**Interfacial engineering affects the photocatalytic activity of poly(3-hexylthiophene)-modified TiO₂**

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In this study, oxidation polymerization was used to synthesize poly(3-hexylthiophene) (P3HT)-modified TiO₂ nanoparticles (NPs) and then the effect of the interface between the TiO₂ NPs and the P3HT coating on the system’s photocatalytic ability under visible light was investigated. The photocatalytic properties of the TiO₂ NPs were enhanced from the UV to the visible after incorporation of P3HT. Moreover, charge transfer between the TiO₂ NPs and the P3HT coating was promoted when a self-assembled monolayer (SAM) of 2-thiophene carboxylic acid was present at their interface; this SAM decreased the barrier for charge transfer between the TiO₂ NPs and the P3HT coating, leading to improved photocatalytic activity under visible light.

**Introduction**

Photocatalysis has emerged as a successful technology for purifying wastewater from industrial sources and from households. Among the many transition metal oxides that exhibit photocatalytic properties,4–6 TiO₂ is a particularly excellent photocatalyst because of its high physical and chemical stability, low cost, high availability, nontoxicity, and unique electronic and optical properties. Nevertheless, electron–hole recombination within TiO₂ nanoparticles (NPs) leads to poor photocatalytic activity. Another issue with TiO₂ is its wide band gap (E_g > 3.2 eV), which limits the application of its particles to photocatalysis under UV irradiation only.5

In recent years, nanocomposites of many conductive polymers and inorganic particles have been prepared that exhibit photocatalytic responses in the visible range. The combination of TiO₂ and a conjugated polymer with suitable energy levels can lead to charge transfer between the polymer and TiO₂ and, thereby, prevent the electron and hole from recombinating. Moreover, when the conjugated polymer acts as an electron donor, its photo-excitation can also produce electron–hole pairs, leading to better use of the solar light over the range from the UV to the visible. TiO₂–polyaniline,6–10 TiO₂–polypyrrole,11,12 TiO₂–P3HT,13–15 and graphitic carbon(n) nitride–polymer16 composites can be synthesized through in situ oxidative polymerization—a simple, rapid method for preparing metal oxide–polymer composites on a large scale. Several problems remain to be solved, however, if we are to improve the photocatalytic activity of TiO₂ composites. The adhesion of the metal oxide to the polymer has generally been the result of physical adsorption, leading to composites having poor stability; in addition, the resistance resulting from the presence of the interface has also been large, thereby disfavoring charge transfer. Only a few researchers have investigated the effects of chemical bonding between TiO₂ and polymers on the photocatalytic activity of their composites.6,17–19

Direct chemical bonding of polymers onto the surfaces of TiO₂ NPs might improve the charge transfer ability and chemical stability of the resulting TiO₂–polymer composites. In this study, therefore, 2-thiophencarboxylic acid was used to form self-assembled monolayers (SAMs) on the surfaces of TiO₂ NPs, thereby allowing subsequent surface oxidative graft polymerization to form dense P3HT layers. To investigate the effect of the SAM on the charge transfer properties, corresponding TiO₂–P3HT composites were also prepared without surface modification.

**Experimental section**

TiO₂–P3HT nanocomposites and dye-sensitized solar cells

TiO₂ powder was stirred in a solution of 2-thiophencarboxylic acid (4 × 10⁻⁴ M) in CHCl₃ for 12 h at room temperature and then filtered off and washed with CHCl₃ to remove any nonbonded 2-thiophencarboxylic acid. In a 100 mL three-necked flask, FeCl₃ (20 mmol) was dissolved in dry CHCl₃ (35 mL) under N₂. The TiO₂ powder featuring SAMs of 2-thiophencarboxylic acid was immersed into the FeCl₃ solution. A solution of 3-hexylthiophene (5 mmol) in dry CHCl₃ (10 mL) was added dropwise; its polymerization occurred while stirring for 24 h at room temperature under N₂. Finally, the TiO₂ composite was filtered off and washed sequentially with CHCl₃.
(to remove any monomeric, oligomeric, and polymeric materials that had not reacted with the SAM of 2-thiophenecarboxylic acid on the TiO$_2$ NPs), MeOH, and deionized water (to remove residual FeCl$_3$). This sample is denoted herein as mTiO$_2$–P3HT. The procedures are displayed in Scheme 1. As a control, neat TiO$_2$–P3HT composite NPs were also prepared through chemical oxidative polymerization of 3-hexylthiophene in the presence of as-received TiO$_2$ particles without SAM pretreatment; these composite NPs are denoted herein as TiO$_2$–P3HT. A thermal plastic spacer (Surlyn1702; thickness: 25 mm; Solaronix S. A., Aubonne, Switzerland) was used to seal the electrodes and control the distance between the two electrodes. The liquid electrolyte was an 3-methoxypropionitrile (MPN) solution containing 0.6 M DMPII, 0.1 M LiI, 0.05 M I$_2$, and 0.5 M TBP. The electrolyte was injected into the space separated by the thermal plastic spacer through a capillary effect. The Pt thin film counter electrode (CE) was sputter-deposited onto an indium tin oxide (ITO) substrate using a Cressington 108 auto sputter coater (Cressington Scientific Instruments, Watford, UK), controlled at 40 mA and 130 s.

**Characterization**

The morphologies of the samples were observed using scanning electron microscopy (SEM, Hitachi S-4700). Chemical compositions were confirmed through Fourier transform infrared (FTIR) spectroscopy. The structures of the TiO$_2$ NPs their composites were measured using X-ray diffraction (XRD). The absorption spectra of the TiO$_2$ composites were recorded using a UV-Vis spectrophotometer (Jasco-V-670) equipped with an integrated sphere. The photocatalytic activities of the obtained nanocomposites were evaluated by monitoring the photo-degradation of methyl orange (MO) in aqueous solution; an aliquot of NPs (10 mg) was dispersed into an aqueous MO solution (2 × 10$^{-4}$ M, 20 mL); while stirring, the mixed solution was irradiated for a certain period and then a portion of the solution (5 mL) was sampled and its absorbance measured. Dye-sensitized solar cells (DSSCs) were energized using a light source comprising a 450 W Xe lamp (#6266, Oriel) equipped with a water-based infrared (IR) filter and an AM 1.5 filter (#81075, Oriel). The TiO$_2$ and P3HT electrodes were characterized using electrochemical impedance spectroscopy (EIS) and a three-electrode system equipped with an FRA2 module in the presence of 1.0 mM redox couples and 0.1 M LiClO$_4$ in an aqueous solution; the impedance spectra were recorded at the formal potential of the redox couple in the frequency range from 0.1 Hz to 1 MHz.

**Results and discussion**

In this study, SAMs and the graft polymerization of 3-hexylthiophene were employed to prepare mTiO$_2$–P3HT hybrid composites. FTIR spectroscopy confirmed the chemical anchoring of the SAMs onto the TiO$_2$ surfaces and the subsequent polymerization of P3HT. Fig. 1 compares the FTIR absorption spectra of the TiO$_2$ NPs, the SAM-coated TiO$_2$ NPs (mTiO$_2$), and the mTiO$_2$–P3HT NPs. The absorption band of TiO$_2$ at 1641 cm$^{-1}$ represents the vibration of its OH groups. The bands at 1510 and 1414 cm$^{-1}$ of mTiO$_2$ originated from the vibrations of the carboxylate groups of the SAM, indicating that 2-thiophenecarboxylic acid had been anchored successfully onto the TiO$_2$ NPs. For the mTiO$_2$–P3HT composite, the absorption bands of the hexyl groups and thiophene rings appeared at 2935 and 1310 cm$^{-1}$, respectively; these new bands provide evidence for the successful graft polymerization of 3-hexylthiophene.

UV-Vis diffuse reflectance spectra were recorded to study the optical response of the mTiO$_2$–P3HT composite. The adsorption edges of pure TiO$_2$ and of the TiO$_2$–P3HT composite appeared at 393 and 657 nm, respectively (Fig. 2a). The absorption plateau for the composite in the region 400–670 nm resulted from the presence of P3HT. Moreover, the absorption spectra of mTiO$_2$–P3HT and TiO$_2$–P3HT were almost identical, suggesting that the SAM had no effect on the optical properties of the composite. The band gap energies of the mTiO$_2$–P3HT nanocomposites were lower than that of the neat TiO$_2$ NPs, allowing the mTiO$_2$–P3HT nanocomposites to be excited to produce electron–hole pairs under visible light and, therefore, to exhibit photocatalytic

![Scheme 1](image)  
**Scheme 1** Preparation of the mTiO$_2$–P3HT composite.

![Fig. 1](image)  
**Fig. 1** FTIR spectra of (a) neat TiO$_2$, (b) mTiO$_2$, and (c) mTiO$_2$–P3HT.
activity under visible light. The loading of P3HT influenced the photocatalytic activity of the nanocomposites. Although the very similar UV-Vis spectra suggested that the P3HT loadings in mTiO2–P3HT and TiO2–P3HT were similar, TGA was performed for further confirmation. Fig. 2b displays TGA curves for TiO2, TiO2–P3HT, and mTiO2–P3HT. The weight losses at temperatures below 200 °C were due mainly to the loss of absorbed H2O. Another stage of weight loss occurred at 310 °C, due to thermal decomposition of P3HT. TiO2–P3HT and mTiO2–P3HT both underwent weight losses of approximately 81% in the range from 30 to 800 °C. Because these two nanocomposites exhibited almost identical TGA curves, their loadings of P3HT were presumably very similar.

Because the morphologies and degrees of aggregation of the NPs will influence their specific surface areas and, therefore, their photocatalytic activities, SEM and XRD were used to investigate the structures of the neat TiO2, TiO2–P3HT, and mTiO2–P3HT. Although all of the NPs had spherical morphologies (Fig. 3), the degree of aggregation of TiO2–P3HT was slightly greater than those of TiO2, and mTiO2–P3HT. This behavior would presumably decrease the contact area between the TiO2–P3HT photocatalyst and MO, leading to weaker photocatalytic activity. The XRD patterns of the prepared composites (Fig. 3) reveal that the degrees of crystallinity of the TiO2–P3HT and mTiO2–P3HT composites were lower than that of the neat TiO2 NPs; the diffraction patterns of the composites were otherwise the same as that of the TiO2 NPs. Therefore, the coating of P3HT on the surface of the TiO2 NPs had no influence on the crystallization of the TiO2 NPs.

To examine the photocatalytic efficiencies of the as-prepared powders, the photodegradation of MO under UV and visible light was investigated at room temperature. Fig. 4a displays the decreases in the concentration of MO with respect to the reaction time for photocatalysis under UV light in the presence of the various samples; all of the samples exhibited similar photocatalytic activities, with MO degrading totally after 180 min. This finding suggests that the coating of P3HT had no effect on the photocatalytic properties of the TiO2 NPs under UV light. Under visible light (Fig. 4b), TiO2 did not degrade MO; its concentration remained constant after 180 min of illumination. In contrast, the TiO2–P3HT and mTiO2–P3HT composites exhibited significant photocatalytic activities under visible light, presumably as a result of excitation of their P3HT units, with subsequent charge transfer between TiO2 and P3HT expanding the range of suitable wavelengths of solar light. Hence, P3HT functioned as a sensitizer for TiO2. After illumination with visible light for 180 min, the absorbance intensity of MO at 463 nm decreased from 0.82 to 0.47 in the presence of TiO2–P3HT and to 0.3 in the presence of mTiO2–P3HT. The greater photocatalytic activity of mTiO2–P3HT was presumably due to the structure at its interface: the SAM presumably decreased the barrier for charge transfer between P3HT and TiO2, leading to improved performance. Fig. 4c presents the UV-Vis spectra of MO recorded after various illumination times. The intensities of the signals in these spectra decreased upon increasing the irradiation time, but without any changes in their shape, suggesting that MO had decomposed completely without forming any intermediates. The results of these photocatalytic tests imply a photocatalytic mechanism under visible light that can be explained by the energy diagram in Fig. 4d. When the mTiO2–P3HT composite was illuminated under
visible light, both TiO2 and P3HT absorbed the photons at their interface, where charge separation then occurred. Because the conduction band of TiO2 and the energy level of the lowest unoccupied molecular orbital (LUMO) of P3HT are well matched for charge transfer, the electrons that were promoted through $\pi$-$\pi^*$ absorption of the outer P3HT film under visible light were readily injected into the conduction band of the inner TiO2 NPs; in contrast, electrons in the valence band of TiO2 were transferred into the P3HT, leaving holes behind. Therefore, the excited-state electrons were injected readily into the conduction band of TiO2 and transferred to the nanocomposite surface to react with O2 to yield superoxide radicals $\cdot$O2/$\cdot$O2$^-$. At the same time, positively charged holes ($h^+$) were formed by electrons migrating from the TiO2 valence band to the P3HT $\pi$-orbital; they reacted with OH$^-$ or H2O to generate $\cdot$OH. These two radicals, $\cdot$O2$^-$ and $\cdot$OH, were responsible for the degradation of MO. Thus, charge transfer between P3HT and TiO2 expanded the range of solar light available for the TiO2 photocatalyst from the UV to the visible.

To further investigate the mechanism behind the visible-light photocatalytic activity of the mTiO2–P3HT composite, DSSCs incorporating mTiO2–P3HT were fabricated to study the effect of P3HT on the photocurrent. Compared with the performance of the neat TiO2 electrode, the photocurrent increased after incorporation of P3HT (Fig. 5a) as a result of excitation of the P3HT units.31 Moreover, the DSSC incorporating mTiO2–P3HT exhibited a photocurrent higher than that of the TiO2–P3HT-containing electrode, presumably because the better quality of the interface between the TiO2 and P3HT led to more-efficient charge transfer. This result is consistent with the tested photocatalytic activities under visible light. Fig. 5b presents the monochromatic incident photon-to-electron conversion efficiency (IPCEs) of the DSSCs. The IPCE of TiO2–P3HT was wider than that of neat TiO2, again due to the absorption of P3HT. Furthermore, the IPCE of mTiO2–P3HT was higher than that of TiO2–P3HT as a result of the higher quality of its interface.

To investigate the kinetics of electron transfer at the TiO2–P3HT interface, the polymer films were characterized using EIS. Fig. 6 displays the impedance spectra of the polymer films characterized under 1.0 mM Fe(CN)$_6^{3-}$/Fe(CN)$_6^{4-}$ and 0.1 M LiClO$_4$ as the supporting electrolyte. The semicircle of TiO2–P3HT is smaller than that of TiO2, suggesting that the TiO2–P3HT composite featured a smaller charge transfer resistance ($R_{ct}$) contributed from the highly conductive P3HT. Moreover, the value of $R_{ct}$ decreased further after modification of the interface between TiO2 and P3HT; that is, the EIS spectrum of mTiO2–P3HT featured the smallest semicircle among the three tested systems. This finding is consistent with the interfacial modification promoting charge transfer between TiO2 and P3HT, leading to a lower value of $R_{ct}$.

Conclusions

TiO2–P3HT nanocomposites have been prepared through oxidative polymerization. The coating of P3HT on the TiO2 NPs expanded the range of useable solar light from the UV to the visible. To improve the quality of the interface between TiO2 and...
P3HT, 2-thiophenecarboxylic acid was used to form a SAM on the surface of the TiO2 NPs. The resulting SAM-containing TiO2–P3HT composite exhibited superior photocatalytic activity under visible light; this enhanced performance can be attributed to the lower energy barrier for charge transfer between the TiO2 NPs and the P3HT coating.

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