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Sulphonic acid functionalized porphyrin grafted ZnO nanorods: Synthesis, characterization and applications in the solid state dye sensitized solar cells

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This work presents the chemical modification of ZnO nanorods with a sulphonic acid functionalized porphyrin derivative. The interaction between semiconducting nanorods and the porphyrin through sulphonic groups proved enough effective that the free base porphyrin behaved as metallated porphyrin under the grafted conditions which is a better donor than its free base counterpart. The soret band of grafted dye was red-shifted by 08 nm with respect to the reference. Additionally, two out of the four Q-bands of reference dye were found missing in the post grafting UV–Visible Spectrum. Fluorescence spectra of the dye before and after grafting were found completely different from each other supporting the UV–visible data. These modified ZnO nanorods in combination with P3HT were employed in the hybrid solar cells. The cells gave better efficiencies at low concentrations of the dye than the corresponding reference device consisting of ZnO nanorods and P3HT. At high concentration of the dye the efficiency of the device was decreased.

1. Introduction

Dye sensitized solar cells are the promising alternatives to the traditional silicon based solar cells owing to their low manufacturing cost, wide choice of photoactive materials and easy processing from solutions [1–6]. In these cells a sensitizer anchored to the surface of a semiconductor absorbs solar radiations and transfers the photo-excited electrons to the conduction band of semiconductor whereas the hole is transferred to the conducting polymer which takes it towards the anode. With a view to obtain higher efficiency, researchers have attempted to optimize potential of the key components of DSSC for not only harvesting solar energy but also separating and carrying charges to the respective electrodes efficiently. Out of the key components of the dye sensitized solar cells the chemical nature and structure of the dye molecules have been thoroughly studied. In this context a wide variety of inorganic dyes such as transition metal polyperidyl complexes have been used as photosensitizers with appreciable efficiency [7]. Similarly organic dyes have also been extensively used as photosensitizers [8–13]. Organic dyes with D–π–A structures, anchored to the surface of semiconductors through carboxylic functionalities have been found efficient sensitizers [14–16]. Solar devices using these photosensitizers have rendered 10% efficiency [14–17]. Above all photoelectrochemical devices have attained 12% efficiency with metallated porphyrins (Zinc porphyrin) as photo-sensitizers [18]. As these devices suffer from the unexpected problems associated with the corrosive and volatile nature of the liquid electrolyte, so switching over to the solid state DSSC's which are comparably more stable and use solid polymeric electrolytes seem to be the successful alternatives. Semi-conducting nanoparticles such as ZnO and TiO_2 in combination with organic polymers have been investigated as constituents of the photoactive blend in the solid state devices [19,20]. Surface functionalization of TiO_2 nanorods with dyes has recently been reported to have improved the efficiency to 2.2% [21].

Porphyrins have high absorption co-efficient and have shown pronounced solar energy harvesting efficiency [22–25]. They have been successfully grafted on ZnO nanospheres, nanorods and tetrapods using different anchors [26–28]. Aurore Said et al. investigated the effect of porphyrin (functionalized with four COOH groups) modified ZnO nanorods on the cell conversion efficiency. They observed additional bands in the EQE spectra but the overall conversion efficiency remained low which was ascribed to the poor blend morphology and charge recombination [29]. Here we demonstrate that sulphonic acid functionalized porphyrins are superior to their COOH functionalized counterparts as regards their

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interaction with ZnO nanorods. Upon grafting they not only get converted into Zinc porphyrin [30] but also enhance the overall efficiency of the device as compared to the reference cell consisting of bare ZnO nanorods and P3HT. However higher concentrations of the dye on ZnO surface resulted in aggregation of the dye and consequently decreased the efficiency of the device.

2. Material and methods

All solvents and chemicals were of reagent grade quality, purchased commercially and used without further purification.

2.1. Synthesis

Wet chemical method was adopted for the synthesis of ZnO nanoparticles [31]. The procedure is described below.

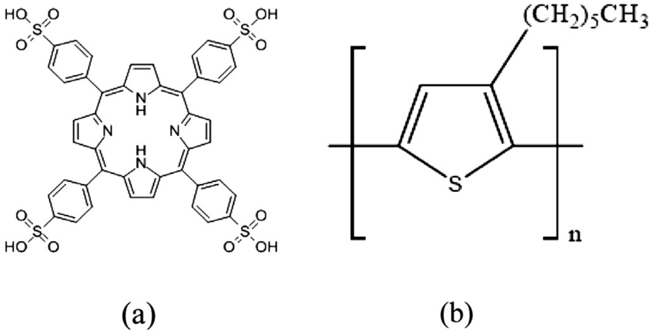
To a solution of 4.15 g of zinc acetate in 214.15 mL of purified distilled methanol, 1.5 mL of distilled water was added. The solution was heated at 60 °C until zinc acetate was completely dissolved. Next in separate flask 1.40 g of sodium hydroxide was dissolved in 117.15 mL of distilled methanol by ultra-sonification. This solution was added dropwise to the solution of zinc acetate under argon atmosphere. The reaction mixture was kept under constant magnetic stirring at 60 °C throughout the synthesis. The progress of reaction was indicated by the changes in the colour of the reaction mixture i.e. upon the addition of alkali, the solution turned milky, then passed through a transparent phase and finally, it became milky once again. After 2 h and 15 min, ZnO nanoparticles of an average diameter of 5 nm were obtained. The colloidal solution of ZnO nanoparticles was concentrated by using rotary evaporator under reduced pressure at 55 °C until it became colourless against its milky appearance. The concentrated solution was replaced in an oil bath at 60 °C for a further duration of 48 h under constant magnetic stirring. Immediately after which the reaction was stopped and the nanorods were left to decant. The white solid precipitate consisting of the nanorods was washed three times with distilled methanol, each time waiting till complete decantation of ZnO and then throwing away the supernatant methanol. These thoroughly washed ZnO nanorods were stored in the dark.

2.2. Functionalization of ZnO nanorods with porphyrin

It was carried out by grafting the dye on the surface of ZnO nanorods. The general procedure is described as, solutions of four different concentration of the dye i.e. 4×10^{-5} M, 8×10^{-5} M, 1.2×10^{-4} M, 1.6×10^{-4} M were prepared by dilution from the mother solution. In a separate flask a solution of ZnO nanorods (1 mg/mL) was prepared in the same solvent. In the next step 5 mL from each concentration of dye solution were mixed with 5 mL of 1 mg/mL ZnO nanorods solution in small glass bottles. These mixtures were kept stirring at room temperature for 16 h. All the grafted samples were prepared in distilled methanol. These samples were then subjected to optical and morphological analysis after proper dilution.

2.3. Construction of solar cell

For the fabrication of solar cells the dye was grafted on to the surface of ZnO in several concentrations by the same general procedure as already discussed. The resulting hybrid samples were termed as solutions A. P3HT solution (20 mg/mL) was prepared by heating 80 mg of the polymer in 4 mL of the methanol at 60 °C for 15 min under argon atmosphere. The solution was named as solution B. Equal volumes of solution A and B were mixed together. This operation reduced the actual concentration of ZnO and that of P3HT to 10 mg/mL. As a substrate, glass sheets of 3 × 2 cm^2 covered with indium tin oxide of 80 nm thickness were used. A small portion of ITO comprising of 1/3 of the total length of substrate was removed by etching with 32% hydrochloric acid for an hour. The remaining portion of the substrate was covered with scotch tape so as to protect it from the effect of acid. After the process of etching, the substrates were rinsed with water many times to remove any traces of the acid and left overnight to dry. The next day the scotch tapes were removed and the slides were washed with acetone in an ultrasonic bath. Deposition of the p-type PEDOT-PSS polymer was done on the clean substrate by spin coating for 50 s at a speed of 5000 rpm and an acceleration of 7000 rpm. The function of the thin layer of PEDOT-PSS is to remove the roughness of the ITO surface and help in the hole conduction towards ITO. Active layer is in fact a blend of dye-sensitized ZnO nanoparticles and P3HT polymer. The blend was deposited by spin coating for 25 s at a speed of 1600 rpm and acceleration of 1800 rpm next a second spin was done for 25 s at a rate of 600 rpm and 100 rpm/minute in order to evaporate the solvent. Al was deposited by thermal evaporation under high vacuum conditions to act as cathode. This was done in the metal evaporator and 80 nm thick cathodic contacts were made to extract and guide electrons to the external circuit. The device was annealed finally at 85 °C for 20 min under argon flow to attain nice morphological distribution of the active blend.



Scheme 1. Chemical structures of (a) sulphonic acid functionalized porphyrin and (b) Poly (3-hexylthiophene).

2.4. Characterization

UV-visible (Shimadzu 1601) and fluorescence spectrophotometer (Perkin Elmer LS 55) were used to determine the optical

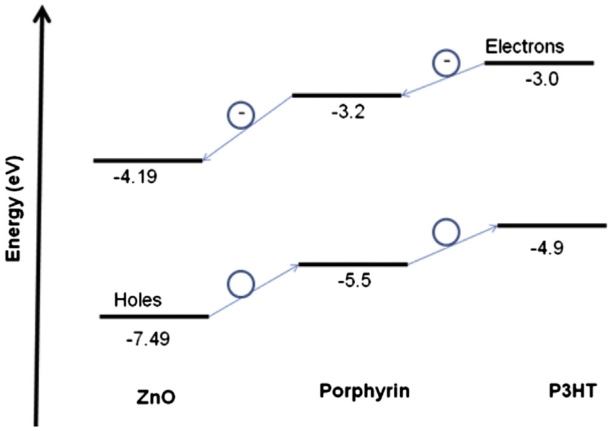


Fig. 1. Energy level diagram showing the LUMO/HOMO levels of the components of photoactive blend.