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Novel porous CuO microrods: synthesis, characterization, and their photocatalysis property

Jiarui Huang [a,b,*], Guijun Fu [a], Chengcheng Shi [a], Xinyue Wang [a], Muheng Zhai [a,*], Cuiping Gu [a,*]

[a] College of Chemistry and Materials Science, Center for Nano Science and Technology, Anhui Normal University, Wuhu, 241000, P.R. China
[b] School of Chemical Engineering, Yeungnam University, Gyeongsan, Gyeoungbuk, 712749, Republic of Korea

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ABSTRACT

Porous copper oxide microrods have been synthesized via calcining copper glycinate monohydrate microrod precursor which was prepared in mild conditions without any template or additive. Several techniques, such as X-ray diffraction, field emission scanning electron microscopy, thermogravimetric analysis, Fourier transform infrared spectroscopy, and Brunauer–Emmett–Teller (BET) N_2 adsorption–desorption analyses, were used to characterize the structure and morphology of the products. Scanning electron microscopy (SEM) analyses show that the precursor consists of a large quantity of uniform rod-like micro/nanostructures with typical lengths in the range of 25–40 μm and diameters in the range of 0.1–0.35 μm. The microrod-like precursors transformed into porous microrod products after calcination at 450 °C in flow air for 2 h. The BET surface area of the porous CuO microrods was calculated to be 8.5 $m^2\,g^{-1}$. In addition, the obtained porous CuO microrods were used as catalysts to photodegrade rhodamine B (RhB), methyl orange, methylene blue, eosin B, and *p*-nitrophenol. Compared with commercial CuO powders, the as-prepared porous CuO microrods exhibit superior properties on photocatalytic decomposition of RhB due to their porous hierarchical structures.

1. Introduction

Porous micro/nanostructure materials have attracted constant interest due to the potential of these materials to offer sustainable solutions to global issues, such as increasing energy demands, rigorous environmental standards for industrial pollutants, depletion of resources, health improvement, and so on. The existence of pores can impart exceptional chemical and physical properties, which differ markedly from those of bulk or dense materials and have potential application in many fields, such as electronics, catalysis, drug delivery, sensors, pigmentation, and magnetic material science, optical material science, and so on [1–5]. During many physical and chemical processes, the different local environment of atoms exposed at solid surfaces compared to atoms in the bulk is the driving force for vital activities. The design of porous surfaces, namely, creating an open pore network within the bulk of the solids can increase the number of surface atoms in solids. This is a strategy toward increasing the surface area of solids and hence the reactivity of the material. Recently, a large number of porous metal oxide micro/nanostructures containing accessible and uniform nanopores are synthesized to maximize the fraction of exposed atoms to the surface [6–9].

Cupric oxide, as an important p-type semiconductor metal oxide with a narrow band gap of 1.21–1.51 eV [10], has attracted great interests in recent years owing to its wide applications in gas sensors [11,12], magnetic storage media [13], lithium batteries [14,15], and solar cells [16] due to its photoconductive and photochemical properties. Similar to many functional semiconductors, many novel CuO micro/nanostructures, such as nanosheets [17,18], nanowalnuts and nanoribbons [19], caddice clew [20], micro/nanoflower [21], and thin films [22] have been synthesized. Among them, porous CuO micro/nanostructures have got much more attention owing to their intrinsic advantages such as low density, high surface area, and unique surface properties, which are good for their applications in gas sensors, catalysts, coating and encapsulating agents [11]. Especially, porous micro/nanostructures can usually provide excellent channels and "surface accessibility" for the mass transportation of target gases and reactive reagents [23]. By now, CuO micro/nanostructures have been fabricated by a range of techniques, including chemical vapor deposition, hydrothermal methods, and some solution processes. Among the various synthesis methods, a facile precursor calcination method was demonstrated for the effective

* Corresponding authors. Tel.: +86 553 3869 303; fax: +86 553 3869 303.
E-mail addresses: jrhuang@mail.ahnu.edu.cn (J. Huang), jrhlab1@mail.ahnu.edu.cn (C. Shi), mhzhai9966@163.com (M. Zhai), cpgu2008@mail.ahnu.edu.cn (C. Gu).

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fabrication of porous oxide materials with desired micro/nanostructure [24]. For instance, Cao et al. reported the preparation of a novel kind of α-Fe_2O_3 hollow core/shell hierarchical nanostructures by the solvothermal process combined with subsequent thermal treatment [25]. Wang et al. synthesized one-dimensional (1D) highly porous CuO nanorods with tunable porous size ranging from ~0.4 to 22 nm in a gram scale by solution precipitation using $CuCl_2 \cdot 2H_2O$ and NaOH as raw materials and subsequent calcination at 200 °C and 400 °C, respectively, which possess a smaller specific surface area compared with the microbelt-like CuO structures [26]. Wu et al. prepared a porous worm-like CuO structure by thermal decomposition of $Cu_4(OH)_6SO_4$ precursor at 700 °C [27].

Recently, many studies about CuO micro/nanomaterials have focused on their applications in photocatalysis for decolorization and degradation of pollutants [17,28]. The treatment of toxic and persistent organic pollutants has recently taken much attention, which is also one of the most important challenges facing environmental scientists. Among the pollutants, dyes are not easily biodegradable and cause so many problems once entering the environment. Semiconductor photocatalysis has proved to be an efficient method for decolorization and degradation of dyes [29]. As we have known, mesoporosity and large surface area of the materials are necessary for efficient substrate adsorption, mass transfer, and light harvesting. The nanomaterials with porous structures represent useful applications in catalysts, because the catalytic reactivity of nanostructures depends on the shape and the exposed crystal planes, in other ways, their specific surface area due to the porosity [30]. A large surface area can supply more active sites and adsorb more pollutants [25]. This implies the importance of the necessity of controlled morphological synthesis of CuO for enhanced practical applications. However, it is still a major research challenge to produce unique, porous CuO structure in large quantities with realizing the improvement of properties for degeneration the dye pollutants, especially via a simple and friendly process.

In this study, we report a simple and novel method for the preparation of porous CuO microrods on a large scale by a facile chemical solution method, combined with subsequent calcination. The photocatalysis property of the porous CuO microrods is also investigated. Compared with commercial CuO powders, the as-prepared porous CuO microrods exhibit superior property on photocatalytic decomposition of rhodamine B (RhB) due to their porous hierarchical structures. Furthermore, the as-prepared porous CuO microrods also exhibited high photocatalytic activities in the photodegradation of other dye pollutants, including methyl orange (MO), methylene blue (MB), eosin B, and *p*-nitrophenol.

2. Experimental details

2.1. Synthesis of the samples

All of the chemical reagents were of analytic grade and were used as received without further purification. A typical synthesis procedure of the porous CuO microrods was as follows: 1.25 mmol glycine (H_2NCH_2COOH) was dispersed in 35 mL absolute ethanol under vigorous stirring, followed by addition of 1.25 mmol lithium hydroxide (LiOH). Subsequently, 10 mL of 0.0625 M cupric chloride bihydrate ($CuCl_2 \cdot 2H_2O$) solution was added into the above mixed solution under vigorous stirring at 60 °C for 10 min, resulting in a blue precipitate. The mixture was then kept standing at 60 °C for 5 h. After the reaction was complete, the resulting blue products (copper glycinate monohydrate, CGM) were washed with absolute ethanol several times and then dried at 50 °C in air for 12 h. To synthesize the porous CuO microrods, the as-obtained precipitates were then calcinated at 450 °C in a flow air for 2 h with a heating rate of 15° min^{-1}.

2.2. Characterization

The products were characterized by X-ray diffraction (XRD, Shimadzu XRD-6000 (Kyoto, Japan), with high-intensity Cu Kα radiation with a wavelength of 1.54178 Å), field emission scanning electron microscopy (FESEM, Hitachi S-4800 (Tokyo, Japan), operated at 5 kV), thermogravimetric analysis (TGA, SDT Q600 (New Castle, America), heating rate 10° min^{-1} in flow air), Fourier transform infrared spectroscopy (FTIR, IRPrestige-21), and Brunauer–Emmett–Teller(BET) nitrogen adsorption–desorption (Nova 2000E). The pore size distribution was determined from the adsorption branch of the isotherms using the Barrett–Joyner–Halenda (BJH) method.

2.3. Photocatalysis measurement

The photocatalytic experiments were carried out by adding 20 mg of porous CuO microrods or commercial compact CuO powders (scanning electron microscope (SEM) images are given in Fig. S1 in Supplementary materials) into 50 mL RhB aqueous solution with the concentration of 10 mg L^{-1}. The suspension was ultrasonicated for 30 min and then stirred for another 30 min in the dark to obtain adsorption equilibrium of dye molecules before illumination. Then, the suspension was irradiated with a 365 nm ultraviolet (UV) light (Philips, 300 W) (Shenzhen, China) with an intensity of 11280 μW cm^{-2}. During the full irradiation process, the suspension was stirred continuously. At a given time interval, 3 mL of suspension was taken out and immediately centrifuged to eliminate the solid particles. The absorbance of the filtrate was measured by a Hitachi U-3010 UV–vis absorption spectrophotometer (Tokyo, Japan) at the maximum absorbance peak (552 nm). By the same method, the photodegradation rates of other pollutants in the presence of porous CuO microrods were also measured. The maximum absorption wavelengths of MO, MB, eosin B, and *p*-nitrophenol are 462 nm, 665 nm, 517 nm, and 320 nm, respectively.

3. Results and discussion

3.1. Structure and morphology

The CGM microrod precursor was obtained from a chemical solution process. Calcination of the precursor yielded porous CuO microrods. The crystal phase of the CGM precursor is characterized by XRD, and the data are shown in Fig. 1a. All the diffraction peaks of the precursors can be ascribed to triclinic phase $Cu(NH_2CH_2CO_2)_2 \cdot H_2O$ (JCPDS 18-1714) [31,32]. The XRD peaks shown in Fig. 1b, when the sample was heat-treated at 450 °C in a flow of air for 2 h, are completely different from those of the

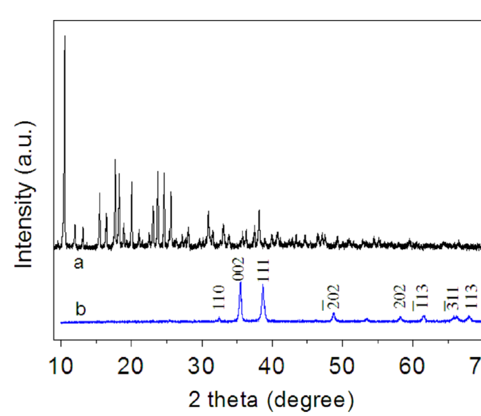

Fig. 1. XRD patterns of (a) CGM precursor and (b) calcined CuO product of the CGM precursor.