



Facile route to prepare film of poly(3,4-ethylene dioxythiophene)-TiO₂ nanohybrid for solar cell application

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ABSTRACT

Composite using poly(3,4-ethylenedioxythiophene) (PEDOT) as electronic conducting polymer and nanocrystalline titanium dioxide (TiO₂) as host matrix were prepared by the template method. We applied an original in situ photopolymerization technique to synthesize PEDOT inside the TiO₂ pore and characterized the polymer and pore filling by different analysis (cyclic voltammetry, atomic force microscopy, spectroscopy and thermogravimetric measurements). Results were compared with those obtained on PEDOT films synthesized by monomer oxidization in the presence of FeCl₃. In situ generation of PEDOT by photopolymerization was observed to be higher and self-limiting after 22% filling of the mesoporous TiO₂ network. Hybrid materials were used to fabricate an indium–tin oxide/nano-crystalline TiO₂/PEDOT/Au device. The current–voltage characteristics indicate that a built-in electrical field has been created at the nano-crystalline TiO₂/PEDOT interface with energy conversion efficiency of 0.09% without dye.

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1. Introduction

Organic/inorganic polymer hybrid materials have a wide variety of attractive potentialities to introduce original structural design in material sciences and to derive innovative functions for device applications. In particular, a hybrid associating an electronic conducting polymer and a metal oxide semiconductor is one of the most advantageous combinations for photoelectronic devices including photovoltaics. Interpenetration of the two phases at the nanoscale can yield materials whose collective performance is greatly enhanced compared to that of each constituent.

Hybrid materials from inorganic oxide layer are typically created either by infiltration or by in situ polymerization techniques. The infiltration strategy is widely used for TiO₂-conjugated polymer or TiO₂-molecular glasses for photovoltaic application. Devices incorporating, 2,2',7,7'-tetrakis-(*N,N*-di-*p*-methoxyphenylamine)-9,9'-spirobifluorene as organic hole conductor lead to efficiencies up to 5% [1,2]. Others molecular glasses like triphenylamine [3], triazine [4] or hydrazone [5] derivatives are other promising candidates. Concerning polymer infiltration, the best way is obtained from a pre-formed polymer casted on a mesoporous TiO₂ film and heated to induce infiltration [6,7]. In situ chemical polymerization has been demonstrated in the creation of polyaniline filaments [8,9] or polythiophene shell on TiO₂ surface [10,11]. Finally, in situ electropolymerization can be used to generate

the polymeric phase around a mesoporous inorganic electrode: Fox and Worthen [12] described the combination of electrochemistry and photochemistry for covering TiO₂ with polypyrrole. Similar results are obtained by Idris et al. whereas polythiophene-TiO₂ composite were prepared electrochemically [13,14]. However, in these techniques, the inorganic phase acts as a template for the organic phase but does not play an active role in its formation especially for photovoltaic application [15–17].

An alternative approach is to utilize in situ photopolymerization by optical excitation of the inorganic semiconductor. Photon absorption by an inorganic semiconductor can generate oxidative and reductive equivalents to drive chemical reactions, such as polymerization. This technique leads to well adhering contact between the polymeric materials and the inorganic sensitizing material. Polypyrrole [18,19] or poly(3,4-ethylenedioxythiophene) (PEDOT) [20,21] titanium dioxide particles were also formed by an UV irradiation source and starting photopolymerization by the activation of TiO₂.

Photopolymerization is initiated wherever hole carriers in the inorganic surface can oxidize monomer. A good electronic contact between the polymer and the inorganic semiconductor takes place because the polymerization reaction is locally initiated by charge transfer across the inorganic semiconductor–electrolyte interface. In this paper, we studied the photopolymerization of 3,4-ethylene dioxythiophene (EDOT) in mesoporous TiO₂ layer for photovoltaic application. PEDOT is an excellent hole-conducting polymer with both high chemical stability and appropriate highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels for photovoltaic application. This system relies on optical

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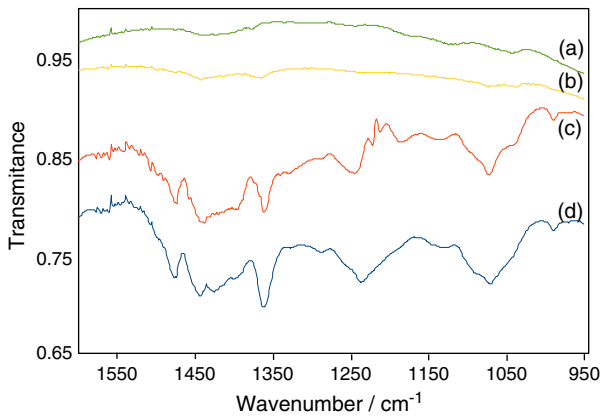


Fig. 1. Fourier Transform Infrared (FTIR) spectra of TiO₂ (a) before (green curve) and after (b) 36 s (yellow curve), (c) 72 s (red curve), (d) 108 s (blue curve) of UV photopolymerization.

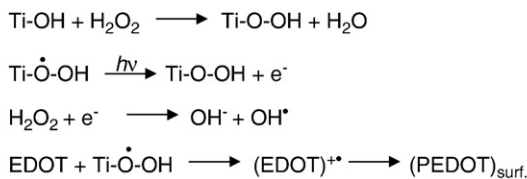
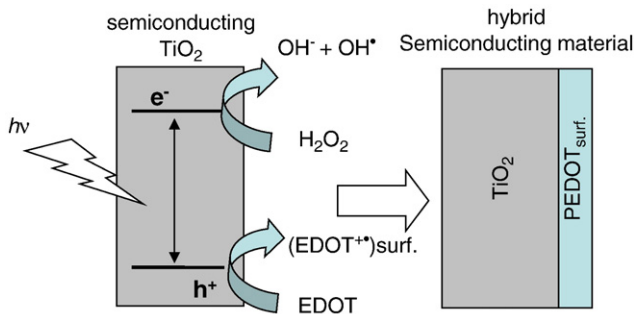
excitation of TiO₂ to generate the oxidative potential necessary to polymerize EDOT monomer (Scheme 1). Photopolymerization of EDOT can occur at any point on the mesoporous TiO₂ surface because both EDOT-containing solution and UV photons penetrate the mesoporous network.

2. Experimental details

2.1. Reagents and experimental techniques

3,4-Ethylenedioxythiophene monomer (Bayer AG) was purified by distillation under reduced pressure and stored in a refrigerator at 4 °C before use. The oxidant, iron trichloride (FeCl₃; Fluka), and stabilizer-free H₂O₂ (Merck) were used as received. The commercially available nanoxide-HT paste (Solaronix®) was used for fabrication of nanoporous TiO₂ layer.

VIS–NIR Reflective (VIS–NIR) absorption spectra were measured between 400 and 1600 nm on a JASCO V570 spectrophotometer using an integrated sphere (diameter 60 mm) at 1000 nm min⁻¹. Infra-red spectra were measured on a BRUKER Vector27 in attenuated total reflectance mode. Atomic force microscopy (AFM) was performed on a Dimension D3100 controlled by a Nanoscope IIIa and a Tuna extension



Scheme 1. Mechanism of photopolymerization reaction.

module (Veeco). The topography and current images were recorded simultaneously in open air with the contact mode using a conducting probe (ElectriCont by BudgetSensor, Cr/Pt coated, spring constant of 0.2 N/m, and a resonant frequency of 13 kHz). The load force was maintained at 2–6 nN to avoid damages to the sample. A +5 V voltage was applied between the tip and the sample, the latter being connected to ground. Electrochemical experiments were carried out in a conventional three-electrode cell in acetonitrile/tetraethylammonium perchlorate (0.1 M). A PGSTAT30 Autolab (Ecochemie, The Netherlands) potentiostat was used for Cyclic Voltamperometry (CV) experiments. CV were performed at $v = 100$ mV/s between -0.5 V and $+0.5$ V using the fluoride tin oxide (FTO) as working electrode, a silver wire as pseudo-reference electrode (Ferrocen is calibrated at 205 mV vs. Ag) and a platinum grid as counter electrode.

The current density–voltage characteristics of the devices were measured from a Keithley 2400 source measurement unit with solar simulator Atlas Solar Constant 575 PV. Under AM1.5 G conditions, the radiant light power was adjusted with respect to a standard reference cell to one-sun intensity (100 mW/cm²).

Thermogravimetric analysis (TGA) has been realized with a TA Instrument Q50 and was done in air at a heating rate of 20 °C mn⁻¹. The pore filling was then calculated as following. Assuming that the PEDOT density is equal to $d_{\text{PEDOT}} = 1.6$ g/cm³ [22], the titanium dioxide density $d_{\text{TiO}_2} = 4$ and the mesoporous TiO₂ (Solaronix®) porosity $\Phi = 0.5$, the pore filling ratio is given by:

$$\text{Pore filling \%} = \frac{V_{\text{PEDOT}}}{V_{\text{pore}}} \times 100 = \frac{\frac{m_{\text{PEDOT}}}{d_{\text{PEDOT}}}}{\Phi \cdot V_{\text{Solaronix}}} \times 100$$

where V_{PEDOT} represents, the PEDOT volume inside the TiO₂ pores. Moreover,

$$V_{\text{Solaronix}} = \frac{m_{\text{TiO}_2}}{d_{\text{TiO}_2} \cdot (1-\Phi)}$$

Then, Eq. (1) is obtained

$$\text{Pore filling \%} = \frac{\frac{m_{\text{PEDOT}}}{d_{\text{PEDOT}}}}{\Phi \cdot \frac{m_{\text{TiO}_2}}{d_{\text{TiO}_2} \cdot (1-\Phi)}} \times 100 \tag{1}$$

The PEDOT weight percentage, X , determined from TGA results, can be expressed by:

$$X = \frac{m_{\text{PEDOT}}}{m_{\text{TiO}_2} + m_{\text{PEDOT}}} \times 100 \tag{2}$$

Eq. (3) results of Eqs. (1) and (2):

$$\text{Pore filling \%} = \frac{X}{\Phi \cdot \frac{100-X}{d_{\text{TiO}_2} \cdot (1-\Phi)}} \times 100 = \frac{X}{0.625 \times (100-X)} \times 100. \tag{3}$$

2.2. Synthesis of PEDOT and TiO₂-PEDOT nanohybrid

The nanohybrids were prepared by a photochemical polymerization of EDOT as follows: initially, the TiO₂ electrode used in this study were fabricated as follows: fluorine doped tin oxide (FTO) coated glass sheets (25 Ω/cm² Solaronix) were etched with zinc powder and HCl (4 N) to give the required electrode pattern. The sheets were subsequently cleaned with soap (2% helmanex in water), distilled water, acetone, ethanol and finally treated under UV illumination for 10 min to remove any organic residues. An ethanol solution of titanium tetra-isopropoxide (Aldrich) containing few drops of HNO₃ (pH = 2), was stirred during

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