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Vanadium doped barium germanate microrods and photocatalytic properties under solar light

L.Z. Pei*, S. Wang, H.D. Liu, N. Lin, H.Y. Yu*

Key Lab of Materials Science and Processing of Anhui Province, School of Materials Science and Engineering, Anhui University of Technology, Ma'anshan, Anhui 243002, PR China

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ABSTRACT

Vanadium doped barium germanate microrods have been prepared by a facile hydrothermal process. The obtained vanadium doped barium germanate microrods are proved to be hexagonal $BaGe_4O_9$ and orthorhombic $Ba_2V_2O_7$ phases by X-ray diffraction. Scanning electron microscopy shows that the vanadium doped barium germanate products consist of microrods with the diameter of microscale size. The diameter of the mirorods decreases from 800 nm to 150 nm with the vanadium doping mass percentage increasing from 1% to 10%. Solid UV–vis diffuse reflectance spectra show that the band gap of the vanadium doped barium germanate is smaller than that of the undoped barium germanate. The photocatalytic activity has been greatly enhanced by the vanadium doping. The vanadium doped barium germanate microrods exhibit great application potential for the photocatalytic degradation of methylene blue under solar light irradiation.

1. Introduction

Alkaline earth barium germanate, as an important semiconductor, shows great application potential for lithium ion batteries and photocatalysts owing to their good electrochemical and photocatalytic performance [1]. In general, bulk barium germanate was prepared by high temperature reaction and ultra-rapid quenching process [2,3]. In our previous research, barium germanate with special morphology, such as barium germanate microrods have been synthesized by a facile hydrothermal process without any surfactants [4]. The barium germanate microrods exhibit good photocatalytic activity for the degradation of methylene blue (MB) under ultraviolet (UV) light irradiation. However, only about 3% UV light exists in natural solar light. Barium germanate microrods are difficult to degrade MB under visible light irradiation due to wide band gap. Therefore, it is of important significance to improve the photocatalytic activity of the barium germanate microrods under visible light irradiation.

The semiconductors with wide band gap can only absorb UV light which cannot degrade organic pollutants under visible light. The band gap of these semiconductors can be greatly improved by doping metal cations, such as Yb, Er co-doped $BiVO_4$ [5], Mn, co-doped TiO_2 [6], Bi doped TiO_2 [7] and Ce doped $SiO_2@TiO_2$ nanocomposite [8]. Organic pollutants can be efficiently photocatalytic degraded by these metal doped semiconducors under solar light irradiation. Vanadium belongs to important transition metal which can enhance the photocatalytic activity of the photocatalysts under visible light. Song et al. [9] developed a sol–gel method to prepare vanadium doped TiO_2 nanocrystalline at low temperature with a red-shift of the absorption spectrum to 445 nm. The vanadium doped TiO_2 nanocrystalline can be excited by visible light and is a good photocatalyst under daylight. Yamashita et al. [10] reported the synthesis of vanadium doped TiO_2 by hydrothermal method in the presence of NH_4F which shows high photocatalytic activity under visible light.

In the present work, transition metal vanadium ions were chosen as the dopant to vanadium doped barium germanate microrods. The vanadium doped barium germanate microrods were prepared by a hydrothermal process using germanium dioxide, barium acetate and sodium vanadate as the raw materials. The role of doping vanadium on the structure, morphology and optical absorption property of the vanadium doped barium germanate microrods were analyzed. The photocatalytic activity for the degradation of MB using vanadium doped barium germanate microrods has been investigated under solar light irradiation in detail.

2. Experimental

High pure GeO_2 powders (purity: $\geq 99.99\%$), $Ba(CH_3COO)_2 \cdot H_2O$ (AR grade), sodium vanadate (AR grade) and MB (AR grade) were purchased from Sinopharm Chemical Reagent Co., Ltd. of P.R. China. All

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* Corresponding authors. Fax: +86 5552311570.
E-mail addresses: lzpei@ahut.edu.cn, lzpei1977@163.com (L.Z. Pei), yuhy@ahut.edu.cn (H.Y. Yu).

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raw materials were used as received without further purification. In a typical procedure, 0.16 g GeO_2, 0.84 g $Ba(CH_3COO)_2 \cdot H_2O$ and sodium vanadate were dissolved in 60 mL deionized water. The mass ratios of vanadium and barium germanate are 1:99, 3:97, 5:95 and 10:90, correspondingly. The $Ba(CH_3COO)_2 \cdot H_2O$ and sodium vanadate solution were added to GeO_2 solution with vigorous stirring. Then, the mixture was placed in a 100 mL autoclave with a Teflon liner. The autoclave was maintained at 180 °C for 24 h. Subsequently the autoclave was cooled naturally in air. The white precipitates were filtered, washed with deionized water for several times and dried at 60 °C in air. Finally, white vanadium doped barium germanate products were obtained.

X-ray diffraction (XRD) patterns of the vanadium doped barium germanate products were performed on a Bruker AXS D8 X-ray diffractometer equipped with a graphite monochromatized Cu-Kα radiation ($\lambda = 1.5406$ Å). The vanadium doped barium germanate samples were scanned at a scan rate of 0.05°/s in 2θ range of 20–80°. SEM observation was performed using nova nanoSEM FEI 430 SEM with a 15 kV accelerating voltage. Solid UV–vis diffuse reflectance spectra of the undoped and vanadium doped barium barium microrods were carried out using a UV3600 UV–vis spectrometer (Shimadzu International Co., Ltd. of Japan) and a thermo Electron Corporation with a reflectance diffuse accessory.

Photocatalytic activity of the vanadium doped barium germanate was analyzed for the photocatalytic degradation of MB under solar light irradiation in a OCRS-IV photocatalytic system with a quartz reactor. The photocatalytic system was purchased from Kaifeng Hongxing Technology Co., Ltd. of Henan province of P.R. China. The photocatalytic tests were carried out using 5–40 mg vanadium doped barium germanate suspended in 20 ml MB solution with 2.5–20 mg L^{-1} MB in a quartz glass cell. Prior to the solar light irradiation, the mixture was maintained in the dark for 20 min with the stirring to reach the adsorption equilibrium. All photocatalytic tests were carried out under natural sunlight irradiation in air. The MB solution was separated from vanadium doped barium germanate by filter unit. The obtained solution was analyzed by UV756 UV–vis spectrometer (Shanghai Youke Instrument Co., Ltd. of P.R. China). The initial MB concentration (C_0) and MB concentration (C) after a certain reaction time (t) were obtained by measuring the absorbance of the reactant solution at 665 nm during the photocatalytic reaction process. C/C_0 ratio was used to analyze the photocatalytic activity of the vanadium doped barium germanate.

3. Results and discussion

XRD patterns of the vanadium doped barium germanate products prepared from 180 °C for 24 h are shown in Fig. 1. The XRD patterns of the vanadium doped barium germanate with different vanadium mass percentages are similar. All diffraction peaks belong to hexagonal $BaGe_4O_9$ phase (JCPDS card no. 43-0644) and orthorhombic $Ba_2V_2O_7$ phase (JCPDS card no. 32-0092). The hexagonal $BaGe_4O_9$ phase is same to that of the undoped barium germanate microrods prepared under same hydrothermal conditions [4]. No other phases, such as vanadium or vanadium oxide, exist in the vanadium doped barium germanate microrods besides hexagonal $BaGe_4O_9$ and orthorhombic $Ba_2V_2O_7$ phases. The intensities of the diffraction peaks of hexagonal $BaGe_4O_9$ phase decrease obviously with the increase of the vanadium doping mass percentage. Even some diffraction peaks located at $2\theta = 23.04°$, 36.05° and 61.07° of the hexagonal $BaGe_4O_9$ phase disappear. However, the intensities of the diffraction peaks of the orthorhombic $Ba_2V_2O_7$ phase increase greatly by increasing the vanadium doping mass percentage.

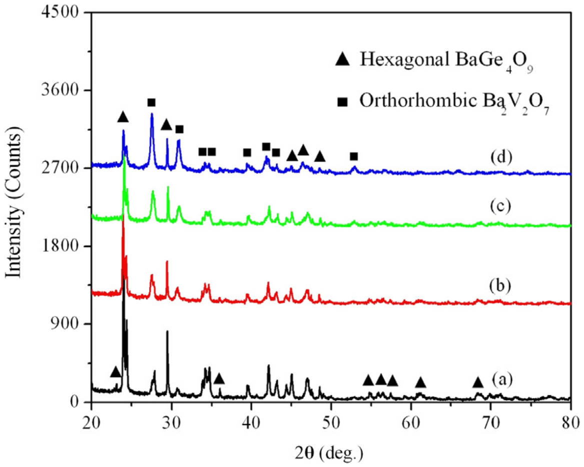

Fig. 1. (Color online) XRD patterns of the vanadium doped barium germanate with different vanadium doping mass percentage. (a) 1%, (b) 3%, (c) 5%, and (d) 10%.

The typical morphology and size of the vanadium doped barium germanate are shown in Fig. 2. It is observed that the morphology of the vanadium doped barium germanate with different vanadium mass percentage is similar. The vanadium doped barium germanate products are composed of short rod-shaped morphology which is also similar to that of the undoped barium germanate microrods prepared from same hydrothermal conditions [4]. The length of the microrods with flat tips is about 2 μm. However, the diameter of the vanadium doped barium germanate microrods with different vanadium doping mass percentage is very different. The average diameter of the microrods is about 800 nm (Fig. 2(a)) when the vanadium mass percentage is 1%. The average diameter decreases to 500 nm (Fig. 2(b)), 250 nm (Fig. 2(c)) and 150 nm (Fig. 2(d)), respectively, with the increase in the vanadium doping mass percentage to 3%, 5% and 10%. Therefore, it is concluded that the diameter of the vanadium doped barium germanate microrods depends on the vanadium doping mass percentage. The diameter of the microrods decreases obviously with the increase of the vanadium doping mass percentage.

Fig. 3 shows the solid UV–vis diffuse reflectance spectra of the undoped barium germanate microrods and vanadium doped barium germanate microrods. Table 1 shows the band gap of the undoped barium germanate microrods and vanadium doped barium germanate microrods. From the intercept on the wavelength axis for a tangent line drawn on the absorption spectrum, the absorption edge (λ) of the undoped barium germanate microrods is estimated to be 249 nm (inset in the upper-right part of Fig. 3). However, the absorption edge of the vanadium doped barium germanate with different vanadium doping mass percentage has the red-shift to 425–443 nm. The band gap (E_g) can be determined by the Planck's equation. $E_g = hc/\lambda = 1240/\lambda$, where E_g is the band gap (eV), c is the light velocity (m s^{-1}), h is the Planks constant and λ is the absorption threshold wavelength (nm). The band gap decreases from 4.98 eV (undoped barium germanate microrods) to 2.80–2.90 eV (vanadium doped barium germanate microrods). The red-shift of the optical absorption edge of the barium germanate to visible light originates from the vanadium doping. The vanadium doped barium germanate microrods indicate higher absorption ability in visible light region than that of undoped barium germanate microrods. Therefore, vanadium doped barium germanate microrods are strong absorbers of photons under solar light irradiation owing to their narrow band gap.

The photocatalytic degradation of MB in aqueous solution under visible light has been carried out so as to test and verify