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Regular Article

Quasi-noble-metal graphene quantum dots deposited stannic oxide with oxygen vacancies: Synthesis and enhanced photocatalytic properties

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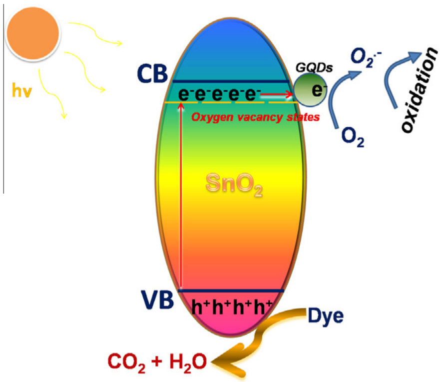
GRAPHICAL ABSTRACT

The nanocomposite photocatalysts of quasi-noble-metal graphene quantum dots (GQDs) deposited SnO_2 with oxygen vacancies (VOs) were prepared through a simple two-step reactions process. The obtained nanocomposites exhibited much enhanced photodegradation activity for the extended visible-light response as well as raised charge-separation efficiency.



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ABSTRACT

Quasi-noble-metal graphene quantum dots (GQDs) deposited stannic oxide (SnO_2) with oxygen vacancies (VOs) were prepared by simply sintering SnO_2 and citric acid (CA) together. The redox process between SnO_2 and GQDs shows the formation of oxygen vacancy states below the conduction band of stannic oxide. The produced VOs obviously extend the optical absorption region of SnO_2 to the visible-light region. Meanwhile, GQDs can effectively improve the charge-separation efficiency via a quasi function like noble metal and promote the visible-light response to some degree. In addition, the samples calcinated at 450 °C reveals the best performance because of its relatively high concentrations of VOs. What is more, the possible degradation mechanism has been inferred as extended visible-light response as well as raised charge-separation efficiency has also been put forward. Our work may offer a simple strategy to combine the defect modulation and noble metal deposition simultaneously for efficient photocatalysis.

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1. Introduction

Semiconductor photocatalysis has been widely regarded as a kind of potential technique which considerably meets the requirements for the current issues on environment and energy [1–3]. Earlier work done by Markham and co-workers described the phenomena of catalytic oxidation of organic compounds under UV light by some metal oxides like ZnO, Sb_2O_3, and TiO_2. Decades of research have been carried on to answer many of the fundamental questions in regard to the intricacies of semiconductor photocatalysis [4–8]. However, the intrinsic issues of semiconductor photocatalysis still exist, and an ideal photocatalyst should own both a wide photo-absorption range and a low recombination rate of the photogenerated charge carriers [9–11].

Generally speaking, there are plenty of strategies to extend the scope of light response and increase the separation efficiency of electron-hole pairs such as doping elements, defect engineering, noble metal deposition, coupling semiconductors with narrow-band semiconductors to form hybrid heterojunctions or composite [12–14]. Among these approaches, defect modulation has been regarded as an effective method to elongate photoresponse range which can be achieved by several synthetic approaches including doping with other elements, thermal treatment under oxygen depleted conditions, high energy bombardment and self-doping by reduction treatment [15,16]. Recently, self-doped semiconductor photocatalysts has attracted much attention. Ti^{3+}-doped TiO_2 has been reported to show visible-light absorption and enhanced photocatalytic activity. It has been verified that the Ti^{3+} species induced Ov states between the valance and the conduction bands is responsible for the ideal separation efficiency of photogenerated electron-hole pairs. In addition, the corresponding metal ion defects also extend the optical absorption of wide-bandgap semiconductors into the visible region [17–20]. Moreover, to reduce the recombination rate of the photogenerated charge carriers, depositing of noble metal is commonly used. Lately, GQDs has received much attention. Compared with two-dimensional graphene nanosheets and one dimensional nanoribbons, zero-dimensional GQDs possess strong quantum confinement and edge effects when their sizes are down to 10 nm, which induce new physical properties. Hence, GQDs can be applied in many fields, such as photovoltaics, light-emitting diodes, and photocatalysis [21–23]. What is more, GQDs is quite cheap compared with noble metal like Pt, Pd, Ag which can affect the nature of the surface of semiconductor via altering the distribution of electron. Schottky barrier formed in the interface of GQDs and semiconductor captures excites electron and prevents the recombination of electron-hole pairs, thus improving the photocatalytic activities. Though there are numerous reports on defect modulation or depositing of noble metal [24,25], the reports integrating both two catalytic mechanisms of oxygen vacancies and GQDs-replacement noble metal together are rarely.

In this study, SnO_2 was selected which has been widely used in photocatalysis, sensors, detectors, and solar cells [26,27] due to its low cost, nontoxicity, commercial availability and excellent chemical stability. Nevertheless, SnO_2 is a poor absorber of photons in the visible portion of the solar spectrum limited by the wide energy band gap (3.6 eV at 300 K). Hence we employed a simple process to realize the integration of SnO_2 and GQDs and the reduction of SnO_2 by GQDs, which are produced by pyrolyzing of citric acid (CA). Oxygen vacancies (VOs) are generated after the redox reaction, meanwhile GQDs remain in the GQDs@SnO_2 composite, taking part in the photocatalysis process. Thus we successfully accomplish a combination of two types to enhance photocatalytic performance in one semiconductor. Obviously, the GQDs@SnO_2-VOs nanocomposites ameliorated with dual modifying mechanisms exhibit much enhanced photodegradation activity of methylene blue than bare one. Additionally, experiment parameters have been optimized and the mechanism of enhancement of photocatalytic activity is also discussed in detail.

2. Experimental

2.1. Catalyst synthesis

2.1.1. Preparation of SnO_2 nanorods

All the reagents were of analytical grade and used without further purification. The SnO_2 nanorods were prepared by a simple hydrothermal method. In the typical synthesis, 6 mmol sodium stannate (Na_2SnO_3) was dissolved in 20 mL deionized water under magnetic stirring. After stirring for 30 min at room temperature, 60 mL absolute ethyl alcohol was slowly added, stirring for 60 min. Then the above solution was transferred into a dried Teflon-lined stainless steel autoclave with a capacity of 100 mL at ambient temperature, followed by hydrothermal treatment of the mixture at 210 °C for 48 h. After hydrothermal reaction, the white precipitate was collected by centrifuge, washed with deionized water and ethyl alcohol for three times, and then dried in an oven at 60 °C for 24 h.

2.1.2. Preparation of GQDs@SnO_2-VOs nanocomposites

The SnO_2-GQDs nanocomposites were synthesized firstly by calcining the mixtures of SnO_2 and citric acid. To put it simply, SnO_2 powder was mixed with CA by a mass ratio of SnO_2 to CA (5/1) in the compound. Then, the mixture was transferred to a crucible and calcinated at 200 °C for 3 h in the air. After the pyrolytic reaction of CA, the SnO_2/GQDs nanocomposites were obtained. Afterwards, the gained powder was calcinated in the nitrogen gas environment in a muffle furnace. A typical reduction reaction between GQDs and SnO_2 occurred during the process. To explore the effect of the concentration of VOs generated in the reduction course on the photocatalytic performance of SnO_2, SnO_2-GQDs nanocomposites was calcinated at different temperature (350 °C, 450 °C, 550 °C, 650 °C) in the nitrogen gas environment. The obtained materials were labeled as GQDs@SnO_2-VOs-3, GQDs@SnO_2-VOs-4, GQDs@SnO_2-VOs-5 and GQDs@SnO_2-VOs-6, respectively.

2.2. Characterization

Structural properties of all the samples were carried out using X-ray diffraction (XRD) with an X-ray diffractometer (XRD, Bruker D8 ADVANCE) equipped with X'Pert High Score under Cu Kα (λ = 1.5405 Å) radiation. The X-ray machine was operated at 45 kV whereas the scanning range of (2θ) was from 10° to 90°. Morphological studies of the synthesized materials were performed by high resolution transmission electron microscopy (HRTEM, JEOL JSM-2010). UV–vis absorption spectrum was obtained using a UV–vis spectrometer (Shimadzu UV-3600). Raman spectra were recorded on a Raman spectrometer (Renishaw InVia). Electron paramagnetic resonance spectra (EPR) were recorded at 110 K on a Bruker EMX-10/12 EPR spectrometer. Thermogravimetric analysis (TG) was conducted using a Pyris 1 DSC analyzer (PerkineElmer).

2.3. Photocatalytic activity measurement

Photodegradation experiments were carried out in a 250 mL beaker with 0.1 g photocatalysts and solution of MB (7.5 ppm, 200 mL). Before exposure to UV–vis light irradiation, the suspension was stirred in the dark for 30 min, thereby establishing absorption-desorption equilibrium between the organic molecules