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Optical properties of poly(3-hexylthiophene) and interfacial charge transfer between poly(3-hexylthiophene) and titanium dioxide in composites

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ABSTRACT

The optical properties of poly(3-hexylthiophene) (P3HT), in pristine form or with added anatase titanium dioxide (TiO₂) nanoparticles have been investigated, and the interfacial charge transfer between P3HT and TiO₂ have been studied by steady-state luminescence spectroscopy analysis. The photoluminescence results revealed that incorporation of TiO₂ nanoparticles in concentrations up to 0.3 mM significantly enhanced the luminescence intensity of P3HT when exposing to light of energy higher than TiO₂ bandgap. The observed variation suggested an energy transfer from TiO₂ nanoparticles to P3HT. Meanwhile, when P3HT/TiO₂ composites were exposed to light of energy below TiO₂ bandgap, TiO₂ nanoparticles gradually quench the fluorescence of P3HT, demonstrating the injection of excited electrons from lowest unoccupied molecular orbit of P3HT to the conduction band of TiO₂.

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1. Introduction

Poly(3-hexyl thiophene) (P3HT), as a typical conjugated polymer with wide sunlight absorption range, outstanding flexibility, low density and relatively high photostability, has significant advantages over inorganic semiconductors for making large scale solar-energy related productions, including photovoltaic cells and photocatalysts [1,2]. However, the efficiency of P3HT for converting solar energy is relatively low as compared to its inorganic counterpart [3]. So far, incorporation of inorganic semiconductors, like titanium dioxide (TiO₂) into P3HT has been proved to be very promising for using solar energy by combining the advantages from both conjugated polymers and inorganic semiconductors, and P3HT/TiO₂-based hybrid photocatalysts might be one of the most exceptional examples. Previous investigations in our group [4–6] revealed that the photo-responding range of P3HT/TiO₂ composites was successfully extended to the visible part of solar spectrum, leading to an enhancement of the photo-degradation performance. Meanwhile, other conjugated polymers/inorganic composites also show excellent photocatalytic performance [7–9]

in degrading organic pollutants. For a given conjugated polymers/TiO₂ composite system, the optical absorption and emission behavior of the conjugated polymers and the interfacial charge transfer between the conjugated polymers and the TiO₂ will strongly affect the photocatalytic performance of the composites. Although a few investigations exist for understanding interfacial phenomena such as charge traps and interfacial dipoles in TiO₂-P3HT-based hybrid solar cell devices [10], the energy and charge-transfer mechanisms at the polymer-inorganic interface are still under active investigation and hence the affection of the interfacial charge/energy transfer processes on the photocatalytic performance is not well elucidated so far.

Focusing on the optical behavior, the present paper will investigate the optical absorption and emission properties of the P3HT, and then the influence of TiO₂ on the optical behavior of P3HT by using UV-vis absorption and steady-state luminescence spectroscopy analyses to gain fundamental understanding of the energy and charge-transfer mechanisms between the conjugated polymer and the inorganic nanoparticles.

2. Experimental

Anatase titanium dioxide (HR-3) with an average diameter of 15 nm was purchased from Zhoushan Minri Nanometer Material Co., Ltd. (Zhoushan, China). The P3HT polymer was prepared by a

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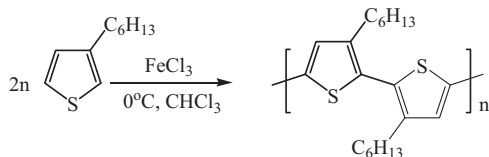
typical in-situ chemical oxidative polymerization of 3-hexylthiophene, using anhydrous FeCl_3 as catalyst [11]. The polymer was dissolved in chlorobenzene to form solution with a concentration of 40–500 mg/L. Composite samples were prepared by adding TiO_2 nanoparticles to P3HT solutions, followed by an ultrasonic bath for 1 h to improve the dispersion of nanoparticles. UV-visible absorption spectra of the chlorobenzene solution of P3HT and P3HT/ TiO_2 composites were recorded on a Shimadzu UV2100 UV-vis spectrophotometer (UV2100, Shimadzu, Japan). Steady state photoluminescence (PL) spectra were collected from a fluorescence spectrophotometer (F4600, Hitachi, Japan) using a xenon lamp (500 W) as the excitation source at room temperature.

3. Results and discussion

3.1. Synthesis and optical properties of P3HT

3.1.1. Synthesis

As shown in schematic representation in Scheme 1, P3HT was prepared by a typical in-situ chemical oxidative polymerization of 3-hexylthiophene in chloroform at 0 °C using anhydrous FeCl_3 as catalyst. The as-prepared P3HT powder was further reduced by extracting with refluxing methanol [12]. And after 72 h extraction, the color of P3HT powder changed from black to red, indicating the reduction of P3HT from oxidized state to neutral (undoped) state. The chemical structure of P3HT was studied by solution 400 MHz ^1H NMR spectroscopy, and the chemical shift bands and their assignments are shown in Fig. 1. Chemical shift data were found to be in agreement with those reported in the literature [13]. Meanwhile, multi-chemical shift bands for the proton in the 4-position of the thiophene ring are observed in the ^1H NMR spectrum (δ , 6.97–7.06, g-proton in Fig. 1), indicating that the thiophene proton bears multi different chemical environments. As the thiophene proton is very sensitive to the substitution pattern



Scheme 1. Schematic representation of the process for polymerization of 3-hexylthiophene.

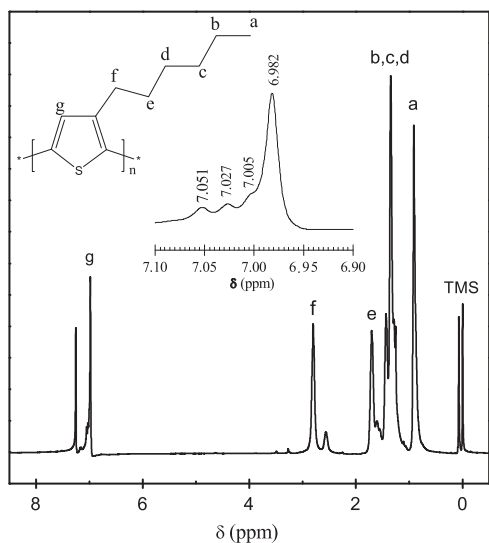


Fig. 1. ^1H NMR spectrum of P3HT.

in the polymer backbone [14,15], the result clearly demonstrates that the as-prepared P3HT had a regiorandom chain structure. The molecular weights and corresponding polydispersity index of P3HT were determined (relative to polystyrene standard) by gel permeation chromatography in chloroform, and the GPC curve (Fig. 2) shows that the M_n and PDI of the as-prepared P3HT were 2.55×10^4 g/mol and 2.96, respectively.

3.1.2. Optical properties

The UV-vis and fluorescence spectra of P3HT in chlorobenzene are shown in Fig. 3. It can be clearly seen that the chlorobenzene solution of P3HT has a long wavelength absorption band in the range from 250 nm to 575 nm with a maximum absorption at 433 nm for the π - π^* transition. Thus, either light in the ultraviolet region (below 400 nm) or visible light below 575 nm can excite P3HT. In order to examine the influence of the excitation energy on the photoluminescence of P3HT, the emission spectrum of P3HT in chlorobenzene solution excited at 275 nm is depicted in Fig. 3. Meanwhile, the emission spectrum of P3HT excited at 400 nm is also shown in Fig. 3. Comparing the PL properties of P3HT after excitation at various wavelengths, it can be seen that the maximum of the conjugated polymer-derived photoemission did not significantly change by using excitation at either 275 nm or 400 nm. The consistent energy of PL emission may be due to the relative conjugated length of as-prepared P3HT chains as well as the aggregation state and conformation of P3HT chain in chlorobenzene solution [16,17]. Conversely, the intensity of the PL

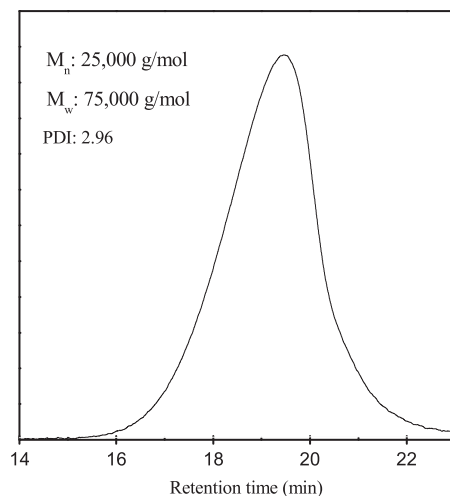


Fig. 2. GPC curve of P3HT.

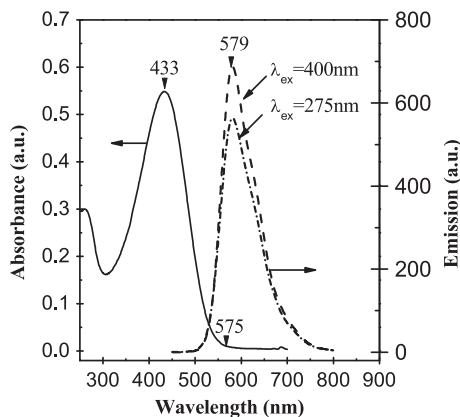


Fig. 3. UV-vis absorption and fluorescence emission spectra of chlorobenzene solution of P3HT (80 mg/L). (—): UV-vis; (---): fluorescence.

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