UNIVERSITI PUTRA MALAYSIA

INTEGRATION OF PHOTO-SUPERCAPACITOR UTILIZING POLYPYRROLE/REDUCED GRAPHENE OXIDE INTERMEDIATE BIFUNCTIONAL ELECTRODE

LAU SIAW CHENG

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UNIVERSITI PUTRA MALAYSIA

BERILMU BERBAKTI

INTEGRATION OF PHOTO-SUPERCAPACITOR UTILIZING POLYPYRROLE/REDUCED GRAPHENE OXIDE INTERMEDIATE BIFUNCTIONAL ELECTRODE

By

LAU SIAW CHENG

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfillment of the Requirements for the Degree of Master of Science

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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Master of Science

INTEGRATION OF PHOTO-SUPERCAPACITOR UTILIZING POLYPYRROLE/REDUCED GRAPHENE OXIDE INTERMEDIATE BIFUNCTIONAL ELECTRODE

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October 2017

Chairperson: Associate Professor Janet Lim Hong Ngee, PhD
Faculty : Science

With the continued industrialization and development of the world economy, the need for a clean source of renewable energy is becoming ever more urgent. Furthermore, despite the recent rise in global oil production due to fracking, on a time horizon of one or two hundred years, oil reserves will ultimately dwindle, along with supply. Sunlight is an abundant energy source that is more than capable of providing for the world's energy needs. In order to generate and simultaneously store the photo-generated energy for substantial use even during the night, a supercapacitor is coupled with solar cell, which turned into an integrated photo-supercapacitor.

In this work, a photo-supercapacitor with three electrodes configuration was fabricated by the integration of titania (TiO_2)-based dye-densitized solar cell (DSSC) with a symmetrical supercapacitor utilizing polypyrrole/reduced graphene oxide (PPy/rGO) as an electrode active material. The photoanode of DSSC was composed of compact and mesoporous TiO_2 layer. Compact TiO_2 layer was formed via aerosol-assisted chemical vapor deposition (AACVD) method while the mesoporous TiO_2 layer was deposited using doctor's blade method. The PPy/rGO materials were formed through electrochemical deposition. Double-sided-electrodeposited PPy/rGO material served as an intermediate electrode which was bifunctional; acting as a counter electrode for the DSSC to permit electrolyte regeneration, and charge storage for the supercapacitor.

Before the integration, the isolated DSSC and supercapacitor were characterized, and the power conversion efficiency (PCE) of DSSC was 2.4 %, while the specific capacitance of the supercapacitor was 308.1 F/g. The performance of the integrated photo-supercapacitor was tested under a light illumination of 100 mW/cm^2. The photo-supercapacitor experienced a small voltage drop of 0.024 V with high charge/discharge durability and long lifetime. Remarkably, the photo-supercapacitor possessed a specific

capacitance of 124.7 F/g and a retention percentage of 70.9 % was obtained after 50 consecutive cycles of charge/discharge.

This cheap graphene-based and light-weight integrated device showed a promising performance in both effectiveness and stability, thus it opened the door for future self-powered electrochemical energy storage system. To further improve this device, development on the intermediate electrode and device packaging should be taken into consideration.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia
sebagai memenuhi keperluan untuk ijazah Master Sains

INTEGRASI FOTO-SUPERKAPASITOR MENGGUNAKAN *POLIPIROL*/GRAFIN SEBAGAI ELEKTROD PERANTARAAN DWIFUNGSI

Oleh

LAU SIAW CHENG

Oktober 2017

Pengerusi: Profesor Madya Janet Lim Hong Ngee, PhD
Fakulti : Sains

Dengan perindustrian yang berterusan dan pembangunan ekonomi dunia, keperluan untuk sumber tenaga bersih yang boleh diperbaharui menjadi semakin mendesak. Tambahan pula, walaupun kenaikan dalam pengeluaran minyak dunia baru-baru ini disebabkan oleh "fracking" (process pengekstrakan minyak), dalam jangka masa satu atau dua ratus tahun, rizab minyak akhirnya akan berkurang, bersama-sama dengan bekalannya. Cahaya matahari adalah sumber tenaga yang banyak yang mampu menampung keperluan tenaga dunia. Dalam usaha untuk menjana dan pada masa yang sama menyimpan tenaga foto yang dihasilkan untuk kegunaan yang banyak walaupun pada waktu malam, superkapasitor yang digandingkan dengan sel solar, yang bertukar menjadi foto-superkapasitor bersepadu.

Dalam karya ini, foto-superkapasitor dengan tiga konfigurasi elektrod telah direka dengan penyepaduan sel suria kepekaan pencelup (DSSC) berdasarkan titania (TiO_2) dengan superkapasitor simetri yang menggunakan *polipirol*/grafin (PPy/ rGO) sebagai bahan aktif elektrod. Foto-anod DSSC terdiri daripada lapisan TiO_2 padat dan berliang meso. Lapisan TiO_2 padat dibentuk melalui kaedah pemendapan wap kimia yang dibantu oleh aerosol (AACVD) manakala lapisan TiO_2 berliang meso dimendapkan menggunakan kaedah *doctor's blade*. Bahan PPy/rGO dibentuk melalui pemendapan elektrokimia. Electro-mendapan bermuka dua bahan PPy/rGO berfungsi sebagai elektrod perantaraan yang bersifat dwifungsi; bertindak sebagai elektrod bertentangan untuk DSSC bagi membenarkan regenerasi elektrolit, dan caj penyimpanan untuk superkapasitor.

Sebelum integrasi, DSSC dan superkapsitor terpencil telah dicirikan,dan kecekapan penukaran kuasa (PCE) untuk DSSC ialah 2.4 %, manakala kapasitans khusus bagi

superkapasitor adalah 308.1 F/g. Prestasi foto-superkapasitor bersepadu telah diuji di bawah pencahayaan cahaya 100 mW/cm^2. Foto-superkapasitor mengalami penurunan voltan kecil sebanyak 0.024 V dengan daya ketahanan caj/nyahcaj yang tinggi dan jangka hayat yang panjang. Hebatnya, foto-superkapasitor mempunyai kapasitans khusus sebanyak 124.7 F/g dan peratusan pengekalan sebanyak 70.9% yang telah diperolehi selepas 50 kitaran berturut-turut bagi caj/nyahcaj.

Peranti bersepadu berasaskan grafin yang murah dan ringan ini telah menunjukkan prestasi yang menjanjikan dalam kedua-dua keberkesanan dan kestabilan, dengan itu ia telah membuka pintu untuk sistem penyimpanan tenaga elektrokimia janaan sendiri. Untuk mempertingkatkan lagi peranti ini, pembangunan pada elektrod perantaraan dan pembungkusan peranti harus dipertimbangkan.

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I could not have completed this project without anyone of them. Thank you very much, all.

I certify that a Thesis Examination Committee has met on 24 October 2017 to conduct the final examination of Lau Siaw Cheng on her thesis entitled "Integration of Photo-Supercapacitor Utilizing Polypyrrole/Reduced Graphene Oxide Intermediate Bifunctional Electrode" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Master of Science.

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

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I hereby confirm that:

- this thesis is my original work;
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This is to confirm that:

- the research conducted and the writing of this thesis was under our supervision;
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Signature: ______________________________
Name of Member of Supervisory Committee: Dr. Thahira Begum

Signature: ______________________________
Name of Member of Supervisory Committee: Dr. Mohd. Hanif Bin Yaacob

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AACVD	Aerosol-assisted chemical vapor deposition
AC	Activated carbon
ACF	Activated carbon fibers
a-Si	Amorphous silicon
CI(G)S	Copper indium gallium (di)selenide
CNT	Carbon nanotube
C_s	specific capacitance
c-Si	Crystalline silicon
CV	Cyclic voltammetry
DSSC	Dye-sensitized solar cell
EDLC	Electric double-layer capacitor
EIS	Electrochemical impedance spectroscopy
ESR	Equivalent series resistance
GCD	Galvanostatic charge/discharge
GO	Graphene oxide
hEDLC	Hybrid electric double-layer capacitor
HTM	Hole transporting material
ITO	Indium tin oxide
J_{sc}	Short-circuit voltage

N3 dye	Ruthenizer 535-bisTBA
NHE	Normal hydrogen electrode
OECD	Organisation for Economic Co-operation and Development
OPV	Organic photovoltaic
P25	Titanium (IV) oxide
P3HT	Poly(3-hexylthiophene)
PANI	Polyaniline
PCE	Power Conversion Efficiency
PEDOT	Poly(3,4-ethylenedioxythiophene)
PEDOT:PSS	Poly(3,4-ethylenedioxythiophene)-poly(styrenesulphonate)
PPy	Polypyrrole
PV	Photovoltaic
PVA	Polyvinyl alcohol
QDSC	Quantum dot solar cell
R_{ct}	Charge transfer resistance
rGO	Reduced graphene oxide
S	Sensitizer
spiro-OMeTAD	2,2',7,7'-tetrakis(N,N-di-p-methoxyphenylamine)-9,9'-spirobifluorene
SQL	Shockley-Queisser limit
ssDSSC	Solid-state dye-sensitized solar cell
TC	Templated porous carbons

TCS	Trichlorosilane
TFSC	Thin-film solar cell
TTIP	Titanium (IV) tetraisopropoxide
V_{oc}	Open-circuit voltage
WEO	World Energy Outlook
WHO	World Health Organization

CHAPTER 1

INTRODUCTION

1.1 Renewable Energy Resources

Energy is inevitable to human life and a continuous energy supply is crucial for the sustainability of modern societies and continued human development. With increasing human population and modernization, the global energy demand is rapidly increasing. To cope with the current energy requirements, fossil fuels such as oil, gas and coal plays an important role in the world energy market. According to the World Energy Outlook (WEO) 2007, fossil fuels energy is expected to provide more than 80% of the global energy demand in 2030 (Asif & Muneer, 2007; Shafiee & Topal, 2009). However, fossil fuels energy usage is facing several problems, which are the depletion of the unrenewable fossil fuels reserves, increasing fuel price and environmental issues such as global warming. For the latter, climate changes driven by the greenhouse gas emissions due to the use of fossil fuels are having enormous implications on our environment and ecosystem (Asif & Muneer, 2007). As shown in Figure 1.1, the total world CO_2 gas emissions increased from 21.5 billion tons in 1990 to 23.9 billion tons in 2001 before climbing to above 27.0 billion tons in 2010. In 2025, the CO_2 gas production is expected to reach 37.1 billion tons (Asif & Muneer, 2007).

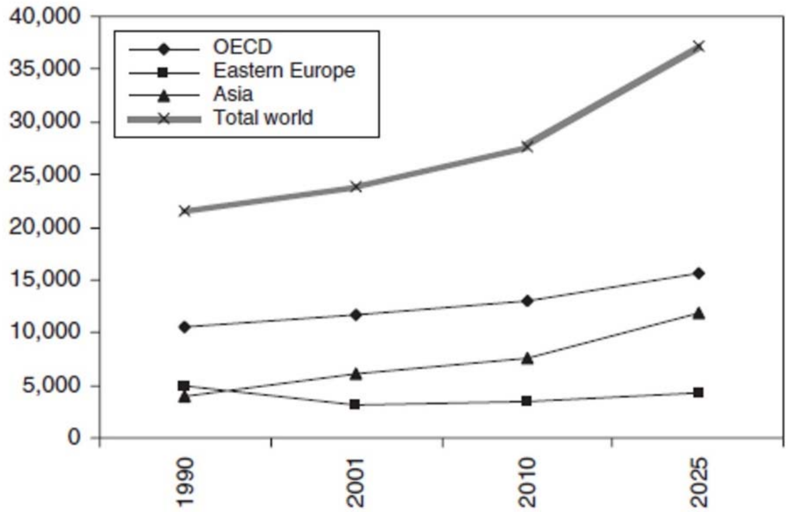

Figure 1.1: CO_2 gas emissions in millions of tons.
(Source: Renewable and Sustainable Energy Reviews (Asif & Muneer, 2007))

According to the World Health Organization (WHO), 160,000 people die every year because of the side-effects of climate change like malaria, malnutrition and diarrhea, resulting from higher atmospheric temperatures, droughts and floods. More importantly, the numbers are expected to be almost double by 2020 (Asif & Muneer, 2007; Petinrin & Shaaban, 2015). On the other hand, in spite of the increase in global oil production due to fracking, the oil reserves will eventually diminish (Asif & Muneer, 2007; Christians *et al.*, 2013; He *et al.*, 2014; Noel *et al.*, 2014; Shafiee & Topal, 2009). Also, the locked up CO_2 from these reserves will be released due to fracking and this causes adverse effects to humankind (Christians *et al.*, 2013; Jeon *et al.*, 2013; Noh *et al.,* 2013; Snaith, 2013; Zhu *et al.*, 2014). Obviously, presently employed fossil fuels energy systems will not be able to cope with the future energy necessities since they are significantly affecting human health, ecological balance and biological diversity.

The aforementioned problems have prompted a worldwide research into clean sources of renewable energy to substitute fossil fuels, which guarantee the life of current and future generations (Zhang & Zhao, 2009). Integration of renewable energy in the power system has the potential to form a robust and viable power transmission and distribution system. Renewable energy sources that use natural resources such as the sun, wind, biomass and wave, are abundant and able to produce energy with almost nil emissions of both greenhouse gases and air pollutants, thus they are free from related global warming effects (Asif & Muneer, 2007; Petinrin & Shaaban, 2015). Moreover, with the current total global power requirements of 15TW, and that of 30TW by year 2050, renewable energy is believed to be the best candidate to meet those needs (Cheng *et al.*, 2009; Ramanujam *et al*., 2016). At present, 15-20 % of the world's total energy demand is supported by renewable energy sources (Petinrin & Shaaban, 2015).

Sunlight is an abundant and reliable energy source that is more than capable to provide such global energy needs (Christians *et al*., 2013; Docampo *et al.*, 2013; Noel *et al*., 2014; Snaith, 2013). Approximately 70% of the energy radiated from the sun is absorbed by the ocean, land masses and clouds while the other is free back into the space. The absorbed energy is useful to keep our Earth surface at about 14ºC. Moreover, green plants carry out photosynthesis and convert solar energy into chemical energy, which produces food, wood and biomass. This is where fossil fuel is derived. Notably, all renewable energy derive their energy from the sun except tidal and geothermal energy (Petinrin & Shaaban, 2015). Surprisingly, the energy needs could be fulfilled if only 0.1% of the Earth surface is covered with solar panels with an average efficiency of 10%. This is because in every second, the sun produces a power of 3×10^{26} W, which approximately equals 500,000 years of current energy needs (Ramanujam *et al*., 2016). In an hour, the energy produced by the sun exceeds the annual energy consumption of humans (Crabtree & Lewis, 2007; Lewis & Nocera, 2006). Figure 1.2 shows the availability of various non-renewable and renewable energy sources as compared to the world energy consumption per year (Asif & Muneer, 2007).

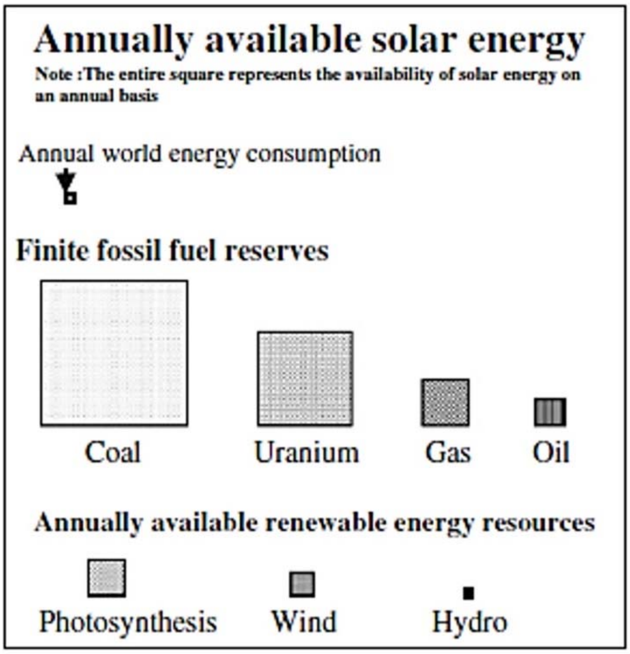

Figure 1.2: Comparison between annually available energy sources and global energy consumption.
(Source: Renewable and Sustainable Energy Reviews (Asif & Muneer, 2007))

In order to harvest energy from the sun, different methods have been utilized. For example, solar cells have been developed to absorb sunlight and convert photons to electrical energy, and solar thermal collectors have been used to absorb and convert solar energy into heat energy. Generally, the working mechanism of solar cells or photovoltaic devices are based on charge separation at an interlayer between two materials with different conduction mechanism. The solar energy conversion has three requirements, which are electrons (negative charges), holes (positive charges) and a potential which acts as a driving force to transport the charges to an external circuit (Grätzel, 2003; Hadipour *et al*., 2006). Photovoltaic devices have two main advantages of energy independence and environmental compatibility, where they require free fuels (sunlight), and their operations do not produce air, water and noise pollution (Ong *et al.*, 2011).

To date, the photovoltaic market is dominated by silicon solar cells, the semiconductor-based solid-state junction devices due to their high power conversion efficiencies. Despite the good device performances, there are drawbacks since they involve rare earth elements and have a high manufacturing cost (Kozma & Catellani, 2013). In fact, they are now being challenged by the emergence of third generation solar cells, which are based on nanocrystalline structures and conducting polymers thin films. Third generation solar cells have the potential to be low cost in fabrication and deviate completely from the typical solid-state junction devices. The latter is by replacing the contacting phase to the semiconductor by an electrolyte in the form of liquid, solid or gel, resulting in a photo-electrochemical cell. The employment of nanocrystalline materials has thus brought up new ways for the development of solar cells. In addition, further involvement of mesoscopic semiconductors showed comparable efficiencies to the conventional cells.

Dye-sensitized solar cells (DSSC) are good representatives with mesoporous nanoparticles (Grätzel, 2003). The typical device architecture and operating mechanism of DSSC is shown in Figure 1.3. The photoactive layer, which is the mesoporous metal oxide layer, is made up of sintered semiconductor nanoparticles responsible for electronic conduction. The most preferably metal oxide is titanium dioxide (TiO_2), other material choices are zinc oxide (ZnO) and niobium(V) oxide (Nb_2O_5). Ruthenium dye is well-distributed on the surface of the nano-sized mesoporous semiconductor layer. Upon photo excitation of the dye molecules, electrons are injected into the conduction band of the oxide materials. Subsequently, the loss of electrons of the dye molecules is compensated by electron donation from the redox electrolyte, with the most common redox couple used being a triiodide/iodide (I_3^-/I^-) couple. Dye regeneration then occurs by the reduction of triiodide at the counter electrode. Thus, the circuit is completed by the transportation of electrons *via* the external load (Grätzel, 2003).

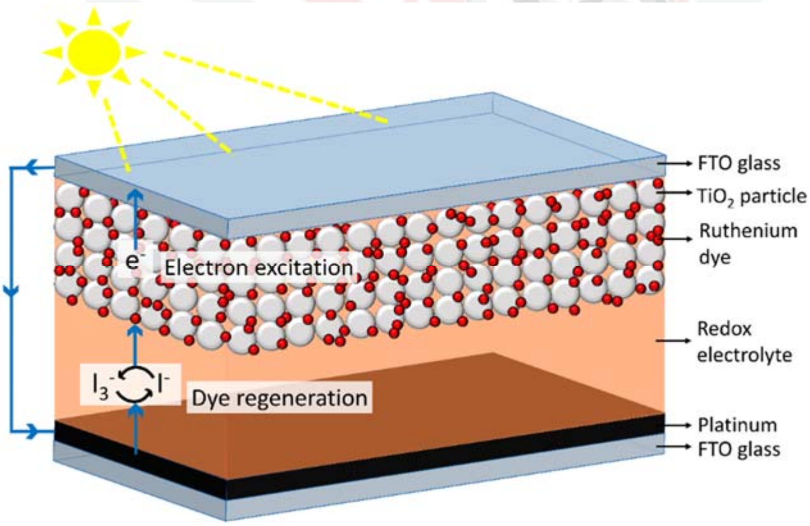

Figure 1.3: Schematic diagram of a DSSC with blue arrows representing the movement of electrons after electron excitation.

1.2 Energy Demand and Renewable Energy in Malaysia

Since Malaysia's independence in 1957, the development in economy and infrastructure showed tremendous growth which was characterized by advanced technology like the SMART tunnel and Petronas Twin Towers. Such development was supported by the affordable and reliable electricity sector of the country. From 2005 to 2008, the growth rate of final energy consumption was 5.6%. In the future by 2030, the final energy consumption is expected to triple the 2002 level (Mekhilef *et al.*, 2014). The energy supply is mostly consumed by industrial sector followed by transportation sector (Ong *et al*., 2011). Every year, electricity demand in Malaysia increases 5-8% with a projection of 10 GW is needed by 2020 (Petinrin & Shaaban, 2015). Currently, the main energy supply in Malaysia are coal, crude oil and natural gas. Somehow, the depletion of fossil fuels and global warming issue call for the use of renewable energy sources as alternative energy supply, especially for rural areas far from utility grids (Petinrin & Shaaban, 2015). Decrease in domestic gas supply and shortage of coal supply have urged the government to promote renewable energy and thus come up with some policies, programmes and incentives, to reduce the over-dependence on fossil fuels. Besides, the importance of renewable energy is further reinforced in the Tenth Malaysia Plan (2011-2015), which focus on energy generation and utilization efficiency with firm agreement of environmental objectives. According to the plan, the percentage of renewable energy of total electricity generation has to increase from < 1% in 2009 to 5.5% by 2010, with amounts of 41.5 MW and 985 MW, respectively (Mekhilef *et al*., 2014). Biomass, hydro and solar energy are three major renewable energy resources in Malaysia. The abundance of sunshine throughout the year favours the development of solar energy, with an average monthly solar radiation of 400-600 MJ/m^2 (Mekhilef *et al*., 2012).

As an equatorial country, Malaysia has uniform temperature throughout the year with average solar radiation of 4.7-6.5 kWh/m^2 per day. The lowest solar radiation is in December while that of the highest is in August and November with estimated values of 0.61 kWh/m^2 and 6.8 kWh/m^2, respectively. Table 1.1 shows the yearly average solar radiation in different towns in Malaysia. Kota Kinabalu has the highest yearly irradiance while the lowest radiation is experienced by Kuching. Despite the adequate sunlight throughout the year which is a primary advantage, the efficiency of solar devices needs to be improved in order to convince the government to invest and rely on solar energy, which could meet the energy needs in rural areas (Petinrin & Shaaban, 2015). Even though solar devices have great potential as a future sustainable energy source especially for rural areas, it involves high cost for mass power generation. This is because our country has no local photovoltaic device manufacturer due to high initial system cost, and thus all solar modules and inverters have to be imported from overseas (Ong *et al*., 2011).

Table 1.1: Yearly average solar radiation in different towns in Malaysia.
(Source: Renewable and Sustainable Energy Reviews (Petinrin & Shaaban, 2015))

Town	Yearly irradiance (kWh/m^2)
Bandar Baru Bangi	1487
Bayan Lepas	1809
George Town	1785
Ipoh	1739
Johor Bahru	1625
Kota Baru	1705
Kota Kinabalu	1900
Kuala Lumpur	1571
Kuala Terengganu	1714
Kuantan	1601
Kuching	1470
Petaling Jaya	1571
Seremban	1572
Senai	1629
Taiping	1768

1.3 Electrical Energy Storage Systems

The development of renewable and sustainable energy resources is the main focus of today's research interests due to the growing energy crisis, and to ensure uninterrupted human development. However, renewable energy resources such as solar and wind power are intermittent. The sun is not shining at night and the wind is not blowing whenever necessary. Nanogenerators that convert mechanical energy into electrical energy has the potential to operate easily and effectively. But, their outputs are significantly affected by the ambient environment changes, causing unstable output electric power. Therefore, efficient energy storage methods are essential to ensure the availability of energy by providing a durable output. The most commonly used energy storage systems are capacitors, supercapacitors, batteries and fuel cells (Jahromi *et al.*, 2015; J. Wang *et al.*, 2015).

Supercapaciors also called electrochemical capacitors or ultracapacitors, are a high-energy type of conventional capacitors, where their energy per unit volume or mass are hundreds of times more than that of capacitors. Both the capacitance of supercapacitor and conventional capacitor are affected by three main factors which are effective area of the electrodes, the separation distance of the electrodes, and the dielectric constant of the separating medium. For conventional capacitor, it obtains its effective area from a flat and conductive plates while supercapacitor gets the area from a porous carbon-based material. The porous structure resulted in a very high effective surface area and minimal distance of electrodes, thus leading to a higher capacitance of supercapacitor compared to a conventional capacitor (Cultura II & Salameh, 2015).

Supercapacitors have the advantages of long cycle life (4100 000 cycles), high power and energy densities, simple working principle, fast charge-discharge processes and environmental benignancy (Jahromi *et al*., 2015; Lee *et al.*, 2009; J. Wang *et al*., 2015; Zhang & Zhao, 2009). They have the potential to be a bridging function for the energy/power gap between conventional capacitors, which have high power output, and between batteries and fuel cells, which have high energy storage.

Supercapacitors contain two porous electrodes in contact with electrolyte that store charge electrostatically. Their capacitance is significantly affected by the active area and separation distance of the electrodes, in addition to the dielectric constant of the separating medium. Remarkably, the capacitance per unit volume of supercapacitors is 100 to 1000 times of that of capacitors (Cultura II & Salameh, 2015). Supercapacitors are useful for high power density applications like hybrid electrical vehicles, load cranes, forklifts and power back-up systems, in addition to low power devices such as camera-flash equipment and pulsed-light generators (Li *et al*., 2009; Wang *et al*., 2009; Zang & Li, 2011). Recently, supercapacitors have been employed in emergency doors on the Airbus A380, signifying the reliable performance of supercapacitors. Moreover, their use and promising performance in hybrid electric vehicles and fuel cell vehicles, where they couple with batteries and fuel cells respectively, highlighting their equal importance to batteries in the near future (Zhang & Zhao, 2009). With the involvement of supercapacitors, energy can be stored so efficiently such that the vehicles can have enough energy to be used during acceleration or startup (Zhang *et al*., 2009).

Basically, supercapacitors are made up of electrodes (anode and cathode), electrolytes, conducting charge paths and separators that electrically separates the two electrodes. Supercapacitors play an important role in the energy storage market as they provide high power capacility (60-120 s), excellent reversibility (90-95 %), and long cycle life (> 10^5). They usually possess a capacitance value which is 20-200 times higher than conventional capacitors (Zhang *et al*., 2009).

In this work, DSSC was coupled with a supercapacitor to form a photo-supercapacitor as shown in Figure 1.4. It shows the configuration of a three-electrode photo-supercapacitor, which includes sandwiched multi-layered electrodes made up of a dye-sensitized TiO_2 nanoparticle photoanode (positive electrode) and polypyrrole/reduced graphene oxide (PPy/rGO) in contact with iodolyte, and two PPy/rGO electrodes in contact with a hydrogel electrolyte. Two electrolytes work simultaneously on each side (Chen *et al*., 2010). The bottom-most PPy/rGO electrode acts as a negative electrode. The operating principle of a photo-supercapacitor is similar to that of a DSSC, where a photon excites an electron of a dye molecule, and the excited electron is injected into the conduction band of the TiO_2 semiconductor and diffused through the mesoporous TiO_2 layer. After the charge separation, the injected electron travels through the external circuit. The oxidized dye will be regenerated by accepting an electron from the redox iodolyte. The oxidized I_3^- ion will diffuse to the intermediate electrode and gains an electron for reduction back to I^- ion. This progress continues to drain electrons from the intermediate electrode, resulting in a positive charge of the active layer of intermediate electrode near the supercapacitor, and formation of mostly anions in its adjacent hydrogel electrolyte. Simultaneously, photo-excited electron travels to the bottom-most negative electrode where they form electrostatic double layer of negative charges accumulate at the negative electrode and mostly cations in its adjacent hydrogel electrolyte (Bagheri *et al*., 2014; Peng, 2015; Cohn *et al*., 2015). The electrons flow of the integrated device is shown in Figure 1.5. During the discharge process, the stored charge can be used to supply electrical energy without solar energy conversion. An efficient photo-supercapacitor can be fabricated with the utilization of simple preparation and integration methods.

By focusing only the supercapacitor part, electric double-layer capacitor (EDLC) and pseudo-capacitor combination is used, with rGO working synergistically with PPy as the active electrode material to achieve a high capacitance value with good stability. The embedded PPy particles between the graphene layers can help to prevent aggregation of graphene sheets, therefore maximizing the surface area of graphene and simultaneously enhancing the device performance. Besides, this graphene-based hybrid electric double-layer capacitor (hEDLC) also acts as an intermediate electrode in the three-electrode photo-supercapacitor to further enhance the life time and stability of the integrated device.

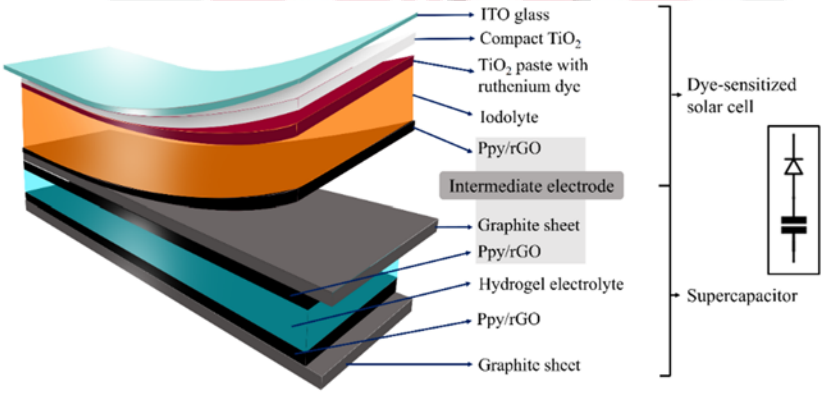

Figure 1.4: Device configuration of the three-electrode photo-supercapacitor which consists of a DSSC and a symmetrical PPy/rGO-based supercapacitor, where both the DSSC and supercapacitor share a PPy/rGO electrode. A corresponding circuit diagram is shown in the inset.

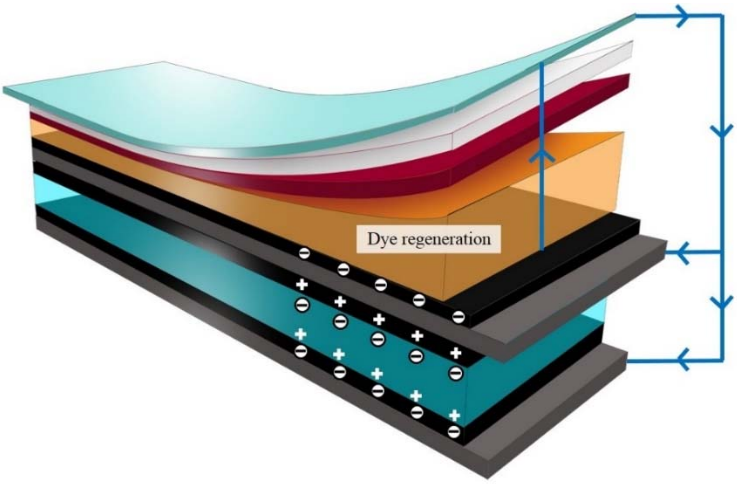

Figure 1.5: Electrons flow of the three-electrode photo-supercapacitor indicated by the blue arrows.

1.4 Problem Statement

The integration of a solar cell and energy storage component into one self-powered electrochemical energy storage device is challenging due to the instability of the hybridized system. Therefore, to maximize the efficiency of solar cell, the photoactive layer must be mesoporous to achieve a better dye absorption for photon excitation. On the other hand, to store the generated energy effectively, the supercapacitor plays an important role. The challenge has always been the criteria of high energy and power density, and high stability upon continuous charging and discharging cycles. The aforementioned criteria are hard to achieve by the two types of supercapacitor, either the electric double layer capacitor or the pseudo-capacitor, since they have generally suffered from low energy density and low cycle stability respectively (Chee *et al.*, 2015). Therefore, the two types of supercapacitor have to been coupled together to overcome this problem.

In addition, the interface between solar cell and energy storage plays a vital role in the integrated devices but the current research have used expensive materials like platinum (Chen *et al*., 2010), gold (Lee *et al*., 2016), silver (Skunik-Nuckowska *et al*., 2013) or other conductive materials, which significantly increased the overall production cost. Besides, the information regarding stability of the currently reported self-powered electrochemical energy storage device is lacking. By using platinum interlayer, 80% retention was achieved after 10 cycles (Hsu *et al.*, 2010), and that using PEDOT:Carbon interlayer could achieve 96.8% after 50 cycles (Xu *et al.*, 2016). For the rest of the reported single solar cell-charging integrated device, no stability data was provided. This major problems of high cost solar cell/supercapacitor interface with limited stability data have urged the researchers for a cheaper and relatively more stable interface's replacement.

1.5 Objectives

The main objective of this study was to develop an effective and stable DSSC-based photo-supercapacitor in a three-electrode configuration, utilizing an appropriate solar cell/supercapacitor graphene-based interface. The objectives can be sub-divided into the following points:

a. To fabricate and achieve a DSSC with minimum power conversion efficiency (PCE) of 2 % using a PPy/rGO counter electrode material that is the same as the supercapacitor's active material.
b. To fabricate a stable supercapacitor with specific capacitance retention percentage of at least 90 % after 500 cycles based on PPy/rGO active materials.
c. To develop an integrated photo-supercapacitor and then to analyze its photo-generated electrical energy and charge storage.

1.6 Thesis Organisation

This thesis is organized into five chapters and the contents of each chapter are described briefly as follows.

Chapter 1 introduces about the worldwide necessity of renewable energy and the emerging of solar power as a promising substituent of fossil fuels. Also, it discusses about the energy demand and renewable energy, especially solar energy, in Malaysia. Then, the text proceeds with the introduction of supercapacitors, as storage systems for solar power. Next, this chapter explains about the device configuration of the integrated photo-supercapacitor in this work, which is the coupling between DSSC and a symmetrical PPy/rGO-based supercapacitor. In addition, it states about the problems encountered throughout this research, followed by the corresponding objectives.

Chapter 2 reports about the dominance of crystalline silicon solar cells in the photovoltaic market with their drawback of high price. Besides, it reports the advantages and disadvantages of each type of solar cells. For better understanding of the background of photovoltaic devices, it reports about the historic evolution of solar cell technology. Next, it focuses on operating principle and leads of DSSCs and it tells about the efforts done on improving their performance, typically in the aspects of photoanodes, electrolytes, dye molecules and counter electrode materials. This chapter then proceeds to report about the supercapacitors, mainly on their advantages, types and categories, and improvements made to enhance their energy storage capabilities. Then, it focuses on the details of graphene-based materials as well-known supercapacitor electrode materials, and it compares the properties and performance of various carbon-based supercapacitors. In addition, it explains about the two working mechanisms of supercapacitors, the double layer charge storage or by the Faradaic reaction. In the last part of this chapter, it reports about the photo-charging mechanism of integrated photo-supercapacitors, with their advantages and significance to ensure substantial and constant power supply.

Chapter 3 lists down all the materials used in this work, which their product information that are enough to identify the chemicals accurately and precisely. Then, it covers all the preparing, fabricating, integrating and testing procedures related to this research. In brief, it tells about the simplified Hummer's method for the preparation of graphene oxide (GO), the aerosol assisted chemical vapour deposition (AACVD) and Dr's blade method for the fabrication of DSSC, and electrochemical deposition method for fabrication of PPy/rGO supercapacitor, followed by the integration between DSSC and PPy/rGO supercapacitor. Besides, it shows the samples preparation ways and types of machines used for each characterization techniques, which includes FESEM, Raman spectroscopy and electrochemical measurements.

Chapter 4 shows the significant data and results obtained throughout this research. It shows the current response and thus PCE of DSSCs with different photoanodes to signify the importance of each components in the DSSCs. It compares the FESEM images of compact TiO_2 layer and mesoporous TiO_2 paste deposited onto compact TiO_2 layer to signify the porosity of the latter. For the characterization of supercapacitor, it first shows the FESEM images of PPy/rGO materials, and then the Raman spectra of PPy, rGO and PPy/rGO materials to prove the coupling effect between them PPy and rGO. Next, it reports the results of various electrochemical measurements for the supercapacitors, which include cyclic voltammetry (CV), galvanostatic charge/discharge (GCD), electrochemical impedence spectroscopy (EIS) and life cycle stability, to tell about the specific capacitance, equivalent series resistance (ESR), charge transfer resistance (R_{ct}) and retention percentage of the device. On the other hand, this chapter continues to discuss on the results of the integrated photo-supercapacitor. It shows the photo-current response and the photocharge/galvanostatically discharge curve of the integrated device to prove that the charging source is certainly from the solar simulator. Then, it shows the life cycle stability of the device and it compares the obtained results against previously reported photo-supercapacitor.

Chapter 5 concludes the results on the integrated photo-supercapacitor, and it highlights the advantages, overall device performance and novelty of the device. Then, it tells some recommendations to further improve the device, focusing on the intermediate electrode and device packaging.

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