



Hierarchical yolk-shell WO₃ microspheres with highly enhanced photoactivity for selective alcohol oxidations

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ABSTRACT

Hierarchical WO₃ microspheres with controllable interior structures from solid, yolk-shell, to hollow were synthesized through sonochemical precipitation and hydrogen ion-exchange routes followed by thermal treatment. During the photocatalytic selective oxidation of aromatic alcohols to their corresponding aldehydes in aqueous medium under light irradiation with full wavelengths, the yolk-shell WO₃ microspheres exhibited much higher photocatalytic activity than those WO₃ microspheres with solid and hollow structures, respectively. This superior activity of the yolk-shell WO₃ microspheres can be attributed to the synergistic promoting effect of the following factors: firstly, the porous structure constructed by self-assembly of the interconnected nanosheets together with high surface area promoted the light harvesting and also facilitated the adsorption and diffusion of reactant molecules; secondly, the small crystallite size favored the rapid transfer of photoelectrons, which diminished the transfer distance of photoelectrons and thus inhibited their recombination with holes; thirdly, the yolk-shell structure enhanced light harvesting *via* multiple reflections in the yolk-shell chambers. Meanwhile, all the WO₃ photocatalysts displayed excellent durability against structural collapse due to the robust hierarchical structures. This work identifies the important role of yolk-shell structure played in photocatalytic selective oxidation of aromatic alcohols.

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1. Introduction

Selective oxidation of alcohols to carbonyl compounds as one of the most important functional group transformations in industrial chemistry has received much attention, because carbonyl compounds such as aldehydes and ketones are widely used in fragrance, confectionary, and pharmaceutical industries [1–4]. Traditional organic reactions for selective oxidation of alcohols to carbonyl compounds not only involve environmentally harmful and corrosive stoichiometric oxidants (e.g. Cr and Mn salts or V₂O₅) in organic solvents, but also produce large amounts of hazardous wastes under harsh conditions (e.g. high temperature and pressure) [2–4]. In order to overcome these drawbacks, great efforts have been devoted to exploiting clean processes for green organic synthesis [5–9]. Recently, photocatalysis emerged as a green and promising technique for organic synthesis, which is frequently carried out in aqueous medium under mild conditions without using toxic solvents and reagents [5–9].

The photocatalyst plays the critical role in determining the photocatalytic efficiency [10–20]. Until now, most studies are focused on TiO₂ photocatalyst due to its advantages of earth abundance, non-toxicity, and strong stability [15–20]. Since TiO₂ must be irradiated by UV lights because of its large intrinsic band gap (3.2 eV), intense attention has been paid to explore visible-light activated photocatalysts [21–32]. Presently, two strategies are mainly developed to achieve visible photocatalysts: one is to design TiO₂ doped with metal or nonmetal elements while they usually display poor activity and durability in practical applications owing to their limited amount and easy leaching of dopants [21–24], and the other is to explore non-titania photocatalysts with intrinsic narrow energy gaps (e.g. CdS, Bi₂O₃, WO₃, Ag₃PO₄, and Bi₂WO₆) [25–32]. Among them, WO₃ has been considered as one of the most ideal candidates owing to its outstanding stable physicochemical properties and wide applications in secondary batteries, gas sensors, electrolysis, and heterogeneous photocatalysis [30–32]. Monoclinic WO₃ with a distorted ReO₃-type structure is higher stable phase than any other forms (e.g. orthorhombic and hexagonal) and possesses a narrow intrinsic band gap (2.6 eV) [30–36], which extends the light absorption into the visible-light region, making it more suitable for photocatalytic applications.

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In addition to achieve visible-light activated photocatalysts, the nanostructure of photocatalysts also strongly influences the photocatalytic performances [34–46]. Many studies from both theoretical prediction and experimental results demonstrate that the activity and stability are strongly related to the particle size and morphology, together with the porous structure [37–46]. For example, the small particle size together with high surface area facilitates the adsorption and diffusion of reactant molecules while crystal facet with high surface energy, e.g. (001) facet in anatase TiO₂ and orthorhombic WO₃ crystal, favors the activation of reactant molecules [7,20,33,34]. Li's group reported that TiO₂ with flower-like, nanotube, hollow, and yolk-shell structures promoted the light harvesting via multiple reflections and thus enhanced the photocatalytic activity especially the yolk-shell structure [41–43,46]. After that, Quan's group investigated that PANI modified core-shell TiO₂ microspheres exhibited remarkable improvement in photocatalytic degradation of Rhodamine B and 4-chlorophenol due to the enhanced light harvesting via multiple reflections in the yolk-shell chambers [44]. Recently, Jiang's group also exhibited the similar results in studying the N-doped yolk-shell TiO₂ photocatalyst for the degradation of Rhodamine B [45]. More recently, we also found that SnS₂-TiO₂ with yolk-shell structure boosted the photocatalytic efficiency in Cr(VI) reduction by synergistic promoting effect of high surface area, strong SnS₂-TiO₂ interaction, and enhanced light harvesting via multiple reflections in yolk-shell chambers [22]. Recent research interest in inorganic semiconductor photocatalysts has been extended to the hierarchical nanostructures.

Herein, hierarchical yolk-shell WO₃ microspheres were synthesized through hydrogen ion-exchange route followed by thermal treatment, aiming to enhance light harvesting via multiple reflections and extend light response into visible region. Meanwhile, the structural effect on photocatalytic efficiency was also systematically investigated by using hierarchical WO₃ microspheres with solid and hollow structures as the counterparts, respectively. As expected, the hierarchical yolk-shell WO₃ microspheres exhibited the highest photocatalytic activity during selective oxidation of aromatic alcohols to their corresponding aldehydes in aqueous medium under light irradiation with full wavelengths, which can be attributed to the synergistic promoting effect of the porous structure together with high surface area, small crystallite size, and enhanced light harvesting via multiple reflections in yolk-shell chambers. Moreover, all the WO₃ photocatalysts displayed excellent durability against structural collapse due to the robust hierarchical structures.

2. Experimental

2.1. Sample preparation

The hierarchical WO₃ microspheres with controllable interior structures from solid, yolk-shell, to hollow denoted as WSS, WYS, and WHS in this work, respectively, were synthesized by the modified methods according to the previous literatures [47,48]. For WSS, 4.0 mmol Na₂WO₄·2H₂O and 5.5 mmol oxalic acid were completely dissolved in 16 mL H₂O under stirring, and then 6 mL 3.0 mol/L HCl solution was added into the above solution, which was then continuously sonicated for 1.0 h. After that, the product was collected and dried at 60 °C for 24 h, and finally calcined at 450 °C for 4.0 h to get the WSS. For WYS and WHS, the PbWO₄ precursor was firstly synthesized by the following route: a transparent solution containing 1.0 mmol Na₂WO₄·2H₂O, 1.0 mmol PbAc₂·3H₂O, 1.0 mmol CTAB, and 50 mL ethylene glycol was added into a 100 mL autoclave and kept at 160 °C for 10 h, and then the product was collected and dried at 60 °C for 2.0 h to obtain the PbWO₄ precursor (see Fig. S1). After

that, 1.0 mmol PbWO₄ was firstly immersed in 100 mL 4.0 mol/L HNO₃ for 12 h, and then the sample was collected and dried at 60 °C for 12 h. Subsequently, the acid-treatment sample was secondly immersed in 100 mL 4.0 mol/L HNO₃ for another 36 h, and then the after-treatment was the same as WSS to obtain WYS. The WHS was synthesized by the same method to WYS except that the PbWO₄ precursor was immersed in 100 mL 4.0 mol/L HNO₃ solution for 48 h by one-pot operation. The crushed yolk-shell WO₃ microspheres were prepared through strongly grinding WYS by hand at room temperature, and denoted as CWYS.

2.2. Characterization

The crystal structure and morphology were characterized by using X-ray diffraction (XRD, BRUKER D2 PHASER with Cu K α radiation), field emission scanning electron microscopy (FESEM, Hitachi S4800), high-resonance transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) on a JEOL JEM-2100. N₂ adsorption-desorption isotherms were determined on Micromeritics ASAP 2460 at 77 K, from which, the surface area (S_{BET}), pore volume (V_{p}) and pore diameter (D_{p}) were calculated by applying Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) models on the desorption branches. Photoluminescence spectroscopy (PLS), UV-vis diffuse reflectance spectra (UV-vis DRS) and Fourier-transform infrared (FTIR) spectra were collected on Varian Cary-Eclipse 500, MC-2530, and NEXUS-470, respectively. The photocurrent measurements were conducted on a self-made three-electrode quartz cell containing 30 mL 0.50 mol/L Na₂SO₄ aqueous solution with PAR VMP3 Multi Potentiostat apparatus and BAS Epsilon workstation, and the testing system was equipped with a 300 W xenon lamp with full wavelengths. The Pt plate and the Ag/AgCl electrode were used as the counter and reference electrodes, respectively, and the work electrode was prepared by depositing 10 mg photocatalyst onto fluoride-tin oxide (FTO) conductor glass. The photocatalytic products of selective oxidation of aromatic alcohols were detected by GC-MS (Agilent 6890N/59731).

2.3. Activity test

The photocatalytic selective oxidation of aromatic alcohols were carried out at 25 °C in a self-designed 50 mL reactor (see Fig. S2) containing 0.10 g photocatalysts, 10 mL distilled H₂O and 0.10 mmol benzyl alcohol or its derivatives in air atmosphere. All the photocatalytic reactions were conducted under irradiation by using a 300 W xenon lamp with full wavelengths located at 20 cm away from the reactor. After reacting 5.0 h, the reaction products were extracted with diethylether and analyzed by a gas chromatograph (Shimadzu, GC-2014C) equipped with a TB-1 column and a flame ionization detector (FID). Blank experiments demonstrated that no measurable amounts of oxidation products for aromatic alcohols occurred in the absence of either light irradiation or the WO₃ photocatalyst. The capturing experiment of active species was also conducted by the same method except addition of different scavengers with amount of 40 mmol. The reproducibility of all the activity tests was checked by repeating each result at least three times and found to be within acceptable limits ($\pm 3.0\%$).

3. Results and discussion

3.1. Structural characteristics

The XRD patterns in Fig. 1 demonstrated that all the WO₃ samples were present in monoclinic phase with high crystallization degree, corresponding to the 2 θ at 23.1°, 23.6°, 24.4°, and 26.6° indicative of the (002), (020), (200), and (120) diffractions (JCPDS

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