



3DOM InVO₄-supported chromia with good performance for the visible-light-driven photodegradation of rhodamine B



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ABSTRACT

Three-dimensionally ordered macroporous (3DOM) monoclinic InVO₄ and its supported chromia (yCrO_x/3DOM InVO₄, y denotes as the weight percentage of Cr₂O₃, y = 5, 10, 15, and 20 wt%) photocatalysts were fabricated using the ascorbic acid-assisted polymethyl methacrylate-templating and incipient wetness impregnation methods, respectively. Physicochemical properties of the materials were characterized by means of a number of analytical techniques. Photocatalytic activities of the samples were evaluated for the degradation of rhodamine B (RhB) in the presence of H₂O₂ under visible-light illumination. Compared to 3DOM InVO₄ and 15CrO_x/bulk InVO₄, yCrO_x/3DOM InVO₄ showed much better visible-light-driven photocatalytic performance for RhB degradation, with the 15CrO_x/3DOM InVO₄ sample performing the best. It is concluded that the CrO_x loading, higher surface area and surface oxygen vacancy density and lower bandgap energy as well as the better quality of 3DOM structure were responsible for the good photocatalytic performance of 15CrO_x/3DOM InVO₄ for the degradation of RhB.

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1. Introduction

In recent years, semiconductor photocatalysis has received much attention since it can be used to deal with wastewater and atmospheric pollutants and produce hydrogen via the splitting of water [1–4]. As a novel photocatalyst, InVO₄ attracts increasing interests due to its capability of responding to visible light. Up to now, there have been various methods to fabricate InVO₄ photocatalysts, such as solid-state high-temperature reaction [5,6], ‘chimie douce’ [7,8], sol–gel [9–11], and hydrothermal approaches [12–14]. It is well known that performance of a sample is intimately related to its surface area, crystal structure, and morphology [15]. For example, Noh et al. [16] fabricated InVO₄ microspheres via a facile template-free hydrothermal route, and observed an excellent visible-light-driven photocatalytic activity for the degradation of rhodamine B (RhB) under visible-light illumination. By adopting a hydrothermal method, Li et al. [17] obtained orthorhombic InVO₄ with a chrysanthemum-like hierarchical microstructure, which

showed a high discharge capacity and acceptable capacity retention when it was used as an electrode material in lithium ion battery.

It has been shown that the bandgap energy of a photocatalyst can be narrowed by doping some metal (i.e., Ni and Co) or metal oxides (i.e., Cr₂O₃ and In₂O₃), hence enhancing the photocatalytic performance under visible-light illumination [18–23]. For example, Zou et al. [19] doped Ni to InTaO₄ and narrowed the bandgap energy from 2.6 to 2.3 eV, thus achieving an increased visible-light-driven catalytic activity. Yang et al. [24] synthesized NiO/InVO₄ composite photocatalysts with a high visible-light absorption capacity via a high-temperature solid-phase reaction route. By adopting a sol–gel approach, Li et al. [25] prepared Ni-doped InVO₄ thin films, over which the degradation rate of methylene blue (MB) under visible-light illumination increased from 77 to 91%. Working on the hydrothermal preparation and photocatalytic ciprofloxacin degradation of Pt/InVO₄, Yan et al. [26] observed excellent visible-light-driven photocatalytic activity. To the best of our knowledge, however, there have been no reports on the fabrication and photocatalytic applications of three-dimensionally ordered macroporous (3DOM) InVO₄-supported chromia for the degradation of RhB under visible-light illumination.

In recent years, our group has prepared and characterized a number of BiVO₄ with various morphologies using the surfactant-

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assisted hydrothermal or alcohol-hydrothermal strategies [27–31] and heteroatom-doped BiVO₄ [32,33]. As an extension work, we herein report for the first time the fabrication, characterization, and photocatalytic performance of monoclinic 3DOM-structured InVO₄-supported chromia (yCrO_x/3DOM InVO₄) for the degradation of RhB in the presence of a small amount of H₂O₂ under visible-light illumination.

2. Experimental

2.1. Catalyst preparation

The well-arrayed hard template polymethyl methacrylate (PMMA) microspheres with an average diameter of ca. 300 nm were synthesized according to the procedures described elsewhere [34]. The monoclinic 3DOM-structured InVO₄ with mesoporous skeletons were fabricated by adopting the ascorbic acid (AA)-assisted PMMA-templating strategy with In(NO₃)₃·4.5H₂O and NH₄VO₃ as the metal source, and ethylene glycol (EG) and absolute methanol (MeOH) as the solvent. The typical fabrication procedure is as follows: 10 mmol of In(NO₃)₃·4.5H₂O and 10 mmol of AA were added to a mixture of EG (1.5 mL), MeOH (7.5 mL), and deionized water (7.0 mL) under stirring. 10 mmol of NH₄VO₃ was dissolved in the above mixture for 1 h. 3.0 g of well-aligned PMMA microspheres was then soaked in the mixed solution for 3 h. After being filtered, the as-obtained wet PMMA template was in turn dried at room temperature (RT) for 12 h, calcined in a N₂ flow of 100 mL/min in a tubular furnace at a ramp of 1 °C/min from RT to 300 °C and kept at this temperature for 3 h, and in an air flow of 100 mL/min at the same ramp to 500 °C and maintained at 500 °C for 4 h, thus generating the 3DOM InVO₄ photocatalyst.

3DOM InVO₄-supported chromia photocatalysts were fabricated using the incipient wetness impregnation method. The typical fabrication procedure is as follows: 0.5 g of 3DOM InVO₄ was impregnated with the desired amount of chromium nitrate solution for 10 min. After that, the mixture was dried at 110 °C for 12 h, and then calcined in an air flow of 100 mL/min at a ramp of 1 °C/min from RT to 450 °C and kept at this temperature for 4 h. For the sake of clear presentation, we denote the as-obtained photocatalysts as yCrO_x/3DOM InVO₄ (y denotes as the weight percentage of Cr₂O₃, y = 5, 10, 15 and 20 wt%), as clearly described in Table 1. For comparison purposes, we also prepared nonporous InVO₄ (denoted as bulk InVO₄) and 15CrO_x/bulk InVO₄ photocatalysts using the solid-state reaction [5] and incipient wetness impregnation methods, respectively.

All of the chemicals (A.R. in purity) were purchased from Beijing Chemical Reagent Company and used without further purification.

2.2. Catalyst characterization

X-ray diffraction (XRD) patterns of the as-obtained samples were recorded on a Bruker D8 Advance diffractometer with Cu K α radiation and nickel filter ($\lambda = 0.15406$ nm), and the operating voltage and current was 40 kV and 35 mA, respectively. Crystal phases of the samples were identified by referring to the JCPDS

Database. BET (Brunauer–Emmett–Teller) surface areas of the samples were measured via N₂ adsorption at –196 °C on a Micromeritics ASAP 2020 analyzer with the samples outgassed at 300 °C for 2.5 h under vacuum before measurement. The scanning electron microscopic (SEM) images of the samples were recorded on a Gemini Zeiss Supra 55 apparatus (operating at 10 kV). Transmission electron microscopic (TEM) images and the selected-area electron diffraction (SAED) patterns of the samples were obtained on a JEOL-2010 equipment (operating at 200 kV). X-ray photoelectron spectroscopy (XPS, VG CLAM 4 MCD analyzer) was used to determine the In 3d, V 2p, Cr 2p, O 1s, and C 1s binding energies (BEs) of surface species using Mg K α ($h\nu = 1253.6$ eV) as the excitation source. The instrumental resolution was 0.5 eV. In order to minimize the amounts of OH[–] and carbonate species on the surface, the samples were calcined in an O₂ flow of 20 mL/min at 450 °C for 1 h and then cooled in the same atmosphere to RT before XPS measurements. After such a pretreatment, the samples were mounted and transferred to the spectrometer in a transparent Glove Bag (Instruments for Research and Industry, USA) filled with helium. The samples were then outgassed in the preparation chamber (10^{–5} Torr) for 0.5 h and introduced into the analysis chamber (3 \times 10^{–9} Torr) for spectrum recording. The C 1s signal at 284.6 eV was taken as the reference for BE calibration. The ultraviolet–visible diffuse reflectance spectra (UV–Vis DRS) of the samples in the range of 200–800 nm were recorded on a Shimadzu UV-2450 spectrophotometer with BaSO₄ as the standard.

2.3. Photocatalytic evaluation

Photocatalytic activities of the as-obtained samples were evaluated in a quartz reactor (QO250, Beijing Changtuo Sci. & Tech. Co. Ltd.) for the degradation of RhB under visible-light irradiation. A 300-W Xe lamp was used as the light source, and an optical cut-off filter was used to only permit illumination at $\lambda \geq 400$ nm. The photocatalytic process was conducted at RT as follows: 0.1 g of the photocatalyst and 0.6 mL of H₂O₂ aqueous solution (30 wt%) were added to 100 mL of RhB aqueous solution (initial RhB concentration C₀ = 5, 10, 15, and 20 mg/L). Before illumination, the mixed solution was ultrasonically treated for 15 min and then stirred for 20 min in the dark to allow the system to establish the adsorption-desorption equilibrium. With the aid of flowing cool water, the temperature of reactant solution was kept at ca. 25 °C. 4 mL of the mixed solution was taken out at 20 min intervals and centrifuged to remove the photocatalyst particles for the analysis of RhB concentration. The RhB concentration (C_t) after a certain reaction time (t) was monitored by checking the absorbance of the reactant solution at ca. 553 nm on a Shimadzu UV–Vis equipment. The C_t/C₀ ratio was used to evaluate the photocatalytic activity.

3. Results and discussion

3.1. Crystal phase composition

Fig. 1 shows the XRD patterns of the as-fabricated samples. By referring to the XRD patterns of the standard InVO₄ (JCPDS PDF#

Table 1
Crystal phases, morphologies, BET surface areas, and bandgap energies of the samples.

Sample	Crystal phase	Morphology	Macropore size (nm)	Mesopore size (nm)	Surface area (m ² /g)	Bandgap energy (eV)
CrO _x /bulk InVO ₄	Monoclinic	Irregular	–	–	4.6	2.50
3DOM InVO ₄	Monoclinic	3DOM	130–140	5–40	52.3	2.50
5CrO _x /3DOM InVO ₄	Monoclinic	3DOM	160–170	2–30	41.3	2.38
10CrO _x /3DOM InVO ₄	Monoclinic	3DOM	150–165	5–20	42.5	2.24
15CrO _x /3DOM InVO ₄	Monoclinic	3DOM	155–165	2–40	45.0	2.10
20CrO _x /3DOM InVO ₄	Monoclinic	3DOM	160–170	2–30	42.6	2.10

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