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Photovoltaic properties of liquid-state photoelectrochemical cells based on PPAT and a composite film of PPAT and nanocrystalline titanium dioxide

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ABSTRACT

We have studied the optical and photoelectrical properties of liquid state photoelectrochemical cells (PECs) based on photoactive electrodes based on poly (phenyl azo methane thiophene) (PPAT) and a composite film of nano-crystalline titanium dioxide (nc-TiO_2) and PPAT. The device fabricated with nc-TiO_2/PPAT photoactive electrode shows better performance with an open circuit voltage (V_{oc}) 0.56 V, short circuit photocurrent (J_{sc}) = 0.87 mA/cm^2 and fill factor (FF) = 0.58 under illumination with white light intensity of 10 mW/cm^2. We have analyzed the experimental results by comparing the IPCE spectra of both devices. It is observed that the device with nc-TiO_2/PPAT photoactive electrode shows better photovoltaic response as compared to the device based on PPAT photoactive electrode. This indicates that PPAT shows its p-type semiconducting behavior in the device based on PPAT, while in the device based on nc-TiO_2/PPAT photoactive electrode, the PPAT acts as a sensitizer to nano-crystalline TiO_2. The PEC based on TiO_2/PPAT photoelectrode exhibit an exponential increase of low frequency device capacitance due to the diffusion of electrons along TiO_2 network. Effect of iodine doping in PPAT on the photovoltaic performance of PEC have been also studied.

1. Introduction

Lot of research and technological applications of solar energy utilization have been carried out in converting light energy into electrical energy. Increasing efforts have been made into the development of different types of photovoltaic devices based on organic molecules and polymeric materials. In organic photovoltaic systems, light absorption leads to the production of excited, bound electron–hole pairs commonly known as excitons. To achieve a substantial amount of photocurrent, the excited charge pairs thus produced to be dissociated into free charge carriers, through the assistance of electric field at interface of materials with different electron affinities. Several reports have been already adopted to achieve the efficient exciton dissociation [1–6]. So far, the method of blending conjugated polymers with suitable electron donors has most successfully demonstrated in the most efficient photovoltaic devices with power conversion efficiency greater than 4% [7–12].

Substituted polythiophenes exhibit interesting properties as semiconducting photoactive materials due to π and π^* orbitals and are used for conversion of optical energy into electrical energy. They are possible alternatives to conventional inorganic semiconductors because of their high optical absorption in the visible region of the electromagnetic spectrum and because of properties such as ease of fabrication, large area coating, low cost, and the possibility to control the band gap through molecular engineering. In polymer organic solar cells, the light absorbing material is a conjugated polymer. These types of photovoltaic devices have been investigated studied in the form of solid-state devices [13–16] and liquid junction [17,18] devices.

The regenerative photoelectrochemical cells (PECs) based on photosensitization of nano-crystalline titanium dioxide (nc-TiO_2) have been regarded as potentially low-cost and easily processable alternatives to conventional inorganic solar cells. In a number of studies of dye-sensitized nc-TiO_2 PECs, Rubipyridyl based dyes have been used as sensitizers to nc-TiO_2 [19–22]. In these devices, the dye absorbs light and electrons are excited from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The excited electrons are then injected to the conduction band (CB) of the TiO_2 and transported to the external circuit. The positive charges created in the dye are transferred to the redox mediator. The oxidized mediator gets reduced back at the counter electrode resulting with no net chemical

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reaction while converting light energy to electricity. The power conversion efficiencies of such PECs reached 10.4% Although, the dye-sensitized nc-TiO_2 PECs showed high power conversion efficiencies, their commercial applications have not been realized. This is due to problems associated with the evaporation and degradation of the electrolyte and technological difficulties associated with large module production. To alleviate these problems, solid-state PECs have been designed where the liquid electrolyte was replaced by hole-conducting amorphous organic materials [23] or polymer electrolytes that conduct ions [24–26].

Semiconducting polymers can also be used in combination with inorganic semiconductors such as TiO_2, ZnO and $CuInSe_2$ [27–32]. In these hybrid organic/inorganic devices, the good electron accepting and conducting properties of the inorganic semiconductors can, in principle, be combined with cheap, solution processing of the semiconducting polymers. The disadvantages of many of these systems are the low hole-mobility in semiconducting conjugated polymers compared to the electron-mobility in inorganic semiconductors [33] and the incomplete filling of the nano-pores of the inorganic semiconductor by the polymers [34].

The sensitization of inorganic semiconductors by conjugated polymers [35,36] has been investigated in liquid-state PECs where the hole-mobility is facilitated by the redox couple. In this work we report a comparative study on the photo response behavior of liquid-state PECs where the photoactive electrodes consist of PPAT, and a composite film of nc-TiO_2 and PPAT (nc-TiO_2/PPAT). PPAT was chosen since it is known to have good solubility, good electrical properties [37] and suitable HOMO–LUMO energy level positions with respect to TiO_2 and I_3^-/I^- redox couple. Under illumination the excited electrons may be transferred from the LUMO of PPAT to the conduction band of nc-TiO_2 (sensitizing behavior) or to the electrolyte solution (p-type semiconducting behavior). The higher photocurrent in the device having nc-TiO_2/PPAT photoelectrode is due the fact that the composite of PPAT with nc-TiO_2 forms the bulk heterojunction with increased interfacial area which enhance the dissociation of excitons into free carriers formed under illumination.

2. Experimental details

Indium tin oxide (ITO) coated glass sheets of 2.0 cm × 2.0 cm were clean successively with de-ionized water, acetone and isopropyl alcohol and dried in air. Nano-crystalline titanium dioxide (nc-TiO_2) films were prepared by the hydrolysis of titanium isopropoxide using following method as adopted by many researchers [34,1]. 0.5 ml of titanium isopropoxide was slowly added to a mixture of 2.5 ml glacial acetic acid, 7.5 ml of isopropanol and 2.5 ml of de-ionized water with constant stirring during the mixing. The solution was constantly stirred for 12 h to obtain the viscous solution. The nc-TiO_2 colloidal solution was applied on the surface of ITO glass and distributed with a glass rod sliding over an adhesive tape that covered the glass edge. The adhesive tape controls the thickness of nc-TiO_2 which is in the range of few microns. After drying in air, the TiO_2 was sintered at 450 °C for 30 min in a furnace and then cooled to room temperature slowly.

PPAT was synthesized in our laboratory as reported earlier [37]. The PPAT was dissolved in dicholorobenzene (DCB) and the solution was drop cast on the nc-TiO_2 coated ITO glass sheet. After drying in air, the PPAT film at edges was cleaned with DCB for the electrical contact. The film was dried in vacuum for 24 h. The PPAT and nc-TiO_2/PPAT photoelectrodes combined with an ITO counter-electrode by insertion of an electrolyte solution containing I^-/I_3^- redox system in PEO. The two electrodes were separated by a Teflon space to prevent shorting. The iodine doping in PPAT was performed by exposing the PPAT sensitized TiO_2 film to the saturated solution of iodine hexane before the introduction of electrolyte. The systematic layout of photoelectrochemical device used for present investigation and chemical structure of PPAT were shown in Fig. 1. The optical spectrum of material was carried out using Perkin Elmer UV–visible spectrophotometer. The fluorescence spectra of the materials used for photoelectrode are recorded with Hitachi fluorescence spectrophotometer. The PEC was mounted in a sample holder inside a metal box having 2 cm × 2 cm light entrance window. The current–voltage characteristics of the devices were recorded using a Keithley electrometer with built in power supply in dark as well as under illumination. A 100 W halogen lamp was used for illumination the PEC. The white light intensity of the incident light was measured with electronic luxmeter. The photo action spectra of the devices were measured employing a monochromator and the resultant short circuit photocurrent was recorded with Keithley electrometer.

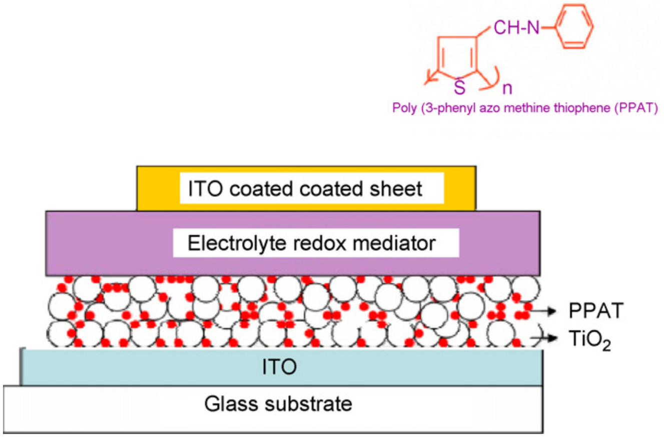

Fig. 1. Chemical structure of PPAT and structure of the photoelectrochemical cell based on TiO_2/PPAT photoelectrode.

3. Results and discussion

3.1. Optical properties of photoactive electrode

The absorption spectra of the PPAT and nc-TiO_2/PPAT are shown in Fig. 2. The polymer PPAT belongs to a class of π-conjugated polymers which has an absorption band ranging from 400 to 600 nm having an absorption peak at 520 nm and an absorption edge around 580 nm. The HOMO–LUMO energetic difference (energy gap) of PPAT estimated from the absorption spectra is around

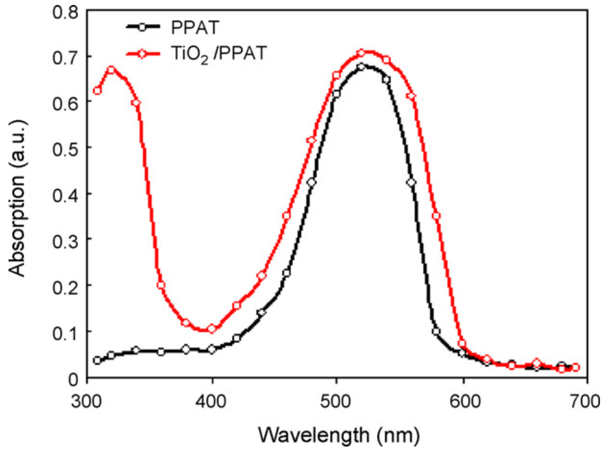

Fig. 2. Optical absorption spectra of PPAT and nc-TiO_2/PPAT photoelectrodes.