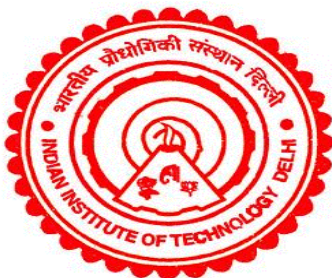


STUDIES ON DYE-SENSITIZED SOLAR CELLS

Garima Dwivedi



Department of Chemical Engineering

Indian Institute of Technology, Delhi

OCTOBER, 2017

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STUDIES ON DYE-SENSITIZED SOLAR CELLS

By

Garima Dwivedi

Submitted

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to the



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Dedicated to my Maa who has the
highest regard for education

CERTIFICATE

This is to certify that the thesis entitled “**Studies on Dye-Sensitized Solar Cells**” being submitted by **Garima Dwivedi** to the Department of Chemical Engineering, Indian Institute of Technology, New Delhi, in partial fulfillment of the requirements for the award of the degree of **Doctor of Philosophy**, is a record of bonafide work carried out by her. She has worked under my guidance and supervision and has fulfilled the requirements, which to my knowledge, have reached the requisite standard for the submission of the thesis.

The research report and results presented in this thesis have not been submitted, in part or full, to any other university or institute for the award of any degree or diploma.

Ashok N. Bhaskarwar

Professor

Department of Chemical Engineering

Indian Institute of Technology Delhi

New Delhi 110016, India

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ABSTRACT

In the 21st century, the biggest challenge is to replace fossil fuels with renewable-energy sources. With increasing population, the demand for energy is also steeply increasing. Solar energy is one of the best alternatives to meet this increasing energy demand. While fossil fuels emit CO₂, thereby causing the greenhouse effect, solar energy has the advantages of being eternally available and totally clean. By the successful combination of nano-structured electrodes and efficient charge-injection dyes Professor Grätzel and his team developed the first solar cell with energy conversion efficiency of 7 %. This solar cell is called the dye-sensitized nano-structured solar cell or simply the Grätzel cell.

Dye-sensitized solar cells (DSSCs) have attracted attention of many researchers and companies because of their low-cost and a reasonable photochemical conversion efficiency (13 %) for liquid state DSSCs having a Co(II/III) tris (bipyridyl)-based redox electrolyte in conjunction with a custom synthesized donor-p-bridge-acceptor zinc porphyrin dye. The highest reported efficiency is 15 % till date, for a solid-state DSSC with an inorganic-organic composite material having a perovskite structure (e.g., CH₃NH₃PbI₃) as a dye sensitizer and with an organic material as hole transport material (HTM) in place of an electrolyte.

For the first generation solar cells, the costs are high mainly because of the mono-crystalline silicon being used. For the second generation solar cells, the thin active layer has a low absorption capacity for sunlight, and comparatively a low-cost. The third generation solar cells offer a good performance and also have a low-cost. Further, the DSSCs can be assembled by simple assembly techniques.

A DSSC consists of a working-electrode, a counter-electrode, and an electrolyte in between the electrodes. A working-electrode (fluorine doped tin oxide (FTO) glass coated with TiO_2 nanoparticles with dye-adsorbed on it) acts as a photo-anode. Counter-electrode (FTO glass with platinum deposited on it) acts as the cathode and the electrolyte contains a redox couple.

When light is incident on the working-electrode (photo-anode), it passes through the transparent conducting glass (TCO) sheet. The dye gets excited and transfers its electrons to the TiO_2 layer, and with this removal of electrons the dye gets oxidized. The electrons travel from TiO_2 layer to the FTO glass through the load, and finally to the counter-electrode, thus completing the outer circuit. The oxidized dye gets regenerated by the electrons from the electrolyte, and the electrolyte is regenerated by the electrons from the counter-electrode. Thus, the photons from the light generate electricity.

In the present study, the techniques for construction of a standard DSSC using FTO glass, TiO_2 nanoparticles, N719 dye and electrolyte containing I^-/I_3^- redox couple, with an efficiency of 7.18 % have been established. The use of platinum as a counter-electrode catalyst is one of the costliest aspects of DSSCs. As platinum is a noble metal, replacement of platinum with plant-derived low-cost material has been explored. The use of hemp-derived interconnected carbon nano-sheets (ICNS) for platinum replacement decreases the cost of a DSSC with a reasonable efficiency of 4.01 %. Effect of loading of different weight percentages of platinum in the ICNS-based formulation was also studied.

Replacement of TiO_2 nanoparticles in the scattering-layer with modified semiconductor-nanoparticles in the scattering-layer of working-electrode has also been studied.

On Further, DSSC assembled using TiO_2 shell and magnetic core nanoparticles in the scattering- layer in place of TiO_2 nanoparticles showed improvement in efficiency to 7.87 %. Electrochemical impedance studies (EIS) were also performed for determination of different parameters like electron transport resistance, diffusion coefficient, diffusion length of the standard DSSC, also for the DSSC using TiO_2 shell with magnetic core nanoparticles in the scattering-layer.

21 वीं सदी में, अक्षय ऊर्जा स्रोतों से जीवाश्म ईंधन को बदलने की सबसे बड़ी चुनौती है बढ़ती आबादी के साथ, ऊर्जा की मांग भी बढ़ती जा रही है सौर ऊर्जा ऊर्जा की बढ़ती मांग को पूरा करने के लिए सबसे अच्छा विकल्प है। जबकि जीवाश्म ईंधन CO_2 का उत्सर्जित करते हैं, जिससे ग्रीनहाउस प्रभाव होता है, सौर ऊर्जा का सदाबहार होने और पूरी तरह से साफ होने के फायदे हैं। नैनो संरचित इलेक्ट्रोड और कुशल प्रभारी इंजेक्शन रंगों के सफल संयोजन से प्रोफेसर ग्रेटेल और उनकी टीम ने 7% की ऊर्जा रूपांतरण दक्षता वाले पहला सौर सेल विकसित किया। इस सौर कोशिका को डार्क-संवेदीकृत नैनो-संरचित सौर कोशिका या केवल ग्रेटसेल सेल कहा जाता है।

डार्क-संवेदी सौर कोशिकाओं (डीएसएससी) ने कई शोधकर्ताओं और कंपनियों का ध्यान आकर्षित किया है क्योंकि उनकी तरलता वाली राज्य डीएसएससी के लिए कम लागत और उचित फोटोकैमिकल रूपांतरण दक्षता (13%) के कारण सह (II / III) ट्राइस (बीआईपीआईडीआईएल) आधारित एक कस्टम संश्लेषित दाता-पी-पुल-स्वीकर्ता जस्ता पोर्फिरिन डार्क के साथ संयोजन के साथ रेडॉक्स इलेक्ट्रोलाइट। उच्चतम रिपोर्टिंग दक्षता आज तक 15% है, एक ठोस-राज्य डीएसएससी के लिए एक अवर्तक-कार्बनिक कम्पोजिट सामग्री के साथ एक प्रतिस्कोप वाली संरचना (उदाहरण के लिए, सीएच 3 एनएच 3 पीबीआई 3) डार्क सेंसिटाइज़र के रूप में और छेद परिवहन सामग्री (एचटीएम) के रूप में कार्बनिक सामग्री के साथ एक इलेक्ट्रोलाइट का

पहली पीढ़ी के सौर कोशिकाओं के लिए, मुख्य रूप से मोनो क्रिस्टलीय सिलिकॉन की वजह से लागतें अधिक होती हैं दूसरी पीढ़ी के सौर कोशिकाओं के लिए, पतली सक्रिय परत में सूर्य के प्रकाश के लिए कम अवशोषण क्षमता होती है, और अपेक्षाकृत कम लागत होती है। तीसरी पीढ़ी के सौर कोशिकाओं में अच्छा प्रदर्शन होता है और कम लागत भी होती है। इसके अलावा, डीएसएससी को साधारण विधानसभा तकनीक से इकट्ठा किया जा सकता है।

एक डीएसएससी में इलेक्ट्रोड के बीच कार्य-इलेक्ट्रोड, एक काउंटर-इलेक्ट्रोड और एक इलेक्ट्रोलाइट होता है। एक कार्य-इलेक्ट्रोड (फ्लोरिन डॉस्ड टिन ऑक्साइड (एफटीओ) कांच जिसे टीओओ 2 नैनोकणों के साथ डार्क-एडोरेड युक्त रखा गया है) एक फोटो-एनोड के रूप में कार्य करता है। काउंटर-इलेक्ट्रोड (प्लैटिनम युक्त एफटीओ ग्लास) कैथोड के रूप में कार्य करता है और इलेक्ट्रोलाइट में एक रेडॉक्स जोड़ी होती है।

जब प्रकाश काम-इलेक्ट्रोड (फोटो-एनोड) पर एक घटना है, यह पारदर्शी संचालन कांच (टीसीओ) शीट से गुजरता है। डार्क उत्तेजित हो जाती है और अपने इलेक्ट्रॉनों को टीओ TiO_2 परत पर स्थानांतरित करती है, और इस इलेक्ट्रान को हटाने से डार्क ऑक्सीकरण हो जाता है। इलेक्ट्रान लोड के माध्यम से TiO_2 परत से एफटीओ ग्लास तक जाता है, और अंत में काउंटर इलेक्ट्रोड को जाता है, इस प्रकार बाहरी सर्किट को पूरा करता है। ऑक्सीकृत डार्क इलेक्ट्रोलाइट से इलेक्ट्रॉनों द्वारा पुनर्जन्म हो जाता है, और इलेक्ट्रोलाइट को इलेक्ट्रॉनों द्वारा काउंटर-इलेक्ट्रोड से पुनर्जीवित किया जाता है। इस प्रकार, प्रकाश से फोटॉन बिजली उत्पन्न करता है।

वर्तमान अध्ययन में, एफटीओ ग्लास, TiO_2 नैनोपेण्टिक्ल्स, N719 डाई और इलेक्ट्रोलाइट का इस्तेमाल करते हुए मानक डीएसएससी के निर्माण की तकनीकों को 7.18 % की दक्षता के साथ आई / आई 3-रेडॉक्स जोड़ी की स्थापना की गई है। प्लैटिनम का उपयोग प्रति-इलेक्ट्रोड उत्प्रेरक के रूप में डीएसएससी के सबसे महंगी पहलुओं में से एक है। चूंकि प्लैटिनम एक महान धातु है, प्लैटिनम की जगह पौधों से प्राप्त कम लागत वाली सामग्री का पता लगाया गया है। प्लैटिनम प्रतिस्थापन के लिए भांग-युक्त परस्पर कार्बन नैनो शीट (आईसीएनएस) का उपयोग डीसीएससी की लागत 4.01 % की उचित दक्षता के साथ घटाता है। आईसीएनएस आधारित प्रपत्र में प्लैटिनम के विभिन्न वजन प्रतिशत लोड करने का प्रभाव भी अध्ययन किया गया था।

कार्य-इलेक्ट्रोड की बिखरने वाली परत में संशोधित अर्धचालक-नैनोकणों के साथ बिखरने वाली परत में TiO_2 नैनोकणों का प्रतिस्थापन भी अध्ययन किया गया है।

इसके अलावा, TiO_2 नैनोकणों के स्थान पर बिखरने वाली परत में TiO_2 शेल और चुंबकीय कोर नैनोकणों का उपयोग कर डीएसएससी ने दक्षता में 7.87% की वृद्धि दर्ज की। इलेक्ट्रॉन ट्रांसपोर्ट रोधी, प्रसार गुणांक, मानक डीएसएससी की प्रसार की लंबाई, बिखरने वाली परत में चुंबकीय कोर नैनोकणों के साथ TiO_2 शेल का उपयोग करने वाले डीएसएससी के लिए भी विभिन्न पैरामीटरों के निर्धारण के लिए इलेक्ट्रोकेमिकल प्रतिबाधा अध्ययन (ईआईएस) किया गया था।

TABLE OF CONTENTS

SECTION	Page Number
Abstract	iv
List of Figures	xiii
List of Tables	xviii
List of Abbreviations	Xix
CHAPTER 1. INTRODUCTION	1
1.1 Structure and operating principle of a Dye-Sensitized Solar Cell (DSSC)	2
1.2 Aim and scope	5
CHAPTER 2. LITERATURE SURVEY	7
2.1 Introduction	7
2.2 Components of DSSC	10
2.2.1 Conducting glass substrate	10
2.2.2 Working-electrode/Photo-anode	11
2.2.3 Dye/Sensitizer	14
2.2.4 Electrolyte	20
2.2.5 Counter-electrode	22
2.2.6 Sealant and methodologies for sealing	23
2.3 Details regarding different counter-electrode catalysts and methods of deposition	24
2.4 Different structures of semiconductor particles in the scattering-layer of DSSC and application of magnetic-field	26
2.5 Electrochemical impedance spectroscopy	32
2.5.1 EIS studies of counter-electrode: Symmetric cell using CE-CE electrode	33
2.5.2 EIS spectra of DSSC	34

CHAPTER 3. EXPERIMENTAL WORK	38
3.1 Introduction	38
3.2 Materials	39
3.3 Instruments used	40
3.3.1 Physical characterization	30
3.3.2 Electrochemical characterization	41
3.4 Preparation of a standard Dye-Sensitized Solar Cell (DSSC)	41
3.4.1 Different components of a standard DSSC	42
3.4.2 Assembly of a DSSC	49
3.4.3 Testing of the cell	51
3.5 Development of a low-cost counter-electrode (CE): DSSC with hemp-derived Interconnected Carbon Nano-Sheets (ICNS)	52
3.5.1 Preparation of Interconnected Carbon Nano-Sheets (ICNS)	54
3.5.2 Effect of loading different weight percentages of platinum along with ICNS-FTO based counter-electrode and DSSC assembled	60
3.5.3 EIS studies of symmetric cell: (a) Pt-FTO and (b) ICNS-FTO counter-electrodes	61
3.6 Development of a new working-electrode (WE): DSSC with TiO ₂ shell and magnetic core nano-particles (250 nm) in the scattering-layer	62
3.6.1 Synthesis of TiO ₂ shell with magnetic core 250 nm nano-particles for scattering-layer	64
3.6.2 Preparation of working-electrode	65
3.6.3 EIS studies of DSSCs: (a) standard DSSC and (b) DSSC with TiO ₂ shell and magnetic core nanoparticles in the scattering-layer	66

CHAPTER 4. RESULTS AND DISCUSSION	68
4.1 Introduction	68
4.2 Standard Dye-Sensitized Solar Cell (DSSC)	69
4.2.1 Working-electrode (WE) with compact-layer only, and its characterization	69
4.2.1.1 Compact-layer paste formulation: Optimum ratio of TTIP:TiO ₂	69
4.2.2 Preparation of counter-electrode (CE) and its characterization	72
4.2.2.1 Cyclic Voltametry (CV)	72
4.2.2.2 EIS studies: Equivalent circuit fit of the Nyquist plot to obtain R _{ct} of Pt-FTO counter-electrode	74
4.2.3 The assembly of standard DSSC and its characterization	78
4.3 DSSC with hemp-derived Interconnected Carbon Nano-Sheets (ICNS) as a counter-electrode catalyst	81
4.3.1 Characterization of ICNS	83
4.3.2 Counter-electrode paste formulation and deposition	83
4.3.3 Performance evaluation of DSSCs with ICNS as CE catalyst	85
4.3.4 Electrochemical Impedance spectroscopy (EIS) studies	86
4.3.5 DSSCs with different weight percentages of platinum along with ICNS	91
4.3.6 EIS studies: Equivalent circuit fit (CE with different weight percentages of Pt along with ICNS) of the Nyquist plot to obtain R _{ct}	97
4.4 DSSC with TiO ₂ shell and magnetic core nanoparticles (250 nm) in the scattering-layer	101
4.4.1 Characterization of TiO ₂ shell with magnetic core 250 nm nanoparticles	101
4.4.2 Performance evaluation of DSSC	101
4.4.3 EIS studies of DSSC: Working-electrode with TiO ₂ shell and magnetic core nanoparticles in the scattering-layer and	104

standard DSSC for parameter estimation

CHAPTER 5. CONCLUSIONS AND RECOMMENDATIONS	114
REFERENCES	116
APPENDICES	
APPENDIX A	125
APPENDIX B	126
APPENDIX C	134
BIODATA	148

LIST OF FIGURES

Figure Number	Title	Page Number
Chapter 1.		
1.1	Schematic diagram of a DSSC.	3
1.2	Schematic diagram showing the structure and operating principle of a DSSC.	
Chapter 2.		
2.1	The molecular structures of various Ruthenium based dyes.	16
2.2	Types of electrolytes.	20
2.3	Different counter-electrode catalysts.	24
2.4	Light pathway illustration of (a) TiO ₂ nanoparticles. (b) Shell in shell TiO ₂ hollow spheres.	27
2.5	Schematic diagram illustration for light scattering by (a) TiO ₂ -NP, and (b) STCS-NP on the basis of geometric optics.	28
2.6	Schematic diagram showing the scattering effect by core shell TiO ₂ nanoparticles.	29
2.7	Schematic diagram of a dye-sensitized solar cell under external magnetic-field.	30
2.8	Schematic diagram illustration of faster electron transportation in TiO ₂ nanocrystals with magnetic-field applied.	31
Chapter 3.		
3.1	Set-up for Pt deposition on FTO glass.	48
3.2	Schematic diagram of (a) Working-electrode. (b) Counter-electrode. (c) An electrolyte injection in the DSSC. (d) DSSC assembled.	50
3.3	J-V plot of standard dye-sensitized solar cell.	52
3.4	(a) Schematic diagram of hemp stem. (b) Schematic diagram of set-up for activation of hydrothermally treated hemp bast fiber. (c), (d) Enlarged schematic image of set-up for activation of hydrothermally treated hemp bast fiber.	56

3.5	Cyclic Voltammetry (CV) set-up.	60
3.6	Schematic diagram of (a) Counter-electrode with Surlyn film. (b) Counter- electrode. (c) Assembled symmetric cell.	62
Chapter 4.		
4.1	(a) SEM of TiO ₂ compact-layer on FTO glass with TTIP:TiO ₂ , 1:7. (b) At high resolution, SEM of TiO ₂ compact-layer on FTO glass with TTIP:TiO ₂ , 1:7.	70
4.1	(c) SEM of TiO ₂ compact-layer on FTO glass with TTIP:TiO ₂ , 1:8. (d) At high resolution, SEM of TiO ₂ compact-layer on FTO glass with TTIP:TiO ₂ , 1:8.	70
4.1	(e) SEM of TiO ₂ compact-layer on FTO glass with TTIP:TiO ₂ , 1:9. (f) At high resolution, SEM of TiO ₂ compact-layer on FTO glass with TTIP:TiO ₂ , 1:9.	71
4.1	(g) SEM of TiO ₂ compact-layer on FTO glass with TTIP:TiO ₂ , 1:10. (h) At high resolution, SEM of TiO ₂ compact-layer on FTO glass with TTIP:TiO ₂ , 1:10.	71
4.2	(a) Image of FTO glass. (b) TiO ₂ paste deposited on FTO glass and TiO ₂ electrode after dye uptake.	71
4.3	(a) Cyclic voltammograms (CV) of the Pt-FTO electrode at a scan rate of 50 mV s ⁻¹ in 10 mM LiI, 1 mM I ₂ acetonitrile solution containing 0.1 M LiClO ₄ as the supporting electrolyte. (b) Relationship between the number of cycles and the resulting redox peak currents by Pt-CE.	73
4.4	(a) Nyquist plot of symmetric cell with platinum, deposited on FTO glass. Inset equivalent circuit model for symmetric cell.	74
4.5	Comparison of J-V plots of DSSCs with different ratios of TTIP:TiO ₂ in the compact-layer of working-electrode paste formulation.	76
4.6	(a) SEM of TiO ₂ scattering-layer on FTO glass with TTIP:TiO ₂ , 1:8. (b) At high resolution, SEM of TiO ₂ compact-layer on FTO glass with TTIP:TiO ₂ , 1:8.	77

4.7	Working-electrode view of the color intensity of dye adsorption (a) Scattering-layer side (b) Compact-layer side.	78
4.8	J-V plot of standard dye-sensitized solar cell.	80
4.9	Schematic diagram of synthesis of hemp-derived ICNS.	82
4.10	(a) J-V plot of DSSC assembled. (b) Counter-electrode formulation using TiO ₂ nanoparticles along with ICNS.	84
4.11	Image of the (a) ICNS. (b) Counter-electrode paste formulation with ICNS deposition on FTO glass.	85
4.12	(a) J-V plot of DSSCs with CE formulation with ICNS. (b) Comparison plot for standard DSSC (Pt-FTO) and DSSC with CE formulation with ICNS.	85
4.13	Cyclic voltammograms of Pt-FTO and ICNS-FTO electrodes at a scan rate of 50 mV s ⁻¹ in 10 mM LiI, 1 mM I ₂ acetonitrile solution containing 0.1 M LiClO ₄ as the supporting electrolyte.	87
4.14	Relationship between the number of cycles and the resulting redox peak currents by Pt-CE.	88
4.15	Relationship between the number of cycles and the resulting redox peak currents by ICNS-CE.	88
4.16	(a) Cyclic voltammograms of Pt-FTO based counter-electrode at different scan rate in 10 mM LiI, 1 mM I ₂ acetonitrile solution containing 0.1 M LiClO ₄ as the supporting electrolyte. (b) Relationship between anodic and cathodic peak current density with the square root of scan rate for Pt-FTO based counter-electrode.	89
4.17	(a) Cyclic voltammograms of ICNS-FTO based counter-electrode at different scan rate in 10 mM LiI, 1 mM I ₂ acetonitrile solution containing 0.1 M LiClO ₄ as the supporting electrolyte. (b) Relationship between anodic and cathodic peak current density with the square root of scan rate for ICNS-FTO based counter-electrode.	90
4.18	Nyquist plot of symmetric cell with counter-electrode paste formulation with ICNS, deposited on FTO glass.	91

4.19	J-V plot of DSSCs with CE formulation using ICNS and loading with 12 weight percentage of Pt as that of the conventional Pt electrode in the counter-electrode formulation.	92
4.20	J-V plot of DSSCs with CE formulation using ICNS and loading with 16 weight percentage of Pt as that of the conventional Pt electrode in the counter-electrode formulation.	92
4.21	J-V plot of DSSCs with CE formulation using ICNS and loading with 18 weight percentage of Pt as that of the conventional Pt electrode in the counter-electrode formulation.	93
4.22	Comparison J-V plots of DSSCs with different CE formulations deposited on FTO glass.	93
4.23	Effect of loading of different weight percentages of platinum as that of the conventional Pt electrode along with ICNS on the fill factor of DSSC assembled.	94
4.24	Effect of loading of different weight percentages of platinum as that of the conventional Pt electrode along with ICNS on the open-circuit voltage of DSSC assembled.	94
4.25	Effect of loading of different weight percentages of platinum as that of the conventional Pt electrode along with ICNS on the current density of DSSC assembled.	95
4.26	Effect of loading of different weight percentages of platinum as that of the conventional Pt electrode along with ICNS on the efficiency of DSSC assembled.	95
4.27	Nyquist plot of symmetric cell with paste 12 weight percentage of Pt as that of the conventional Pt electrode in counter-electrode paste formulation along with ICNS, deposited on FTO glass.	98
4.28	Nyquist plot of symmetric cell with paste 16 weight percentage of Pt as that of the conventional Pt electrode in counter-electrode paste formulation along with ICNS, deposited on FTO glass.	98
4.29	Nyquist plot of symmetric cell with paste 18 weight percentage of Pt as that of the conventional Pt electrode in counter-electrode paste	99

	formulation along with ICNS, deposited on FTO glass.	
4.30	Comparison of the Nyquist plot of symmetric cell with paste containing different weight percentages of platinum as that of the conventional Pt electrode in counter-electrode paste formulation along with ICNS, deposited on FTO glass.	99
4.31	(a) SEM of TiO ₂ shell with magnetic core (250 nm) nanoparticles. (b) TEM of TiO ₂ shell with magnetic core (250 nm) nanoparticles. (c) Photo showing that TiO ₂ shell with magnetic core nanoparticles are magnetically responsive.	102
4.32	J-V plot for DSSC using TiO ₂ shell with magnetic core nanoparticles in the scattering-layer.	103
4.33	Nyquist plot of standard DSSC.	106
4.34	Experimental Nyquist plot of (a) DSSC using TiO ₂ shell with magnetic core. (b) Standard DSSC.	109
4.35	Nyquist plot (theoretical and experimental): (a) DSSC using TiO ₂ shell with magnetic core nanoparticles in the scattering-layer. (b) Standard DSSC.	110

LIST OF TABLES

Table Number	Title	Page Number
Chapter 2.		
2.1	Efficiencies of DSSCs assembled using different nanostructures in working-electrode/photo-anode.	13
2.2	Different types of sensitizers and other components required for fabrication of DSSC.	17
2.3	List of different carbon materials and polymers explored as the counter-electrode catalyst.	25
Chapter 4.		
4.1	Efficiencies of DSSCs assembled with different ratios of TTIP:TiO ₂ in the compact-layer of WE paste formulation.	76
4.2	Comparison table for standard DSSC and DSSC with compact-layer only.	79
4.3	Comparison table for standard DSSC (Pt-FTO) and DSSC (ICNS-FTO) as CE catalyst.	86
4.4	Comparison table for DSSCs assembled using hemp with Pt loading as counter-electrode catalysts.	96
4.5	Comparison table for DSSCs assembled using various counter-electrode catalysts.	100
4.6	Comparison table for DSSC with TiO ₂ shell magnetic core nanoparticles and standard DSSC.	103
4.7	Parameters for DSSCs.	111
4.8	Calculated values of various parameters obtained for DSSCs.	112

LIST OF ABBREVIATIONS

DSSC	Dye-Sensitized Solar Cell
WE	Working-electrode
CE	Counter-electrode
FTO	Fluorine doped tin oxide
TCO	Transparent conducting oxide
TTIP	Titanium iso-propoxide
TiO ₂	Titanium di-oxide
TBOT	Titanium butoxide
CTAB	Cetyltrimethyl ammonium bromide
DI	De-ionized water
CNT	Carbon nanotube
NP	Nano particles
Ppy	Polyprrole
PANI	Polyaniline
PEDOT	Poly (3,4-ethylenedioxythiophene)
V_{oc}	Open-circuit voltage (V)
J_{sc}	Short-circuit current density (mA cm ⁻²)
P_{max}	Maximum power
P_{in}	Power of incident light
η	Efficiency (%)
ICNS	Interconnected Carbon Nano-Sheets
EIS	Electrochemical Impedance Spectroscopy
QD	Quantum dots

CV	Cyclic Voltammetry
I_{pa}	Anodic peak current
I_{pc}	Cathodic peak current
ΔE_{pp}	Peak to peak separation
R_{ct}	Counter-electrode charge transport resistance
Z	Impedance of the TiO ₂ electrode (Ω)
Z_p	Impedance of Pt electrode (Ω)
Z_n	Finite Warburg impedance (Ω)
Z_s	Total impedance (Ω)
R_w	Electron transport resistance in TiO ₂ (Ω)
R_k	Electron transport resistance related to recombination of electrons (Ω)
Ω	Modulation frequency (s^{-1})
r_p	Resistance at the Pt surface (Ω)
R_{dc}	DC resistance of impedance of diffusion of tri-iodide (Ω)
D_1	Diffusion coefficient of I ₃ ⁻
D_{eff}	Effective diffusion coefficient of electrons ($cm^2 s^{-1}$)
δ	Thickness of spacer (μm)
Z'	Real part of impedance (Ω)
Z''	Imaginary part of impedance (Ω)
L_n	Diffusion length (μm)
τ_n	Effective lifetime of electrons (s)
k_{eff}	Effective rate constant for recombination (s^{-1})