



Oxygen vacancy-rich mesoporous ZrO₂ with remarkably enhanced visible-light photocatalytic performance

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ABSTRACT

Introducing oxygen vacancies is an effective strategy to tail the absorption band-edge of ZrO₂ photocatalyst into visible-light region and modifying its surface feature can promote the adsorption affinity toward organic molecules, resulting in the enhancement of visible-light photocatalytic degradation of organic pollutants. Herein, we prepared mesoporous ZrO₂ with rich oxygen vacancy through a template-free solvothermal method followed by an annealing process, which was used as a catalyst to photodegrade tetracycline hydrochloride (TCH). The photocatalytic performance was found to be dependent on both oxygen vacancies and adsorption affinity. Comprehensive analysis revealed that, despite a certain reduction in both specific surface area and the amount of charged oxygen vacancy after annealing at 350 °C in air, the increased adsorption affinity toward TCH could promote its visible-light photocatalytic properties, along with good recyclability. Finally, a possible pathway and mechanism for the degradation of TCH was proposed.

1. Introduction

Photocatalysis has been recognized as a promising technology not only for the conversion of solar energy into chemical energy [1,2] but also for degradation of pollutants [3,4]. Especially, the removal of antibiotics from aqueous environment by reactive oxygen species [5], is highly expected as a potential application because even a very low concentration can give rise to the development of antibiotic-resistant bacteria, which pose adverse health effects to humans [6].

Intensive efforts have been devoted to develop high-efficient photocatalysts, such as metal-free [7,8] and metal-containing semiconductors [9–11]. Among metal-containing semiconductors, ZrO₂ has potentially technological application in the field of catalysis due to unique acid-base and redox characteristics. However, intrinsic ZrO₂ with a bandgap of ~ 5.0 eV is found to be only responsive to ultra-violet (UV) light, which is impracticable for the use of the visible (VIS) light. For the best use of solar energy, incorporating metal [12,13] or non-metal [14,15] ions into ZrO₂ lattice is widely used to form impurity state, which can shift its absorption edge into the VIS light region.

Another strategy to extend absorption edge into the VIS light region is to incorporate oxygen-vacancy (V_O) into ZrO₂ lattice, similar to TiO₂ [16] and ZnO [17,18] systems, which produces a new energy band near Fermi level. It was reported that V_O-rich black ZrO_{2-x} with a bandgap of 1.52 was prepared by a controllable magnesiothermic reduction in 5%

H₂/Ar atmosphere from white ZrO₂ with a bandgap of ~ 5.0 eV [19]. In our previous study, V_O-rich ZrO₂ nanocrystals with specific surface area of ~ 76 m²/g showed highly VIS light photocatalytic performance for degradation of tetracycline hydrochloride (abbreviated as TCH), and we considered that both photoexcitation of electron(e⁻)-hole(h⁺) pairs and photosensitive charge transfer process [20] at the liquid-solid interface contribute to VIS light photocatalytic degradation of TCH [21]. The mesoporous structured photocatalyst is more promising due to enhanced light-harvesting resulting from the enlarged surface and multiple scattering.

Generally, the photocatalytic performance of a catalyst is also dependent on reduction/oxidation rates on its surface and e⁻-h⁺ recombination rate besides light absorption property [22]. It has been suggested by Zheng et al. that the photocatalytic activity of V_O-rich ZnO nanocrystals mainly depends on the type and concentration of oxygen defects (eg. doubly charged oxygen vacancies V_O^{••} and interstitial oxygen defects) [23]. Recently, Rahman et al. has suggested that both types (singly charged oxygen vacancies V_O[•], V_O^{••} and neutral oxygen vacancies V_O^x) and relative amounts of these V_O controlled ferromagnetic properties of ZrO₂ nanostructures [24]. As for ZrO₂ photocatalyst, how about the relationships between VIS light photocatalytic properties and relative amounts of these V_O?

Solvothermal alcoholysis has been widely used to prepare TiO₂ because of controllable morphology and porous structure as well as

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high crystallinity [25]. Herein, we report a simple and cheap approach for preparing mesoporous ZrO_2 via a solvothermal process without any template agents. Further, the influence of solvothermal and annealing temperatures on relative amounts of these V_0 in mesoporous ZrO_2 is investigated. Subsequently, TCH, extensively used as antibacterial agents in clinical treatment and livestock industry, is chosen as the substrate to evaluate VIS light photocatalytic performance of ZrO_2 catalysts. The relationships between VIS light photocatalytic properties and relative amounts of these V_0 is also investigated in depth.

2. Experimental section

2.1. Synthesis of ZrO_2 catalysts

ZrO_2 catalysts was synthesized by using zirconium *n*-propoxide ($\text{Zr}(\text{OC}_3\text{H}_7)_4$), acetylacetone (Hacac), 2-ethoxyethanol and lactic acid as the starting chemicals. 0.01 mol $\text{Zr}(\text{OC}_3\text{H}_7)_4$ was dissolved in the mixture of 25 ml Hacac and 25 ml 2-ethoxyethanol by stirring, which further mixed with 0.01 mol lactic acid. After the above mixed solutions turned clear, the resultants were transferred into a 100 ml Teflon-lined autoclave to treat solvothermally at 150 °C and 220 °C for 24 h, respectively. The precipitates were centrifuged and alternately washed six times with distilled water and ethanol. The products were dried at 110 °C overnight and then annealed at various temperature for 4 h in air. The samples were marked as ZrO_2 -*x*-*y*, in which *x* and *y* indicated the solvothermal and annealing temperature, respectively.

2.2. Characterization

Crystal structure of samples was characterized by means of X-ray diffraction (XRD, Bruker AXS D2 PHASER, Germany) with $\text{CuK}\alpha$ radiation. Microstructure was characterized by using transmission electron microscope (TEM, JEOL 2100F, Tokyo, Japan). Specific surface area and pore size distribution of samples were measured on a Micromeritics ASAP 2020M analyzer. X-ray photoemission spectra (XPS) were measured using an Axis Ultra DLD spectrometer with monochromatic $\text{AlK}\alpha$ radiation and peak fitting of XPS spectra was performed by using Casa software. Electron spin resonance (ESR) of the samples was examined at room temperature on a Bruker A300 ESR spectrometer (Karlsruhe, Germany), operating in 9.86 GHz microwave frequency with a field modulator frequency of 100 kHz. UV–VIS diffuse reflectance spectra were measured by using a Shimadzu UV-3600 UV–VIS spectrophotometer equipped with an integrating sphere using BaSO_4 as a reference.

Photocurrent tests were performed on CHI 660E electrochemical workstation equipped with 300 W xenon lamp ($\lambda > 420$ nm cutoff filter), in which ZrO_2 samples on FTO substrates were used as working electrode. In addition, Pt wire and $\text{Hg}/\text{Hg}_2\text{Cl}_2$ were used as counter and reference electrode, respectively. The working electrode area was 1 cm^2 with 0.5 M Na_2SO_4 solution as a supporting electrolyte for the photocurrent test under on-off light conditions.

Temperature-programmed desorption (TPD) of adsorbed NH_3 on ZrO_2 samples was carried out using a Micromeritics AutoChem II 2920 Chemisorption Analyzer. In a typical NH_3 -TPD experiment, the samples were initially flushed at 200 °C for 2 h and then cooled down to 100 °C in a He flow (50 ml/min). Afterwards, NH_3 was adsorbed from a He flow (50 ml/min) containing 10% NH_3 for 40 min. The samples were then cooled down to 50 °C and flushed under a He flow for 30 min. The NH_3 -TPD was performed from 50 to 700 °C in flowing He (50 ml/min) with a heating rate of 10 °C/min.

2.3. VIS light photocatalytic performance measurements

Photocatalytic performance of various catalysts was evaluated by degradation of TCH solution under VIS light ($\lambda > 420$ nm) irradiation. The irradiation was acquired by a 200 mW/cm^2 300 W xenon lamp with

an UV cutoff filter ($\lambda > 420$ nm). In a typical experiment, 100 mg photocatalyst was dispersed in 100 ml of 40 mg/l TCH aqueous solution. Before irradiation, the above suspension was stirred in the dark for 60 min to reach the adsorption-desorption equilibrium. Then the suspension was illuminated under VIS light, sampled at regular intervals of 30 min and centrifuged to remove the catalyst at 8000 rpm for 10 min. The peak absorbency of the centrifuged TCH solutions at 357 nm was used to determine its concentration by using a Shimadzu UV-3600 UV–VIS spectrophotometer at room temperature. The initial concentration (C_0) was considered to be the TCH concentration after adsorption-desorption equilibrium.

2.4. Active species trapping experiments

2 mM Tert-butyl alcohol (TBA), 0.5 mM benzoquinone (BQ) and 2 mM disodium ethylenediaminetetraacetate (EDTA) were employed as the scavengers for trapping $\cdot\text{OH}$, $\cdot\text{O}_2^-$ and h^+ radicals, respectively [26]. The method was similar to the former photocatalytic properties test. Additionally, room temperature ESR signals of spin-trapped species were recorded under VIS light ($\lambda > 420$ nm) irradiation for 5 min in order to detect superoxide ($\cdot\text{O}_2^-$) and hydroxyl ($\cdot\text{OH}$) radicals, in which $\cdot\text{O}_2^-$ radicals were detected in methanol with 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) and $\cdot\text{OH}$ radicals were examined in ultrapure water with DMPO [27].

3. Results and discussion

3.1. Phase and textural structure characterizations

As shown in Fig. 1, XRD patterns clearly demonstrate that the precipitates solvothermally derived at 150 °C are amorphous, while those at 220 °C exhibit stably monoclinic ZrO_2 (*m*- ZrO_2 , according to JCPDF no. 78-1807). Based on the thermal analysis of supplementary Fig. S1, the different temperature was chosen to thermally treat the precipitates in air. After annealing at 350 °C in air, only metastably tetragonal ZrO_2 (*t*- ZrO_2 , JCPDF no. 79-1770) can be obtained for the precipitates derived at 150 °C [28], while those derived at 220 °C still maintain purely monoclinic phase. For the ZrO_2 -220-350 and ZrO_2 -150-350 samples, pure phase was also confirmed by Raman symmetry analysis (Fig. S2) [29,30].

N_2 adsorption-desorption isotherms of the precipitates derived at 150 and 220 °C shown in Fig. 2(a1) are IV-type behavior with triangular hysteresis loop, typical of mesoporous materials. Accordingly, a narrow pore size distribution centered at 3.6 nm is obtained for those precipitates (Fig. 2(a2)). Brunauer-Emmett-Teller (BET) measurements show that specific surface area (S_{BET}) of the precipitates derived at 150 and 220 °C is 232.7 and 203.3 m^2/g , respectively. This well-structured mesoporosity of the ZrO_2 -220-0 sample with high S_{BET} is comparable to mesoporous ZrO_2 synthesized via P123 template [31,32], of which the proposed synthesis pathway is depicted in Fig. S3. As shown in Fig. 2(b1), the morphology of the ZrO_2 -220-0 sample exhibits significant grain dispersion with the size of several nanometers, probably ascribed to the existence of unidentate carboxylic ligands [33], as shown in Fig. S4.

After annealing at 350 °C in air, a type IV isotherm is observed for the ZrO_2 -220-350 sample (Fig. 2(a1)), in which a gradual increase in slope starts at $P/P_0 = \sim 0.4$, followed by a sharp adsorption uptake at $P/P_0 = 0.6$ – 0.9 . The gentle upward slope from $P/P_0 = \sim 0.4$ is typical for mesoporous materials, corresponding to pore size distribution of a weak peak at ~ 3.4 nm (Fig. 2(a2)) [34]. The further increase at higher P/P_0 indicates substantial interparticle porosity, which is directly associated to a rather broad peak at ~ 9.0 nm. Additionally, the ZrO_2 -220-350 sample exhibits the uniformly fine grains (Fig. 2(b2)) together with relatively high S_{BET} of 131.3 m^2/g . Nevertheless, no adsorption of N_2 was observed in the ZrO_2 -150-350 sample, indicating the absence of mesoporous structure. This is due to the collapse of mesopores resulting

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