



Facile synthesis of α -Ag₃VO₄ hollow nanospheres with improved photocatalytic activities



Xiaoxiao Zhao, Jianfeng Huang^{**}, Liangliang Feng^{*}, Liyun Cao, Jiayin Li, Lei Zhou

School of Material Science and Engineering, Shaanxi University of Science and Technology, Xi'an, Shaanxi 710021, PR China

ARTICLE INFO

Article history:

Received 10 January 2017

Received in revised form

8 May 2017

Accepted 9 May 2017

Available online 10 May 2017

Keywords:

α -Ag₃VO₄

Hollow structure

pH-dependent

Photocatalytic activity

ABSTRACT

The development of efficient photocatalysts is of paramount significance for sustainable availability of solar energy. Herein, hollow α -Ag₃VO₄ photocatalysis crystallites were successfully synthesized via a facile one-pot hydrothermal approach without modifier. The morphology, phase composition and crystal structure of α -Ag₃VO₄ crystallites are strongly dependent on the pH values of the precursor solution, and the formation of hollow α -Ag₃VO₄ nanospheres merely occurs at pH = 10. Furthermore, hollow α -Ag₃VO₄ nanospheres exhibit superior photocatalytic activities compared with bulk α -Ag₃VO₄ for the degradation of Rhodamine B (Rh B) under the simulated solar light, achieving up to 97% degradation in 2 h irradiation. This improved photocatalytic performance of hollow α -Ag₃VO₄ nanospheres is primarily attributed to the synergistic effect of the improved electron-transfer efficiency, the extended light absorption range and effective separation of electron-hole pairs.

© 2017 Published by Elsevier B.V.

1. Introduction

Semiconductor-based photocatalysts have been receiving the extensive attention in terms of the elimination of organic dye pollutants and solar energy conversion [1–3]. To make sufficient use of solar light, a variety of visible-light-driven photocatalysts have been developed. Among these, silver vanadium oxides (SVOs) can be seen as one of the most promising photocatalysts for the degradation of dye pollutants, water treatment and environment cleaning. Since Konta et al. [4] reported the photophysical and photocatalytic properties of silver vanadates, silver vanadium oxides (SVOs) have been the hot issues of materials research fields during the past few years and exhibited promising application in electrochemical [5], biological [6], electronic [7], catalytic [8] and other fields. And previously, there are three polymorphs of Ag₃VO₄: α -type [9], β -type [10], and γ -type [11], α -Ag₃VO₄ has aroused intensive attention as a photocatalyst owning the wide responsiveness to visible light. For α -Ag₃VO₄, the valence band consist of hybridized Ag 4d₁₀ orbitals and O 2p₆ orbitals, resulting in a narrow bandgap (~2.2 eV) [12]. Therefore, α -Ag₃VO₄ possess potential applications in degradation of dye pollutants, water

treatment and environment cleaning.

Compared to traditional bulk materials, nanomaterials with unique morphologies exhibit a special size, shape, crystallizability and surface condition [13–15], making it have a relatively higher surface area, more catalytic active sites, wider spectral response and higher utilization of sunlight. Especially, unlike the solid materials, hollow nanospheres have unique properties [16–19], such as large specific surface area, good ability of electron capture and large internal space, thus having a broad application prospect in the field of photocatalysis. Till now, most fabricated α -Ag₃VO₄ are particles [20] of nanoscale or microscale, few are nanostars and flower-like [21], but these synthetic methods all use surfactant or modifier [22–25]. The regulating effect of template could form a more orderly and rigorous structure, while the process of removing template will result in problems of impurities pollution and structure damaged. However, to the best of our knowledge, the preparation of hollow α -Ag₃VO₄ nanospheres without template has seldom been reported.

Herein, template-free α -Ag₃VO₄ hollow nanospheres were synthesized by a plain hydrothermal method without any modifier. The electron transfer phenomenon was revealed by photoluminescence (PL) and transient photocurrent studies. Furthermore, SEM, TEM, XPS, the porosity (large surface area) and the high catalytic activity of the resulting hollow α -Ag₃VO₄ nanomaterial can also highlight the importance of this free-template strategy.

* Corresponding author.

** Corresponding author.

E-mail addresses: huangjfsust@126.com (J. Huang), fengl@sust.edu.cn (L. Feng).

2. Experimental

2.1. Synthesis of hollow α - Ag_3VO_4 nanospheres

All starting materials in the experiment were of analytical purity and used without further purification. The procedure of preparation was as follows. Firstly, 0.23 g of ammonium vanadate (NH_4VO_3) was dispersed to the distilled water under vigorous stirring for 30 min at the temperature of 80 °C. Secondly, 60 mL 0.1 mol/L of AgNO_3 was slowly added to the above solution with stirring. Successively, the mixture was stirred at room temperature for 1 h, and 0.2 mol/L of sodium hydroxide was used to adjust the pH value of solution. Then the above mixture solution was sealed in a 100 mL Teflon-lined stainless and maintained at 120 °C for 8 h. When the autoclave was cooled naturally to room temperature, the products were harvested by centrifugation, washed several times using deionized water and absolute ethyl alcohol, respectively, and dried in an oven at 60 °C for 12 h. For comparative purposes, bulk α - Ag_3VO_4 powders (denoted hereafter as bulk) without the hollow structure were prepared using a precipitation method as previously reported [26].

2.2. Characterizations

X-ray diffraction (XRD) patterns were recorded on a Rigaku D/max2200PC X-ray diffractometer with Ni-filtered $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406$ nm, 40 kV and 40 mA). Field emission scanning electron microscope (FESEM) measurement was performed by a Vega 3 SBH instrument (TESCAN, Česko) operated at an accelerating voltage of 10 kV. Transmission electron microscope (TEM) images, and high resolution transmission electron microscope (HRTEM) images were obtained from a FEI Tecnai G2 F20 S-TWIN instrument (FEI, America) at an accelerating voltage of 200 kV to get the surface morphology and lattice fringes. X-ray photoelectron spectroscopy (XPS) measurements were performed on a PHI5000 Versa Probe electron spectrometer using Al $\text{K}\alpha$ radiation (Ulvac Phi, England) to identify the surface chemical composition and chemical states of the samples. The UV–vis diffuse reflectance spectra (DRS) were recorded on a Cary 5000 UV–Vis–NIR Spectrophotometer (America) with BaSO_4 as the background in the wavelength range of 200–800 nm. The photoluminescence (PL) spectra were obtained with a Spectrofluorometer FS5 (EDINBURGH, England) equipped with 150 W Xe lamp source at an excitation wavelength of 315 nm. Brunauer–Emmett–Teller (BET) surface area measurements were measured by nitrogen adsorption and desorption method using a ASAP 2460 analyser (Mac, America) to get the surface area and porosity.

2.3. Photocatalytic and electrochemical measurements

To investigate the photocatalytic activities of the as-fabricated samples, the photocatalytic degradation of Rhodamine B (Rh B) aqueous solution was conducted in a photoreactor at room temperature using a 1000 W Xenon lamp as light source. In brief, 50 mg of photocatalyst was dispersed in 50 mL of a 10 mg L^{-1} aqueous solution of Rh B in a photoreactor with a double layer, which was cooled by running water to keep the temperature unchanged. Adsorption was pre-carried out in the dark for 40 min to achieve adsorption–desorption equilibrium between the catalyst and the simulating pollutant, and then degradation proceeded at $t = 0$. About 5 mL aliquots were collected and then centrifuged to remove catalysts for analysis at certain time intervals of light irradiation. Then the supernatants were analyzed to study the photocatalytic degradation of the target pollutants by a 2600 UV–VIS Spectrophotometer. In contrast, the photocatalytic activity of P25 was also

carried out.

The photocatalytic activities were carried out in a BL-GHX-V photoreactor. A 1000 W Xenon lamp was used as lamp source. The photocurrent was carried out by a CHI 660B electrochemical analysis station (Chenhua Instrument Company) in a standard three-electrode system. A platinum wire was used as counter electrode, and a saturated calomel electrode served as a reference electrode. A 0.5 M Na_2SO_4 aqueous solution was used as the electrolyte. The working electrode was prepared as follows: Firstly, FTO glasses were treated ultrasonically with water, acetone and ethyl alcohol for 20 min in each, and dried in dry N_2 atmosphere. Secondly, 2 mg of catalyst was dispersed in a mixture solution which contained 1 mL of ethylene glycol and 0.5 mL of Nafion to form a uniformly distributed slurry. Thirdly, the slurry was drop-cast onto the precleaned FTO glass electrode, and left to dry at 60 °C in the dark for 12 h (this gave the mass loading of $\sim 1 \text{ mg/cm}^2$). A 500 W Xenon lamp was utilized as the light source. The light irradiation came from the backside of fluorine doped tin oxide (FTO) glass for all cases.

3. Results and discussion

As shown in Fig. 1, it can be seen that the pH values of the precursor solution (pH = 10) plays an important role in the formation of the α - Ag_3VO_4 material. VO_2 began to form when the precursor pH value was adjusted to 9. Whereas when the pH value of the precursor solution was decreased to 9, the mixed phase of $\text{Ag}_4\text{V}_2\text{O}_7$ (JCPDS No. 77-0977) and α - Ag_3VO_4 (JCPDS No. 43-0542) was detected. Only at pH = 10, all of the diffraction peaks could be well-indexed to pure phase monoclinic α - Ag_3VO_4 (JCPDS No. 43-0542), and which exhibited good crystallinity. The major diffraction peaks at 2θ values of 32.33° and 30.86° were well corresponded to (121) and (−121) planes, separately. And small peaks at 19.20°, 35.07°, 35.94°, 38.92° and 54.06° were indexed to (011), (301), (202), (022) and (331) planes of α - Ag_3VO_4 , respectively. Furthermore, the bulk α - Ag_3VO_4 sample was also carefully characterized for comparative purposes (XRD and SEM, Fig. S1, ESI†).

XPS analysis was carried out to investigate the elemental composition and chemical state of as-fabricated hollow α - Ag_3VO_4 samples. As shown in Fig. 2a, three elements including Ag, V and O are observed in this material. The peaks at 513.6 eV and 521.3 eV can be assigned to the $\text{V } 2p_{3/2}$ and $\text{V } 2p_{1/2}$ binding energies of V^{5+} in

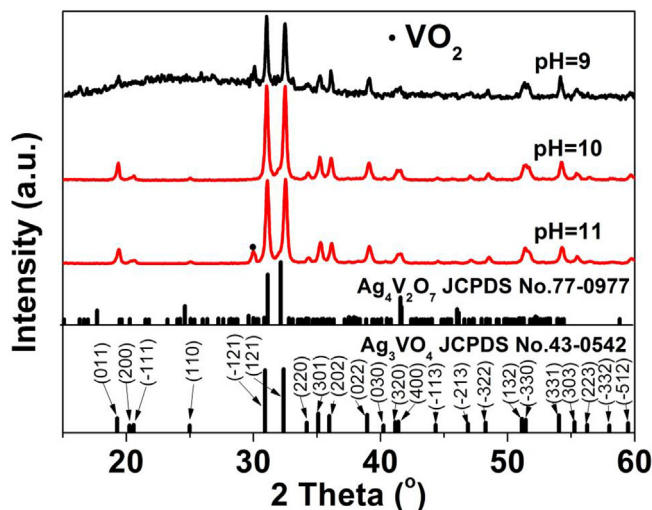


Fig. 1. XRD patterns of as-fabricated silver vanadates photocatalysts at different pH values.

Download English Version:

<https://daneshyari.com/en/article/5459418>

Download Persian Version:

<https://daneshyari.com/article/5459418>

[Daneshyari.com](https://daneshyari.com)