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Graphene oxide quantum dot-sensitized porous titanium dioxide microsphere: Visible-light-driven photocatalyst based on energy band engineering

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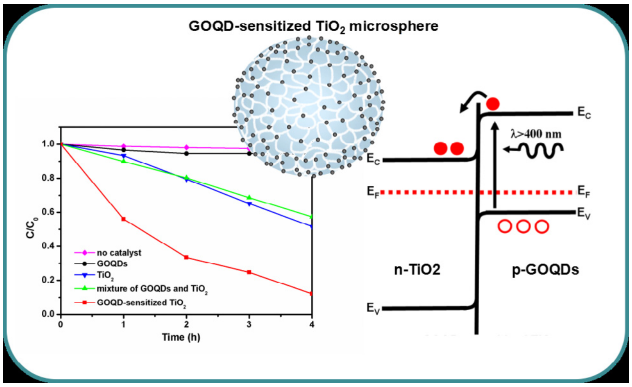
GRAPHICAL ABSTRACT



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ABSTRACT

We report a novel graphene oxide quantum dot (GOQD)-sensitized porous TiO_2 microsphere for efficient photoelectric conversion. Electro-chemical analysis along with the Mott-Schottky equation reveals conductivity type and energy band structure of the two semiconductors. Based on their energy band structures, visible light-induced electrons can transfer from the p-type GOQD to the n-type TiO_2. Enhanced photocurrent and photocatalytic activity in visible light further confirm the enhanced separation of electrons and holes in the nanocomposite.

1. Introduction

Solar energy harvesting through photoelectric conversion on semiconductor has attracted much attention due to the rising energy crisis and environmental issues [1–8]. Over the past years, TiO_2 and ZnO have been widely studied in solar cells and photocatalysis due to their excellent photoelectric properties [9–17]. However, the wide band gap energy of TiO_2 and ZnO, >3.0 eV, greatly hindered them to utilize the largest proportion of the solar spectrum. To develop efficient visible-light active photoelectric materials, one promising way is the construction of heterogeneous structure coupling the wide-band-gap semiconductors with those of narrow band gap, which can generate electrons and holes by

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absorbing visible light. If two coupled semiconductors have matched energy band structures, photoinduced electrons and holes would be promisingly separated through the heterostructure interface [18–20].

Semiconductor quantum dots (QDs) sensitization is considered to be a good way to prepare heterogeneous structure. There are some specific advantages in using quantum dots as light harvesting media [21–23]. Firstly, the energy band of quantum dots can be adjusted by controlling the particle size due to quantum size effect, thus the energy band engineering can be implemented. Secondly, there is a high area of interface that can be constructed between the two semiconductors, resulting in enhanced separation of photoinduced electrons and holes. Thirdly, it has been shown that the QDs can generate multiple charge carriers with a single photon. Inorganic QDs including CdS, CdSe CdTe, PbS, InP have been used to sensitize TiO_2 or ZnO for improving efficiency [24–28]. However, their toxicity and hazardous nature are serious impediments for large-scale device applications. Therefore, benign and green semiconductor quantum dots with similar properties are needed.

Graphene oxide (GO) is a graphene compound with a basal plane, immense surface area and an edge bearing oxygen functionalities [29,30]. Electronic structural analysis reveals that GO has conduction band minimum (CBM) and valence band maximum (VBM) levels which are suitable for photoelectric conversion. Among graphene nanostructures, quantum-sized GO as semiconductors will also possess quantum size effect [31,32]. Thus, the graphene oxide quantum dot (GOQD) would be a green sensitizer when comparing to conventional toxic and hazardous QDs. Recently, Yeh et al. have studied the energy band structure and photocatalytic properties of N-doped GOQDs [33]. They found that N-doping resulted in the formation of p-n type photochemical diodes, in which the n-conductivity was caused by embedding nitrogen atoms, and the p-conductivity by oxygen functionalities. The p-n type photochemical diodes will benefit the separation of photogenerated electrons and holes in the photocatalytic reaction. Long et al. made a theoretical investigation on the interfacial electronic structure and charge transfer properties of GOQDs adsorption on the TiO_2 surface [34]. They confirmed that the work function difference can drive electron transfer from GOQD into TiO_2, leading to charge separation across the GOQD–TiO_2 interface. In light of these results, nanostructures based on p-type GOQDs-sensitized TiO_2 might be constructed as a promising photoelectric material. In this work, we report a p-type GOQD-sensitized TiO_2 with porous and micro spherical structure. The porous structure of TiO_2 could load QDs more sufficiently and uniformly. In addition, the energy band structures of p-type GOQDs and n-type TiO_2 were confirmed to be matched. The as-prepared sample showed enhanced photocurrent and photocatalytic activity under visible light illumination.

2. Experimental

2.1. Synthesis of GOQDs

GOQDs were prepared from Vulcan CX-72 carbon black by refluxed with concentrated nitric acid [35]. 0.25 g of CX-72 carbon black was put into 50 mL (6 mol/L) HNO_3, which was followed by refluxing for 24 h. After cooling to room temperature, the suspension was centrifuged for 20 min to obtain sediment, which was washed with 1 M HCl followed by centrifuging three times and then drying under vacuum. While the dried sample was dissolved in 50 mL H_2O, the solution was centrifuged for 30 min to obtain a reddish-brown supernatant. Finally the supernatant was ultrafiltered through a centrifugal filter device with a 100 kDa molecular weight cut off membrane. The filtrate was collected and dried.

2.2. Synthesis of porous TiO_2 microspheres

TiO_2 porous microspheres were synthesized according to our previous method [36]. Tetrabutyltitanate was utilized as a Ti source. 1 mL of tetrabutyl titanate (Sinopharm Chemical Reagent Co., ≥98.0%) was put into 25 mL ethylene glycol (Sinopharm Chemical Reagent Co.) in a flask under vigorously stirring. At the same time, the system was bubbled with nitrogen for about 10 min to remove oxygen and water. Then, the system was sealed tightly with parafilm and stirred for 24 h. After that, the above solution was poured into an acetone bath (100 mL) containing 1 mL ultrapure water, then under vigorous stirring for 10 min. After aging for about 16 h at 25 °C, titanium glycolate microspheres were obtained by centrifugation, and washed with acetone and absolute alcohol for 5 times to remove residual ethylene glycol from the surface of the titanium glycolate microspheres. After the washing treatment, the samples were dried at 40 °C for 12 h.

1 g of the dried titanium glycolate microspheres was dispersed in 80 ml of deionized water and transferred into a Teflon-lined stainless steel autoclave. The autoclave was sealed and placed in an oven at 180 °C for 4 h. After the hydrothermal reaction, the autoclave was taken out and cooled down to room temperature. The white precipitate was harvested by centrifugation and then was washed with deionized water and ethanol several times. At last, the samples were dried at 50 °C overnight for characterization and preparation of electrodes.

2.3. Preparation of GOQDs-sensitized TiO_2 porous microsphere

In a typical procedure to synthesize GOQDs/TiO_2, GOQDs (1 mg/mL) were dissolved in distilled water under stirring. A stable aqueous dispersion of GOQDs was obtained. Then, 50 mg of TiO_2 porous microsphere were added into the solution under stirring for 5 h. The obtained sample was separated by centrifuge, washed with distilled water and dried at 45 °C in air. Residual GOQDs will stay in the solution due to its water soluble character.

2.4. Characterization

The transmission electron microscopic (TEM) imaging was performed on a HITACHI H-7650 microscope. Scanning electron microscopy (SEM) and EDX spectra were carried out using a FESEM JSM-6700F microscope. The optical absorption measurements were performed in an UV–vis spectrophotometer (Shimadzu UV–2550). An SDT Q600 Simultaneous DSC-TGA instrument (TA Corp., USA) was used to investigate the thermal stability of the nanocomposites in the temperature range from room temperature to 990 °C under air atmosphere at a rate of 10.0 °C min^{-1}. The FTIR spectra were recorded on a Perkin Elmer 1600 FT-IR Spectrophotometer. The zeta-potential data were obtained by using a Zeta-Plus4 instrument (Brookhaven Corp., USA).The photocatalytic activity of the samples was estimated by the degradation of Rhodamine B (RhB) in an aqueous solution (20 mL, 20 mg L^{-1}) under visible irradiation. A 500 W xenon lamp (CHFXQ500W, Beijing Trusttech Co. Ltd) was used as the light source, and a filter plate ($\lambda > 400$ nm) (Beijing Trusttech Co. Ltd) was used to control the wavelength of light. The photocatalyst powder (0.025 g) was dispersed in 20 mL of the RhB solution and sonicated for 15 min to break-up the agglomerates. Before visible irradiation, the suspension was stirred magnetically in the dark for 1 h to reach an equilibrium state. After visible irradiation, one-milliliter aliquots were taken at certain time intervals (30 min) and centrifuged to separate the particles from the solution. The decomposition of RhB was monitored using a UV–Vis spectrometer (Lambda Bio20, Perkin Elmer). The photocurrent experiment has been used to describe the mechanism of photocatalytic reaction. Doctor-blade technique