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Facile fabrication of $CeVO_4$ microspheres with efficient visible-light photocatalytic activity

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ABSTRACT

$CeVO_4$ microspheres were synthesized by a simple hydrothermal method using glycerine as surfactant. The products were characterized by XRD, SEM, HRTEM, XPS, DRS and PL. The results showed that $CeVO_4$ microspheres were self-assembled with nano-hexahedron, and its absorption edge and energy gap was about 800 nm and 1.49 eV, respectively. Meanwhile, its photocatalytic property was investigated by the degradation of MB under visible light irradiation, and the highest efficiency of 99% was obtained within 300 min.

1. Introduction

Cerium orthovanadate ($CeVO_4$) is an interesting phase of the Ce-V-O ternary system and has a tetragonal zircon-type structure belonging to the space group $I4_1/amd$ [1]. This tetragonal zircon-type structure stabilizes Ce^{3+} ion even under oxidizing conditions. Thus, it has wide potential application in various fields, such as in laser host materials, catalysts, gas sensors, phosphors and so on [2]. As a consequence, the design and synthesis of $CeVO_4$ nanostructures with various morphologies have attracted a lot of attention [3]. Such as, $CeVO_4$ hollow spheres were assembled by small single crystal nanorods with a simple hydrothermal synthesis method and used as an active catalyst for the oxidative dehydrogenation of propane [4]. $CeVO_4$ particles with pindle-shaped structures or rectangular morphology were obtained by a hydrothermal method and $CeVO_4$/graphene aerogels with honeycomb-like 3D porous architectures were prepared by the electrostatic-driven self-assembly method, which were applied in the degradation of MB under visible light radiation [5]. $CeVO_4$ nanorods (NRs) were prepared and exhibited high ethanol sensing behavior below breath analyzer (200 ppm) at a reasonable optimum operating temperature (250 °C) [6]. $CeVO_4$ nanosquares and nanorods were successfully synthesized by PEG-assisted hydrothermal reaction and the highest efficiency of 98.03% (MB) was obtained under UV radiation [7]. To the best of our knowledge, there have been no reports on the fabrication of $CeVO_4$ microspheres assembled by nano-hexahedron.

In this research, $CeVO_4$ microspheres were successfully synthesized by glycerine-assisted hydrothermal method. The prepared samples showed excellent MB removal efficiency under visible light irradiation.

2. Experimental

The $CeVO_4$ photocatalyst was prepared by a hydrothermal process. In a typical synthesis procedure, 0.005 mol $Ce(NO_3)_3{\cdot}6H_2O$ and 0.005 mol NH_4VO_3 were dissolved into 50 ml 80 °C deionized water. Then, 10 mL glycerine was added into the solution and stirred for 30 min. The obtained solution was then transferred into a 100 mL Teflon-lined stainless steel autoclave and maintained at 180 °C for 8 h. After being cooled to room temperature, the separated products were washed, dried at 110 °C for 12 h, and calcined at 300 °C for 5 h.

The final products were characterized by X-ray diffraction (XRD, Bruker Advance D-8), scanning electron microscopy (SEM, Hitachi S-4300), high resolution transmission electron microscopy (HRTEM, TECNAI G2), X-ray photoelectron spectra (XPS, VG ESCALAB Mark II), UV–vis diffuse reflectance spectra (DRS, UV-2550) and photoluminescence (PL, Fluoromax-4P, 360 nm excitation wavelength).

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Photocatalysis was evaluated by the photodegradation of methylene blue (MB) under visible light radiation. About 100, 200, 300, 400 or 500 mg $CeVO_4$ (or 500 mg TiO_2) was added into 200 mL of 50 mg/L MB solution, which was magnetically stirred in the dark for 1 h to reach the adsorption–desorption equilibrium. Subsequently, the photocatalytic reaction was initiated by irradiating the system using a 500 W Xe lamp with a 420 nm cut-off filter. After illumination for a certain time, 5 mL of the reaction solution was extracted and separated by centrifugation. The filtrate was analyzed by recording UV–vis spectra on a UV1100 spectrophotometer and the MB concentration was determined at its characteristic absorption wavelength of 664 nm. In addition, the total organic carbon (TOC) was investigated according to the reported papers [8,9].

3. Results and discussion

The chemical composition of the as-synthesized products was characterized by powder XRD. As shown in Fig. 1a, the XRD pattern can ascertain the successful synthesis of tetragonal $CeVO_4$, because a serial of peaks are in accordance well with those from the standard JCPDS card no. 12-0757. In contrast to the diffraction peaks, the growth rate of the (200) lattice plane is faster than the other lattice planes. Besides, slight presence of V_2O_3 phase (JCPDSNo. 01-071-0344) is also detected. To visually investigate the morphology of $CeVO_4$ particles, the SEM images were conducted. As seen from Fig. 2b, the $CeVO_4$ is composed of uniform microspheres with an average diameter as about 2 μm. Moreover, the microspheres are self-assembled with a great deal of nano-hexahedrons with an average grain size as about 100 nm. To further investigate elemental composition and distribution uniformity, the elemental maps of the selected area on $CeVO_4$ are displayed in Fig. 1c, indicating that homogeneous distribution of Ce, V and O constituting elements in the sample. Besides, peaks attributed to Ce, V, O are examined by EDS analysis (Fig. 1c), showing that the $CeVO_4$ components present in the system. From Fig. 2d, the HRTEM images of $CeVO_4$ microspheres indicate that the lattice fringes of 0.49 and 0.37 nm are indexed to the (101) and (200) crystallographic planes of $CeVO_4$ phase, respectively, demonstrating that the $CeVO_4$ microspheres have the [001] preferred growth direction [7].

The chemical composition of $CeVO_4$ was further analyzed by XPS. Fig. 2a shows wide XPS spectrum of the $CeVO_4$, indicating the presence of Ce 4p, V 2p, O 1s, V 2s, Ce MNN and Ce 3d. The C 1s peak appears due to the testing electrodes, confirming the high chemical purity of the $CeVO_4$. As shown in Fig. 2b, the core level binding energies of Ce $3d_{5/2}$ are at approximately 881.1 and 884.9 eV, and those of Ce $3d_{3/2}$ are at approximately 899.8 and 903.2 eV, indicating a valence state of +3 for Ce in the sample. The V 2p spectrum is fitted with two spin-orbit doublets (Fig. 2c), characteristic of V^{5+} and V^{3+}. The binding energies at approximately 516.8 and 524.4 eV are attributed to V $2p_{3/2}$ and V$2p_{1/2}$ of V^{5+}, while those at about 515.4 and 522.6 eV are assigned to V $2p_{3/2}$ and V$2p_{1/2}$ of V^{3+}. The O 1s spectrum is fitted with two peaks at 529.4 and 531.1 eV, respectively (Fig. 2d). The former is the peak of the O^{2-} ions at the lattice sites of $CeVO_4$, while the latter is related to the O^{2-} ions at the lattice sites of V_2O_3 phases [6].

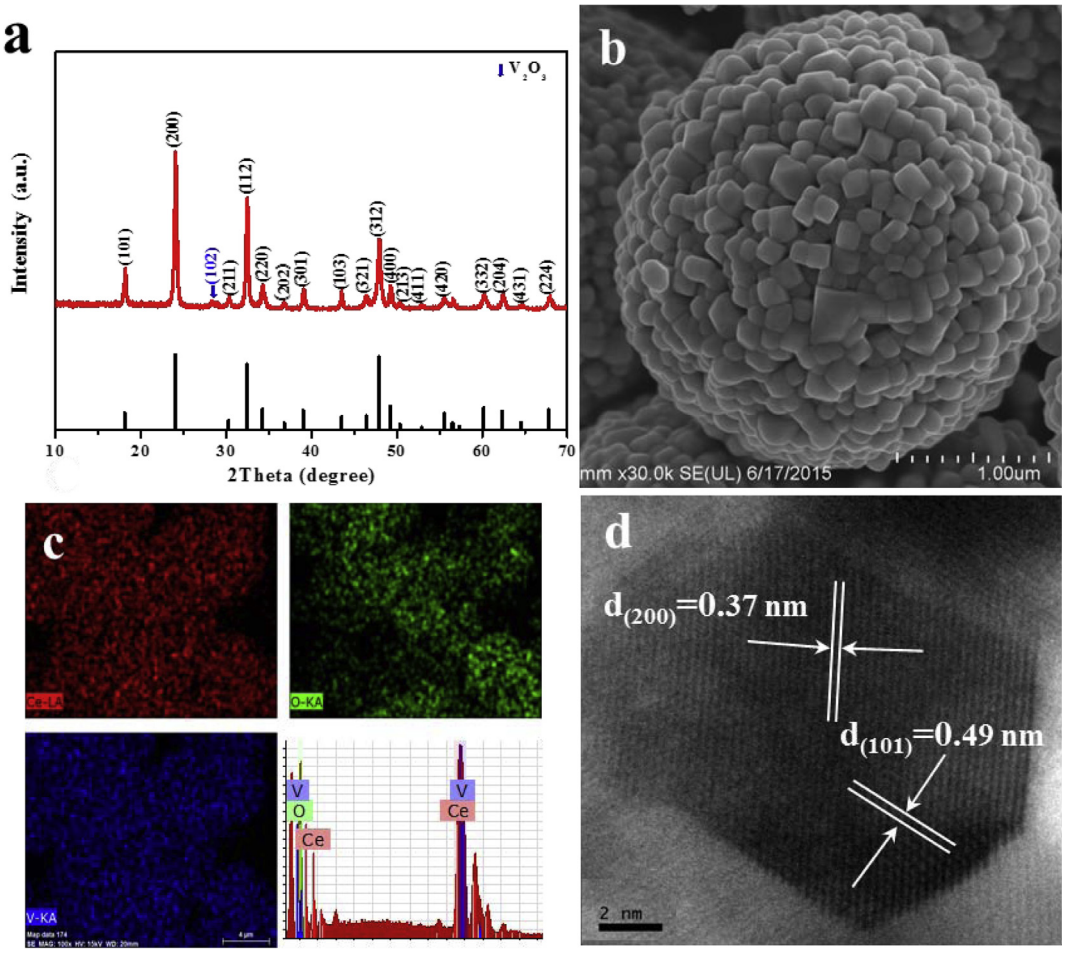

Fig. 1. (a) XRD pattern; (b) SEM images; (c) the corresponding elemental mapping images for Ce, O and V and EDX image; (d) HR-TEM images.