

Novel poly(3-methylthiophene)-TiO₂ hybrid materials for photovoltaic cells

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Abstract

Organic–inorganic hybrid materials based on poly(3-methylthiophene) (P3MeT) and TiO₂ were developed and investigated. The TiO₂ nanoparticles were deposited on ITO-coated glass by spin coating, and characterized with scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray diffraction (XRD) and Brunauer–Emmett–Teller (BET) equation. The P3MeT films were then electrodeposited onto the porous TiO₂ film for junction formation. Instruments of AFM and electron spectroscopy for chemical analysis (ESCA) were utilized to examine the surface morphology and chemical composition of the P3MeT/TiO₂ hybrids, respectively. The performance of the photovoltaic cell fabricated from as-prepared donor/acceptor hybrid was evaluated.

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1. Introduction

Photovoltaic cells containing organic semiconductors have attracted considerable attention [1–3] because their electrical and optical properties can be varied widely, and generally they can be fabricated more easily than inorganic photovoltaic cells. However, the use of organic molecules or conducting polymers to fabricate photovoltaic cells remains impractical because of the small overlap of the electronic transition absorption spectrum of organic materials with the solar spectrum and ineffective charge transport to electrodes. Since the diffusion range of excitons in conjugated polymers typically ranges between 5–15 nm [4–7], a large interface area is required between the electron donor and electron acceptor to achieve a high efficiency of charge separation.

This work describes a new route for preparing organic–inorganic hybrid as a photoactive material in ultrathin photovoltaic device using an electrochemical polymerization technique. Because of the higher accessibility to small pores for thiophene monomer than for the polythiophene (PTh) chain, the interface area between the PTh phase (electron donor) and

TiO₂ phase (electron acceptor) is expected to increase. Moreover, the subject method does not require the polymer to be soluble in the solvent, since monomers without solubilizing side chains or with very short side chains can be used. In this study, we chose nanoporous TiO₂ as the inorganic semiconductor and 3-methylthiophene as the monomer for electropolymerization. Polythiophene [8] was selected because of its good environmental stability and high hole-mobility.

2. Experimental

2.1. Synthesis and characterization of nanoporous titania film

Titanium isopropoxide, 2-propanol and nitric acid were purchased from Acros and used without further purification. TiO₂ colloid solutions were prepared by sol–gel reaction of titanium isopropoxide, Ti(OCH(CH₃)₂)₄, as follows: under a stream of dry nitrogen, 25 mL of Ti(OCH(CH₃)₂)₄ was added to a dropping funnel containing 4 mL of 2-propanol. The mixture was added to 150 mL of deionized water over 10 min with vigorous stirring. Within 10 min of the alkoxide addition, 1.14 mL of 65% nitric acid was further added to the system. The reaction was continued for 8 h at 80 °C. The resulting sol was then concentrated under vacuum at room temperature until the TiO₂ concentration was about 80 gL⁻¹. Finally, two drops of nonionic surfactant, Triton-X 100, were added to the

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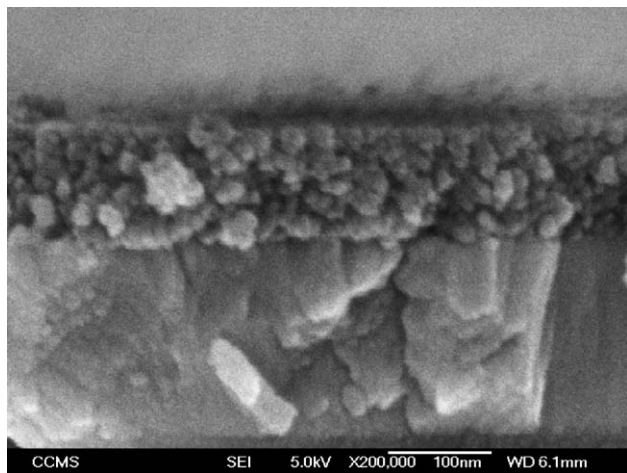


Fig. 1. SEM image of the cross section of a sintered TiO₂ film.

solution and the solution then was stirred for several hours to enhance the colloidal stability and size uniformity of TiO₂.

Nanoporous TiO₂ films were formed on ITO coated glass through spin coating at 2500 rpm. The films were heated to 450 °C at a heating rate of 5 °C min⁻¹ and held at 450 °C for 1 h. The morphology of the TiO₂ films was examined by scanning electron microscopy (JOEL). Surface area of TiO₂ nanoparticles was determined from Brunauer–Emmett–Teller (BET) equation. X-ray diffraction measurements (Philips, X'Pert PRO) with monochromatic CuK_α radiation were taken to examine the crystal structure of the particles. Film thickness was measured on an ellipsometer (GAERTNER, L116D). The typical film thickness following calcinations was approximately 70 nm. XRD and ellipsometry measurements were conducted on films prepared on silicon wafers. Photoluminescence spectra were taken using a Fluorolog-Tau-3 spectrometer (Jobin Yvon) by photoexcitation at 480 nm. The depth profile of elemental compositions in the P3MeT/TiO₂ hybrid was examined by electron spectroscopy for chemical analysis (ESCA) technique, which were performed on a VG Scientific ESCALAB 250 spectrometer under a Mg K_α (1253.6 eV) radiation source. Sample etching was undertaken in situ using a VG Scientific ESCALAB 250 EX05 argon ion etcher with an emission current of 15 mA. The etched crater was 2 × 5 mm².

2.2. Electropolymerization of 3-MeT into nanoporous titania films

Electropolymerization of 3-methylthiophene in nanoporous titania films was carried out in acetonitrile using Bu₄NBF₄ (Aldrich) as the electrolyte. Acetonitrile was distilled before use, while other chemicals were used as received. The monomer and electrolyte concentrations were 0.1 and 0.02 M, respectively. The electropolymerization was controlled by an Electrochemical Analyzer (CH Instrument, Model 614A) using platinum and Ag/AgCl as the counter electrode and reference electrode, respectively. During the electropolymerization, a constant potential of 2.0 V was applied for several minutes to establish a highly BF₄⁻ doped P3MeT layer on and inside the porous TiO₂ matrix. The samples were undoped at -0.8 V for

5 min then rinsed with fresh acetonitrile. The overgrown polymer layers were removed mechanically.

2.3. Fabrication of photovoltaic cells

Photovoltaic cells were fabricated by spin-coating a thin layer of poly(3-hexylthiophene) on the top of P3MeT/TiO₂/ITO prepared above to avoid direct contact of the TiO₂ and top electrode, followed by the evaporation deposition of a 60 nm thick of Al electrode under vacuum. The effective cell area was adjusted to about 0.25 cm². The measurement of the *I*-*V* characteristic of the cell was conducted while the cell was illuminated by an Xe lamp with intensity of 88 mW/cm².

3. Results and discussion

This study produced nanoporous TiO₂ films via the sol-gel method using titanium isopropoxide as precursor, and then calcining the films at 450 °C. Fig. 1 illustrates the SEM cross-section image of a sintered TiO₂ film deposited on conducting glass substrate. The figure reveals that the TiO₂ film comprised a three-dimensional network of interconnected particles with an average size of approximately 14 nm. The BET surface area of the TiO₂ powders was about 89.45 m²/g. Fig. 2 displays X-ray diffraction pattern of the TiO₂ powders. Nanoparticle size was determined based on the diffraction peak by the use of Scherrer's equation [9]. This approach calculated that the crystallite size of the TiO₂ particle was approximately 9.8 nm.

Fig. 3 illustrates the surface morphologies of TiO₂ and P3MeT/TiO₂ films, as determined using atomic force microscope in the tapping mode. From the AFM images, the nanostructured TiO₂ in Fig. 3a comprised interconnected and nanometer sized TiO₂ particles and pores. The TiO₂ particles in the film have been observed to be uniform (root mean square surface roughness around 2.0 nm) with average diameter 18 nm. Fig. 3b shows the measurements performed following the deposition of the in situ formed P3MeT on the nanoporous TiO₂-coated ITO glass. The surface roughness is significantly higher (rms roughness of 63.0 nm) for the composite films compared to the parent TiO₂ film. Comparison of the surface

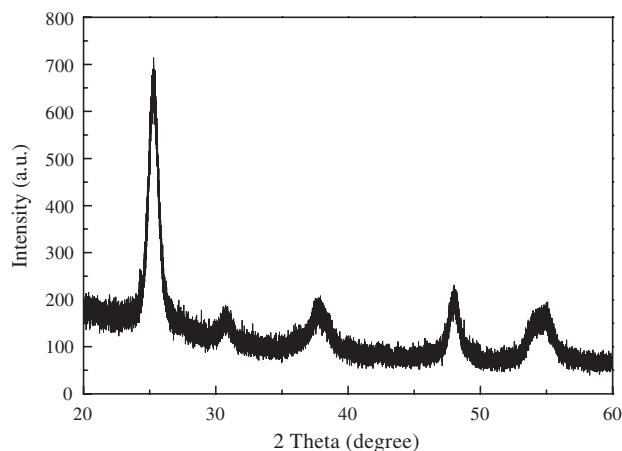


Fig. 2. X-ray diffraction pattern of TiO₂ nanoparticles.

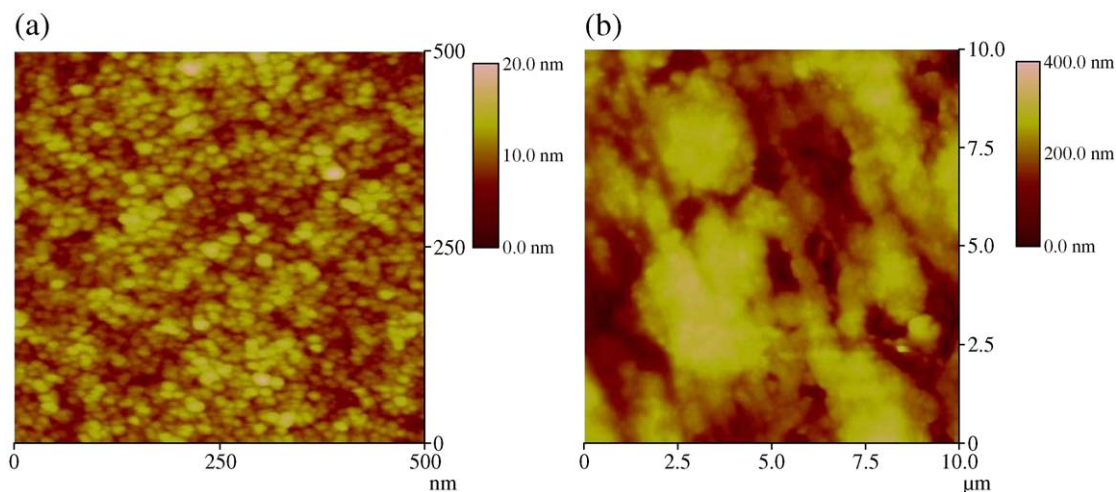


Fig. 3. AFM images of (a) TiO_2 and (b) P3MeT/ TiO_2 film.

morphologies of the TiO_2 layer with P3MeT coated TiO_2 layers from the AFM pictures in Fig. 3 reveals that the surface of the TiO_2 network was covered by the polymer layer.

Fig. 4 displays the absorption spectra of P3MeT/ITO and P3MeT/ TiO_2 /ITO. Compared to P3MeT deposited on ITO, the maximum absorption of P3MeT grown inside nanoporous TiO_2 is blue-shifted, which indicates that the P3MeTs synthesized from the TiO_2 /ITO substrate possessed a smaller average conjugation length than those prepared directly from ITO substrate. This phenomenon may result from low molecular weight and twist chain conformation of P3MeT.

Electron spectroscopy for chemical analysis (ESCA) was employed to elucidate the P3MeT distribution in the depth profile, by examining the elemental compositions of the composite film. Fig. 5a displays the ESCA spectra of the surface of the P3MeT/ TiO_2 film prepared by the electropolymerization of 3-methyl thiophene and the removal of the top layer of pure P3MeT, as specified in the Experimental section. The signals at 459.0, 530.4, 285.0 and 164.0 eV correspond to the binding energies of $\text{Ti}(2p_{3/2})$, $\text{O}(1s)$, $\text{C}(1s)$ and $\text{S}(2p_{3/2})$ [10–12], respectively, proving the coexistence of TiO_2 and P3MeT in the thus-synthesized film. Fig. 5b depicts the sulfur

signal from the thiophene rings in the ESCA spectra of P3MeT/ TiO_2 /ITO at various depths. Letters A to G are the numbers of etchings of the sample by Ar ions, starting from the film surface. The lack of sulfur signal in curve G is probably due to the complete removal of P3MeT from the sample by Ar ions.

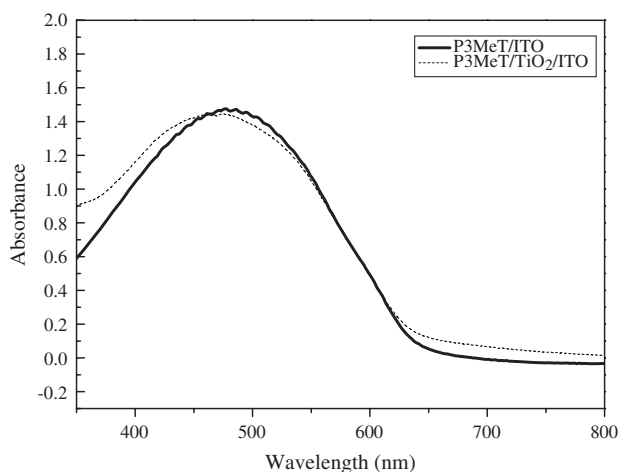


Fig. 4. UV-vis absorption spectra of P3MeT and P3MeT/ TiO_2 .

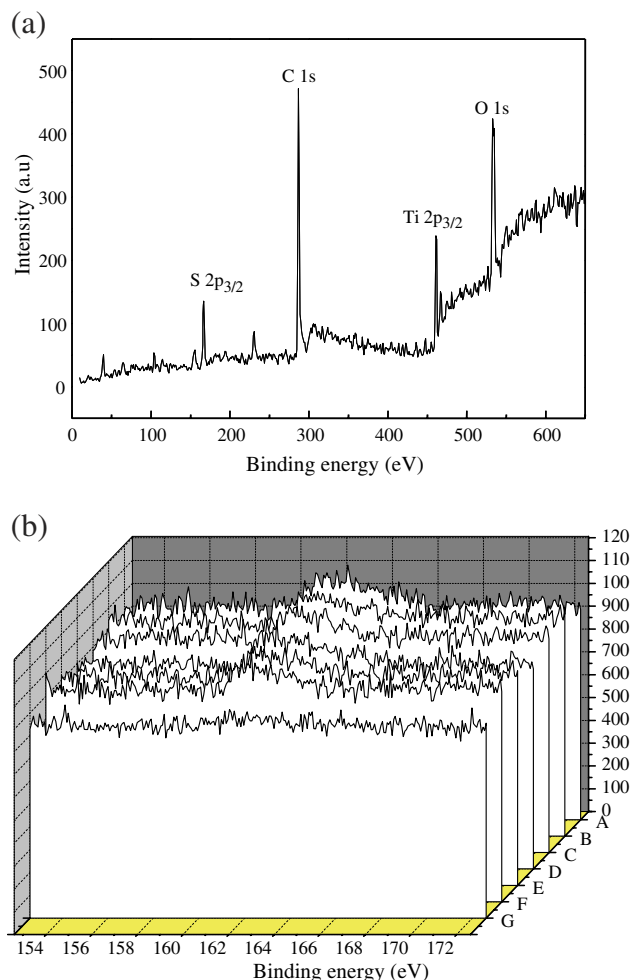


Fig. 5. ESCA spectra of (a) the surface of P3MeT/ TiO_2 film, and (b) P3MeT/ TiO_2 /ITO at various depths.

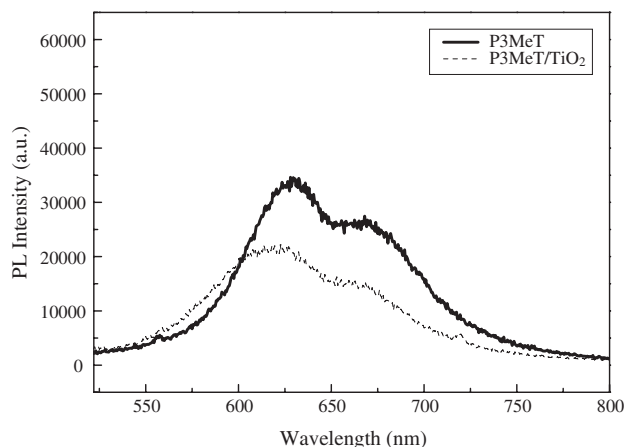


Fig. 6. PL spectra of P3MeT and P3MeT/TiO₂.

Interestingly, the normalized intensity of the S(2p_{3/2}) signal at 164 eV is almost the same for curves A to F, revealing that the composition ratio of TiO₂ to P3MeT, is nearly fixed throughout the sample and the electropolymerization of 3-MeT in the TiO₂ matrix probably began from the bottom ITO electrode, before the pores were filled. This also indicated that P3MeT chains were uniformly grown inside the porous TiO₂ film. Furthermore, the thickness of the P3MeT/TiO₂ film can be estimated from the etching depth before all of the P3MeT has been removed. It was determined to be approximately 60 nm, close to the value of 70 nm determined by the α -stepper.

Charge transfer is known to normally occur with a very high efficiency if excitons are formed in conducting polymer within approximately 10–20 nm [13,14] of a titania interface. The PL measurements in Fig. 6 show that the excitons in the polymer are visibly quenched, suggesting that polymer chains were successfully synthesized inside the pores of TiO₂ matrix, and electron transfer occurred from the polymer to TiO₂. The quenching efficiency of each film can be determined by calculating the integrated area beneath each curve [15]. The quenching efficiency of P3MeT/TiO₂ was found to be 31%.

The current–voltage characteristics of Al/P3HT/P3MeT/TiO₂/ITO device were measured under Xe-lamp illumination with an intensity of 88 mW/cm². The short-circuit current, open-circuit voltage, fill factor and power conversion efficiency of the cell were determined to be 23.3 μ A/cm², 160 mV, 0.19 and a 3.22 $\times 10^{-3}$ %, respectively. Two possible reasons are responsible for the rather low quenching efficiency of the hybrid film and low power conversion efficiency of the cell. Firstly, the incompatibility of inorganic particles and organic polymers results in a poor contact between polymer and TiO₂ surface after electropolymerization process, reducing the efficiency of photo-induced electron transfer. Secondly, the pore size of the porous TiO₂ film used here is still small relative to the polymer chain-length, which causes a coiled and twisted chain conformation for the poly(3-hexylthiophene)s grown inside the pores, thus lowering the hole mobility and blue-

shifting the UV–vis absorption spectrum. However, this study provides a facile and successful route for growing conducting polymer from the porous TiO₂ film. The cell power conversion efficiency could be further improved by optimizing the in situ polymerization conditions, polymer structures, film morphologies, and contacts of metal/polymer/inorganic interfaces.

4. Conclusions

A method of developing an organic–inorganic hybrid as a photoactive material in ultrathin photovoltaic devices via in situ polymerization technique is described. UV–vis and photoluminescence spectroscopy measurements suggest that the polymer chains are coiled inside the nanoporous titanium films. ESCA spectra indicate the P3MeT chains were successfully electropolymerized and packed inside the porous TiO₂ matrix. The photovoltaic cell fabricating from the prepared P3MeT/TiO₂ film demonstrates an open-circuit voltage of 0.16 V, a short-circuit current density of 23.3 μ A/cm², a fill factor of 0.19, and a power conversion efficiency of 3.22 $\times 10^{-3}$ %.

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