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Effect of urea on the synthesis of Al-doped ZnO nanoparticle and its adsorptive properties for organic pollutants

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ABSTRACT

Al-doped ZnO nanoparticles were synthesized through a solution combustion synthesis derived from zinc nitrate, aluminum nitrate and urea mixed solution. The effects of fuel/oxidizer molar ratio (ϕ) on the morphology, physical properties, and adsorptive properties for organic pollutants of Al-doped ZnO have been systematically investigated. The results indicated that the homogeneous Al-doped ZnO powders might be prepared by selecting an optimum ϕ in solution. The results of XRD pointed toward a significant pure wurtzite ZnO phase for 2 mol% Al-doped ZnO powders prepared with different ϕ. With the increase of ϕ, the morphology of the products changes from clusters of irregular particles into flakes. A well-distributed and smaller crystallite size varying from 30 nm to 50 nm was observed from 2 mol% Al-doped ZnO sample ($\phi = 4$). In addition, the Al-doped ZnO sample ($\phi = 4$) showed a higher absorption ability and shorter equilibration time for organic pollutants compared to other samples.

1. Introduction

Removal of colored materials and dyes from water is becoming more and more important to improve environment, therefore considerable attentions have been paid to water treatments in recent years [1,2]. Many physicochemical methods have been developed to remove these pollutants from waste water, such as adsorption, coagulation–flocculation, biological treatment, and photocatalysis, etc. [3–6]. Among these methods, adsorption is believed to be the most convenient, and it is widely used in water treatment [7]. In this case, adsorbents play a key role to efficiently remove pollutants from water. Usually, the removal capacity of any adsorbents largely depends on their physicochemical properties [8]. Materials with mesoporous structure, larger pore volumes, and chemical inertness, etc., possess high removal capacities, and they are often used as adsorbents [9].

Recently, a great deal of work have been reported on Al-doped ZnO, which possesses attractive properties for potential applications as thermoelectric materials [10], gas sensing materials [11] and wastewater treatment [12]. Al-doped ZnO is a solid solution consisting of ZnO and Al_2O_3, which both have wurtzite hexagonal structure. And the comparable ionic radius (Zn^{2+} = 0.60 Å and Al^{3+} = 0.39 Å), serves as a possibility for the solid solution formation. During the past few years, various techniques, including hydrothermal method [11], microwave-activated thermal decomposition [10], and solution combustion synthesis (SCS) [12], have been employed to synthesis Al-doped ZnO. Among the available chemical processes, SCS is one of the proper methods to prepare materials, which exhibit well-defined chemical composition with homogeneous distribution of the elements [13]. Besides, the SCS method can save energy, rendering simple and instantaneous combustion reaction [14]. This method involves exothermic chemical reaction between oxidizer and fuel. Many reports have demonstrated that the fuel type and fuel to oxidizer ratio have been shown to alter the combustion behavior, oxidation state, morphology and grain size of the products [15–17], these issues significantly affect the applications of the resulting materials as catalysts and adsorbents. In particular, urea is proposed as the most convenient fuel for its ready availability, high exothermicity [18,19] and effective complexion of amine group (i.e., $—NH_2$) from urea with transition metals [20,21,26–31]. Although some reports [12,22] have been documented about the synthesis of Al-doped ZnO powders by SCS method, however, there are no significantly systematic studies about the effects of fuel/oxidizer molar ratio on the synthesis Al-doped ZnO. In the paper, Al-doped ZnO powders have been synthesized successfully by SCS method, in which zinc

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nitrate and aluminum nitrate as oxidizer, urea as fuel have been utilized. The influences of fuel/oxidizer molar ratio on the morphology, the crystallite size, physical properties, and adsorptive properties for organic pollutants of synthesis Al-doped ZnO have been studied in detail.

2. Experimental procedure

2.1. Synthesis

A series of samples of Al-doped ZnO were prepared by solution-combustion synthesis using zinc nitrate [$Zn(NO_3)_2{\cdot}6H_2O$] and aluminum nitrate [$Al(NO_3)_3{\cdot}9H_2O$] as the oxidant, urea [$CO(NH_2)_2$] as the fuel. Analytical reagent grade chemicals were purchased commercially. As a typical sample preparation procedure, Zn $(NO_3)_2{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$ and $CO(NH_2)_2$ were dissolved into 250 mL deionized water under stirring to obtain a homogeneous solution. The mixture was filled into a 1000 mL glass, and was heated in air in an electrical furnace whose temperature could be controlled.

2.2. Characterization

Phases of the calcined powders were investigated by X-ray diffraction (XRD, MXP21VAHF) at room temperature. The 2θ angle was varied from 10° to 90° in 0.02° increments. Morphology of the calcined powders was characterized by scanning electron microscopy (SEM, JSM-6510) and transmission electron microscopy (TEM, Tecnai G2 F30 S-TWIN). The nitrogen adsorption and desorption isotherms of the calcined samples were collected using a Quantachrome-1000e surface area analyzer. The specific surface area (SSA) of the calcined samples was determined by the Brunauer–Emmett–Teller (BET) method using an Automated Surface Area & Pore Size Analyzer (QUADRASORB SI-MP, Quantachrome Instruments, BoyntonBeach, FL). Pore diameter and pore volumes of the calcined samples were calculated from the desorption branch of the Barret–Joyner–Halenda (BJH) model.

2.3. MO adsorption

All adsorption experiments were carried out at room temperature. With the aim of investigating the adsorption performance of the Al-doped ZnO materials toward the adsorption of organic pollutants, we selected methylene orange (MO) as a model contaminant for adsorption experiments. For the adsorption rate tests, 60 mg Al-doped ZnO adsorbents were added to 60 mL of MO (10 mg/L) solutions, and solutions were under stirring for a certain time of 30 min at room temperature. The measurements of MO concentrations were carried out using a UV–visible spectrophotometer (UV–vis spectrophotometer, Varian Cary 5000). The MO concentration was determined by measuring the solution absorbance at 466 nm.

3. Results and discussion

3.1. Synthesis and characterization of the products

SCS is a self-sustained reaction in homogeneous solution. The solution of zinc nitrate, aluminum nitrate and urea was filled into a 1000 mL glass and heated in air in an electrical furnace whose temperature could be controlled. As heating continued, the solution evaporated and formed a gelatinous mass. Upon further heating, the resultant mass swelled suddenly coupled with flame and the release of a lot of gases. The whole process of swelling and combustion of gel appeared to undergo a self-propagating and exothermic reaction and took only several minutes, resulting in finally a porous and foamy powders. It was observed that the powders are of brownish color. Then the powders were calcined at 750 °C for 1 h, and the color of products changes to white. The SCS process can be shown as the following Eq. (1):

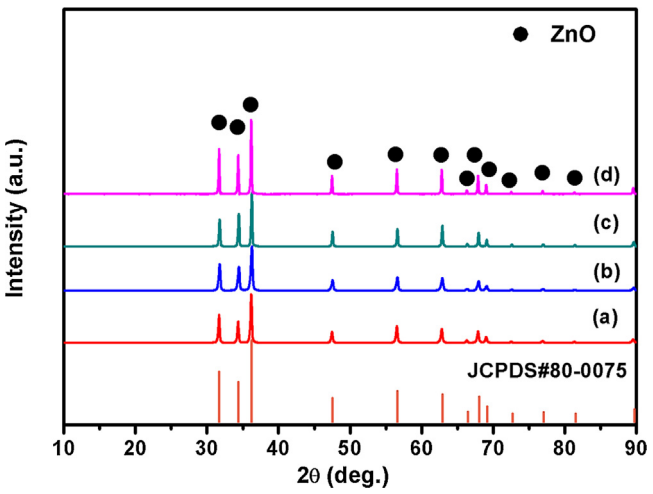

Fig. 1. XRD of calcined 2 mol% Al-doped ZnO samples prepared with different ϕ: (a) 1, (b) 1.7, (c) 4, and (d) 6.

$$(1-\chi)Zn(NO_3)_2 + \chi Al(NO_3)_3 + \left(\frac{5+3\chi}{3}\right)CO(NH_2)_2 \rightarrow Zn_{1-\chi}Al_\chi O + \left(\frac{5+3\chi}{3}\right)CO_2 + \left(\frac{16+9\chi}{6}\right)N_2 + 2\left(\frac{5+3\chi}{3}\right)H_2O \quad (1)$$

Some researches [10,23–25] propose the solid solubility for Al in ZnO is less than 3 mol%, and the content of Al (χ) in the paper is 2 mol%. Here, the amount of zinc nitrate was 0.1 M, and the fuel to oxidizer ratio $\left(\frac{5+3\chi}{3}\right)$, denoted by ϕ, represents a tunable parameter, where $\phi = 1.7$ means the stoichiometric ratio, while $\phi > 1.7$ (<1.7) implies fuel-rich (lean) conditions. The ϕ in the paper is in the

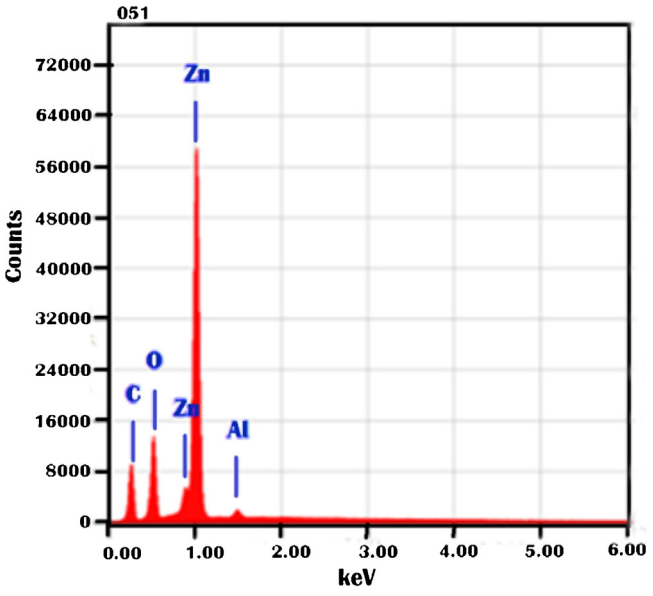

Fig. 2. EDX spectra of calcined 2 mol% Al-doped ZnO particles prepared with ($\phi = 4$).