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Short communication

Microwave-hydrothermal synthesis of CuO nanorods and their catalytic applications in sodium humate synthesis and RhB degradation

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Abstract

CuO nanorods have been prepared through a facile microwave-hydrothermal method with the aid of polyethylene glycol 400, ethylene glycol and urea. The X-ray diffraction and transmission electron microscopy results showed that the prepared CuO nanocrystalline had a rod-like shape with diameters of 15–20 nm and the average length of 80 nm. Compared with commercial CuO powder, the CuO nanorods showed an enhanced catalytic activity for the synthesis of sodium humate and the degradation of Rhodamine B. The yield of sodium humate catalyzed by CuO nanorods was 75.78%, which was higher than that of the commercial CuO powder (52.8%). In addition, the CuO nanorods showed a relatively faster degradation rate of RhB. The CuO nanorods prepared by this facile method demonstrated their potential applications in the field of catalysis.

Keywords: A. Microwave processing; C. Chemical properties; D. Transition metal oxides; E. Functional applications

1. Introduction

Nanostructured materials have been intensively studied due to their size and shape-induced chemical and physical properties [1]. The controlled synthesis of nanomaterials with certain morphology is one of the most challenging issues in chemistry and materials science [2]. Moreover, a significant number of studies have focused on the relationship between catalytic performance and the size or the shape of nanomaterials [3–5]. Among various nanostructured materials, nanorods as one-dimensional nanostructured materials have attracted much attention due to their peculiar properties, which originate from their high surface area and low dimensionality [6–8]. CuO nanorods, as one type of important 1D semiconductor nanostructured materials, have been demonstrated to be effective catalysts for the degradation of organic wastewater and other catalytic reactions [9,10].

A number of methods have been developed to prepare CuO nanorods such as hydrothermal method, wet chemical route and thermal decomposition process [9–12]. Zhu et al. have prepared CuO nanorods via a facile hydrothermal process, which exhibited excellent catalytic oxidation performance [9]. Anandan et al. have synthesized vertically aligned CuO nanorods arrays using a wet chemical method, and found that the as-prepared CuO nanorods are promising hole-transport media of dye-sensitized hetero-junctions for solar energy conversion [11]. Gao et al. have reported a thermal decomposition approach for the preparation of CuO nanorods, and the products displayed an active photocatalytic property for the decolorization of methyl orange [12]. Although several groups have reported the synthesis of CuO nanorods, the synthetic procedure used often required a long reaction time or complicated synthetic steps. Therefore, it is desirable to develop a facile and rapid method to prepare CuO nanorods.

Humic substances, which can be derived from lignite or weathered coal, are commonly used as natural fertilizer and soil conditioner to remediate soil structure and to improve plant growth [13,14]. They have complex structures involving

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proportions of condensed aromatic rings with a different number of hydroxyl and carboxyl groups [15]. Sodium humate (SH) is one of the most important humic substances due to its environmentally sound application in agriculture, which can be extracted from lignite or weathered coal with the aid of NaOH [16,17]. The high efficient extraction of sodium humate is significant for energy saving and price reduction. Therefore, a series of solid catalysts, such as Fe–Zr composite solid acid and $NiSO_4$, have been used to improve the extraction efficiency due to they are easily separable and recyclable [18,19]. However, the total extraction yield of sodium humate still has the potential to be improved (e.g. less than 60%) [20,21]. Therefore, a highly efficient catalyst for improving the yield of sodium humate is indispensable.

Recently, CuO nanorods with excellent gas sensing properties have been reported by our group [22]. In the present study, we have developed a facile microwave-hydrothermal (MH) approach for the preparation of CuO nanorods. The as-prepared CuO nanorods displayed an excellent catalytic activity for the synthesis of sodium humate, and the yield reached 75.78%, which is reported for the first time to our knowledge. The degradation of Rhodamine B (RhB) results indicated that the as-prepared CuO nanorods show an enhanced catalytic activity compared to commercial CuO powder. The results showed that CuO nanorods are promising candidates for application in catalytic field.

2. Experimental

2.1. Synthesis of the CuO nanorods

All reagents used here were analytically pure and purchased from commercial sources except polyethylene glycol 400 (PEG-400), which was chemically pure. CuO nanorods were prepared using a modification of our previous synthesis method by replacing PEG-400 with a 1: 4 solution of ethylene glycol (EG) and PEG-400 [22]. An aqueous solution (180 mL), containing $CuSO_4 \cdot 5\,H_2O$ (2.5 g), EG (2 mL), PEG-400 (8 mL), distilled water (110 mL) and urea (10 g), was heated to 60 °C. Subsequently, 60 mL of NaOH solution (2 M) was poured into the above solution. Then, 180 mL of the obtained mixture was transferred into a 270 mL Teflon-line autoclave. Next, the autoclave was heated by microwave irradiation to 120 °C within 5 min and hold for another 15 min. After the autoclave cooled to room temperature, the product was centrifuged, washed with distilled water and ethanol, and finally dried at room temperature.

2.2. Characterization

The commercial CuO powder (C-CuO) and as-prepared CuO nanorods (N-CuO) were characterized by X-ray diffraction (XRD) using a Bruker D8 X-ray diffractometer at a scanning rate of $6^{o}\ min^{-1}$ ranging from 5^{o} to 80^{o} with Cu $K\alpha$ radiation ($\lambda = 1.54178$ Å). Transmission electron microscopy (TEM) images were carried out on a Hitachi H-600 transmission electron microscope with an accelerating voltage of 100 kV.

2.3. Synthesis of sodium humate

The raw coal residues used in this study are weathered coal residues from Double Dragons Humic Acid Co., Ltd. Xinjiang, China. The preparation method was similar to that of H. Motojima's work [23]. The details were as follows: 0.2 g of the CuO, 0.3 g of sodium hydroxide, 10.0 g of weathered coal residues and 30 mL of H_2O_2 (1 wt%) were mixed under continuous stirring for 1 h. Finally, the resulting suspension was centrifuged in order to separate sodium humate and residues. The residues were dried at 110 °C for 4 h and cooled to room temperature. The reaction procedure was repeated four times with the previous residues as the starting materials. The crude yield of sodium humate was calculated as the weight of extracted sodium humate per unit of residues. The actual yield of sodium humate was obtained after subtracting the moisture and ash content.

2.4. Catalytic oxidation degradation of RhB

The catalytic activities of the as-obtained N-CuO and C-CuO powder were evaluated by the degradation of a model pollutant RhB. In a typical experimental process, 10 mg of CuO was dispersed in 50 mL of RhB aqueous solution with a concentration of $10\ mg\ L^{-1}$ in conical flask, and the solution was continuously stirred for 1 h in the dark to ensure the establishment of an adsorption-desorption equilibrium. Then, 0.5 mL aqueous H_2O_2 (30 wt%) was added in the reaction mixture and was allowed to react under stirring. The concentration of RhB during the degradation was monitored by colorimetry with a UV–vis spectrophotometer (Shimadzu UV-2450 PC).

3. Results and discussion

The phase of the C-CuO and as-prepared N-CuO was characterized by XRD. As shown in Fig. 1, all the diffraction peaks can be indexed as a monoclinic phase of tenorite, which are well matched with the values in the standard card (CuO, JCPDS No. 48-1548). No peaks from impurities are detected from this pattern, confirming the pure phase of all the samples.

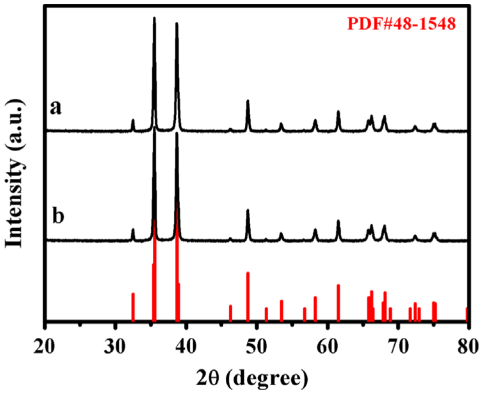

Fig. 1. XRD patterns of (a) commercial CuO powder, (b) as-synthesized CuO nanorods.

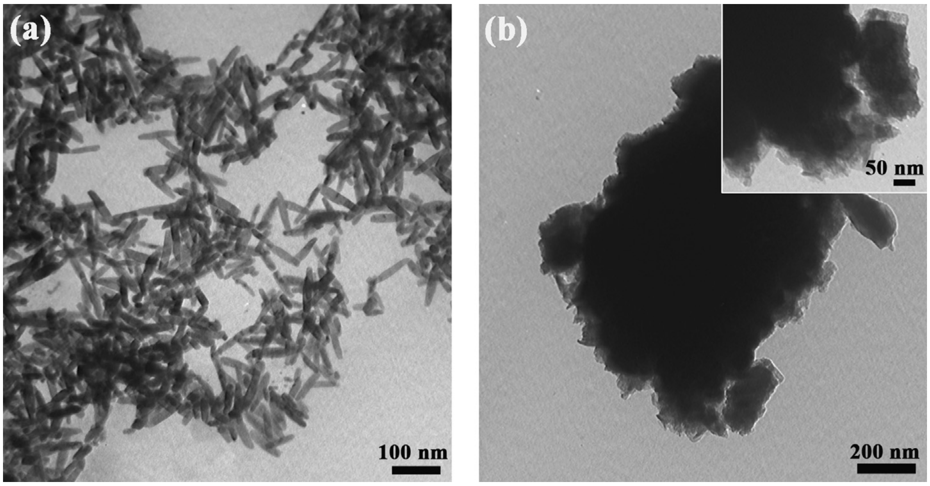

Fig. 2. TEM images of (a) as-synthesized CuO nanorods, (b) TEM images of commercial CuO powder and high-magnification TEM images (inset).

Table 1
The yield of SH prepared with various condition.

Condition	Yield of crude SH/(%)	Moisture/(%)	Ash content/(%)	Actual yield of SH/(%)
Blank	67.2 ± 2.37	0.97 ± 0.03	24.61 ± 0.07	41.61
N-CuO	69.4 ± 2.78	5.31 ± 0.19	34.47 ± 0.14	29.62
H_2O_2	75.3 ± 3.21	5.62 ± 0.09	35.02 ± 0.15	34.67
N-CuO+H_2O_2	95.71 ± 2.20	1.14 ± 0.37	18.8 ± 0.23	75.78
C-CuO+H_2O_2	80.2 ± 1.38	7.14 ± 0.34	20.26 ± 0.30	52.8

The strong and narrow diffraction peaks indicated that the product has good crystallinity.

The size and morphology of the C-CuO and as-prepared N-CuO were further investigated by TEM. Fig. 2a shows the TEM images of the as-synthesized CuO nanocrystals, and all of the as-prepared products have a rod-like shape with diameters of 15–20 nm and the average length of 80 nm. For comparison, the morphology of the C-CuO was also investigated, as shown in Fig. 2b. It can be seen that the powder was composed of irregular bulks with a large size up to several micrometers. From the inset in Fig. 2b, the plate-like morphology with a thickness of 50 nm can be found.

The C-CuO and synthesized N-CuO were used as the catalysts for the preparation of SH. The results of the reaction are shown in Table 1. The yield of SH reached 52.8% and 75.78% with the C-CuO and N-CuO as catalysts, respectively. The data indicated that as-prepared N-CuO had a better catalytic activity in the catalytic synthesis of SH from the weathered coal residues compared with the C-CuO. The excellent catalytic activity of the CuO nanocrystals may be due to the small size and rod-shape of the catalyst [9]. Many active sites of the surface of the N-CuO are exposed due to its special nanostructures, which can promote catalytic reaction on the fabrication of SH.

The catalytic activity of the C-CuO and synthesized N-CuO was also investigated for the degradation of RhB in the presence of H_2O_2 at room temperature. Fig. 3a shows UV–vis adsorption spectrums of the aqueous solution of RhB in the presence of the N-CuO and H_2O_2 at different reaction time. Obviously, the characteristic adsorption peak of RhB at 553 nm dropped with the prolonging of reaction time. The catalytic activity of the C-CuO was also investigated, as can be seen in Fig. 3b. It can be detected that the characteristic absorption peak diminished slower than the N-CuO. Fig. 3c displays a plot of degradation extent of RhB molecules as a function of catalytic time by different catalysts. It is obvious that the degradation of RhB can reach 80% within 60 min in the presence of the N-CuO. However, the degradation of RhB is just 25% in the presence of C-CuO. This demonstrated that the degradation catalytic activity of the N-CuO is better than that of the C-CuO. The N-CuO have enhanced catalytic performance with 95% decomposition of RhB after 3 h, which was much higher than the reported value of 50% [24]. The degradation rate of present CuO nanorods within 60 min reached 80%, which is similar with the result at the degradation time of 240 min as reported in Ref. [25]. The as-prepared N-CuO show an enhanced catalytic activity for the degradation of the organic dyes, which may be attributed to the effect of particle size and rod-shape.

4. Conclusions

In summary, CuO nanorods have been fabricated by a facile MH method with the aid of PEG, EG and urea. The as-prepared CuO nanorods showed a high catalytic activity for the synthesis of sodium humate and an excellent catalytic property for the degradation of RhB. The results indicated that

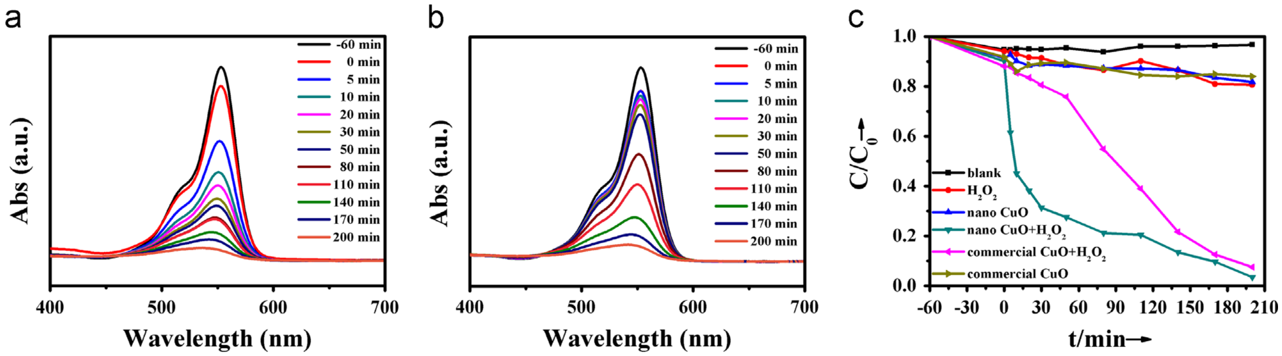

Fig. 3. (a and b) UV–vis absorption spectrum of RhB as a function of catalytic time using the commercial CuO and CuO nanorods as catalysts; (c) a plot of the degradation extent of RhB as a function of catalytic time for the blank and different catalysts.

the as-prepared CuO nanorods have promising application in the catalytic synthesis of sodium humate, degradation of organic contaminants and other areas.

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