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Original Research Paper

Preparation of CuO nanopowders and their catalytic activity in photodegradation of Rhodamine-B

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ABSTRACT

CuO nanopowders have been successfully synthesized in two different morphologies from same precursor using a facile gel to crystalline (reflux) and co-precipitation synthesis routes. SEM and TEM observations indicate that the morphology of the products depends on preparation technology, while XRD shows the formation of CuO nanocrystals with monoclinic crystal system in both cases. A comparison of morphological characterization of CuO nanopowders showed flower-like and aggregated nanoparticles in the form of clusters using reflux and co-precipitation techniques, respectively. Photocatalytic activity of the products in the aqueous solution of Rhodamine-B has been investigated under UV-light for a given time using UV–visible spectroscopy and the mineralization of organic substance was measured by total organic carbon (TOC) analysis. It was observed that the photocatalytic activity in the presence of flower-like CuO nanopowders was higher than that of observed with aggregated nanoparticles. Also the mechanisms for the formation of CuO nanopowders and the obtained results of photocatalytic degradation of Rhodamine-B are discussed.

1. Introduction

Semiconductor nanostructures fall into an important class of materials, which have various applications in optoelectronic device technologies, catalysis, cosmetics and biosensors [1–3]. The oxides of transition metals perform an important class of semiconductors. Among various semiconductors, Cu and its oxides have attracted a great deal of attention in both fundamental researches and technical applications because of their outstanding catalytic, optical, electrical conductivity, chemical stability, low cost, and other properties [4,5]. CuO is known as *p*-type semiconductor, exhibiting narrow band gaps ($E_g = 1.2$ eV), which has been widely exploited for diverse applications, such as an active electrode material for Li-ion batteries, magnetic storage media, heterogeneous catalysts, gas sensors and solar cells [6,7].

The controlled synthesis of semiconductor oxide materials is very interesting due to their applications both in practical and theoretical points of view. Various synthesis techniques including wet chemical methods [8], microwave irradiation [9], ultrasound-assisted methods [10], sol–gel techniques [11], electro deposition [12], thermal decomposition of different precursors [13], gas-phase oxidation [14], electrochemical methods [15], thermal oxidation [16], one-step solid state reaction methods at room temperature [17], co-implantation of metal and oxide ions [18], high-temperature combustion [8], quick-precipitation [19,20] and so on, have been applied to the preparation of semiconductor oxide materials to achieve special chemical, optical and electronic properties. Among several techniques, simple wet-chemical methods have been widely used for the preparation of nanostructures. These methods effectively control the morphology and chemical composition of prepared powder, but these methods require high temperature to produce the final product. Therefore low temperature synthesis of metal oxide semiconductors is a novel and suitable synthesis method.

The crystalline metal oxide nanostructures that can be synthesized by gel to crystalline conversion method (reflux method) helps to obtain final products at temperatures around 100 °C [21]. The reflux method differs from others in two aspects: (i) no expensive alkoxide reactants are required and (ii) no need of higher temperature calcinations to produce the final product [22]. The method of gel to crystalline conversion is reported in the literature

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for the preparation of multi-component oxides, such as perovskites and spinels [23] and single-component oxides, such as ZnO, Co_3O_4, SnO_2 Fe_3O_4 and TiO_2 [24]. As a novelty, this is the first report about the synthesis of CuO nanopowders by a simple method (i.e. gel to crystalline conversion). Other advantages of this method includes using copper nitrate as the sole copper precursor, cost-effective and lower synthesis temperature.

Water pollution due to release of chemicals from industrial sectors is an important source of environmental contamination. The major constituents of these pollutants are heavy metals, pesticides, dyes, aliphatic and aromatic detergents, degreasing agents, volatile organics and chlorophenols [25]. Organic dyes are extensively used for various industrial applications including textile dyeing, photographic, coating and photochemical industries. Most of the dyes used as coloring materials are toxic to aquatic organisms [26]. Rhodamine-B (RhB) is one of the most common xanthenes dyes which was applied in textile industries, found to be potentially toxic and carcinogenic [27]. In addition, wastewaters from dyeing and textile industries easily produce toxic trihalomethanes when chlorinated [28]. Therefore, the removal of these pollutants from the environment is an important challenge in ecological systems, because of their toxicity and carcinogenic properties.

Many conventional methods have been proposed to remove these pollutants. Photocatalytic elimination process is one of the famous removal methods in this field. The pollutants can be effectively removed from wastewater by the photocatalytic process using semiconductor photocatalysts. Nowadays, remarkable progresses have been made in the photodegradation of dye pollutants under ultraviolet light [29,30]. Among several metal oxides, CuO is one of the suitable photocatalysts for this purpose, because of its photocatalytic activity, reusability, nontoxicity and other properties [31–33].

In the present work, CuO nanostructures have been synthesized using two simple reflux and co-precipitation methods from the same copper hydroxide precipitated gel precursor. Morphological, structural and optical properties and thermal behavior of the products have been identified using scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), Fourier transformer infrared (FTIR) spectroscopy, UV–visible–NIR spectroscopy and thermal gravimetric (TG) and differential thermal analysis (DTA) techniques. The other aim of the present work is the investigation of the photocatalytic degradation of RhB under UV-light radiation and using of CuO nanopowders with different morphologies. Actually the most novelty of this work is the degradation of RhB in the presence of flower-like CuO nanopowders as an efficient and inexpensive photocatalyst nanomaterial.

2. Experimental

2.1. Materials

Analytical grade copper nitrate ($Cu(NO_3)_2{\cdot}3H_2O$, purity: 99.5%), ammonium hydroxide solution (25% NH_3 in water) and Rhodamine-B ($C_{28}H_{31}ClN_2O_3$, purity: 95%) were purchased from Sigma-Aldrich and were used as received without further purification.

2.2. Instruments

Thermal behavior of precursor was characterized by thermal gravimetric (TG) and differential thermal analysis (DTA) using Linseis STA PT-1000 instrument at a heating rate of 10 °C/min in N_2 atmosphere with Al_2O_3 as reference. X-ray diffraction (XRD) patterns were recorded by a Bruker D8-advance diffractometer using Cu Kα radiation (λ = 1.5406 Å). Surface morphologies of products were characterized by using a LEO-1430 VP scanning electron microscopy (SEM) with an accelerating voltage of 15 kV. TEM images were prepared on a Philips EM 208 transmission electron microscope operated at an accelerating voltage of 100 kV. Fourier transform infrared (FTIR) spectra were recorded on a Bruker-vertex70 spectrophotometer in KBr pellets. The optical properties of sample were monitored on a UV–visible spectrophotometer (model Carry 5, Varian). UV–visible spectra of RhB were performed with a Shimadzu UV-265 spectrophotometer using a quartz cell. Total organic carbon (TOC) analyzer (multi N/C 3000; Analytik Jena) was used to measure TOC concentration in the filtered samples.

2.3. Synthesis

2.3.1. Synthesis of CuO nanopowders via reflux method

In a typical synthesis, 1.5 M NH_4OH was added drop wise into a 1 M aqueous solution of $Cu(NO_3)_2{\cdot}3H_2O$ while stirring to precipitate copper as a light-blue hydroxide gel. The molar ratio of NH_4OH:Cu was 1.5. The hydrated precipitated gel filtered off and washed several times with deionized water until achieving to pH = 7. The precipitated gel was equally divided into two parts and separately transferred to a flask and then fitted with a water condenser. These two samples were stirred under reflux condition for 4 (denoted as CuO-4 h) and 6 h (denoted as CuO-6 h) and temperature was maintained around 90–100 °C. The color of precipitates turned from light-blue to splendid black while gradually converted to suspension state during the reflux which explained the formation of copper oxide crystallite. Finally, the solid products were filtered off and washed with ammonium hydroxide and then with deionized water for several times and dried at 80 °C in an oven.

2.3.2. Synthesis of CuO nanopowders via co-precipitation method

In a typical synthesis, similar to reflux method, copper hydroxide was precipitated with 1.5 M NH_4OH while stirring for 30 min at room temperature. The obtained gel was repeatedly washed with deionized water till the gel was devoid of any impurities. The remaining solid was dried in air at ambient temperature and calcined at 350 °C (denoted as CuO-P350) and 450 °C (denoted as CuO-P450) for 2 h, respectively. The reaction conditions were varied to explore the effect of different reaction parameters on the size and morphology of the products.

2.4. Photocatalytic performance

Photodegradation efficiency of synthesized CuO nanostructures was evaluated by photocatalytic degradation of RhB aqueous solution at room temperature (25 °C). The experiments were performed in a jacketed column quartz reactor. The high pressure Hg UV lamp (300 W) was positioned centrally in the reactor, inside a quartz tube with wavelength irradiation of 254 nm. In a typical procedure, 150 mL of 2.0×10^{-5} M artificially polluted water with RhB was prepared. Then, this solution was equally divided to several parts in two groups labeled group-A and group-B. 10 mg of nanostructured CuO-4 h were dispersed using ultrasonic apparatus in all members of group-A, and labeled from RR-0 to RR-5. Similar to group-A, 10 mg of nanostructured CuO-P350 were dispersed using ultrasonic apparatus in all members of group-B, and labeled from RP-0 to RP-5. The suspensions were placed in the dark for 30 min before irradiation to allow sufficient adsorption of RhB onto copper oxide. After UV-light irradiation, the reaction solution was filtered, and then the absorbance of RhB aqueous solution was measured by UV–visible spectrophotometer.