



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.

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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 photovoltage 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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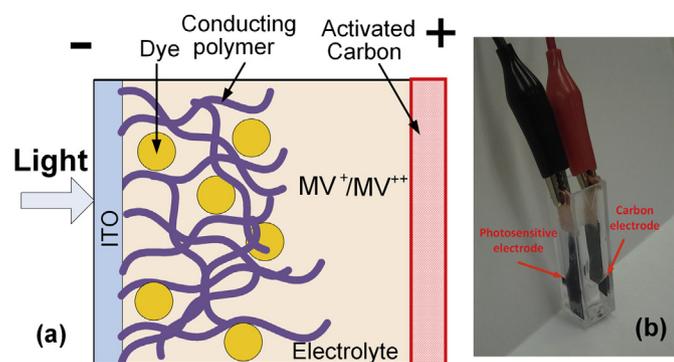


Fig. 1. (a) Schematic of an electrochemical device with a composite of a conducting polymer and a dye as the photosensitive anode electrode (– terminal). Methyl viologen (MV^+/MV^{2+}) was applied as the redox material in the electrolyte. (b) A fabricated photoelectrochemical cell using the composite 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 photovoltaic 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 plastic), porphyrin dye (5,10,15,20-tetraphenyl-21h,23h-porphine-Zinc), also known as ZnTPP, PEDOT:PSS (1.3 wt% dispersion in water), 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 experiments, 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 sonicated for 5–20 min to achieve a homogeneous solution. Kapton tape was used to make a rectangular mask ($1.0 \text{ cm} \times 0.5 \text{ cm}$) on the ITO electrode. $10 \mu\text{l}$ of the mixed solution was drop casted on the electrode and dried on a hotplate for 5 min at $120 \text{ }^\circ\text{C}$ 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

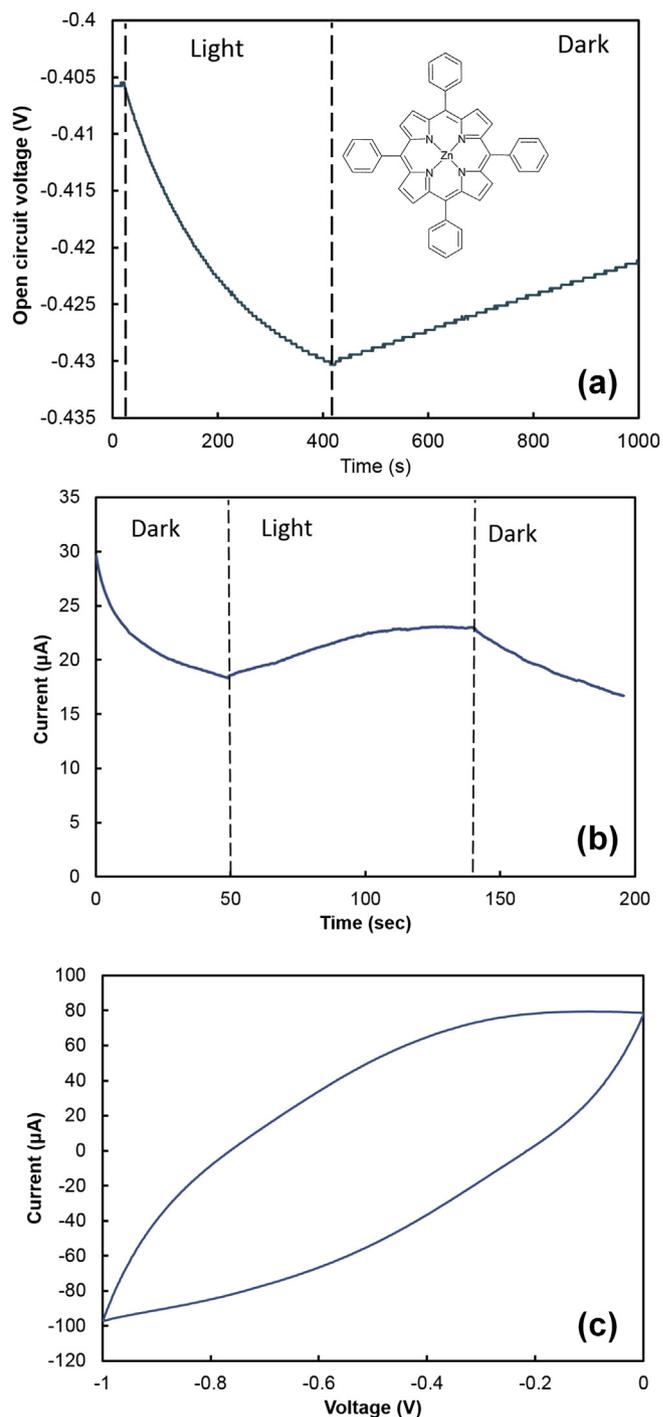


Fig. 2. Photovoltaic and energy storage effect in the cell with PEDOT:PSS-porphyrin dye composite electrode. (a) Open circuit voltage and (b) short circuit current in the dark and light. (c) CV in the dark with scan rate of 50 mV s^{-1} . The voltages were measured with respect to the counter electrode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

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