Development and characterization of solar energy conversion devices based on nanocomposite semiconductors

PhD Dissertation

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To my family
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Abstract

This doctoral dissertation presents the study of the development and characterization of solar energy conversion devices based on nanocomposite semiconductors. The PhD research is focused on third generation solar cells, namely in dye−sensitized solar cells (DSSCs) and perovskite solar cells (PSCs). The innovation of this study is detected on the use of novel materials by well−known methods in order to intervene in the structural and morphological properties of the photoelectrode, the investigation of newly synthesized sensitizers and hybrid organic/inorganic materials employed in quasi−solid state electrolytes for their jellification, alternative counter electrodes to replace platinum and composite anodes for efficient electron transport to enhance the electrical characteristics of the final devices. Additionally the upscaling of transparent strip−shaped DSSC of various lengths (1 cm to 45 cm) was carried out by inkjet printing the electrodes to ensure the reproducibility and the accuracy of the research findings and the obtained results are evaluated.

The study regarding DSSCs is limited on TiO₂ solar cells and is divided into individual sections each one confining in one of the components of a DSSC. Firstly, the research is concentrated on the photoanode and specifically on different approaches to modify the films to optimize the performance of the corresponding devices. The methods that were tested were the incorporation of a small amount of carbonaceous materials (carbon black powder (CBP) or multi−walled carbon nanotubes (MWCNTs)), the surface treatment of the TiO₂ photoanode films by soaking them in a TiO₂ solution and the testing of different TiO₂ precursor materials or surfactants.

The use of template free P25−TiO₂ solutions modified with CBP or MWCNTs showed that the incorporation of MWCNTs improved the overall performance of the DSSCs, in both sintering temperatures examined (100°C and 500°C) with the highest efficiency recorded for the devices employing P25−TiO₂ electrodes with 0.1 wt% of MWCNTs. However, the CBP modified P25−TiO₂ films resulted in poorer performing devices for all cases tested. The DSSCs with the post−treated P25−TiO₂ films, where the anodes were immersed in two TiO₂ solutions used for the first time (Titanium(IV) (triethanolaminato)isopropoxide and Titanium(IV) bis(ammonium lactate)dihydroxide
solution) followed by annealing at 300°C and 500°C, demonstrated improved short-circuit current density promoting their overall efficiency up to 26–30% compared with solar cells with untreated electrodes. Among the titanium precursor materials used to fabricate transparent TiO₂ films for DSSC, the solar cells with the Titanium(IV) butoxide photoanodes displayed the best electrical parameters and an 11.2% higher power conversion efficiency compared with the solar cells with the Titanium(IV) isopropoxide anode. In contrast, the last modification method tested using the surfactant Dioctyl sulfosuccinate sodium salt (AOT) in the TiO₂ solution which could be easily removed by rinsing without damaging the film, didn’t reach to the desired results and the attempt to simplify the fabrication of TiO₂ films through this procedure was given up.

Regarding the dye complexes tested as sensitizers in quasi-solid state DSSCs, initially six newly synthesized ruthenium dye complexes with different pyridine and bipyridine side groups were studied. The DSSCs that were sensitized with the dyes having two bipyridines (bpy-bpy) in their structure demonstrated almost the same performance as the solar cells that were sensitized with the commercially available dye D907 which has a similar structure as the new complexes. In particular, the solar cell sensitized with the dye CS28 displayed a slightly better power conversion efficiency than the one corresponding to the DSSC sensitized with D907 (3.28% and 3.26% respectively). Subsequently, two new triphenylamine based organic dyes with or without the additional electron donating hexyloxy groups, having a benzimidazole derivative as π-bridge were studied. The DSSCs sensitized with the dye without the additional hexyloxy groups (MZ−341) were more efficient compared with the ones sensitized with the dye with the hexyloxy groups (MZ−235) because of the higher absorbance of the former on the TiO₂ photocathode. Finally, a water based natural dye solution was prepared by extracting the phycoerythrin pigment from red algae and was used as a sensitizer for DSSCs. The best results were obtained for an acidic dye solution (pH=3) and for a temperature of 35°C during the sensitization of the anode.

In the electrolyte solution only a minor alteration was examined regarding the hybrid material used for the gradual solidification of the electrolyte. All five hybrid organic/inorganic materials that were synthesized with polypropylene or polyethylene of different oligomer chain length as organic sub-phase demonstrated good thermal stability up to 150°C with ED600−ICS slightly standing out. Nevertheless no obvious
differences were detected in the electrical parameters of the DSSCs that employed these hybrid materials in their electrolyte solution. As far as the alternative counter electrodes tested to replace platinum is concerned, DSSCs with the nickel doped CoS$_2$ and the polypyrrole counter electrode displayed better electrical characteristics compared with the solar cells with platinum. In fact in both cases an enhanced short−circuit current density was recorded improving the solar cells’ overall efficiency.

Proceeding to the manufacture of large area transparent DSSCs with electrodes fabricated by inkjet printing, the main variations observed at these strip−shaped DSSC of various lengths (1 cm−45 cm) were at the $J_{sc}$ and the FF values which decreased as the length increased. Even so, the construction of strip−shaped DSSCs of intermediate length (20 cm−25 cm) connected in order to form a solar module in an almost square form could be a viable solution providing satisfactory results.

Finally, the PSCs with the TiO$_2$–In$_2$O$_3$ binary electron transport layer which was used as a scaffold in order for the mixed halide perovskite (CH$_3$NH$_3$I$_{3-x}$Cl$_x$) to infiltrate exhibited a maximum power conversion efficiency of 12.86% which improved the efficiency of the PSCs with the pristine TiO$_2$ over 28%. This is attributed to the better interfacial connection between TiO$_2$–In$_2$O$_3$/CH$_3$NH$_3$I$_{3-x}$Cl$_x$, the efficient electron transport due to optimized alignment of the energy levels of the mixed oxides and the perovskite, as well as the reduction of the recombination processes. Baring in mind that all manufacturing processes for the perovskite solar cells were carried out in ambient conditions renders these results quite impressive.

Overall, it is presumed that the obtained research results, their interpretation and the final conclusions derived from this work will give an insight for future research prospects on third generation solar cells.
Περίληψη

Η παρούσα διδακτορική διατριβή μελετά την ανάπτυξη και το χαρακτηρισμό διατάξεων μετατροπής της ηλιακής ενέργειας βασισμένων σε νανοσύνθετους ημιαγωγούς. Η έρευνα επικεντρώνεται στις ηλιακές κυψελίδες τρίτης γενιάς και συγκεκριμένα στις ευαισθητοποιημένες με χρωστική ηλεκτροχημικές κυψελίδες (dye-sensitized solar cells, DSSCs) και στις ηλιακές κυψελίδες περοβσκιτών (perovskite solar cells, PSCs). Η πρωτοτυπία αυτής της μελέτης εντοπίζεται στην εφαρμογή γνωστών μεθόδων χρησιμοποιώντας νεότερα υλικά στη δοκιμή και μελέτη νέων ευαισθητοποιητών και υβριδικών οργανικών/ανάγλυφων υλικών που χρησιμοποιούνται στους ημι-στερεούς ηλεκτρολόγωτες για την προμηθεία, εναλλακτικά αντιηλεκτρόδια για αντικατάσταση αυτών της πλατίνας και σύνθετες ανάδειξες για την αποτελεσματική μεταφορά των ηλεκτρονίων και την ενίσχυση των ηλεκτρολογικών χαρακτηριστικών των τελικών διατάξεων. Επιπλέον, κατασκευάστηκαν διαφανείς ευαισθητοποιημένες με χρωστική ηλεκτροχημικές κυψελίδες μεγάλων διαστάσεων σε μορφή λωρίδας διαφόρων μηκών (1 cm έως 45 cm) με εναπόθεση των ηλεκτροδίων μέσω εκτύπωσης inkjet ώστε να εξασφαλίσει την επαναληπτικότητα της διαδικασίας και η ακρίβεια στα ερευνητικά αποτελέσματα τα οποία προέκυψαν.

Η μελέτη των ευαισθητοποιημένων με χρωστική ηλεκτροχημικές κυψελίδων εστιάστηκε αποκλειστικά σε ηλιακές κυψελίδες διοξειδίου του τιτανίου (TiO\textsubscript{2}) και χωρίστηκε σε επιμέρους ενότητες σε καθεμία από τις οποίες εξετάστηκε κάποια τροποποίηση σε ένα από τα ενεργά συστατικά τους. Αρχικά, η έρευνα επικεντρώθηκε στην τροποποίηση των υμειών της φωτοανόδου με διάφορες εναλλακτικές ώστε να βελτιστοποιηθεί η επαναληπτικότητα της δεξαμενής ενέργειας. Οι μέθοδοι οι οποίοι εξετάστηκαν ήταν η επανακατασκευή μιας κυρίας ποσότητας ανθρακωδών υλικών (σκόνη μαύρου άνθρακα−carbon black powder (CBP) ή νανοσωλήνες άνθρακα με πολλαπλά τομείματα (multi−walled carbon nanotubes (MWCNTs)), η επιφανειακή επεξεργασία των υμειών TiO\textsubscript{2} της ψητοόξυδου μέσω εμβαπτισμού σε διάλυμα TiO\textsubscript{2} και η δοκιμή διάφορων πρόδρομων υλικών διοξειδίου του τιτανίου ή επιφανειοδραστικών υλικών.
Η δοκιμή διαλυμάτων P25−TiO2 τροποποιημένων με CBP ή MWCNTs, χωρίς την προσθήκη επιφανειοδραστικών ουσιών απέδειξε ότι η ενσωμάτωση MWCNTs βελτίωσε τη συνολική απόδοση των ευαισθητοποιημένων με χρωστική ηλεκτροχημική κυψελίδων και για τις δύο θερμοκρασίες πυροσυσσωμάτωσης που εξετάστηκαν (100°C και 500°C) με την υψηλότερη απόδοση να καταγράφεται για τις διατάξεις με τη φωτοανόδο P25−TiO2 τροποποιημένη με 0.1 wt% MWCNTs. Ωστόσο, οι ηλιακές κυψελίδες με τα τροποποιημένα υμένια P25−TiO2 με CBP οδήγησαν σε διατάξεις με χειρότερη απόδοση συγκριτικά με τις κυψελίδες αναφοράς για όλες τις υπό μελέτη περιπτώσεις. Οι ευαισθητοποιημένες με χρωστική ηλεκτροχημική κυψελίδες με τα υμένια φωτοανόδου τα οποία μετά την εναπόθεση της P25−TiO2 υποβλήθηκαν σε περαιτέρω επεξεργασία χρησιμοποιώντας διαλύματα TiO2 που δοκιμάστηκαν για πρώτη φορά (Titanium(IV) (triethanolaminato)isopropoxide και Titanium(IV) bis(ammonium lactate)dihydroxide) και στη συνέχεια πραγματοποιήθηκε πυροσυσσωμάτωση στους 300°C ή στους 500°C, παρουσίαζαν βελτιωμένη πουσότητα γράμμων βραχυκύκλωσης ενισχύοντας τη συνολική απόδοσή τους έως 26–30% σε σύγκριση με τις ηλιακές κυψελίδες των οποίων οι φωτοανόδοι δεν είχαν υποστεί επεξεργασία. Μεταξύ των προδρόμων ουσιών του τιτανίου που χρησιμοποιήθηκαν για την κατασκευή διάφανων υμένων TiO2 για την κατασκευή DSSCs, οι ηλιακές κυψελίδες με τη φωτοανόδο από διάλυμα Titanium(IV) butoxide παρουσίαζαν τα καλύτερα αποτελέσματα και μια απόδοση αυξημένη κατά 11.2% συγκριτικά με τις ηλιακές κυψελίδες με την άνοδο από διάλυμα Titanium(IV) isopropoxide. Εντούτοις, η τελευταία μέθοδος τροποποίησης της φωτοανόδου που δοκιμάστηκε με τη χρήση της επιφανειοδραστικής ουσίας Dioctyl sulfosuccinate sodium salt (AOT) στο διάλυμα του TiO2, η οποία μπορεί να απομακρυνθεί εύκολα με έκπλυση με νερό χωρίς να καταστρέφει το υμένιο, δεν επέφερε τα επιθυμητά αποτελέσματα και η προσπάθεια απλοποίησης της κατασκευής των υμενίων μέσω αυτής της διαδικασίας εγκαταλείφθηκε.

Όσον αφορά τα σύμπλοκα χρωστικών που δοκιμάστηκαν ως ευαισθητοποιητές σε ημι−στερεού τύπου ηλεκτροχημικές κυψελίδες, αρχικά μελετήθηκαν έξι νέα σύμπλοκα χρωστικών ρουθηνίου με διαφορετικές πλευρικές ομάδες πυριδίνης και διπυριδίνης. Τα DSSCs που ευαισθητοποιήθηκαν με τις χρωστικές που είχαν στη μοριακή δομή τους δύο διπυριδίνες, είχαν σχεδόν την ίδια απόδοση με ηλιακές κυψελίδες οι οποίες είχαν ευαισθητοποιηθεί με την εμπορικά διαθέσιμη χρωστική D907 η οποία έχει παρόμοια δομή με τα νέα σύμπλοκα που συντέθηκαν. Πιο συγκεκριμένα οι ηλιακές κυψελίδες οι οποίες είχαν ευαισθητοποιηθεί με τη χρωστική CS28 εμφάνιζαν ελαφρώς καλύτερη απόδοση.
συγκριτικά με αυτή των κυψελίδων που είχαν ευαισθητοποιηθεί με την D907 (3.28% και 3.26% αντίστοιχα). Στη συνέχεια, μελετήθηκαν δύο νέες οργανικές χρωστικές τριφαινυλαμίνης με ή χωρίς επιπρόσθετες ομάδες δοτών ηλεκτρονίων με παράγωγο βενζιμιδαζόλης ως π−γέφυρα. Οι ηλεκτροχημικές κυψελίδες οι οποίες είχαν ευαισθητοποιηθεί με τη χρωστική χωρίς τις πρόσθετες ομάδες δοτών ηλεκτρονίων (MZ=−341) ήταν πιο αποδοτικές σε σύγκριση με εκείνες που είχαν ευαισθητοποιηθεί με τη χρωστική με τις πρόσθετες ομάδες δοτών ηλεκτρονίων (MZ=−235) εξαιτίας της υψηλότερης απορρόφησης της πρώτης στο υμένιο TiO₂ του φωτοηλεκτροδίου. Τέλος, παρασκευάστηκε μια φυσική υδατοδιαλυτή χρωστική μέσω της εκχύλισης της φυκοερυθρίνης από κόκκινα φύκια η οποία χρησιμοποιήθηκε ως ευαισθητοποιητής σε ηλιακές κυψελίδες. Τα καλύτερα αποτελέσματα ελήφθησαν για οξίνο διάλυμα φυσικής χρωστικής (pH=3) και για θερμοκρασία 35°C κατά την ευαισθητοποίηση των υμενίων TiO₂.

Στο διάλυμα του ηλεκτρολύτη εξετάστηκε μόνο μια μικρή τροποποίηση που αφορά το υβριδικό υλικό το οποίο χρησιμοποιείται για τη σταδιακή στερεοποίησή του. Όλα τα πέντε νέα υβριδικά οργανικά/ανόργανα υλικά, τα οποία συντάχθηκαν έχοντας ως οργανικό μέρος πολυπροπυλένιο ή πολυαιθυλένιο με διαφορετικό μήκος αλυσίδας, είχαν καλή θερμική σταθερότητα έως τους 150°C, με το υλικό που ονομάστηκε ED600−ICS να υπέρεχε ελαφρώς συγκριτικά με τα υπόλοιπα. Παρόλα αυτά, δεν εντοπίστηκαν σημαντικές διαφορές στις ηλεκτρικές παραμέτρους των ηλιακών κυψελίδων οι οποίες παρασκευάστηκαν έχοντας το διάλυμα του ηλεκτρολύτη κάποια από τα παραπάνω υβριδικά οργανικά/ανόργανα υλικά. Αναφορικά με τα εναλλακτικά αντιηλεκτρόδια που δοκιμάστηκαν ως πιθανοί αντικαταστάτες του αντιηλεκτροδίου πλάτινας, οι ηλιακές κυψελίδες τόσο με το αντιηλεκτρόδιο CoS₂ ντοπαρισμένο με νικέλιο όσο και αυτές με το αντιηλεκτρόδιο πολυπυρρόλης εμφάνισαν καλύτερα ηλεκτρικά χαρακτηριστικά σε σύγκριση με αυτά των ηλεκτροχημικών κυψελίδων με αντιηλεκτρόδιο πλάτινας. Στην πραγματικότητα και στις δύο περιπτώσεις παρατηρήθηκε αύξηση της πυκνότητας τεχνητής βελτιώνης βελτιώνοντας τη συνολική απόδοση των ηλιακών κυψελίδων.

Συνεχίζοντας την έρευνα των ευαισθητοποιημένων με χρωστική ηλεκτροχημικών κυψελίδων πραγματοποιήθηκε η κατασκευή διάφανων ηλεκτροχημικών κυψελίδων μεγάλων διαστάσεων σε μορφή λωρίδων με διάφορα μήκη (1 cm−45 cm) με την εκτύπωση των ηλεκτροδιών να έχει πραγματοποιηθεί μέσω εκτύπωσης με ψεκασμό μελάνης (inkjet printing). Οι κύριες μεταβολές παρατηρήθηκαν στις τιμές της πυκνότητας θερμακτώσσως βελτιώνοντας την συνολική απόδοση των ηλιακών κυψελίδων.
βραχυκύκλωσης (Jsc) και σε αυτές του παράγοντα πλήρωσης (FF) οι οποίες μειώνονταν με αύξηση του μήκους. Όμως η κατασκευή ηλεκτροχημικών κυψελίδων σε μορφή λωρίδων με ενδιάμεσο μήκος (20 cm–25 cm) συνδεδεμένα ώστε να σχηματίζουν ένα πλαίσιο με σχεδόν τετράγωνη μορφή θα μπορούσε να είναι μια βιώσιμη λύση που να παρέχει ικανοποιητικά αποτελέσματα.

Τέλος, οι ηλιακές κυψελίδες περοβσκιτών με το σύνθετο στρώμα μεταφοράς ηλεκτρονίων TiO$_2$−In$_2$O$_3$, το οποίο χρησιμοποιήθηκε ως μέσο για να μπορέσει ο περοβσκίτης (CH$_3$NH$_3$I$_3$−xCl$x$) να διεισδύσει, παρουσίασαν μέγιστη απόδοση 12.86% η οποία ήταν κατά 28% υψηλότερη συγκριτικά με την απόδοση των ηλιακών κυψελίδων περοβσκιτών με απλό στρώμα μεταφοράς ηλεκτρονίων TiO$_2$. Αυτό αποδίδεται στην καλύτερη διασύνδεση της διεπιφάνειας TiO$_2$−In$_2$O$_3$/CH$_3$NH$_3$I$_3$−xCl$x$, στην αποτελεσματικότερη μεταφορά ηλεκτρονίων λόγω της βέλτιστης αυθηγοδόμησης των ενεργειακών επιπέδων των οξειδίων TiO$_2$, In$_2$O$_3$ και του περοβσκίτη, καθώς και στη μείωση του ανασυνδυασμού. Δεδομένου ότι όλες οι διεργασίες κατασκευής των ηλιακών κυψελίδων περοβσκιτών πραγματοποιήθηκαν σε συνθήκες περιβάλλοντος καθιστά τα παραπάνω αποτελέσματα ιδιαίτερα εντυπωσιακά.

Συνολικά, εκτιμάται ότι τα ερευνητικά αποτελέσματα τα οποία προέκυψαν από αυτή τη διδακτορική διατριβή, η επεξεργασία τους καθώς και τα τελικά συμπεράσματα θα δώσουν μια άφθοση για μελλοντικές προοπτικές άρευνας πάνω στις ηλιακές κυψελίδες τρίτης γενιάς.
# Table of Contents

Chapter 1 Introduction .................................................................................1

1.1 Dissertation objective ........................................................................1

1.2 The p-n junction − Structure of a solar cell .....................................2

1.3 Operating principle of a DSSC .........................................................3

1.4 Operating principle of a PSC ..........................................................6

References ...............................................................................................8

Chapter 2 Individual materials development for DSSC ...............................9

2.1 Transparent conducting substrate ..................................................9

2.2 Photoanode .....................................................................................9

2.2.1 Nanocrystalline semiconductors .............................................10

2.2.2 Combining or doping semiconductors ....................................14

2.2.3 Photoanodes’ deposition methods .........................................15

2.3 Sensitizers ....................................................................................17

2.3.1 Metal complexes .....................................................................18

2.3.2 Porphyrins and Phthalocyanines ..........................................20

2.3.3 Organic dyes ...........................................................................21

2.3.4 Natural pigments ...................................................................22

2.3.5 Co-sensitization ....................................................................23

2.3.6 Co-adsorbers .........................................................................23

2.4 Electrolytes ..................................................................................24

2.4.1 Liquid state electrolytes .......................................................25

2.4.2 Quasi-solid state electrolytes ............................................26

2.4.3 Redox couples ......................................................................28
Chapter 4 Experimental methods ................................................................. 74

4.1 Characterization techniques ................................................................. 74

4.1.1 Scanning electron microscopy .......................................................... 74
4.1.2 Ultraviolet−Visible spectroscopy ...................................................... 75
4.1.3 Porosimetry ....................................................................................... 76
4.1.4 X−ray diffraction ............................................................................. 77
4.1.5 Fourier transform infrared spectroscopy ........................................... 79
4.1.6 Thermal gravimetric analysis−Differential scanning calorimetry .... 79
4.1.7 Incident photon to current efficiency ................................................ 80
4.1.8 Electrochemical impedance spectroscopy ........................................ 81
4.1.9 Open−circuit voltage decay .............................................................. 82

References .................................................................................................... 83

Chapter 5 Experimental results−photoanode of DSSC .............................. 84

5.1 Modification of the TiO$_2$ photoanode with carbonaceous materials .... 84

5.1.1 Preparation method for the CBP−TiO$_2$ and MWCNTs−TiO$_2$ photoanodes ................................................................. 84

5.1.2 Structural properties of pure and modified TiO$_2$ films..................... 86
5.1.3 Fabrication of quasi−solid state DSSCs and electrical characterization. 91

5.2 Surface treatment of the TiO$_2$ photoanode films ................................ 96

5.2.1 Preparation method for the pure and surface treated TiO$_2$ films ...... 97
5.2.2 Structural properties of pure and surface treated TiO$_2$ films............ 98
5.2.3 Fabrication of quasi−solid state DSSCs and electrical characterization101

5.3 Transparent TiO$_2$ photoanode films ................................................... 104

5.3.1 Preparation method for the transparent TiO$_2$ photoanode films ...... 104
5.3.2 Structural properties of the transparent TiO$_2$ photoanode films ....... 105
5.3.3 Fabrication of quasi-solid state DSSCs and electrical characterization 109

5.3.4 Electrochemical characterization .............................................................. 111

5.4 Simple procedure for porous TiO₂ photoanode with an amphiphilic surfactant ................................................................. 115

5.4.1 Preparation method for the porous TiO₂ photoanode with AOT as a surfactant ................................................................. 115

5.4.2 Morphological and structural properties of the AOT–TiO₂ photoanode films ................................................................. 116

5.4.3 Fabrication of quasi-solid state DSSCs. Electrical and electrochemical characterization ................................................................. 119

References .................................................................................................. 122

Chapter 6 Experimental results—sensitizer of DSSC .............................................. 124

6.1 Newly synthesized ruthenium(II) complexes .............................................. 124

6.1.1 Absorption and electrochemical data of the Ruthenium complexes .... 125

6.1.2 Fabrication of DSSCs ................................................................................. 129

6.1.3 Electrical and electrochemical characterization of DSSCs ................ 130

6.2 New metal free D−π−A sensitizers ............................................................... 136

6.2.1 Electrochemical and FTIR data of the D−π−A sensitizers .................. 136

6.2.2 Fabrication of DSSCs sensitized with the D−π−A sensitizers .............. 139

6.2.3 Electrical and electrochemical performance of DSSCs sensitized with the D−π−A sensitizers ................................................................. 139

6.3 Natural sensitizer extracted from red algae .............................................. 143

6.3.1 Red algae pigment extraction and optical characterization .......... 143

6.3.2 DSSC’s electrical and electrochemical characterization .................... 146

References .................................................................................................. 152

Chapter 7 Experimental results—electrolyte of DSSC ........................................... 155
7.1 Preparation of hybrid organic/inorganic materials and quasi-solid state electrolytes. ................................................................. 155

7.2 Thermogravimetric analysis, differential scanning calorimetry and ionic conductivity measurements of the quasi-solid state electrolytes. ............................................ 156

7.3 Fabrication and characterization of quasi-solid state DSSCs ............ 159

7.3.1 Fabrication of TiO₂ photoanode and structural properties .......... 159

7.3.2 DSSCs' manufacture-Electrical and electrochemical performance .... 162

References ........................................................................................................ 167

Chapter 8 Experimental results-counter electrode of DSSC .................. 168

8.1 Nickel doped cobalt sulfide counter electrode .................................. 168

8.1.1 Preparation of the nickel doped cobalt sulfide counter electrode....... 168

8.1.2 Fabrication of the DSSCs, electrical and electrochemical characterization .................................................................................................................... 170

8.2 Polypyrrole counter electrode ................................................................. 173

8.2.1 Preparation of the Polypyrrole counter electrode ......................... 173

8.2.2 Performance comparison of DSSCs with Pt and PPy counter electrodes ................................................................................................................................. 174

References ........................................................................................................ 175

Chapter 9 Experimental results-Upscaling of DSSCs ......................... 176

9.1 Transparent strip-shaped TiO₂ DSSCs .............................................. 176

9.2 Performance of strip-shaped DSSCs .................................................. 177

References ........................................................................................................ 181

Chapter 10 Experimental results-PSCs ................................................. 182

10.1 Electron transport layer fabrication ............................................... 182

10.2 Perovskite synthesis and monolithic mesoscopic PSCs fabrication .... 183
10.3 Morphological and structural properties of the complex photoelectrodes ........................................................................................................................................ 185

10.4 PSCs’ electrical and electrochemical characterization ........................................... 190

References .......................................................................................................................... 195

Chapter 11 Conclusions—Future research prospects .................................................. 197

11.1 Conclusions ................................................................................................................ 197

11.2 Future research prospects ......................................................................................... 200
<table>
<thead>
<tr>
<th>Abbreviations</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>PV</td>
<td>photovoltaic</td>
</tr>
<tr>
<td>c-Si</td>
<td>crystalline silicon</td>
</tr>
<tr>
<td>mc-Si</td>
<td>multicrystalline silicon</td>
</tr>
<tr>
<td>a-Si</td>
<td>amorphous silicon</td>
</tr>
<tr>
<td>DSSC</td>
<td>dye–sensitized solar cell</td>
</tr>
<tr>
<td>QDSSC</td>
<td>quantum-dot sensitized solar cell</td>
</tr>
<tr>
<td>PSC</td>
<td>Perovskite solar cell</td>
</tr>
<tr>
<td>VB</td>
<td>Valence band</td>
</tr>
<tr>
<td>CB</td>
<td>Conduction band</td>
</tr>
<tr>
<td>FTO</td>
<td>Fluorine doped tin oxide</td>
</tr>
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<td>ETL</td>
<td>Electron transport layer</td>
</tr>
<tr>
<td>HTM</td>
<td>Hole transport material</td>
</tr>
<tr>
<td>TCO</td>
<td>Transparent conductive oxide</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium tin oxide</td>
</tr>
<tr>
<td>PCE</td>
<td>Power conversion efficiency</td>
</tr>
<tr>
<td>NIR</td>
<td>Near infrared</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>PGM</td>
<td>Platinum group metal</td>
</tr>
<tr>
<td>MLCT</td>
<td>Metal–to–ligand charge transfer</td>
</tr>
<tr>
<td>ICT</td>
<td>Intramolecular charge transfer</td>
</tr>
<tr>
<td>IL</td>
<td>Ionic liquid</td>
</tr>
<tr>
<td>VOCs</td>
<td>Volatile organic compounds</td>
</tr>
<tr>
<td>4−TBP</td>
<td>4-tert-butylpyridine</td>
</tr>
<tr>
<td>Guan SCN</td>
<td>Guanidine thiocyanate</td>
</tr>
<tr>
<td>CE</td>
<td>Counter electrode</td>
</tr>
<tr>
<td>PEDOT</td>
<td>Poly(3,4-ethylenedioxythiophene)</td>
</tr>
<tr>
<td>PANI</td>
<td>Polyaniline</td>
</tr>
<tr>
<td>PPy</td>
<td>Polypyrrole</td>
</tr>
<tr>
<td>MA</td>
<td>Methylammonium</td>
</tr>
<tr>
<td>FA</td>
<td>Formamidinium</td>
</tr>
<tr>
<td>HTL</td>
<td>Hole transport layer</td>
</tr>
<tr>
<td>ETM</td>
<td>Electron transport material</td>
</tr>
<tr>
<td>OPV</td>
<td>Organic photovoltaic</td>
</tr>
<tr>
<td>GBL</td>
<td>γ-butyrolactone</td>
</tr>
<tr>
<td>DMF</td>
<td>N,N-dimethylformamide</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethyl sulphoxide</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>UV−Vis</td>
<td>Ultraviolet−Visible</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>--------------------------------------------------</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer–Emmett–Teller</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width at half maximum</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermal gravimetric analysis</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>IPCE</td>
<td>Incident photon to current efficiency</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical impedance spectroscopy</td>
</tr>
<tr>
<td>EQE</td>
<td>External quantum efficiency</td>
</tr>
<tr>
<td>CBP</td>
<td>Carbon black powder</td>
</tr>
<tr>
<td>MWCNTs</td>
<td>Multi-walled carbon nanotubes</td>
</tr>
<tr>
<td>MW</td>
<td>Molecular weight</td>
</tr>
<tr>
<td>ICS</td>
<td>3-isocyanatopropyltriethoxysilane</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>AcOH</td>
<td>Acetic acid</td>
</tr>
<tr>
<td>MPII</td>
<td>1-methyl-3-propylimidazolium iodide</td>
</tr>
<tr>
<td>CPE</td>
<td>Constant phase element</td>
</tr>
<tr>
<td>TTAI</td>
<td>Titanium(IV) (triethanolaminato)isopropoxide solution</td>
</tr>
<tr>
<td>TALD</td>
<td>Titanium(IV) bis(ammonium lactate)dihydroxide solution</td>
</tr>
<tr>
<td>TTIP</td>
<td>Titanium(IV) isopropoxide</td>
</tr>
<tr>
<td>TTBU</td>
<td>Titanium(IV) butoxide</td>
</tr>
<tr>
<td>Ti(AcAc)</td>
<td>Diisopropoxytitanium bis(acetylacetonate)</td>
</tr>
<tr>
<td>AOT</td>
<td>Dioctyl sulfosuccinate sodium salt</td>
</tr>
<tr>
<td>nZEB</td>
<td>Nearly zero-energy buildings</td>
</tr>
<tr>
<td>CBD</td>
<td>Chemical bath deposition</td>
</tr>
<tr>
<td>HMT</td>
<td>Hexamethylenetetramine</td>
</tr>
<tr>
<td>MAI</td>
<td>Methylammonium iodide</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy dispersive X-ray</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
</tbody>
</table>
Chapter 1 Introduction

1.1 Dissertation objective

As noted by the latest statistical review [1], based on the current extraction rate of fossil fuel, coal will last for about 113 years and the crude oil and natural gas reserves will be exhausted in 2067 and 2069 respectively. Thus, in an effort to address the climate change and the continuous depletion and cost increase of fossil fuel, mankind focused their attention to the renewable energy sources. Solar energy reaching the surface of Earth is an unlimited energy source and its exploitation can meet the world’s energy consumption, while contributing to fulfilling the climate targets.

Photovoltaics (PVs) are devices employing semiconductor materials converting the incident solar light to electrical energy and they can be classified into three categories. Crystalline and multicrystalline silicon solar cells (c-Si, mc-Si) are photovoltaics categorized to the first generation technology and they are the current dominants of the photovoltaic market. Single crystalline silicon solar cells have reached an efficiency of 27.6% a value which starts to approximate the Shockley-Queisser limit. Second generation technology include thin film solar cells like amorphous silicon (a-Si) or polycrystalline compounds such as copper indium gallium (di)selenide (CIGS) and cadmium telluride (CdTe). Optimized CIGS solar cells have reached a record efficiency of 23.3%, although the toxicity and the lack of abundance of certain elements (In, Cd, Te) is still a major concern. Intensive research has also been launched on third generation photovoltaic cells, as dye–sensitized solar cells (DSSCs), quantum-dot sensitized solar cells (QDSSCs) and lately perovskite solar cells (PSCs) recording 11.9% [2], 10.6% and 22.1% respectively highest cells’ efficiencies (Fig. 1.1) [3]. Especially, it is highly promising that the overall efficiency values reached for small lab scale PSCs are comparable with commercial available silicon solar cells.
The objective of this thesis is the development and characterization of solar energy conversion devices based on nanocomposite semiconductors. The dissertation is focused on the research of two types of third generation photovoltaics, the dye-sensitized solar cells and the perovskite solar cells, which have numerous advantages as compared to photovoltaic cells from other technologies, such as low total cost, simple preparation and manufacturing processes, with low impact in the environmental problem. This PhD thesis is going to investigate each of the components of the DSSC and the PSC individually, in an attempt to optimize them either by increasing their overall efficiency or by lowering their total fabrication cost or by increasing their stability.

1.2 The p-n junction – Structure of a solar cell

Conventional solar cells are based on semiconductors which have a dual role: to absorb the incident light and to separate the charge carriers. The working principle of first and second generation photovoltaic solar cells is based on the p-n junction. A p-n junction is formed when two oppositely charged semiconductors, an n-type and a p-type semiconductor, are in contact. The electrons from the n-doped semiconductor
that are close to the p-n interface diffuse in the p-doped semiconductor forming anions in the p-region and leaving cations in the n-region. Similarly, holes from the p-doped semiconductor that are close to the p-n interface diffuse in the n-doped semiconductor forming cations in the n-region and leaving anions in the p-region. As a result the regions near the p-n interface cease to be neutral and the so-called depletion region is formed (Fig. 1.2). Due to the formation of the depletion region an electric field is formed which counteracts the diffusion of electrons and holes.

![Figure 1.2: Scheme of a p-n junction in equilibrium.](image)

When the semiconductor is illuminated it absorbs photons with energy higher or equal to its energy band gap, creating an exciton (a bound electron-hole pair). The electron is promoted from the valence band (VB) to the conduction band (CB) of the semiconductor leaving behind a hole which is attracted to the electron by Coulomb forces leading to a bound electron-hole pair. Charges that are not collected at the contacts are eventually lost by recombination.

### 1.3 Operating principle of a DSSC

The operation of a dye–sensitized solar cell resembles the photosynthesis procedure taking place in all flora organisms. Chlorophyll is a pigment which is contained inside the chloroplasts of the plant cells and is responsible for absorbing light from the sun and converting it into chemical energy. This chemical energy is used to convert the CO₂ and water into oxygen and energy-rich organic compounds, mainly hydrocarbons. Likewise, in dye–sensitized solar cells sensitizers (dyes or natural pigments) are used in order to absorb the incident light and convert it in electrical energy.
The operating principle of a DSSC is based on the layout shown in Figure 1.3. The cell consists of two transparent conductive substrates (glass, fluorine doped tin oxide, FTO). On one of the glasses is deposited a semiconductor (i.e. TiO₂, ZnO, etc.) which plays the role of the anode, while in order to make the cathode, a counter electrode is deposited on the surface of the second conductive glass. On the surface of the semiconductor is adsorbed a suitable sensitizer and afterwards a couple of drops of the electrolyte solution are placed on top of the anode and the counter electrode is pushed by hand on the top.

The sensitizer’s molecules (S) absorb the incident light of the cell and they reach an excited state (S*), resulting in the injection of an electron into the conduction band of the semiconductor leaving the dye in its oxidized state (S⁺). The dye is restored to its ground state by an electron transfer from the redox couple of the electrolyte which acts as an electron donor. The electrolyte is an organic solution containing a redox system (A/A⁻) which is regenerated in turn by a reduction reaction at the counter electrode. Finally, the circuit is completed by an electron migration through the external load. These processes can be described by the following reactions.

\[ S + hv \rightarrow S^* \]  
Absorption (1.1)

\[ S^* \rightarrow S^+ + e^- \]  
Electron injection (1.2)

\[ S^+ + A^- \rightarrow S + A \]  
Regeneration (1.3)

\[ A + e^- \rightarrow A^- \]  
Cathode reduction (1.4)

Thus, an essential difference can be spotted between traditional solar cells and DSSCs regarding their operating principle. While the sunlight absorption and the charge separation are carried out at the same material in the former, those two procedures are sundered in the case of the latter. Particularly, in DSSCs the photoelectrons are obtained from the excitation of the sensitizer, whereas the charges are separated at the interface between the semiconductor, the dye and the electrolyte.

However, the operating principle previously described is rather simplified, as there are also unwanted pathways that the conduction band electrons might follow. The injected electrons can recombine before being successfully collected from the contacts, either with the oxidized dye molecules or with the electrolyte’s redox couple (reactions 1.5, 1.6). This back electron transfer is considered to be responsible for the dark current and the main reason of DSSCs’ power losses [5]. As a result the redox mediator of the
electrolyte needs to have the ability to regenerate quickly the dye, in order to intercept the recapture of the conduction band electrons by the oxidized dye molecules. Moreover, co-adsorbers or a blocking layer covering the semiconductor’s layer can also be used to decrease the recombination rate, which will be discussed in detail in later subparagraphs.

\[ A + e_{\text{CB}}^- \rightarrow A^- \]  
(1.5)

\[ S^+ + e_{\text{CB}}^- \rightarrow S \]  
(1.6)

\[ b \nu \]

**Figure 1.3:** Structure of a typical dye-sensitized solar cell.
1.4 Operating principle of a PSC

A perovskite solar cell (PSC) is another type of third generation photovoltaic cell employing a perovskite as a light absorber, instead of a dye as in the case of DSSCs. The nomenclature “perovskite” is used for all compounds adopting the general formula $A MX_3$. In photovoltaic applications, perovskites are direct bandgap semiconductors with exceptional properties, such as broad optical absorption from the visible to the near infrared (NIR) region, ambipolar carrier transport, long electron–hole diffusion lengths and high dielectric constant leading to low exciton binding energy [6,7]. In organic–inorganic halide perovskites ($A MX_3$) $A$ is a cation, usually $\text{CH}_3\text{NH}_3^+$, $\text{CH}(\text{NH}_2)_2^+$, $\text{Cs}^+$ or a mixture of them, $M$ is divalent or trivalent metal, usually $\text{Pb}^{2+}$, $\text{Sn}^{2+}$, $\text{Bi}^{3+}$, $\text{Sb}^{3+}$ and $X$ is a halogen anion, usually $\text{I}^-$, $\text{Br}^-$, $\text{Cl}^-$ or a combination of them.

Unlike the DSSCs devices, which usually employ two different substrates for the anode and the cathode (Fig. 1.3), the device structure of the PSCs is monolithic, namely only one conductive glass substrate is required for the deposition of all films, where the perovskite is confined between an n−type and a p−type material. The PSCs can be fabricated following the mesoscopic (mesostructured) or the planar (thin film) configuration (Fig. 1.4). In the mesoscopic structure, the perovskite absorber infiltrates the mesoporous electron transport layer (ETL). As soon as the incident light is absorbed by the perovskite, excitons are formed; the generated electrons are injected to the mesoporous ETL and they are transported to the anode through which they are extracted, while the generated holes are transferred to the hole transport material (HTM) and they are collected at the cathode. In the planar architecture, when the perovskite absorbs the incident light, the generated charges are directly transported to the selective contacts through the perovskite, which, as earlier mentioned, is an ambipolar charge conducting material.

As in DSSCs, so in PSCs the photogenerated electrons might also get lost before being successfully collected at the selective contacts. The photo−induced electrons may follow an undesired pathway leading to radiative or non−radiative charge recombination (reactions 1.7a and b) or recombination at the PSC’s interfaces (reactions 1.8-1.10) [8,9]. These processes have a negative effect on the cells’ overall efficiency and notably at the open−circuit potential ($V_{oc}$).
Introduction

\[(e^- ... h^+)_{\text{perovskite}} \rightarrow h \cdot v\]  
Exciton annihilation (1.7a)

\[(e^- ... h^+)_{\text{perovskite}} \rightarrow \text{carriers loss}\]  
(1.7b)

e_{CB(ETL)}^+ + h^+_{(\text{perovskite})} \rightarrow \text{carriers loss}  
Back electron transfer at the ETL surface (1.8)

h^+_{(HTM)} + e^-_{(\text{perovskite})} \rightarrow \text{carriers loss}  
Back charge transfer at the HTM surface (1.9)

e_{CB(ETL)}^- + h^+_{(HTM)} \rightarrow \text{carriers loss}  
Charge recombination at the ETL/HTM interface (1.10)

Figure 1.4: (a) Mesoscopic (mesostructured) and (b) planar (thin film) perovskite solar cells’ configuration.
References


2.1 Transparent conducting substrate

Although DSSCs can be fabricated using either rigid or flexible substrates, the glass substrates are the most commonly used as they outweigh their plastic counterparts. Transparent conductive oxides (TCOs), as indium tin oxide (ITO) and fluorine doped tin oxide (FTO, SnO$_2$:F), are thin, transparent and electrically conductive layers coated on glasses, which are frequently used in photovoltaic applications including dye-sensitized solar cells.

Fluorine doped tin oxide glasses are generally preferred compared with indium tin oxide glasses as they are cheaper. On the market there is a variety of FTO glasses with different properties, such as sheet resistance (Ohms/□), thickness (mm), light transmittance (%) and haze (%) to suit according the application (Fig. 2.1).

<table>
<thead>
<tr>
<th>Product</th>
<th>Thickness (mm)</th>
<th>Light Transmittance (%)</th>
<th>Solar Direct Transmittance (%)</th>
<th>Sheet Resistance (Ohms/□)</th>
<th>Haze (%)</th>
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<tbody>
<tr>
<td>NSG TEC™ A7</td>
<td>2.2</td>
<td>82</td>
<td>70</td>
<td>7</td>
<td>5</td>
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<tr>
<td>NSG TEC™ A9</td>
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<td>70</td>
<td>8</td>
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<td>NSG TEC™ A9K</td>
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<tr>
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<tr>
<td>NSG TEC™ T11X</td>
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<td>81</td>
<td>76</td>
<td>12</td>
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</tr>
<tr>
<td>NSG TEC™ T12X</td>
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<td>82</td>
<td>76</td>
<td>12</td>
<td>11-15</td>
</tr>
<tr>
<td>NSG TEC™ C10</td>
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<td>72</td>
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<td>69</td>
<td>&lt; 15</td>
<td>1-2</td>
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<td>91</td>
<td>87</td>
<td>N/A</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Figure 2.1: Properties of FTO glass products (Source: Pilkington [1]).

2.2 Photoanode

The mesoporous photoanode is formed by the deposition of a semiconductor film on the conducting glass substrate, which is afterwards sintered in high temperature for a
few minutes in order to remove any organic residues and electrically connect the nanoparticles composing the film.

The mesoporous anode should satisfy a number of requirements in order for the resulting cell to be efficient. Firstly, the film should possess high crystallinity and large surface area, as rough and porous films have larger active area for the dye molecules to be adsorbed, leading to increased light harvesting and eventually to DSSCs with high quantum efficiency. Moreover, a metal oxide film with high porosity (ideally 50–60%) could also facilitate the electrolyte penetration to ensure the fast regeneration of the dye molecules. In addition, the semiconductor which is going to be used for the anode, needs to have suitable energy levels, namely its conduction band must be lower than the lowest unoccupied molecular orbital (LUMO) of the dye molecules to ensure the injection of the electrons to the CB of the semiconductor. The thickness of the nanocrystalline semiconductor film also plays a significant role. Photoanode films with small thickness can lead to reduced dye adsorption and films with thickness higher than the electron diffusion length, \( L \), can obstruct the electron transport increasing the recombination of photo-injected electrons with the oxidized dye molecules or the redox mediator of the electrolyte [2]. Finally, the metal oxide films should have simple preparation procedures and at the same time low cost. While TiO\(_2\) is the most studied semiconductor for the fabrication of DSSCs’ photoanode, resulting in cells with the highest efficiencies, other semiconductors have also been tested, such as ZnO, SnO\(_2\) and Nb\(_2\)O\(_5\).

### 2.2.1 Nanocrystalline semiconductors

Titanium dioxide, TiO\(_2\), is the most common compound of titanium, having a broad range of applications in pharmaceuticals, pastes, paints, photocatalysts and solar cells. TiO\(_2\) is a wide bandgap semiconductor which has three main crystalline polymorphs: anatase, rutile and brookite (Fig. 2.2) [3]. All TiO\(_2\) polymorphs are composed of distorted TiO\(_6\) octahedra which are connected in a different way for each one of them. Brookite has an orthorhombic structure with the distorted TiO\(_6\) octahedra sharing three edges and corners with adjoining octahedra. Brookite is seldom studied, as it’s not stable and it is difficult to be synthesized. Anatase and rutile both have a tetragonal structure with adjacent octahedra sharing edges and corners. The most important structural differences between them are the way the moieties are assembled into crystals and the distortion degree of the octahedra [4]. In anatase the distortion
degree of the octahedra is more distinct than rutile’s, as in anatase each TiO$_6$ octahedra is abut with eight other octahedra on four sharing edges and four sharing corners, whereas in rutile each TiO$_6$ octahedra abuts with ten other octahedra on two sharing edges and the remaining eight connecting through sharing corners. Thus, these structural differences in the two crystals denote that anatase can form more hydroxyl groups (–OH) on the surface of TiO$_2$ when compared with rutile [4-6]. The hydroxyl groups are essential for sensitizers bearing carboxylate groups (–COOH) which bind on the TiO$_2$ surface via an ester–like bond formed between the –OH and –COOH groups [7]. In conclusion, while rutile is more thermodynamically stable than anatase, the preferred polymorph for DSSCs is anatase as it has wider bandgap (3.2 eV for anatase (Fig. 2.3) vs. 3.0 eV for rutile), higher conduction band edge ($E_{\text{CB}}$) and it’s easy to exhibit a larger specific surface area to increase the dye loading.

**Figure 2.2:** Crystalline polymorphs of TiO$_2$: anatase, rutile and brookite [3].

There are many methods to synthesize different anatase nanostructures such as nanoparticles, nanowires, nanotubes, nanorods, nanosheets and nanoflowers. Indicatively, some of these methods include sol–gel, chemical vapor deposition, micelle or inverse micelle, hydrothermal, electrodeposition and microwave deposition methods. In DSSCs the most commonly used method for the preparation of the photoanode film is the sol–gel which is ideal for making thin films. The typical sol–gel route involves the hydrolysis of a metal alkoxide, although another sol–gel route is based on the organic acid solvolysis of the alkoxide. The organic acid solvolysis, for example acetic acid
solvolysis, is carried out in two steps where the intermediate step includes an esterification reaction. The hydrolysis and the case of acetic (AcOH) acid solvolysis are presented by the subsequent reactions (reactions 2.1 and 2.2) in which, for simplicity reasons, only one metal-bound ligand is considered. M represents a metal (i.e. titanium) and R is a small alkyl chain (i.e. methyl, ethyl or propyl) [8].

- **Hydrolysis**

\[
M - OR + H_2O \rightarrow M - OH + ROH \quad (2.1a)
\]
\[
M - OH \rightarrow M - O - M + H_2O \quad (2.1b)
\]

- **Acetic acid solvolysis**

\[
M - OR + AcOH \rightarrow M - OAc + ROH \quad (2.2a)
\]
\[
ROH + AcOH \rightarrow ROAc + H_2O \quad \text{Condensation (2.2b)}
\]
\[
M - OAc + ROH \rightarrow ROAc + M - OH \quad (2.2c)
\]
\[
M - OR + M - OAc \rightarrow ROAc + M - O - M \quad (2.2d)
\]

The hydroxide species of the hydrolysis reaction (M–OH) are highly reactive which after inorganic polymerization produce the end product of the sol–gel method, the oxide M–O–M. The organic acid solvolysis is a more complicated case of the sol–gel method as there might be different routes to obtain the end product M–O–M. Reaction 2.2a is necessary for the occurrence of the subsequent reactions. Reaction 2.2b leads to the formation of water which can lead to hydrolysis, reaction 2.2c produces the reactive species M–OH which can lead to the formation of the M–O–M linkage, while reaction 2.2d leads to the immediate production of M–O–M.

The structure of the TiO\textsubscript{2} electrode is usually based on the deposition of a thin compact layer consisting of small sized particles, on the conductive glass. The applied compact layer blocks the recombination and provides better contact between the conductive glass and the mesoporous layer. The top layers can be transparent, semitransparent or opaque. An alkoxide precursor solution can be used to apply multiple layers to gradually build up the electrode’s final thickness; otherwise a thick layer of TiO\textsubscript{2} paste can be applied to directly complete its thickness. The deposition of each film is
followed by sintering at about 500°C in air to remove the organic residues and to achieve the connection between the nanoparticles. The mesoporous photoanode film can be subjected to surface treatment to improve the power conversion efficiency (PCE) of the solar cell. Materials used for the TiO$_2$ post-treatment, such as the regularly used TiCl$_4$, improve the sensitizer’s adsorption due to the alteration of the structural properties of the photoanode, such as increased roughness [9,10].

**Figure 2.3**: Band gaps and band positions of n-type semiconductors.

Zinc oxide, ZnO, is also a wide bandgap semiconductor used as a photoanode for DSSCs and it has three main polymorphs: wurtzite, zinc–blend and rocksalt. The wurtzite is the most stable form with a direct bandgap of 3.4 eV at room temperature (Fig 2.3) [11,12]. Compared with TiO$_2$, ZnO has higher electron mobility and easier synthesis of nanostructures with high crystallinity and in different structures, such as nanoparticles, nanowires (or nanorods), nanotubes, nanosheets, nanobelts and nanoflowers [13]. The dye adsorption time for ZnO films is substantially lower than the TiO$_2$ films due to the poor chemical stability of ZnO, as it dissolves under acidic and basic conditions. The acidic carboxylic anchoring groups of sensitizers can lead to a partial dissolution of the ZnO film forming Zn$^{2+}$ ions, followed by the formation of
aggregates between the sensitizer and the ions. In case of an increased immersing time of the ZnO films in the sensitizer’s solution, the aggregation effect is promoted, decreasing drastically the solar cell’s power conversion efficiency. This ZnO films’ instability is one of the primary reasons the ZnO DSSCs efficiencies are lying notably lower than their TiO₂ counterparts (7.5% vs. 13%) [14,15].

Tin dioxide, SnO₂, is another n−type semiconductor with a wide bandgap of 3.6 eV (Fig. 2.3) suitable for various applications, such as gas sensing [16], lithium ion batteries [17,18], supercapacitors [19,20] and dye−sensitized solar cells [21]. While SnO₂ has higher electron mobility and a more positive conduction band edge than TiO₂, the DSSCs based on SnO₂ have very low efficiencies [22,23]. The more positive conduction band edge increases the recombination losses limiting the open−circuit voltage and enhancing the dark current reducing the efficiency [24]. Furthermore, the SnO₂ surface has an acidic character, due to its lower isoelectric point, which hinders the dye adsorption, restricting the short−circuit current of the cell [25].

Niobium pentoxide, Nb₂O₅, is an n−type semiconductor with an energy bandgap of 3.4 eV (Fig. 2.3) and a higher conduction band edge than TiO₂ which suggests that Nb₂O₅ solar cells can reach higher open−circuit voltage and power conversion efficiency. The most usual polymorphs for Nb₂O₅ include: pseudohexagonal, orthorhombic, tetragonal and monoclinic, with the monoclinic form to be the most thermodynamically stable and the pseudohexagonal the most unstable. While a power conversion efficiency of 3.05% has been reached for solar cells employing pseudohexagonal Nb₂O₅ photoelectrodes under 1 sun, a higher efficiency of 5% has been reached under lower intensities (0.1 sun) [26,27].

### 2.2.2 Combining or doping semiconductors

One of the most important reasons that the DSSCs haven’t reached even higher efficiencies is the recombination losses. In order to suppress charge recombination the photoanode film can be synthesized by combining different semiconductors in a core−shell structure instead of a pure semiconductor. Capping the photoanode’s surface with another semiconductor can introduce an energy barrier at the photoanode/electrolyte interface, retarding the electron transport and at the same time filling the deep trap states stemming from surface defects. The overcoating layer might also enhance the dye loading increasing the short−circuit current and consequently the DSSC’s power
conversion efficiency. Some of the composite metal oxide photoanode films that have been studied include ZnO–TiO$_2$ [28], TiO$_2$–SnO$_2$ [29], Al$_2$O$_3$–TiO$_2$, MgO–TiO$_2$, TiO$_2$–Nb$_2$O$_5$ [30], SiO$_2$–TiO$_2$ [31], TiO$_2$–ZrO$_2$ [32], Sb$_2$S$_3$–TiO$_2$ [33], ZnO–SnO$_2$, MgO–SnO$_2$, ZrO$_2$–SnO$_2$, Al$_2$O$_3$–SnO$_2$, Y$_2$O$_3$–SnO$_2$ [25].

A different method adopted to alter the chemical, optical and electrical properties of the photoanode is doping the semiconductor with metal (Ce, Mg, Nb, F, Cu, Ag, Au, Pt, Ga, Al, In, Sn, Sb) or nonmetal ions (N, C, S, I, B, P) [34–41]. The surface modification of the anode by doping can tune up the conduction band edge of the semiconductor, reduce the recombination, minimizing the energy losses and improve the charge transfer processes.

2.2.3 Photoanodes’ deposition methods

While there are many coating and printing methods (Fig. 2.4) to apply the solution containing the semiconductor’s precursor, in order to form the photoanode, in this thesis the techniques that were used was one of the following: dip coating (or dipping), spin–coating, doctor blading and inkjet printing. In each experiment, a suitable coating method was selected based on the desired characteristics of the final photoanode film, such as the film’s transparency and thickness.

![Solution deposition methods](image)

**Figure 2.4:** Solution deposition methods [42].

In the dip coating method, the conductive glass is immersed in the semiconductor solution; after a couple of seconds the glass is withdrawn from the solution, it is drained, so that the excess solution is removed and finally it is dried and sintered to complete the formation of one layer of the photoanode film. This procedure is repeated several times
to increase the thickness of the photoanode. While this is a simple technique, it is important to keep the withdraw rate of the glass constant, in order to ensure that all films will have layers with even thickness. Moreover, a rather big amount of solution is needed, in order to make sure that once the glass is immersed in the solution it is going to be sufficient to cover the desirable area and in case the backside of the FTO glass isn’t covered with a tape, cleaning it thoroughly is essential before sintering it.

Spin-coating is a useful laboratory coating method which is used to deposit uniform thin films on glass substrates. Typically, this technique involves depositing a few drops of a solution on a glass substrate and then spinning the substrate in a high speed. The thickness of the wet film which is formed is a complex interplay between the spinning speed (rounds per minute, rpm), the spinning time, the rate at which the solution’s solvent evaporates and in general the physical and chemical properties of the solution (i.e. viscosity). Although spin-coating is a very reproducible method, it’s not suitable for industrial use, as it is difficult to deposit an even film on a large substrate. In addition, it’s a wasteful technique as far as the solution needed is concerned. In reality, most of the solution which is deposited on the glass substrate is ejected from the outskirts of the substrate while spinning and it is lost inside the spin-coater. Nonetheless, it’s an extremely reproducible technique which is used for preparing the majority of the solar cells reported in literature today. For the spin-coating method Spin150, APT Automation was used.

Doctor blading is a coating technique which is used to apply viscous solutions, such as pastes. An amount of the paste was placed on the glass substrate and it was spread on the active area manually using a rod. The thickness of the wet film was determined by using clear scotch tape (Scotch® Magic™ Tape 3M with thickness 62.5 μm) as a spacer, as it can be easily removed from the glass without leaving glue traces.

Inkjet printing is a well-recognized printing technique from the daily home or office use that gradually entered the industrial sector. In this technique, the solution is sprayed out on the substrate through fine nozzles, using a piezoelectric system. There are two inkjet printing systems: the droplet on demand system, where a drop of a few Pico liters of solution is squeezed out whenever wanted, and the continuous droplet system, where droplets are generated at all time and then an electric field is used to deflect them onto the substrate. Inkjet printing is a digital printing technique with a very high
resolution which can be used to print different patterns with no extra cost. In this method, the solution’s rheology and viscosity, as well as the size of the semiconductor particles in the solution are important. The size of the particles in the precursor solution needs to be small; otherwise they will clog up the fine nozzles of the printhead. In the future inkjet printing might be the preferred technique as it is a reproducible technique, suitable for making thin, transparent films in different patterns without additional cost. In this technique, the photoanode films were manufactured using DMP−2800 Fujifilm Dimatix materials printer or DMP−5000 for electrode strips with even larger active area.

2.3 Sensitizers

The sensitizer is one of the crucial elements of a DSSC, as it can significantly affect the solar cell’s power conversion efficiency and long term stability, thus, its characteristics should fulfill certain requirements.

- The sensitizer ought to have a broad absorption spectrum covering the entire visible region (390 nm−700 nm) and extending to a part of the near infrared (NIR) region (700 nm−2500 nm).
- The molecular structure of the photosensitizer should bear anchoring characteristic groups, such as carboxylate (−COOH), dihydrogen phosphite (−H₂PO₃⁻) and hydrogen sulfite (−HSO₃⁻) groups in order for the sensitizer to bind onto the photoanode’s surface.
- In case that a n-type semiconductor is used for the solar cell’s photoanode (n-type DSSC), the LUMO (lowest unoccupied molecular orbital) energy level of the sensitizer’s excited state should be higher than the conduction band edge of the n-type semiconductor so that the electron transfer from the excited dye molecules to the conduction band of the semiconductor is accomplished. In case of a p-type DSSC, the HOMO (highest occupied molecular orbital) energy level of the sensitizer’s excited state should be more positive than the valence band edge of the p-type semiconductor.
- In order for the dye regeneration reaction to take place, the energy level of the dye’s oxidized state must be more positive than the electrolyte’s redox potential.
The dye aggregation on the photoanode must be avoided either by modifying the molecular structure of the sensitizer or by using co-adsorbers to prevent the formation of aggregates, which is going to be elaborated in a later paragraph.

The sensitizer must have thermal, electrochemical and irradiation stability.

Over the past decades and since the overall concept of DSSCs is based on the photosynthetic process occurring in plants, naturally derived dyes and pigments have been extracted from flora organisms and have been tested along with synthetic sensitizers designed to satisfy the previously mentioned requirements. Apart from the natural dyes, sensitizers can be divided into metal complexes, porphyrins, phthalocyanines and organic dyes.

2.3.1 Metal complexes

Metal complex photosensitizers consist of a central metal ion, usually ruthenium (Ru(II)) or less often osmium (Os(II)), rhenium (Re(I)), iron (Fe(II)), platinum (Pt(II)) or copper (Cu(I)), with anchoring and ancillary ligands. The anchoring ligands are the parts of the dye bearing the chromophoric groups and are responsible for the dye’s adsorption onto the photoanodes surface. Ancillary (or auxiliary) ligands aren’t directly involved in the dye’s adsorption but can be used to stabilize the metal complex or contribute to its properties. Thereby, by modifying a part of the complex (anchoring or ancillary) one can attain optimized electron injection, dye regeneration kinetics, alter the photophysical and electrochemical properties of the dyes or adjust the energy levels.

So far, the ruthenium complexes have resulted in cells with high photovoltaic parameters, as they have broad absorption spectrum, good electrochemical stability, suitable energy levels and long excited state lifetime [43]. Two of the most representative Ru(II) complexes dyes, which have been used as a reference for synthesizing new Ru sensitizers, are the dyes abbreviated N3 and N719 (Fig. 2.5). N719 is the result of the deprotonation of two of the carboxylic acid groups of the N3 structure (a hydrogen cation $\text{H}^+$ is removed and replaced with a tetrabutylammonium cation (TBA$^+$)). In the structure of the Z907 dye (Fig. 2.5) two alkyl chains were introduced on the bipyridyl ligand which improved the dye’s thermal stability [44,45]. While the thiocyanate ligands (SCN), which are present in most ruthenium dyes, is an unstable part of the dyes, substituting thiocyanate with other ligands reduces the overall efficiency possibly because of the decrease in the visible light absorption [46,47].
Figure 2.5: (a) cis-Bis(isothiocyanato) bis(2,2’-bipyridyl-4,4’-dicarboxylato ruthenium(II) (known as N3) (b) Di-tetrabutylammonium cis-Bis(isothiocyanato)bis(2,2’-bipyridyl-4,4’-dicarboxylato)ruthenium(II) (known as N719) (c) cis-Bis(isothiocyanato)(2,2’-bipyridyl-4,4’-dicarboxylato)(4,4’-di-nonyl-2’-bipyridyl)ruthenium(II) (known as Z907).

Alternatively, osmium, which is also a platinum group metal (PGM), just like ruthenium, is the very next choice. Osmium (II) complexes possess a more red-shifted metal–to–ligand charge transfer (MLCT) transition that renders osmium sensitizers an excellent option for expanding the spectral response into the NIR region. Yet, the reduced oxidation potential of Os(II) complexes, compared with their Ru(II) analogues, results in a delayed dye regeneration by the $\Gamma^–/I_3^–$ redox couple in most electrolytes, which can facilitate the recombination with the conduction band electron ($e_{CB}$), leading to DSSCs with poor performance [48-51].

Dyes based on rhenium, iron, copper or platinum metal complexes have also been explored as sensitizers for DSSCs, unfortunately with low overall solar to electric conversion efficiencies. Re(I) complexes with benzathiazole ligands were tested and the best obtained efficiency was 1.72%, while solar cells sensitized with newly designed dinuclear hydrido–carbonyl rhenium complexes exhibited a power conversion efficiency of 1% [52-54]. Despite the fact that the main obstacle of the Fe(II)–polypyridine sensitizers is the short lifetime of the photoactive MLCT states preventing the injection of electrons into the conduction band of the semiconductor, recently researchers came up with an iron–based N–heterocyclic carbine sensitizer that possess an injection yield of 92%, whereas Ru complexes have a yield almost 100%, which gives prospect to use earth abundant, environmentally friendly and cheap materials for the sensitization of solar cells [55,56]. In the meantime, platinum and copper complexes are been studied in an attempt to modify their structure in order to improve the photovoltaic performance [57,58].
2.3.2 Porphyrins and Phthalocyanines

Since the report of a 13% record efficiency for a porphyrin–sensitized solar cell (Fig. 2.6), researchers have been stimulated to find new porphyrin dyes that can boost photovoltaic performances to even greater values [15]. Porphyrins are promising sensitizers that exhibit a strong Soret band in the 400–450 nm region and moderate Q bands in the 500–700 nm region [59]. The intrinsic advantages of the porphyrin dyes also include appropriate LUMO and HOMO energy levels, versatile modification of their core and facile tuning of their optical, physical, electrochemical and photovoltaic properties [60]. Different classes of porphyrin dyes have been synthesized and tested in an attempt to optimize the designing strategy for highly efficient DSSCs. Among the various parameters that have been examined in order to investigate how they affect the dye’s characteristics and consequently the solar cells’ performance include the different central metal ions (Zn(II), Cu(II)), the type of anchoring group (−COOH, −PO$_3$H$_2$) and the linker’s length, the position of the anchoring group (meso− or β−position) and modification on the dye’s molecular structure to expand the absorption in the visible region. Porphyrin dyes containing Zn and carboxylate anchoring groups exhibited higher PCE than Cu containing porphyrins and in addition solar cells sensitized with porphyrins containing phosphonate anchoring groups showed lower efficiencies than those with carboxylate linkers [61].

![Figure 2.6: Molecular structure of the porphyrin dye used for the fabrication of DSSC with record efficiency. The dye features a porphyrin core and a bulky bis(2′,4′−bis(hexyloxy) −[1,1′−biphenyl] −4−yl) amine donor and a benzothiadiazole group for acceptor [15].](image)

Phthalocyanines sensitizers, which are structurally related with porphyrins, are interesting dyes that exhibit a moderate Soret band in the 300–400 nm region and intense Q bands in the 600–750 nm region, but they lack of absorption between
400–600 nm [59,62]. They have high molar extinction coefficients in a wide region of the spectrum, promising electrochemical and photochemical properties, excellent thermal stability [59,63]. However, these conjugated macrocycles have poor solubility and thus their structural optimization is obligatory to facilitate the sensitization process [43]. Another major obstacle that hinders the vast use of these light harvesters is the fact that they tend to aggregate on the semiconductor’s surface, which entails the use of co-adsorbers [43,63,64]. The highest efficiency reached so far for a phthalocyanine-sensitized solar cell is 6.01% at 1 sun, in absence of any coadsorber, with the addition of chenodeoxycholic acid as a disaggregation agent [62,65]. The molecular formula of the phthalocyanine sensitizer used to record the highest power conversion efficiency is illustrated in Fig. 2.7. Essentially, remarkable progress could be expected if phthalocyanines are combined with appropriate dyes having complementary absorption spectra to attain DSSCs with panchromatic absorption.

Figure 2.7: Molecular structure of the phthalocyanine dye abbreviated TT40 used to sensitize the most successful phthalocyanines-sensitized solar cell [65].

2.3.3 Organic dyes

Compared with dyes containing metal complexes, organic dyes have many merits, such as simple designing, synthesizing and purifying process, high molar extinction coefficients, low cost and high efficiency. The general structure used for these sensitizers is the Donor–π-bridge–Acceptor structure (D–π–A), where moieties such as triphenylamine, triarylamine, indoline, coumarin and fluorine can be employed as electron donors, carboxylate, cyanoacrylate and rhodamine groups can be used as acceptors and polyene and oligothiophene can be added as the π-bridge [53]. When the
dye molecules absorb the incident light this D−π−A structure can induce the intramolecular charge transfer (ICT) from the donor to the acceptor through the π-bridge (Fig. 2.8) [43,66].

This structure facilitates designing new dyes, incorporate different light-absorbing groups into the organic framework to broaden the light-harvesting region of the dyes from the visible to the NIR region, tune the HOMO and LUMO energy levels and complete the intramolecular charge transfer [67-69]. Thereby, numerous organic dyes with adjusted properties have been used to sensitize DSSCs over the past years. Among them, indoline and triarylamine dyes have demonstrated power conversion efficiencies very close to 10% and over 10.3% respectively, with the latter being a record efficiency for the organic sensitizers [66,70].

Figure 2.8: Schematic diagram of the D−π−A structure of the organic dyes and intramolecular charge transfer for a DSSC.

2.3.4 Natural pigments

Since the operating principle of DSSCs resembles the photosynthesis procedure and the expenses for the sensitizer constitute the largest part of the solar cells' cost, research has been focused on testing natural dyes and pigments extracted from flora organisms, in order to replace the synthetic ones and reduce the total fabrication cost [71-76]. Natural pigments have certain advantages as there are no resource limitations, they don't cause any harm to the environment and are easily prepared [77]. Also, they have high absorption coefficients and light harvesting efficiency [75].

The natural pigments can be classified into three categories (a) chlorophylls, (b) carotenoids and (c) phycobilins [78]. The type of solvent used for the extraction, determines which natural pigment will be isolated. Chlorophylls (a, b, c and d) and carotenoids (carotenes and xanthophylls) are both insoluble in water and so organic solvents must be used to isolate them, whereas phycobilins are water soluble as they are attached to water-soluble proteins [78]. Up until now many natural dyes have been
extracted and tested for sensitizing dye-sensitized solar cells and although employing a natural pigment as a sensitizer doesn’t lead to the fabrication of highly efficient cells, it could be a viable alternative for cheaper manufacturing processes which could further promote the investigation of natural dyes.

2.3.5 Co-sensitization

Co-sensitization is a technique involving the use of two or more sensitizers with appropriate HOMO and LUMO energy levels for the sensitization of the DSSC’s photoanode to broaden the absorption spectrum of the solar cell and thus increase its power conversion efficiency. There are two methods for the co-sensitization procedure: the stepwise sensitization and the dye cocktail method. The stepwise sensitization comprises sequential dipping of the photoanode into each dye solution, so the sensitizers are adsorbed in turn onto the photoanode’s surface. After removing the photoanode from the first dye solution, any vacant spaces of the photoanode will be filled by the dye molecules of the next dye solution. Issues that need to be considered when using this method is the dipping order and time the concentration of the dye solutions and other conditions that may prevent the expansion of the absorption spectrum and consequently the overall efficiency of the solar cell. In the dye cocktail method, a mixture of dyes is used to sensitize the photoanode with all dyes at once. While in this method the only consideration is the mixing ratio of the dyes, the drawback is the competitive adsorption of the dyes used in the mixture and in general the intermolecular interactions between the dyes, which could threaten the efficiency increase [79]. Beside the combination of dyes from the same class, attempts have also been made combining dyes from different categories [80-84].

2.3.6 Co-adsorbers

An alternative strategy to increase the power conversion efficiency of DSSCs is the use of co-adsorbers (or co-adsorbents). In general, co-adsorbers are compounds or ions which are added to the dye’s solution and are adsorbed onto the photoanode’s surface simultaneously with the dye molecules during the sensitization process. Co-adsorbers should possess the following characteristics: a suitable molecular structure to avoid the competitive adsorption among dyes while hindering the dye aggregation, the ability to reduce the recombination of conduction band electrons by forming some kind
of capping layer covering the photoanode’s surface and a large molar extinction coefficient ($\varepsilon$) in the infrared region [85,86].

Co-adsorbers commonly used include cholanic acid derivatives, such as chenodeoxycholic acid and Li$^+$ cations. Chenodeoxycholic acid (Fig. 2.9) is an organic compound which can strongly attach to the photoanode’s surface and affect the dye by preventing the formation of aggregates. The reduction of the dye aggregation increases the electron injection which enhances the photocurrent and improves the solar cell’s efficiency. On the other hand, Li$^+$ cations mostly affect the photoanode. The small size of the Li$^+$ cations expedites their adsorption on the photoanode’s surface that it’s gets positively charged. The presence of the Li$^+$ cations affects the flat band potential of the metal oxide and shifts downward its conduction band edge facilitating the electron injection. However, lowering the CB edge also limits the theoretical maximum voltage generated under illumination, thus a middle ground settlement between the photocurrent enhancement and the minimization of the photovoltage should be considered when using Li$^+$ cations as co-adsorbers [87].

Figure 2.9: Structure of chenodeoxycholic acid.

2.4 Electrolytes

Electrolytes are one of the main components of a DSSC having an essential role for the operation of the solar cell. As previously mentioned in Chapter 1, electrolytes are basically organic solutions containing a redox couple which is responsible for restoring the oxidized molecules to their ground state. It is vital for the smooth operation of the DSSCs the electrolyte to fulfill certain requirements [88]:

- The electrolyte must efficiently transport the charge carriers. As soon as the electron is injected in the CB of the photoanode, the redox couple in the electrolyte must
have the ability to regenerate the oxidized dye molecules to their ground state quickly to hamper the recombination.

- The electrolyte must vouch the fast diffusion of the charge carriers, namely it must have high conductivity and good interfacial contact with the mesoporous semiconductor layer and the counter electrode.

- The electrolyte must have chemical, thermal, optical, electrochemical, interfacial and long-term stability. Moreover, the use of an electrolyte mustn’t lead to desorption or degradation of the adsorbed dye.

- The electrolyte solution should have negligible absorption in the visible light region, so it doesn’t reduce the dye’s light absorption.

Electrolytes can be classified into three categories, based on their state: liquid quasi-solid state electrolytes or solid, an overview of which is going to be unfolded in the upcoming paragraphs.

2.4.1. Liquid state electrolytes

Liquid electrolytes are easily prepared and they possess certain merits compared with the other types of electrolytes, such as high conductivity and low viscosity, which is beneficial for penetrating the electrodes, ensuring good interfacial connection between them and thus DSSCs with high power conversion efficiencies [89,90]. Regarding the solvents used for the liquid electrolyte solutions, they must comply with some prerequisites. Specifically solvents should have low volatility and they should be compatible with the sealing material to avoid degradation of the sealant that could increase the leakage or the evaporation of the electrolyte solution. The use of water or other protic solvents, such as ethanol or other lower alcohols, isn’t proposed because many dyes are prone to hydrolysis [43,89]. Among nitriles, acetonitrile is considered to be a good choice, as it has low viscosity, it dissolves a number of salts and organic molecules and it also has excellent chemical stability. Nitriles containing methoxy groups (i.e. 3-methoxypropionitrile) have also been extensively used for electrolyte solutions, as they exhibit lower toxicity compared with plain nitriles and higher boiling point rendering it unlikely for the electrolyte solution to evaporate under operating conditions even in an outdoor environment [89]. A different approach to prepare liquid electrolytes is by using ionic liquids (ILs) instead of solvents. Ionic liquids are molten salts with low vapor pressure (low volatility), high ionic conductivity, with thermal, chemical and
electrochemical stability. They are also considered having a “greener” character compared to solvents, as they don’t emit volatile organic compounds (VOCs) because of their negligible volatility. Imidazolium containing ILs were the first ones used in electrolyte solutions, but due to their high viscosity, ion diffusion is slow, which negatively affects the electrical parameters of a solar cell (short-circuit current density and efficiency are decreased) [91]. Other types of ILs which have been applied to DSSCs include trialkylsulphonium (R₂R’S), tetralkylammonium (NR₂R₂’), asymmetric phosphonium and pyridinium groups [88,91]. Apart from being used as a replacement of solvents, ILs have also been employed in electrolytes as a solidification medium, which is going to be unfolded in the next paragraph.

### 2.4.2. Quasi-solid state electrolytes

To address the leakage and the sealing problems, as well as the solvent’s volatilization issues of liquid electrolytes, researchers turned their attention to the quasi-solid state electrolytes. Liquid electrolytes can be transformed to quasi-solid state electrolytes by using organic/inorganic materials, polymerizable precursors or ionic liquids [92]. In the beginning, the electrolyte solution must be liquid so that a good pore filling of the semiconductor’s network can be realized and progressively solidify. While the quasi-solid state electrolytes combine the merits of the liquid and the solid-state electrolytes, such as high ionic conductivity and good penetration at the photoanode, DSSCs employing quasi-solid state electrolytes exhibit lower conversion efficiencies compared to solar cells with liquid electrolyte due to limited transport of the redox mediator species [43,90].

The organic/inorganic materials consist of two subphases, the organic subphase (usually surfactants or polyether chains) and the inorganic subphase (silicon dioxide or titanium dioxide). These materials can be divided into two categories depending on the bonds and the interactions formed between the two subphases. Classification I contains simple mixtures of the organic and inorganic materials, where weak bonds and interactions are developed between them. Classification II contains materials which result after strong chemical bonding between the two subphases (hybrid materials). These organic/inorganic hybrid materials often have better properties than Classification I materials [93]. One way to prepare these hybrid organic/inorganic materials is through the sol–gel method previously described in paragraph 2.2.1. As an indication, for the
formation of ureasils, (3-isocyanatopropyl)triethoxysilane (ICS) can be mixed with poly(propylene glycol) bis(2-aminopropyl ether) and tetrahydrofuran in a reflux at 64°C for 6 hours. Between the isocyanate and the amine groups an amine alkylation reaction takes place creating urea bonds that leads to the formation of a ureasil sol–gel precursor (Fig. 2.10) [94].

![Chemical structures of (a) (3-isocyanatopropyl)triethoxysilane (ICS), (b) poly(propylene glycol) bis(2-aminopropyl ether), and (c) the final ureasil sol–gel precursor.]

Polymer gel electrolytes consist of a polymer material (gelator) which can be added in a liquid electrolyte to jellify it. The gelation process is attained through the formation of a self-organized network of the gelator within the organic solvent. There are two distinct cases of polymer electrolytes depending on whether they have or lack the ability to reversibly change their physical state with temperature; in the former case the aforementioned network is destroyed in elevated temperatures and is reformed upon cooling and the corresponding electrolytes are known as thermoplastic polymer electrolytes, while electrolytes in the latter case are known as thermosetting polymer electrolytes [90,95-97]. Some of the polymers that are often used in polymer electrolytes include poly(ethylene oxide) (PEO also known as poly(ethylene glycol) PEG), poly(acrylonitrile) (PAN), poly(vinylpyrrolidinone) (PVP), polystyrene (PS), poly(vinyl chloride) (PVC), poly(vinylidene ester) (PVE), poly(vinylidene fluoride) (PVDF) and poly(methyl methacrylate) (PMMA). One more way to prepare quasi-solid state electrolytes is the use of ionic liquids, where the solidification process starts with the addition of the IL and can be expedited by incorporating a polymer or inorganic material.
to improve the photovoltaic properties of the DSSC [44]. Iodide containing ILs, such as 1-methyl-3-propylimidazolium iodide, can also act as an iodide source in $\Gamma^-/I^-_3$ electrolytes.

2.4.3. Redox couples

The main scope of the redox couple is to transfer electrons from the counter electrode in order to restore the oxidized dye molecules to their ground state. Thus, an appropriate redox shuttle should ensure a fast regeneration of the oxidized dye molecules and a slow electron recombination (reaction 1.5). Moreover, the redox mediator should be soluble in organic solvents and have a high ionic mobility [98]. Until now the most frequently used redox couple is iodide/triiodide ($\Gamma^-/I^-_3$) due to its desirable kinetics’ properties, namely the regeneration of the oxidized dye molecules by $\Gamma^-$ is in the microsecond scale, while the reduction of $I^-_3$ by the injected electrons at the conduction band of the semiconductor is slow, which assures low recombination and high charge collection [43,99]. Despite the advantages that the iodide/triiodide electrolytes are displaying, they also have certain disadvantages. The $\Gamma^-/I^-_3$ electrolytes have a dark amber color and as a result their light absorption is in the blue part of the spectrum limiting the solar cells’ absorption, hence reducing their corresponding current and their efficiency. Moreover, the discrepancy of the redox potential of the $\Gamma^-/I^-_3$ electrolyte and the HOMO levels of typical dyes lowers the DSSCs’ open−circuit photovoltage. Likewise, one shouldn’t avoid leaving out the corrosive effect of the $\Gamma^-/I^-_3$ redox couple with the current collectors of DSSCs modules or the counter electrodes [98].

In order to confront and overcome the aforementioned drawbacks researchers started seeking alternative redox couples. The bromide/tribromide ($Br^-/Br^-_3$) redox system was considered for substituting the $\Gamma^-/I^-_3$ due to its more positive redox potential, which could lead to solar cells with a higher open−circuit voltage ($V_{oc}$). Devices of 5.22% efficiency have been achieved with $Br^-/Br^-_3$ employing electrolyte, nonetheless with comparable corrosive effects as $\Gamma^-/I^-_3$ electrolytes [100]. An exceptional choice for iodine−free electrolytes is ferrocene/ferrocenium (Fe/Fe$^+$) redox shuttle which also has a more propitious redox potential compared with $\Gamma^-/I^-_3$. DSSCs
employing ferrocene/ferrocenium electrolyte exhibit a higher PCE than solar cells with iodide/triiodide electrolyte owing to their higher open-circuit voltage [101]. Cobalt complexes seem to be a viable replacement of the \( \Gamma^-/I^- \) redox couple and so far many different cobalt redox mediators with different ligands have been examined [102]. Researchers were fascinated by the fact that the redox potential of cobalt complexes can be easily synthetically tuned and their noncorrosive character against metal electrodes [103]. Moreover, DSSCs with very high efficiencies (13%) have been reported, displaying increased open-circuit voltage, with the current record efficiency (14.3%) to be achieved by combining co-sensitization processes and Co(III/II) complexes [104,105]. However, the cobalt electrolytes are challenged by some limitations related with stability issues and reduced mass transport [106,107].

Copper complexes have also been tested as redox mediators and although the first DSSCs’ efficiencies were discouraging, high PCEs were recorded (10.3%) by dye optimization, with open-circuit photovoltages higher than 1 V as a result of reduced losses [108,109]. Particularly, recent articles have been published highlighting the promising use of copper shuttles in DSSCs and also trying to fully demonstrate their electrochemical characteristics [110,111]. Other redox mediators that have been employed in iodine-free electrolytes include Ni(III/IV), V(IV/V), \( S^{2-}/S_n^{2-} \), \( SCN^-/(SCN)_2 \), \( SeCN^-/(SeCN)_2 \) and also organic redox couples [112].

2.4.4. Additives

Additives are regularly employed in electrolyte solutions in order to enhance the electrical parameters of the DSSCs. A large number of the compounds tested as additives bear pyridines or other N-heterocyclic compounds, with the most commonly used to be 4-\textit{tert}-butylpyridine (4−TBP). Several papers have been published describing the effect of 4−TBP in TiO\(_2\) and few in ZnO DSSCs, whereas all of them were in regard with \( \Gamma^-/I^-_3 \) electrolytes [113-116]. Briefly, 4−TBP improves significantly the open-circuit voltage of the solar cells which is an important parameter affecting notably the cells’ overall efficiency, while the corresponding short-circuit current remains unaffected or slightly reduced. 4−TBP is adsorbed on the surface of the photoanode, blocking the reduction sites and decreasing the direct contact between the semiconductor’s nanoparticles and the triiodide ions, suppressing in turn the recombination processes. Moreover, the
addition of 4–TBP negatively shifts the conduction band edge of the semiconductor limiting the incident photon to current efficiency in the red part of the spectrum. [113,115].

Another frequently used additive is guanidine thiocyanate (Guan SCN) which has the opposite effect than 4–TBP. Guan SCN positively shifts the conduction band edge of the semiconductor, suggesting that it is adsorbed onto its surface, increasing the electron injection rate [43,114,117]. Also, when Guan SCN is added in the electrolyte solution it reduces the recombination, followed by a sequential dark current suppression, all of which improves the open–circuit voltage [114, 118]. The synergy of 4–TBP and Guan SCN can be ensured by adopting an optimized ratio between them reaching the maximum $V_{OC}$ and the optimum overall DSSCs’ efficiency [119].

2.4.5. Hole conductors

Though it is widely recognized that quasi–solid state electrolytes have certain advantages compared with their liquid counterparts, the solvent’s evaporation at high temperatures, along with the long term stability of the cells are still matters of concern. HTMs are p–type materials that can potentially be used in solid state solar cells replacing the electrolytes. The features that the hole conductors should have are similar to those of electrolytes. Namely, the HTMs shouldn’t absorb in the visible spectrum, they ought to have a HOMO level above the ground state of the absorber, good hole mobility and pore filling and an amorphous nature [120]. These materials can be divided into two categories based on their compositional parts: organic or inorganic hole conductors [43,121].

The organic hole conductors can be further classified into conducting polymers and small molecule HTMs. Conducting polymers, such as Poly(3-hexylthiophene-2,5-diyl) (P3HT), Poly(triaryl amine) (PTAA) and Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) (Fig. 2.11) can be easily deposited by simple spin–coating techniques, however their main disadvantage is that the size of the polymer chain may limit their penetration inside the pores [122]. Small molecule organic HTMs, such as the state of the art $\text{N}_2\text{N}_2\text{N}_2\text{N}_2\text{N}_7\text{N}_7\text{N}_7\text{N}_7$-octakis(4-methoxyphenyl)-9,9'-spirobi[9H-fluorene]-2,2',7,7'-tetramine (Spiro-MeOTAD) (Fig. 2.12), are also regularly used. Due to their low hole mobility, the addition of certain compounds in their solutions is rather common. Except the 4–TBP additive, the effect of which was
previously described, lithium Bis(trifluoromethane)sulfonimidate (Li−TFSI) is employed to enhance the cell’s efficiency. Li−TFSI downward shifts the CB edge of the metal oxide increasing the electron injection and as a result the solar cell’s current density.

Figure 2.11: Chemical structures of conducting polymers (a) P3HT (b) PTAA and (c) PEDOT:PSS.

On the contrary, inorganic HTMs, such as copper iodide (CuI), copper thiocyanate (CuSCN) and nickel oxide (NiO), have high hole conductivities, can be easily synthesized with low cost and they don’t have stability issues, mainly seen when organic HTMs are used [120,122]. Over the years, solid state solar cells (DSSCs and PSCs) with various inorganic HTMs have been reported, exhibiting high efficiencies [123].

Figure 2.12: Chemical structure of small molecule organic HTM Spiro-MeOTAD.

2.5 Counter electrodes

The primary role of the counter electrode (CE) is the reduction of the redox species which are contained in the electrolyte solution. In case of an electrolyte solution employing iodide/triiodide redox couple, triiodide is reduced to iodide according to reaction 2.3.
$I_3^- + 2e^- \rightarrow 3I^-$  \hspace{1cm} (2.3)

Throughout the years, extensive research has been devoted to different kinds of counter electrodes like platinum, carbon materials, conducting polymers and alternative materials. The selection of the counter electrode can be dictated by the redox couple of the electrolyte or the intended application of the DSSCs or even the transparency, the stability and the cost of the solar cell. For example, in case of a DSSC intended to be integrated as a photovoltaic window, a transparent counter electrode must be employed, with small sheet resistance to maximize its performance. However, in case the aim is to manufacture low cost solar cells, one must consider using low cost counter electrodes such as carbon materials [124,125].

2.5.1 Platinum

Platinum (Pt) is the most commonly preferred electrocatalyst for DSSCs, as the CE films have high electrical conductivity, thermal stability and corrosion resistance and low resistance in the CE/electrolyte interface. There are several deposition techniques, such as thermal decomposition, electrodeposition, spray pyrolysis, vapor deposition and sputtering, some of which are not suitable for the fabrication of flexible DSSCs, others they require large amount of expensive platinum, while others have as a result CE films with low transparency [124-126]. So far, the best performance and long-term stability has been reported for platinum metal clusters deposited by thermal decomposition [127].

2.5.2 Carbon materials

Carbon materials are an attractive alternative to replace platinum, due to their good catalytic activity for triiodide reduction, electrical conductivity, thermal stability, corrosion resistance towards iodine and large surface area which are combined with the merit of reduced cost. Various carbonaceous materials have been studied so far as counter electrodes, such as carbon black, carbon nanotubes, graphene, graphite and activated carbon with satisfactory results. A power conversion efficiency of 6.7%, for a cell with a monolithic geometry, employing a counter electrode from a mixture of graphite with carbon black, was the first reported result of using carbon materials [128]. Moreover, other results have been published reporting carbon black coated graphite CEs with 0.2 mm thickness prepared by spin–coating which had an efficiency of 6.46%, which was even higher than the corresponding efficiency of platinum CE (6.37%).
prepared through thermal decomposition [129]. Additionally, graphene based composite materials have been studied. DSSC with Pt/graphene CE have achieved higher efficiency (7.88%) than DSSC with common Pt cathode (6.51%) [130]. Despite that, the power conversion efficiency and the fill factor of cells employing carbon materials as CE depend greatly on the thickness of the CE, and although they are low cost materials, a large amount of them is required in order to ensure the catalysis process, while their long term stability can be jeopardized by the poor adhesion of carbon films on the substrate [124,125,131,132].

2.5.3 Conducting polymers

Conducting polymers is another class of promising materials that can be used as counter electrodes for solar cells, due to their high conductivity and catalytic activity, stability and easy synthesis [133]. Poly(3,4-ethylenedioxythiophene) (PEDOT), polyaniline (PANI) and polypyrrole (PPy) are some of these polymers that have been more frequently employed as CE. The main advantages of PANI CEs are that they have higher catalytic activity towards $\Gamma^-/\Gamma$ and lower resistance in the CE/electrolyte interface than platinum CEs. Also, results of solar cell with PANI CE have been reported with power conversion efficiency as high as 8.8% [134]. However, the main issue that still remains is the deposition of uniform films with satisfactory surface area and adequate conductivity. PPy is another material that can replace platinum owing to its good catalytic ability, low cost, stability and simple synthesis. The higher efficiency reached so far is 7.66% for a solar cell with CE from PPy nanoparticles prepared through a synthetic chemical method [135]. Yet the performance of the PPy CE solar cell highly depends on the synthesis method of the CE and its morphology and PPy films have high resistance corresponding to the CE/electrolyte interface and lower conductivity compared with other materials. PEDOT has a high conductivity and catalytic activity as well as thermal and chemical stability. PEDOT can also be doped with a polyanion, such as polystyrenesulfonate (PEDOT–PSS), in order to work better with aqueous electrolytes. Unfortunately, the cost of PEDOT is comparable with that of platinum and solar cells with PEDOT CEs and $\Gamma^-/\Gamma$ electrolyte have poor performance, as PEDOT forms charge transfer complexes with iodide. Thus, in case of solar cells with PEDOT counter electrode, an electrolyte with a non–iodide redox couple should be employed [131-133].
2.5.4 Alternative materials

Many inorganic compounds, such as metal sulfides, nitrides, carbides, oxides, selenides and phosphides, have also been investigated and identified as possible catalysts [131,132]. High power conversion efficiencies have been reached with numerous of these inorganic compounds, such as nickel–cobalt sulfide (NiCo$_2$S$_4$) with PCE 6.14% [136], titanium nitride nanotube arrays (TiN) with PCE 7.73% [137], titanium carbide (TiC) with PCE 6.50% [138] and tungsten oxide (W$_{18}$O$_{49}$) with PCE 7.94% [139].

2.6 Contacts

The contacts for the current collection were mainly made using a silver paste (Agar Scientific electrodag 1415 G3692) with a sheet resistance lower than 0.015 Ω/□ at 25 μm coating thickness. In some cases where large area DSSCs were examined, a copper conductive foil tape (Kemtron 9115−6 with 13 mm width and 1−1.5 Ω resistance) was used instead of the silver paste, to limit the total fabrication cost. In general, unless otherwise specified, the silver paste was used for the contacts of the solar cells.
References


Chapter 2


Chapter 3 Individual materials development for PSC

3.1 A brief introduction

As earlier stated, perovskites are semiconductors represented by the formula AMX₃. The A cation can be an organic amine derivative (methylammonium–MA, CH₃NH₃⁺ or formamidinium–FA, CH(NH₂)₂⁺), an inorganic cesium ion (Cs⁺) or a mixture of them, M is also a cation, usually Pb²⁺ or Sn²⁺ and X is an anion, usually I⁻, Br⁻, Cl⁻ or a combination of them. Perovskites form a MX₆ octahedron, where M is in the center and X at the vertices of the prism (Fig. 3.1). Several of these octahedra form a more complex network where each vertex of the prism is connected with a vertex from an adjacent prism and the A cation is located in the center of this lattice [1]. This A−site cation must fit through the space created by the four connected octahedra which suggest that its dimensions can’t be unlimited large.

![Figure 3.1: Ball−and−stick model of cubic perovskites [1].](image)

Perovskites can form different crystalline phases (cubic, tetragonal, orthorhombic) with three, two, one or zero−dimensional structures [1,2]. In some cases, which depend on the size and nature of the perovskite’s components, the interactions between the A−site cation and the MX₆ octahedra and the temperature, the ideal cubic structure of the perovskites (Fig. 3.1) can get distorted, altering its physical properties [1,3-5]. Specifically, among these properties, the bandgap and the color of the perovskite can be tuned by changing its composition, for instance by simply altering the halogen used or the ratio between halogens, in case of mixed halide perovskites [6,7]. Moreover,
perovskites often have a polycrystalline structure which can be easily attained by simple thin−film deposition procedures.

3.2 An overview of early perovskite reports in photovoltaic cells

The perovskite solar cells have emerged in 2009 as a new class of third generation photovoltaic cells and though the first results could be described as slightly discouraging, compared to those anticipated due to the unique properties of the perovskites, it didn’t take long until the first efficient PSCs were launched in 2012. The first reports about the perovskite compounds on solar cells were related to their use as visible light harvesters, instead of sensitizers or quantum dots, due to their optical properties. In contrast to what was earlier stated in Chapter 1, in regard to the monolithic design which is now the exclusive structure used for manufacturing perovskite solar cells, the first PSCs employed separate conducting glasses for the deposition of the photoanode and the cathode, just as in DSSCs and QDSSCs [8-10]. These PSCs also included an electrolyte solution, containing an iodide or a bromide redox couple and a platinum counter electrode. Albeit their efficiencies ranged between 2.4%−6.5%, their stability was poor due to the presence of the electrolyte solution.

Since 2013 rapid progress has been made, further increasing their efficiencies and paving their way for future progress which could highlight their paramount role. This sudden advance was strongly associated with the fact that the researchers adapted the structure of the PSCs to monolithic. Their formation, including the materials used and the procedures followed, will be developed in the upcoming paragraphs. Since both dye−sensitized solar cells and perovskite solar cells are third generation solar cells, some of their structural units are common. As a result, a number of them, such as the conducting glass substrates, some of the semiconductors used for the formation of the photoanode and the HTMs have been presented in depth in the previous Chapter. Thus, this Chapter will emphasize in the rest of the materials needed for the fabrication of the PSCs and primarily to the perovskites.
3.3 Monolithic perovskite solar cells

The monolithic perovskite solar cells can be distinguished into different categories based on the morphology of the ETL or which layer the incident light first reaches (Fig. 3.2). In the first case the PSCs are classified into mesoscopic (mesostructured, sensitized) or planar (thin film) solar cells depending on whether the ETL is mesoporous or compact respectively. In the second case the PSCs are classified into regular (n−i−p) or inverted (p−i−n) solar cells depending whether the light beams encounter first the electron transport or the hole transport layer (HTL) respectively. The mesoscopic PSCs (pore diameter 2 nm−50 nm) have a relatively thick mesoporous ETL, while planar PSCs have a thinner and compact ETL. The pore filling of the perovskite, as well as its morphology and crystallinity are strongly dependent on the thickness of the ETL [11,12].

Figure 3.2: Mesoscopic (a) n-i-p and (c) p-i-n and planar (b) n-i-p and (d) p-i-n perovskite solar cells’ structures.

A certain particularity found in the p-i-n structured PSCs is that the ETL is deposited after the deposition of the perovskite, which suggests that low temperature fabrication methods must be adopted for the ETL in order to prevent the perovskite’s decomposition [13]. As a result an organic electron accepting material is used, instead of a metal oxide as the ones reported for DSSCs. These organic materials include a wide
variety of fullerene (C$_{60}$) and its derivatives such as [6,6]-phenyl-C$_{61}$-butyric acid methyl ester (PC$_{61}$BM) [14-16].

In order to manufacture monolithic PSCs the conductive glasses must be patterned before cleaning them and depositing the films. There are a number of techniques for etching, such as laser scribing (vanadate laser, Nd:YVO$_4$ or Nd:GdVO$_4$, Nd:LuVO$_4$) or chemical etching [17,18]. The former is an expensive technique as it requires special equipment and while it ensures a higher precision, the latter can be easily used for simple patterning (i.e. linear patterns), with very low, almost zero cost and thus is the one usually preferred for solar cells. The chemical etching is done by using concentrated or diluted hydrochloric acid (HCl) and zinc powder (Zn).

![Diagram of perovskite solar cells](image)

**Figure 3.3:** (a) Mesoscopic and (b) planar perovskite solar cells with branches.
Chapter 3

After determining the pattern, the area of the conducting glass that won’t be etched can be covered with insulating tape or any other kind of tape which is resistant to acid to protect the conductive substrate. Once this preparation step is completed a small amount of Zn powder can be spread uniformly on the part of the glass that will be etched before starting to drop the HCl acid. An exothermic reaction takes place between these two materials described by the following reaction.

\[
\text{Zn} + \text{HCl} \rightarrow \text{ZnCl}_2 + \text{H}_2
\]  

(3.1)

The removal of the conducting substrate can be optically detected and also can be verified by measuring the resistance of the glass with a multimeter set in the resistance mode. The glasses can be cleaned and prepared for the following fabrication steps. As an example, a detailed image of the completed structure of n-i-p mesoscopic and planar PSCs with three branches is presented in Figure 3.3.

3.4 Electron transport materials for PSCs–doping and combining them

The most frequently used electron transport materials (ETMs) for PSCs are the same metal oxides which are also primarily used in DSSCs as photoanodes and were presented in the previous Chapter. Except the anatase TiO\textsubscript{2} that is basically the metal oxide of choice for most of the third generation solar cells, it might came as a surprise that the insulating Al\textsubscript{2}O\textsubscript{3} has successfully replaced the mesoporous n-type semiconductor film at PSCs. The PSCs which employ the wide band gap Al\textsubscript{2}O\textsubscript{3} (7 eV–9 eV) also have an underlining thin compact layer of TiO\textsubscript{2}. The alumina film simply works as a scaffold for the deposition of the perovskite [19]. Clearly, the perovskite’s photogenerated electrons cannot get injected to the CB of Al\textsubscript{2}O\textsubscript{3} so they remain at the perovskite through which they are transported, while the holes are transferred to the HTL. It has been established that the electron transport through the perovskite is faster compared to TiO\textsubscript{2} and that the charge collection is faster in Al\textsubscript{2}O\textsubscript{3} based PSCs. Moreover, they exhibit improved open−circuit voltage, with reported values even higher than 200 mV, which significantly contributes to their power conversion efficiencies.
Following the same principles as in DSSCs, it can be assumed that doping the ETM or combining it with an additional layer can improve the device’s performance. Doping the ETM can enhance the electron transport or lower the CB edge of the anode to facilitate the electron injection. Metal ions that have been deliberately inserted into the TiO$_2$ lattice to modify its properties include Nb$^{5+}$, Y$^{3+}$, In$^{2+}$ and Li$^+$ [20-23]. In particular, lithium doped TiO$_2$ PSCs have demonstrated prominent electronic properties with high power conversion efficiency [24]. Likewise, the combination of two or more metal oxides can alleviate the recombination by reducing the energy-level mismatch or by passivating the surface defect sites [25,26]. Both mechanisms can improve the device’s performance since limiting the recombination raises the short-circuit current density and the fill factor and suppresses the dark current which elevates the open-circuit voltage. Though the combination of ETMs has been investigated in depth in solar cells and photocatalysis, the only puzzling aspect of this topic still remaining is that in literature there are many different terms used to describe the top layer deposited over the photoanode (passivating layer, barrier layer) or the combination of them (bilayer, complex or composite ETL).

As far as inverted PSCs are concerned, due to the requirement of low temperature procedures for the deposition of the ETM, attention has been drawn to organic materials which are already well known from their use in organic photovoltaics (OPVs). However, the use of these materials for the fabrication of efficient solar cells comes along with certain challenges. PCBM has an energy level mismatch with the metal contacts which affects the electron extraction and in order to overcome this obstacle the use of an additional layer over PCBM is necessary (i.e. C$_{60}$/2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP), TiO$_x$, ZnO, LiF) [27-31]. Similarly, the formation of a uniform thin film of pristine fullerenes such as C$_{60}$ or C$_{70}$ through solution deposition processes is difficult because they have low solubility in common organic solvents and tend to aggregate during the drying step [32]. Therefore, it is really complex to choose an appropriate ETM and a suitable deposition process to manufacture stable PSCs with high overall efficiencies.

### 3.5 Perovskites

The outstanding performance of the PSCs is, to a large extent, due to their high open-circuit voltage, which results from the high energy bandgap of the perovskite compounds (AMX$_3$). The perovskite’s energy bandgap, determined by the energy
difference between the valence band maximum and the conduction band minimum, varies depending on the cation at the A and M positions and the anion at the X position. Therefore, the perovskite’s bandgap can be tuned by substituting the halide anion, as it alters the position of the VB maximum \[7,33\]. Changing the cations employed at the A and M site of the perovskite compound can affect its crystal structure, modifying indirectly the energy bandgap, or shift the conduction band respectively \[34\].

Key role on the optoelectronic performance of the devices plays the diffusion length, \(L_{\text{d}}\), of the perovskite’s carriers. The diffusion length of electrons or holes describes the distance that a carrier can travel before extraction or recombination and it can be calculated from the following equation

\[
L_{\text{d}} = (D \cdot \tau)^{1/2}
\]

where \(D\) is the diffusion coefficient and \(\tau\) the charge’s lifetime. The carrier diffusion length can range depending on the perovskite, as well as the defects or the grain boundaries of the corresponding film. Long diffusion lengths can boost the PSCs’ fill factor and PCEs to high values. The methylammonium (MA) lead triiodide perovskite absorber \((\text{CH}_3\text{NH}_3\text{PbI}_3)\) has an electron–hole diffusion length of about 100 nm, whereas the diffusion length of the mixed halide (I/Cl) perovskite \((\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x)\) exceeds 1 \(\mu\)m \[35\]. Stuningly the carrier diffusion length of \(\text{CH}_3\text{NH}_3\text{PbI}_3\) single crystals surpassed 175 \(\mu\)m under one sun illumination \[36\]. A crystalline solid material is formed by a periodic distribution of its atoms. When this periodic distribution of the atoms is carried out in one single way this crystalline material is called single crystal or monocrystalline material and they can form continuous films with no grain boundaries. The effect of the replacement of the A site cation on the diffusion length of lead iodide and lead bromide perovskites has also been investigated \[37,38\]. Remarkably, the diffusion lengths of electrons on lead bromide perovskites (MAPbBr\(_3\), FAPbBr\(_3\), CsPbBr\(_3\)) were an order of magnitude shorter than that of holes. Long carrier diffusion lengths have also been acquired for tin perovskites \[39,40\].

### 3.6 Perovskite’s fabrication

The fabrication of solution processed perovskite films can be carried out by a single step (one-step) or a sequential (two-step) deposition method. The spin-coating
technique is perhaps the most widely adopted solution deposition process as it has limited cost compared with other techniques, i.e. vacuum vapor deposition methods. Our interest is going to be focused only on this technique as it's the one that is going to be exclusively used in the experimental methods of the PSCs. In lead perovskites, the one-step deposition process involves the preparation of a solution containing the lead salt (PbX₂) and the organic methylammonium or formamidinium halide or the inorganic cesium halide, dissolved in anhydrous γ-butyrolactone (GBL), N,N-dimethylformamide (DMF), dimethyl sulphoxide (DMSO) or a mixture of two of them. This solution is then deposited onto the substrate (ETL or HTM) forming the perovskite film, followed by a drying in order to convert it to its final form. The transition from the initial precursor perovskite film to the final one can be visually perceived as the color gradually changes from yellow to dark grey/brown.

The sequential deposition method involves the preparation of two separate solutions; one containing the lead salt (PbX₂) and the other one containing the methylammonium, the formamidinium or the cesium halide, dissolved in an alcohol, usually ethanol or 2-propanol. The PbX₂ precursor material isn’t easily dissolved in the solvent, thus the solution must be kept at 70°C to expedite its dissolution. The deposition of the first solution is followed by a drying step. As soon as the second solution is dropped onto the PbX₂ substrate the film darkens suggesting the formation of the perovskite at the interface of the two materials. A loading time is required before spin-coating the second solution in order for the organic or inorganic halide to penetrate deeper into the underlying PbX₂ film and facilitate their reaction [41]. In an effort to optimize the perovskite films, the effect of the loading time on the structural and electronic properties of the perovskite, as well as on the performance of the PSCs has been studied [42]. Finally, the perovskite formation via the two-step deposition method is completed by a drying step.

3.6.1. Morphological control of perovskite films

In order to attain high performance PSCs, major attention must be devoted to the morphology of the perovskite films for the fabrication of uniform thin films, with complete surface coverage and absence of pinholes. The morphology of the perovskite film is highly dependent on the crystallization of the perovskite (nucleation and growth). The perovskite’s crystallization starts to occur during the deposition process and it
depends on the evaporation rate of the solvent used in the perovskite’s solution (boiling point) and the spin–coating settings (speed, acceleration, time). The crystallization can progress by speeding up the solvent’s evaporation through the introduction of an inert gas flow during the deposition method [43,44].

The morphology of the perovskite film can be modified by using either solvent engineering or solvent annealing. The solvent engineering procedure (also known as solvent treatment or antisolvent dripping) can be applied to improve the grain growth, the perovskite’s crystallization and ultimately its morphology. Firstly the perovskite solution is casted over the active area followed by spin–coating. Several seconds before the spin–coating program is completed a solvent is dripped on the substrate; this solvent mustn’t dissolve the precursor perovskite materials and must be able to form homogeneous mixtures with the solvents used for the perovskite solution. Toluene and chlorobenzene meet the above criteria and can be used in this process to launch the perovskite’s crystallization which will be finalized after the thermal annealing [45,46]. In the solvent annealing process, the perovskite’s film morphology is improved by eliminating the grain boundaries. The perovskite films are thermally annealed in solvent vapor atmospheres and some of the solvents that have been tested are DMF, DMSO, n-propanol and acetone [47]. In the sequential deposition, it is unlikely that all the lead salt is going to react with the organic or inorganic halide to fully transform into perovskite [48]. Hence, the solvent annealing technique can enhance the conversion of the lead salt to perovskite contributing in the manufacture of PSCs exhibiting high PCEs [47].

3.6.2 Instability of perovskite compounds

All perovskite compounds are more or less susceptible to ambient conditions, such as moisture, ultraviolet (UV) light, oxygen and temperature, with the most detrimental being moisture. Taking as an example the methylammonium lead triiodide compound the deterioration can be described by the following reactions [49,50]. Reaction 3.3 describes the decomposition of methylammonium lead triiodide, in the presence of moisture (H₂O), to the materials from which it was originally produced (CH₃NH₃I, PbI₂). Then, CH₃NH₃I dissociates to CH₃NH₂ and HI aqueous solutions (reaction 3.4) and the produced HI can finally react either with oxygen, producing iodine and water molecules (reaction 3.5a) or photodegrade to hydrogen and iodine molecules (reaction 3.5b). Indicatively, methylammonium lead triiodide PSCs demonstrate low
degradation at humidity lower than 50%, whereas the procedure is speeded up when the relative humidity is over 55% [6]. Evidently exposing the perovskite compounds or the PSCs simultaneously to two or more of the factors responsible for their instability can accelerate the degradation process [51-53].

\[
\text{CH}_3\text{NH}_3\text{PbI}_3(s) \leftrightarrow \text{PbI}_2(s) + \text{CH}_3\text{NH}_3\text{I(aq)} \quad (3.3)
\]

\[
\text{CH}_3\text{NH}_3\text{I(aq)} \leftrightarrow \text{CH}_3\text{NH}_2(aq) + \text{HI(aq)} \quad (3.4)
\]

\[
4\text{HI(aq)} + \text{O}_2 \leftrightarrow 2\text{I}_2(s) + 2\text{H}_2\text{O} \quad (3.5a)
\]

\[
2\text{HI(aq)} \xrightleftharpoons[ hv ]{ } \text{H}_2 \uparrow + \text{I}_2(s) \quad (3.5b)
\]

Combining I with Br or Cl, forming mixed halide perovskite compounds, seems to improve the stability in terms of humidity, although without totally obstructing its effect [53]. Cesium trihalide perovskites are reported to be more stable to the environmental degradation, therefore except mixing the halides, combining different cations is an additional approach towards achieving thermally and structurally stable perovskite compounds [6,54]. Moreover, the use of UV filters can almost diminish the degradation of PSCs demonstrating nearly constant short-circuit current density for over 1000 h of continuous illumination [55]. Ultimately, the deposition of a buffer layer and/or the use of encapsulation seem to be a prerequisite to establish a long term stability [49,56].

### 3.6.3 Toxicity of perovskite materials

Beside the long term stability issues lingering the commercialization of PSCs, the toxicity of lead incorporated in some materials is also an inhibitory factor. Lead and lead compounds are very toxic pollutants that enter the food chain through plant uptake. When lead concentration in a human body exceeds the safe levels, most lesions are concentrated to the neurological and cardiovascular system [57,58]. Particularly susceptible to the severe damages that lead can cause are embryos, children and women. Specifically embryos and young children may show developmental delay, reduced performance, concentration disorders and behavioral changes. Furthermore, pregnant women are very prone to the exposure to high Pb concentrations, which can lead to spontaneous abortion, stillbirth, pre-term delivery or low birth weight of the fetus [59].
The main concern for the environmental impact of the PSCs (manufacturing, operating, disassembly and disposal phase) lies in the fact that for the synthesis of perovskite compounds lead halide salts are extensively used. These lead salts are partially soluble in water with chloride being more soluble than bromide and bromide more soluble than iodide (Cl$^-$>Br$^-$>I$^-$). The perovskite compound of a perovskite solar cell or module operating under ambient conditions can degrade or decompose due to its interaction with external factors (presence of water or moisture, oxygen, UV light, temperature) even if the cell or module is encapsulated. A defective encapsulation or a breach at it isn’t unlikely; this can provide a pathway for the moisture to insert, dissolve the perovskite followed by the production of lead salts. These harmful compounds will eventually reach the soil contaminating it and finally will end up in the aquifer polluting the water.

Thus, reducing or eliminating the use of lead compounds in PSCs is the long-term goal of the scientific community. Towards this direction tin and germanium based perovskites have been tested as viable alternatives [60-62] although they have instability issues due to their oxidation states. Other potential replacements for lead free perovskites could be bismuth or antimony which has a similar distribution of electrons [63,64].

3.7 Buffer layers

Extended research has been devoted to buffer layers which can functionally improve the PSCs through various ways. Buffer layers can obstruct the formation of shunt paths which can adversely affect the fill factor and the open-circuit voltage of the PSCs. Moreover, a homogeneous coverage of the perovskite film with a buffer layer can protect the perovskite from the HTL. The solutions of the HTMs often employ additives, such as 4−TBP and lithium and/or cobalt salts that regardless their positive impacts in some of the PSCs’ parameters, they also come with some negative effects. In fact, 4−TBP is a polar solvent, similar to GBL, that can disintegrate the perovskite and also lithium and/or cobalt salts can damage Sn-based perovskite films, leading to poor functioning devices [16,65,66]. Equally, the addition of a buffer layer can protect the perovskite film from humidity expanding the long term stability of the PSCs. The buffer
layers can also form a porous film to assist in the deposition of the HTL. As a result the hole transport can be facilitated and the charge recombination can be confined.

The most typical choice for a buffer layer, between the HTL and the perovskite film, is aluminum oxide ($\text{Al}_2\text{O}_3$) even though there are many other materials that can also be used, some of which include montmorillonite, graphene oxide (GO) and molybdenum disulfide ($\text{MoS}_2$) [56,67-70]. The thickness of the buffer layer should be small so that the solar cell’s resistances remain unaffected [56]. On the contrary, an increment of the total resistance would have a negative effect on the electrical parameters, reducing the open-circuit voltage and the fill factor of the solar cell. In essence, employing a thin buffer layer is crucial in order to prevent the recombination, to improve the electrical response of the cell and elongate the PSC’s stability by confining the interaction of the perovskite layer with moisture and oxygen.

3.8 Hole transport materials

Most of the materials that are used to form the hole transport layer in PSCs are the same as the ones that are used in solid state DSSCs as hole conductors, again with the use of additives (cf. subsection 2.4.5). Still, an equally important group of materials that has been tested as HTM in PSCs is phthalocyanines, which are already known from their use in DSSCs as light harvesters. While phthalocyanines have photochemical and electrochemical stability they are being challenged with aggregation issues. Even so, these issues don’t constitute a problem for HTMs and also phthalocyanines can be sublimated instead of being deposited via solution processed methods (i.e. spin-coating), though in this case no additives can be used. Therefore a number of Cu(II) and Zn(II) phthalocyanines have been synthesized and investigated as HTMs [67,69,71-76]. The resulting PSCs exhibited low to moderate efficiencies, then again with the possibility of improvement by changing the buffer layer, modifying the phthalocyanine or mixing it with other HTM, such as Spiro-MeOTAD [69,72-76].

Since perovskite materials are ambipolar charge conductors, the HTL can be eliminated simplifying the assembling process and reducing the fabrication cost. HTM free PSCs have been manufactured and studied paying much attention to creating perovskite films with no defects (i.e. pinholes) to prevent the formation of shunt paths.
In these PSCs different approaches were considered and tested in order to fabricate efficient solar cells, such as solvent treatment and the application of an insulating layer over the ETL [77-79]. The PSCs employed a carbon black counter electrode and displayed mediocre efficiencies (10%−12%) but given that they were manufactured under ambient conditions the results were reasonable [77-79]. Another report describes the use of Cu cathode for PSCs without a HTM. Those cells had low efficiency however after storing them in a drying cabinet for several days, the corroding perovskite reacted with the copper cathode forming the CuI, which improved the PCE to some extent [80].

3.9 Counter electrodes and contacts

The most commonly used materials as counter electrodes for PSCs are gold (Au), silver (Ag), aluminum (Al) and carbon materials (i.e. graphite, carbon black). The deposition of Au, Ag and Al can be carried out by solution processes but usually is performed by placing the solar cells into a high vacuum chamber where an amount of the metal is sublimed and the desired pattern can be attained by using a mask. While PSCs with Au counter electrode are the most efficient, the high cost of the CE increases tremendously the total manufacturing cost. On the other hand, Ag and Al might be cheaper but the efficiency of the corresponding PSCs is lower and reduces even more dramatically over time [81,82]. Carbon materials are thought to be a promising choice for electrodes because they are low cost, abundant and water−repelling materials that can extend the stability of PSCs. Many types of carbon electrodes have been applied and tested, even in HTM free PSCs, and while the procedures for synthesizing these materials might be complicated, their deposition is simpler ordinarily by screen−printing techniques [83,84]. As far as the contact for the current collection is concerned, it can be made using the same material and deposition method as the one that is used for the counter electrode or simply by using a silver paste.

3.10 Hysteresis in PSCs

Except the instability and the toxicity of the perovskite materials, it is typical for the completed perovskite devices to be also faced with hysteretic behavior. Hysteresis is
observed at the current density–voltage characteristic curve and it is manifested as an
improvement in the performance of the cell on the reverse scan (from open–circuit to
short–circuit state) compared to the forward scan (from short–circuit to open–circuit
state). The predominant difference that can be identified is in the fill factor of the PSC in
the region adjacent to the maximum power point exhibiting an increased current density
in the reverse sweep. Owing to this response, calculating the overall efficiency of a PSC
with accuracy has been a concern from the beginning of their emersion.

Several origins for the J–V hysteresis have been suggested but this behavior is still
debatable and not fully determined. Some of these possible origins are the ferroelectric
polarization of perovskite, the high density of trap sites and the ion migration within the
perovskite film [85,86]. Beside the scan direction, the hysteresis depends on a number of
parameters such as the cell’s architecture, the voltage range and the scan rate [87-90]. The
extent of the hysteretic behavior is very affected by the scan rate and it is more
prominent at medium scan rate [88,90]. The voltage change cause dynamic processes (i.e.
ion migration) and so by selecting a low scan rate can provide enough time for these
processes to be resolved before measuring the corresponding current, leading at the same
time to a recession of the PSC’s hysteresis. A different approach for limiting the
hysteresis could be choosing a high scan rate. In that case, the dynamic processes which
are caused by the bias change won’t be completed before the corresponding current is
measured. In other words the dynamic processes won’t influence the measurement and
the hysteresis will be negligible, but the J–V characteristic curve won’t be a
representative response of the device [91]. Furthermore, it has been reported that the
hysteresis is intrinsic to the perovskite material and it can also get affected by the device’s
structure. Planar devices having a thin compact TiO₂ layer are displaying a more distinct
hysteresis compared with mesoscopic devices incorporating a mesoporous TiO₂ layer,
while replacing the mesoporous TiO₂ with a mesostructured Al₂O₃ scaffold intensifies
even further the hysteresis [90, 92-94].
Chapter 3

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Chapter 4 Experimental methods

4.1 Characterization techniques

In this paragraph a short presentation of the characterization techniques used for the fabricated materials, films and the completed DSSC and PSC devices will be introduced.

4.1.1 Scanning electron microscopy

The surface morphology and the film thickness of the different photoanodes prepared can be examined by using a scanning electron microscope. In this technique, the surface of a sample is excited by an electron beam which causes electrons to be emitted from its surface; this transmission results in the formation of the desired images. Scanning electron microscopy (SEM) can reveal in depth information regarding the morphology and structure of a sample or a selected area of it. In order to prepare the samples for the SEM measurements, it must be ensured that they have the appropriate size to fit into the high vacuum chamber, before applying a thin layer of a conducting material (gold, silver or carbon) on a small area of them. An example of a scanning electron microscopy image is presented in Figure 4.1 where the corresponding sample is a TiO₂ film. The scanning electron microscope that was used to characterize the samples was by FEI (Inspect™ F50).

![SEM image of a TiO₂ film](image)

**Figure 4.1:** SEM image of a TiO₂ film.
4.1.2 Ultraviolet−Visible spectroscopy

In the Ultraviolet−Visible (UV−Vis) optical absorption spectroscopy a beam of light in the UV−Vis range is incident on a sample (solution or solid sample) and the attenuation of this beam is measured at a given wavelength or over an extended spectral range after passing through the sample. This reduction in the light’s intensity after it passes through a sample can be described by using one of the related processes, the absorption or the transmittance. The operating principle of the UV−Vis spectroscopy is based on the general Beer−Lambert law expressed through the mathematical equation

\[ A = a(\lambda) \cdot b \cdot c \]  

(4.1)

where \( A \) is the measured absorption of the sample, \( a(\lambda) \) is the wavelength−dependent absorptivity coefficient, \( b \) the path length and \( c \) the sample’s concentration. Equation 4.1 can be written in the form of equation 4.2 when units of molarity (M) are used for the concentration and \( \varepsilon \) is the wavelength−dependent absorptivity coefficient measured in M\(^{-1}\)cm\(^{-1}\). However, there are factors limiting the linearity relation expressed through the Beer−Lambert law such as stray light or non−monochromatic radiation and light scattering due to particulates in the sample.

\[ A = \varepsilon \cdot b \cdot c \]  

(4.2)

UV−Vis spectrophotometers use two lamps with a different spectral response covering a wavelength range within 190 nm to 1100 nm. The instruments usually incorporate a tungsten−halogen (WI) lamp and a deuterium (D2) lamp as a light source for the visible and the ultraviolet spectrum respectively. In a double−beam UV−Vis spectrophotometer the light generated by the lamp is reflected through a prism and enters a monochromator through an entrance slit (Fig. 4.2). The monochromatic light is split into two beams before reaching the reference and the test sample. A detector measures the sample’s beam and the data (the absorption or the transmittance spectrum) are recorded on a computer. Absorption spectra presented in this dissertation thesis were recorded using Hitachi U−2900 spectrophotometer controlled by the UV solutions 2.2 program.
4.1.3 Porosimetry

Porosimetry is a technique used to characterize the structural features of materials. It involves the intrusion of an inert gas into a material, commonly nitrogen that doesn’t react with material surfaces as adsorbates, to measure the specific surface area, pore volume, pore diameter, pore width and pore size distribution. This measurement is carried out on powder after the powder is purified by degass while heating in a purging-gas, degassing unit to remove adsorbed contaminants from the surface and the pores of the sample. The powder of the sample results by scratching films of the material deposited on glass microscope slides and grinding the obtained flakes to break all agglomerations. The specific surface area can be determined by nitrogen sorption–desorption measured as a function of relative pressure through the Brunauer–Emmett–Teller (BET) method. The adsorption curve is formed as the pressure of the gas increases, whereas desorption occurs as the pressure reduces [2].

The shape of the adsorption–desorption isotherm is representative for the material’s surface and pore characteristics and they can be classified in six types (Fig. 4.3). Type I or Langmuir adsorption isotherm present an almost horizontal plateau and it is encountered in micropore solids whose pores don’t exceed 2 nm in diameter. Type II and Type IV isotherms have similar shapes with the only difference being that Type II isotherm exhibits no hysteresis between the adsorption and desorption branches. Type II isotherm occurs in non-porous or macropore solids having pores larger than 50 nm in diameter. Type IV isotherm corresponds to mesoporous materials with pore diameter ranging between 2 nm-50 nm. Type III and Type V isotherms also have similar shapes, just like Type II and Type IV isotherms, but they don’t display a plateau. Type III isotherm is observed for solid having large pores, while Type V isotherm, which exhibits
hysteresis, is correlated with mesoporous materials. Finally, Type VI isotherms present non-porous adsorbent having uniform multilayers [3].

![Figure 4.3: Types of adsorption isotherms [3].](image)

In addition, to the BET method, the Barrett–Joyner–Halenda (BJH) analysis can provide the pore size distribution [4]. The porosimetry measurements were performed using Micromeritics Tristar 3000 controlled by Tristar 3000 v6.08.

### 4.1.4 X-ray diffraction

X-ray diffraction (XRD) analysis is a method used to determine the crystallinity of a material. This technique can be used to verify if a material is crystalline or amorphous, the presence of different polymorphs, the crystal structure, the distance between atoms in the crystal lattice and the size of particles or crystallites. X-rays are generated by a cathode ray tube, usually a Ni-filtered Cu to provide radiation wavelength $\lambda = 1.54$ Å, by bombarding a metal surface with accelerated electrons. The electrons acquire their acceleration from the constant high voltage applied at the ends of the ray tube. Once the electrons reach the metal surface their velocity is zero. Based on the law of conservation
of energy the kinetic energy that they had isn’t destroyed; it is transformed mainly into heat and only a very small part of it is transformed into X radiation.

According to W. L. Bragg’s law, X-ray beams, with wavelength comparable to the distance between atoms or ions in a solid, are diffracted by atoms periodically arranged in different planes of a crystal, undergoing constructive interference. Bragg considered that the crystal solid consisted of parallel horizontal planes of atoms having an interplanar distance \( d \) (Fig. 4.4). The Bragg’s law is described by equation 4.3

\[
n \cdot \lambda = 2 \cdot d \cdot \sin \theta
\]  

(4.3)

where \( n \) is a positive integer, \( \lambda \) is the wavelength of the incident X-ray and \( \theta \) is angle of incidence [5,6]. As the X-rays are diffracted the imaging of the crystal’s structure is created.

![Figure 4.4: X-ray diffraction from a crystal](image)

After a typical XRD measurement is completed a characteristic XRD pattern (diffractogram) is acquired, which can be used to calculate the size of the particles or crystallites of the sample by using the Scherrer equation. The Scherrer formula is expressed through equation 4.4

\[
D = \frac{K \cdot \lambda}{B \cdot \cos \theta}
\]  

(4.4)

where \( D \) is the mean diameter of the particles or crystallites of the sample, \( K \) represents a constant (usually equal to 0.9), \( \lambda \) is the X-ray wavelength (usually \( \lambda = 1.54 \, \text{Å} \)), \( B \) is the full
width at half maximum (FWHM) in radians and \( \theta \) is the Bragg angle in degrees. The phase composition of the samples was determined by using Bruker D8 advance diffractometer, with Ni−filtered CuK\( \alpha \) radiation (\( \lambda = 1.54 \text{ Å} \)). XRD patterns were obtained from film samples or directly from powders obtained by scratching the corresponding films in a 2\( \theta \) range of 2° to 70° at a scanning rate of 2°/min.

4.1.5 **Fourier transform infrared spectroscopy**

Fourier transform infrared (FTIR) spectroscopy is a technique used to obtain the absorption of a sample in the infrared spectrum as a function of the wavenumber. This method can identify the functional groups that are present in a compound and it can also be used to determine if a sample is pure or contains impurities. In FTIR spectroscopy the monochromator of a classical spectrometer is replaced with a Michelson interferometer and rather than using a monochromatic beam to irradiate a sample, a polychromatic beam is used instead. When the molecules of a sample absorb infrared radiation their dipole moment change as a result of vibrational (stretching or bending) or rotary movement. Throughout the years, scientists have recorded the location of infrared absorptions associating them with a number of chemical bonds and registering all these data to tables (infrared spectroscopy correlation table) to facilitate the interpretation of an FTIR spectrum [8]. The FTIR measurements were performed with Jasco FTIR−4100, wavenumber range from 4000 cm\(^{-1}\) to 350 cm\(^{-1}\), which was controlled by Spectra Manager software.

4.1.6 **Thermal gravimetric analysis−Differential scanning calorimetry**

Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) are methods which are used to thermally analyze the chemical and physical properties of samples. TGA can provide information about the mass loss of a material as a function of temperature which changes linearly with time. The sample’s mass loss can be either due to the decomposition of some of the sample's components or due to loss of volatiles (solvents, moisture). Differential scanning calorimetry is a technique that studies the thermal transitions of materials, usually polymers. After the measurement, a curve of heat flow versus temperature can be obtained having some peaks, representing exothermic or endothermic reactions occurring in the material, the interpretation of which can help in the characterization of the studied material. For the purposes of this thesis, both
measurements were conducted using Perkin Elmer Simultaneous Thermal Analyzer STA6000 controlled by Pyris Manager Software.

### 4.1.7 Incident photon to current efficiency

As described in previous paragraphs, when a solar cell is illuminated, photons are absorbed and consequently excitons are created. The incident photon to current efficiency (IPCE) or external quantum efficiency (EQE) corresponds to the current density which is produced by the cell when it’s illuminated with a monochromatic light. In simple words IPCE is a measure of the device efficiency in terms of electrons generated per incident photons. The IPCE as a function of wavelength $\lambda$ (nm) can be calculated from equation 4.5 where $J_{sc}$ is the photocurrent density generated by the device when illuminated with monochromatic light with wavelength $\lambda$ and power intensity $P$

$$IPCE(\lambda) = \frac{1240(V \cdot nm) \cdot J_{sc} (mA/cm^2)}{\lambda (nm) \cdot P (mW/cm^2)}$$

(4.5)

![IPCE configuration diagram](image)

**Figure 4.5:** IPCE configuration diagram.
The principle of the IPCE measurement is based on illuminating a sample with a monochromatic beam which is produced after the light from the light source pass through a filter monochromator. The configuration of an IPCE apparatus is presented in Figure 4.5. By changing the frequency of the light the entire IPCE spectrum can be obtained as a function of wavelength. The IPCE spectrum of a device can be monitored over time to study its degradation. Any reduction observed at the corresponding spectrum indicates the decay of the photoconversion properties of the active material, while a discrepancy to the form of the spectrum may suggest morphological changes to the absorbing layer [9]. The IPCE was measured with Thetametrisis PM−QE with Xenon (Xe) light source using a filter monochromator (Oriel Cornerstone™ 260 1/4 m, Newport) which was controlled by PM−Monitor® software.

4.1.8 Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) is a characterization technique that can give fundamental information about solar cells and can also be used to examine the electrochemical behavior of electrodes and electrolyte materials. Typically, a sinusoidal potential \( v(t) = V_m \sin(\omega t) \) is applied to a cell and the resulting current response \( i(t) = I_m \sin(\omega t + \theta) \) is measured as a function of frequency \( f = \omega / 2\pi \), where \( \theta \) is the phase shift between the voltage and the current. The impedance spectrum of a solar cell (DSSC or PSC) can be described by an equivalent circuit consisting by elements (resistors (R), capacitors (C), constant phase elements (CPE), Warburg elements (W) etc) connected in series or in parallel, having real or imaginary values. The results of the EIS analysis of a DSSC can provide values for numerous electrical quantities, such as the series resistance, the charge transfer resistance of the counter electrode, the charge transport and recombination resistance, the diffusion resistance of the redox species in the electrolyte and the electron lifetime, \( \tau_e \) [10]. Accordingly, the EIS results of a PSC can provide information on recombination processes which might take place at the ETL/perovskite interface and on charge transfer properties at the HTM/counter electrode interface.

Impedance measurements were carried out either under illumination using a Xe light source or in the dark, without the use of a mask, with Metrohm Autolab 3.v potentiostat galvanostat (Model PGSTAT 128N) through a frequency range of 100 kHz−0.01 Hz, using a perturbation of ±10 mV over the open−circuit potential. The instrument was controlled by Nova 1.10 software which was also used for fitting the
experimental data. The same instrument was used for measuring the ionic conductivity of electrolytes and for the electrodeposition technique.

4.1.9 Open−circuit voltage decay

An alternative way to calculate the electron lifetime, $\tau_n$, and examine the recombination processes in a solar cell, is by applying the open-circuit voltage decay (OCVD) method. For this procedure cells are illuminated until they reach a steady open-circuit voltage, then the light is interrupted abruptly and the charge on the electrodes is allowed to decay in the dark. The electron lifetime is estimated from the gradient of the OCVD plot by using equation 4.6

$$\tau_n = -\frac{k_B \cdot T}{e} \left( \frac{dV_{OC}}{dt} \right)^{-1}$$

(4.6)

where $k_B \cdot T$ is the thermal energy and $e$ the elementary charge ($k_B \cdot T/e = 25.6\text{ mV}$).

The measurements were recorded by using the same configuration that was used to obtain the photocurrent−voltage curves, namely the cells were connected to a Keithley Source Meter (model 2601A) which was controlled by Keithley computer software (LabTracer) [11].

82
Chapter 4

References


83
In this chapter the results of the research on the optimization of the TiO$_2$ photoanode of DSSCs and the improvement of their performance will be presented. The TiO$_2$ photoanode films were either opaque and thick or transparent and they were modified following different approaches to increase the dye adsorption and porosity in order to enhance the DSSCs’ efficiency. The modifications of the photoanode were attempted by incorporating a small amount of carbonaceous materials, by surface treating the photoanode films before immersing them to the dye solution and by testing different TiO$_2$ precursor materials or surfactants.

5.1 Modification of the TiO$_2$ photoanode with carbonaceous materials

A simple method for modifying the TiO$_2$ photoanode films is used, without employing a template material in order to be able to prepare films at a relative low temperature (100°C) which could potentially be formed on flexible plastic electrodes. An amount of a carbonaceous material, carbon black powder (CBP) or multi-walled carbon nanotubes (MWCNTs), was added to the mixture for the preparation of the TiO$_2$ films to improve the electron transport by enhancing the charge carrier mobility [1,2]. By varying the amount of the added carbon material the porosity of the TiO$_2$ films is altered and the corresponding surface area can be controlled. A number of different weight ratios of the CBP and the MWCNTs in the TiO$_2$ solution were tested and the films were sintered either in low (100°C) or high (500°C) temperature before being used to manufacture the DSSC devices and measure their electrical parameters.

5.1.1 Preparation method for the CBP–TiO$_2$ and MWCNTs–TiO$_2$ photoanodes

The photoanodes were formed by using a TiO$_2$ paste which was made by adding an amount of the commercially available Degussa P25–TiO$_2$ powder, which contains nanoparticles of anatase and rutile phases in a ratio of about 70:30 and Titanium(IV) isopropoxide (TTIP). Specifically, the mixture that was used for the preparation of the photoanode films in this experimental procedure contained 1 g of P25–TiO$_2$ powder which was added in 10 mL of ethanol followed by magnetic stirring to obtain a homogeneous dispersion. Then, the optimum concentration of TTIP (0.053M TTIP) was added in the previous dispersion under stirring [3]. In order to reach to this optimum
result the concentration of the TTIP in P25–TiO$_2$ solution varied until the minimum quantity needed for the formation of stable films on FTO glass substrates was concluded. The TTIP/P25–TiO$_2$ molar ratio varied from 0–0.1 where the P25–TiO$_2$ quantity was kept constant at all times. When the TTIP/P25–TiO$_2$ molar ratio was less than 0.02 the adhesion of the film on the glass was poor, while the best adhesion was achieved for 0.053 molar ratio which from then on was kept constant to all experiments. This result was quite expected as a certain amount of TTIP is needed for the interconnection of P25–TiO$_2$ particles due to $-\text{O}^-\text{Ti}^-\text{O}^-$ network formation after alkoxide’s hydrolysis/condensation in ambient humidity according to the reaction (5.1):

$$\text{TiO}_2(\text{P25}) + n\text{Ti}(\text{OC}_3\text{H}_7)_4 + 2n\text{H}_2\text{O} \rightarrow (n+1)\text{TiO}_2 + 4n\text{C}_3\text{H}_7\text{OH}$$ (5.1)

Less than the optimum amount of alkoxide (TTIP) in the solution resulted in poor film adhesion as a large part of the TiO$_2$ film was peeled off the substrate. On the other hand, higher alkoxide content in the solution than the optimum quantity could create more amorphous TiO$_2$ phase in the films due to the presence of untreated TTIP and as a consequence inferior performing DSSCs could be obtained. As earlier stated, no surfactants were used as templates to the solutions which were ultrasonicated for 15 min. For the CBP–TiO$_2$ films, carbon black (CABOT, VULCAN-XC72R) was added in the solution varying the weight ratio from 0.05 to 1 wt%. The MWCNT–TiO$_2$ films were prepared by the addition of MWCNTs (Sigma-Aldrich) varying the weight ratio from 0.02 to 0.15 wt% into the initial solution. All films were made by dip-coating in a speed 12 cm/min to create films with active surface area around 1 cm$^2$. All films were left to dry for 1h at room temperature to prevent the creation of cracks. The thickness of the pure and modified TiO$_2$ films was in all cases around 5 μm. Then films were calcined in a multi-segment programmable furnace (PLF 110/30, Protherm) at a ramp rate of 5°C/min to 100°C or alternatively to 500°C for 30 min and after the calcination step they were left to cool down naturally. The durability of the films in water rinsing (sometimes violently) was very strong. In the presence of carbon black or MWCNTs the adhesion of the composite films on FTO glass was also very strong while the durability is comparable with that measured for pure TiO$_2$ films. The durability of composite films was checked for a variety of carbon black or MWCNTs quantities (0–0.1 wt%) and the results were similar in all cases.
5.1.2 Structural properties of pure and modified TiO\textsubscript{2} films

The porosity of TiO\textsubscript{2} films is one of the key factors determining how efficient the photoelectrodes constructed can be for dye adsorption. Thus, the as-prepared pure or modified TiO\textsubscript{2} films were examined with porosimetry through nitrogen (N\textsubscript{2}) sorption–desorption analysis in order to specify their textural properties. The measurements were carried out on powder which was carefully scratched from thick films. The N\textsubscript{2} sorption–desorption isotherms of as-prepared TiO\textsubscript{2} film at relatively low temperature (100°C) with 0.053M TTIP molar ratio in P25–TiO\textsubscript{2} powder are presented in Figure 5.1a. The hysteresis loop appears in relatively high pressure region (0.8<P/P\textsubscript{0}<1.0), which suggests that Degussa P25–TiO\textsubscript{2} particles could lead to the formation of larger pores. The shape of the isotherms is typical for mesoporous materials (Fig. 5a–c). The Brunauer–Emmett–Teller (BET) specific surface area and Barrett–Joyner–Halenda (BJH) pore volume of as-prepared films were relatively high at 57.8 m\textsuperscript{2}/g and 0.24 cm\textsuperscript{3}/g, respectively. In the presence of 0.5 wt% in carbon black or 0.1 wt% MWCNTs in TTIP/P25–TiO\textsubscript{2} films at 100°C the results were almost similar (Table 5.1).

**Figure 5.1:** Sorption–desorption isotherms for optimized (a) pure P25–TiO\textsubscript{2}, (b) CBP–P25–TiO\textsubscript{2} and (c) MWCNT–P25–TiO\textsubscript{2} at low and high temperature. Pore size distribution (MWCNT–P25–TiO\textsubscript{2}) measured at 500°C is presented as figure (d).
In particular, the specific surface area for MWCNT/TTIP/P25−TiO$_2$ is a little bit higher (58.9 m$^2$/g) than that measured for pure TTIP/P25−TiO$_2$ which is rather expected because of the presence and specific nature of nanotubes in films. The pore diameter varied between 15.4–16.6 nm for pure and carbon treated films. These large pores are expected to favor the pore filling and wetting of the TiO$_2$ films from the electrolyte solution. When the as−prepared pure and carbon modified films were heated at high temperature, as anticipated, a decrease to all structural characteristics of the films was recorded due to the intense calcination, namely the total pore volume, the specific surface area and the pore diameter was reduced (Table 5.1). However, the maximum measured decrease was 33% in total pore volume, 13% in specific surface area, 20% in total porosity and 38% in mean pore diameter. As an example, the pore size distribution plot for high temperature prepared 0.1% MWCNT/TTIP/P25−TiO$_2$ film (Fig. 5.1d) showed an average pore size of 10.5 nm.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Sample</th>
<th>Total pore volume V$_p$ (cm$^3$/g)</th>
<th>Specific surface area S (m$^2$/g)</th>
<th>Total porosity (%)</th>
<th>Mean pore diameter D$_{por}$ (nm)</th>
</tr>
</thead>
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<td></td>
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<td>45.5</td>
<td>16.6</td>
</tr>
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<td>58.9</td>
<td>46.6</td>
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</tr>
<tr>
<td>500</td>
<td>TiO$_2$−P25</td>
<td>0.16</td>
<td>57.9</td>
<td>37.8</td>
<td>10.2</td>
</tr>
<tr>
<td></td>
<td>0.5% CBP/TiO$_2$−P25</td>
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<td>49.8</td>
<td>37.8</td>
<td>12.9</td>
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<tr>
<td></td>
<td>0.1% MWCNT/TiO$_2$−P25</td>
<td>0.16</td>
<td>55.8</td>
<td>37.8</td>
<td>10.5</td>
</tr>
</tbody>
</table>

FTIR studies of the TTIP/P25−TiO$_2$ film at 100°C show the characteristics of the formation of high−purity material while similar behavior was monitored for MWCNT/TTIP/P25−TiO$_2$ and CBP/TTIP/P25−TiO$_2$ films at the same temperature. The FTIR spectrum of Figure 5.2 clearly shows the peaks corresponding to TiO$_2$. Peaks located in the area of 400−650 cm$^{-1}$ correspond to the vibration of Ti−O and Ti−O−O bonds. On the other hand, the absence of peaks at 1000 cm$^{-1}$ proves the absence of peroxo (O−O) groups. Furthermore, FTIR spectrum firmly suggests the presence of −OH groups which is absolutely necessary for dye adsorption in DSSCs’ fabrication. Thus, the as−prepared TTIP/P25−TiO$_2$, MWCNT/TTIP/P25−TiO$_2$ and
CBP/TTIP/P25−TiO₂ films after washing with pure water consisted of pure TiO₂ particles without any significant organic contaminants, which is an important advantage in the evaluation of DSSCs’ efficiency made with these TiO₂ electrodes. However, in the case of MWCNT/TTIP/P25−TiO₂ and CBP/TTIP/P25−TiO₂ films there wasn’t any peak related to the reaction of MWCNT and CBP with P25−TiO₂ host material.

Figure 5.2: FTIR spectra of pure P25−TiO₂ and CBP and MWCNT in optimum quantities annealed at 100°C.

The films with optimum TTIP content (0.053M), 0.5 wt% CBP/TTIP/P25−TiO₂ and 0.1 wt% MWCNT/TTIP/P25−TiO₂ were examined with scanning electron microscopy (SEM) to determine the homogeneity of the films and the interplay among carbon and P25−TiO₂ particles. The SEM image (Fig. 5.3a) of the pure TiO₂ film reveals that it consisted of 25–30 nm particles uniformly distributed in the film. The film thickness of the photoanode, which is an important factor for the evaluation of the efficiency of the DSSC constructed with this specific film, was measured to be 5 μm. This thickness was not affected by CBP or MWCNT modification as this quantity even at its higher value, was very low compared to the P25−TiO₂ content. As far as the CBP modification is concerned (Fig. 5.3b) larger particles of carbon were homogeneously dispersed in the nanocomposite TiO₂ host material while having a good connection between them. Finally, when carbon nanotubes were introduced in films the characteristic shape of the nanotubes appeared in the SEM images while no serious
deviations to the film’s shape and homogeneity was detected compared to pure TTIP/P25−TiO$_2$ (Fig. 5.3c).

**Figure 5.3:** SEM images of (a) pure P25−TiO$_2$, (b) CBP and (c) MWCNT in optimum quantities annealed at 500°C.
The structural properties of the TiO$_2$ films were also examined by testing their effectiveness on the dye adsorption. All the TiO$_2$ films prepared on FTO glass substrates were immersed in a 0.4 mM (ethanol/acetonitrile 50:50 v/v) solution of N719 dye and were left there for 24h to complete the sensitization process. When the sensitized films were removed from the dye solution they were thoroughly washed with ethanol to remove the excessive dye molecules and dried in air to remove any ethanol or humidity that could be present in the pores of the films. In order to determine the amount of the dye uptake in each film, pure or modified, the films were exposed to a 1M aqueous solution of NaOH for 10 min. Figure 5.4 shows the absorbance of N719 dye after detachment from all TiO$_2$ films. The concentration of the adsorbed dye was calculated using the absorption values and the molar extinction coefficient and was found to range between 0.00588 mM−0.0354 mM [4,5].

![Figure 5.4: UV−Vis absorption of dye N719 detached from pure P25−TiO$_2$ samples and CBP or MWCNT modified films after exposed in 1M NaOH.](image)

It is obvious that the quantity of the dye detached from the untreated P25−TiO$_2$ samples is higher than those detected for CBP or MWCNT modified samples. In contrast to the structural properties obtained from the porosimetry measurements the CBP/P25−TiO$_2$ films seem to absorb a greater quantity of the N719 dye, while the MWCNT/P25−TiO$_2$ films showed the poorest adsorption capacity among the three
different films. However, it was verified that the temperature increase was beneficial for the film’s dye adsorption capacity. This can be attributed to the water content of the TiO$_2$ films which significantly diminishes with annealing temperature, indicating that samples annealed at 100°C retain much more water than samples annealed at higher temperatures.

5.1.3 Fabrication of quasi−solid state DSSCs and electrical characterization

In order to manufacture the DSSCs a quasi−solid state electrolyte was used. For the gelification of the electrolyte solution an organic/inorganic material was prepared by mixing poly(propylene glycol) bis(2-aminopropyl ether) (molecular weight, (MW)~230) and 3-isocyanatopropyltriethoxysilane (ICS; molar ratio ICS/diamine=2) with tetrahydrofuran (THF) under reflux conditions (64°C) for 6 h. As stated in subsection 2.4.2, under these conditions the isocyanate group of ICS reacts with the amino groups of poly(propylene glycol) bis(2-aminopropyl ether) (acylation reaction), producing urea connecting groups between the polymer units and the inorganic part. The remaining THF was evaporated by using a rotary evaporator and a viscous precursor was obtained, which was stable at room temperature for several months [6,7]. The abbreviated name used for this precursor material is PPG230−ICS, referring to the materials mixed to prepare it and the molecular weight 230 of the poly-(propylene glycol).

The quasi−solid state electrolyte was synthesized by dissolving 0.175 g of the functionalized alkoxide precursor PPG230−ICS in 0.4 g of sulfolane and 0.2 g of methoxypropionitrile under vigorous stirring. Then 0.092 g glacial acetic acid (AcOH) followed by 0.03 g 1-methyl-3-propylimidazolium iodide (MPII), 0.03 g LiI and 0.015g I$_2$ were added. Finally 0.051 g of 4-tert-butylpyridine (4−TBP) and 0.0089 g of guanidine thiocyanate (Guan SCN) were also added. 1-Methyl-3-propylimidazolium iodide was used in order to avoid crystallization of LiI, while the presence of LiI was necessary since these small mobile ions allow increase in ionic conductivity.

On the top of the TiO$_2$ films, which were sensitized using the N719 dye as previously described, a couple of drops of the obtained electrolyte solution were placed and a second slightly platinized FTO counter electrode was pushed by hand over the working electrode in a sandwich construction. The platinized FTO glass was made by casting a few drops of chloroplatinic acid hexahydrate (H$_2$PtCl$_6$) solution (5 mg/1 mL of iso-propanol) followed by thermal decomposition at 500°C for 10 minutes. The two
electrodes tightly stuck together by –Si–O–Si- bonds developed by the presence of PPG230–ICS.

The electrical measurements, namely the current density under light and dark conditions versus the devices’ voltage, where recorded by connecting the DSSCs to a Keithley Source Meter (model 2601) which was controlled by a Keithley computer software (LabTracer). Under light, an appropriate mask was used to confine the active area of all solar cells to 0.3 cm² and the illumination intensity was 100 mW/cm² originating from a Solar Light Co solar simulator (model 16S-300) equipped with AM 0 and AM 1.5 direct Air Mass filters and a Xe light source to simulate solar radiation at the surface of the earth. The obtained results for the CBP–TiO₂ and MWCNT–TiO₂ at different sintering temperatures and for a variety of carbon black powder and multi–walled carbon nanotubes concentrations in relation to the TiO₂ weight ratios are summarized in Table 5.2.

For films sintered at low temperature (100°C) the DSSCs’ maximum overall efficiency was obtained for films fabricated with 0.5 wt% CBP–TiO₂ and 0.1 wt% MWCNT–TiO₂ weight ratios in the solution compared with the TiO₂ weight content. However, in the case of carbon black powder the overall efficiency of the corresponding devices was always lower than the devices with the pure TiO₂ films, while in the case of multi–walled carbon nanotubes for 0.1 wt% percentage 6% increase was observed. The current density–voltage (J–V) characteristic curves of quasi–solid state dye–sensitized solar cells for low temperature TiO₂ films with varying CBP and MWCNT content prepared on FTO substrates are presented in Figure 5.5a and b respectively. Notably in the case of the CBP modified films when the concentration of carbon black powder was high the electrical characteristics of the cells rapidly decreased.

Similarly, all the electrical data of the cells with the previous as–prepared pure and modified films sintered at high temperature (500°C) are also presented in Table 5.2. The efficiencies of the cells for all cases increased compared with the acquired results at low temperature. This was an expected result as TiO₂ particles treated at high temperature give improved charge collection efficiencies because of the firm necking between them and the crystallization of the TiO₂ content due to the presence of TTIP, while the carbon connection with the TiO₂ particles is also improved. The current density–voltage (J–V) characteristic curves of the quasi–solid state solar cells prepared with the TiO₂ films with
varying CBP and MWCNT content fabricated on FTO substrates and treated at high temperature are presented Figure 5.6a and b respectively. However, the somewhat lower efficiencies calculated at low temperature is counterbalanced by the lower cost for the preparation of the TiO$_2$ electrode. As far as the modification with CBP is concerned, there is no evidence for better performance of the DSSCs in comparison with those employing pure TiO$_2$, while in the presence of MWCNT in variable quantities in modified films the measured efficiencies were always higher than that obtained for DSSCs with pure TiO$_2$ film. This means that the electrical conductivity in the films was improved as there is no direct correlation with the structural properties of the films which are not improved in the case of MWCNT modification.

**Table 5.2:** Cell performances measured for CBP–TiO$_2$ and MWCNT–TiO$_2$ for different weight ratios measured at 100 mW/cm$^2$ and AM 1.5 simulated solar light.

<table>
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<th>Sample</th>
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<th>Weight ratio (%)</th>
<th>J$_{sc}$ (mA/cm$^2$)</th>
<th>V$_{oc}$ (mV)</th>
<th>FF</th>
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Figure 5.5: Photocurrent-voltage curves of DSSCs based on (a) CBP and (b) MWCNT treated TiO$_2$ nanocrystalline films annealed at low temperature (100°C).

Moreover, the recombination processes at low and high temperature treated photoelectrodes were examined by measuring the dark current density characteristic curves (Fig. 5.7). In the case of CBP presence in the TiO$_2$ matrix, there is an increase in the dark current values either the films were treated at low or at high temperature. The acceleration in the recombination reaction is more distinct for photoelectrodes treated at low temperature most likely due to the presence of amorphous TiO$_2$ originating from the TTIP and the carbon black content. Similar results were recorded for pure and MWCNT
modified P25–TiO₂ samples treated at low temperature. This effect acts cumulatively to
the decay of the V₆₀ values which is already expected when using gel electrolytes, due to
a large concentration of polyiodides species. However, in the case of MWCNT modified
P25–TiO₂ films a lower recombination was monitored which is mainly attributed to the
fact that the MWCNT facilitate the electron transport because of their improved
interconductivity with TiO₂.

![Figure 5.6](image)

**Figure 5.6:** Photocurrent-voltage curves of DSSCs based on (a) CBP and (b) MWCNT treated
TiO₂ nanocrystalline films annealed at high temperature (500°C).
5.2 Surface treatment of the TiO$_2$ photoanode films

As earlier reported (cf. 2.2.1), a procedure used in order to improve the overall performance of DSSCs is the surface treatment of photoanode with materials such as TiCl$_4$, which is selected by the vast majority of researchers as a means to enhance the photoanode’s dye adsorption by interfering with its structural properties. Based on this premise, TiO$_2$ photoanodes were surface treated using two novel materials and their structural and electrical characteristics were examined. After the TiO$_2$ nanocomposite films were formed, they were dipped in a solution containing the surface modifier molecules and remained there for a short period of time achieving the particles coverage according to the chemical bath deposition technique. The two solutions used for the post−treatment of the TiO$_2$ photoanodes employed either Titanium(IV) (triethanolaminato)isopropoxide or Titanium(IV) bis(ammonium lactate)dihydroxide and their effect to the electrical parameters of the quasi−solid state dye−sensitized solar cells was investigated and the results were associated with differences monitored at the structural properties of the films. DSSCs with TiO$_2$ films treated with the two aforementioned titanium precursors were compared against reference cells having TiO$_2$ photoelectrode films which weren’t surface treated to determine which electrical
parameters are most affected. Furthermore, the effect of the annealing temperature of the treated films was also tested.

5.2.1 Preparation method for the pure and surface treated TiO$_2$ films

A TiO$_2$ thin compact layer was deposited on FTO glasses using a TiO$_2$ solution which was prepared by mixing 0.72 g of the surfactant Triton X-100 (99.8%, Fisher Scientific) with 4 mL of ethanol, followed by the addition of 0.4 mL of glacial acetic acid and 0.32 mL of Titanium(IV) isopropoxide (Sigma-Aldrich) under vigorous stirring [8]. After a few minutes of stirring, the FTO glasses were dipped in the above solution and removed with a withdrawal rate of 2 cm/s. The FTO glasses were heated up to 500°C for 30 minutes using 20°C/min heating ramp rate and the final film thickness of the TiO$_2$ layer was approximately 150 nm. Then a layer of TiO$_2$ paste was deposited using the doctor blading technique followed by sintering at 500°C. For the fabrication of TiO$_2$ paste 3 g of Degussa P25–TiO$_2$ powder was mixed with 0.5 mL of acetic acid in a mortar for about 3 min. After that, 2.5 mL of millipore water and 17.5 mL of ethanol were alternately added to break all TiO$_2$ aggregates and form a homogenous solution. The solution was transferred to a crucible with 50 mL of ethanol and was mixed with 10 g of terpineol and an amount of ethyl cellulose. The solution was ultrasonicated for about 2 minutes and then the crucible was placed in a rotary evaporator at 40–45°C to remove the excessive solvent and form the TiO$_2$ paste.

After cooling down at around 100°C, some of the glasses were dipped for 30 minutes either to the 1 M Titanium(IV) (triethanolaminato)isopropoxide solution (hereafter denoted as TTAI) or to the 1 M Titanium(IV) bis(ammonium lactate)dihydroxide solution (hereafter denoted as TALD). After the post–treatment of the TiO$_2$ films two different annealing temperatures were used for sintering them, 300°C and 500°C and the corresponding films were accordingly denoted as i.e. TTAI-300, TTAI-500 meaning that the films were dipped in 1 M Titanium(IV) (triethanolaminato) isopropoxide solution and sintered at 300°C and 500°C respectively for 10 minutes. These surface–treated photoanodes were compared with photoanodes that weren’t dipped in any of the above solutions and sintered at 500°C for equal time, stated as reference.
5.2.2 Structural properties of pure and surface treated TiO$_2$ films

The morphology of the surface−treated TiO$_2$ films was examined through SEM images which were paralleled with those corresponding to reference TiO$_2$ films (Fig. 5.8). As it can be seen the untreated film consists of nanoparticles with an average size of 25 nm as it was expected because of the use of Degussa P25−TiO$_2$ as starting material. However, no serious deviations are displayed in the presence of TTAI or TALD after films’ treatment. The homogeneity of the films and the particle average size look similar among the three images of Figure 5.8.

![SEM images](image)

Figure 5.8: SEM images of: (a) pure P25−TiO$_2$, (b) TTAI modified P25−TiO$_2$ and (c) TALD modified P25−TiO$_2$ films sintered at 500°C.
This means a very thin coverage of TiO₂ particles in films which does not affect the increase of the total thickness of the film and particle size. Finally, TTAI and TALD treated P25–TiO₂ films look more porous than untreated films, therefore porosimetry measurements were performed to estimate structural properties of all films. The final thickness of the TTAI or TALD treated films were approximately 3.7 and 3.8 μm respectively.

The structure of the untreated and the TTAI or TALD treated TiO₂ nanocrystalline films was analyzed by N₂ adsorption and desorption. The BET surface area and the pore structure results are summarized in Table 5.3 and the corresponding plots are presented in Figure 5.9a and b. From Figure 5.9a, the hysteresis loop appear in relatively high pressure region (0.8 < P/P₀ < 1.0), which indicates that Degussa P25–TiO₂ particles form large pores. Moreover, treated samples seem to exhibit relatively wider pore size distribution (22–26 nm) compared to the untreated and treated at lower temperature samples (14–15 nm). Such large pores favor the pore filling and wetting of the TiO₂ films from the electrolyte solution. However, the specific surface area of particles is lower in the case of treated samples sintered at 500°C. From Table 5.3, it can be seen that the BET surface area of the untreated TiO₂ films is 53.01 m²/g which is getting lower ~51 m²/g for treated TiO₂ films at 300°C and it reduces to even lower values (47–48 m²/g) for treated samples at 500°C. Nevertheless, the difference between untreated and treated samples at 500°C is only 11%.

Table 5.3: Structural characteristics of treated and untreated TiO₂ films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pore size (nm)</th>
<th>Porosity, P (%)</th>
<th>Total pore volume, Vₚ (cm³/g)</th>
<th>Specific surface area, S (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference</td>
<td>14.86</td>
<td>42.8</td>
<td>0.197</td>
<td>53.01</td>
</tr>
<tr>
<td>TTAI-300</td>
<td>13.99</td>
<td>40.8</td>
<td>0.181</td>
<td>51.67</td>
</tr>
<tr>
<td>TALD-300</td>
<td>14.96</td>
<td>42.1</td>
<td>0.191</td>
<td>51.01</td>
</tr>
<tr>
<td>TTAI-500</td>
<td>22.14</td>
<td>50.5</td>
<td>0.269</td>
<td>48.57</td>
</tr>
<tr>
<td>TALD-500</td>
<td>26.32</td>
<td>54.1</td>
<td>0.310</td>
<td>47.11</td>
</tr>
</tbody>
</table>

Before manufacturing DSSCs with the treated and untreated TiO₂ photoanodes, the films were sensitized with the ruthenium N719 sensitizer. The films were immersed overnight in a N719 solution with a concentration of 5·10⁻⁴ M where ethanol and acetonitrile were used as solvents (1:1 v/v). Figure 5.10 shows the absorbance of N719
dye after detachment from all TiO$_2$ films exposed to 1M NaOH for the same time (10 min).

Figure 5.9: Sorption–desorption isotherms (a) and pore size distribution (b) for treated and untreated TiO$_2$ films.

It is obvious that the quantity of the dye detached from all treated samples is higher than the untreated sample. The exact intensity of the dye’s absorbance at both wavelengths in the visible is presented at Table 5.4. TTAI, TALD surface treatment of TiO$_2$ films increased the amount of adsorbed dye. This may be caused due to the passivation of the TiO$_2$ surface and increased pore size distribution, pore volume and porosity of the films.
Figure 5.10: UV−Vis absorption of dye N719 detached from untreated and TTAI, TALD treated TiO$_2$ nanocrystalline films after exposition in 1M NaOH.

Table 5.4: Absorbance of N719 dye after detachment from TiO$_2$ films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Wavelength (nm)</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference</td>
<td>372.5</td>
<td>0.173</td>
</tr>
<tr>
<td></td>
<td>500.5</td>
<td>0.171</td>
</tr>
<tr>
<td>TTAI-300</td>
<td>356.5</td>
<td>0.316</td>
</tr>
<tr>
<td></td>
<td>490.5</td>
<td>0.191</td>
</tr>
<tr>
<td>TALD-300</td>
<td>371.5</td>
<td>0.294</td>
</tr>
<tr>
<td></td>
<td>497.0</td>
<td>0.219</td>
</tr>
<tr>
<td>TTAI-500</td>
<td>374.5</td>
<td>0.183</td>
</tr>
<tr>
<td></td>
<td>499.0</td>
<td>0.226</td>
</tr>
<tr>
<td>TALD-500</td>
<td>377.0</td>
<td>0.205</td>
</tr>
<tr>
<td></td>
<td>499.0</td>
<td>0.178</td>
</tr>
</tbody>
</table>

5.2.3 Fabrication of quasi−solid state DSSCs and electrical characterization

The sensitization of all the TiO$_2$ electrodes in the visible region was performed as previously described. For the construction of the DSSCs the same type of counter electrode and quasi−solid state electrolyte was used as the ones described in paragraph 5.1.3. The quasi−solid state electrolyte was chosen as a promising approach to DSSC technology as it combines the high ionic conductivity of liquids while it reduces the risk
of leaks and minimizes sealing problems in the cells. The DSSCs fabricated with the surface−treated photoanodes (TTAI, TALD) were compared with cells with photoanodes that weren’t dipped in any of the above solutions (Reference). For each case two devices were manufactured and tested under the same conditions in order to ensure the accuracy of the results. The active area of all the DSSCs was constant to 0.3cm² by using an appropriate black mask.

The photocurrent density−voltage (J−V) characteristic curves of quasi−solid state DSSCs for all TiO₂ films are presented in Figure 5.11. The DSSCs constructed with treated and untreated TiO₂ films showed different energy to power conversion efficiencies under AM 1.5 simulated Xe−light of 100 mW/cm². In the case of solar cell with the TALD treated TiO₂ film the overall efficiency was slightly higher than that of the solar cell with the TTAI surface treated TiO₂ film (Table 5.5). In particular, the open−circuit voltage for the solar cell with the TTAI-500 treated sample was 0.71 V and the short−circuit current density was 8.35 mA/cm² with a calculated overall efficiency of 4.04%. For the cell employing the TALD-500 treated photoelectrode, with exactly the same electrolyte composition, the open−circuit voltage was measured 0.74 V and the short−circuit current density was 8.42 mA/cm². The overall efficiency for this cell was slightly increased to 4.25%.

![Figure 5.11: Photocurrent density−voltage curves of DSSCs based on treated and untreated TiO₂ nanocrystalline films.](image-url)
The difference observed in the overall efficiencies of the solar cells was attributed to the textural and morphological variations of the two films as they were earlier described. Specifically, the difference may be explained by the higher number of active sites for the adsorption of dye molecules, the larger average pore size for effective mass transfer of electrolyte and light harvesting. It is worth noting that the efficiency of the untreated TiO$_2$ sample is much lower (2.97%) mainly due to the lower current density recorded. Consequently, a 26.5% and 30.1% increase to the overall efficiency was recorded for the TTAI and TALD treated photoanodes respectively. Finally, the solar cells with the surface treated samples heated at lower temperature (300°C) exhibited poor performance mainly due to the presence of carbon residues, as the film’s calcination temperature wasn’t high enough to completely remove all of them.

Table 5.5: Solar cells parameters for DSSCs with TTAI, TALD treated or untreated TiO$_2$ photoelectrodes.

<table>
<thead>
<tr>
<th>Sample</th>
<th>J$_{sc}$ (mA/cm$^2$)</th>
<th>V$_{oc}$ (V)</th>
<th>FF</th>
<th>n (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference-500</td>
<td>5.71</td>
<td>0.72</td>
<td>0.721</td>
<td>2.97</td>
</tr>
<tr>
<td>TTAI-300</td>
<td>3.11</td>
<td>0.55</td>
<td>0.753</td>
<td>1.29</td>
</tr>
<tr>
<td>TALD-300</td>
<td>2.26</td>
<td>0.51</td>
<td>0.693</td>
<td>0.80</td>
</tr>
<tr>
<td>TTAI-500</td>
<td>8.35</td>
<td>0.71</td>
<td>0.683</td>
<td>4.04</td>
</tr>
<tr>
<td>TALD-500</td>
<td>8.42</td>
<td>0.74</td>
<td>0.684</td>
<td>4.25</td>
</tr>
</tbody>
</table>

Figure 5.12: Dark current–voltage characteristic curves of dye-sensitized solar cells before and after TTAI, TALD treatment.
Chapter 5

The TiO$_2$ treated samples were also examined as efficient photoelectrodes in DSSCs measuring the dark current suppression. Figure 5.12 shows that the electron leakage, in the cells made with TTAI, TALD surface treated TiO$_2$ films at 300°C is noticeably higher compared to the cells with untreated and TTAI, TALD treated TiO$_2$ films at 500°C which leads to a reduced overall performance under light exposure. Among untreated and treated with TTAI, TALD photoelectrodes sintered at 500°C a slightly lower dark current suppression is monitored for the cell with the TTAI treated photoanode.

5.3 Transparent TiO$_2$ photoanode films

The research and development of transparent photoanodes with suitable properties is of great importance so that the corresponding DSSCs can have the prospect to be integrated on building facades as structural elements capable for energy production. Thus, it was examined whether the TiO$_2$ photoanode films can be modified by altering the TiO$_2$ precursor material used while maintaining the same preparation method for optically transparent photoelectrodes. Four different TiO$_2$ precursors have been used and the structural and morphological characteristics of the films as well as the electrical behavior of the DSSCs employing these TiO$_2$ photoanodes were tested.

5.3.1 Preparation method for the transparent TiO$_2$ photoanode films

The different titania precursors used for the preparation of the TiO$_2$ solutions were Titanium(IV) isopropoxide, Titanium(IV) butoxide, Titanium(IV) (triethanolaminato) and Diisopropoxytitanium bis(acetylacetonate) hereafter abbreviated as TTIP, TTBU, TTAI and Ti(AcAc) respectively. The TiO$_2$ photoanode films were synthesized via the sol–gel method where the hydrolysis rate minimizes as the isopropoxide groups are substituted by butoxy groups and reduces even more as they are partially replaced by the acetylacetonate groups [9,10]. The titanium molar ratio was kept constant to all solutions which were prepared by mixing 0.72 g of the surfactant agent Triton X-100 (99.8%, Fisher Scientific) with 4 mL of ethanol, followed by the addition of 0.4 mL of glacial acetic acid and 1.08 mmoles of the titanium precursor under vigorous stirring. After a few minutes of stirring, the solutions were deposited on FTO glasses (TEC8, 8 Ohm/square) which were purchased from Pilkington NSG Group with a spin coating
device (Spin150, APT Automation) at 1200 rpm for 10s. The films were sintered up to 500°C for 30 minutes using 20°C/min heating ramp rate. This procedure was repeated several times until a satisfactory film thickness was obtained.

5.3.2 Structural properties of the transparent TiO₂ photoanode films

The structural properties of the powders which were obtained by carefully scratching the TiO₂ films prepared with the different titanium dioxide precursors as previously described were analyzed with N₂ sorption–desorption isotherms. The particle surface area and pore structure of all measured samples are summarized in Table 5.6 while the results are presented in Figure 5.13a–d and Figure 5.14.

![Graphs showing sorption–desorption isotherms for powders obtained from TiO₂ solutions employing different precursors: TTIP, TTBU, TTAI, and Ti(AcAc).](image)

**Figure 5.13:** Sorption–desorption isotherms for powders obtained from the TiO₂ solutions employing (a) TTIP, (b) TTBU, (c) TTAI and (d) Ti(AcAc).

**Table 5.6:** Structural properties of powders obtained from the TiO₂ solutions employing all four precursors.

<table>
<thead>
<tr>
<th>TiO₂ precursor</th>
<th>Porosity (%)</th>
<th>$S_{BET}$ (m²/g)</th>
<th>Pore diameter (nm)</th>
<th>Pore volume (cm³/g)</th>
<th>Pore width (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TTIP</td>
<td>27.14</td>
<td>64.04</td>
<td>4.40</td>
<td>0.098</td>
<td>6.14</td>
</tr>
<tr>
<td>TTBU</td>
<td>26.51</td>
<td>60.46</td>
<td>4.45</td>
<td>0.095</td>
<td>6.31</td>
</tr>
<tr>
<td>TTAI</td>
<td>26.97</td>
<td>60.33</td>
<td>4.75</td>
<td>0.097</td>
<td>6.48</td>
</tr>
<tr>
<td>Ti(AcAc)</td>
<td>27.94</td>
<td>76.08</td>
<td>3.93</td>
<td>0.102</td>
<td>5.40</td>
</tr>
</tbody>
</table>
Chapter 5

It can be seen (Fig. 5.13) that the hysteresis loop for all the TiO$_2$ films appears at low relative pressure (0.4<P/P$_0$<0.8) which is attributed to the smaller mesoporosity of the material. The sample’s BET specific surface area was high, while the BJH pore volume (Fig. 5.14) was relatively low at 0.09−0.1 cm$^3$/g. Moreover, all the powders which resulted from the TiO$_2$ films with the different precursors had a small mean pore diameter, with the powder obtained by the films were the Ti(AcAc) precursor was used appearing the smallest pore diameter among all (Table 5.6).

![Figure 5.14: Pore size distribution for powders obtained from the TiO$_2$ solutions employing all four precursors.](image)

The particle’s size was also verified through the SEM images of the surface of the films which are presented in Figure 5.15a−d. The films employing TTIP and TTBU had similar particle size (9−13 nm) while Ti(AcAc) had the smallest particle size (6−9 nm). It is obvious that all films prepared from the four different titanium precursors consisted of TiO$_2$ particles of very small size. In addition, based on SEM cross section images, the films were thin and their thickness was approximately between 1.5−2 μm. Indicatively, Figure 5.16 shows the cross section of the film prepared with the TTBU precursor.

The XRD patterns of the powders prepared from the different TiO$_2$ precursors are shown in Figure 5.17a−d. The diffraction peak at around 25° represents the anatase form of TiO$_2$ while the peak’s intensity observed which is higher for the case of TTBU suggests a larger amount of TiO$_2$. The grain size for anatase TiO$_2$ particles has been
calculated from XRD patterns using Scherrer’s formula (equation 4.4). The crystallite size for TiO$_2$ prepared from TTIP, TTBU, TTAI, Ti(AcAc) precursors is calculated as 9.5 nm, 12.7 nm, 14.8 nm and 7.3 nm respectively which is in good accordance to the SEM images. Moreover, the peak at around 27° corresponds to the rutile form of TiO$_2$ though this peak isn’t distinctive for the case of TTAI and Ti(AcAc).

Figure 5.15: SEM images of (a) TTIP, (b) TTBU, (c) TTAI and (d) Ti(AcAc).

Figure 5.16: Cross section of the film employing TTBU.
Figure 5.17: XRD patterns for powders obtained from the TiO\textsubscript{2} solutions employing (a) TTIP, (b) TTBU, (c) TTAI and (d) Ti(AcAc).

Figure 5.18: UV−Vis absorption spectra of TiO\textsubscript{2} films obtained using different precursors.

Figure 5.18 shows the absorption spectra of the different TiO\textsubscript{2} films. Beside the spectrum corresponding to the film employing TTAI, all the other spectra exhibit interference fringes. Since the TiO\textsubscript{2} molar ratio was kept constant for all starting solutions, the quantity of titanium was the same for all films. Thus, the fact that fringes occur to thicker films, indicates that films which resulted from the solutions containing...
TTIP, TTBU and Ti(AcAc) were more porous (or less dense). However, the TTAI films weren’t uniform throughout the surface which would also have a negative impact on the sensitization of the films (poor dye adsorption). Additionally, from the steep part of the spectra at the absorbance threshold wavelength the energy band gap of the TiO$_2$ was calculated to be 3.4 eV which is in accordance to the values obtained for mesoporous films reported in literature [11].

5.3.3 Fabrication of quasi−solid state DSSCs and electrical characterization

The TiO$_2$ films prepared by the formerly described procedure on FTO glass substrates were sensitized with N719 dye and the same quasi−solid state electrolyte and platinum counter electrodes were used for completing the DSSCs as reported in previous paragraphs. Figure 5.19 presents the current density−voltage (J−V) characteristic curves of quasi solid−state dye−sensitized solar cells for all the TiO$_2$ precursors tested. All J−V measurements were carried out using a mask with an active area of 0.3 cm$^2$. The electrical parameters measured and calculated for all cells are summarized in Table 5.7. The cells’ open−circuit voltage was relatively constant while differences were detected on the short−circuit current density measured. The obtained $J_{SC}$ values were sufficiently high, given the fact that the photoanodes’ thickness was relatively small and the fact that the cells had high transparency.

![Figure 5.19: Photocurrent−voltage curves of DSSCs with photoanodes obtained using different TiO$_2$ precursors.](image-url)
It was interesting to note that cells manufactured with photoanodes which resulted from the use of TTBU, showed higher short-circuit current density compared with the ones employing the commonly used TTIP. Specifically, the obtained $J_{sc}$ value for the TTBU was almost 9% higher than the one recorded for the TTIP, which resulted in an 11.2% increase of the cell’s overall efficiency. The photoanodes of the cells prepared with TTAI weren’t properly sensitized due to the dissimilarity of the TiO$_2$ film which justifies the resulting low $J_{sc}$ value.

Table 5.7: Solar cells parameters for DSSCs with TiO$_2$ photoelectrodes obtained using different precursors.

<table>
<thead>
<tr>
<th>TiO$_2$ precursor</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>n (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TTIP</td>
<td>6.1</td>
<td>0.692</td>
<td>0.62</td>
<td>2.61</td>
</tr>
<tr>
<td>TTBU</td>
<td>6.7</td>
<td>0.693</td>
<td>0.64</td>
<td>2.94</td>
</tr>
<tr>
<td>TTAI</td>
<td>1.1</td>
<td>0.694</td>
<td>0.59</td>
<td>0.46</td>
</tr>
<tr>
<td>Ti(AcAc)</td>
<td>4.8</td>
<td>0.673</td>
<td>0.65</td>
<td>2.07</td>
</tr>
</tbody>
</table>

Figure 5.20: Dark current density−voltage characteristic curves of dye-sensitized solar cells with different TiO$_2$ precursors.

The dark current suppression was also examined to perceive the extent of the back electron transfer. Figure 5.20 shows that dark current density of the solar cells made with the different titanium precursors. The onset of the dark current for the DSSCs fabricated
with TTIP, TTBU and Ti(AcAc) occurred at lower voltage compared with TTAI cells, despite the poor dye adsorption of the photoanodes with this alkoxide.

### 5.3.4 Electrochemical characterization

From the impedance spectroscopy measurements of the solar cells with the different titanium precursors the Nyquist and Bode plots are obtained (Fig. 5.21a–b). The first semicircle corresponds to the Pt/electrolyte interface, \( R_{pt} \). The charge transfer resistance at the counter electrode (\( R_{ct} \)) is represented as a semicircle in the impedance spectra and a peak in the Bode phase angle plot. The resistance element related to the response in the intermediate frequency represents the charge transport at the \( \text{TiO}_2/\text{dye/electrolyte interface} (R_{int}) \) and shows diode like behavior. The semicircle at the low frequency is attributed to the diffusion in the electrolyte (\( R_{dif} \)) and the intercept of the horizontal axis stands for the resistance of the sheet resistance of the FTO substrate and the contact resistance of the FTO/\( \text{TiO}_2 \) (\( R_h \)).

The total series resistance of the solar cell can be calculated by using equation 5.1.

\[
R_s = R_h + R_{pt} + R_{dif}
\]

The total series resistance of the solar cell can be calculated by using equation 5.1.

\[
R_s = R_h + R_{pt} + R_{dif}
\]  

(5.1)

The equivalent circuits which were used to fit the experimental data are presented in Figure 5.22. For electrodes having a rough surface the capacitance element in Figure 5.22a is replaced by a constant phase element (CPE, \( Q \)) which depends on the parameters \( Y_o \) and \( N \) where \( Y_o \) is the admittance of an ideal capacitance and \( N \) an empirical constant with values ranging from 0 to 1 (Fig. 5.22b). It is possible to convert a CPE element, which is in parallel with a resistance, to a pseudo capacitance using equation 5.2.

\[
C_{pseudo} = Y_o^{1/N} \cdot R^{\left(\frac{1}{N-1}\right)}
\]

(5.2)

As shown from equation 5.2 for \( N=1 \) the CPE element describes a pure capacitor while for \( N=0 \) an ideal resistor. Moreover for \( N=0.5 \) the CPE element is equivalent to the Warburg element often used to describe the diffusion in the electrolyte. It is generally though to arise from the lack of homogeneities in the electrode–material system. The fitted parameters are presented in Table 5.8. The solar cells whose photoanodes resulted from TTBU had the highest short-circuit current density which can be attributed to the
fact that they had the smallest total series resistance $R_s$. As indicated above (Fig. 5.19), DSSCs with TTIP outperformed the ones with Ti(AcAc), however the total series resistance of the former was higher than the latter. Nevertheless, this inconsistency can be ascribed to the fact that the value of $R_h$ of the solar cells with Ti(AcAc) was nearly half compared with the one corresponding to the solar cells with TTIP. Since all the DSSCs were manufactured using the same type of conductive substrate this difference is due to the contact resistance of the FTO/TiO$_2$. The use of Ti(AcAc) leads to the formation of smaller nanoparticles tightly bind on the FTO glasses which results in a small $R_h$ value.

Figure 5.21: a) Impedance spectra and b) Bode phase plots of dye-sensitized solar cells with different titanium precursors measured at open-circuit voltage at 1 sun illumination.
Table 5.8: Fitted parameters derived from electrochemical impedance spectroscopy.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>( R_h ) (Ω)</th>
<th>( R_{pt} ) (Ω)</th>
<th>( C_{pt} \cdot 10^{-4} ) (F)</th>
<th>( R_u ) (Ω)</th>
<th>( C_u \cdot 10^{-3} ) (F)</th>
<th>( R_{dif} ) (Ω)</th>
<th>( C_{dif} \cdot 10^{-2} ) (F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TTIP</td>
<td>19.50</td>
<td>2.01</td>
<td>0.237</td>
<td>9.10</td>
<td>3.34</td>
<td>3.43</td>
<td>9.32</td>
</tr>
<tr>
<td>TTBU</td>
<td>8.07</td>
<td>1.43</td>
<td>0.371</td>
<td>6.56</td>
<td>3.57</td>
<td>3.99</td>
<td>5.35</td>
</tr>
<tr>
<td>TTAI</td>
<td>14.40</td>
<td>3.46</td>
<td>0.646</td>
<td>53.20</td>
<td>0.40</td>
<td>34.00</td>
<td>0.39</td>
</tr>
<tr>
<td>Ti(AcAc)</td>
<td>10.10</td>
<td>1.73</td>
<td>0.512</td>
<td>8.92</td>
<td>5.14</td>
<td>6.70</td>
<td>3.87</td>
</tr>
</tbody>
</table>

Table 5.9: Electron lifetime derived from the Bode phase plots.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>( f ) (Hz)</th>
<th>( \tau_n \cdot 10^{-2} ) (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TTIP</td>
<td>5.57</td>
<td>2.86</td>
</tr>
<tr>
<td>TTBU</td>
<td>7.64</td>
<td>2.09</td>
</tr>
<tr>
<td>TTAI</td>
<td>14.24</td>
<td>1.12</td>
</tr>
<tr>
<td>Ti(AcAc)</td>
<td>4.04</td>
<td>3.94</td>
</tr>
</tbody>
</table>

From the peak at the Bode phase plots (Fig. 5.21b) the electron lifetime can be calculated using equation 5.3. The results are summarized in Table 5.9 [12-14].

\[
\tau_n = \frac{1}{2 \cdot \pi \cdot f}
\] (5.3)

Ti(AcAc) had the highest electron lifetime, followed by TTIP and TTBU. These results are not in accordance to the \( J_{sc} \) values obtained from \( J-V \) curves. However, the small
size of TiO$_2$ particles obtained for films prepared from Ti(AcAc) precursor could prevent the electrons recombination due to better contact of the particles.

\[ \text{Figure 5.23: a) Open-circuit voltage decay measurement of DSSCs with electrodes obtained with different TiO}_2 \text{ precursors to illumination excitation (AM 1.5G solar light (100 mWcm}^{-2}). b) Electron lifetime curves in relation to the open-circuit voltage for electrodes obtained with different TiO}_2 \text{ precursors.} \]

The electron lifetime can also be calculated by the open-circuit voltage decay (OCVD) technique (Fig. 5.23a) by using equation 4.6. In this measurement we only included cells with TTIP, TTBU and Ti(AcAc) to compare and determine any differences between them, while the cell with TTAI was excluded as we anticipated a
poor representation mainly due to the poor sensitization of the anode [15]. It was observed that the OCVD response of the DSSC with the TiO$_2$ made out of TTBU was much slower than that made out of TTIP or Ti(ACAc). Electron lifetime ($\tau_n$) was proposed to quantify the extent of electron recombination with the redox electrolyte and has been proven to be effective. Figure 5.23b compares the results of the dependence of electron lifetime on the open–circuit voltage of DSSCs with the photoanodes prepared with the different titanium precursors. It is obvious than in the case of TTBU solar cells the electron lifetime was longer than those obtained for the other two precursors. This suggests that for the case of the TTBU fabricated DSSCs the electrons injected from the excited dye molecules can survive longer without undergoing losses.

5.4 Simple procedure for porous TiO$_2$ photoanode with an amphiphilic surfactant

A simple procedure was used to fabricate TiO$_2$ photoanodes via the sol–gel method by using a TiO$_2$ solution that contained a surfactant which can be easily removed from the films without destroying them just by rinsing them with deionized water. Since the organic surfactant is washed away from the FTO electrodes by rinsing, low sintering temperature can be applied, rendering this TiO$_2$ fabrication process applicable even for flexible DSSC. The surfactant that was employed as a template agent was Dioctyl sulfosuccinate sodium salt (AOT, Sigma-Aldrich).

5.4.1 Preparation method for the porous TiO$_2$ photoanode with AOT as a surfactant

For the preparation of the TiO$_2$ solution a mixture of two solvents, cyclohexane and n-propanol, was used along with TTIP and AOT. Different solution compositions were tested varying the solvents’ ratios, the AOT or titanium precursor quantity to evaluate the resulting films and conclude to the optimal one before using it as a photoanode for DSSC. The TiO$_2$ films were deposited on FTO conducting glasses (TEC8, 8 Ohm/square) by dip coating and the criteria used to evaluate the various TiO$_2$ solutions tested were the film adherence on those glasses and the film’s uniformity across the active area. Between the dipping into the TiO$_2$ solution and the rinsing, a few minutes (5–10 minutes) of drying in air mediated to ensure that the TiO$_2$ film wouldn’t peel off the glass. All TiO$_2$ films had an effective surface area of 1·2 cm$^2$ and the back
side of the conducting glasses were cleaned with acetone to maintain a clear and uncovered surface.

The quantity of AOT tested varied between 0.36 g and 0.54 g but optimal results were obtained for 0.36 g of AOT. Similarly different alkoxide quantities were tested (0.45 mL–0.63 mL of TTIP) and the final solution consisted of a 50:50 volume concentration of cyclohexane/n-propanol, 0.36 g of AOT and 0.54 mL of Titanium(IV) isopropoxide. Since the surfactant was drifted away with water films could be sintered in low temperature, however films were calcined at 500°C for 10 minutes to increase their crystallinity. The procedure was repeated several times until a satisfactory film thickness was obtained. Figure 5.24 presents the AOT–TiO₂ films that were formed by using some of the solutions that were tested in comparison with the films that resulted from the one with the optimum composition. The final AOT–TiO₂ films were almost opaque, had good adherence on the conducting glass and they were uniformly deposited throughout the desired area.

Figure 5.24: Films prepared with some of the AOT–TiO₂ solutions tested.

5.4.2 Morphological and structural properties of the AOT–TiO₂ photoanode films

The surface morphology of the AOT–TiO₂ film and its thickness were studied through scanning electron microscopy images (Fig. 5.25). It can be seen that a highly porous network with aggregated particles is formed (Fig. 5.25a–c). The presence of large clusters of aggregated particles with large volume of free void could be advantageous for the electrolyte filling in the DSSCs. The AOT–TiO₂ particles have almost similar size
9–10 nm) and they are interconnected in a fine network with high porosity which favors the dye uptake. In addition, the thickness of the photoanode was approximately between 4.2–4.7 μm, measured by a cross section image (Fig. 5.25d).

![SEM images of: (a−c) the top view of the AOT−TiO\(_2\) film and (d) cross section.](image)

Figure 5.25: SEM images of: (a−c) the top view of the AOT−TiO\(_2\) film and (d) cross section.

The structural properties of the AOT−TiO\(_2\) film were investigated through porosimetry measurements and its corresponding phase composition was determined by X-ray diffraction analysis. The measurement for the porosity of the AOT−TiO\(_2\) film was carried out on powder which resulted by scratching thick films made on glass microscope slides and grinding the obtained flakes to break all agglomerations. The sample was degassed for 1 h at 400°C before N\(_2\) sorption analysis. The particle surface area and pore structure of the TiO\(_2\) powder are summarized in Table 5.10 and the obtained graphs are presented in Figure 5.26a−b.

The hysteresis loop in Figure 5.26a has a wide relative pressure region (0.5<P/P\(_0\)<1) which suggests that the TiO\(_2\) solution employing AOT can lead to the formation of pores over a broad range of sizes (mesopores to macropores). The sample’s BET specific surface area wasn’t high, as well as the BJH pore volume which was 0.11
It is also worth noting that the pore size distribution plot for the TiO$_2$ powder shown in Figure 5.26b displayed two peaks: one located at 3.7 nm and the other one at a larger average pore size of 6.33 nm.

![Sorption-desorption isotherms and pore size distribution for powder obtained from the AOT-TiO$_2$ films.](image)

**Figure 5.26:** (a) Sorption-desorption isotherms and (b) pore size distribution for powder obtained from the AOT-TiO$_2$ films.

**Table 5.10:** Structural properties of the AOT-TiO$_2$ powder obtained from the corresponding film.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Porosity (%)</th>
<th>$S_{BET}$ (m$^2$/g)</th>
<th>Pore diameter (nm)</th>
<th>Pore volume (cm$^3$/g)</th>
<th>Pore width (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AOT-TiO$_2$</td>
<td>29.30</td>
<td>30.31</td>
<td>11.94</td>
<td>0.109</td>
<td>14.48</td>
</tr>
</tbody>
</table>
5.4.3 Fabrication of quasi–solid state DSSCs. Electrical and electrochemical characterization

The AOT–TiO$_2$ films prepared by the previously described procedure on FTO glass substrates were sensitized with N719 dye following exactly the same procedure as earlier reported. The quasi–solid state electrolyte used and the platinum counter electrode were the same as in previous experiments. Once the gelation of the quasi–solid state electrolyte progressed, electrical and electrochemical measurements were performed at the fabricated DSSCs.

The DSSCs were illuminated using a mask that limited the active area of all solar cells to 0.174 cm$^2$. Figure 5.28 shows the photocurrent density–voltage curve corresponding to the solar cells with the AOT–TiO$_2$ photoanodes and the obtained results of the electrical parameters are presented in Table 5.11. In general, the short–circuit current density was relatively satisfactory considering the specific surface area and the porosity values of the AOT–TiO$_2$ film. The current density had a relatively sharp decrease which results in a low fill factor value. Regarding the cell’s open–circuit voltage, all the cells fabricated using the various solutions had a constant value at around 0.7 V. Finally the efficiency of the DSSC with the AOT–TiO$_2$ photoanode was moderate compared with the efficiencies calculated for the other photoanode modifications tested (cf. subparagraphs 5.1.3, 5.2.3, 5.3.3).
The solar cells were also characterized through electrochemical impedance spectroscopy measurements. The Nyquist plot and the equivalent circuit used to fit the experimental data are shown in Figure 5.29 and the fitted parameters are summarized in Table 5.12. The total series resistance \( R_s \) was calculated by using equation 5.1 to be 25.59 \( \Omega \), which was considered a high value, probably because of the high value of the sheet resistance \( R_h \), as no compact layer was employed at the anode. The compact layer is usually applied on the FTO glass, prior to the deposition of the main TiO\(_2\) film, to block the recombination and improve the contact between the FTO and the TiO\(_2\).

![Figure 5.28: Photocurrent density–voltage curve of the AOT–TiO\(_2\) DSSC.](image)

**Table 5.11:** Electrical parameters for AOT–TiO\(_2\) DSSC.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( J_{sc} ) (mA/cm(^2))</th>
<th>( V_{oc} ) (V)</th>
<th>FF</th>
<th>n (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AOT–TiO(_2)</td>
<td>7.13</td>
<td>0.705</td>
<td>0.51</td>
<td>2.55</td>
</tr>
</tbody>
</table>

**Table 5.12:** Electrochemical impedance spectroscopy fitted parameters of AOT–TiO\(_2\) DSSC.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( R_h ) (( \Omega ))</th>
<th>( R_{pt} ) (( \Omega ))</th>
<th>( C_{pt} \times 10^{-4} ) (F)</th>
<th>( R_u ) (( \Omega ))</th>
<th>( C_u \times 10^{-3} ) (F)</th>
<th>( R_{dif} ) (( \Omega ))</th>
<th>( C_{dif} \times 10^{-2} ) (F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AOT–TiO(_2)</td>
<td>14.6</td>
<td>2.38</td>
<td>0.314</td>
<td>11.8</td>
<td>5.418</td>
<td>8.61</td>
<td>0.324</td>
</tr>
</tbody>
</table>

Although the procedure to fabricate the AOT–TiO\(_2\) photoanode was simple and AOT can be easily removed by rinsing with distilled water leaving pure titania film
without requiring high sintering temperature, the investigation of this method was suspended due to the fact that the other modification methods that were tested led to better results.

Figure 5.29: Nyquist plot of AOT−TiO$_2$ dye−sensitized solar cell measured at open−circuit voltage at 1 sun illumination. As an inset the DSSC’s electrical equivalent circuit used to fit the experimental data from the EIS measurement.
References


Chapter 6 Experimental results—sensitizer of DSSC

In this chapter the TiO$_2$ photoanodes are sensitized with new dyes representative of some of the basic categories (ruthenium, organic or natural sensitizers) and the corresponding results of the DSSCs’ performance are presented and analyzed in detail. First, six newly synthesized ruthenium(II) complexes are tested, followed by two metal free D−π−A sensitizers and finally a natural sensitizer extracted from red seaweed. All DSSCs were fabricated using a quasi−solid state electrolyte and a platinum counter electrode.

6.1 Newly synthesized ruthenium(II) complexes

The DSSCs employing ruthenium(II) sensitizers are known to display high solar−to−electric energy conversion efficiencies and numerous reports have been published regarding the synthesis and investigation of new ruthenium(II) complexes with different ligands with an aim to further improve the device’s efficiency and stability. In general, these dyes are assembled by incorporating bipyridines and thiocyanate ligands. The recent research in ruthenium sensitizers is focused on structure modification of the ligands to improve the light harvesting, the electron injection efficiency and finally the efficiency of the DSSCs [1,2]. Ligand modifications could also contribute to the better collaboration between the ruthenium dye molecules and electrolytes, especially in the case that quasi−solid state electrolytes are used.

The six new ruthenium(II) complexes synthesized had different side groups and their molecular structures are presented in Figure 6.1. These dyes’ structures were chosen with the aim to provide a possible solution for two general problems appearing in DSSC based on ruthenium sensitizers; the solubility of the dye that may cause aggregation of the dye on the TiO$_2$ surface, and water adsorption of the dye that affects the performance of the solar cell. The Ru(II) complexes were characterized spectroscopically and electrochemically. Moreover, the influence of the molecular side groups on the electrical performance of quasi−solid state DSSCs was investigated by studying the DSSCs sensitized with the new ruthenium(II) dyes in comparison with solar cells sensitized with a commercially available ruthenium dye having a similar structure (D907−Everlight, Taiwan).
6.1.1 Absorption and electrochemical data of the Ruthenium complexes

Initially dye solutions were prepared with the new ruthenium(II) complexes using DMF as solvent (1 mM) in order to optically examine them through UV−Vis absorption spectroscopy. The UV−Vis spectra illustrated in Figure 6.2a were recorded in a 1 cm path length quartz cell and the obtained maximum absorption wavelengths, with the calculated molar absorption coefficients are summarized in Table 6.1. The absorption spectra of ruthenium complexes show bands between 370 and 533 nm that are assigned to MLCT transitions. In the UV region, the bands below 306 nm are observed due to the \(\pi−\pi^*\) transitions of bipyridine and pyridine ligands [3,4]. The bpy-bpy molecules containing branching and non−branching side groups (CS27, CS28, CS32, CS43) exhibit similar maximum absorption wavelengths and molar absorption coefficients (Fig. 6.2a, Table 6.1). This indicates that the branching of side groups didn’t have an important effect on the absorption properties [3]. The absorption spectra of bpy-py molecules (Fig. 6.2a) show blue shifted the lowest−energy MLCT band from 533 nm to 530 nm in the bpy-py molecule with −C−O−C− molecular group in the side group (CS17). The blue shift is attributed to the donor character of 4-(2-ethyl-hexyloxy)-pyridine ligands containing oxygen in side group which cause a slight increase in the energy of the LUMO
of the complex [5]. This results that the $\pi-\pi^*$ and MLCT transitions occur at higher energy.

![Absorption spectra](image)

**Figure 6.2:** (a) UV–Vis absorption spectra of $4\cdot10^{-5}$ M solution of bpy-bpy ruthenium complexes (CS27, CS28, CS32, CS43) and bpy-py ruthenium complexes (CS17, CS22) in DMF, (b) UV–Vis absorption spectra of ruthenium dyes adsorbed on TiO$_2$ film.

In comparison to bpy-bpy molecules (CS27, CS28, CS32, CS43), the lowest–energy MLCT band of bpy-py molecules (CS17, CS22) is red shifted by 12 nm while the molar extinction coefficient decreases. The red shift is due to the fact that the pyridine rings in bpy-py molecules may rotate free into the optimum overlap
Chapter 6

configuration [6]. The more conjugated character of bpy-bpy molecules result in an increase in the molar extinction coefficient. It is well known that sensitizers with high molar extinction coefficients display increased solar light harvesting capacity [7]. Therefore, improving the molar extinction coefficients of sensitizers can result in an increased efficiency in DSSC applications. The dye solutions with the bpy-bpy molecules exhibit similar molar extinction coefficients (ε: 1.05–1.34·10^4 M^{-1}·cm^{-1}) compared to the one reported in literature for the commercially available D907 ruthenium dye, with the similar structure as the new ruthenium complexes, which was used as a reference (ε: 1.16·10^4 M^{-1}·cm^{-1}) [3].

Table 6.1: Absorption and electrochemical data of the ruthenium complexes in DMF.

<table>
<thead>
<tr>
<th>Complex</th>
<th>λ_{max}, (nm)</th>
<th>ε/10^4 M^{-1}·cm^{-1}</th>
<th>π→π*</th>
<th>d π→π*</th>
<th>E_{ox} (V) (ΔE_p (V))</th>
<th>E_{red1} (V)</th>
<th>E_{red2} (V) (ΔE_p (V))</th>
<th>E_{red3} (V) (ΔE_p (V))</th>
</tr>
</thead>
<tbody>
<tr>
<td>CS27</td>
<td>299 (4.78)</td>
<td>369 (1.25) 517 (1.13)</td>
<td>0.96 (0.010)</td>
<td>-1.12</td>
<td>-1.46 (0.056)</td>
<td>-1.77 (0.013)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CS28</td>
<td>299 (4.48)</td>
<td>370 (1.20) 518 (1.08)</td>
<td>0.99 (0.009)</td>
<td>-1.09</td>
<td>-1.45 (0.065)</td>
<td>-1.76 (0.021)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CS32</td>
<td>298 (4.50)</td>
<td>370 (1.17) 518 (1.05)</td>
<td>0.97 (0.008)</td>
<td>-1.10</td>
<td>-1.42 (0.009)</td>
<td>-1.76 (0.017)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CS43</td>
<td>299 (5.43)</td>
<td>369 (1.34) 518 (1.20)</td>
<td>0.99 (0.010)</td>
<td>-1.11</td>
<td>-1.43 (0.009)</td>
<td>-1.77 (0.017)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CS17</td>
<td>306 (3.23)</td>
<td>382 (0.71) 530 (0.41)</td>
<td>1.25 (0.096)</td>
<td>-0.73</td>
<td>-1.34</td>
<td>-1.61</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CS22</td>
<td>305 (2.60)</td>
<td>386 (0.85) 533 (0.50)</td>
<td>1.25 (0.104)</td>
<td>-0.71</td>
<td>-1.33</td>
<td>-1.57</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In order to obtain concrete results about the adsorbed amount of dye on TiO_2 films which could be later correlated with the electrical characterization results, UV–Vis absorption measurements were performed to examine the light absorption spectra of the sensitized TiO_2 films (Fig. 6.2b). All TiO_2 films were immersed in the ruthenium dye solutions overnight in order to complete the sensitization. As a reference some TiO_2 films where sensitized using a 1 mM acetonitrile solution of D907. It is obvious that the absorbance of the two complexes CS28 and CS32 is directly compared with that obtained for D907 while the absorbance of the other two bpy-bpy molecules CS43 and CS27 is a little lower. In accordance to Figure 6.2a the absorbance of the two bpy-py molecules CS17 and CS22 is much lower while the visual impression of the sensitized TiO_2 films is a very pale purple color.

The electrochemical properties of the complexes were investigated by cyclic voltammetry. Cyclic voltammograms were obtained in a cell containing a glassy carbon working electrode, a silver wire reference electrode, a platinum wire counter electrode and a supporting electrolyte consisting of 0.1 M tetrabutylammonium
hexafluorophosphate (TBAPF₆) in DMF with a scan rate of 100 mV·s⁻¹. The ferrocenium/ferrocene couple was used as an internal standard (0.65 V vs. Ag/Ag⁺).

The electrochemical data are summarized in Table 6.1 and the cyclic voltammograms of CS27 and CS17 are given in Figure 6.3 and 6.4. The cyclic voltammogram of the bpy-bpy molecules (CS27, CS28, CS32, CS43) show one reversible oxidation peak around 0.97 V vs. Ag/Ag⁺, which is attributed to the Ru (II/III) couple (Fig. 6.3a). The quasi-reversible oxidation peaks of bpy-py (CS17, CS22) (Fig. 6.4a) show anodic shift from 0.97 V to 1.25 V compared to bpy-bpy molecules (CS27, CS28, CS32, CS43). This means that the electron density of ruthenium metal for bpy-py is less than that for bpy-bpy complexes [8]. This is attributed to the chelating effect of bidentate bipyridine ligands. The chelating effect increases the interaction between ruthenium and bipyridyl nitrogens (Ru–N), the greater the π−back bonding, which leads to a shorter Ru–N bond length compared to monodentate coordination [8]. This interaction occurs by the electron donation from bipyridine ligand to empty ruthenium metal d orbital and followed by the π−back bonding from the filled ruthenium metal d orbital to the empty π* orbital of ligand. This interaction increases the electron density in the ruthenium metal t₂g orbital in the presence of bipyridine ligand which coordinates to ruthenium metal with two electron donating nitrogens [9-11]. This result in a cathodic shift for bpy-bpy molecules compared to bpy-py molecules. The cyclic voltammograms of the bpy-bpy and bpy-py molecules (Fig. 6.3b and 6.4b) show three reduction peaks. The reduction peaks are assigned to the reduction of carboxylic acid protons, 4,4'-dicarboxy- 2,2'-bipyridine and the bipyridine, respectively [3]. The reduction potentials of bpy-bpy molecules are shifted cathodically which are related to the stronger electron donor property of bipyridine ligands.

Consecutive cyclic behaviors of the complexes (Fig. 6.3c and 6.4c) were investigated in order to determine their electrochemical stability. The bpy-bpy molecules have more electrochemical stability compared to the bpy-py molecules. No significant change in peak currents and potentials of anodic and cathodic areas are observed in bpy-bpy molecules. Furthermore, the reversibility of the redox peaks exhibits more stability of bpy-bpy molecules. It indicates that the chelating effect enhances stability in the presence of bipyridine ligand [8]. The energy levels and electrochemical stability of the complexes are in agreement with the reported values for the related classes of
ruthenium(II) complexes, indicating that they can be used as photosensitizers in DSSCs [3-5].

Figure 6.3: (a) Cyclic voltammograms of CS27, (b) differential of CS27 voltammogram, (c) 5 consecutive cyclic voltammograms of CS27 measured in DMF solutions with scan speed of 100 mV·s⁻¹.

Figure 6.4: (a) Cyclic voltammograms of CS17, (b) differential of CS17 voltammogram, (c) 5 consecutive cyclic voltammograms of CS17 measured in DMF solutions with scan speed of 100 mV·s⁻¹.

6.1.2 Fabrication of DSSCs

The TiO₂ photoelectrode films were fabricated in two steps using a compact TiO₂ blocking layer and a layer of TiO₂ paste (cf. subsection 5.2.1). The TiO₂ films were
sensitized overnight in the dye solutions and when they were removed from the solutions they were thoroughly washed with the corresponding solvent (DMF or acetonitrile) to remove the excessive dye molecules. The sensitized TiO₂ films were dried in air before completing the manufacture process of the final DSSC device using platinum counter electrodes and an I⁻/I₃⁻ quasi−solid state electrolyte as reported in previous paragraphs.

6.1.3 Electrical and electrochemical characterization of DSSCs

In order to obtain the current density−voltage (J−V) characteristic curves (Fig. 6.5) of the quasi−solid state DSSCs, for all the dye complexes tested a black mask was used confining the solar cell’s active area to 0.3 cm². In general, the solar cells sensitized with the new dye complexes showed almost the same overall performance compared with the ones that were sensitized with D907. In the case of the solar cells sensitized with CS28 a slight better performance was monitored than this obtained for D907. Some of the new dyes weren’t adsorbed that well (Fig. 6.2b), thus they didn’t sensitize sufficiently the TiO₂ films which had a direct impact on the DSSCs’ performance reflected mainly to the measured current density values.

![Figure 6.5: Photocurrent−voltage curves of DSSCs with TiO₂ nanocrystalline films sensitized with different newly fabricated ruthenium dyes.](image)

The electrical parameters measured and calculated for all solar cells are summarized in Table 6.2. The bpy-bpy molecules (CS28, CS32, CS43) showed higher overall efficiencies in the range of 2.9%−3.3% compared to the bpy-py molecules (CS17, CS22).
The more conjugated character of bpy-bpy molecules result in an increase in the molar extinction coefficients. This can enhance the solar light harvesting capacity and improve the conversion efficiencies of DSSCs [12]. In fact the solar cells sensitized with the dyes CS28, CS32 and CS43 showed a slightly increased open–circuit voltage compared with D907. The cell efficiency of CS27 decreased in the presence of two branching alkyl chains when compared to other bpy-bpy molecules. This increase in the efficiency of the DSSCs can be attributed to the decreasing steric effect of side groups. The efficiency of solar cell sensitized with CS17 is higher than that of CS22 which may be attributed to more electron donor properties of pyridine ligand containing oxygen in side group of CS17. The performance of the new dyes as TiO₂ sensitizers for DSSCs was also explained in terms of the external quantum efficiency measured for each solar cell sensitized with the six ruthenium complexes. Figure 6.6 presents the IPCE spectra of the solar cells at different wavelengths. It can be seen that the maximum of the solar cells’ efficiency almost coincides with the maximum of the dye absorption spectra of the dyes on TiO₂. Moreover, the better J_{sc} values obtained for D907 can be attributed to the extension of the IPCE spectrum at longer wavelengths compared to that obtained for CS28 and CS32. However, values exceeding 80% are obtained for these dyes (CS28, CS32) while 70% and 45% IPCE values are monitored for the remaining two bpy-bpy molecules CS43 and CS27 respectively. Finally, low IPCE values for the two bpy-py molecules are obtained which are in line with J–V data.

Table 6.2: Solar cells parameters for DSSCs with TiO₂ photoelectrodes sensitized with different ruthenium dyes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>J_{sc} (mA/cm²)</th>
<th>V_{oc} (V)</th>
<th>FF</th>
<th>n (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CS27</td>
<td>3.0</td>
<td>0.63</td>
<td>0.77</td>
<td>1.46</td>
</tr>
<tr>
<td>CS28</td>
<td>7.0</td>
<td>0.66</td>
<td>0.72</td>
<td>3.28</td>
</tr>
<tr>
<td>CS32</td>
<td>6.7</td>
<td>0.66</td>
<td>0.67</td>
<td>2.95</td>
</tr>
<tr>
<td>CS43</td>
<td>6.1</td>
<td>0.69</td>
<td>0.69</td>
<td>2.91</td>
</tr>
<tr>
<td>CS17</td>
<td>1.2</td>
<td>0.59</td>
<td>0.69</td>
<td>0.47</td>
</tr>
<tr>
<td>CS22</td>
<td>0.5</td>
<td>0.53</td>
<td>0.62</td>
<td>0.16</td>
</tr>
<tr>
<td>D907</td>
<td>7.3</td>
<td>0.65</td>
<td>0.69</td>
<td>3.26</td>
</tr>
</tbody>
</table>
**Figure 6.6:** Incident photon to current efficiency of the manufactured DSSCs with TiO$_2$ nanocrystalline films sensitized with different newly fabricated ruthenium dyes.

**Figure 6.7:** Dark current−voltage characteristic curves of dye−sensitized solar cells with different dyes.

The solar cells sensitized with the different ruthenium dyes were also examined by measuring the dark current suppression. Figure 6.7 shows that the dark current density of the DSSCs sensitized with the new dyes does not have substantial differences compared to that obtained for D907. However, the electron leakage, of the DSSCs sensitized with the dyes CS17 and CS22 is noticeably higher compared to those sensitized with CS28, CS32, CS43 and D907 which can be attributed to the poor adsorption of the former at
the TiO$_2$ mesoporous films eventually leading to a reduced overall performance of the solar cells under light exposure.

![Impedance spectra and Bode phase plots](image)

**Figure 6.8:** (a) Impedance spectra and (b) Bode phase plots of dye−sensitized solar cells with different dye complexes measured at open−circuit voltage at 1 sun illumination.

Figure 6.8a and b show the Nyquist and Bode plots respectively obtained from the electrochemical impedance spectroscopy measurements for all the solar cells sensitized with the different ruthenium dyes. The experimental data are presented by scattering symbols while lines represent the fitted plots arising from the software used to handle the
Metrohm Autolab equipment. The Nyquist plots (Fig. 6.8a) are displaying three characteristic semicircles each one corresponding to a frequency range high, intermediate and low, ascribed to the parallel combination of a capacitor or a CPE with the charge transfer resistance at the counter electrode \( R_{pt} \), the charge transport at the \( \text{TiO}_2/dye/electrolyte \) interface \( R_{tr} \) and the diffusion resistance \( R_{dif} \) respectively [13]. Correspondingly the Bode phase plots (Fig. 6.8b) also feature three frequency peaks which are related with each one of the Nyquist characteristic peaks.

The equivalent circuits which were used to fit the experimental data were either a \( R(RC)(RC)(RC) \) or a \( R(RQ)(RQ)(RQ) \) electrical circuit and the CPE elements (represented by \( Q \) in the equivalent circuit) were converted to capacitor elements using equation 5.2. The fitted parameters are presented in Table 6.3. The values of \( R_{pt} \), \( C_{pt} \), \( R_{dif} \) and \( C_{dif} \) were almost invariable as all cells were fabricated using the same electrolyte solution and the same type of counter electrode. The main variation was observed in \( R_{tr} \) and \( C_{tr} \) values. Cells with less dye adsorbed, exhibit an increased charge transport resistance at the \( \text{TiO}_2/dye/electrolyte \) interface. A small \( R_{tr} \) value with a simultaneous high \( C_{tr} \) value denotes a fast charge transport at the interface of \( \text{TiO}_2/dye/electrolyte \), which explains the better overall performance of the cells sensitized with the dyes CS32, CS28, CS43 and D907 [14].

**Table 6.3:** Fitted parameters derived from electrochemical impedance spectroscopy.

<table>
<thead>
<tr>
<th>Complex</th>
<th>( R_h ) (Ω)</th>
<th>( R_{pt} ) (Ω)</th>
<th>( C_{pt} \cdot 10^{-4} ) (F)</th>
<th>( R_{tr} ) (Ω)</th>
<th>( C_{tr} \cdot 10^{-3} ) (F)</th>
<th>( R_{dif} ) (Ω)</th>
<th>( C_{dif} \cdot 10^{-2} ) (F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CS27</td>
<td>11.10</td>
<td>1.59</td>
<td>0.42</td>
<td>5.60</td>
<td>1.31</td>
<td>0.81</td>
<td>6.5</td>
</tr>
<tr>
<td>CS28</td>
<td>10.00</td>
<td>1.56</td>
<td>0.40</td>
<td>7.37</td>
<td>1.40</td>
<td>1.48</td>
<td>3.9</td>
</tr>
<tr>
<td>CS32</td>
<td>7.96</td>
<td>1.75</td>
<td>0.38</td>
<td>4.40</td>
<td>1.72</td>
<td>1.00</td>
<td>5.5</td>
</tr>
<tr>
<td>CS43</td>
<td>10.10</td>
<td>1.63</td>
<td>0.46</td>
<td>6.00</td>
<td>1.50</td>
<td>0.99</td>
<td>15.6</td>
</tr>
<tr>
<td>CS17</td>
<td>5.07</td>
<td>2.00</td>
<td>0.65</td>
<td>11.70</td>
<td>1.63</td>
<td>8.02</td>
<td>1.2</td>
</tr>
<tr>
<td>CS22</td>
<td>13.20</td>
<td>2.02</td>
<td>0.35</td>
<td>16.40</td>
<td>1.64</td>
<td>2.58</td>
<td>9.3</td>
</tr>
<tr>
<td>D907</td>
<td>8.78</td>
<td>1.91</td>
<td>0.45</td>
<td>5.70</td>
<td>1.58</td>
<td>1.03</td>
<td>7.5</td>
</tr>
</tbody>
</table>

The electron lifetime \( \tau_{el} \) in DSSC is of great importance to determine the recombination dynamics in the cell. Thus, the electron lifetime of all the solar cells was calculated using equation 5.3 and the values are summarized in Table 6.4. The electron lifetime for the solar cells with CS28 was slightly higher than the ones with D907. Particularly, the electron lifetime was 8.10 and 8.08 ms for the cells with CS28 and D907.
respectively which sounds as an improvement for the solar cells employing the newly synthesized CS28 dye.

Table 6.4: Electron lifetime derived from electrochemical impedance spectroscopy.

<table>
<thead>
<tr>
<th>Complex</th>
<th>f (Hz)</th>
<th>$\tau_n$ (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CS27</td>
<td>27.00</td>
<td>5.89</td>
</tr>
<tr>
<td>CS28</td>
<td>19.66</td>
<td>8.10</td>
</tr>
<tr>
<td>CS32</td>
<td>26.91</td>
<td>5.91</td>
</tr>
<tr>
<td>CS43</td>
<td>19.11</td>
<td>8.07</td>
</tr>
<tr>
<td>CS17</td>
<td>29.38</td>
<td>5.42</td>
</tr>
<tr>
<td>CS22</td>
<td>30.33</td>
<td>5.25</td>
</tr>
<tr>
<td>D907</td>
<td>19.69</td>
<td>8.08</td>
</tr>
</tbody>
</table>

Table 6.5: Electron diffusion length derived from electrochemical impedance spectroscopy.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\frac{R_n}{R_{dif}}$</th>
<th>$L_n$ (( \mu )m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CS27</td>
<td>6.91</td>
<td>13.15</td>
</tr>
<tr>
<td>CS28</td>
<td>4.98</td>
<td>1.16</td>
</tr>
<tr>
<td>CS32</td>
<td>4.00</td>
<td>10.49</td>
</tr>
<tr>
<td>CS43</td>
<td>6.06</td>
<td>12.31</td>
</tr>
<tr>
<td>CS17</td>
<td>1.46</td>
<td>6.04</td>
</tr>
<tr>
<td>CS22</td>
<td>6.36</td>
<td>12.61</td>
</tr>
<tr>
<td>D907</td>
<td>5.53</td>
<td>11.76</td>
</tr>
</tbody>
</table>

The electron collection efficiency is vitally important to determine the photovoltaic performance of a DSSC. The electron collection in the conducting substrate can be described in terms of electron diffusion length, $L_n$. Using the electrochemical parameters from the impedance spectroscopy results and the thickness of the TiO$_2$ film, $L_n$ can be calculated from equation 6.1,

$$L_n = L \cdot \sqrt{ \frac{R_n}{R_{dif}} }$$  \hspace{1cm} (6.1)

where $L$ is the TiO$_2$ film thickness [15]. For a relative thickness of about ~5 micrometers TiO$_2$ layer the data for all aforementioned solar cells employing the different ruthenium dyes (newly synthesized and commercially available dye) are presented in Table 6.5. It is worth noting that most of the DSSCs made with the new dyes showed quite comparable
results with the solar cell employing the commercial dye D907. The L<sub>n</sub> values were calculated in the range of 10−13 micrometers.

6.2 New metal free D−π−A sensitizers

Two new organic dyes with D−π−A structure were synthesized and used as sensitizers in DSSCs. The D−π−A sensitizers abbreviated MZ−341 and MZ−235 (Fig. 6.9), had a triphenylamine group as an electron donor which in the case of MZ−235 was coupled to additional electron donating hexyloxy groups.

![Chemical structures of MZ−341 and MZ−235 dyes](image)

**Figure 6.9:** Chemical structures of (a) MZ−341 and (b) MZ−235 dyes.

The π−conjugated bridge between donor and acceptor was benzimidazole derivative. The benzimidazole group, used between the triphenylamine group (donor) and the carboxylic acid (acceptor), is a weak acceptor and was used in order to lower the reduction potential and to facilitate the charge transfer. TiO<sub>2</sub> quasi−solid state DSSCs were fabricated using these D−π−A sensitizers and were electrically and electrochemically characterized. The effect of the additional electron donating hexyloxy groups of MZ−235 on the DSSCs’ properties was also examined.

6.2.1 Electrochemical and FTIR data of the D−π−A sensitizers

The electrochemical properties of the MZ−341 and MZ−235 dyes were examined by cyclic voltammetry using an electrolyte solution containing 0.1 M solution of
tetrabutylammonium hexafluorophosphate (Bu$_4$NPF$_6$) in acetonitrile with a scan rate of 100 mV·s$^{-1}$. A glassy carbon was used as the working electrode, platinum as the counter electrode and Ag/AgCl as the reference electrode. The cyclic voltammograms for both dyes are presented in Figure 6.10.

![Cyclic voltammograms of (a) the MZ−341 and (b) MZ−235 dyes.](image)

**Figure 6.10:** Cyclic voltammograms of (a) the MZ−341 and (b) MZ−235 dyes.

The oxidation potentials were found at 0.89 V and 0.78 V (vs. ferrocenium/ferrocene couple, Fc$^+$/Fc) for MZ−341 and MZ−235, respectively and they are assigned to the oxidation of the triphenylamine donor moiety. Accordingly, the
reduction potentials were found at -1.13 V and -1.67 V for MZ−341 and at -1.16 V and -1.56 V for MZ−235 and they are assigned to the reduction of the benzimidazole and carboxylic acid acceptor that can be anchored to the TiO₂ surface. The presence of the electron-donating groups, coupled to the triphenylamine backbone, reduces the oxidation potential. The HOMO levels for both dyes were calculated from the oxidation potentials, while the LUMO levels were calculated from the reduction potentials. The HOMO levels are located at 5.30 eV and 5.18 eV, while the LUMO levels at 3.27 eV and 3.24 eV for MZ−341 and MZ−235 respectively.

Figure 6.11: FTIR spectra of (a) MZ−341 and (b) MZ−235 dyes.

The dyes were also characterized through FTIR spectroscopy to identify if the carboxylate functional groups (−COOH) were integrated on them. The FTIR spectra obtained for MZ−341 and MZ−235 are presented in Figure 6.11. The O−H bonds of
the dyes resonate at around 3400 cm\(^{-1}\) and they are believed to arise from the carboxylate groups (–COOH). The peak at around 1700 cm\(^{-1}\) is based on the C=O stretch of the carboxylic acid group. Aromatic and aliphatic –CH groups exhibited characteristic absorption bands around 2900 cm\(^{-1}\) and 2800 cm\(^{-1}\). The three aforementioned peaks are the most important ones confirming that the carboxyl groups are successfully integrated on the MZ−341 and MZ−235 dyes.

6.2.2 Fabrication of DSSCs sensitized with the D−π−A sensitizers

The DSSCs were manufactured using transparent TiO\(_2\) photoanode films the preparation of which is described in an earlier paragraph (cf. subsection 5.3.1). Subsequently, the TiO\(_2\) films were sensitized in the dye solutions (10\(^{-5}\) M) for about 30 minutes before completing the fabrication process using a quasi–solid state electrolyte and platinized counter electrodes following the same procedure as in previous cases.

6.2.3 Electrical and electrochemical performance of DSSCs sensitized with the D−π−A sensitizers

A series of three DSSCs were fabricated for each dye and tested under the same conditions. In order to perform the current density–voltage (J–V) measurements under light illumination (1000 W/m\(^2\)) a black mask was used to ensure that all solar cells had an active area 0.28 cm\(^2\). The J–V characteristic curves of the solar cells sensitized with the newly synthesized dyes MZ−341 and MZ−235 are presented in Figure 6.12a and the average values of the electrical characteristics measured and calculated are summarized in Table 6.6. The quasi–solid state DSSCs constructed with MZ−341 showed an overall efficiency of 3.4% which was slightly better than that obtained for the solar cells sensitized with MZ−235 (3.0%). The open–circuit voltage for both dyes was measured around 660 mV, while the short–circuit current density was 6.83 and 6.45 mA/cm\(^2\) for MZ−341 and MZ−235 respectively. These rather low short–circuit current density values can be ascribed to one of the two factors: The low extinction coefficient value and the ineffective visible light utilization. Indeed, the relatively lower values of the electrical characteristics obtained for MZ−235 can be explained in terms of lower absorption of the sensitized TiO\(_2\) photoelectrode compared to that measured for MZ−341 as it can be seen in the inset of Figure 6.12a. Moreover, the unsealed devices showed good stability when subjected to light soaking tests for 300 h of 1 sun continuous solar irradiation.
Figure 6.12: (a) Current density–voltage characteristic curves of quasi–solid state DSSCs employing MZ−341 and MZ−235 dyes under illumination (1.5 A.M, 1000 W/m²) and (b) in dark. Inset of Fig. 6.12a: the absolute absorbance of sensitized TiO₂ films with both dyes.

Table 6.6: Electrical parameters of DSSCs with TiO₂ photoelectrodes sensitized with MZ−341 and MZ−235.

<table>
<thead>
<tr>
<th>Dye</th>
<th>J&lt;sub&gt;SC&lt;/sub&gt; (mA/cm²)</th>
<th>V&lt;sub&gt;OC&lt;/sub&gt; (mV)</th>
<th>FF</th>
<th>n* (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MZ−341</td>
<td>6.83±0.02</td>
<td>663±2</td>
<td>0.74</td>
<td>3.4</td>
</tr>
<tr>
<td>MZ−235</td>
<td>6.45±0.02</td>
<td>662±2</td>
<td>0.69</td>
<td>3.0</td>
</tr>
</tbody>
</table>

*Probable error for the efficiency values of the order 10⁻⁴*

The solar cells with the two dyes were also examined by measuring the dark current suppression. Figure 6.12b shows that even though there isn’t a substantial difference between the dark current density of the DSSCs sensitized with the two different D−π−A organic dyes, the electron leakage of the solar cells made with the dye
MZ−235 is higher compared to the solar cells made with MZ−341. This result corroborates with the slightly reduced overall performance of the MZ−235 DSSCs under light irradiation compared with the ones sensitized with MZ−341.

The Nyquist and Bode plots obtained from the EIS measurements for the solar cells with the two organic dyes are shown in Figure 6.13a and b respectively. The equivalent circuit which was used to fit the experimental data is also presented in Figure 6.13a as an inset and the fitted parameters are summarized in Table 6.7. The solar cells with MZ−341 and MZ−235 dyes exhibit nearly equal values for the charge transport resistance \( (R_{tr}) \) corresponding to the TiO\(_2\)/dye/electrolyte interface. However, using equation 5.1, an increased value for the total series resistance \( (R_s) \) for the solar cells employing MZ−235 dye is obtained, which agrees with the slightly smaller energy conversion efficiency of these DSSCs.

Table 6.7: Fitted parameters derived from electrochemical impedance spectroscopy.

<table>
<thead>
<tr>
<th>Dye</th>
<th>( R_h ) (Ω)</th>
<th>( R_{pt} ) (Ω)</th>
<th>( C_{pt} \times 10^{-4} ) (F)</th>
<th>( R_{tr} ) (Ω)</th>
<th>( C_{tr} \times 10^{-3} ) (F)</th>
<th>( R_{dif} ) (Ω)</th>
<th>( C_{dif} \times 10^{-2} ) (F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MZ−341</td>
<td>6.09±0.03</td>
<td>1.13±0.03</td>
<td>0.35</td>
<td>3.38±0.18</td>
<td>0.125</td>
<td>&lt;&lt;0.810</td>
<td>-</td>
</tr>
<tr>
<td>MZ−235</td>
<td>7.22±0.03</td>
<td>0.669±0.03</td>
<td>0.53</td>
<td>3.85±0.18</td>
<td>0.799</td>
<td>0.810±0.18</td>
<td>18.8</td>
</tr>
</tbody>
</table>

From the Bode plots in the medium frequency range, the characteristic frequency peak is associated with the electron transport in the mesoscopic TiO\(_2\) film and the back reaction at the TiO\(_2\)/electrolyte interface. The electron lifetime in the TiO\(_2\) electrodes for both solar cells employing MZ−341 and MZ−235 was calculated using equation 5.3, where \( f \) is the frequency corresponding to the middle peak at the Bode phase plots [15]. The electron lifetime of the DSSCs with MZ−235 was calculated to be 2.8 ms which was slightly lower than the one obtained for MZ−341 (3.5 ms). This is in line with the better performance of the solar cells employing MZ−341 as a photosensitizer. Moreover, the low and high frequency peak observed in the Bode plots correspond to the triiodide diffusion in the electrolyte and the charge transfer at the counter electrode, respectively. The lack of differences at least for the high frequency peaks implies that no unexpected reaction had occurred within the electrolyte and counter electrode for the two dyes.

Overall, by assessing the gathered results it was ascertained that the smaller solar cell efficiency of the DSSCs prepared with MZ−235 was in agreement with the EIS results, such as higher total series resistance and smaller electron lifetime in the TiO\(_2\)
electrodes, compared to the cells made with MZ−341. Another possible explanation for
the lower performance of the solar cells in the hexyloxy substituted sensitizer could be a
faster recombination of the injected electrons with the dye cations since the hexyloxy
groups are expected to increase the positive charge on the triphenylamine moiety of the
dye [16].

Figure 6.13: (a) Nyquist and (b) Bode phase plots of MZ−341 and MZ−235 sensitized DSSCs
performed under 1 sun illumination measured at open−circuit voltage.
6.3 Natural sensitizer extracted from red algae

In the context of testing various dyes as photosensitizers for DSSCs, red seaweed were collected and their pigment was extracted with a simple procedure in order to be used as sensitizer for TiO$_2$ electrodes and manufacture solar cells. The red algae of the genus *Laurencia Oltusa* were collected at the island of Kefallinia, Greece (38°15′N 20°30′E) and different solvents were used to extract the seaweed’s natural pigment. The absorption spectra of the resulting solutions were tested and the dye solution which had the wider absorption over the visible spectrum was further studied. Finally, dye–sensitized solar cells were fabricated, using the natural dye solutions as sensitizers and they were characterized electrically and electrochemically.

6.3.1 Red algae pigment extraction and optical characterization

After the red seaweed species were collected, they were stored at a closed container at 9°C until used. The red color of the seaweed (Fig. 6.14a) is ascribed to the presence of the chromophore phycoerythrobilin in phycoerythrin (Fig. 6.14b). Initially, four dye solutions were prepared employing different solvents so that each time a different natural pigment could be isolated. The solvents that were tested were methanol, ethanol, a mixture of acetone with millipore (ultra pure) water (acetone/millipore water 80:20 v/v) and millipore water. To prepare the dye solutions, 5 g of the seaweed were soaked in 30 mL of solvent overnight and then it was filtered, to ensure that it didn’t contain any residues from the algae strain.

![Figure 6.14](image.png)

*Figure 6.14:* (a) Red marine algae used for the extraction of natural pigment and (b) the chromophore phycoerythrobilin in phycoerythrin.

The natural dye solutions with the different solvents were optically characterized and their absorption spectra are presented in Figure 6.15. The color of the dye solution employing methanol as a solvent was yellow; the one with ethanol was green, while the
dye solutions employing the mixture of acetone with millipore water or just millipore water as a solvent were red. The yellow methanol dye solution mainly contains carotenoids, whereas the green color of the ethanol dye solution suggests that chlorophyll is the main pigment extracted.

\[\text{Figure 6.15: UV–Vis absorption spectra of natural dye pigments extracted using different solvents.}\]

Absorption over a broad range of the light spectrum is a prime indication of an efficient sensitizer. The three dye solutions in alcohols and a mixture of acetone and water were used for the pigment extraction, showed main characteristic peaks at 415 nm, 472 nm, 530 nm and 668 nm. Although the dye solution with millipore water as a solvent exhibited only one characteristic peak at 518 nm, nevertheless it had the wider absorption spectrum. The peaks at around 415 nm and at 668 nm which are present to all the dye solutions employing an organic solvent are ascribed to chlorophyll a. This shouldn’t be considered as a paradox, based on the red color of the algae species (Fig. 6.14a), as no plant capable of photosynthesis is found without containing chlorophyll a. Chlorophyll a is present in brown or red algae where the characteristic green color is covered by other pigments. Similarly, all photosynthetic cells contain carotenoid pigments whose color is masked by chlorophylls. The peak at around 472 nm is ascribed to these carotenoid pigments. This peak isn’t prominent for the dye solution where the mixture of an organic and inorganic solvent was used, possibly because of the presence of the water. The peak at 518 nm of the dye solution with millipore water is ascribed to phycobilins, as they are
the only water soluble pigment. Although the absorption spectrum of this dye solution exhibits only one peak, it has a wide light absorption, thus it was characterized as the best dye solution which was used for the remaining absorption and infrared spectroscopy experiments.

Additionally, methods to increase the dye adsorption on TiO$_2$ films were examined in order to obtain optimal characteristics. Particularly the dye adsorption on the transparent TiO$_2$ films was tested as a factor of the temperature and the pH of the dye solution. Since the millipore water dye solution had the wider absorption spectrum, acetic acid was added only to that dye solution to modify its pH from neutral to acidic (pH=3) to try to enhance the light harvesting efficiency by reducing the aggregation of the dye molecules [17]. The photoanodes were immersed into the dye solutions and were left overnight to complete their sensitization. Various dye solutions’ temperatures were tested (35°C, 45°C and 55°C) to examine if and in what extent the temperature affects the dye adsorption on TiO$_2$ films and the solar cells’ electrical parameters. The dye uptake of the TiO$_2$ films increased with the addition of acetic acid for all the temperatures tested (Fig. 6.16). The highest absorption spectrum was obtained for a dye solution temperature of 35°C and pH 3. As the temperature further increased, the absorption spectrum decreased, probably because the TiO$_2$ films weren’t efficiently sensitized.

![Temperature and pH of the dye solution](image)

**Figure 6.16:** Absorption spectra of natural dye—adsorbed on TiO$_2$ film for several adsorption temperatures and dye solution’s pH.
The FTIR spectra of the pigment extracted from acidic and neutral solutions are presented in Figure 6.17. In general the two spectra didn’t have any distinguishable differences, which might suggest that the addition of an amount of acetic acid to the dye solution doesn’t change its consistency and it only limits the aggregation effect. The carboxylate group which is present in the phycoerythrin (Fig. 6.14b) show a strong peak ascribed to the O−H stretch. The peak at 3318 cm$^{-1}$ at the FTIR spectrum is an indication of a high concentration of hydroxyl groups $\text{–OH}$ which are necessary to ensure the dye adsorption. The presence of the dye’s carboxylate groups helps in creating an ester−like bond between the carboxylate groups and the $\text{–OH}$ groups on the surface of TiO$_2$. The N−H stretch also occurs in the region 3400−3250 cm$^{-1}$, however these bands are weaker and sharper than those of the O−H stretch. The stretching vibration of the C=C bond, which is usually detected in the region of 1670−1640 cm$^{-1}$, shows a peak at around 1638 cm$^{-1}$. Peaks at about 1645 cm$^{-1}$ and 1530 cm$^{-1}$ can also be ascribed to amide I and amide II protein vibrations and are probably due to the presence of a component at the external part of the cell wall of the algae and of the medullary area of the algae [18]. The peak at 1125 cm$^{-1}$ corresponds to the C−O stretch vibration.

![Figure 6.17: FTIR spectra of acidic and neutral red seaweed natural dye.](image)

**6.3.2 DSSC’s electrical and electrochemical characterization**

The DSSCs were manufactured using transparent titania photoanodes which were fabricated via the sol−gel method employing a quasi−solid state electrolyte and platinum
counter electrodes (cf. subsection 5.3.1 and 5.1.3). All photocurrent density–voltage (J−V) measurements were carried out using a black mask with an aperture area of 0.174 cm². The electrical parameters of all the fabricated solar cells sensitized with all five dye solutions at all temperatures tested (35°C, 45°C and 55°C) are reported in Table 6.8. The measured and calculated electrical values were satisfactory compared with the corresponding ones published for DSSCs sensitized with pigments derived from seaweed [19,20]. Figure 6.18 presents the J−V characteristic curves of the DSSCs sensitized with the natural dye from the red seaweed pigment using millipore water as a solvent at different dye solution’s temperature and pH=3. As a comparison, the corresponding J−V plot of the DSSC sensitized with the neutral dye solution (pH=7) at 35°C is also included.

![Figure 6.18](image)

**Figure 6.18:** Photocurrent−voltage curves of DSSCs for several adsorption temperatures and acidic natural dye solution.

At a first glance it is obvious that the performance of the DSSCs changes drastically when altering the dye solution temperature during photoanode sensitization (Fig. 6.18). The best results were obtained for cells with photoanodes that were sensitized at a dye solution temperature of 35°C with J_{SC} of 1.26 mA/cm², V_{OC} of 0.66 V, FF of 0.63 and efficiency of 0.52%. While the absorption spectrum of the TiO₂ films sensitized with the natural dye solution at a temperature of 45°C didn’t have significant differences with the one corresponding at 35°C, the current values of the former decreased by a factor of almost 64% compared with the latter. Additionally, as the sensitization
temperature increased from 45°C to 55°C the short-circuit current density further decreased, reaching the value of 0.5 mA/cm². The $V_{oc}$ was also affected by the temperature increase, probably because the photoanodes were inefficiently sensitized. The fill factor was more or less satisfactory for all the fabricated cells; however the overall efficiency was low compared with the efficiencies that have been achieved for DSSCs sensitized with commercial dyes due to the low current density values. Nevertheless, it is worth noting that the collected efficiency for the quasi-solid state transparent DSSCs sensitized with the aforementioned pigment could be even higher in the case that thick non-transparent TiO₂ films were used in combination with liquid electrolytes.

**Table 6.8:** Solar cells’ parameters varying the solvent and the temperature for the dye solution during the adsorption of red seaweed natural dye.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Sample</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>$V_{oc}$ (V)</th>
<th>FF (%)</th>
<th>n (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>Millipore water, pH=3</td>
<td>1.26</td>
<td>0.66</td>
<td>0.63</td>
<td>0.52</td>
</tr>
<tr>
<td></td>
<td>Millipore water, pH=7</td>
<td>0.65</td>
<td>0.48</td>
<td>0.65</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td>Methanol</td>
<td>0.50</td>
<td>0.42</td>
<td>0.71</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>Ethanol</td>
<td>0.42</td>
<td>0.45</td>
<td>0.69</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>Acetone:Millipore water (4:1)</td>
<td>0.60</td>
<td>0.46</td>
<td>0.69</td>
<td>0.19</td>
</tr>
<tr>
<td>45</td>
<td>Millipore water, pH=3</td>
<td>0.70</td>
<td>0.44</td>
<td>0.54</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td>Millipore water, pH=7</td>
<td>0.60</td>
<td>0.42</td>
<td>0.71</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>Methanol</td>
<td>0.42</td>
<td>0.41</td>
<td>0.54</td>
<td>0.093</td>
</tr>
<tr>
<td></td>
<td>Ethanol</td>
<td>0.40</td>
<td>0.40</td>
<td>0.59</td>
<td>0.094</td>
</tr>
<tr>
<td></td>
<td>Acetone:Millipore water (4:1)</td>
<td>0.55</td>
<td>0.40</td>
<td>0.64</td>
<td>0.14</td>
</tr>
<tr>
<td>55</td>
<td>Millipore water, pH=3</td>
<td>0.50</td>
<td>0.43</td>
<td>0.54</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>Millipore water, pH=7</td>
<td>0.41</td>
<td>0.42</td>
<td>0.55</td>
<td>0.094</td>
</tr>
<tr>
<td></td>
<td>Methanol</td>
<td>0.37</td>
<td>0.41</td>
<td>0.66</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>Ethanol</td>
<td>0.23</td>
<td>0.39</td>
<td>0.68</td>
<td>0.061</td>
</tr>
<tr>
<td></td>
<td>Acetone:Millipore water (4:1)</td>
<td>0.38</td>
<td>0.42</td>
<td>0.44</td>
<td>0.070</td>
</tr>
</tbody>
</table>

The short-circuit current density values were also verified by the IPCE measurements (Fig. 6.19). The limited performance of the solar cells sensitized with red seaweed natural dye can be ascribed not only to the low IPCE values, but also to the fact that the IPCE spectrum drops to zero after around 600 nm. However, in literature, even lower IPCE values than those obtained have been reported for solar cells sensitized with natural dyes [19].

148
The fabricated solar cells which were sensitized with the different natural dye solutions at 35°C were also examined by measuring the dark current suppression (Fig. 6.20). The dark current is due to the recombination of the injected electrons with the $I_3^-$ in the electrolyte and occurs at the TiO$_2$/electrolyte interface where no dye molecules are adsorbed. The dark current onset of all the solar cells started around 0.4 V, however the electron leakage was higher for the cases where methanol or ethanol was used as solvents.
to extract the dye pigments, due to the poor sensitization of the corresponding photoanodes. Furthermore, the fact that acetic acid was added in the natural dye solution with millipore water in order to decrease the dye aggregation and increase the dye adsorption on the TiO₂ films, had a positive effect as the dark current increased in a slower rate compared with the values of the other solar cells. An increase of the photoanodes’ dye uptake could reduce the dark current and raise the open–circuit voltage, enhancing the overall cells’ performance.

Figure 6.21: (a) Electrochemical impedance spectroscopy spectra fitted with the equivalent circuit shown as an inset and (b) Bode phase plots for solar cell sensitized with red seaweed natural dye, measured at open–circuit voltage at 1 sun illumination.
In order to determine the internal resistances corresponding to the optimum solar cell’s interface, electrochemical impedance spectroscopy measurements were carried out. Figures 6.21a and b demonstrate the typical Nyquist and Bode plot for the DSSC with the red seaweed natural dye and the fitted parameters are summarized in Table 6.9. When changing the dye used to sensitize the photoanode, the only difference should be detected to the fitted parameters corresponding to the TiO$_2$/dye/electrolyte interface ($R_n$ and $C_m$). The desired results would be a small charge transport resistance, $R_n$, with a simultaneous high $C_m$ value, which is an indication of a fast charge transport at the interface. However, the $R_n$ was relatively high and the $C_m$ value was low, probably because the dye adsorption on the TiO$_2$ films wasn’t as strong as when using a commercially available dye [14]. The electron lifetime, $\tau_n$, namely the average time for an electron to recombine (equation 5.3) was calculated 5.89 ms (Table 6.9) which is comparable even with electron lifetimes of newly synthesized ruthenium dye complexes [21].

Table 6.9: Fitted parameters derived from electrochemical impedance spectroscopy.

<table>
<thead>
<tr>
<th>$R_n$ (Ω)</th>
<th>$R_{pt}$ (Ω)</th>
<th>$C_{pt}\cdot10^{-4}$ (F)</th>
<th>$R_m$ (Ω)</th>
<th>$C_m\cdot10^{-3}$ (F)</th>
<th>$R_{dif}$ (Ω)</th>
<th>$C_{dif}\cdot10^{-2}$ (F)</th>
<th>$\tau_n$ (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.1</td>
<td>2.80</td>
<td>0.267</td>
<td>17.1</td>
<td>0.539</td>
<td>10.4</td>
<td>0.815</td>
<td>5.89</td>
</tr>
</tbody>
</table>

Considering the analysis of the natural red seaweed sensitizers it is quite obvious that although employing an algal pigment doesn’t lead to highly efficient solar cells, it could be a viable alternative for fabricating DSSCs with cheap and eco–friendly manufacturing processes even as a demonstration for educational purposes.
Chapter 6

References


Chapter 6


[18] M. Sekkal, C. Declerck, J.-P. Huvenne, P. Legrand, B. Sombret, M.-C. Verdus, Direct structural identification of polysaccharides from red algae by FTIR


Chapter 7 Experimental results—electrolyte of DSSC

Taking as a starting point the quasi-solid state electrolyte employed throughout the previous experimental parts, in this chapter, five different hybrid organic/inorganic materials were synthesized with the organic sub-phase being polypropylene or polyethylene of different oligomer chain length and the inorganic sub-phase consisting of silica. These hybrid organic/inorganic materials were used to prepare five quasi-solid state electrolytes which were characterized through thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) to evaluate their thermal stability. Their electrical conductivity was also measured before utilizing them for the fabrication of transparent quasi-solid state dye-sensitized solar cells. Finally, the performance of the solar cells was examined through electrical and electrochemical measurements.

7.1 Preparation of hybrid organic/inorganic materials and quasi-solid state electrolytes.

Five precursor materials, either O,O’-Bis(2-aminopropyl) polypropylene glycol of various molecular weights (MW~230, 400, 2000), O,O’-Bis(2-aminopropyl) polyethylene glycol (MW~900) or O,O’-Bis(2-aminopropyl) polypropylene glycol-block-polyethylene glycol-block-polypropylene glycol (MW~600) (Fig. 7.1) and 3-isocyanatopropyltriethoxysilane were mixed with THF under reflux conditions (64°C) for 6 h to prepare five different hybrid organic/inorganic materials. The organic/inorganic materials, abbreviated according to the precursor materials that were used to fabricate them and their molecular weight (PPG230–ICS, PPG400–ICS, PPG2000–ICS, PEG900–ICS and ED600–ICS) were subsequently employed as gelator agents and ionic conductors for quasi-solid state electrolytes in dye-sensitized solar cells.

For the preparation of each quasi-solid state electrolyte, various amounts of the corresponding hybrid organic/inorganic material were used until the quantity that led to the optimum solar cell’s performance was concluded. Each quasi-solid state electrolyte was synthesized using the materials and the ratios previously reported (cf. subparagraph 5.1.3) following the same procedure. Among the electrolyte solutions (Fig. 7.2) the one that contained the hybrid organic/inorganic material PPG2000–ICS jellified faster than the others, probably because of the higher molecular weight of the precursor material used.
Chapter 7

Figure 7.1: Molecular structure of the precursor materials (a) O,O’-Bis(2-aminopropyl) polypropylene glycol (b) O, O’-Bis(2-aminopropyl) polyethylene glycol and (c) O,O’-Bis(2-aminopropyl) polypropylene glycol-block-polyethylene glycol-block-polypropylene glycol (Jeffamine® ED-600) used to prepare the hybrid organic/inorganic materials.

Figure 7.2: Synthesized $\Gamma^-/I_3^-$ quasi-solid state electrolytes with different organic/inorganic hybrid material after their jelification.

7.2 Thermogravimetric analysis, differential scanning calorimetry and ionic conductivity measurements of the quasi-solid state electrolytes

As noted, there are future prospects for integrating transparent dye-sensitized solar cells on building facades for energy production towards nearly zero-energy buildings (nZEB). Taking into consideration that these DSSCs could replace common windows used in buildings, their operating temperature and as a result the electrolyte temperature could reach $80^\circ C$ according to solar cell testing standards. Hence, the thermal stability of the electrolytes was examined by testing the materials responsible for the jellification of the electrolytes, namely the hybrid organic/inorganic materials and the acetic acid which were diluted in the electrolyte solvents (sulfolane and 3-...
methoxypropionitrile). The materials were mixed under vigorous stirring and the resulting solutions were left in open bottles to expedite the gelation process. The formed gels were analyzed through TGA and DSC measurements at an extended temperature range from 15°C to 440°C.

![Graph of TGA analysis](image1)

![Graph of DSC analysis](image2)

Figure 7.3: (a) Thermal gravimetric analysis and (b) differential scanning calorimetry curves of the formed gels.

From the thermal gravimetric analysis curves (Fig. 7.3a) the weight of the gels started to slightly reduce after 50°C. The fact that the weight starts to reduce at a temperature lower than 100°C probably is an indication of water presence in the samples.
Chapter 7

[1]. The weight loss increased significantly between the temperature range of 150°C−250°C for all five samples probably because of the evaporation of the gels’ solvents. The fastest weight loss was noted for the gel sample containing the hybrid material PPG230−ICS, while the curve corresponding to ED600−ICS decreased at a slower rate compared with all the samples. In the differential scanning calorimetry curves (Fig. 7.3b), the endotherm transitions are represented by a downward peak. The melting temperature (T_m) of the samples, where they change from gel to liquid phase, was in the range of 210°C−260°C. The higher melting temperatures indicate good thermal stability of the electrolytes and therefore of the solar cells.

The ionic conductivity of the electrolytes with the five different hybrid organic/inorganic materials was examined by electrochemical impedance spectroscopy using an electrochemical cell consisting of the electrolyte solution sandwiched between two copper electrodes. The electrolyte solutions used for these measurements didn’t contain the additives 4−TBP and Guan SCN as these materials don’t have any influence on the ionic conductivity. Figure 7.4 shows the Nyquist impedance spectra for all electrolytes which consist of a shifted from zero semicircle fitted by a resistance R_s in series with a parallel combination of the bulk resistance, R_b, and its corresponding capacitance C_b and a line with a 45° slope to low frequencies extending to infinity fitted using a Warburg element, W in series, which is characterized by the parameter Y_0 (inset of Fig. 7.4). The Warburg element is a sub−indent of a CPE which depends on the admittance of an ideal capacitance Y_0 and the empirical constant N (N=\frac{1}{2}) [2]. The ionic conductivity can be calculated using equation 7.1

\[ \sigma = \frac{d}{R_b \cdot A} \]  

(7.1)

where d is the thickness of the electrolyte samples, R_b the bulk resistance taken as the intercept of the completed semicircle with the real axis and A is the area of the samples [3]. All the calculated values of the ionic conductivity, summarized in Table 7.1, seem to be close to one another while a relatively higher value was obtained for ED600−ICS. The conductivity values could be considered low compared with the corresponding values of liquid electrolytes, however in the case of quasi−solid state electrolytes, as the gelation process progresses, the conductivity is reduced because the ion diffusion is also
reduced. Then again, it’s not the first time that quasi-solid state electrolytes with ionic conductivity values of the same order of magnitude have been reported [4,5].

![Nyquist impedance plots of electrolyte gels measured in dark at room temperature.](image)

**Figure 7.4:** Nyquist impedance plots of electrolyte gels measured in dark at room temperature.

**Table 7.1:** Ionic conductivities for the five different gel electrolytes studied at room temperature.

<table>
<thead>
<tr>
<th>Hybrid organic/inorganic material</th>
<th>Conductivity $\sigma$ (S·cm$^{-1}$·10$^{-4}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPG230–ICS</td>
<td>7.47</td>
</tr>
<tr>
<td>PPG400–ICS</td>
<td>8.09</td>
</tr>
<tr>
<td>PPG2000–ICS</td>
<td>7.58</td>
</tr>
<tr>
<td>PEG900–ICS</td>
<td>7.54</td>
</tr>
<tr>
<td>ED600–ICS</td>
<td>8.47</td>
</tr>
</tbody>
</table>

7.3 Fabrication and characterization of quasi-solid state DSSCs

7.3.1 Fabrication of TiO$_2$ photoanode and structural properties

The TiO$_2$ photoanodes were fabricated via the sol–gel method with minor alterations at the solution’s synthesis reported in subparagraph 5.3.1. Since TiO$_2$ DSSCs manufactured using Titanium(IV) butoxide as a precursor material for the TiO$_2$ films displayed superior performance, TTBU was used as a starting material for their
fabrication. Furthermore, instead of using Triton X-100 and ethanol, Pluronic P123 and n-propanol were employed as a surfactant agent and solvent in the TiO$_2$ solution respectively. In particular, 0.498 g of Pluronic P123 was mixed with 4 mL of n-propanol, followed by the addition of 0.4 mL of glacial acetic acid and 0.37 mL of titanium(IV) butoxide under vigorous stirring. The solution was kept in a well closed vessel when it wasn’t used to slow down alkoxide’s hydrolysis due to ambient moisture. After a few minutes of stirring, the solution was deposited on the FTO glasses with the spin coating device following the procedure described in subparagraph 5.3.1, with intermediate sintering steps. The procedure was repeated several times until an optimum film thickness was obtained for maximum electrical performance of the solar cells.

The TiO$_2$ solution employing Pluronic P123 was examined for the first time after the completion of the experiments for the DSSCs’ photoanode (cf. Chapter 5) and was tested only in this series of experiments. Pluronic P123 was chosen because reports came to our attention regarding the fact that this surfactant can lead to the formation of pores over a wide range of sizes [6]. Therefore to determine the structural properties of the TiO$_2$ films nitrogen sorption–desorption measurements were carried out on powder which resulted by scratching thick films made on glass microscope slides. The particle surface area and pore structure of the TiO$_2$ powder are summarized in Table 7.2, while the results are presented in Figure 7.5a and b.

The hysteresis loop in Figure 7.5a has a wide relative pressure region (0.5<P/P$_0$<1) which suggests that the TiO$_2$ solution employing P-123 can in fact lead to the formation of pores over a broad range of sizes (mesopores to macropores) [6]. The porosity of the TiO$_2$ film was rather high considering that the calculated value (46.1%) was almost comparable with the corresponding values obtained for the TiO$_2$ pastes (cf. subparagraphs 5.1.2 and 5.2.2) combined with the fact that the TiO$_2$ films maintained their transparency. The sample’s BET specific surface area was high, as well as the BJH pore volume which was 0.23 cm$^3$/g. It is also worth noting that the pore size distribution plot for the TiO$_2$ powder (Fig. 7.5b) showed two peaks, one located at 3.6 nm and the other one at larger average pore size of 11.37 nm.

The particles and the surface of the film they form on FTO glasses were also studied through SEM at an acceleration voltage of 10 kV. From the TiO$_2$ film’s images (Fig. 7.6a and b) it can be seen that a highly porous network with aggregated particles is
formed. Indeed, the presence of large clusters of aggregated particles with large volume of empty space could be advantageous to the electrolyte filling in the DSSCs. TiO$_2$ particles have almost similar size ($9-10$ nm) and they are interconnected in a fine network with high porosity (Fig. 7.6b), which favors the dye uptake. In addition, the thickness of the photoanode was approximately between $3.6-4.2$ μm, measured by a cross section image suggesting a rather medium thick but transparent film.

**Table 7.2:** Structural properties of the TiO$_2$ powder obtained from the solution used for the film fabrication.

<table>
<thead>
<tr>
<th>Porosity (%)</th>
<th>$S_{BET}$ (m$^2$/g)</th>
<th>Pore diameter (nm)</th>
<th>Pore volume (cm$^3$/g)</th>
<th>Pore width (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>46.1</td>
<td>60.1</td>
<td>11.37</td>
<td>0.225</td>
<td>14.97</td>
</tr>
</tbody>
</table>

**Figure 7.5:** (a) Sorption−desorption isotherms and (b) pore size distribution for powder obtained from the TiO$_2$ solution used to fabricate the photoanodes.

**Figure 7.6:** (a), (b) SEM images of the TiO$_2$ particles of the film used as photoanode.
7.3.2 DSSCs’ manufacture—Electrical and electrochemical performance

The as−prepared TiO$_2$ films were sensitized with N719 dye solution (0.5 mM) overnight. Afterwards, the glasses were removed from the dye solution and were rinsed meticulously. For each case, two quasi−solid state solar devices were manufactured following the same procedure used so far and tested under the same conditions. The complete DSSCs are shown in Figure 7.7, where their high transparency is obvious. Figure 7.8 presents the photocurrent density−voltage characteristic curves of the dye−sensitized solar cells employing the five different quasi−solid state electrolytes (Fig. 7.8). All the electrical measurements were carried out using a black mask that confined the active area of the solar cells to 0.26 cm$^2$ and the obtained values of the electrical parameters are summarized in Table 7.3.

![Image of solar cells](image-url)

**Figure 7.7:** The transparent quasi−solid state dye−sensitized solar cells.

In general, the solar cells that employed four out of five tested electrolytes had almost the same electrical parameter values and only the DSSCs with the electrolyte that contained PPG230−ICS exhibited a deviation as far as the measured photocurrent is concerned. Regarding the solar cells’ open−circuit voltage, the obtained values were relatively invariant as all electrolytes contained the same redox couple, so the redox potential remained constant. Specifically, the solar cells employing the quasi−solid state
electrolyte PPG230−ICS exhibited the lowest photocurrent density affecting the acquiring efficiency. Moreover, even though cells with ED600−ICS and PPG2000−ICS demonstrated the highest short−circuit current densities; the highest solar cell’s overall efficiency was recorded for the case of PEG900−ICS due to its better fill factor.

![Figure 7.8: Photocurrent−voltage curves of DSSCs with quasi−solid state electrolytes employing different hybrid organic/inorganic material.](image)

**Table 7.3:** Electrical solar cells’ parameters for DSSCs with quasi−solid state electrolytes employing different hybrid organic/inorganic material.

<table>
<thead>
<tr>
<th>Hybrid organic/inorganic material</th>
<th>J_{sc} (mA/cm^2)</th>
<th>V_{oc} (V)</th>
<th>FF (%)</th>
<th>n (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPG230−ICS</td>
<td>7.89</td>
<td>0.73</td>
<td>0.59</td>
<td>3.4</td>
</tr>
<tr>
<td>PPG400−ICS</td>
<td>8.80</td>
<td>0.72</td>
<td>0.57</td>
<td>3.6</td>
</tr>
<tr>
<td>PPG2000−ICS</td>
<td>8.98</td>
<td>0.74</td>
<td>0.56</td>
<td>3.7</td>
</tr>
<tr>
<td>PEG900−ICS</td>
<td>8.88</td>
<td>0.73</td>
<td>0.60</td>
<td>3.9</td>
</tr>
<tr>
<td>ED600−ICS</td>
<td>8.98</td>
<td>0.73</td>
<td>0.57</td>
<td>3.7</td>
</tr>
</tbody>
</table>

In order to examine the recombination processes between the injected electrons and the I_{3}− in the electrolyte, the dark current suppression was studied. From the dark current curves of the DSSCs with the quasi−solid state electrolytes employing different hybrid organic/inorganic material (Fig. 7.9) the dark current onset started after 0.65 V and it was almost the same for all the DSSCs regardless of the quasi−solid state
electrolyte used. The low dark current values are an indication of a suppressed electron recombination which consequently is an evidence for an increased short−circuit current density. Overall the different length of the oligomer’s chain and the molecular weight of the organic sub−phase of the hybrid material had no apparent impact on the electrical performance of the DSSCs.

![Graph showing dark current−voltage characteristic curves of dye−sensitized solar cells with quasi−solid state electrolytes employing different hybrid organic/inorganic material.](image)

**Figure 7.9:** Dark current−voltage characteristic curves of dye−sensitized solar cells with quasi−solid state electrolytes employing different hybrid organic/inorganic material.

The electrochemical impedance spectroscopy was used as an efficient method to examine each dye−sensitized solar cell’s interface and elucidate which parameters are affected by changing one of the DSSCs’ components. Figure 7.10 demonstrates the typical Nyquist plots for the DSSCs with the different quasi−solid state electrolytes. The equivalent circuit used to fit the experimental data was either a R(RC)(RC)(RC) or a R(RQ)(RQ)(RQ) circuit (Fig. 5.22) and the obtained fitted parameters are summarized in Table 7.4. Since the only difference between the solar cells was the quasi−solid state electrolyte used, the main variations should be limited at the EIS parameters that correspond to the interfaces with which the electrolyte interacts, namely the parameters of the TiO₂/dye/electrolyte interface (R_tr, C_tr) and the ones describing the diffusion in the electrolyte (R_dif, C_dif).

Notably, the values corresponding to the first semicircle describing the Pt/electrolyte interface (R_pt, C_pt) were constant, while unexpected variations were observed regarding the R_h values. The R_h discrepancies could be originating from the
uneven use of silver paste for the solar cells’ contacts due to the manual application with a brush. As far as the other parameters are concerned, owing to the fact that a small $R_u$ value with a simultaneous high $C_u$ value denotes a fast charge transport at the interface of TiO$_2$/dye/electrolyte could explain the better results obtained for the case of PEG900–ICS. Finally, although the main differences were anticipated to be recorded for the $R_{\text{dif}}$ and $C_{\text{dif}}$ values, there were no such indications, from which it was concluded that altering the hybrid organic/inorganic material used as a gelator in the electrolyte, doesn’t affect the $I_3^-$ diffusion in the electrolyte [7].

All things considered, the quasi–solid state electrolytes tested exhibited satisfactory thermal stability and ionic conductivity and only minor differences were detected among them, with ED600–ICS displaying slightly superior results. For the fabricated DSSCs employing the electrolytes with the different hybrid organic/inorganic materials a maximum overall efficiency of almost 4% was recorded which is rather competitive considering their high transparency. In particular, the efficiencies of the DSSCs, with the photoanode films prepared from the TiO$_2$ solution employing Pluronic P123 which were subsequently sensitized with N719, were the highest recorded throughout all the previous experiments regarding transparent TiO$_2$ solar cells fabricated through the sol–gel method.

![Impedance spectra of dye-sensitized solar cells with quasi-solid state electrolytes employing different hybrid organic/inorganic material measured at open-circuit voltage at 1 sun illumination.](image)

**Figure 7.10:** Impedance spectra of dye–sensitized solar cells with quasi–solid state electrolytes employing different hybrid organic/inorganic material measured at open–circuit voltage at 1 sun illumination.
Table 7.4: Fitted parameters derived from electrochemical impedance spectroscopy.

<table>
<thead>
<tr>
<th>Hybrid organic/inorganic material</th>
<th>$R_h$ (Ω)</th>
<th>$R_{pt}$ (Ω)</th>
<th>$C_{pt} \cdot 10^{-4}$ (F)</th>
<th>$R_n$ (Ω)</th>
<th>$C_n \cdot 10^{-3}$ (F)</th>
<th>$R_{dif}$ (Ω)</th>
<th>$C_{dif} \cdot 10^{-2}$ (F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPG230−ICS</td>
<td>12.3</td>
<td>1.13</td>
<td>0.43</td>
<td>8.49</td>
<td>6.77</td>
<td>1.41</td>
<td>0.9</td>
</tr>
<tr>
<td>PPG400−ICS</td>
<td>9.3</td>
<td>1.48</td>
<td>0.43</td>
<td>9.72</td>
<td>7.53</td>
<td>1.27</td>
<td>1.1</td>
</tr>
<tr>
<td>PPG2000−ICS</td>
<td>7.3</td>
<td>1.68</td>
<td>0.34</td>
<td>10.20</td>
<td>6.93</td>
<td>0.82</td>
<td>2.1</td>
</tr>
<tr>
<td>PEG900−ICS</td>
<td>10.2</td>
<td>1.69</td>
<td>0.36</td>
<td>8.53</td>
<td>7.65</td>
<td>1.39</td>
<td>1.1</td>
</tr>
<tr>
<td>ED600−ICS</td>
<td>8.1</td>
<td>1.71</td>
<td>0.40</td>
<td>8.37</td>
<td>7.09</td>
<td>1.28</td>
<td>1.4</td>
</tr>
</tbody>
</table>
References


The common material of choice for the counter electrode of DSSCs is platinum, as it is a great electrocatalyst that can be easily prepared by thermal decomposition of chloroplatinic acid [1]. However, other less expensive materials have also been used and tested (cf. paragraph 2.5) in order to replace platinum and lower the total DSSCs’ fabrication cost. The ultimate purpose of almost every research regarding third-generation photovoltaics, as DSSCs, is to optimize their efficiency and long-term stability, having as a prerequisite their transparency in order to be able to use them in a variety of applications in the future for power generation. In an attempt not to compromise between the counter electrode’s transparency and its electrocatalytic ability, the case of a nickel doped cobalt sulfide cathode and polypyrrole (PPy) were investigated. Nickel doped cobalt sulfide counter electrode was chosen as an alternative CE for DSSCs based on research reports that suggested an enhancement of the solar cells’ power conversion efficiency when compared with solar cells employing Pt CE [2]. The solar cells that were used for the aforementioned study employed liquid electrolyte, thus in order to examine the effect of this CE on the electrical characteristics of DSSCs employing a quasi-solid state electrolyte a similar nickel doped cobalt sulfide synthesis was tested. Likewise, the conducting polymer PPy was used as a counter electrode as it can be applied by electrodeposition, which does not require high temperature annealing, hence, it can be employed on flexible plastic electrodes [3].

8.1 Nickel doped cobalt sulfide counter electrode

8.1.1 Preparation of the nickel doped cobalt sulfide counter electrode

Cobalt sulfide CEs have been tested as an alternative to platinum CEs due to their exceptional electrocatalytic ability toward $\Gamma^-/I_3^-$ [4,5]. Nickel can be used as a dopant in cobalt sulfide CEs in order to further enhance their electrocatalytic activity and improve the performance of the solar cells by reducing the energy losses. Thus, the counter electrode that was fabricated and tested was a nickel doped cobalt sulfide (Ni doped...
CoS$_2$) as literature reports indicated that this CE could supersede and perhaps substitute the platinum counter electrode.

The nickel doped cobalt sulfide counter electrode was fabricated through the chemical bath deposition (CBD) method. The materials that were used to fabricate the nickel doped cobalt sulfide counter electrode were substantially cheaper than platinum and the deposition method didn’t require annealing at high temperature, which suggests that this counter electrode could be also used for manufacturing flexible DSSCs. For the solution synthesis we used 0.1 M cobalt(II) nitrate hexahydrate, 0.2 M thiourea, 0.2 M thioacetamide in 3 mL of Millipore water. To the above solution, a small amount of nickel(II) acetate tetrahydrate (0.0471 g, 1.5% w/w) was added to complete the doping. The FTO glasses were placed horizontally into a closed glass bottle containing the solution and then the container was placed in a furnace at 90°C for 2 hours. The parts of the FTO glass that needed to remain without the CE solution to be deposited were covered with an insulating tape, which was removed after the completion of the deposition. When the container was transferred out of the furnace, the FTO glasses were removed from the glass bottle and were rinsed using Millipore water and ethanol. Finally, the FTO glasses annealed at 60°C for half an hour to dry. The platinized CEs were made as reported before by casting a few drops of a chloroplatinic acid solution on the FTO glasses followed by heating at 500°C for 10 minutes.

**Figure 8.1:** Transparent platinum counter electrode (on the left) and nickel doped cobalt sulfide counter electrode (on the right).

The resulting counter electrodes are presented in Figure 8.1 from which it can easily be ascertained their high transparency. At some point during the CBD process for the Ni doped CoS$_2$ counter electrodes formation one of the caps of the glass bottles popped out resulting in the evaporation of some amount of the solvent (Millipore water), making the solution more dense, which resulted in a thicker and less transparent counter electrode. However, it was decided to use both the thinner and the thicker nickel doped counter electrode for solar cells to compare it against each other.
8.1.2 Fabrication of the DSSCs, electrical and electrochemical characterization

The TiO\textsubscript{2} photoanodes were prepared using a compact layer of TiO\textsubscript{2} and TiO\textsubscript{2} paste, following the exact procedure reported in subparagraph 5.2.1, and then they were sensitized overnight in an ethanol/acetonitrile solution of N719. For the manufacture of the solar cells, a quasi–solid state electrolyte was used. Among the quasi–solid state electrolytes tested in the previous Chapter, the gel electrolyte abbreviated ED600–ICS was chosen because of the slightly superior characteristics (stability and ionic conductivity) and performance.

The electrical measurements of the fabricated solar cells were performed using a mask with an aperture area of 0.26 cm\textsuperscript{2}. The photocurrent density–voltage curves of the solar cells with the platinum and the nickel doped CoS\textsubscript{2} CE are illustrated in Figure 8.2 and the obtained parameters are presented in Table 8.1. The solar cell with the thinner nickel doped CoS\textsubscript{2} CE had a higher $J_{sc}$ value compared with the one employing the Pt CE. In general, cobalt sulfide counter electrodes have lower conductivity compared with Pt and lower electrocatalytic ability for reducing $I_{3}^{-}$. However, the use of a small amount of nickel as a doping agent for the CoS\textsubscript{2} seems to enhance the catalytic ability and increase the current density.

![Figure 8.2: Photocurrent density–voltage characteristic curves of dye–sensitized solar cells with different counter electrodes.](image-url)
Since the solar cells with the thicker nickel doped cobalt sulfide CE were outperformed by the ones with platinum CE they weren’t taken into account for the remaining measurements and calculations. The $V_{OC}$ values recorded for the different cells had small variations as expected, since the same anode and electrolyte was used for manufacturing the solar cells. Finally, the fill factor values were nearly the same (0.68 and 0.67 for the DSSC with the Pt and the Ni doped CoS$_2$ counter electrode respectively).

**Table 8.1:** Electrical characteristics of DSSCs employing different counter electrodes.

<table>
<thead>
<tr>
<th>Counter Electrode</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>$V_{OC}$ (V)</th>
<th>FF</th>
<th>n (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>6.6</td>
<td>0.764</td>
<td>0.68</td>
<td>3.44</td>
</tr>
<tr>
<td>Ni doped CoS$_2$</td>
<td>7.8</td>
<td>0.733</td>
<td>0.67</td>
<td>3.76</td>
</tr>
</tbody>
</table>

The dark current suppression was also examined to investigate the back electron transfer. Figure 8.3 shows that dark current of the solar cells made with the different counter electrodes. The onset of the dark current for the DSSCs fabricated with the platinum CE occurred at lower voltage compared with the solar cells employing the nickel doped CoS$_2$ counter electrode, which was an additional indication for the better performance of the solar cells with the latter counter electrode.

**Figure 8.3:** Dark current–voltage characteristic curves of dye-sensitized solar cells with different counter electrodes.
Figure 8.4 shows the electrochemical impedance spectra obtained for the solar cells with the different counter electrodes. The equivalent circuits used to fit the experimental data are the same ones as those presented in Figure 5.22a and b, where each parallel RC or RQ combination represents an arc (Fig. 8.4) and the fitted parameters are summarized in Table 8.2. The fact that the only difference between the cells was the counter electrode that was used, the main variations should be expected to be noticed at the EIS parameters that correspond to that interface, in other words, at the CE/electrolyte interface. The $R_{CE}$ was smaller for the solar cells with the nickel doped CoS$_2$ counter electrode indicating its better electrocatalytic performance, however their higher $R_{dif}$ value suggest a slower $I_3^-$ diffusion in the electrolyte. Moreover, difference was also observed at the $R_s$ values, while the total series resistance was calculated using equation 5.1 and the results were comparable. Specifically, $R_s$ was 23.15 $\Omega$ for the cell with the platinum counter electrode, whereas $R_s$ was 23.56 $\Omega$ for the cell with the Ni doped CoS$_2$ counter electrode.

![Figure 8.4](image)

**Figure 8.4:** Impedance spectra of dye–sensitized solar cells with different counter electrodes measured at open–circuit voltage at 1 sun illumination.

**Table 8.2:** Electrochemical impedance spectroscopy fitted parameters for dsscs with different counter electrodes.

<table>
<thead>
<tr>
<th>CE</th>
<th>$R_h$ (Ω)</th>
<th>$R_{CE}$ (Ω)</th>
<th>$C_{CE} \times 10^4$ (F)</th>
<th>$R_s$ (Ω)</th>
<th>$C_s \times 10^3$ (F)</th>
<th>$R_{dif}$ (Ω)</th>
<th>$C_{dif} \times 10^2$ (F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>14.4</td>
<td>6.62</td>
<td>0.141</td>
<td>20.6</td>
<td>1.25</td>
<td>2.13</td>
<td>0.198</td>
</tr>
<tr>
<td>Ni doped CoS$_2$</td>
<td>14.6</td>
<td>4.46</td>
<td>0.138</td>
<td>12.3</td>
<td>1.28</td>
<td>4.5</td>
<td>1.04</td>
</tr>
</tbody>
</table>
8.2 Polypyrrole counter electrode

8.2.1 Preparation of the Polypyrrole counter electrode

The Polypyrrole counter electrode was formed through the electrochemical polymerization of pyrrole. For the preparation of the solution for the electrodeposition procedure 0.1 M of sodium sulfate (\(\text{Na}_2\text{SO}_4\)) was dissolved in about 47 mL of Millipore water under stirring. A few drops of sulfuric acid were added to the solution in order to adjust the solution’s pH to 1 [6]. Finally, under continuous stirring 1.5 mL of pyrrole (Pyrrole 98%) was added to complete the solution.

For the three-electrode cell setup, the blue reference electrode was Ag/AgCl, the black counter electrode was a Pt sheet and the red electrodes (working electrode and sense) were connected together holding an FTO glass half immersed in the above solution (Fig. 8.5). The applied potential was +0.5 V vs. Ag/AgCl and argon (Ar) inert gas was flowing in the Autolab glass vessel (1−50 mL, code 6.1415.110) where the pyrrole solution was transferred. There was no need for the back side of the FTO glass to be covered as the electrodeposition took place only on the conducting side. Once the procedure was completed the FTO glasses were rinsed with Millipore water and were left to dry in air before use. By varying the deposition time, different film thicknesses were obtained and in particular the longer the deposition lasted the darker the resulting counter electrodes were. As the deposition time increased over 25−30 minutes the resulting PPy films peeled off the FTO substrate and thus the maximum deposition time which was finally used was 20 minutes (4 cycles each one lasting 5 minutes) and while the resulting counter electrode was black however it retained some transparency.

![Figure 8.5: Metrohm Autolab PGSTAT cables and the color code used [7].](image-url)
8.2.2 Performance comparison of DSSCs with Pt and PPy counter electrodes

The photoanode TiO$_2$ films, which were sensitized with N719 for the manufacture of the DSSCs with the different counter electrodes, consisted of a compact TiO$_2$ layer and TiO$_2$ paste (cf. subparagraph 5.2.1). Among the solar cells employing PPy CEs the best electrical performance was recorded for the solar cell which was fabricated with the PPy CE with the longest deposition time (20 min) and its performance was compared with DSSC with platinum CE (Fig. 8.6). While DSSCs with the PPy CE displayed slightly better electrical characteristics compared with the solar cells with the Pt CE (Table 8.3) the transparency of the final devices were significantly lower which was inhibitory for the further research of the use of this conductive polymer as a CE. Hence, this research was put on hold and eventually ended not only because of the aforementioned results but also because of the high safety precautions needed to be taken before handling pyrrole due to the many hazards regarding toxicity.

![Figure 8.6: Photocurrent density−voltage characteristic curves of dye−sensitized solar cells with platinum and polypyrrole counter electrodes.](image)

**Table 8.3:** Electrical characteristics of DSSCs employing platinum and polypyrrole counter electrodes.

<table>
<thead>
<tr>
<th>Counter Electrode</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>n (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>6.03</td>
<td>0.676</td>
<td>0.55</td>
<td>2.24</td>
</tr>
<tr>
<td>PPy</td>
<td>6.89</td>
<td>0.662</td>
<td>0.50</td>
<td>2.28</td>
</tr>
</tbody>
</table>
References


9.1 Transparent strip–shaped TiO$_2$ DSSCs

Among the renewable energies, it is proven beyond reasonable doubt that the solar energy may successfully meet the ever increasing energy demands and photovoltaics can assist towards this direction. Hence, third generation solar cells, as dye–sensitized solar cells, have attracted intense interest due to their numerous merits such as simple and environmentally friendly fabrication procedures, low cost and the fact that it is possible to manufacture transparent solar cells that can operate by front–face light incidence, but also by diffuse light and even by back–face light incidence [1,2]. The long–term goal motivating researchers has always been the attainment of a satisfactory efficiency and an increased life expectancy for the third generation solar cells in order to transit from the laboratory scale to large area solar devices, which would also promote their commercialization and their industrially mass production. Over the past years, efforts have been made by many research groups to manufacture large area dye–sensitized solar modules, trying to overcome the arising difficulties which will eventually lead to the fabrication of an optimized device [3-6].

Under this scope, quasi–solid state dye–sensitized solar cells of increasing size were manufactured and their performance was examined in depth. Since strips can be considered as the structural units of large area devices, strip–shaped DSSCs with fixed width (1 cm) and varying length (1–45 cm) were fabricated and studied. In order to ensure the uniformity of the solar cells the electrodes, photoanode and counter electrode, were fabricated through inkjet printing (Dimatix Materials Printer DMP-5000). The lengths of the strip–shaped DSSCs prepared were 1, 2, 3, 4, 5, 10, 15, 20, 25, 30, 35, 40 and 45 cm (Fig. 9.1). The transparent TiO$_2$ photoanodes were fabricated using the solution described in paragraph 5.3 and were subsequently sensitized with an ethanol/acetonitrile N719 solution. In terms of materials it was a costly project because of the large number of samples that needed to be constructed (2 samples for each of the 13 cases examined) and to reduce the total fabrication cost a copper conductive foil tape was used for the contacts instead of using silver paste. The large active area of the DSSCs dictated that they couldn’t be illuminated by the solar simulator which was used in all the previous experiments because of the limited illuminating surface created by the beam.
Instead, the solar cells were subjected to outdoor solar irradiation with an almost constant light intensity of 1000 W/m² measured with a Newport power meter (Model 843-R) without the use of a mask.

Figure 9.1: Strip-shaped DSSCs of variable lengths from 1 to 45 cm and constant width 1 cm.

9.2 Performance of strip-shaped DSSCs

The changes of the electrical parameters were recorded in relation to the increase in the length of the fabricated transparent TiO₂ DSSCs. The electrical parameters are summarized in Table 9.1 and the photocurrent density–voltage curves are depicted in Figure 9.2a–c.

Table 9.1: Electrical parameters of strip-shaped DSSCs of variable lengths.

<table>
<thead>
<tr>
<th>Strip size (cm²)</th>
<th>J_{sc} (mA/cm²)</th>
<th>V_{oc} (V)</th>
<th>FF</th>
<th>n (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1x1</td>
<td>9.33</td>
<td>0.73</td>
<td>0.48</td>
<td>3.27</td>
</tr>
<tr>
<td>1x2</td>
<td>9.07</td>
<td>0.72</td>
<td>0.47</td>
<td>3.07</td>
</tr>
<tr>
<td>1x3</td>
<td>9.03</td>
<td>0.73</td>
<td>0.45</td>
<td>2.97</td>
</tr>
<tr>
<td>1x4</td>
<td>9.05</td>
<td>0.73</td>
<td>0.43</td>
<td>2.84</td>
</tr>
<tr>
<td>1x5</td>
<td>9.26</td>
<td>0.73</td>
<td>0.42</td>
<td>2.84</td>
</tr>
<tr>
<td>1x10</td>
<td>8.84</td>
<td>0.73</td>
<td>0.39</td>
<td>2.52</td>
</tr>
<tr>
<td>1x15</td>
<td>8.70</td>
<td>0.74</td>
<td>0.40</td>
<td>2.58</td>
</tr>
<tr>
<td>1x20</td>
<td>8.85</td>
<td>0.73</td>
<td>0.36</td>
<td>2.33</td>
</tr>
<tr>
<td>1x25</td>
<td>8.12</td>
<td>0.75</td>
<td>0.33</td>
<td>2.01</td>
</tr>
<tr>
<td>1x30</td>
<td>7.94</td>
<td>0.73</td>
<td>0.32</td>
<td>1.85</td>
</tr>
<tr>
<td>1x35</td>
<td>7.38</td>
<td>0.73</td>
<td>0.33</td>
<td>1.78</td>
</tr>
<tr>
<td>1x40</td>
<td>7.71</td>
<td>0.73</td>
<td>0.30</td>
<td>1.69</td>
</tr>
<tr>
<td>1x45</td>
<td>6.8</td>
<td>0.73</td>
<td>0.31</td>
<td>1.54</td>
</tr>
</tbody>
</table>
Figure 9.2: Photocurrent density–voltage characteristic curves of dye-sensitized solar cells of lengths from (a) 1 to 5 cm (b) from 10 to 25 and (c) from 30 to 45.
The main variations were noticed at the short−circuit current density and the fill factor values and as a result to the overall efficiency measured. The open−circuit voltage values recorded for the solar cells with the different strip length were almost constant as expected, since the same photoanode and quasi−solid state electrolyte was used for their manufacture. Regarding the short−circuit current density values, a small discrepancy was observed as the length increased from 1 to 5 cm. As the strip’s length further increased the J_{SC} gradually decreased at a higher rate. As far as the efficiency of the DSSCs is concerned, if a comparison was made for the calculated values of the small sized solar cells of this Chapter (i.e. strip size 1x1 cm²) which were illuminated with outdoor solar irradiation and without the use of a mask, with the corresponding ones reported in paragraph 5.3 a slight inconsistency would be found. In particular, the absence of use of a mask on the electrical measurements leads to a small overestimation of the J_{SC} values and as a result of the efficiency, because the diffused light from the glass can also contribute to the illumination of the solar cell’s active area [7].

![Impedance spectra](image)

**Figure 9.3:** Impedance spectra of dye−sensitized solar cells of varying length measured at open−circuit voltage under outdoor illumination.

The decrease of the fill factor values with the increasing strip’s length could be better explained through EIS measurements, as it could be attributed to the fact that the size of the solar cell affects its total internal in series resistance (R_s). Due to the limited time available in which the outdoor irradiation would be stable and the fact that each EIS measurement lasts longer than the J−V measurements only some of the strip−shaped
solar cells with an average length were electrochemically characterized as an indication. Figure 9.3 depicts the impedance spectra of the DSSCs with strip length 15, 20 and 25 cm and the corresponding fitted parameters are presented in Table 9.2. Since the tested solar cells had different length, namely different active area, it wouldn’t be accurate to compare their total series resistance in Ω as it is obtained when equation 5.1 is used. Instead, the values derived from equation 5.1 were multiplied with the active area of each solar cell and the comparison was made using these final values which were measured in Ω·cm². The value of the total series resistance $R_s$ of the solar cells with strip length 15 cm, 20 cm and 25 cm were 91.05 Ω·cm², 94.8 Ω·cm² and 98 Ω·cm² respectively. It can be seen from these values that the total series resistance didn’t increase significantly as the length increased, which was very encouraging for the transition to large scale. Finally, considering all the above results it was concluded that a solar module consisting of individual strip−shaped DSSC connected with an almost square form and dimensions between 20 and 25 cm for each side could provide adequately satisfactory results.

Table 9.2: Electrochemical impedance spectroscopy fitted parameters for strip−shaped DSSCs with varying length.

<table>
<thead>
<tr>
<th>Strip size (cm²)</th>
<th>$R_s$ (Ω)</th>
<th>$R_{pt}$ (Ω)</th>
<th>$C_{pt} \cdot 10^{-4}$ (F)</th>
<th>$R_{ct}$ (Ω)</th>
<th>$C_{ct} \cdot 10^{-3}$ (F)</th>
<th>$R_{dif}$ (Ω)</th>
<th>$C_{dif} \cdot 10^{-2}$ (F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1x15</td>
<td>3.44</td>
<td>0.54</td>
<td>0.41</td>
<td>7.86</td>
<td>2.61</td>
<td>2.09</td>
<td>7.3</td>
</tr>
<tr>
<td>1x20</td>
<td>1.97</td>
<td>0.50</td>
<td>0.80</td>
<td>3.49</td>
<td>5.53</td>
<td>2.27</td>
<td>6.4</td>
</tr>
<tr>
<td>1x25</td>
<td>1.41</td>
<td>0.55</td>
<td>1.27</td>
<td>2.15</td>
<td>8.40</td>
<td>1.96</td>
<td>19.5</td>
</tr>
</tbody>
</table>
Chapter 9

References


Chapter 10 Experimental results—PSCs

In this chapter all the results of the research on the perovskite solar cells will be presented. In early 2016 the NAML group published its first article on PSCs with promising results given the fact that the solar cells were constructed in ambient air without the use of advanced and highly expensive laboratory equipment [1]. Considering these results as a starting point an optimization study began trying to further promote the PSCs’ efficiency maintaining the simple preparation procedures under ambient conditions of temperature and humidity. Since similar basic principles apply for the construction and operation of DSSCs and PSCs, the combination of two semiconductors with appropriate energy levels was examined for constructing the electron transport layer of PSCs, as it has already been tested for DSSCs’ photoanodes (cf. subparagraph 2.2.2).

Perovskite solar cells with TiO$_2$/SrTiO$_3$ or BaTiO$_3$ ETL bilayers have displayed enhanced photovoltaic performance [2,3]. The introduction of composite semiconductors as ETL can enhance the power conversion efficiency of the PSC by providing a better energy level alignment between the CB of the perovskite and the ETL and thereby facilitating the electron transport and minimizing the recombination processes. Among the many semiconductors that could be selected to be combined with TiO$_2$ for the complex ETL, indium oxide was the one chosen and examined because of its slightly higher CB edge compared with TiO$_2$, which was considered that it would be helpful for the more efficient transferring of the photogenerated electrons from the perovskite to the TiO$_2$. In this chapter, the results regarding the morphological and structural properties of the combined TiO$_2$–In$_2$O$_3$ bilayer, along with the electrical characterization of the PSCs will be presented and analyzed.

10.1 Electron transport layer fabrication

Before depositing the various layers needed for manufacturing monolithic mesoscopic perovskite solar cells, the FTO glasses (8 Ω/□, Pilkington) were chemically etched in order to obtain a pattern as the one shown in Figure 3.3a to prevent any short–circuit phenomenon and cleaned with detergent, deionized water and acetone. Afterwards, a compact TiO$_2$ layer (c-TiO$_2$) was deposited on the FTO glasses by spin–
coating at 2000 rpm for 10 s a solution that was prepared by further diluting titanium diisopropoxide bis(acetylacetonate) (75 wt% in isopropanol, Aldrich) in isopropanol (10% v/v). For the formation of the mesoporous TiO$_2$ layers (mp-TiO$_2$) 0.37 mL Titanium(IV) butoxide, 0.4 mL glacial acetic acid and 0.5 g Pluronic P123 were mixed under stirring with 4 mL of isopropanol. A number of layers were deposited by spin–coating a couple of drops of the as–prepared solution at 1200 rpm for 20 s until the desired thickness was obtained. Each layer deposition, for the c-TiO$_2$ or for the mp-TiO$_2$, was followed be a drying step and then annealing at 500°C for 10 minutes in order to remove the organic residues and create porous films.

For the fabrication of the complex ETL, on top of the mp-TiO$_2$ films an additional In$_2$O$_3$ layer was deposited, which was formed by spin–coating at 3000 rpm for 10 s a precursor solution containing an amount of indium(III) acetylacetonate, 0.007 g hexamethylenetetramine (HMT, ≥99% Aldrich) and 0.1 g Triton X–100 in 1 mL of ethanol. Specifically, three different molar concentrations of the indium precursor material in the solution were tested (46 mM, 50 mM and 56 mM) and the resulting films, hereafter abbreviated as TiO$_2$–In$_2$O$_3$ (1), TiO$_2$–In$_2$O$_3$ (2) and TiO$_2$–In$_2$O$_3$ (3) respectively, were compared with pristine TiO$_2$ films (pristine TiO$_2$). The indium solutions were used only once for the deposition of a single In$_2$O$_3$ layer followed by drying and annealing at 500°C for 30 minutes.

10.2 Perovskite synthesis and monolithic mesoscopic PSCs fabrication

For the fabrication of the perovskite films a mixed halide methylammonium lead (CH$_3$NH$_3$I$_{3-x}$Cl$_x$) perovskite solution was prepared by the one–step deposition method as reported in an earlier publication by NAML group [1]. All the processes were carried out under ambient conditions of temperature and relative humidity. For the preparation of the 40 wt% mixed halide perovskite solution, methylammonium iodide (MAI, CH$_3$NH$_3$I) and lead chloride (PbCl$_2$) were dissolved in anhydrous DMF in a molar ratio 3:1. The MAI powder was synthesized by mixing under stirring 20 mL of ethanol, 12 mL methylamine (33 wt% in ethanol) and 5 mL of hydroiodic acid (HI, 57 wt% in water, Aldrich) at a round bottomed flask under nitrogen flow at 0°C. The HI was added dropwise because of its exothermic reaction with methylamine in order to maintain the
solution’s temperature low. After 2 hours the flask was adjusted on the rotary evaporator to remove the ethanol and the water and attain the crystallization of MAI. The resulting powder was washed off several times with anhydrous diethyl ether until a white colored powder was obtained confirming the success of the recrystallization process. The perovskite solution was spin–coated onto the ETLs at 2000 rpm for 45 s and the coated films were placed on a hot plate at 100°C for 30 minutes in order to obtain the crystalline phase of perovskite which was indicated by the changed color from yellow to grey (Fig.10.1).

**Figure 10.1:** ETLs coated with perovskite solution on a hot plate at 100°C during the drying procedure of the perovskite films.

The perovskite films were coated with a P3HT solution for the formation of the HTL. The HTM solution was prepared by dissolving 15 mg of P3HT in 1 mL chlorobenzene and adding 7.18 mg of lithium bis(trifluoromethanesulfonyl) imide and 10.3 mg of 4−TBP. The P3HT layer was casted by spin–coating the solution over the perovskite films at 1200 rpm for 10 s, followed by drying on a hot plate at 60°C for 5 minutes. Two P3HT layers were deposited for the formation of the final HTL, the one above the other, to acquire a homogenous layer. To complete the PSCs the coated glasses were placed inside a vacuum chamber to thermally evaporate gold as the top electrode, while silver paste was used for the contact on the un–etched area of the substrate. The resulting structure of the mesoscopic PSC was FTO/c-TiO₂/mp-TiO₂/(In₂O₃)/CH₃NH₃IₓClₓ/P3HT/Au (Fig. 10.2).

**Figure 10.2:** The final perovskite solar cells.
10.3 Morphological and structural properties of the complex photoelectrodes

In order to verify the morphological characteristics and the thickness of the TiO$_2$ and TiO$_2$–In$_2$O$_3$ photoelectrode films samples were microscopically examined through top view and cross section SEM images (Fig. 10.3 and 10.4). Assessing the top view images of all films the formation of nanoparticles with an average size of 10–14 nm is evident (Fig. 10.3a–d). The images corresponding to the pristine TiO$_2$ and TiO$_2$–In$_2$O$_3$ films show no obvious differences probably due to the fact that TiO$_2$ and In$_2$O$_3$ have similar nanoparticles’ size forming clusters, making it hard to distinguish the two oxide particles from one another. Comparing the three TiO$_2$–In$_2$O$_3$ films with each other, the different concentrations of indium precursor in the indium oxide solution don’t seem to affect the morphology of the films. According to the cross section images, the mesoporous TiO$_2$ and TiO$_2$–In$_2$O$_3$ film’s relative thickness was estimated to be around 1–1.2 μm (Fig. 10.4). It has been reported that with the use of such thick films the obtained PSCs’ overall efficiency is higher than the one corresponding to PSCs with thinner photoelectrode films [1,4]. In fact these highly porous and rough films of one micrometer relative thickness are ideal scaffolds for the growth of perovskite.

![SEM images](image_url)

**Figure 10.3:** SEM images of (a) pristine TiO$_2$, (b) TiO$_2$–In$_2$O$_3$ (1), (c) TiO$_2$–In$_2$O$_3$ (2) and (d) TiO$_2$–In$_2$O$_3$ (3) films.
To specify the surface area and the pore size distribution of the TiO$_2$ and TiO$_2$–In$_2$O$_3$ powders which resulted from the corresponding films, the BET method was used. The powders were degassed with nitrogen and helium inert gases to acquire the adsorption–desorption isotherms (Fig. 10.5). The hysteresis seen between the adsorption (lower) and desorption (upper) branch indicates the existence of mesoporosity \[5,6\], which suggests a pore width of 2–50 nm, which is of great importance for the penetration of the perovskite and therefore the efficient contact between the perovskite and the pristine TiO$_2$ or the TiO$_2$–In$_2$O$_3$. Likewise, the BET specific surface area also plays a crucial role for the infiltration of perovskite in the mesoporous film. The highest specific surface area was calculated for TiO$_2$–In$_2$O$_3$ (2) (48.98 m$^2$/g), which was almost 17% higher than that of pristine TiO$_2$ (41.80 m$^2$/g) (Table 10.1).

The pore size distribution has been estimated from the adsorption branch of the isotherm, the analysis of which describes the size of the voids and their distribution (Fig. 10.5b). A wide pore size distribution was observed for all samples, ranging from 2–30 nm. A maximum pore size has been found, corresponding to 3.4 nm and 6.1 nm pore diameter peaks for the pristine TiO$_2$ as well as to 3.4 nm and 6.1–7.7 nm for the TiO$_2$–In$_2$O$_3$ (2). The pore diameter of the samples, calculated by the BET measurement, is required to be high enough in order to achieve efficient pore filling of the perovskite solution. Specifically, even though TiO$_2$–In$_2$O$_3$ (3) presents higher specific surface area than pristine TiO$_2$, the pore diameter is rather low, hindering the efficient contact of the perovskite solution with the TiO$_2$–In$_2$O$_3$ (3) nanoparticles. Thus, solar cells with the TiO$_2$–In$_2$O$_3$ (3) photoanode are expected to present lower performance \[7\].

Figure 10.4: SEM cross section images of (a) pristine TiO$_2$ and (b) TiO$_2$–In$_2$O$_3$ films.
Figure 10.5: (a) Sorption–desorption isotherms of the TiO$_2$ and TiO$_2$–In$_2$O$_3$ powders and (b) pore size distribution of the TiO$_2$ and TiO$_2$–In$_2$O$_3$ powders.

Table 10.1: Structural properties of the powders obtained from the TiO$_2$ and TiO$_2$–In$_2$O$_3$ films.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$S_{BET}$ (m$^2$/g)</th>
<th>Pore diameter (nm)</th>
<th>Pore volume (cm$^3$/g)</th>
<th>Pore width (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine TiO$_2$</td>
<td>41.80</td>
<td>15.26</td>
<td>0.217</td>
<td>20.80</td>
</tr>
<tr>
<td>TiO$_2$–In$_2$O$_3$ (1)</td>
<td>44.01</td>
<td>12.62</td>
<td>0.191</td>
<td>17.35</td>
</tr>
<tr>
<td>TiO$_2$–In$_2$O$_3$ (2)</td>
<td>48.98</td>
<td>15.27</td>
<td>0.247</td>
<td>20.18</td>
</tr>
<tr>
<td>TiO$_2$–In$_2$O$_3$ (3)</td>
<td>45.06</td>
<td>11.33</td>
<td>0.169</td>
<td>14.97</td>
</tr>
</tbody>
</table>
For the elemental composition energy dispersive X-ray (EDX) analysis was carried out at TiO$_2$ and TiO$_2$–In$_2$O$_3$ films deposited on borosilicate glass microscope slides. The EDX spectra (Fig. 10.6a and b) showed that the films consisted of titanium, oxygen, indium and a high concentration of silicon derived from the silicon dioxide at the glass substrate. The XRD measurements were performed using the same films used for the EDX analysis, namely the pristine TiO$_2$ and one of the TiO$_2$–In$_2$O$_3$ films, as the concentration of the added indium(III) acetylacetonate in the indium precursor solution doesn’t affect the crystallinity of the sample. The diffraction peaks of the XRD pattern at around 25.2º, 37.7º and 55º represent the TiO$_2$ anatase phase, while the peaks at 30.8º, 35.5º, 51.3º and 60.8º represent In$_2$O$_3$ (JCPDS 76–0152) (Fig. 10.7). The grain size of
In$_2$O$_3$ was calculated 12–13 nm, using the Scherrer’s formula (equation 4.4), which is close to the nanoparticles’ size determined by the SEM images.

![XRD pattern of the as-prepared ETLs.](image)

**Figure 10.7:** XRD pattern of the as-prepared ETLs.

To confirm the presence of indium oxide at the TiO$_2$–In$_2$O$_3$ photoanode X-ray photoelectron spectroscopy (XPS) analysis was carried out at samples deposited on ITO glass substrate (Fig. 10.8 and 10.9). The photoemission experiments were carried out in an ultra high vacuum system using unmonochromatized AlK$\alpha$ line at 1486.6 eV and an analyzer pass energy of 97 eV, giving a FWHM of 1.7 eV for the Au 4f7/2 peak. Survey scan (Fig. 10.8) shows the presence of indium and oxygen peaks. In fact, the XPS survey spectrum of In$_2$O$_3$ thin film contains only the core level XPS In4d, In3d, and In3p peaks together with XPS O1s peak. It can also be seen that for freshly deposited In$_2$O$_3$ films no carbon contamination was detected. Figure 10.9a and b show the In3d doublet and O1s XPS core level peak respectively. In particular, binding energy of 445.15 eV, can be attributed to the indium species in indium oxide thin films [8,9]. However Ti2p region was not detected on the surface of the films which means that In$_2$O$_3$ layer uniformly covered the thicker TiO$_2$ films making it hard to be discriminated as XPS is a surface technique. Using the total peak area of O1s and In3d5/2 peaks, and the appropriate sensitivity factors the atomic ratio of In to O was determined, In/O=1.6±0.1 which is also an extra evidence for the formation of indium oxide on the TiO$_2$ films.
10.4 PSCs’ electrical and electrochemical characterization

The electrical performance of the devices made with the pristine TiO$_2$ and the three different composite TiO$_2$–In$_2$O$_3$ films was examined through the current density–photovoltage characteristic curves (Fig. 10.10) and the obtained electrical parameters are summarized in Table 10.2. The PSC devices with the incorporated indium oxide layer exhibited an improved open-circuit voltage ($V_{OC}$) compared with the devices with the pristine TiO$_2$. As earlier mentioned In$_2$O$_3$, which is a semiconductor with an indirect band gap of 2.7 eV, has a higher conduction band edge than TiO$_2$ (Fig. 10.11), leading to a better tuning of the energy levels of the perovskite with the composite ETL. Consequently, the electron transfer from the perovskite to the TiO$_2$ (via the In$_2$O$_3$.
interface) occurs efficiently, decreasing the recombination rate and ultimately improving the charge collection efficiency. In$_2$O$_3$ could be also passivating the surface defects of the TiO$_2$ that would otherwise act as recombination sites [10].

![Photocurrent density−voltage characteristic curves of the PSCs.](image)

**Figure 10.10:** Photocurrent density−voltage characteristic curves of the PSCs.

<table>
<thead>
<tr>
<th>Samples</th>
<th>J$_{SC}$ (mA/cm$^2$)</th>
<th>V$_{OC}$ (V)</th>
<th>FF (%)</th>
<th>n (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine TiO$_2$</td>
<td>18.74</td>
<td>0.85</td>
<td>0.63</td>
<td>9.98</td>
</tr>
<tr>
<td>TiO$_2$−In$_2$O$_3$ (1)</td>
<td>21.29</td>
<td>0.92</td>
<td>0.58</td>
<td>11.44</td>
</tr>
<tr>
<td>TiO$_2$−In$_2$O$_3$ (2)</td>
<td>23.81</td>
<td>0.92</td>
<td>0.59</td>
<td>12.86</td>
</tr>
<tr>
<td>TiO$_2$−In$_2$O$_3$ (3)</td>
<td>17.73</td>
<td>0.87</td>
<td>0.56</td>
<td>8.69</td>
</tr>
</tbody>
</table>

Minimizing the recombination leads to a short−circuit current density increment, that successively enhances the PCE and reduces the dark current. The suppression of the dark current (Fig. 10.12) can also be reflected as an increase of the V$_{OC}$. In general, the short−circuit current density of the PSCs increased with the addition of In$_2$O$_3$ overlayer. However, when the molar concentration of indium(III) acetylacetonate was 56 mM, all the solar cells’ electrical characteristics were reduced and specifically the J$_{SC}$ dropped significantly to even lower values than the ones corresponding to the pristine TiO$_2$ PSCs. This could be attributed to the formation of a denser In$_2$O$_3$ layer constraining the
infiltration of the perovskite. The optimum performance was recorded for the TiO$_2$–In$_2$O$_3$ (2) PSCs and showed an overall improvement of the efficiency of over 28% compared with the pristine TiO$_2$ cells.

Figure 10.11: Energy level diagram.

Figure 10.12: Dark current–voltage characteristic curves of the PSCs.

The PSCs with the pristine TiO$_2$ and the TiO$_2$–In$_2$O$_3$ (2) ETLs were also characterized through electrochemical impedance spectroscopy under dark conditions. The acquired Nyquist plots and the simplified equivalent circuit used in order to fit the experimental data are presented in Figure 10.13a and b respectively and the
corresponding fitted parameters are summarized in Table 10.3 [11]. Two partially distorted and merged semi-arcs can be observed which are arising from the parallel combination of a resistance with a constant phase element. The CPEs were converted to capacitances (C₁ and C₂) using equation 5.2 and these values were included in Table 10.3 along with the other EIS parameters. The arc at the low frequencies resulting from R_{REC} and C₁ represent the recombination processes which take place at the ETL/perovskite interface. The arc at intermediate frequencies is ascribed to R_{HTM} and C₂ which are used to describe the charge transfer properties at the HTM/gold interface. Finally, the resistance in high frequencies (Rₚ) is related to the series resistance of the solar cell. Larger values of the R_{REC} indicate suppressed recombination processes, namely charges are harder to transfer from the ETL/perovskite interface [12-14].

![Figure 10.13: (a) Nyquist plots of the PSCs measured under dark conditions and (b) equivalent circuit used to fit the experimental data.](image)

**Table 10.3: EIS fitted parameters.**

<table>
<thead>
<tr>
<th>Samples</th>
<th>Rₛ (Ω)</th>
<th>R_{REC} (Ω)</th>
<th>C₁·10⁻⁶ (F)</th>
<th>R_{HTM} (Ω)</th>
<th>C₂·10⁻⁶ (F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine TiO₂</td>
<td>19.0</td>
<td>296</td>
<td>3.23</td>
<td>202</td>
<td>0.56</td>
</tr>
<tr>
<td>TiO₂−In₂O₃ (2)</td>
<td>18.3</td>
<td>361</td>
<td>3.72</td>
<td>286</td>
<td>0.66</td>
</tr>
</tbody>
</table>

The hysteretic behavior of the optimum performing PSCs (namely TiO₂−In₂O₃ (2)) was examined by scanning them with forward and reverse bias. Generally, perovskite solar cells tend to exhibit a lower J−V curve when scanned with a forward bias than with a reverse. In our case, the PSCs with the mesostructured composite electron transport
layer showed almost no hysteresis phenomenon (Fig. 10.14). Notably, as expected, the short-circuit current density and the open-circuit voltage remained constant and only a small difference was observed for the fill factor of the examined PSCs. This is an indication that the carrier trapping at the interface which is created between the perovskite and the ETL is limited. Bearing that in mind, it is safe to suggest that the power conversion efficiency of the PSCs was determined accurately.

**Figure 10.14:** Photocurrent density–voltage characteristic curve for best performing TiO$_2$–In$_2$O$_3$ (2) cells with forward and reverse bias.
Chapter 10

References


Chapter 11 Conclusions—Future research prospects

The purpose of this dissertation is the development and characterization of solar energy conversion devices based on nanocomposite semiconductors with the main research being focused on dye-sensitized and perovskite solar cells. With this aim different approaches were examined to impart desired characteristics to each of the components of the DSSC and the PSC and to optimize the final device either by increasing its power conversion efficiency or by simplifying the manufacturing processes and lowering its total fabrication cost or by increasing its stability.

11.1 Conclusions

- **DSSC**
  - **Photoanode**
  - The results from the use of template free P25–TiO$_2$ solutions modified with CBP and MWCNTs to fabricate films at low and high temperatures showed that the incorporation of MWCNTs improved the overall performance of the DSSCs, in both sintering temperatures examined. The highest efficiency recorded was for the devices employing P25–TiO$_2$ electrodes with 0.1 wt% of MWCNTs which was to a large extent due to the enhanced photocurrent density measured, attributed to the improved interconnectivity between the TiO$_2$ particles and the MWCNTs that facilitated the electron transport through the film. Unlike the improved results that the DSSCs with the MWCNT modified P25–TiO$_2$ films exhibited, the CBP modified P25–TiO$_2$ films resulted in poorer performing devices for all cases examined.
  - The surface treatment of P25–TiO$_2$ films with two solutions tried for the first time (TTAI and TALD) was tested followed by sintering the films at relatively low and high temperature (300°C and 500°C). The post treated P25–TiO$_2$ films adsorbed more dye than the corresponding untreated films. As a result the DSSCs with the TTAI and TALD modified P25–TiO$_2$ films as photoanodes displayed improved short-circuit photocurrent density values which improved their overall efficiency up to 26–30% compared with the solar cells with the untreated electrodes.
  - Four titanium precursor materials were used in order to fabricate transparent TiO$_2$ films through the sol–gel method, namely TTIP, TTBU, TTAI and Ti(AcAc). While the titanium molar ratio was kept constant for all solutions, the DSSC with the TTBU
photoanodes displayed the highest values for the electrical parameters and an 11.2% higher power conversion efficiency compared with the solar cells that employed the widely preferred TTIP films for their anode.

- Finally, the effort made in order to simplify the fabrication of TiO$_2$ films via the sol–gel method by using a surfactant in the TiO$_2$ solution that could be easily removed by rinsing with deionized water without damaging the film didn’t produce promising results in order to further push the research. In fact while the easy removal of AOT could allow sintering at low temperatures, which could render the process applicable to flexible DSSC, the sintering at 500°C was chosen in order to increase the crystallinity of the AOT–TiO$_2$ films. However even this didn’t led to better results compared with the previous methods used to modify the TiO$_2$ photoanodes in order to optimize the performance of the DSSCs.

- **Sensitizer**

- Six newly synthesized ruthenium dye complexes with different pyridine and bipyridine side groups were studied and tested as sensitizers in sol–gel quasi–solid state DSSCs. The absorption and the electrochemical properties of the sensitizers were unaffected by the branching side groups. Moreover, the more conjugated character of the dyes having two bipyridines (bpy-bpy) in their structure resulted in an increase in the molar extinction coefficient compared with the ones having a bipyridine and a pyridine (bpy-py). The bpy-py dyes (CS17 and CS22) were poorly adsorbed on the TiO$_2$ mesoporous films leading to DSSCs with low electrical characteristics. The DSSCs that were sensitized with the bpy-bpy dyes demonstrated almost the same performance as the solar cells that were sensitized with a commercially available dye with a similar structure as the newly synthesized ruthenium(II) complexes (D907). Specifically, the conversion efficiency of the solar cell sensitized with CS28 was a slightly better than the one corresponding to the DSSC sensitized with D907 (3.28% and 3.26% respectively).

- Among the two newly synthesized triphenylamine based organic dyes with or without the additional electron donating hexyloxy groups, having a benzimidazole derivative as π–bridge that were studied, the DSSCs sensitized with the dye without the additional hexyloxy groups (MZ–341) were more efficient compared with the ones sensitized with the dye with the hexyloxy groups (MZ–235) because of the higher absorbance of the former on the TiO$_2$ photodelectrode.
Red algae of the genus *Laurencia Obtusa* were collected in order to extract from them the phycoerythrin pigment and make water based natural dye solution to be used as a sensitizer for DSSCs. Testing the dye adsorption as a factor of the temperature and the pH of the dye solution, the addition of acetic acid decreased the dye aggregation and increased the dye uptake on the TiO$_2$ films, while the increment of solution’s temperature had a negative effect on the absorption. The best results were obtained for a dye solution with pH 3 and for a temperature of 35°C during the sensitization of the anode. Given the fact that the use of a natural sensitizer limited the total DSSC’s fabrication cost to the minimum, the optimum obtained electrical results ($J_{sc}$=1.26 mA/cm$^2$, $V_{oc}$=0.66 V, FF=0.63 and n=0.52%) were reasonable values for a natural seaweed dye on transparent TiO$_2$ photoelectrodes and higher than the published values reported so far.

**Electrolyte**

As far as the electrolyte solution is concerned, a minor alteration was examined regarding the hybrid material used for the gradual solidification of the electrolyte. All five hybrid organic/inorganic materials that were synthesized with polypropylene or polyethylene of different oligomer chain length as organic sub-phase demonstrated good thermal stability up to 150°C with ED600–ICS slightly standing out. Nevertheless no obvious differences were detected in the electrical parameters of the DSSCs that employed these hybrid materials in their electrolyte solution.

**Counter electrode**

While DSSCs with the Ni doped CoS$_2$ and the PPy counter electrode displayed better electrical characteristics compared with the solar cells with the Pt CE, certain restrictions hindered the further research of these electrodes as a replacement for platinum. For the former case, limitations arose from the manufacturing process regarding the dimensions of the CE. The fact that the glasses had to be placed horizontally in a container with a lid closing tightly, before placing them in the furnace, complicated the fabrication step. For the latter case, the transparency of the PPy counter electrode and hence of the final devices was significantly lower compared with the Pt CE. This fact, combined with the high safety considerations for handling pyrrole reduced our incentive for thorough examination of PPy.

**Upscaling**
The results from the upscaling of the transparent strip-shaped DSSC of various lengths ranging from 1 cm−45 cm, with electrodes fabricated by inkjet printing demonstrated that as the length increased the main variations were noticed for the \( J_{SC} \) and the FF values; as the length increased, the \( J_{SC} \) also increased while the FF decreased. Nevertheless, a middle ground solution could be the construction of strip-shaped DSSCs of intermediate length (20 cm−25 cm) which could be connected in order to form a solar module in an almost square form that could provide quite satisfactory results.

\section*{PSC}

The manufactured PSCs, where the TiO\(_2\)−In\(_2\)O\(_3\) binary electron transport layer was used as an efficient scaffold for the CH\(_3\)NH\(_3\)I\(_3−x\)Cl\(_x\) perovskite infiltration demonstrated a maximum PCE value of 12.86% which corresponds to an improved efficiency of over 28% compared with pristine TiO\(_2\) PSCs. Given that all processes for the perovskite solar cells construction were carried out in ambient conditions renders these findings quite impressive. These aforementioned results prove the better interfacial connection between TiO\(_2\)−In\(_2\)O\(_3\)/CH\(_3\)NH\(_3\)I\(_3−x\)Cl\(_x\), the efficient electron transport due to optimized alignment of the energy levels of the mixed oxides and the perovskite, as well as the reduction of the recombination processes.

\section*{11.2 Future research prospects}

Within the scope of the fabrication of efficient and long-lasting dye-sensitized solar cells, there are a myriad of investigations to be undertaken to further optimize the final devices. The issues that need further improvement cover three main key areas: increment of the efficiency levels, device stability, reduction of the materials’ and the devices’ cost. Though DSSCs perform better under diffuse light and high temperature conditions compared with photovoltaic solar cells from other technologies, their efficiency needs to improve in order to be more competitive against existing technologies. Since the margin for synthesizing a panchromatic sensitizer has narrowed, it is more likely that in the coming years emphasis will be given to the introduction of perovskite nanocrystals into DSSC instead of a dye. To avoid the perovskite dissolution from the electrolyte and to address the leakage problems it is possible that the electrolyte will be replaced from hole conductors. Similarly, the commonly used platinum counter
electrode will be replaced by graphene materials to ensure an extended lifetime for dye-sensitized solar modules.

Given that the research on dye-sensitized solar cells has been limited in part, the focus has mainly shifted to perovskite solar cells. The latest trends regarding the perovskite solar cells that could also be proposed as an extension to this dissertation are:

- Methods to improve the band alignment of the applied materials to boost the fill factor and the short-circuit current densities.
- Research on the introduction of a large organic cation into the perovskite structure to improve the perovskite’s thermal and environmental stability.
- Synthesis of new low cost and stable materials with enhanced properties in order to improve the devices’ overall performance and stability.
- Realization of upscaling towards perovskite modules.
Curriculum Vitae

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