Chemical Engineering Journal 218 (2013) 73–80

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Synthesis, characterization, and visible photocatalytic performance of Zn_2GeO_4 nanobelts modified by CdS quantum dots

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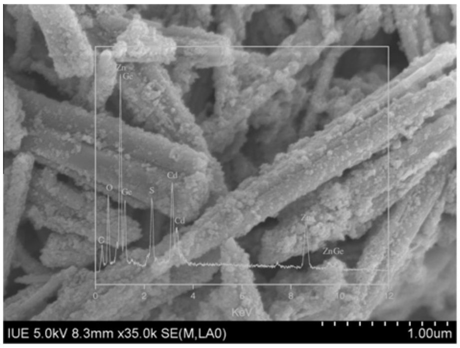
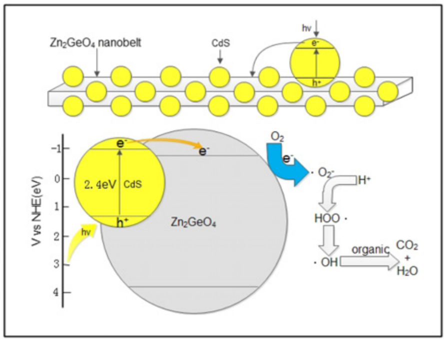
HIGHLIGHTS

- The first example of quantum dots to sensitize the photocatalyst of Zn_2GeO_4.
- Zn_2GeO_4/CdS exhibited higher photocatalytic activity under visible light.
- The composite shows no obvious deactivation after three recycles experiments.

GRAPHICAL ABSTRACT

Zn_2GeO_4 nanobelts modified by CdS quantum dots (Zn_2GeO_4/CdS) were prepared successfully by chemical bath deposition. The as-obtained samples demonstrated high photocatalytic performance to decolorize dye wastewater under visible light irradiation ($\lambda > 400$ nm).





ARTICLE INFO

Article history:
Received 7 August 2012
Received in revised form 16 November 2012
Accepted 10 December 2012
Available online 19 December 2012

Keywords:
Zn_2GeO_4
CdS
Photocatalysis
Visible light
Rhodamine B

ABSTRACT

Zn_2GeO_4 nanobelts modified by CdS quantum dots (Zn_2GeO_4/CdS) were prepared successfully by chemical bath deposition. The novel photocatalyst was characterized by X-ray diffraction, scanning electron microscopy, X-ray photoelectron spectroscopy and UV–Vis diffuse reflectance spectroscopy. It was found that Zn_2GeO_4/CdS consisted of uniform rhombohedral phase Zn_2GeO_4 nanobelts with highly dispersed cubic phase CdS quantum dots, and the Zn_2GeO_4/CdS exhibited strong visible light absorption at about 510 nm. The photocatalytic activities of the catalysts were evaluated by the discoloration of Rhodamine B under visible light illumination and were compared with that of pure Zn_2GeO_4 nanobelts. The results suggested that the composite photocatalyst had much higher photocatalytic activities than pure Zn_2GeO_4 nanobelts under irradiation of visible light. Meanwhile, no obvious deactivation of Zn_2GeO_4/CdS was observed after the three recycles experiments in photodegradation of RhB. The possible mechanism of visible light photocatalytic degradation is also proposed.

1. Introduction

For past decades, the research of various photocatalytic materials has attracted much attention due to their potential application in clean energy sources and degradation of environmental pollutants [1–3]. Currently, TiO_2 is undoubtedly the most widely used photocatalyst because of its biological and chemical stability, non-toxicity, cost effectiveness and high activity [4–6]. However, it still involved some disadvantages, such as limited activity and reduced sensitivity to the visible region of sunlight [7]. Therefore, recently new photocatalysts have been extremely explored that

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http://dx.doi.org/10.1016/j.cej.2012.12.031

may overcome the limitation of TiO_2. To this end, many non-TiO_2 photocatalysts were developed with the appropriate band gap and high quantum yield, such as red P [8], S [9], Ag_2CO_3 [10], BiOI/BiOBr [11], Bi_2WO_6 [12] $BiYWO_6$ [13], GaN [14], V_2O_5/Al_2O_3 [15], ZnO/SnO_2 [16] and (CuO, Pt)/WO_3 [17]. Recently, the Zn_2GeO_4 has been reported as a promising photocatalyst to degrade organic pollutant [18–20]. Unfortunately, Zn_2GeO_4 with a wide band gap of 4.68 eV [21,22] still can only response to high-energy UV light. It is well known that less than 5% of the solar spectrum is UV light. In contrast, about 45% of the solar spectrum is visible light. Therefore, the modification of Zn_2GeO_4 is necessary towards its practical applications in the environmental and chemical engineering.

Though noble metal has been deposited on the Zn_2GeO_4 to improve the photocatalysis due to better electron–hole separation of composite under irradiation of UV light [13–15,23–25], in order to improve activities more efficiently, some promising approaches have also been developed to tune the visible-light response of Zn_2GeO_4, which include non-metal atom doped [26–28]. Coupled with a smaller band gap semiconductor with a more negative conduction band (CB) level has been verified as an efficient way to extend the response of wide band gap semiconductor to visible light [29]. In this way, the charges from the CB of smaller band gap semiconductor can be injected into that of the wide band gap semiconductor, which could improve the efficiency of separation of photogenerated electron–hole pairs as well as the photocatalytic activity. Until now, a number of quantum dots (QDs), such as CdS [30–33], CdSe [34,35], PbS [36,37], ZnS [38], $Zn_xCd_{1-x}S$ [39] have been attempted to sensitize wide band gap semiconductor, such as TiO_2. The response of the resulted composite photocatalyst can be extended to the visible light and even near infrared light by this assembly. It was reported that the composites not only overcome the disadvantages of the individual components but also induce a synergistic effect, such as reduce of recombination probability of electrons and holes pairs and enhancement of photostability [40]. Very recently, we reported the assembly of CdS QDs onto the TiO_2 nanotubes, and the excellent photocatalytic activity and stability of the composites have been proved [41]. However, to the best of our knowledge, so far there is no report of any kinds of QDs to sensitize the photocatalyst of Zn_2GeO_4. Herein, in order to extend the response of Zn_2GeO_4 to visible light, a facile and straightforward approach has been demonstrated to synthesize the nanocomposites photocatalyst Zn_2GeO_4/CdS with Zn_2GeO_4 nanobelts decorated by CdS QDs employing a sequential chemical bath deposition (CBD) method. The as-prepared photocatalyst has been characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and UV–Vis diffuse reflectance spectroscopy (UV–Vis DRS). The visible-photocatalytic activity has also been evaluated by use of rhodamine B (RhB) as a pollutant model. The experiment results suggested that the CdS QDs defined as cubic CdS phase were deposited on Zn_2GeO_4 nanobelts successfully and the Zn_2GeO_4 nanobelts coupled with CdS QDs showed a high photocatalytic activity under visible light. Meanwhile, the mechanism of photocatalysis of Zn_2GeO_4/CdS under visible light was also proposed.

2. Material and methods

2.1. Chemicals

GeO_2 (⩾99.999%) and cadmium nitrate tetrahydrate (AR) were purchased from Aladdin, $Zn(CH_3COO)_2{\cdot}2H_2O$ (⩾99.0%), sodium sulfide nonahydrate (⩾98%), rhodamine B (AR) and ethylenediamine (⩾99.0%) were purchased from Sinopharm Chemical Reagent. All the reagents are used without any further purification.

2.2. Synthesis of Zn_2GeO_4 nanobelts

The Zn_2GeO_4 nanobelts were prepared using a hydrothermal synthesis reported previously [24]. In a typical synthesis, GeO_2 (0.312 g) and $Zn(CH_3COO)_2{\cdot}2H_2O$ (0.66 g, molar ratio of Zn to Ge is 2:1) were added to mixed solvents comprised of 3 mL deionized water and 6 ml ethylenediamine. After being stirred (300 r/min) for 40 min, the mixture was transferred to a stainless Teflon-lined autoclave with 25 mL inner volume. The solvothermal synthesis was performed under an auto-generated pressure at 180 °C for 36 h, followed by cooling to room temperature naturally. The product was collected by centrifugation (13800g), washed thoroughly with deionized water and alcohol several times, and then dried at 60 °C overnight. A white Zn_2GeO_4 powder was finally obtained and denoted as ZC-0 (pure Zn_2GeO_4 nanobelts).

2.3. Deposition of CdS QDs on Zn_2GeO_4 nanobelts

CdS QDs were deposited on Zn_2GeO_4 nanobelts employing a sequential chemical bath deposition (CBD) method. Typically, the Zn_2GeO_4 nanobelts were immersed in a solution of $Cd(NO_3)_2$ (0.005 M) and sonicated for 5 min, then rinsed with deionized water until no Cd^{2+} in supernatant detected, then immersed in a Na_2S (0.005 M) solution (pH = 10.00) for another 5 min followed by another rinsing with deionized water, and then a yellow product was obtained. The ration of Cd^{2+} to S^{2-} in the preparation of quantum dot was 1:1. These processes were repeated several times (5, 10, 15, 20), and the as-prepared samples were named as ZC-5, ZC-10, ZC-15 and ZC-20, respectively.

2.4. Characterization

XRD patterns were recorded at room temperature with an X'Pert Pro diffractometer with Cu Kα irradiation. Diffraction were performed between 20° and 80° with a step width of $0.02° s^{-1}$. The morphology and structure of the samples were checked by a Hitachi Model S-4800 field-emission scanning electron microscope (FESEM) system. A SEM system equipped for energy-dispersive X-ray (EDX) spectroscopy was used to determine the composition of the samples. XPS analysis was conducted on a ESCALAB 250 photoelectron spectroscopy (Thermo Fisher Scientific Inc.) at 3.0×10^{-10} mbar with monochromatic Al Kα radiation (E = 1486.2 eV). UV–Vis absorption spectra of various liquid samples were recorded by a UV-2450 spectrophotometer (Shimadzu, Japan), and the DRS of the pure Zn_2GeO_4 nanobelts and Zn_2GeO_4/CdS with different deposition cycles were obtained from Shimadzu UV-2450 UV–Vis spectrophotometer equipped with an integrating sphere, and the baseline correction was done using a calibrated sample of barium sulfate.

2.5. Photocatalytic test

The visible-photocatalytic activities of the obtained samples were investigated by the photodegradation of RhB in an aqueous solution under atmospheric condition by using a home-made facility [36,42]. A 500 W tungsten halogen lamp was used as light source, and positioned at a cylindrical Pyrex vessel, cooled by circulating water when irradiation was performed. The light source positioned 10 cm from the reaction glassware. Meanwhile, a cut-off filter was used to remove all light with wavelengths less than 400 nm to ensure irradiation with visible light (Scheme 1). In the photodegradation of RhB, as-prepared sample (0.10 g) was first dispersed in a glass reactor with 100 mL RhB solution (10 mg/L, pH = 4.8). Prior to irradiation, the suspension was stirred in the dark for 60 min to achieve an adsorption/desorption equilibrium between the photocatalyst and RhB solution, and then the suspension was irradiated to induce photocatalytic reactions. At given