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Large-mesopore hierarchical tungsten trioxide hydrate with exposed high energy facets: Facile synthesis and enhanced photocatalysis

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ABSTRACT

Developing highly active photocatalysts for water treatment is of vital importance. A large-mesopore hierarchical WO_3 hydrate photocatalyst with exposed high energy facets was synthesized via a facile hydrothermal method using sodium chloride as structure-directing agent. The forming model of the hierarchical structure was discussed, and photogenerated oxide species were investigated. It is shown that the orthorhombic $WO_3 \cdot 1/3H_2O$ photocatalyst is of a hierarchical structure assembled by various 2-dimension nanosheets and that its average pore diameter reaches approximately 33.2 nm. Besides, it could decompose 92% of rhodamine B (Rh B) under visible light irradiation within four hours. The enhanced photocatalytic efficiency is attributed to the exposed high energy (002) crystal facets of hierarchical structure, and to the large mesopores existing between crossed nanosheets which help to charge carriers separation, adsorption of reactants and desorption of product molecules. Furthermore, the catalyst displays an excellent photocatalytic stability, indicating its broad application in water pollution treatment.

1. Introduction

Water pollution threatens human health and environment, and unavoidably attracts much attention to explore effective wastewater treatment [1]. Among numerous water treatment technologies, photocatalytic technology wins out for the only photo-energy utilization, low operating cost and no secondary pollution [2–6]. Furthermore, TiO_2 has urged explosive research since the find of its ability to produce hydrogen through photocatalytic water splitting which was first reported by Fujishima and Honda [7] in 1970s. Nevertheless, TiO_2 can only absorb UV light owing to its wide band gap, restricting its development in photocatalytic application [8,9].

WO_3 is a known functional material, which has good photochromic, electrochromic, gas ochromic, and photocatalytic properties [10–13]. In addition, its band gap of about 2.7 eV suggests that it could absorb more solar light in the visible region than TiO_2. Despite of its excellent performances in many respects, the relatively easy recombination of charge carrier pairs challenges its further development in the photocatalytic field. Furthermore, fabrication of WO_3 is a complex process, and a slight change in the catalyst phase, morphology and textural properties could evoke a significant difference in the photocatalytic reactivity. It is known that external impurity plays an irreplaceable role in crystal growing. For example, organic agents (EDTA [14], and tartaric acid [15]) were added as structure-directing agents to obtain porous materials, and inorganic mineral substances (Li_2SO_4, CH_3COONH_4 [16], Na_2SO_4 [17], $(NH_4)_2C_2O_4$ [18]) were added to gain different shapes or special structures. It was also reported that sodium chloride could be used as a candidate agent to synthesize tungsten oxide with enhanced electrochromic property [19].

As is well known, surface atomic arrangement and coordination intrinsically determine the adsorption, surface transfer, and desorption; therefore, exposed facets, surface morphology, structure, and particle size have been manipulated extensively for various semiconductor photocatalysts in the literature [20–26]. Although different dimensional nanostructures of WO_3 have been prepared [27–32], three-dimensional layered structure is desirable when applied to photocatalysis, for it might provide much more reactive sites. For instance, Liu et al. [33] reported hollow $WO_3/WO_3 \cdot H_2O$ spheres exhibiting an photocatalytic efficiency that 60% of Rh B (20 mg/L) was degraded within 5 h under visible light (300 W, 100 mW cm^{-2}). Guo et al. [34] prepared hierarchical $WO_3 \cdot H_2O$ hollow microspheres with 94.8% of Rh B (1×10^{-5} M) degradation in 6 h (500 W). Zheng et al. [35] synthesized aggregated nanoparticles of cubic $WO_3 \cdot 0 \cdot 5H_2O$ which could degrade 70% of Rh B (10 mg/L) within 200 min under visible light (300 W). Li et al. [36] reported orthorhombic $WO_3 \cdot 0 \cdot 33H_2O$ with hierarchical nanostructures assembled by cuboid-kike building blocks which could degrade 94.2% of Rh B (15 mg/L) under the

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visible light (300 W) for 100 min. Though these hierarchical structures improve the photocatalytic efficiency significantly, large molecular organic pollutants are difficult to enter the pore channels of these catalysts, influencing the adsorption of contaminants and desorption of products. Therefore, an interest in studying the large-pore hierarchical tungsten trioxide hydrate arises. Moreover, three-dimensional hierarchical structure consisting of 2-dimensional nanosheets with the exposure of highly reactive facets is particularly welcome. However, the nanosheets with the exposure of only one facet, especially the ones with exposed high energy facets, are not easy to be achieved because of the controlled surface energy. Therefore, the tungsten trioxide hydrate photocatalyst still calls for further research and advancement, although a reasonable amount of information is already available concerning its preparation and photocatalytic properties.

In this paper, a large-mesopore hierarchical tungsten trioxide hydrate photocatalyst with exposed high energy facets was prepared by a hydrothermal method using inorganic sodium chloride as a structure-directing agent. Photocatalytic activity was evaluated by decomposing Rh B molecules under visible light irradiation. The possible forming model of $WO_3\cdot1/3H_2O$ nanoparticles was presented. Furthermore, reactive oxide species were analysed by introducing several scavengers into photocatalytic reaction system.

2. Experimental

2.1. Preparation of $WO_3\cdot1/3H_2O$ photocatalysts

All the analytic grade reagents were used without any further purification. Tungsten trioxide hydrate were prepared via a facile hydrothermal method [17]. In a typical synthesis, 3.3 g $Na_2WO_4\cdot2H_2O$ was dissolved into 45 mL deionized water under intense stirring, followed by the addition of 1.0 mol/L HCl until the pH reached 1.0. After a yellow green suspension was formed, a specific amount of sodium chloride was added as a structure-directing agent. Subsequently, the resulting solution was transferred to a 100 mL Teflon-lined stainless steel autoclave and heated at 120 °C for 12 h. After cooling to room temperature, the product was vibrated by ultrasonic wave for 10 min, washed by deionized water and absolute ethanol three times, and then a yellow precipitate was obtained and dried at 60 °C overnight to achieve powder.

The additive amount of the structure-directing agent, defined by mole ratio of sodium tungstate hydrate to sodium chloride, was 1:0, 1:0.25, 1:1, 1:4 and 1:8. And the corresponding photocatalysts prepared were labelled as PC-0, PC-1, PC-2, PC-3 and PC-4, respectively.

2.2. Characterization

The crystal phases of the as-prepared samples were identified by X-ray powder diffraction (XRD; Bruker, D8-Discover), using a Cu target at 40 kV and 30 mA from 10° to 70°. The morphologies and composition of the samples were observed by scanning electron microscopy (SEM, FEI, 3D) and transmission electron microscope (TEM, FEI, G220). The UV–visible diffuse reflectance spectra (DRS) were measured by a Shimadzu UV-3600 spectrophotometer in the region of 200–800 nm using $BaSO_4$ as the reference, and the absorbance of aqueous solution were recorded by a 722N visible spectrophotometer at 556 nm. Nitrogen physisorption was conducted at 77 K on a Micromeritics ASAP 2020 M apparatus, and specific surface area was calculated using the Brunauer-Emmett-Teller (BET) equation. The pore size distribution was calculated according to the Barrett-Joyner-Halenda (BJH) model. Additionally, Raman spectra were measured in a Thermo Fisher spectrometer from 200 to 1200 cm^{-1} using a He-Ne laser.

2.3. Photocatalytic test

The photocatalytic activities of the prepared samples were evaluated by decomposing Rh B aqueous solution at room temperature under visible light irradiation. A 500 W Xe lamp (Shanghai Special Lighting Factory, China) with 400 nm cut off was placed in a 500 mL photocatalytic reactor bottle, and the bottle was inserted into a quartz cold trap to guarantee that reaction temperature was stable throughout the whole process. The whole photocatalytic test system was in a black box of 50 cm × 40 cm × 80 cm with a small sampling window. In a typical reaction test, 0.4 g of a prepared photocatalyst was introduced to 400 mL aqueous solution of Rh B (20 mg/L), followed by ultrasonic vibration for 10 min. Then the solution was kept in dark for 30 min under constant magnetic stirring to obtain adsorption-desorption equilibrium between nanoparticles and Rh B aqueous solution, and the reactive time was indexed t=0 at this time. Then the reaction system was exposed to visible light irradiation. At each 30 min interval, 5 mL of turbid solution was taken and centrifuged to get transparent solution before measuring absorbance at a fixed wavelength or UV–visible absorption spectra using different spectrophotometers. In addition, to examine the photostability, the tested photocatalyst was collected, dried and reused in Rh B degradation by the above procedure for the second, third and fourth time.

3. Results

3.1. Catalyst characterization

Fig. 1 shows XRD patterns of the prepared samples. All the peaks could be well indexed to the $WO_3\cdot1/3H_2O$ orthorhombic phase (JCPDS Card No. 54-1012, space group Fmm2, cell constants: a=12.547 Å, b=7.737 Å, c=7.345 Å). No other impurities have been detected, which indicates that most of Na ions were removed while washing, and that the amount of the Na ions probably adsorbed on the surface of the samples is very small. The diffraction peaks presented at 14°, 22.9° and 24.2° correspond to (200), (020) and (002) planes, respectively. It is noteworthy that the intensity of the peak at 28.1° (diffraction spacing d=3.171 Å) corresponding to (202) plane is higher than those of the other peaks, suggesting that the WO_3 samples grow dominantly from the (202) orientation.

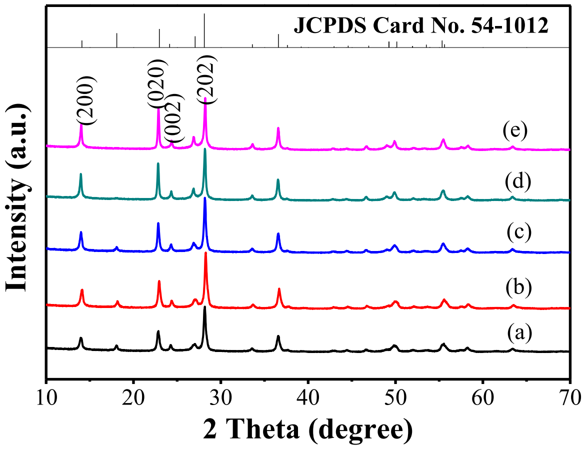

Fig. 1. XRD patterns of (a) PC-0, (b) PC-1, (c) PC-2, (d) PC-3, and (e) PC-4.