UNIVERSITI PUTRA MALAYSIA

FABRICATION OF SUPER CAPACITOR AND PEROVSKITE-SENSITIZED SOLAR CELL FOR THE ASSEMBLY OF PHOTO-SUPER CAPACITOR

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By

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LIST OF ABBREVIATIONS

Spiro-OMeTAD	2,2’,7,7’-tetrakis(N,N-di-p-ethoxyphenylamino)-9,9’-spirobifluorene
P	Poly[[2,5-bus(2-octyldodecyl)-2,3,5,6-tetrahydro-3,6-dioxopyrrolo[3,4-c]pyrrole-1,4-diyl]-alt-[[2,2’-(2,5-thiophene)bis-thieno[3,2-b]thiophen]-5,5’-diyl]]
TiO_2	Titanium dioxide
PProDOT-Et_2	Poly(3,3-diethyl-3,4-dihydro-2H-thieno-[3,4-b][1,4]dioxepine)
HTM	Hole transport mobility
HI	Hysteresis index
ATO	Anodic titanium oxide
$KMnO_4$	Potassium permanganate
Bi_2O_3	Bismuth oxide
H_2SO_4	Sulphuric acid
H_3PO_4	Phosphoric acid
H_2O_2	Hydrogen peroxide
HCl	Hydrogen chloride
Na_2SO_4	Sodium sulphate anhydrous
NapTS	Toluene-4-sulfonic acid sodium salt
$Zn(NO_3)_2.6H_2O$	Zinc nitrate hexahydrate
$Co(NO_3)_2.6H_2O$	Cobalt (II) nitrate hexahydrate
NH_4Cl	Ammonium chloride
FTO	Fluorine-doped tin oxide
ITO	Indium tin oxide
mp-TiO_2	Mesoporous titanium dioxide
$PbBr_2$	Lead (II) bromide

PbI_2	Lead (II) iodide
CsBr	Cesium bromide
Li-TFSI	Bis (trifluoromethane) sulfonimide lithium salt
TBP	4-tert-butylpyridine
TTIP	Titanium (IV) tetraisopropoxide
DMF	Dimethylformamide
$LiClO_4$	Lithium perchlorate
GO	Graphene Oxide
AACVD	Aerosol assisted chemical vapour deposition
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
FTIR	Fourier transform infrared spectroscopy
FESEM	Field Emission Scanning Electron Microscope
TEM	Transmission electron microscopy
UPS	Ultraviolet Photo-Electron Spectroscopy
CV	Cyclic voltammetry
EIS	Electrochemical impedance spectroscopy
J-V	Current density-voltage
EQE	External quantum efficiency
rGO	Reduce graphene oxide
PPy	Polypyrrole
Co_3O_4	Cobalt oxides
$Ni(OH)_2$	Nickel hydroxide
NiO	Nickel oxide
Li	Lithium

Zn	Zinc
PANI	Polyaniline
MnO_2	Manganese dioxide
RuO_2	Ruthenium oxide
ZnO	Zinc oxide
SAED	Selected area electron diffraction
2D	2-Dimensional
3D	3-Dimensional
RZCo	Reduced GO/zinc oxide/cobalt oxide
PyR	Polypyrrole/reduced GO
ZCo	Zinc oxide/cobalt oxide
EIS	Electrochemical impedance spectroscopy
ESR	Equivalent series resistance
R_{ct}	Charge transfer resistance
$CsPbBr_3$	Cesium lead bromide
LUMO	Lowest unoccupied molecular orbital
HOMO	Highest occupied molecular orbital
MgO	Magnesium oxide
PSC	Perovskite solar cell
VB	Valence band
CB	Conduction band
TCO	Transparent conductive oxide
ETL	Electron transporting layer
HTM	Hole transporting material
PVA	Polyvinyl alcohol

KOH	Potassium hydroxide
LED	Light emitting diode
PLQY	Photoluminescene quantum yield
V_{oc}	Open-circuit voltage
J_{sc}	Short circuit current
FF	Fill factor
TF	Thin film
NS	Nanostructure
$CsPbI_3$	Cesium lead iodide
$FAPbI_3$	Formamidinium lead iodide
R_{rec}	Recombination resistance
MoO_3	Molybdenum trioxide
$MAPbI_3$ or $CH_3NH_3PbI_3$	Methylammonium lead iodide
$MAPbX_3$ or $CH_3NH_3PbX_3$	Methylammonium lead halide
EDLC	Electric double layer capacitor
DSSC	Dye-sensitized solar cell
PCE	Power conversion efficiency
Bi_2O_3/MnO_2	Bismuth oxide/manganese oxide
RH	Relative humidity
PEDOT:PSS	Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate
SWCNT	Single-walled carbon nanotubes
MWCNT	Multiwalled carbon nanotubes
IPCE	Photo-to-electrical current conversion efficiency
Al_2O_3	Aluminium oxide or alumina

P3HT	Poly(3-hexylthiophene)
C_E	Specific capacitance per unit electrode active area
SCE	Saturated calomel electrode
YD2-o-C8	Donor-π-bridge-acceptor zinc porphyrin dye
D-π-A	Donor-π-bridge-acceptor
PMMA	Polymethylmethacrylate

LIST OF PUBLICATIONS

Papers published in referred journals

1. **Ng C.H.,** Lim H.N., Hayase S., Zainal Z., Shafie S. and Huang N.M. (2017). Capacitive Performance of Graphene-Based Asymmetric Supercapacitor. Electrochimca Acta. **229**: 173-182.
2. **Ng C.H.,** Ripolles T.S., Hamada K., Teo S.H., Lim H.N., Bisquert J. and Hayase S. (2018). Tunable Open Circuit Voltage by Engineering Inorganic Cesium Lead Bromide/Iodide Perovskite Solar Cells. Scientific Reports. **8**: 2482.
3. **Ng C.H.,** Lim H.N., Hayase S., Zainal Z., Shafie S., Lee H.W. and Huang N.M. (2018). Cesium Lead Halide Inorganic-Based Perovskite-Sensitized Solar Cell for Photo-Supercapacitor Application under High Humidity Condition. Accepted at ACS Applied Energy Materials. DOI: 10.1021/acsaem.7b00103.
4. **Ng C.H.,** Lim H.N., Hayase S., Zainal Z., Shafie S. and Huang N.M. (2018). Effects of Temperature on Electrochemical Properties of Bismuth Oxide/Manganese Oxide Pseudocapacitor. Accepted at Industrial & Engineering Chemistry Research. DOI: 10.1021/acs.iecr.7b04980.
5. **Ng C.H.,** Lim H.N., Hayase S., Harrison I., Pandikumar A. and Huang N.M. (2015). Potential Active Materials for Photo-Supercapacitor: A Review. Journal of Power Sources. **296**: 169-185.

List of involvement/attended seminars/workshops/conferences

1. Workshop on Princeton Applied Research Instruments at Physics Department, University of Malaya on 19th June 2014. (Participant)

2. International Materials Technology Conference & Exhibition (IMTCE) 2014, Organised by Institute of Materials, Malaysia (IMM) on 13th-16th May 2014 at Putra World Trade Centre, Kuala Lumpur, Malaysia. (Committee Member and Poster Presenter)

3. X-Ray Photoelectron Spectroscopy Workshop, Organised by Nano-semiconductor technology on 10th March 2015 at MIMOS Berhad. (Participant)

4. Workshop and Hands On Training in Photoelectrochemistry and Dye-Sensitized Solar Cells on 20th May 2015, held at High Impact Research (HIR) Building, University of Malaya. (Participant)

5. Participated in Young Scientists Network Malaysia: 2nd Creative Science Writing Competition 2015 Organised by Akademic Malaysia. (Consolation Prize)

6. DropSens Miniaturized Electrochemistry Seminar, Organised by Metrohm Malaysia on 19th April 2016. (Participant)

7. 10th International Materials Technology Conference & Exhibition (IMTCE) Organised by Institute of Materials, Malaysia (IMM) on 16th-19th May 2016 at Putra World Trade Centre, Kuala Lumpur, Malaysia. (Committee Member and Oral Presenter)

8. Elsevier Publishing Connect Workshop on 13th June 2016 at Auditorium Faculty of Educational Studies. (Participant)

9. Workshop on Increasing the Impact of Research: Strategies and Practical Guidelines for Universities and Research Institutions, Organised by Perpustakaan Sultan Abdul Samad School of Graduate Studies Center for Academic Development on 1st March 2017. (Participant)

10. UPM-KYUTECH Joint Seminar on Solar Technology at Faculty of Engineering, Universiti Putra Malaysia on 9th March 2017. (Participant)

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ABSTRACT

The coupling of a solar cell with a super capacitor is gaining interest owing to its superior photo-to-electrical conversion efficiency and its in-situ energy storage ability for green and sustainable energy development. In this work, the electrochemical performances of the fabricated super capacitor and perovskite solar cell were individually measured for the fabrication of a photo-super capacitor.

A Bi_2O_3/MnO_2 based symmetrical and asymmetrical super capacitor were fabricated. The symmetrical super capacitor could charge up to 1.0 V, which gave a specific capacitance of 136.4 F/g at a scan rate of 2 mV/s. The power and energy densities of the bismuth-based symmetrical super capacitor were 51.8 W/kg and 7.1 Wh/kg, respectively and were improved to 25.6 Wh/kg and 115.3 W/kg when a Bi_2O_3/MnO_2 positive electrode was integrated to a polypyrrole/reduced graphene oxide (PyR) negative electrode. It thus proven the feasibility of an asymmetrical super capacitor to promote the performance of a super capacitor. The dissatisfying stability performance of the Bi_2O_3/MnO_2//PyR asymmetrical super capacitor (60% capacitance retained) prompted for screening of other pseudocapacitive materials. An asymmetrical super capacitor comprising a positive cobalt oxide/zinc oxide/reduced graphene oxide electrode (RZCo) and a negative polypyrrole/reduced graphene oxide electrode was then fabricated. A wide operational potential range for the RZCo//PyR asymmetrical super capacitor resulted in a high specific capacitance of 470.8 F/g, as opposed to the Bi_2O_3/MnO_2 symmetrical super capacitor of 136.4 F/g and 144.1 F/g for the bismuth-based asymmetrical super capacitor, at a scan rate of 2mV/s, additionally exhibited 1.6-fold higher in energy and power densities, which fulfilling the criteria as the energy storage device for the photo-super capacitor.

Perovskite solar cells were fabricated from a series of cesium based halide mixtures perovskite harvesting materials, denoted as $CsPbBr_{3-x}I_x$, where x = 0-0.3. An optimum iodide concentration of $CsPbBr_{2.9}I_{0.1}$ perovskite solar cell with an efficiency of 3.9% was fabricated. The solar cell achieved an open circuit voltage of more than 1.0 V and a fill factor of 64% by employing *Spiro*-OMeTAD as a hole transporting material with enhanced stability. The performances of the $CsPbBr_{2.9}I_{0.1}$ solar cell with P3HT/MoO_3 hole transporting material was also investigated. The deeper HOMO and shallower LUMO level of the hole and electron transporting materials, respectively has achieved high V_{oc} of 1.23 V, but with lower power conversion efficiency of 2.51% due to reduction in the J_{sc}, implies an additional charge loss processes at the interface of perovskite/HTM. In high humidity of more than 80 percent, the perovskite solar cell comprising $CsPbBr_{2.9}I_{0.1}$ achieved an efficiency of 0.46%. The perovskite solar cell retains 70% of its original efficiency after a week storage in dark and 33% efficiency retained under UV and air exposure at a high relative humidity of more than 80% for 24 hours. The integration of the perovskite solar cell and the asymmetrical super capacitor enabled simultaneous photoconversion and charge storage within the photo-super capacitor. The photovoltage and photocurrent measurements were successfully performed, evidencing that the photo-super capacitor was responsive to light illumination. Referred to the photovoltage measurement, zero voltage was presented at the first 50 s without the shine of light. Subsequently, the photovoltage was abruptly shooted up to ~80 mV and continue increasing to 90 mV for 100 s in the presence of light, and was then decreases drastically when light was switched off. To further proof the energy conversion and storage of the photo-super capacitor, the photocharged integrated device was galvanostatically discharged in dark at the current of 0.1 mA. As the integrated device reaches the cut off potential of 0.07 V, the discharging process took place in dark with the connection of only super capacitor's electrodes, thus shows the workability of the photo-super capacitor. To enable practical application, improvizations such as optimizing thickness of each active layer and encapsulation of the photo-super capacitor are needed to prevent electrolyte loss.

CHAPTER 1

INTRODUCTION

1.1 Background

The photo-super capacitor is a green energy device which utilizes the non-depletable solar energy as the prime energy source for photo-to-electrical conversion, subsequently storing of energy within the energy storage devices such as batteries, capacitors, and the super capacitors. Considerable attention has been allocated on the progression of solar energy conversion and electric energy storage to cope the raising energy demands in daily lives, to minimize the usage of non-renewable energy resources, and to use the harvested solar energy during night when an energy storage device is integrated to an energy conversion device (Xu *et al*., 2014). The present existing photo-super capacitor are composed of dye-sensitized solar cell (DSSC)-battery or DSSC-super capacitor. When a DSSC was incorporated to a lithium ion battery, the power pack device was charged up to 3 V in 8 min and exhibited a total energy conversion and storage efficiency of 0.82%, which is considerably low (Guo *et al*., 2012). To improve the power output performance of the photo-super capacitor, a silicon based photo-super capacitor where the energy conversion device composed of titania based DSSC, while the super capacitor composed of silicon wafer was therefore integrated and rendered an overall efficiency of 2.1% (Cohn *et al*., 2015). In 2017, a photo-super capacitor made up of DSSC and polypyrrole/reduced graphene oxide super capacitor achieved a specific capacitance retention of 70.9% after 50 consecutive charge discharge cycles at a current density of 5 mA/cm^2 (Lau *et al*., 2017). Nevertheless, DSSC-based photo-super capacitor suffered from low charging voltage owing to low open circuit voltage obtained from the DSSC, consequently led to low energy density of photo-super capacitor. In addition, self-discharging of photo-super capacitor could restrain the charge storage ability of the photo-super capacitor. The reason of self-discharging is owing to the energy storage device has certain internal resistance, which in turn consume energy. Additionally, the electrons of the solar cell part flows back to the cathode of the energy storage part and thus recombination between electrons and holes occur. Hence, prioritizing materials used for energy conversion and storage devices is important for energy harvest and storage surge.

So far, the super capacitor has been overriding all kinds of energy storage devices owing to its high power density (2-10 kW/kg), fast charging/discharging, and longer lifespan (10^4-10^6 cycles) properties (Vidyadharan *et al*., 2014; Xia *et al*., 2012; Xie *et al*., 2013). Super capacitor is classified into two classes, namely the electric double layer capacitor (EDLC) and pseudo-capacitor. The distinctive feature between EDLC and pseudo-capacitor solely relies on their charging mechanisms where the EDLC electrode materials are electrochemically inactive and dependence on its accumulation of charges at the electrode/electrolyte interface; whereas the occurrence of faradaic reaction on pseudo-capacitor enables the storage of charges during charging and discharging process (Chen *et al*., 2014; Y. Cheng *et al*., 2013; Lim *et al*., 2013; Lim *et al*., 2014; Wang *et al*., 2012). The EDLC materials such as carbonaceous materials are profound in establishing a cyclic stability, whereas the pseudo-capacitive materials comprise transition metal oxides with multi-oxidative transition states and conducting polymer are of high capacitive spices in the energy storage family. The transition metal oxides are profound in their oxidation and reduction reversibility over the wider potential range which is favorable in the super capacitor application.

Relentless efforts have been done to maximize the super capacitor performances. The limitations of a symmetrical super capacitor such as low overall power and energy density hence prompted the switching of the symmetric configuration of the super capacitor to asymmetric configuration ascribed to narrower potential range applied (Wang *et al*., 2012). An asymmetrical super capacitor is made up of the combination of a battery-type faradaic cathode and a capacitor-type anode that is able to increase the potential window range, subsequently, maximizes the operation voltage of asymmetrical super capacitor (Luan *et al*., 2013; Ng *et al*., 2017; Tang *et al*., 2013) and increases the energy density of the energy storage device (Fan *et al*., 2011; Lin *et al*., 2014). The occurrence of redox reaction with or without the non-Faradaic reaction and EDL (electrostatic adsorption/desorption) on either of the electrodes, respectively, clearly distinguishes the difference between an asymmetric and symmetric configuration of super capacitor (Ng *et al*., 2015; Wang *et al*., 2013).

In an effort to increase the surface area of active materials, tailoring nanostructure electrode is essential as it renders shorter ion insertion/desertion diffusion path to enable efficient charge and mass transfer without compromising its double layer capacitance (Luan *et al*., 2013). In addition, the merit point of binder-less electrode is credited to its excellence in charge transportation (Luan *et al*., 2013), in order to minimize the supercapacitive resistance and "dead volumes" in electrode materials (Fan *et al*., 2011; Liu *et al*., 2011). All in all, the key features to attain high performance super capacitor are large surface area, controlled pore size, layer stacking, and distribution of electrode materials (Brownson *et al*., 2011). These merit points thus revealed that super capacitor is the most considerable candidate for photo-super capacitor association upon integrated with the photovoltaic device.

Taking into consideration of the energy conversion device, owing to the high fabrication cost of the first generation silicon solar cells, focus has therefore diverted to the second-generation thin-film semiconductors (copper indium gallium diselenide) and third-generation DSSCs, which have good cost effectiveness and easy fabrication methods without compromising their high efficiency performances. The efforts to incorporate three-dimensional (3D) perovskite light harvester materials ($CH_3NH_3PbX_3$) into DSSCs produced efficiencies of 3.1% and 3.8% for X = Br and X = I, respectively, in 2009 (Kojima *et al*., 2009). These undesirable efficiencies were ascribed to the ionic crystal of organolead halide perovskite, which is highly soluble in a polar solvent, and subsequently affected the stability in a liquid electrolyte-based sensitized solar cell (Park, 2015a). In addition, the leakage of electrolyte was the main encumbering issue in stabilizing the photovoltaic performances of DSSCs. Thus, in an effort to curb the energy conversion limitation, the focus has switched to the fabrication of perovskite solar cells, where a solid hole transporting material (HTM) is used instead of liquid electrolyte, with the goal of achieving a higher stability relative to DSSCs.

The excellent ability of perovskite solar cells to convert solar energy to electrical energy is unquestionable based on the evidence of the organic-inorganic methylammonium lead iodide perovskite solar cell ($CH_3NH_3PbI_3$ or $MAPbI_3$), which has a high efficiency of 15% (Xing *et al*., 2013; Xu *et al*., 2014). $CH_3NH_3PbI_3$ is excellent at producing optimal band gaps, high absorption coefficients, and long-range exciton diffusion lengths (Choi *et al*., 2014; Xing *et al*., 2013). In addition, photovoltaic (PV) cells with a power conversion efficiency (PCE) of 19% and certified PCE of 20% were reported in 2014 (Park, 2015b; Yakunin *et al*., 2015). Many studies and investigations on the performances of perovskite solar cells are still ongoing in the effort to surpass this PCE of 20%, as well as to establish a stable performance for a perovskite solar cell, in an effort to eliminate costly silicon PV cells (Boix *et al*., 2014). The perovskite solar cell has been expected to be the next most promising light harvesting PV device compared to silicon-based photovoltaic cells and DSSCs, owing to its price effectiveness and high efficiency. To the best of our knowledge, the most suitable light absorbing material band gap for a single junction solar cell is 1.4 eV, according to the Shockley-Queisser limit curve

(Shockley and Queisser, 1961). $CH_3NH_3PbI_3$ has an energy band gap of ~1.55 eV, which surpasses the optimum band gap range of 1.1–1.4 eV (Kitazawa *et al*., 2002; Wang *et al*., 2014). Hence, solar cells with a high open circuit voltage (V_{oc}) such as those that incorporate bromide-based perovskite solar cells with a V_{oc} of ~1.5 eV (Kulbak *et al*., 2016; Xu *et al*., 2015) are highly desirable for electrochemical reactions and a high-energy photon absorber in a system with spectral splitting in order to widen the solar absorption ability (Edri *et al*., 2013; Rühle *et al*., 2009).

Despite perovskite solar cell has achieved impressive PCE of 22.1% in 2016 (Sun *et al*., 2017), however, its low stability performance under operative conditions is apparently the main barrier for commercialization purpose. The $CH_3NH_3PbX_3$ perovskite material is highly sensitive to moisture, ultraviolet light (UV), and thermal stress where irreversible degradation and decomposition happen when the perovskite material is exposed to moisture. A thin film of $CH_3NH_3PbI_3$ thermally degrades to PbI_2 at >85 °C (Sutton *et al*., 2016). Relentless efforts such as using cross-linking additives, compositional engineering, and encapsulation have been done to mitigate photo-instability of perovskite solar cells. However, this approach increases the overall solar cell's fabrication cost and device complexity. Replacing an organic methylammonium cation with an inorganic cesium cation is an approach to decelerate degradation process. $CsPbBr_3$ and $CsPbI_3$ are compositionally stable up to their melting point (>460 °C). At room temperature, $CsPbBr_3$ crystallizes in orthorhombic phase and it transited to tetragonal phase at 88 °C. At 130 °C, the orange cubic perovskite phase is formed. Conversely, an orthorhombic non-perovskite (yellow phase) $CsPbI_3$ is stable at room temperature. When it is heated >300 °C, the orthorhombic non-perovskite $CsPbI_3$ perovskite structure consequently transited to cubic perovskite phase (black phase). However, the $CsPbI_3$ is unstable in black perovskite phase in ambient condition and rapidly reverse to non-perovskite yellow phase. (Sutton *et al*., 2016). Hence, engineering mixed-halide perovskite materials is envisioned to be able to improve its absorption ability, stability, and subsequently the performance of the solar cell.

Though a photovoltaic device (perovskite-sensitized solar cell) accomplishes high energy conversion efficiency, however, its inability to store the converted energy, thus requires an additional energy storage device such as a super capacitor for a storage system, in addition to serve as the main power delivery output in most applications such as optoelectronic devices (Bagheri *et al*., 2014). Considerable attention and efforts have been underway to improve and achieve a strikingly high efficiency, capacitance, and storage ability of a photo-super capacitor by studying and extensively investigating and analyzing the utility of active materials and preparation methods. Overall, the compatibility of active materials is the primary factor ensuring a striking performance for a photo-super capacitor due to the synergic effect of each material, which increases the conversion efficiency of the perovskite solar cell by suppressing electron recombination and simultaneously providing a surge of electrons for storage in the reservoir of the super capacitor, proving the concept of the energy storage system. In this works, the electrochemical performances of super capacitor and perovskite based solar cell were individually being studied towards the coupling of photo-super capacitor. Voltage and current response measurements were performed, thus proved the energy conversion and storage concept of photo-super capacitor.

1.2 Problem Statement/Hypothesis

The depletion of fossil fuels and natural resources has urgently called for green energy substitution. The utilization of solar cell or energy storage device solely cannot be the best solution to minimize energy wastage or to replace the usage of non-replenishing resources as the solar cell could not store energy by its own and the energy storage device still require the sparking of electrical power for energy generation. Herein, the integration of an energy storage and conversion device (photo-super capacitor) as a wholly solar generated power-back device is envisaged to becoming the next energy saver for most optoelectronic applications by applying the energy converting, storage, and delivery system; without any usage of non-renewable sources. The conventional photo-super capacitor was composed of DSSC-battery or DSSC-super capacitor. However, the limitations of present technologies aforementioned are low efficiencies of traditional DSSC and hybrid organic solar cells, leakage of electrolyte, and low storage capacity of the energy storage device. Thus, the super capacitor is employed as the energy storage and power output device for the photo-super capacitor as it bridges the performances gap between the battery and capacitor featuring with fast charging/discharging properties. The electrode materials and super capacitor's configuration are important features for high performing super capacitor.

In realizing the integration of the solar generated power-pack device, firstly, a bismuth oxide/manganese oxide (Bi_2O_3/MnO_2) symmetrical super capacitor was fabricated and was tested through various electrochemical measurements. The limitation of the symmetrical Bi_2O_3/MnO_2 super capacitor, which could only charge up to 1.0 V led to low energy and power densities of 7.1 Wh/kg and 51.8 W/kg, respectively. The energy density performance is proportional to the cell voltage of the super capacitor, which is tunable when both of the super capacitor electrodes are composed of different active materials. Thus, to overcome the limitation of the bismuth-based symmetrical super capacitor, a Bi_2O_3/MnO_2 positive electrode was integrated to a polypyrrole/reduced graphene oxide (PyR) negative electrode. The Bi_2O_3/MnO_2//PyR asymmetrical super capacitor exhibited 3.6-fold and 2.2-fold higher in energy and power densities, respectively when the potential window of the asymmetrical super capacitor was extended to 1.6 V. Despite the electrochemical performances of the bismuth-based asymmetrical super capacitor have been improved, however the cyclic stability is the next shortcoming that needed prompt addresses. The Bi_2O_3/MnO_2//PyR super capacitor could only retain 60% of its original capacitance after 1000 continuous charge/discharge cycles, implies the incompatibility of positive and negative active materials. The non-sustaining cyclic performance of the Bi_2O_3/MnO_2//PyR super capacitor has urged for the next screening of potential active materials that contribute for high capacitance without compromises its cyclic stability. The incorporation of small amount of reduced graphene oxide (rGO) to the hybrid zinc oxide (ZnO) and cobalt oxide (Co_3O_4), in short denoted as RZCo as the positive super capacitor electrode has significantly enhanced the stability performance (1.4-fold increment) upon coupled to a PyR negative electrode.

For the energy conversion device, a highly performing perovskite solar cell is not solely relying on the power conversion efficiency, but also emphasizing on the surface morphology, interfaces of each layer, and stability of the devices. Getting a well-coated and compact film are truly important for efficient charge extraction and delivery system. Thus far, the racing efficiency of a perovskite solar cell is said to be achieved and is still forwarding (efficiency leap), however, the stability performance of the perovskite solar cell is still far left behind, especially under high humidity influence. As per discussed in most literature reports, the organic perovskite material, for instance, methylammonium lead iodide ($CH_3NH_3PbI_3$) is highly vulnerable and prone to materials degradation. The solutions over the stability issue are (i) substituting the organic based perovskite material (methylammonium-based) to an inorganic material (cesium-based), and (ii) varies the halides composition.

Switch to the case in a tropical country with humidity >80% relative humidity (RH), the inorganic perovskite light harvester will be the best choice for solar cell synthesis. The degradation of methylammonium precursor was observed (color of solution turned from colorless to dark brown) during stirring process, which shows the unsuitability of $CH_3NH_3PbI_3$ to be used for perovskite material in an ambient condition. In my work, a series of $CsPbBr_{3-x}I_x$ perovskite materials in the molar ratio of 0, 0.1, 0.2, and 0.3, respectively were synthesized, which not merely enhance the morphological perovskite surface, as well as enhancing its stability performances.

The inaccessibility of the equipment such as the metal evaporator and glove box is one of the encumbers during the fabrication of the solar cells. The metal evaporator is used to prepare the counter electrode or back contact of the solar cell. Due to inaccessibility of the evaporator, a PEDOT:PSS is spin coated as the counter electrode to replace the metal counter electrode. In addition, due to inaccessible glove box, the solar cell fabrication process was conducted in ambient condition, which accelerate the degradation process.

1.3 Research Scope

There are six chapters in total in this thesis, which comprises the Introduction (Chapter 1), Literature review (Chapter 2), Materials and methods (Chapter 3), Results and discussion (Chapter 4 and 5), and Conclusion and recommendations (Chapter 6). Generally, the physical and material properties of the catalysts/active materials used were carried out through X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), fourier-transform infrared spectroscopy (FTIR), field emission scanning electron microscope (FESEM), transmission electron microscopy (TEM), and RAMAN spectroscopy.

A systematic research background (Chapter 1) is presented, which includes an introductory to the super capacitor such as the classification and kinds of super capacitors, as well as the advantageous and disadvantageous of the super capacitor, followed by the discussion on the photovoltaic devices. The history and development of the photovoltaic device, especially the third generation photovoltaic devices (DSSC and perovskite solar cell) are briefly included. Lastly, we will look into the integration of both devices for photo-super capacitor application. Additionally, problem statements and objectives are included in Chapter 1. Chapter 2 is about the thorough literature reviews on the topics which cover the super capacitor, solar cell, and photo-super capacitor; while chapter 3 is reporting on the methodologies of each device's fabrication, characterizations, and measurements.

The results and discussion section is presented in Chapter 4 and 5 where chapter 4 is reporting on the performances of the super capacitors; while chapter 5 is focusing on the photovoltaic device (perovskite solar cell) and towards the emergence of the photo-super capacitor. Firstly, the performances of a symmetrical super capacitor were studied through various electrochemical characterizations such as the cyclic voltammetry (CV), galvanostatic charge discharge, electrochemical impedance spectroscopy (EIS), and cyclic stabilities. The dissatisfactory capacitive performance of the symmetrical super capacitor thus led to the coupling of an asymmetric configured super capacitor, which widen the cell voltage with improved energy and power density performances for photo-super capacitor application.

Chapter 5 presents the photovoltaic performances of the $CsPbBr_{3-x}I_x$ perovskite solar cell ($x = 0, 0.1, 0.2$, and 0.3) evaluated through photocurrent density-photovoltage (J-V) curves, EIS, and stability of the perovskite solar cells. It shows that the perovskite solar cell performs the best when $x=0.1$. The $CsPbBr_{2.9}I_{0.1}$ perovskite solar cell is still performing the best even at high humidity >80% RH. The champion cell was then integrated to the asymmetrical super capacitor for photo-super capacitor application. Conclusions are drawn in Chapter 6, accompanied with recommendations for further improvisation in achieving a highly efficient and stable photo-super capacitor.

1.4 Objectives

The aim of this project is to devise and develop a photo-super capacitor by studying the electrochemical and photovoltaic performances of super capacitor and perovskite solar cell respectively. In line with the increasing demand of energy, the use of renewable, green and clean energy is important for energy sustaining purpose. In this regards, the solar energy, which is one of the most cost effective renewable resources should be fully utilized in most applications. While the efficiency race is still progressing, the stability of the perovskite solar cell should not be compromised though. Thus, the focus of this work is to investigate and evaluate stability of the perovskite solar cell, especially at a high humidity influence. The next objective of this project is to validate the improved charge extraction and power conversion efficiency of the halide mixture solar cell upon the addition of small amount of iodide into the bromide matrix, as well as to examine the morphology of the perovskite surface after the inclusion of iodide.

Apart from the solar cell, the performances of the super capacitor as the primary energy storage and output device are also being investigated. In this context, the energy storage capacity and the rate of power output are essentially important for the photo-super capacitor application. Prioritize the electrode materials for capacitance, energy, and power densities surge for the super capacitor is an objective to be achieved. Attaining a highly reversible and sustainable super capacitor is the next objective to achieve. The super capacitor with high recyclability fits the criteria for practical use and commercialization.

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