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Morphology controlled syntheses of Cu-doped ZnO, tubular Zn(Cu)O and Ag decorated tubular Zn(Cu)O microcrystals for photocatalysis

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HIGHLIGHTS

- The morphology controlled synthesis of Cu^{2+}-doped ZnO crystal was easily carried out.
- In the synthesis Cu^{2+} ion was used as a dopant and a morphology controller.
- The hexagonal prism-like Zn(Cu)O crystal with twinned structure was obtained.
- The tubular Zn(Cu)O materials were easily obtained via selective dissolving by alkali.
- Tubular Zn(Cu)O/Ag sample exhibits higher photocatalytic activity than P25(TiO_2).

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ABSTRACT

Without any assistance of surfactant and/or template the hexagonal prism-shaped Cu^{2+}-doped ZnO (Zn(Cu)O) microcrystals with twinned structures were easily synthesized by one-step co-precipitating under atmospheric pressure and moderate temperature, in which Cu^{2+} ion was used as the dopant and the morphology controller. Because Cu^{2+} ions can be adsorbed on the (0001) and $\{10\bar{1}1\}$ planes the growth on these planes was restrained, resulting in the formation of Zn(Cu)O microcrystals with stubby hexagonal prism shape. Meanwhile, the twinned structure Zn(Cu)O microcrystals were obtained via the electrostatic interaction between adsorbed Cu^{2+} ion and two $(000\bar{1})$ negative planes. When twinned structure Zn(Cu)O sample was etched by NaOH solution the (0001) polar planes at two ends of Zn(Cu)O crystal were dissolved via forming $Zn(OH)_4^{2-}$ complex ion, but the non-polar {0110} planes did not. As a result, the tubular structure Zn(Cu)O microcrystals (T-Zn(Cu)O) were obtained in the absence of template and/or specific protective agent. The metallic Ag decorated tubular Zn(Cu)O (T-Zn(Cu)O/Ag) samples were prepared by auto-catalyzed deposition reaction. The morphological, structural, photoluminescence, as well as photocatalytic properties of Zn(Cu)O, T-Zn(Cu)O and T-Zn(Cu)O/Ag samples were investigated and the results indicated that the Zn(Cu)O sample with a very small amount of doped Cu^{2+} ion showed higher photocatalytic activity than ZnO. Tubular structure Zn(Cu)O samples showed moderately enhanced photocatalytic activities compared to corresponding Zn(Cu)O samples. By decorating metallic Ag on the surfaces the T-Zn(Cu)O/Ag samples exhibited distinctly enhanced photocatalytic activities due to the contribution of Schottky barrier and intensive light absorption in Vis and NIR regions.

1. Introduction

In the last decade zinc oxide (ZnO) has been widely investigated and applied as a field-effect transistor [1], optical device [2], dye-sensitized solar cell [3], photocatalyst [4], and gas sensor [5]. For further improving the performance proper dopants were introduced into ZnO matrix to tune its structural, morphological, optical and magnetic properties [6,7]. Recently, Cu^{2+} ion is considered as an important dopant for ZnO. For examples, Cu-doped ZnO crystalline film was synthesized by hydrothermal method for photoluminescence property [8]. Ferromagnetic ZnO:Cu microstructures were obtained by hydrothermal method with enhanced photocatalytic performance [9]. Nanocrystalline Cu-doped ZnO thin films

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were prepared by advanced spray pyrolysis for H_2S gas sensing [10]. So far, various fabrication techniques have been used, thereinto, hydrothermal or solvothermal method is probably a wise choice due to its moderate synthetic condition and simple operating steps. Besides, it could meet the demand of large-scale industrial fabrication [8,11]. Since various crystal faces of a microcrystal may exhibit different physical and chemical properties, the morphology controlled synthesis of micro/nanocrystals with different shapes and exposed surfaces becomes very important and challenging [12]. In most cases, when the morphology controlled synthesis of ZnO is carried out, the surfactant, special reagent, template substrate, or special procedure is often required [13,14].

It is well known that in addition to the composition, the morphology, particle size, surface area, and the surface state of catalyst also affect the photocatalytic performance [15]. Small particle size and large surface area are beneficial to increase the photocatalytic activity, but they result in difficult separation and low recycling photocatalytic efficiency, especially in large-scale industrial application. However, the hollow structure materials may solve the problem due to their specific characteristics, such as large surface area, low density, good permeation and distinct optical properties. For instance, the three-dimensional center-hollow ZnO architectures with multigonal star-shape have been successfully fabricated via a surfactant-assisted hydrothermal process [16]. Vertically aligned ZnO nanotubes were prepared by etching ZnO rod arrays in aqueous solution, which were previously developed by chemical bath deposition method [17]. Using Zn powder as precursor templates, hollow ZnO microspheres were prepared by thermal evaporation method [18]. Up to now, most of hollow structures materials are obtained via various template-assisted methods [19], in which the template is difficult to remove, resulting in adverse effect on the catalytic performance. Recently, the syntheses of ZnO nanotubes are mainly based on chemical vapor deposition, electrochemical approach or surfactant-assisted chemical etching strategy [20,21]. These syntheses were carried out under harsh conditions, such as multiple steps, complex post-treatments, particular conductive substrates, and especial surfactants. Therefore, exploring the strategy for a green, simple, template/surfactant-free fabrication of hollow or tubular structure ZnO is highly desirable.

In this study, we report a novel, facile, environmental friendly one-step co-precipitating method under atmospheric pressure and moderate temperature for morphology controlled synthesis of Cu^{2+}-doped ZnO with a twinned structure without any assistance of surfactant and/or template. Utilizing the anisortropy of crystal planes, the tubular structure Zn(Cu)O microcrystals were easily obtained via selectively dissolving by a concentrated alkali liquor (NaOH). The cavity diameter and wall thickness of tubular structure material could be tuned by both the reaction time and the alkali concentration. The growth and formation mechanisms of tubular and twinned structures were investigated and the photocatalytic performances were evaluated by photodegrading Acid Orange 7 (AO7). This synthetic technique implies the potential for large-scale industrial application in the synthesis of special structural material under normal condition.

2. Experimental

2.1. The morphology controlled synthesis of Cu-doped ZnO microcrystals

Cu^{2+}-doped ZnO microcrystals were easily synthesized by one-step co-precipitating method using zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$), copper(II) acetate monohydrate ($Cu(CH_3COO)_2{\cdot}H_2O$) and triethanolamine [$(HOCH_2CH_2)_3N$] as raw materials. Generally, 0.025 mol $Zn(CH_3COO)_2$ and $Cu(CH_3COO)_2$ solids, in which the mole fractions of Cu^{2+} are 0, 0.10, 0.20 and 0.30, respectively, were dissolved in 250 mL deionized water (named solution A), meanwhile, 250 mL 0.30 mol L^{-1} triethanolamine solution was prepared (named solution B). When the 1500 mL deionized water loaded in a 2000 mL three-necked bottle was heated to 92 °C, solutions A and B were synchronously added dropwise into the bottle under vigorous stirring. After finishing the adding the suspension was kept at 92 °C for 1 h and then aged for 18 h at room temperature. The product was filtered and washed several times with deionized water until the Cu^{2+} ion in the eluate was not detected, then dried at 60 °C for 24 h. Finally, the Cu-doped ZnO samples with the mole fraction of Cu^{2+} ion in reaction solution at 0, 0.10, 0.20 and 0.30 were prepared and denoted by ZnO, Zn(Cu)O-1, Zn(Cu)O-2, and Zn(Cu)O-3, respectively.

2.2. The preparation of tubular Cu-doped ZnO samples by selectively dissolving

In this paper we report a facile, green and template/surfactant-free method to synthesize tubular structure material via selectively dissolving by strong base solution. Firstly, 0.025 mol of as-prepared Zn(Cu)O sample was ultrasonically dispersed in 250 mL deionized water for 30 min, then the obtained suspension was added into a 2000 mL three-necked flask which loaded 1500 mL deionized water. When the suspension was heated to 94 °C, 250 mL 4 mol L^{-1} NaOH solution (n_{Zn}:n_{OH} = 1:40) was added dropwise into the bottle under mechanically stirring. When finishing the adding, the suspension was kept at the same temperature for 3 h. Then the residues were filtered and washed several times with deionized water, dried at 60 °C for 24 h, and then the tubular structure samples were obtained. The tubular products used ZnO, Zn(Cu)O-1, Zn(Cu)O-2, and Zn(Cu)O-3 as precursors were denoted by T-ZnO, T-Zn(Cu)O-1, T-Zn(Cu)O-2, and T-Zn(Cu)O-3, respectively.

2.3. The preparation of silver decorated tubular Cu-doped ZnO samples

Metallic Ag was decorated on the tubular Cu-doped ZnO sample by photodeposition technique [22]. 0.007 mol of as-prepared tubular sample was ultrasonically dispersed in 700 mL 0.002 mol L^{-1} $AgNO_3$ solution (the molar ratio of Zn/Ag was 1:0.2) for 30 min. Then the suspension was illuminated by a 300 W UV-lamp (predominantly emitting at 365 nm, produced by Philips Electronics Ltd.) for about 3 h until the Ag^+ ion in the suspension was not detected by Cl^- ion. The product was filtered and washed several times with deionized water, dried at 60 °C for 24 h. Finally, the metallic silver decorated products were obtained and denoted by T-ZnO/Ag, T-Zn(Cu)O-1/Ag, T-Zn(Cu)O-2/Ag and T-Zn(Cu)O-3/Ag, respectively.

2.4. Photocatalytic activity testing

In order to evaluate the photocatalytic performances of as-prepared samples, Acid Orange 7 ($C_{16}H_{11}N_2NaO_4S$, M.W. = 350.32, AO7) was chosen as a target compound. The photocatalytic degradation reaction was carried out under illuminating by a 100 W high-pressure metal halide lamp filled with xenon buffer gas (360 nm < λ < 780 nm, the strongest emitting at 595 nm, produced by Sen Bai Lai Lighting Ltd., Shenzhen, China), which was positioned vertically 20 cm away from the liquid surface in the reaction vessel (100 mL beaker). For each condition, 0.05 g sample was ultrasonically dispersed in 50 mL 60 mg L^{-1} of AO7 solution in the darkness for 30 min to establish the adsorption equilibrium, then the beaker was placed in a water bath maintained temperature at 30 ± 0.2 °C, and the degradation reaction started with magnetic stirring. At regular intervals, about 2 mL suspension was