Presented at the DLSU Research Congress 2014
De La Salle University, Manila, Philippines
March 6-8, 2014

Structure, Design and Fabrication of a Novel Conducting Polypyrrole-Based Photovoltaic Cell and Storage Device

Maria Carla Manzano[1,*], Enrique Manzano[1], Chiara Rosario Julia Lanuza[1], and Reuben Quiroga[1]
[1]De La Salle University – Manila
[*]maria.carla.manzano@dlsu.edu.ph

Abstract: Conducting polypyrrole-based photovoltaic cells and storage devices were designed and fabricated as an alternative to silicon-based solar cells to address the world's need for a clean and renewable energy source. The photovoltaic cells and storage devices constructed are (1) indium- tin-oxide/polypyrrole/n-Si/aluminum (ITO/Ppy/n-Si/Al) and (2) indium-tin-oxide/polypyrrole/dielectric/aluminum (ITO/Ppy/dielectric/Al) in a wet, dry, or ionic-solution- impregnated-polypyrrole sandwich configuration. Dielectrics that were used and tested are glass, paper, varnish, and paper/varnish. The device also functions as a storage device, eliminating the need for a battery to store generated electricity. Under halogen lamp illumination, the ITO/Ppy/paper/Al photovoltaic storage device using ionic-solution- impregnated-polypyrrole film obtained an open-circuit voltage as high as 1.128V. Under solar intensity of about 100W/m^2, a short-circuit current as high as 7.35mA was obtained from the ITO/Ppy/paper/varnish/Al photovoltaic storage device using ionic-solution-impregnated- polypyrrole film.

Key Words: solar cell; conducting polypyrrole; photovoltaic cell; storage device

1. INTRODUCTION

The demand for renewable sources of energy such as photovoltaic or solar cells has considerably grown since fossil fuels, the main source of energy nowadays, are becoming more expensive and are already being depleted. Methods on how to harness solar energy are being tested and improved because the amount of sunlight that hits the earth's surface in one hour is enough to power the entire world for one year (Coolearth, 2012). This assures a relatively unlimited supply of energy. Also, the solar energy that is harnessed by photovoltaic cells is free and conversion of this to electricity does not produce toxic waste, pollution, nor greenhouse gases that contribute to global warming. Despite this, the present total solar energy production (from solar cells) contributes only about 1.16% among renewable energy sources and only about 0.1% of the total global primary energy demand (Bosong, 2011). This is mainly because commercially available solar cells are purely inorganic and most are silicon-based. These silicon solar cells are primarily expensive to manufacture, bulky, and inflexible, making electricity derived from them 8 to 10 times more costly than conventional sources. Furthermore, commercially available solar-energy devices need an external storing device for the electrical energy generated thus increasing the system complexity. It would therefore be highly desirable to create photovoltaic devices that can store this energy directly.

As solar energy is free and renewable, the direction of research in this field is towards developing solar cells that are cheap to manufacture and towards increasing their energy conversion efficiencies. Recent studies suggest that solar cells may be produced using conductive polymers. The production cost of polymer-based solar cells is low compared to the conventional silicon-based solar cells. Furthermore, conducting polymers are lightweight, flexible and easy to mass-produce.

Conducting polymers used in recent studies on photovoltaic devices include polyanilines, polythiophenes, poly(p-phenylenevinylenes), and polypyrrole (Ppy). Heterojunction devices have also been formed between n-type silicon and p-type conducting polymers. Although polymer-based materials presently have low energy conversion efficiencies, about 7% at best, open-circuit voltages of up to 1.7V have been obtained (Manzano et.al. 2008). Heterojunction devices been formed between n-type silicon and p-type conducting polymers. Current research are also being made on hybrid solar cells which consist of an inorganic n- type semiconductor (e.g. ZnO and CdSe nanoparticles) dispered in an inorganic solvent and mixed with a p-type polymer semiconductor (e.g. polythiophene or MDMO-PPV).

In this study, a photovoltaic storage device was designed and developed using conducting polypyrrole in a sandwich condiguration. The device, while converting solar energy to electrical energy also stores the same energy in itself. The photovoltaic storage devices designed and fabricated were characterized under illumination by determining open-circuit voltages (V_{OC}), short-circuit current (I_{SC}), current-voltage characteristics (I-V characteristics), and for some of the devices, charging time.

2. METHODOLOGY

Conducting polypyrrole-based photovoltaic storage devices designed and fabricated comprise of indium-tin-oxide (ITO), polypyrrole (Ppy), dielectric, and aluminum (Al) in a wet, dry or ionic-solution-impregnated-polymer sandwich configuration. The conducting Ppy films were first grown on an ITO-coated substrate and then characterized for film thickness, surface morphology and resistivity. Different photovoltaic storage device models were then designed in a wet, dry or ionic-solution-impregnated-polymer sandwich configuration. The fabricated photovoltaic devices were then tested for open-circuit voltage (V_{OC}), short-circuit current (I_{SC}), I-V curve under illumination, and for some of the devices, charging time.

2.1 Synthesis of polypyrrole films

The conducting Ppy films were galvanostatically deposited on either an ITO-coated glass slide or ITO-coated plastic substrate in an aqueous solution containing sodium-paratoluenesulphonate (Na-pTS) and pyrrole monomer. The aqueous solutions were prepared by dissolving an equivalent amount of Na-pTS to produce 0.09M, 0.10M, 0.11M or 0.13M solutions. The amount of pyrrole monomer injected is equivalent to 0.1M when mixed with the solution. Gold-plated stainless steel plates were used as counter electrode and a constant current density of about 3mA/cm^2 was maintained during the course of the polymer synthesis.

2.2 Characterization of polypyrrole films

The conducting Ppy film thickness and surface morphology were determined by scanning electron microscopy using a JEOL JSM-5310 scanning electron microscope (SEM). The measured film thickness and surface morphology were then used to compare the performance of each of the photovoltaic storage device developed. Energy dispersive x-ray (EDX) spectroscopy was used for elemental analysis and Van der Pauw teachnique to determine the resistivity of the films.

2.3 Design and fabrication of the photovoltaic storage devices

Several photovoltaic storage devices in a sandwich-type configuration were designed, fabricated and tested. There were two basic configurations; the ITO/Ppy/n-Si/Al sandwich cell and the ITO/Ppy/dielectric/Al sandwich cell in a wet, dry or ionic-solution-impregnated-polymer configuration. Among the dielectric materials used in the design and construction of the ITO/Ppy/dielectric/Al sandwich cell were glass, paper, varnish and paper/varnish. The following are the different photovoltaic storage devices designed, fabricated and tested:

ITO/Ppy/n-Si/Al (dry)
ITO/Ppy/n-Si/Al soaked in ionic solution
ITO/Ppy/glass/Al soaked in ionic solution
ITO/Ppy/glass/Al using ionic-solution-impregnated Ppy film
ITO/Ppy/paper/Al using ionic-solution-impregnated Ppy film

Presented at the DLSU Research Congress 2014
De La Salle University, Manila, Philippines
March 6-8, 2014

ITO/Ppy/varnish/Al soaked in ionic solution
ITO/Ppy/paper/varnish/Al using ionic-solution-impregnated Ppy film.

2.4 Functionality test and device characterization

After the initial photovoltaic device model/configuration was established and fabricated, the following were tested to show the functionality of the device:

- Presence of an open-circuit voltage
- Presence of a short circuit current
- Ability to charge under various conditions (sunny, partly cloudy, cloudy)
- Sensitivity to various light sources

The devices were then characterized by determining their open- circuit voltage and short-circuit current under illumination, charging time (open-circuit voltage as a function of time), and I-V curve under illumination. Based on the results of the functionality test and device characterization, the model was altered in order to try and improve its output.

3. RESULTS AND DISCUSSION

3.1 Surface morphology, thickness and resistivity of Ppy films

Seven conducting Ppy films were fabricated using electrochemical deposition, one on an ITO coated glass slide (Sample 1) and the other six on an ITO coated clear plastic (Samples 2 to 7). The table below summarizes the synthesis conditions that were used in the study, the film thickness and resistivity.

Table 1. Synthesis conditions, measured thickness and resistivity of conducting Ppy films

Sample	Anion Molarity (M)	Synthesis Time (minutes)	Thickness (μm)	Resistivity (Ω-cm)
1	0.10	120	33.60	-
2	0.09	30	41.04	0.039596
3	0.11	30	48.04	0.033557
4	0.13	30	34.78	0.028028
5	0.13	60	87.16	0.057008
6	0.09	25	10.18	0.030249
7	0.09	20	65.66	0.055188

The surface morphology of all the films is non-fibrillar and non-crystalline but is characterized by the presence of globular structures as evidenced by the two SEM images of Sample 1 shown below.

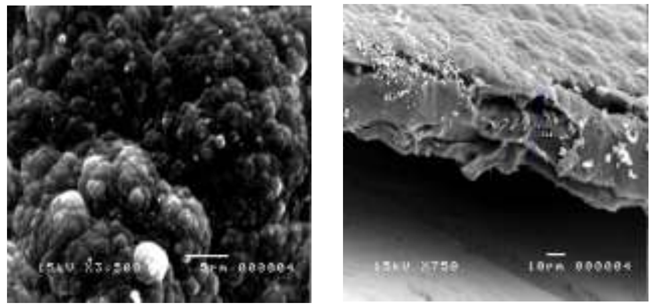

Fig. 1. SEM images for Sample 1

3.2 ITO/Ppy/n-Si/Al photovoltaic cell and storage device

The structure of the photovoltaic storage device was patterned after the sandwich model. The first device developed was an ITO/Ppy/n-Si/Al sandwich cell; the sectional view is shown in Figure 2(a) below. The cell consisted of a glass or transparent plastic, below which were arranged respectively a layer of indium-tin-oxide, a conducting polypyrrole film, an n-type silicon wafer, and an aluminum layer. The indium-tin-oxide (ITO) layer served as the first electrode and the aluminum layer as the second electrode. The ITO, polypyrrole, n-Si, and Al were used to form layers in a sandwich configuration, and the layers were arranged according to the order ITO, polypyrrole, n-Si, and Al.

The dry sandwich configuration of ITO/Ppy/n-Si/Al yielded a maximum open circuit voltage of 181mV when exposed to late afternoon sunlight, with the ITO side exposed to the light. The second sandwich configuration of ITO/Ppy/n-Si/Al that was made was clipped and dipped in an aqueous solution of Na-pTS of about 0.1M. This wet ITO/Ppy/n-Si/Al configuration yielded an initial open circuit voltage of 624mV steadily increasing to 705mV in an hour when exposed to light from an incandescent bulb (Manzano et. al. 2008).

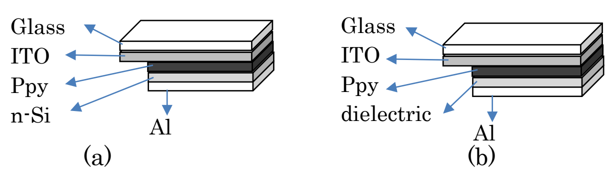

Fig. 2(a). Sectional view of ITO/Ppy/n-Si/Al photovoltaic storage device;
Fig. 2(b). Sectional view of the ITO/Ppy/dielectric/Al photovoltaic storage device

3.3 ITO/Ppy/dielectric/Al photovoltaic cell and storage device

Figure 2(b) is a sectional view of the ITO/Ppy/dielectric/Al photovoltaic storage device composed of a glass or transparent plastic, below which were arranged respectively a layer of indium-tin-oxide, a conducting polypyrrole film, a dielectric layer (glass, paper, varnish, or paper and varnish), and an aluminum layer. The indium-tin-oxide (ITO) layer serves as the first electrode and the aluminum layer as the second electrode. The ITO, polypyrrole, dielectric, and Al are used to form layers in a sandwich configuration and the layers are arranged according to the order ITO, polypyrrole, dielectric, and Al. The various dielectrics tested were glass, paper, varnish and paper/varnish. Both the dry and wet ITO/Ppy/dielectric/Al configurations were characterized. The wet ITO/Ppy/glass/Al sandwich cell was dipped in an aqueous solution containing Na-pTS of about 0.1M. The wet ITO/Ppy/paper/Al and ITO/Ppy/paper/varnish/Al sandwich cell was fabricated by soaking the polypyrrole film with an aqueous solution containing Na-pTS of about 0.1M.

The dry ITO/Ppy/dielectric/Al sandwich cell produced no open-circuit voltage but demonstrated a capacitor-behavior as it was charged by a voltage source and slowly discharged when the source was removed. The different types of dielectric used were varnish, paper, and glass.

It was also observed that when a finger touched the polymer in order to make contact with the aluminum, the device charges to a significant potential. Different persons produced different values of measured open-circuit voltage. It was deduced that the variation was due to the differences in electrolyte levels of a person. This further shows the potential of the device, in dry condition, as a biosensor to measure electrolyte levels in the body.

A wet photovoltaic device using the same configuration was made using varnish coating of the aluminum plate as the dielectric and then immersing the device in an aqueous solution of Na-pTS of about 0.1M. This wet solar cell/storage device is exposed to light and its open-circuit voltage was measured.

When the ITO/Ppy/varnish/Al photovoltaic device was immersed in the ionic solution and then exposed to light, the open-circuit voltage of the device significantly increased to the levels observed when a finger is used to short the aluminum and polymer. This reveals that the finger could be modeled as an electrolyte/ionic solution. Measured open-circuit voltages reached 534mV. The photovoltaic cell/storage device was charged by immersing the device in ionic solution and then exposing it to light.

Another wet photovoltaic device using yet again the same configuration was made using a glass slide as the dielectric and then immersing the device in an aqueous solution of Na-pTS of about 0.1M. This ITO/Ppy/glass/Al photovoltaic device slowly charged from 0.665V to 1.10V when exposed to a halogen lamp. The photovoltaic device was charged by immersing the device in ionic solution and then exposing it to light.

Another device using the same configuration as shown in Figure 2(b) is made using paper as the dielectric and an ionic-solution-impregnated polymer; with all the other components of the device dry. This device was made by soaking the polymer in an aqueous solution of Na-pTS of about 0.1M before creating the sandwich.

The measured open-circuit voltage of the ITO/Ppy/paper/Al photovoltaic storage device stabilized at 834mV and slowly charged to 940mV in 15minutes upon exposure to light from a halogen flashlight. Removal of the light source caused the open-circuit voltage to slowly discharge to 699mV in 6min and 37sec. At any point in the charging cycle where the light source was removed, the open-circuit voltage would start diminishing. The discharge can also be interrupted by again exposing the device to a light source. The short-circuit currents measured from the ITO/Ppy/paper/Al photovoltaic storage device were as high as 2.2mA and open-circuit voltages as high as 1.08V.

This shows another method of charging the photovoltaic storage device. Instead of immersing the whole ITO/Ppy/dielectric/Al device in an ionic solution, only the polymer is momentarily soaked in the ionic solution prior to making the ITO/Ppy/dielectric/Al device. In this case, it is observed that the open-circuit voltage first sought a stable value and the device slowly charged when exposed to light from a halogen lamp. In this configuration, where the polymer used is impregnated with the ionic solution and the device is not immersed in ionic solution, the dielectric must be of porous material such as paper. Another type of dielectric used in this configuration is varnish. Other similar dielectrics may also be used.

Lastly, another device with the same configuration was made but instead of paper, a glass slide was used as a dielectric. The polymer in this device was also impregnated with an aqueous solution of Na-pTS of about 0.1M prior to the assembly. The measured open-circuit voltage of this device hovered at 815mV and slowly charged to 1053mV in 13min 49sec when exposed to light from a halogen lamp. Figure 3 below shows the graph of the open-circuit voltage as a function of time when the ITO/Ppy/glass/Al device was exposed to light from a halogen flashlight. Further experiments on this ITO/Ppy/glass/Al photovoltaic storage device yield a maximum voltage of 1.128V. (Manzano et. al, 2008)

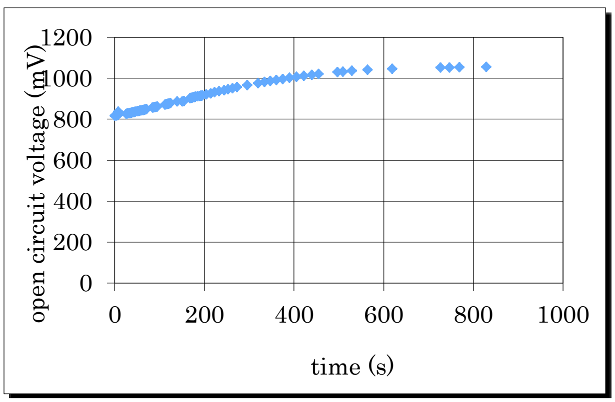

Fig. 3. Open-circuit voltage as a function of time for the ITO/Ppy/glass/Al photovoltaic storage device using ionic-solution-impregnated-Ppy under illumination (Manzano et. al. 2008)

Table 2 below shows a summary of open-circuit voltages measured under illumination from a halogen lamp and for some, the charging time. The ITO layer in the following configurations is on glass substrates and the conducting Ppy films were synthesized at 0.1M for 120 minutes. Open-circuit voltages measured were as high as 1.128V from the ITO/Ppy/paper/Al sandwich configuration using an ionic-solution-impregnated-Ppy film with charging time of 13 minutes and 49 seconds.

Table 2. Open-circuit voltage and charging time measurements under halogen lamp illumination

Photovoltaic Storage Device Configuration	Initial V_{OC} (volt)	Maximum V_{OC} (volt)	Charging Time
ITO/Ppy/n-Si/Al (dry)		0.181	
ITO/Ppy/n-Si/Al soaked in ionic solution	0.624	0.705	1 hour
ITO/Ppy/glass/Al soaked in ionic solution	0.665	1.100	
ITO/Ppy/glass/Al using ionic-solution-impregnated Ppy film	0.834	0.940	15 mins
ITO/Ppy/paper/Al using ionic-solution-impregnated Ppy film	0.815	1.053 1.128 (max)	13mins, 49sec
ITO/Ppy/varnish/Al soaked in ionic solution		0.534	

The ITO/Ppy/paper/Al photovoltaic storage device using ionic-solution-impregnated Ppy film was further characterized by measuring short-circuit current and variation in open-circuit voltages under illumination (halogen lamp) and after removing the light source. Open-circuit voltages of up to 1.080V and short-circuit current of 2.2mA were measured. Charging time was about 15 minutes. From the table it can be seen that removal of the light source caused a decrease in the open-circuit voltage by about 0.24V after 6 minutes.

The ITO/Ppy/paper/Al photovoltaic storage device using ionic-solution-impregnated Ppy film was further characterized by measuring short-circuit current and variation in open-circuit voltages under illumination (halogen lamp) and after removing the light source. Open-circuit voltages of up to 1.080V and short-circuit current of 2.2mA were measured. Charging time was about 15 minutes. From Table 3 below, it can be seen that removal of the light source caused a decrease in the open-circuit voltage by about 0.24V after 6 minutes.

Table 3. I_{SC} and variations in V_{OC} for ITO/Ppy/paper/Al photovoltaic storage device

Maximum V_{OC}		1.080 V
Short-Circuit Current I_{SC}		2.2 mA
Charging under illumination	Initial V_{OC}	0.834 V
	Ending V_{OC}	0.940 V
	Charging time	15 mins
Light source removed	Initial V_{OC}	0.940 V
	Ending V_{OC}	0.699 V
	time	6 min, 37 sec

3.4 ITO/Ppy/paper/varnish/Al Photovoltaic Cell and Storage Device

The I-V characteristics of ITO/Ppy/paper/varnish/Al photovoltaic storage devices using inonic-solution-impregnated Ppy film were measured under solar illumination. By exposure to noontime sun (December) which is approximately equivalent to 100 W/m^2 or 10mW/cm^2 (Collison, 2012), the devices produced open-circuit voltages ranging from 0.710V to 0.989V and short-circuit currents of up to 7.35mA. Figure 3 below shows the I-V characteristics under solar illumination of one of the photovoltaic storage devices.

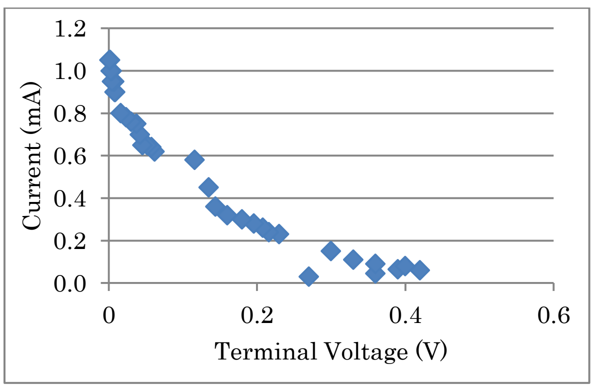

Fig. 3. I-V Characteristics for the ITO/Ppy/paper/varnish/Al photovoltaic storage device using ionic-solution-impregnated-Ppy film (Sample 3) under solar illumination

For the ITO/Ppy/paper/varnish/Al configuration, the highest open-circuit voltage (0.989V) and short-circuit current (7.35 mA) obtained under illumination was using the ionic-solution impregnated-Ppy film deposited on ITO-coated glass substrate (sample 8), as shown in Table 4. This may be due to the lower resistance of the ITO layer on the glass substrate (5-10 Ω) as compared to the ITO layer on plastic substrate (100 Ω). Furthermore, the glass slide has higher light transmittance (greater than 78%) when compared to the plastic substrate.

Among the Ppy films deposited on ITO-coated plastic substrate (samples 2 to 8), the one that produced the highest short-circuit current was the thickest film (sample 5, 87.16μm) and the highest open-circuit voltage was from the thinnest Ppy film (sample 6, 10.18μm).

Table 4. Summary of device characterization for ITO/Ppy/paper/varnish/Al photovoltaic storage device using ionic-solution-impregnated-Ppy film under solar illumination

Ppy Film Sample	Resisti-vity (Ω-cm)	Thick-ness (μm)	V_{OC} (V)	$V_{OC,max}$ (V)	I_{SC} (mA)
2	0.0396	41.04	0.880	0.901	0.75
3	0.0336	48.04	0.850	0.850	2.00
4	0.0280	34.78	0.859	0.859	0.60
5	0.0570	87.16	0.710	0.710	3.00
6	0.0302	10.18	0.820	0.930	0.42
7	0.0552	65.66	0.790	0.830	0.30
8	---	---	0.989	0.989	7.35

4. CONCLUSIONS

Conducting-polypyrrole-based photovoltaic cells and storage devices in a sandwich configuration were designed, fabricated and characterized. These configurations were: ITO/Ppy/n-Si/Al and ITO/Ppy/dielectric/Al in wet, dry and ionic-solution-impregnated-Ppy configurations. Dielectrics tested were glass, paper, varnish and paper/varnish. Two different types of ITO substrates were used, one is ITO-coated glass slide and the other ITO-coated clear plastic substrate.

The first design, a wet configuration of ITO/Ppy/n-Si/Al, produced a maximum open circuit voltage of 0.705V under halogen lamp illumination. This was the sandwich cell that was dipped in the electrolyte solution or the wet cell.

The second design, ITO/Ppy/dielectric/Al, produced open circuit voltages ranging from 0.665V to 1.128V. A maximum open circuit voltage of 1.128V was obtained from the configuration with paper as the dielectric used, an ITO –coated-glass slide and an ionic-solution-impregnated-Ppy film. The constructed device showed characteristics of a capacitor based on its structure and on its charging pattern, which is exponential, characteristic of a capacitor. Charging time was measured to be 13 minutes and 49 seconds. Under about 100W/m^2 solar intensity, short-circuit current as high as 7.35mA were obtained.

The ITO/Ppy/paper/varnish/Al configuration using ionic-solution-impregnated-Ppy films and ITO-coated plastic substrate produced open-circuit voltages ranging from 0.850V to 0.930V under 100W/m^2 solar intensity. The maximum open-circuit-voltage obtained was 0.930V using the conducting Ppy film with synthesis conditions of 0.09M for the anion molarity and 25 minutes for the synthesis time. This film was also found to be the thinnest and had the flattest deposition on the substrate. The maximum short circuit current was measured to be 3.00mA. This was produced by using the thickest Ppy film with following synthesis conditions: 0.13M for anion molarity and 60 minutes for synthesis time. Short-circuit current of 7.35mA and open-circuit voltage of 0.989V was obtained from the ITO/Ppy/paper/varnish/Al configuration using ionic-solution-impregnated-Ppy films and ITO-coated glass substrate.

6. REFERENCES

Beek, W., Wienk, M. and Janssen R. (2005). Hybrid Polymer Solar Cells Based on Zinc Oxide. Journal of Materials Chemistry, 15 2985-2988.

Bossong, K. (2011). *EIA Report: Renewables Surpass Nuclear Output*. Retrieved April 6, 2012 from http://www.renewableenergyworld.com/rea/news/article/2011/07/eia-report-renewables-surpass-nuclear-output

Callison (2012). *Manila, Philippines Climat Analysis*. Retrieved December 19, 2012 from http://urbanizedadaptation.files.wordpress.com/2012/09/manila_int_climate.pdf

Coolearth, n.d. (2012). *Solar* Energy. Retrieved April 6, 2012 from http://www.coolearthsolar.com/faq

Manzano, C. et al. (2008). *Polymer-Based Photovoltaic Cells/Storage Devices*. (n.p., Philippines)

Miyasaka, T., Ikeda, N., Murakami, T., and Teshima, K. (2007). Light Energy Conversion and Storage with Soft Carbonaceous Materials that Solidify Mesoscopic Electrochemical Interfaces. Chemistry Letters, 36 480-487.

Miyakasa, T. and Murakami, T. (2004). The Photocapacitor: An Efficient Self-charging Capacitor for Direct Storage of Solar Energy. Applied Physics Letters, 85 3932-3934.

Murakami, T., Kawashima, N., and Miyasaka, T., (2005). A High-voltage Dye-sensitized Photocapacitor of a Three-electrode System. Chemical Communications, 3346-3348.