UNIVERSITI PUTRA MALAYSIA

ENHANCING POWER CONVERSION EFFICIENCY FOR DYE-SENSITISED SOLAR CELLS USING GRAPHENE QUANTUM DOTS

NOOR FADZILAH BINTI MOHAMED SHARIF

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By

NOOR FADZILAH BINTI MOHAMED SHARIF

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Doctor of Philosophy

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DEDICATION

This thesis is dedicated to my precious parents and siblings

For their prayers and positive support

And to my armies (my husband and our kids “The Iman”)

Especially for my husband, who has always given encouragement and support

and prayed for the completion of this research.

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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Doctor of Philosophy

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February 2020

Chairman: Professor Mohd Zainal Abidin Ab. Kadir, PhD, PEng, CEng
Faculty : Engineering

Traditional dye-sensitised solar cell (DSSC) with Titanium dioxide (TiO_2) works well under low-light condition. However, the use TiO_2 in photoelectrode will cause a random electron transport and high carrier recombination between the TiO_2/dye/electrolyte interface which slow electron diffusion and reduce the charge collection efficiency (CCE). The recombination process can be reduced by Titanium (IV) Chloride ($TiCl_4$) surface treatment at 40mM. A $TiCl_4$ treatment successfully increased charge transfer resistance (R_{ct}) and electron lifetime (τ_n), resulting in suppression of electron recombination and increased CCE at 31.09% compared to untreated DSSC.

In order to enhance the PCE of DSSC, a Design of engineering (DOE) software was employed to study the validity of selection of an independent variable and its parameter for photoelectrode using a statistical method. In this stage, response surface methodology (RSM) was chosen under DOE to undergo three tests, which were: statistical test, regression analysis, and adequacy test on experimental data to develop a model. Based on the RSM test, the most variables that affected the power conversion efficiency (PCE) of DSSC were TiO_2 thickness, then GQDs concentration, and GQDs loading time. The best PCE generated at 8.03% with 16 μm TiO_2 thickness, GQDs concentration at 7.5mg/ml and 18 hours GQDs loading time.

Furthermore, the use of Graphene Quantum Dots (GQDs) into photoelectrode can improve photon absorption which contributes to better PCE and CCE of DSSC. Photoelectrodes were dip-coated in different GQDs concentrations which varied from 2.5, 5.0, to 7.5 and 10 mg/ml. The optimum content of 7.5mg/ml GQDs generated higher photon absorption wavelength of 330 to 600 nm due to the photoluminescent effect by GQDs. Thus, more electron-hole pairs were

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generated in the solar cell with resulting increment of 47% PCE and 53.42% CCE compared to pristine TiO_2 DSSC.

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Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

MENINGKATKAN KECEKAPAN PENUKARAN KUASA UNTUK SEL SOLAR - PEKA WARNA DENGAN MENGGUNAKAN GRAPHENE QUANTUM DOTS

Oleh

NOOR FADZILAH BINTI MOHAMED SHARIF

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Pengerusi : Profesor Mohd Zainal Abidin Ab. Kadir, PhD, PEng, CEng
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Sel solar-peka warna yang biasa (DSSC) dengan Titanium dioksida (TiO_2) boleh berfungsi dengan baik di bawah keadaan cahaya rendah. Walau bagaimanapun, penggunaan TiO_2 yang asli dalam fotoelektrik akan menyebabkan pengangkutan elektron rawak dan penggabungan pembawa yang tinggi antara antara muka TiO_2 / pewarna / elektrolit yang memperlambat penyebaran elektron dan mengurangkan kecekapan pengumpulan caj (CCE). Proses cas rekombinasi boleh dikurangkan dengan rawatan permukaan Titanium (IV) Chloride ($TiCl_4$) pada kepekatan 40mM. Rawatan $TiCl_4$ berjaya meningkatkan rintangan pemindahan rintangan (R_{ct}) dan jangka hayat electron (τ_n). Dengan penurunan cas rekombinasi pada DSSC, kecekapan pengumpulan cas (CCE) meningkat pada 31.09% berbanding dengan DSSC yang tidak melalui rawatan $TiCl_4$.

Untuk meningkatkan PCE DSSC, applikasi Rekabentuk kejuruteraan (DOE) digunakan untuk mengkaji kesahihan pemilihan pembolehubah bebas dan parameternya untuk fotoelektrik dengan menggunakan kaedah statistik. Pada tahap ini, metodologi permukaan respon (RSM) dipilih di bawah DOE untuk menjalani tiga ujian yang dikenali sebagai ujian statistik, analisis regresi dan ujian ketepatan antara data eksperimen dan data model. Berdasarkan ujian RSM, pemboleh ubah yang paling mempengaruhi kecekapan penukaran kuasa (PCE) DSSC adalah ketebalan TiO_2, di ikuti oleh kepekatan GQD dan masa rendaman GQD. PCE yang terbaik dijana pada 8.03% dengan parameter yang di optimumkan ketebalan TiO_2 pada 16μm dengan kepekatan GQDs 7.5mg/ml dan pada masa rendaman GQD pada 18 jam.

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Tambahan pula, penggunaan Graphene Quantum Dots (GQDs) ke fotoelektrik dapat meningkatkan penyerapan foton yang menyumbang kepada PCE dan CCE DSSC yang lebih baik. Photoelectrodes dimasukkan ke dalam kepekatan GQD dari 2.5, 5.0, 7.5 dan 10 mg / ml. Kandungan optimum GQDs pada 7.5mg / ml meningkatkan penyerapan foton yang tinggi pada gelombang 330 hingga 600 nm disebabkan oleh sifat fotoluminescent oleh GQDs. Oleh itu, sel solar dapat menghasilkan lebih banyak pasangan lubang elektron yang akhirnya menghasilkan kenaikan 47% PCE dan 53.42% CCE berbanding dengan sel solar TiO_2 yang asli.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

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Declaration by Members of Supervisory Committee

This is to confirm that:

- The research conducted and the writing of this thesis were under our supervision;
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LIST OF ABBREVIATIONS

AM	Air Mass
ANOVA	Analysis of Variance
CB	Conduction Band
CE	Counter Electrode
CT	Charge Transfer
DOE	Design of Experiment
DSSC	Dye Sensitized Solar Cell
EIS	Electrochemical Impedance Spectroscopy
FESEM	Field Emission Scanning Electron Microscope
FF	Fill Factor
FTIR	Transform Infra-red
FTO	Fluorine doped Tin oxide
GQDs	Graphene Quantum Dots
HOMO	Highest Occupied Molecular Orbital
IQE	Internal Quantum Efficiency
ITO	Indium doped Tin Oxide
J_{sc}	Short circuit current density
LH	Light Harvesting
LHE (λ)	Light harvesting efficiency at wavelength λ
LUMO	Lowest Unoccupied Molecular Orbital
NPs	Nanoparticles
PEDOT	Polypyrrole, poly (3, 4- ethylenedioxythiophene)
PL	Photo-luminescence

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P_{max}	Maximum power
Pt	Platinum
QD	Quantum dot
R	Reflectance
RSM	Response Surface Methodology
TEM	Transmission Electron Microscope
tBA	tertiary Butyl Alcohol
UV-Vis	Ultraviolet-Visible-spectroscopy
XRD	X-ray Diffraction
VB	Valence Band
V_{oc}	Open circuit potential
TCO	Transparent Conducting Oxide

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CHAPTER 1

INTRODUCTION

1.1 Background of the Study

Currently, most of the energy is generated using fossil fuels, but these sources are projected to be depleted. Hence, it is imperative that alternative energy sources are developed before then. In this regard, solar energy, which is clean and abundant, holds great promise.

Dye-sensitised solar cells (DSSCs) have been developed for solar harvesting applications. The solar cell offers several advantages over silicon and thin-film cells due to their low sintering temperature, easy fabrication, non-toxicity and their ability to work under low light conditions [1–2]. Hence, this technology can be commercialised because due to economic reason compared to first and second-generation photovoltaics, if the efficiency could be enhanced significantly. To achieve that goal, it is vital to improve the photoelectrode element. Currently, there are commercial DSSC products available in the market such as wireless remote, solar keyboard for IOS and Android, Gcell sample DSSC and G100 indoor solar powered by G24i group.

Previous work in TiO_2 photoelectrode modification included surface plasmon resonance effect by metal nanoparticle, doping to tune energy band structure, growing graphene layer between FTO and TiO_2, and using graphene type nanomaterial in photoelectrode to enhance power conversion efficiency (PCE) of DSSC [3–5]. Previous studies in the literature proved that two-dimensional (2D) graphene materials can potentially enhance the properties of photoelectrode of DSSC [6–9] due to its unique properties such as high optical transmittance (~98%), good conductivity and large theoretical specific surface area (2630 $m^2\ g^{-1}$) which is suitable for engineering the TiO_2 layer in DSSCs. Graphene also can be downsized by bottom-up technique using organic precursor to modify graphene bandgap and producing zero-dimensional Graphene Quantum Dots (GQDs). The existence of quantum confinement effect in GQDs will modify the optical properties of the TiO_2 photoelectrode in DSSCs. In addition, GQDs material can be used to overcome the drawback of TiO_2, such as high carrier recombination, lack of charge-carrier transport, and poor absorption on visible-region, which is believed to possibly enhance the DSSC efficiency [10 –12].

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1.2 Problem Statement

Photoelectrode is one of crucial elements in DSSC because it holds and transports excited electrons from N719 dye to FTO electrode. Traditionally, TiO_2 is the most promising material for the photoelectrode due to its photostability, biocompatible, wide bandgap, cost-effectiveness and non-toxicity. However, the use of TiO_2 in DSSC cause the electrons to move randomly and increase high electron recombination between the TiO_2/dye/electrolyte interface, which slows down electron diffusion and reduces the current density amount [13 –16]. Thus, it will reduce the PCE of DSSC. In addition, previous research shows less attention being paid to the advantages of pre-and-post-$TiCl_4$, which resulted in easy electron diffusion and enhancement of the PCE of DSSC. To solve these issues, a chemical treatment using titanium tetrachloride ($TiCl_4$) in the photoelectrode was carried out.

Furthermore, there is limited research on how most variables in the photoelectrode element influence the PCE. Thus, this research used Response surface methodology (RSM) to allow simultaneous varying of process variables [17–19]. The application of RSM method in fabricating a TiO_2-GQDs, to investigate more than one independent variable has not been done before. In this research, a statistical method was used to study the validity of selection of the independent variable and its parameter for photoelectrode element. Ultimately, the most variable effect on the PCE was determined.

Moreover, using pristine TiO_2 causes poor light absorption in the visible-region and a lack of charge-carrier transport. Hence, it causes a reduction of photocurrent density [20,21]. Thus, GQDs can be used due to their stable up-conversion photoluminescence property, which may enhance light absorption in the visible region [22]. In this study, GQDs concentration is varied to contribute to higher PCE and charge transport of DSSC. The TiO_2 photoelectrode is sensitised in different concentrations of GQDs then continues with dye adsorption process. The performance of TiO_2-GQDs cells was compared to pristine TiO_2 cell.

1.3 Research Objectives

The key objectives of the current study are listed as follows:

1) To determine the impact of $TiCl_4$ treatment by investigating the carrier transport and recombination rate using electrochemical impedance spectroscopy (EIS). A longer carrier transport shows an improvement of charge collection efficiency (CCE) and power conversion efficiency (PCE).
2) To investigate independent variables and their input parameters of photoelectrode that influence the DSSC performance, to determine an optimised input variable and PCE response by using central composite design (CCM) of RSM.

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3) To use GQDs at different concentrations in the photoelectrode to improve photon absorption in the low visible region which can contribute to higher PCE of DSSC. The TiO_2-GQDs nanocomposite is characterised using field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD), Raman spectrophotometer, and Ultraviolet-visible spectroscopy (UV-vis) to determine its morphology, crystallinity and optical properties.

1.4 Scope and Limitations

1) This research only investigated the DSSC device at 2 cm x 2.5cm with an active area of 1 x 1 cm^2. Then, TiO_2 paste was made by a sol-gel method and screen-printing was selected to deposit TiO_2 paste on FTO glass because the method produces homogenous TiO_2 film.
2) The dip-coated method to incorporate GQDs into DSSC is done based on GQDs nature and the sensitivity of TiO_2 condition, or else the TiO_2 film will be corrugated and it may reduce the PCE of DSSC.

1.5 Research Contributions

1) The effects of pre-and-post-$TiCl_4$ treatment are proven to increase the carrier transport and reduce the recombination rate between TiO_2/dye/electrolyte interfaces. The results also shown higher charge collection efficiency (CCE) and power conversion efficiency (PCE) for DSSC.
2) A quadratic equation with significant variables to predict the PCE value is obtained by Central composite design (CCD). The equation is generated based on statistical approach where the technique can be employed for process optimisation of TiO_2-GQDs based DSSC in the future.
3) A green and acid-free GQDs at concentration of 7.5 mg/ml successfully increased the light absorption in the low visible region, resulting in a higher short-circuit current density and PCE of DSSC.

1.6 Structure of the Thesis

This thesis is divided into five chapters. Chapter one presented the background of the study, problem statement, research objectives, scope of the study, then ended with the research contributions. Chapter Two reviews the literature and discusses a previous work on photoelectrode modification and the use of GQDs to improve the PCE of DSSC. Chapter Three provides information on the preparation of TiO_2-GQDs solar cell via dip-coated method and the characterisation process to determine the performance of new DSSC. Next, Chapter Four presents the results and discussion on the improvement of PCE after GQDs incorporated in the photoelectrode of DSSC. Finally, Chapter Five summarises the research findings and offers recommendations for future work to enhance DSSC efficiency.

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