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Growth study and photocatalytic properties of Co-doped tungsten oxide mesocrystals

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Cobalt-doped tungsten oxide mesocrystals with different morphologies have been successfully generated using a solvothermal method with tungsten hexachloride and cobalt chloride salts as precursors. The resulting mesocrystals were characterized by X-ray diffraction, field emission scanning electron microscopy, transmission electron microscopy, Brunauer–Emmet–Teller analysis of nitrogen sorptometer, and UV–vis diffuse reflectance spectroscopy. The photocatalytic properties of the cobalt-doped tungsten oxide mesocrystals were evaluated on the basis of their ability to degrade methyl orange in an aqueous solution under simulated sunlight irradiation. Results showed that the cobalt doping had obvious effect on the morphologies of the final products, and lenticular and blocky cobalt-doped tungsten oxide mesocrystals could be obtained with 1.0 wt.% and 2.0 wt.% cobalt doping, respectively. The cobalt-doped tungsten oxides exhibited superior photocatalytic activities to that of the undoped tungsten oxide.

1. Introduction

Since the discovery of carbon nanotubes by Ijima, low dimensional nanostructured materials have attracted considerable interests because they exhibit enhanced chemical and physical properties compared to their bulk counterparts [1–3]. Simultaneously, significant progress has been made with regard to the synthesis and fabrication of a broad range of nanomaterials with well-controlled morphology, dimension, size, and composition using various methodologies [4]. The assembly of nanoscale building units into functional devices is prerequisite for the practical applications of nanomaterials. Mesocrystals, a new interesting class of crystal family, are mesoscopically-ordered superstructures that are built up from highly aligned nanocrystals and may be helpful in designing and controlling the assembly of building units into functional nanodevices [5–7].

Tungsten oxides, as one of the important oxide semiconductors, are attracting more special attention since they offer a wide range of potential applications in devices such as electrochromic display, semiconductor gas sensors and photocatalysts due to their outstanding electrochromic, gaschromic, and optochromic properties [8–10]. Till now, a broad range of tungsten oxide nanostructures have been prepared by various strategies, including thermal evaporation, microwave irradiation, sol–gel method, combustion synthesis, and solvothermal method [11–15]. In particular, soft-chemistry route especially solvothermal synthesis is capable of generating tungsten oxide nanostructures with controllable morphology and crystalline structure, such as

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WO_3 nanorods, WO_3 nanosheets, WO_3 nanobelts, WO_3 microflowers, $W_{18}O_{49}$ nanowires, and $W_{18}O_{49}$ nanosheets [16–20]. Recently, much research effort has been paid to the investigation on tungsten oxide mesocrystals, which pave a new way for the assembly of low-dimensional nanostructured tungsten oxides. For example, Pang et al. prepared hexagonal $W_{18}O_{49}$ mesocrystals by using solvothermal method, and they were found to exhibit excellent electrochromic property. Hu et al. fabricated silver indium tungsten oxide mesocrystals by a microwave-assisted approach, which possessed visible-light-driven photocatalytic activity for the degradation of organic dyes [21]. However, the formation mechanisms of the tungsten oxide-based mesocrystals are yet understood clearly. In addition, little attention has been paid to the synthesis of transition metal-doped tungsten oxide mesocrystals.

In our previous work, we successfully prepared transition metal-doped tungsten oxide nanostructures and studied their optical properties [22]. In this paper, we extended our work to investigate the effects of cobalt (Co) doping on the morphologies of the resulting mesocrystals as well as their growth mechanisms. The photocatalytic properties of the Co-doped tungsten oxide mesocrystals under simulated sunlight irradiation were also investigated for the first time.

2. Experimental Details

The Co-doped tungsten oxide mesocrystals were prepared by using solvothermal method with tungsten hexachloride (WCl_6) and cobalt dichloride hydrates ($CoCl_2{\cdot}6H_2O$) as raw materials, and with cyclohexanol as solvent. All chemicals were purchased from Shanghai Chemical Reagent Company and used without further purification. WCl_6 and $CoCl_2{\cdot}6H_2O$ with molar ratios of 1:1 and 1:2 were firstly dissolved in 5 ml of ethanol in a beaker to obtain a solution, which were then transferred into a 100 ml Teflon-lined high-pressure reaction vessel. 60 ml of cyclohexanol was then added to the vessel. The reaction vessel was finally sealed and heated at 200 °C in a Muffle furnace for 12 h. After natural cooling to room temperature, the as-synthesized products were washed thoroughly with distilled water several times, and centrifuged with ethanol and acetone for further examination.

The crystalline structure, morphology, surface specific area, and chemical composition of the as-synthesized products were analysed by using X-ray diffraction (XRD, D/MAX-2500), field emission scanning electron microscope (FESEM, JSM6700F, 15 kV), energy dispersive spectrometer (EDS), transmission electron microscope (TEM, JEOL 2000FX, operated at 120 kV), and Brunauer–Emmet–Teller (BET) analysis of nitrogen sorptometer (Autosorb-1). The absorbance of the as-synthesized products was measured by using UV–vis diffuse reflectance spectroscope (U-3010, HITACHI).

Photocatalytic activities of the Co-doped tungsten oxide mesocrystals were evaluated on the basis of their ability to degrade methyl orange (MO) in an aqueous solution under simulated daylight irradiation provided by a 350 W Xe lamp. Photocatalytic experiments were performed in a photochemical reactor containing a suspension of the Co-doped tungsten oxide photocatalysts (50 mg) in an MO aqueous solution (50 ml, 10 mg/l) with continuing agitation using a magnetic stirrer. Prior to the light irradiation, the MO solutions with the photocatalysts were kept in the dark for 2 h to reach an adsorption–desorption equilibrium. The absorbance of MO solutions before and after degradation by the photocatalysts was analysed by UV–vis diffuse reflectance spectroscopy. The concentrations of MO in aqueous solution were simply determined by the maximum absorbance around 465 nm of wavelength. The degradation efficiency of MO was defined by the equation of $\frac{C}{C_0} \times 100\%$, where C is the concentration of MO aqueous solution after light irradiation, and C_0 is the equilibrium concentration of MO at the equilibrium adsorption state.

3. Results and Discussions

With only WCl_6 as raw material in the solvothermal reaction system, the resulting products are pure monoclinic $W_{18}O_{49}$ (JCPDS Card No. 71-2450), with (010) plane possessing the strongest diffraction intensity, as shown in Fig. 1a. The broad diffraction peak around 26° may be attributed to the presence of a thin amorphous layer on the surfaces of the $W_{18}O_{49}$ nanorods, as discussed in our previous work [23]. As shown in Fig. 1b and c, the diffraction peaks of the resulting product synthesized with mixed WCl_6 and $CoCl_2{\cdot}6H_2O$ as raw materials could also be assigned to monoclinic phase of $W_{18}O_{49}$. EDS spectra (provided in Supporting Information) could verify the existence of Co elements in the resulting products obtained with W/Co molar ratios of 2:1 and 1:1, and their weight percents were about 1.0% and 2.0%, respectively. The broad peak corresponding to amorphous phase almost disappeared, indicating increased crystallinity of the resulting samples with the doping of Co. Notably, the (010) peaks of the 1.0 and 2.0 wt.% Co-doped $W_{18}O_{49}$ shifted to low diffraction angles in comparison with the undoped $W_{18}O_{49}$. Since the ionic radium of Co^{2+} (78 pm) is larger than those of both W^{4+} (68 pm) and W^{6+} (65 pm), the Co doping could inevitably lead to the lattice expansion of monoclinic $W_{18}O_{49}$, and then to the shift of diffraction peaks to low angles.

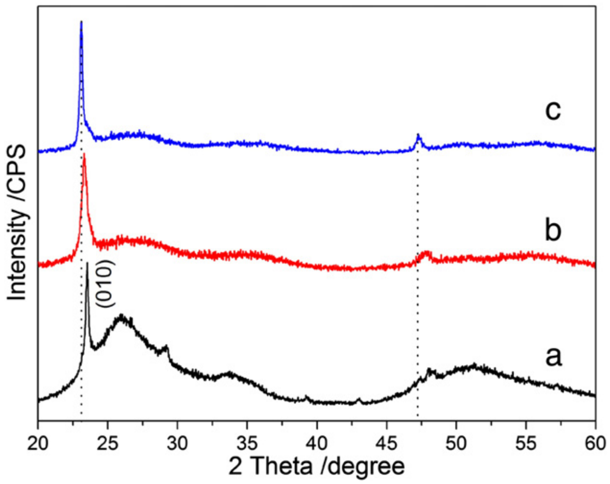

Fig. 1 – XRD patterns of (a) undoped, (b) 1.0 wt.% and (c) 2.0 wt.% Co-doped $W_{18}O_{49}$.