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Adsorption of porphyrin and carminic acid on TiO_2 nanoparticles: A photo-active nano-hybrid material for hybrid bulk heterojunction solar cells

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ABSTRACT

A photo-active nano-hybrid material consisting of titania nanoparticles, carminic acid, and sulphonic acid functionalized porphyrin is reported here. In an attempt to extend the absorption spectrum of titania to visible region by co-adsorbing carminic acid and sulphonic acid functionalized porphyrin on its surface. Interesting changes in the UV–visible and fluorescence spectra were noticed. The adsorption of carminic acid resulted in the formation of charge transfer complex with titania nanoparticles. This was confirmed by the electronic absorption and fluorescence emission spectroscopies. Chemisorption of porphyrin on the carminic acid functionalized titania further boosted the charge transfer effect. This was noticed by the increase in intensity and width of the charge transfer absorption and emission bands. Energy level diagram showed that the interaction among the constituents of the nano-hybrid assembly permitted the flow of electron in a cascade manner from carminic acid to TiO_2.This also allowed direct flow of electrons either from carminic acid or porphyrin toward titania. The material was used as an active blend in hybrid bulk heterojunction solar cells. Co-functionalized TiO_2-based devices were found 3.5 times more efficient than the reference device but morphology of the device proved a major setback.

1. Introduction

Recently, the development of alternate energy sources is one of the main focuses of research for scientists and researchers. Among these alternatives, photovoltaic solar cells are gaining importance day by day owing to the benefits that can be achieved using this technology [1–10]. After silicon, anatase TiO_2 is one of the core materials employed in solar cell fabrication and new records are being formed each day for achieving better efficiencies by introducing various modifications.

The development of dye-sensitized solar cells (DSSCs) by Grätzel [11] created more opportunities to develop low cost and environmental friendly photovoltaic devices [12–15]. DSSCs consist of two integral parts, i.e. the core semiconducting material and a photosensitizer in the form of dye molecules. As a consequence, the light-capturing ability of the semiconductor material is greatly enhanced. This plays a vital role in increasing the efficiency of the device. Based on this idea, higher efficiencies up to 11–12% have been reported using nanocrystalline titania [16]. The production of titania-based solar cells is easy and cost-effective. These cells can prove as an alternative to silicon-based solar cells [17–20]. But the corrosive and volatile nature of the liquid electrolyte put a question mark on the stability of these devices. To cope with this problem effectively, scientists focus on developing solid state and durable alternatives in the form of hybrid bulk heterojunction solar cells. These cells though comparably more stable are less efficient. Efforts are underway to broaden the spectral range of the material by using the modified dye molecules and enhance its light harvesting potential [21–22].

Porphyrin and its derivatives are considered to be highly suitable sensitizers for DSSCs due to their strong absorption in the visible region, i.e. Soret peaks at around 400–450 nm and Q-bands extending from 500 to 700 nm [23]. The efficiency of solar cells using carboxylic and sulphonic acid functionalized porphyrin has been evaluated by our group using ZnO as inorganic core material [23,24]. An enhancement of photocurrent efficiency using nanotitania grafted with carboxylic acid functionalized porphyrin and co-grafted with C_{60} has been reported previously [25] but no work has been done on the co-adsorption of carminic acid and acid functionalized porphyrin.

Carminic acid, an organic chromophore, has carboxylate and phenolate groups through which it anchors itself to the surface of semiconductor. In 2008, Gawęda reported the photosensitization of nanocrystalline titania with carminic acid to enhance the absorption in visible region [26]. He did not observe any charge transfer effect. Co-adsorption of porphyrin and carminic acid on the surface of nanotitania led to charge transfer complexation because LUMO levels of porphyrin and carminic acid [27] were found quite suitable for the stepwise flow of electrons from these potential photosensitizers to the conduction band of titania. These levels also permitted

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direct transfer of electrons from either of these photosensitizers to titania.

This work is aimed at enhancing the visible region absorption of the semiconducting nanotitania by adsorbing carminic acid and porphyrin on its surface to develop a novel photo-active nano-hybrid material. It is also intended to suppress the recombination processes which lower the efficiency of hybrid bulk heterojunction solar cells.

2. Experimental

2.1. Chemicals

Titanium (IV)-iso-propoxide (Ti[OCH(CH_3)$_2$]$_4$, 4,4′,4″,4‴-(Porphine-5,10,15,20-tetrayl)tetrakis(benzenesulfonic acid) and carminic acid (CA)) were bought from Sigma–Aldrich, Analytical grade 1-propanol and deionized water were used as medium in the synthesis procedure.

2.2. Synthesis of TiO_2 Nanoparticles

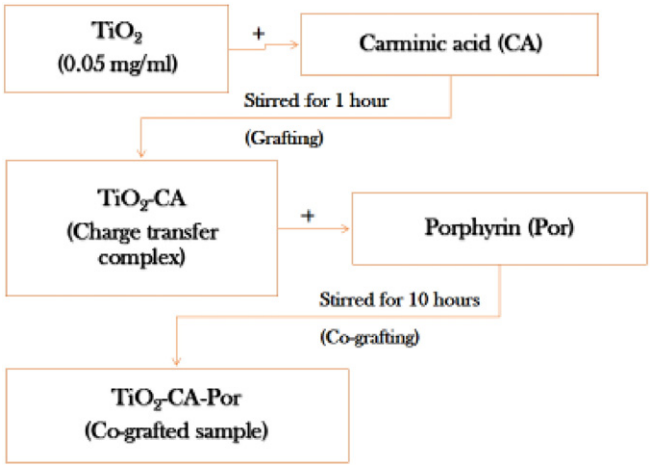
TiO_2 nanoparticles were synthesized using simple sol–gel method as reported in the literature [28]. Titanium (IV)-iso-propoxide (TIP, 100 g) was added to 1-propanol (200 g) and the mixture was well stirred for 5 min using a magnetic stirrer. Thereafter, a mixture of water (25.33 g) and 1-propanol (127 g) was added to the alkoxide solution from burette at the rate of 1 mL/min. In this way, the molar ratio of TIP/H_2O was set to 4:1. After adding the water–alcohol solution, the mixture was stirred for about 24 h at room temperature. The solid product was separated by centrifugation and dried at room temperature overnight. The dried product was calcined at 500 °C for 1 h. The synthesized nanoparticles in 1-propanol were centrifuged and washed three times with the same solvent in order to remove impurities and remnants of the precursor compounds.

2.3. Synthesis of Nano-Hybrid Material

Porphyrin molecules were chemisorbed on the surface of titanium dioxide according to the following procedure. A fixed amount of TiO_2 (0.05 mg/mL) and different concentrations of carminic acid (CA) ranging from 2×10^{-5} M to 6×10^{-5}M were used. In a typical experiment, 5 mL of TiO_2 solution in 1-propanol were mixed with 5 mL of dye solution (CA) in the same solvent. This was repeated for each dye concentration. The mixture was stirred for 1 h. The nano-hybrid material was termed as TiO_2-CA. It was subjected to optical characterization after proper dilution. In a similar way, porphyrin was adsorbed using 0.05 mg/mL of TiO_2 and various concentrations of porphyrin. This nano-hybrid material was termed as TiO_2-Por. In order to co-adsorb both the sensitizers and synthesize TiO_2-CA-Por, the following procedure was adopted. CA was first grafted on TiO_2 by stirring the mixture for 1 h. Afterward, porphyrin was added to the grafted samples and the mixture was stirred for 10 h to ensure complete adsorption. The schematic diagram of the synthesis of nano-hybrid assembly is shown in Scheme 1. The grafted and co-grafted materials were optically analyzed after proper dilution and centrifugation which helped to wash away the negligible fraction of un-adsorbed porphyrin or carminic acid molecules.

2.4. Fabrication of Solar Cell

Solar cells were fabricated on ITO-coated glass (indium-doped tin oxide) slabs measuring 3×2 cm^2 (resistivity 15 Ω/square). ITO-coated glass was rinsed with acetone and deionized water to wash away both organic and inorganic impurities. Thereafter, a thin layer (100 nm) of PEDOT-PSS (poly(ethylenedioxy thiophene)-poly(styrenesulphonate) (CLEVIOS™ P VP AI 4083, dark blue suspension in water) was spin coated on its surface at 4000 rpm for 50 s. This layer was annealed at 50 °C for 15 min to get uniformly distributed and facilitate the transport of holes toward anode. In the subsequent step, the photo-active blend consisting of dye-functionalized titania and poly(3-hexylthiophene) (regioregular Sigma–Aldrich) in a ratio of (70:30) by weight was spin coated at 1600 rpm for 20 s on the top of PEDOT-PSS (layer thickness 200 nm). This was immediately followed by another spin at 600 rpm for 15 s in order to evaporate the solvent. The mixture of P3HT and titania was prepared by dissolving 20 mg of P3HT in 1 mL of chloroform at 60 °C for 15 min in argon atmosphere and then adding 1 mL of 46 mg/mL of titania to the solution of P3HT at 50 °C. This mixing reduced the concentration of P3HT to 10 mg/mL and that of titania to 23 mg/mL. Finally, aluminum metal was thermally evaporated under high vacuum conditions (1×10^{-6} mbar) in the form of thin strips (80 nm) using shadow masks. This acted as cathode. The device was annealed at 85 °C for 25 min in argon atmosphere in order to attain uniform morphological distribution of the active blend.



Scheme 1. Schematic diagram for the synthesis of nano-hybrid assembly.

2.5. Characterization

UV–visible (Shimadzu 1601) and fluorescence spectrophotometer (Perkin Elmer LS55) were used to explore the optical properties of nanoparticles, photosensitizers, and the nano-hybrid samples. The purity and crystalline nature of synthesized nanotitania were confirmed by X-ray diffraction measurements. High-resolution transmission electron microscope(JEOL 2010 working at accelerating voltage of 80 and 200 kV) gave the morphological properties and the crystalline size of titania nanoparticles. Solar simulator with tungsten halogen lamp (150 W, light power density 100 mW/cm^2) and AM 1.5 G (Oriel 81,086) filter was used to characterize the fabricated solar cells. Source Meter (Keithley Model 2400) was employed to record current–voltage (I-V) data. For external quantum efficiency measurements, Cornerstone monochromator (Cornerstone™ 130 1/8 m) was employed. The intensity of light was calibrated with a monocrystalline silicon solar cell.

3. Results and Discussions

Titania nanoparticles (TN) synthesized by sol–gel method constitute the inorganic core while carminic acid and porphyrin act as photosensitizers. Both the organic constituents anchor to the surface of titania using carboxylic and sulphonic functionalities, respectively. (Scheme 2). The organic moieties not only photosensitize the material but also provide a multistep channel to the flow of electrons toward TiO_2. These sensitizers can also help in the direct injection of electrons in the conduction band of TiO_2 and thus contribute their individual shares in charge transfer in the desired direction. This has been discussed with details in the forthcoming section using different instrumental techniques.