Photoactive supercapacitors for solar energy harvesting and storage

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HIGHLIGHTS

- A composite of a conducting polymer and a dye was used to make a photoactive supercapacitor.
- We have found that addition of the dye molecule to the conducting polymer enhances the capacitance.
- The electrochemical impedance of the photoactive supercapacitor was studied in dark and light.

ABSTRACT

In most applications an energy storage device is required when solar cells are applied for energy harvesting. In this work, we have demonstrated that composite films of a conducting polymer and a dye can be used as photoactive electrodes in an electrochemical cell for concurrent solar energy conversion and charge storage. A device was made of poly ethylenedioxythiophene:polystyrene sulfonate and (PEDOT:PSS) and a porphyrin dye which showed a capacitance of ~1.04 mF. The device was charged up to 430 mV (open circuit voltage) under a solar simulated illumination and was able to store the charge for more than 10 min in the dark. Further study on the concentration of the dye revealed the importance of the ratio between the dye and the conducting polymer to optimize the photovoltage and capacitance of the device. Also, the effect of the dye material was studied by using a Ruthenium (Ru) based dye. The device with the Ru dye showed a photovolatge of 198 mV and charge stability of more than 2 h.

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1. Introduction

Due to the intermittent nature of solar energy, energy storage is essential in systems which are powered by harvesting solar energy [1]. Conventionally, external energy storage devices such as batteries and supercapacitors are employed in conjunction with solar cells [2]. In the attempt to store energy in a photovoltaic device, various hybrid devices were fabricated and tested before [3–15]. In a simple form, demonstrated by several groups [3–9,11–15], a cell with two compartments can be designed for accommodating a dye sensitized solar cell (DSSC) and a supercapacitor in a device. Most of those devices are essentially a solar cell and a supercapacitor in one package with three electrodes (one electrode is shared between the capacitor and solar cell). An external circuit, such as a diode switch, is required to connect the solar cell to the capacitor during energy harvesting cycle and prevent the capacitor discharge through the

DSSC [3,4]. In a different approach, Zhang et al., have used a modified counter electrode in a DSSC which demonstrated ~100 mV open circuit voltage with a few minutes energy storage in a two terminal device [10].

Photogalvanic cells (invented in 1970s) are also capable of harvesting and storing energy by using two different ions (positive and negative charge carriers) in the electrolyte of a two terminal device [16]. Different types of photogalvanic cells have been investigated, so far [17,18]. However, the experimental studies and the theoretical analysis show that the storage time is limited to the recombination rate of the positive and negative ions in the electrolyte [19]. Charge storage time in the range of a few minutes can be achieved in a photogalvanic cell by reducing the recombination rate in a cell using semiconducting electrodes [17].

We have devised a new structure which can convert photons to electric charges and at the same time store the charges in the device under the open circuit conditions. As shown in Fig. 1a, the new device is an electrochemical cell with porous working and counter electrodes. The working electrode is a composite film of a conducting polymer (Poly(3,4-ethylenedioxythiophene) Polystyrene sulfonate and — PEDOT:PSS) and a dye deposited on a transparent

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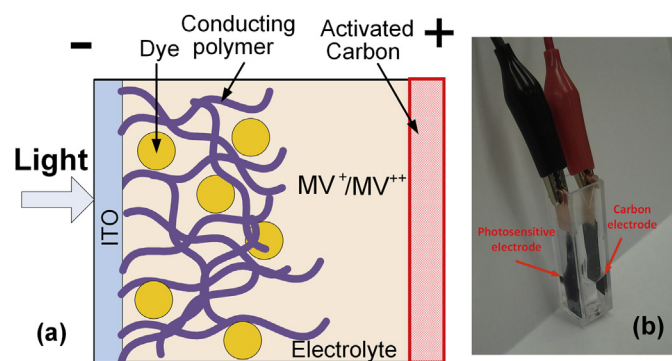
Fig. 1. (a) Schematic of an electrochemical device with a composite of a conducting polymer and a dye as the photosensitive anode electrode (− terminal). Methyl viologen (MV^+/MV^{++}) was applied as the redox material in the electrolyte. (b) A fabricated photoelectrochemical cell using the composite film as the photosensitive electrode.

indium tin oxide (ITO) electrode. The counter electrode is made of a porous activated carbon. Using porous conducting polymer (CP) and activated carbon electrodes, the device is essentially a super-capacitor which can store charges [20–22]. As shown in this work, application of the dye molecules can enhance the photovoltaic effect in the conducting polymer. A photograph of the fabricated cell is shown in Fig. 1b. The presented work includes both the photo-voltaic response and energy storage effect in the new device. Composite electrodes of CP with two different dyes and various concentration of the dye have been investigated. The results show a promising energy storage feature for a photovoltaic device.

2. Experimental

2.1. Materials and equipment

Indium tin oxide coated PET (polyethylene terephthalate plas-tic), porphyrin dye (5,10,15,20-tetraphenyl-21h,23h-porphine-Zinc), also known as ZnTPP, PEDOT:PSS (1.3 wt% dispersion in wa-ter), Triton X-100, ethylene glycol, methyl viologen (MV) and Tris were all purchased from Sigma−Aldrich. The carbon paper, as the counter electrode, was purchased from Y-carbon. The Ru based dye (triisothiocyanato-(2,2′:6′,6″-terpyridyl-4,4′,4″-tricarboxylato) ruthenium(II) tris(tetra-butylammonium)) also known as N749 was from Solaronix. The electrical and electrochemical measurements, including open circuit voltage test, current measurement, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS), were carried out using a desktop computer connected to a VersaSTAT 4 potentiostat. The cells were placed in a dark box connected via an optical fibre to a solar simulator (RST, Radiant Source Technology) with an internal AM 1.0 optical filter which delivered light intensity of 80 mW cm^{-2} at its output. For the ex-periments, the illumination time was controlled manually by turning on and off the instrument shutter. The experimental setup, including the dark box and the shutter mechanism, was designed to eliminate the effect of stray light in the experiment. A picture of the setup is presented in the supplementary data section (see Figure SD1). The optical absorption spectrum was measured using a Thermo Scientific (Evolution 201) UV−Vis spectrophotometer.

2.2. Electrode fabrication

1.25 mg of ZnTPP (or N749) was dissolved in 2.5 ml isopropanol (acetonitrile for N749). 2.5 ml of the conducting polymer solution was made by mixing 5 wt% ethylene glycol and 3 wt% Triton X-100 in the PEDOT:PSS [22]. Different ratio (1:0, 1:1, 1:2, 2:1, and 0:1) of

the conducting polymer and dye solutions were mixed and soni-cated for 5−20 min to achieve a homogeneous solution. Kapton tape was used to make a rectangular mask (1.0 cm × 0.5 cm) on the ITO electrode. 10 μl of the mixed solution was drop casted on the electrode and dried on a hotplate for 5 min at 120 °C to make the composite film on the transparent electrode. The electrode and a piece of Y-carbon (as the counter electrode) were placed in a
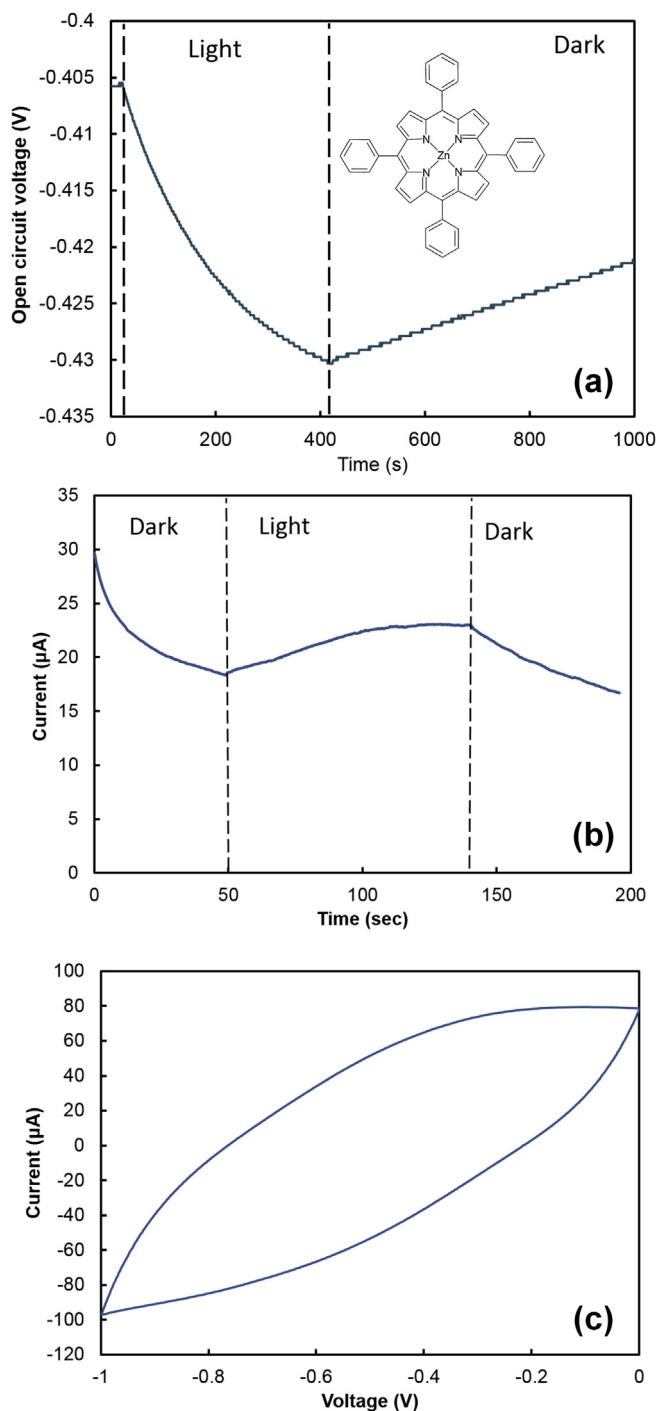

Fig. 2. Photovoltaic and energy storage effect in the cell with PEDOT:PSS- porphyrin dye composite electrode. (a) Open circuit voltage and (b) short circuit current in the dark and light. (c) CV in the dark with scan rate of 50 mV s^{-1}. The voltages were measured with respect to the counter electrode (carbon electrode) potential. The molecular structure of the porphyrin dye (ZnTPP) is shown in the inset of Figure a.

disposable cuvette and it was filled with the electrolyte (1 mM MV in 0.1 M Tris buffer solution) to cover the composite film. The apparent surface area of the carbon electrode in the solution was estimated to 1.0 cm × 0.5 cm. The fabricated cells were not sealed.

3. Results and discussion

First a composite film was made by drop casting a mixed solution of 1:1 ratio of PEDOT and porphyrin dye solutions on an ITO electrode. The molecular structure of the dye (ZnTPP) is shown in Fig. 2a. The electrode with 1:1 CP-dye was used as the working electrode in a cell with a porous carbon electrode (counter electrode) and an electrolyte with 1 mM methyl viologen (MV) in Tris buffer. The cell was kept in the dark for about one hour until a stable open circuit voltage was achieved. Then the cell was illuminated for 400 s, using the solar simulator. As shown in Fig. 2a, the open circuit voltage across the cell in the dark was 405 mV (the negative value shows that the composite film was the negative terminal of the device-see Fig. 1). The cell voltage (absolute value) was increased gradually from 405 mV to 431 mV in 400 s of illumination. After turning off the light, unlike conventional DSSCs [23], the voltage was not dropped to the dark value immediately. Instead a gradual change was observed and the magnitude of the cell voltage reached to 421 mV in 580 s after the cessation of light. The gradual increase in the cell voltage in light implies the energy storage effect (charging the supercapacitor). A simple explanation is that, under the open circuit condition, the photoexcited charges (generated in the composite) accumulate on the conducting polymer and charge the working electrode. The interaction between MV^+ ions in the electrolyte and the positive charge on the composite can also oxidized the ions and convert them to MV^{++} ($MV^+ \rightarrow MV^{++} + e^-$). The oxidized ions ($MV^{++}$) diffuse to the counter electrode where a double layer charge can be formed on the surface of the carbon electrode. The slow change in the voltage after illumination shows the leakage effect in the supercapacitor [24]. Nevertheless, the device was able to store a part of the photogenerated charges after ~10 min. The photovoltaic and energy storage effects were further studied in the device by illuminating the cell for another 400 s under the open circuit conditions. Immediately after turning off the light, the short circuit current was recorded. As shown in Fig. 2b, the stored charges in the device resulted in a dark current which was decreased from 30 μA to 18 μA in 50 s. The low short circuit current and gradual discharge of the device indicates a relatively large internal resistance. While the short circuit current was monitored, the light source was turned on for 90 s. The current was increased to 23 μA at the end of the illumination cycle and decreased again when the light was turned off. The positive current and negative open circuit voltage indicate a photovoltaic power generation by the device. The increase in the short circuit current under illumination also shows the feasibility of delivering a part of the photogenerated charges directly to a load and store some of the charges. It should be mentioned that due to the storage effect, the conventional current–voltage test (scanning voltage and recording the current) cannot be applied to characterize the photovoltaic effect and estimate the efficiency, short circuit current, open circuit voltage, and the fill-factor (FF) of the device. As shown in Fig. 2c, the voltage scan shows a large current even in dark, because of the supercapacitive characteristic of the device ($I = C \cdot dV/dt$ — where I is the current, C is the device capacitance, and dV/dt is the scan rate). However, in the current form, with relatively low short circuit current, the photo conversion efficiency is very low.

The storage capacitance of the device was measured using CV method. Since the working electrode voltage was negative, the voltage range in the CV measurement was set between 0 V

and −1 V (Fig. 2c). The value of the capacitance was estimated to be ~1.04 mF from the width of the CV loop at −0.5 V.

To investigate the effect of dye concentration on the energy storage and photovoltaic effect of the device, various composite electrodes were fabricated with CP-dye ratios of 1:0 (only CP), 1:1, 1:2, 2:1, and 0:1 (only dye). Fig. 3a shows the CV results from the devices with those electrodes. As expected the electrode with only dye coating had very negligible capacitance likely due to the lack of porosity. Although due to the higher amount of CP it was expected to achieve the highest capacitance in the device with only CP, the electrode with one part CP and two parts dye showed the largest capacitance of 1.76 mF and the electrode with only CP had a capacitance of only 0.19 mF. To understand the capacitance increase in the composite electrode, SEM (Scanning Electron Microscopy) images were taken (Fig. 3b and c) which clearly showed the structural difference between the composite and the CP films. It is likely that the micro cracks on the composite material enhanced the film porosity.

The optical absorption of a CP film and a layer of the dye on two electrodes were studied using the UV–Vis spectroscopy method. As shown in Fig. 4, the CP has a broad absorption in the red and infrared range, whereas the dye is responding strongly to 432 nm wavelength. Hence, the high energy photons are more absorbed by the dye and the polymer can absorb low energy photons. Also, the broad absorption spectrum in the CP suggests the photovoltaic effect in the only CP film.

The photovoltaic effect in different electrodes was studied by monitoring the change in the open circuit voltages in the dark and light (Fig. 5). Since the capacitance of the electrode with only dye
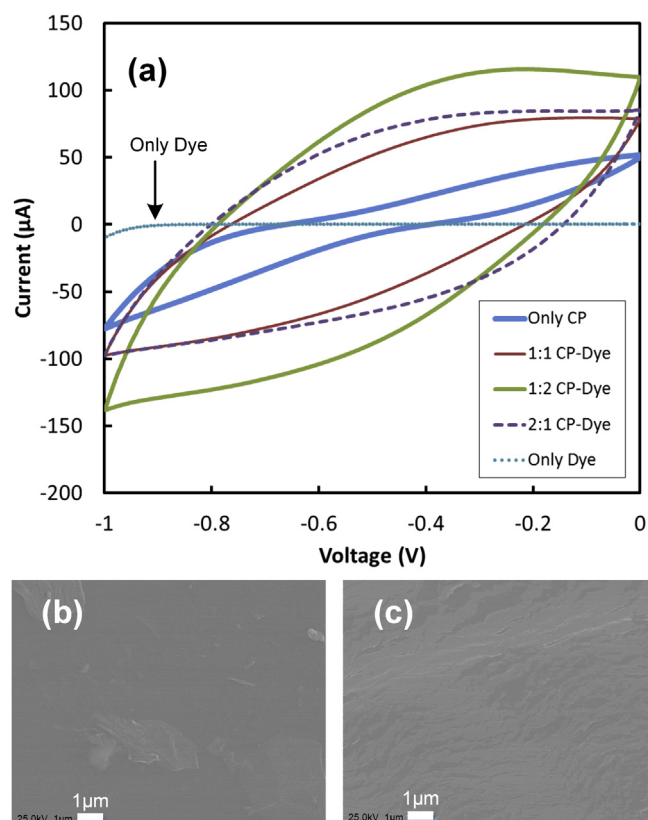

Fig. 3. (a) CV results from devices with only CP, only dye, and 1:1, 1:2, 2:1 CP-dye composite electrodes. The scan rate was 50 mV s^{-1} and the experiment was performed in the dark. SEM images of electrodes with (b) only CP and (c) 1:2 CP-dye composite films.
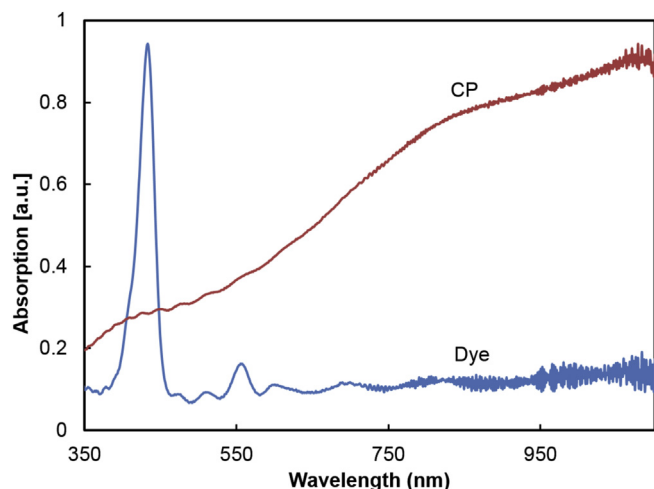
Fig. 4. Optical absorption of the films of only CP and only dye on two ITO electrodes.
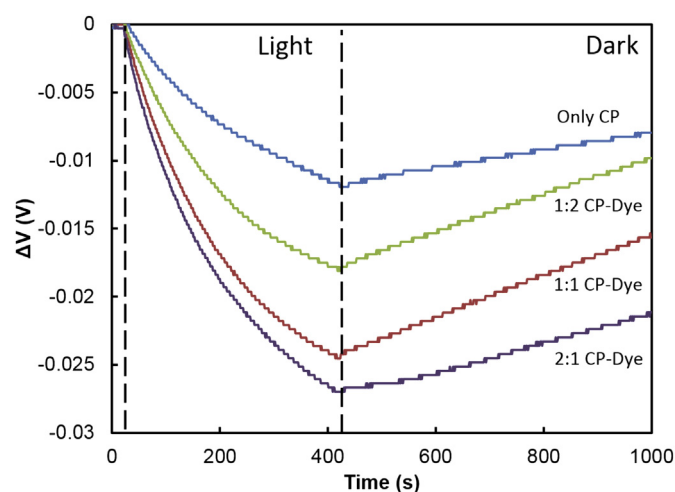

Fig. 5. The change in the open circuit voltage in different cells under illumination and after cessation of light.

is not known yet, but it is likely that the charge is stored on the polymer chains by changing the oxidation state of the polymer film (pseudo capacitive charge storage) [26]. The CV experiment with very low scan rate (2 mV s^{-1}) was performed in the dark and light on the cell (two probe experiment) with 2:1 CP-dye electrode to investigate the oxidation state of the composite film. As shown in Fig. 6a, an oxidation peak was observed at −0.78 V. Also, a very broad reduction peak can be seen around −245 mV (the peak is more pronounced in the CV of the dark experiment-inset Figure). The reduction peak is under influence of the knee current. Due to the small peak amplitudes, the redox peaks could not be seen in the CV with fast scan rate (Fig. 3). Nevertheless, the open circuit voltage of the cell (Fig. 2a) is between the redox peaks. Hence, it is possible to change the redox state by shifting the composite electrode voltage to more negative value [27]. The voltage of the oxidation peak did not change in the dark and light, but the knee in the current was sharper under illumination, which suggests faster charge transfer in light than in the dark. The effect of light on the electrode properties was further studied by performing EIS on the cell with the 2:1 CP-dye electrode. The Nyquist plot is presented in
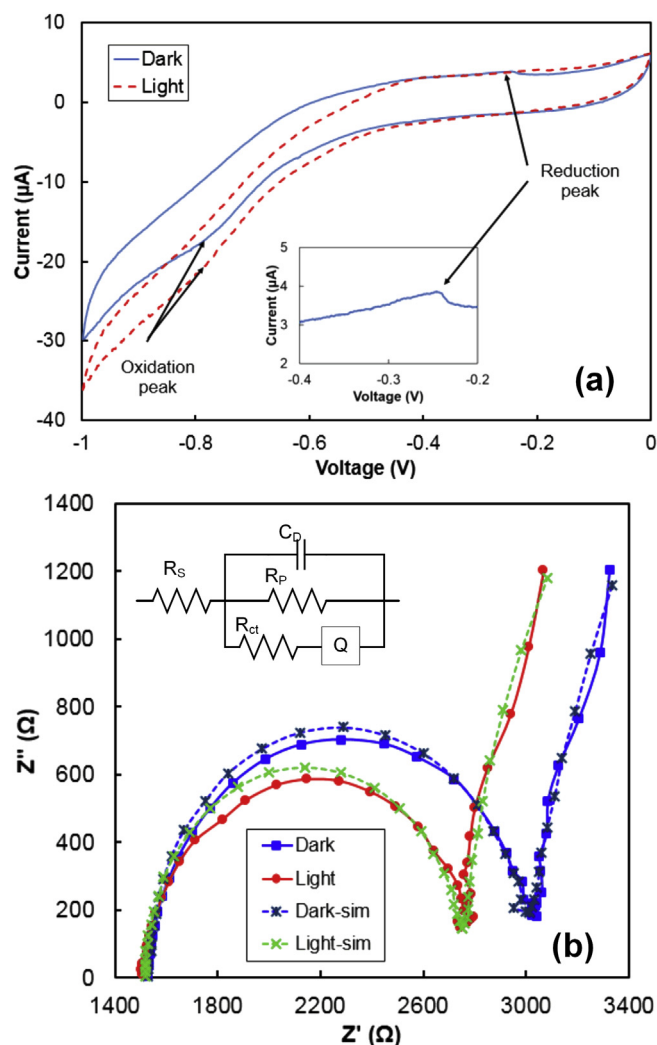
was negligible (Fig. 3a), only the electrodes with the conducting polymers were considered in the photovoltaic test. Due to the energy storage effect, different devices showed different open circuit voltages in the dark, even after keeping devices in the short circuit (in the dark) mode for a few hours. Therefore, for a comparative study, only the change in the open circuit voltage from the dark (ΔV) is presented in Fig. 5. The cell open circuit voltages are demonstrated in Fig. S2 in the supplementary data. The largest ΔV was −27 mV from the device with 2:1 CP-dye composite. The electrode with only CP showed the lowest ΔV (−12 mV). Considering the absorption spectrum in Fig. 4, it seems that the absorption of high energy photons by the dye molecules enhances the photovoltaic effect. However, the larger ΔV in the composite of 2:1 CP-dye than the electrodes with higher dye concentration (1:1 and 1:2 CP-dye) shows the importance of the ratio between the dye and the conducting polymer for the photovoltaic effect.

Considering the semiconducting properties of conducting polymers, the structure of the device is similar to a DSSC in which a porous layer of TiO_2 nanoparticles (semiconducting material) and a layer of dye molecules are applied as the photoactive electrode. However, there is no charge storage in a DSSC [23,25]. The mechanism of the photogenerated charge storage in the composite film

Fig. 6. Photoelectric study of the cell with 2:1 CP-dye composite electrode (a) CVs in dark and light with slow scan rate (2 mV s^{-1}). (Inset) the reduction peak under influence of the current knee. (b) Electro impedance spectroscopy in the dark and light. The proposed model for the cell is shown inside the figure. The simulated results for the dark and light are also presented.

Fig. 6b. The impedance at high frequencies showed a resistive behaviour with the series resistance of 1.52 kΩ. Such a large resistance explains the limited short circuit current in the cell (Fig. 2b). To reduce the resistance, an electrolyte with higher ion concentration can be used. Also the contact resistance between the composite film and the ITO electrode has to be improved. The semi-circle with almost linear tail in the Nyquist plot suggests that the polarization is due to a combination of diffusion and kinetic processes [28]. The presented equivalent circuit model (inset Fig. 6b) was applied to simulate the cell response in the dark and light using ZSim software. In the model, R_S represents the series resistance, C_D is the double layer capacitance, R_P is the parallel resistance, R_{ct} is the charge transfer resistance, and Q is the constant phase element with power of n. The estimated values of the elements in the model are listed in Table 1. In both the dark and light cases, the estimated value for n is close to 1 which implies a capacitive behaviour (transmission line model) [29,30]. The values of C_D, Q, and n were almost the same in the dark and light. Hence, as expected, the effect of light on the capacitive behaviour of the cell was negligible. The largest difference was observed in R_{ct} and R_P, which again shows higher charge transfer rate in light than in the dark and larger cell current in light.

The concept of using a CP-dye composite for making photovoltaic devices with embedded energy storage was further developed by using a Ru based dye molecule (see Fig. 7 for the molecular structure of N749) instead of the porphyrin dye in a 1:1 CP-dye composite. The photovoltaic test of the device showed a much slower charging cycle with a large potential difference under illumination. As shown in Fig. 7, the cell voltage (absolute value) was increased from 42 mV to 240 mV in 2500 s ($\Delta V = 198$ mV). Also, the cell showed an incredibly high charge storage stability. After turning off the light the open circuit voltage was reduced by only 20 mV (~10% of ΔV) in 2 h. However, the short circuit current was in sub micro amp range (the result is not presented). In addition, Ru based dyes are relatively expensive and, potentially, they are not suitable for low cost devices such as the photoactive supercapacitor studied in this work.

The energy diagram in Fig. 8 has been presented to suggest the charge cycle in the devices with ZnTPP/N749 dye molecule. Similar to a DSSC, absorbed photons by the dye molecules (or CP) generate excited states. The electron in the excited state can reduce the PEDOT:PSS polymer. In this situation the electron is not mobile. This resembles a localized charge in a higher energy state in the polymer. Also, the dye molecules receive electrons from methyl viologen through another redox reaction ($MV^+ \rightarrow MV^{++} + e^-$) and MV^{++} ions diffuse toward the counter electrode. Under the open circuit conditions, the reduced polymer at the composite electrode and the oxidized methyl viologen at the counter electrode generate a potential difference across the cell. In the short circuit mode, the carbon electrode delivers electrons to methyl viologen in the electrolyte and ITO removes electrons from PEDOT:PSS. Since holes are more mobile than electrons in the polymer, the generated hole can travel through the polymer film where the stored electron can be released through a recombination process. The energy levels in Fig. 8 have been obtained from reported values in other publications [31–36]. The significant difference between the two dyes is in
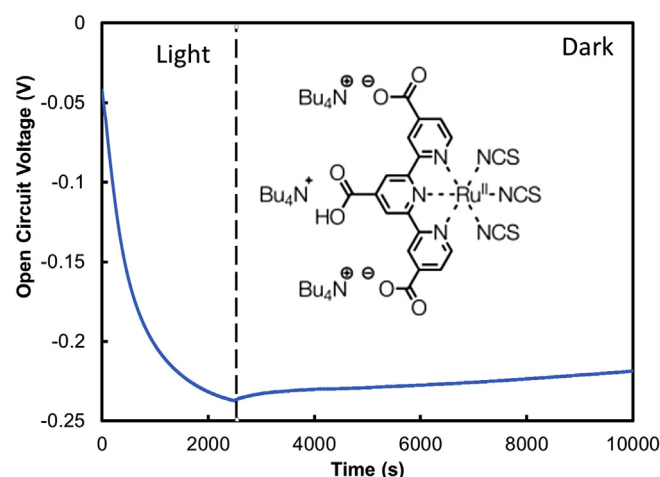
Table 1
Comparison between impedance parameters in the dark and light.

Description	R_S (kΩ)	C_D (μF)	R_P (kΩ)	R_{ct} (kΩ)	Q (S sec^n)	n
Dark	1.52	4.10	9.11	1.77	8.26E-04	0.92
Light	1.52	4.02	6.89	1.51	8.28E-04	0.96

Fig. 7. Open circuit voltage of a cell with CP and N749 dye composite electrode in light and dark. Long storage time of more than 7500 s was achieved with only 20 mV cell voltage change in the dark. The inset Figure shows the molecular structure of N749.
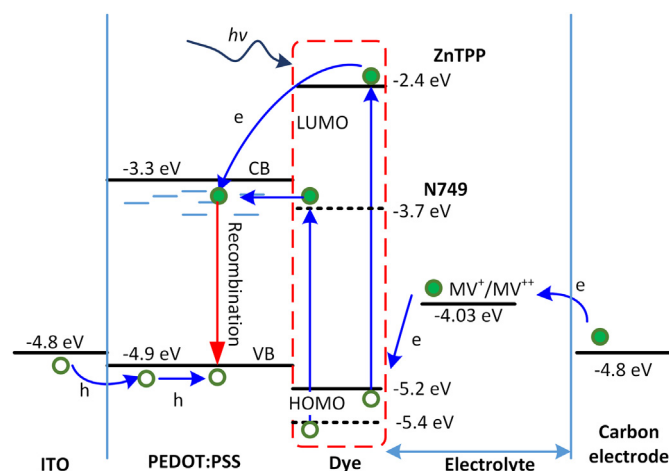

Fig. 8. Energy diagram of the photoactive supercapacitor. The energy levels are versus the vacuum level. The localized states below the conduction band of the polymer show the energy states when the polymer is reduced. The diagram shows the energy levels for both ZnTPP and N749 dyes.

the LUMO level. The excited electrons in ZnTPP can be transferred to the conduction band of the polymer and from there, they would be trapped in the localized states. However, the excited electrons in N749 move directly to the localized states. This can explain the slow increase in the voltage (Fig. 7) and low current in the device with the Ru dye, as the direct electron transfer to the localized states has likely lower probability than trapping the charges from the conduction band in the ZnTPP case. Nevertheless, a bottleneck in the electron cycle is the redox potential of MV. A redox mediator with lower energy than methyl viologen would facilitate the charge circulation. A detail energy study of the composite material is required for better understanding of the mechanism of charge cycle and storage in the device.

Further study on the charge transfer and energy levels at the dye and polymer molecules is required to understand the mechanism of energy storage in the composite film. Also, the effect of ion concentration on the photovoltaic and energy storage effects has to be investigated. Enhancing the photovoltaic effect and optimizing the energy storage properties can lead to a practical solar cell with embedded energy storage feature.

4. Conclusions

Using composite materials of a conducting polymer and dye molecules, a new photoelectrochemical device was introduced which demonstrated an internal energy storage capability. The effect of dye concentration on the energy storage and photovoltaic effects were investigated. It was found that the addition of the dye increases the capacitance in the conducting polymer and enhances the photovoltage in the device. Slow scan CV and EIS study revealed that the electrical properties of the composite electrode changes in presence of light by facilitating the charge transfer. Also, application of N749 dye molecule showed significant improvement in the photovoltage and charge stability in the cell. Further study is required to investigate the effect of materials and concentrations on the photovoltaic and energy storage properties of the device. Additionally, for practical applications, there are technical issues, such as sealing the device, which must be addressed after device development.

Acknowledgements

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jpowsour.2014.10.110.

References

[1] R.A. Messenger, J. Ventre, Photovoltaic Systems Engineering, second ed., CRC Press, 2003.
[2] L.D. Partain, L.M. Fraas, Solar Cells and their Applications, John Wiley & Sons, Hoboken, NJ, 2010.
[3] C.-Y. Hsu, H.-W. Chen, K.-M. Lee, C.-W. Hu, K.-C. Ho, J. Power Sources 195 (2010) 6232–6238.
[4] P. Liu, H.X. Yang, X.P. Ai, G.R. Li, X.P. Gao, Electrochem. Commun. 16 (2012) 69–72.
[5] T. Miyasaka, H. Ina, M. Ikegami, Electrochem. Soc. Meet. Abstr. 2012–02 (2012) 2864.
[6] H. Nagai, H. Segawa, Chem. Commun. (2004) 974–975.
[7] Y. Saito, A. Ogawa, S. Uchida, T. Kubo, H. Segawa, Chem. Lett. 39 (2010) 488–489.
[8] M. Skunik-Nuckowska, K. Grzejszczyk, P.J. Kulesza, L. Yang, N. Vlachopoulos, L. Häggman, E. Johansson, A. Hagfeldt, J. Power Sources 234 (2013) 91–99.
[9] P.A. Mini, S.V. Nair, K.R.V. Subramanian, Prog. Photovoltaics: Res. Appl. 21 (2013) 1153–1157.
[10] X. Zhang, X. Huang, C. Li, H. Jiang, Adv. Mater. 25 (2013) 4093–4096.
[11] X. Huang, X. Zhang, H. Jiang, J. Power Sources 248 (2014) 434–438.
[12] J. Bae, Y.J. Park, M. Lee, S.N. Cha, Y.J. Choi, C.S. Lee, J.M. Kim, Z.L. Wang, Adv. Mater. 23 (2011) 3446–3449.
[13] W. Guo, X. Xue, S. Wang, C. Lin, Z.L. Wang, Nano Lett. 12 (2012) 2520–2523.
[14] P. Liu, Y.l. Cao, G.R. Li, X.P. Gao, X.P. Ai, H.X. Yang, ChemSusChem 6 (2013) 802–806.
[15] Y. Saito, S. Uchida, T. Kubo, H. Segawa, Thin Solid Films 518 (2010) 3033–3036.
[16] W.J. Albery, M.D. Archer, J. Electrochem. Soc. 124 (1977) 688–697.
[17] W.J. Albery, Acc. Chem. Res. 15 (1982) 142–148.
[18] G. Chen, J.M. Zen, F.R.F. Fan, A.J. Bard, J. Phys. Chem. 95 (1991) 3682–3687.
[19] W.J. Albery, M.D. Archer, Nature 270 (1977) 399–402.
[20] G. Wang, L. Zhang, J. Zhang, Chem. Soc. Rev. 41 (2012) 797–828.
[21] A. Laforgue, P. Simon, J.F. Fauvarque, M. Mastragostino, F. Soavi, J.F. Sarrau, P. Lailler, M. Conte, E. Rossi, S. Saguatti, J. Electrochem. Soc. 150 (2003) A645–A651.
[22] Tete Tevi, Shantonio W. Saint Birch, Sylvia W. Thomas, A. Takshi, Synth. Met. 191 (2014) 59–65.
[23] C.C. Wamser, H.-S. Kim, J.-K. Lee, Opt. Mater. 21 (2003) 221–224.
[24] T. Tevi, H. Yaghoubi, J. Wang, A. Takshi, J. Power Sources 241 (2013) 589–596.
[25] M. Grätzel, J. Photochem. Photobiol. C: Photochem. Rev. 4 (2003) 145–153.
[26] G.A. Snook, P. Kao, A.S. Best, J. Power Sources 196 (2011) 1–12.
[27] J.T. Mefford, W.G. Hardin, S. Dai, K.P. Johnston, K.J. Stevenson, Nat. Mater. (2014).
[28] A.J. Bard, L.R. Faulkner, Electrochemical Methods Fundamentals and Applications, second ed., John Wiley, New York, 2001.
[29] D.S. Yoo, A. Mahmoudzadeh, E.C.W. Fok, K. Walus, J.D.W. Madden, Electrochim. Acta 56 (2011) 4711–4716.
[30] M.R. Warren, J.D. Madden, J. Electroanal. Chem. 590 (2006) 76–81.
[31] T. Brown, J. Kim, R. Friend, F. Cacialli, R. Daik, W. Feast, Appl. Phys. Lett. 75 (1999) 1679–1681.
[32] K.A. Nagamatsu, S. Avasthi, J. Jhaveri, J.C. Sturm, (2013).
[33] K.K. Cline, M.T. McDermott, R.L. McCreery, J. Phys. Chem. 98 (1994) 5314–5319.
[34] S. Khan, M. Kaur, J. Heflin, M. Sayyad, J. Phys. Chem. Solids 72 (2011) 1430–1435.
[35] M. Shiraishi, M. Ata, Carbon 39 (2001) 1913–1917.
[36] T. Funaki, H. Funakoshi, O. Kitao, N. Onozawa-Komatsuzaki, K. Kasuga, K. Sayama, H. Sugihara, Angew. Chem. Int. Ed. 51 (2012) 7528–7531.