

Ultrathin films of tetrasulfonated copper phthalocyanine-capped titanium dioxide nanoparticles: Fabrication, characterization, and photovoltaic effect

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Abstract

Tetrasulfonated copper phthalocyanine (CuTsPc)-capped TiO₂ nanoparticle ultrathin films were fabricated by a layer-by-layer (LBL) self-assembly technique. Alternating bilayer structures were formed by consecutive adsorption of CuTsPc-capped TiO₂ nanoparticles with poly(diallyldimethylammonium chloride). Optical and electrical measurements were carried out to characterize the CuTsPc-capped TiO₂ nanoparticle ultrathin films. Optical measurements revealed uniform deposition. The surface morphology of such bilayer films showed a granular morphology similar to other classes of LBL films. Electrical measurements revealed an abnormal phenomenon under white light illumination. Electrochemical and photoelectrochemical measurements on such a bilayer system were carried out to elucidate the electron transport processes and the photovoltaic effect.

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1. Introduction

The development of inexpensive renewable energy sources continues to stimulate new approaches to the production of efficient, low-cost photovoltaic devices. The application of organic-dye-sensitized titanium dioxide (TiO₂) nanoparticles to a new type photovoltaic cell has recently generated much interest [1–6]. In 1991, O'Regan and Grätzel introduced a new approach to efficient large-area photovoltaics using nanoporous dye-sensitized TiO₂ nanocrystalline layers to form efficient electrochemical solar cells [4]. The dye-sensitized TiO₂ solar cell showed conversion efficiencies of 7–10% under standard solar conditions. The high power efficiencies are attributable to ultrafast charge transfer from the dye to the TiO₂, the high internal sur-

face area of the TiO₂ films, the broad absorption of the dye, and the efficient separation of opposite charges into different materials. Therefore, the quantum efficiency and internal electric field are dependent on the relative energy levels and anchoring ability of the photoconducting dye to the porous TiO₂ nanoparticle surface [7–10].

Phthalocyanine (Pc) and its many kinds of derivatives have been used to sensitize TiO₂ nanoparticles [11–13]. As early as 1980, Giraudeau et al. observed photocurrents in the visible light region for phthalocyanine-coated TiO₂ electrodes in aqueous solution [14]. They demonstrated that the Pc molecules have an appropriate energy state with respect to TiO₂, so that the excited electrons in the Pc molecules under white light illumination are able to flow into the conduction band of TiO₂. In this case, dye molecules should be adsorbed onto the nanoparticle surface in a closely packed monolayer for maximum sensitization efficiency [4,15]. Therefore, it is important to design the Pc-TiO₂ interface to improve the light absorption, carrier gen-

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eration, and transport properties. In most cases, the method for sensitizing TiO_2 nanoparticles is to make a sintered network of porous TiO_2 serving as a matrix for the adsorption of the sensitizing dye molecules [11,16]. Takada et al. made organic–inorganic heteromultilayer structure for Pc-sensitized TiO_2 as an optoelectronic device [17]. The device exhibits 40 times higher photoconductivity than a single CuPc layer, but the efficiency was limited by the thickness of both CuPc and TiO_x layers. They suggested that a thin CuPc layer and a thick TiO_2 layer will decrease the probability of recombination, and thus increase the photoconductivity.

In this paper, we present a new way of preparing ordered ultrathin films of copper phthalocyanine (CuPc)-sensitized TiO_2 nanoparticles. Based on this method, the most sufficient surface area of TiO_2 nanoparticle can be coated with a single CuPc molecule layer, and then such CuPc molecule-coated TiO_2 nanoparticles can be fabricated onto various substrates by a layer-by-layer (LBL) self-assembly technique.

2. Experimental details

Copper(II) phthalocyaninetetrasulfonic acid tetrasodium salt (CuTsPc), titanium(IV) propoxide (98%), poly(diallyldimethylammonium chloride) (PDDA) (average molecular weight 200,000–350,000, 20 wt% in water), and other chemicals used herein were purchased from Aldrich. Quartz, indium–tin oxide (ITO)-coated glass plates, interdigitated electrodes, and mica were used as the substrates for the fabrication of CuTsPc-capped TiO_2 and PDDA LBL films. The quartz plates and interdigitated electrodes were treated with a hot concentrated $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ (7:3) bath for 1 h, and the ITO-coated glass plates were cleaned with methanol/chloroform at first. Then, all the substrates were treated in hot $\text{NH}_3/\text{H}_2\text{O}_2/\text{H}_2\text{O}$ (1:1:5) at 60 °C for 30 min. Last, these substrates were carefully rinsed using sufficient deionized water and further dried by nitrogen flux. This procedure creates the hydrophilic substrates. The substrates were kept in deionized water prior to their use for LBL deposition.

The TiO_2 colloidal nanoparticle was synthesized by the method of acid-catalyzed sol–gel formation [9,18]. Typically, 7.4 ml of titanium propoxide was added stepwise into 20 ml of 1 mol dm^{-3} HNO_3 aqueous solution under stirring, followed by vigorous agitation for 2 h to give a transparent TiO_2 colloidal solution. Then 2 ml of 5 mmol dm^{-3} CuTsPc aqueous solution was added slowly into the TiO_2 colloidal solution with vigorous agitation, followed by stirring for another 2 h. The CuTsPc-capped TiO_2 colloidal solution was centrifuged to get rid of any precipitation. Last, the solution was dialyzed in the water with the same pH value to get rid of the unreacted CuTsPc molecules. The resulting colloidal solution was used as a polyanion solution for LBL film formation. The polycation PDDA was diluted by adding water to 2 mg cm^{-3} , and then the pH of the solution was lowered to 4.5 by slowly adding 1 mol dm^{-3} HCl. For these

hydrophilic surfaces, LBL films were fabricated by immersing the substrate first in the PDDA solution and then in the CuTsPc-capped TiO_2 colloidal nanoparticle solution. The hydrophilic substrates were dipped in each solution for 5 min and subsequently rinsed with water containing HCl at pH 4.5 and then nitrogen-dried.

UV–vis spectra of the LBL films deposited on quartz substrates were recorded by using an UV–vis–NIR spectrophotometer (Jasco Model V-570). The electrical characterization was performed using an electrometer (Keithley Model 6517). Current–voltage (I – V) characteristics were obtained by a potential step of 0.5 V. The interdigitated electrode was fabricated on a glass plate by the photolithography technique. Any pair of electrodes was spaced at 50 μm and each tract was spaced at 50 μm in width and 40 nm in height. The electrochemical measurements were made by potentiostat/galvanostat (EG&G PARC, Model 263A). A standard three-electrode configuration was used, where LBL films on an ITO glass plate acted as a working electrode, platinum as a counter electrode, and Ag/AgCl as a reference electrode. A standard electrochemical cell with a three-electrode system was employed for the photoelectrochemical photocurrent response. A white light of 100 W illuminated the working electrode from a fixed distance of 5 cm. The switching on and off of the light was controlled manually.

3. Results and discussion

3.1. Fabrication of the LBL films

The schematics of the preparation of CuTsPc-capped TiO_2 nanoparticles and LBL self-assembly are shown in Fig. 1. The idea of fabricating such LBL films is first to cap TiO_2 nanoparticles with a monolayer of CuTsPc mole-

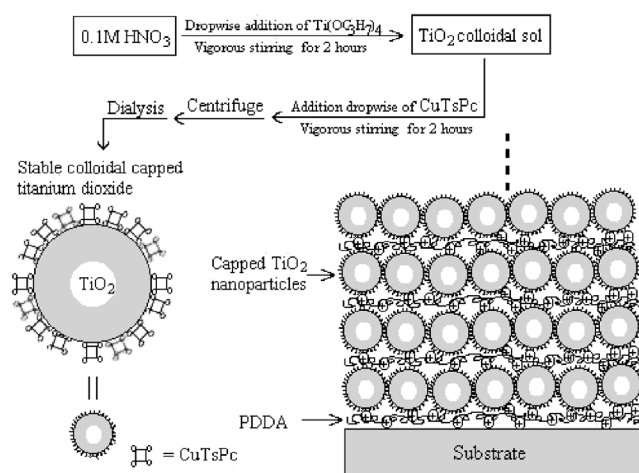


Fig. 1. Schematics of the preparation of CuTsPc-capped TiO_2 nanoparticles and layer-by-layer self-assembly of (PDDA/CuTsPc-capped TiO_2) $_n$ thin films. Titanium(IV) propoxide and copper(II) phthalocyaninetetrasulfonic acid were used to produce a capped TiO_2 nanoparticle.

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