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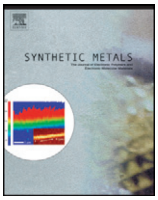

Dye sensitized solar cells (DSSCs) based on modified iron phthalocyanine nanostructured TiO_2 electrode and PEDOT:PSS counter electrode

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ABSTRACT

An iron phthalocyanine with tetra-sulphonated substituents (FeTsPc) was used as photosentizer for the development of dye sensitized nanostructured TiO_2 solar cells. The influence of surface modification (TiO_2 film treated with HCl and HNO_3) and thermal annealing of TiO_2 photo-electrode on the performance of dye sensitized solar cell (DSSC) having structure FTO/TiO_2–FeTsPc/electrolyte/PEDOT:PSS (carbon added)/FTO was investigated through the analysis of current–voltage characteristics under illumination and electrochemical impedance spectra (EIS). The improvement in crystallinity of TiO_2, decrease in the internal surface area and adsorbed amount of dye and increase in the lifetime of injected electrons upon thermal annealing of TiO_2 photo-electrode affects the photovoltaic properties of DSSC. The increase in power conversion efficiency of DSSC based on nitric acid treatment for the photo-electrode is mainly attributed to the increase in photocurrent. A comparative photovoltaic investigation of DSSCs using HCl-treated TiO_2 photo-electrode, indicates that the HNO_3-treated photo-electrode retards back electron transfer at the interface with electrolyte and increases the amount of dye.

1. Introduction

Increasing energy demands and concern about the global warming have lead to a greater focus on renewable energy sources in recent years. Dye sensitized solar cells (DSSCs) have been attracted increasing industrial and academic interests since their discovery in 1991 [1] and have been regarded as promising for next generation photovoltaic device due their attractive features of high power conversion efficiency (>10%) and low production cost [2–8]. DSSC have been studied extensively using wide band gap nano-crystalline TiO_2 sensitized with ruthenium polypyridine complexes [8–15] or metal free organic dyes [16–19] as photo-electrodes. The most successful charge transfer sensitizers employed in DSSC are polypridyl ruthenium complex, which yields power conversion efficiency of 10–11%. In spite of this, the main drawback of ruthenium-based sensitizer is their lack of absorption in the red region of the visible spectrum and their high cost.

In spite of high efficiency achieved by the DSSC based on ruthenium (II) polypyridyl complexes as photo-sensitizer, the main drawback of these sensitizers is the lack of absorption in the far-red/near IR region of the solar spectrum, where the maximum photon flux is exist [20]. To further improve the performance of DSSC's, it is imperative to enhance their response in the above mentioned wavelength region. Phthalocyanines posses intensive absorption in the far-red/near IR region, are well known for their excellent chemical, light and thermal stability, therefore, they are an excellent alternative for solar cell applications [21–23]. These materials also have appropriate redox properties for sensitization of wide band gap semiconductors, i.e. TiO_2 [22,24–26], making them attractive for DSSC. However, there are some problems to be solved for phthalocyanine to be used in DSSC application. They are poorly soluble in organic solvents, for example ethanol and chloroform, which makes it difficult to synthesis, separate and purify these kind of phthalocyanines. The typical phthalocyanines explored for sensitization of wide band gap are free base or metallic ones substituted by carboxylic or sulphonic acid groups for attachment to the semiconductors surface [27–29]. The low efficiency of DSSC incorporating Pc appears to be due to aggregation, insolubility in solvents and lack of directionality [30]. One of the essential requirement for the light harvesting system of DSSC is that the sensitizer posses directionality of its electronic orbitals in the excited states. The directionality should be tuned to provide an efficient electron transfer from the excited dye to the TiO_2 conduction band by good electronic coupling between the lowest unoccupied molecular orbital (LUMO) of the dye and conduction band edge of TiO_2.

In DSSC, a sputtered platinum (Pt) conducting glass is usually employed as a counter electrode to catalyze reduction of I_3^-

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to I^- in redox electrolyte. However, Pt is one of the expensive rare metals in the earth, evolution of the counter electrode with other cheaper materials expected to reduce production cost of the cell is needed. PEDOT doped with poly (4-styrene sulphonated) (PSS) i.e. PEDOT:PSS has attracted much attention during last decades [31–33]. Recently, it was reported that conductivity of the PEDOT:PSS film is enhanced if a liquid organic compound such as dimethyl sulfoxide (DMSO), dimethyl formamide (DMF) or tetrahydrofuran (THF) is added to the PEDOT:PSS aqueous solution [34,35]. Besides the choice of preparation method for depositing conducting polymers on the conducting glass is significant for the determination of efficiency of DSSC. A few methods, such as spin coating [36] and chemical polymerization [32] were employed in order to form a conductive polymers deposited counter electrode, which posses good electrochemically stable.

In the present study, iron tetra-sulphonated phthalocyanine (FeTsPc) substituted by four sulphonic acid groups was synthesized and used as photo-sensitizer and black carbon added DMSO-treated PEDOT:PSS as counter for dye sensitized solar cell. The effect of annealing temperature for nc-TiO_2 electrode on photovoltaic performance of DSSC was investigated in detail. We have also demonstrated that a change in the surface structure of TiO_2 photo-electrode by nitric acid treatment improved the power conversion efficiency.

2. Experimental

2.1. Synthesis of iron tetra-sulphonated phthalocyanine (FeTsPc)

Iron tetra-sulphonated phthalocyanine (FeTsPc) was synthesis as follows: a solid mixture of 4-sulfophthalic acid, ammonium chloride, urea, ammonium heptamolybdate tetrahydrate and iron II sulfate heptahydrate was added to nitrobenzene at 150 °C. The suspension was heated under stirring at 150–190 °C for 6 h. The solid obtained in this way was then washed and purified. The FTIR spectrum of the FeTsPc in KBr pellet displayed the following main absorption bands (in cm^{-1}): 769 (ring breathing, C–H wag), 994 (FePc), 1046 (SO_3 stretch), 1134 (C–H bending), 1194 (SO_3 stretch), 1400, 1489 (isoinode stretch) and 1632 (C=C stretch).

2.2. Preparation of dye sensitized nanostructured TiO_2 electrode

The conducting glass substrates (fluorine-doped tin oxide) (FTO) were cleaned and rinsed with de-ionized water and 2-propanol, and then soaked in propanol for 12 h. The FTO substrates were dried in air prior to film preparation. The TiO_2 colloidal solution was prepared by grinding the TiO_2 (P25 Degussa) powder purchased from Aldrich with 2 ml of distilled water and acetylacetone for 30 min. Finally the 8.0 ml of distilled water and 0.1 ml of Triton X-100 were added with continuous mixing for 10 min. Finally this paste of TiO_2 was coated over FTO by doctor blade technique. After air drying, the TiO_2-coated FTO films were annealed at 250 °C, 350 °C and 450 °C for 30 min, respectively. For the acid treatment, the TiO_2 films (sintered at 450 °C) were immersed in a 0.1 M HCl and HNO_3 solution in de-ionized water for 10 min, respectively. The bare TiO_2 films were immersed in de-ionized water for balancing experimental conditions of acid treated photo-electrodes. Subsequently, the films were rinsed with de-ionized water and then dried at room temperature.

The TiO_2-coated FTO substrates were dipped in the solution of FeTsPc dye dissolved in DMF at 70 °C for 12 h, followed by rinsing with DMF. To decrease the dye aggregation on the semiconductor surface, 10 mM TBP was added to the dye solution and dye sensitized TiO_2 film (sintered at 450 °C) electrodes were obtained by dipping the TiO_2 film into dye solution with additive for 12 h and rinsing with ethanol immediately after removing from dye solution. Sensitized photo-electrodes prepared from dye solutions with additives and without additives are denoted as FeTsPc–TiO_2 and (FeTsPc–$TiO_2)_{add}$, respectively.

2.3. Preparation of counter electrode

PEDOT:PSS aqueous solution (1:3 wt.% dispersion in water) was purchased from Aldrich. The preparation of counter electrode is as follows: the PEDOT:PSS aqueous solution and the organic solvent DMSO was mixed by the volume ratio 3:1. The mixed solution of PEDOT:PSS and DMSO was filtered and stirred continuously for 6 h at room temperature. A small amount of carbon black (C) (0.2 wt.% with respect to the DMSO-PEDOT:PSS aqueous solution) was added to the above solution and stirred for 2 h. The DMSO-treated PEDOT:PSS (C, 0.2 wt.%) films were formed on FTO by spin coating technique. The film was dried at 80 °C for 30 min.

2.4. Assembling of DSSC

The dye sensitized solar cell was assembled by clamping dye sensitized photo-electrode with a DMSO-treated PEDOT:PSS (C added) coated FTO counter electrode to form a sandwiched type structure. The electrolyte solution, which consists of 0.5 M KI, 0.05 M I_2 in 1:1 acetrinitrile–butanol was injected into the inter space between the photo-electrode and the counter electrode. The schematic diagram of the device is shown in Fig. 1.

2.5. Characterization

Structure phase analysis with the X-ray diffraction (XRD) method was performed on XRD with Cu Kα radiation (λ = 0.15418 nm). The TiO_2 powders, which are taken from the prepared photo-electrode were mixed with KBr and pressed into pallets for IR spectroscopy analysis. IR transmission spectra in the range 1000–2000 cm^{-1} were measured at room temperature using FTIR spectrometer. The optical absorption of the photo-electrode was measured by a UV–vis spectrophotometer.

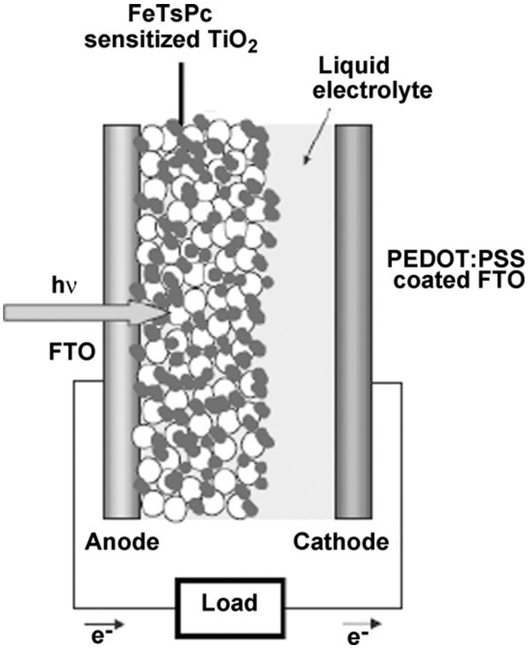

Fig. 1. Schematic structure of dye sensitized solar cell. The white circle represent the TiO_2 nano-particle covered by dye (grey dots).