



Synthesis and microwave modification of CuO nanoparticles: Crystallinity and morphological variations, catalysis, and gas sensing



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ABSTRACT

CuO nanoparticles with different morphologies were synthesized by chemical precipitation and subsequently modified by microwave hydrothermal processing. The nanoparticles were precipitated by the introduction of a strong base to an aqueous solution of copper cations in the presence/absence of the polyethylene glycol and urea additives. The modification of the nanoparticles was subsequently carried out by a microwave hydrothermal treatment of suspensions of the precipitates, precipitated with and without the additives. X-ray powder diffraction analysis indicated that the crystallinity and crystallite size of the CuO nanoparticles increased after the microwave hydrothermal modification. Microscopy observations revealed the morphology changes induced by microwave hydrothermal processing. The thermal decomposition of ammonium perchlorate and the detection of volatile gases were performed to evaluate the catalytic and gas sensing properties of the synthesized CuO nanoparticles.

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1. Introduction

Cupric oxide (CuO), as a p-type semiconductor with a narrow band gap of 1.2 eV, has proven a versatile material for applications in catalysis [1], sensors [2,3], lithium ion batteries [4], and pseudo-capacitors [5]. It is generally agreed that properties of CuO may be tuned or improved by developing materials with well-controlled characteristics such as high crystallinity, uniform size and shape, and large surface area [6–9]. For example, the dominant crystal planes of various CuO nanoparticles affect their catalytic activity of benzene combustion [7]. Belt-like CuO nanoparticles exhibit an enhanced sensing performance toward formaldehyde and ethanol vapors with rapid response and high sensitivity [9]. Rod-like CuO nanoparticles display a significantly improved specific capacitance possible resulting from the increased surface area, compared to irregular CuO nanoparticles [5]. It should be noted that all these cases require the well-controlled synthesis of CuO nanoparticles with high crystallinity, small size, and uniform shape. So, it is desirable to develop a facile and versatile method for the controlled synthesis of CuO nanoparticles.

Several synthetic methods have been reported to fabricate CuO nanoparticles [10–14]. Among them, the chemical precipitation method is relatively simple but useful to scale up synthesis of CuO nanoparticles with different morphologies such as nanowires

and nanobelts [15], nanorods [16], and nanosheets [17]. However, the resultant CuO nanoparticles from this method show broad size distribution, non-uniform morphology, and low crystallinity. Although the crystallinity of the resulting CuO nanoparticles can be enhanced by subsequent high-temperature calcination, such a modification method sometimes suffers from severe agglomeration of particles [18]. Compared to heat treatment, crystallization by hydrothermal treatment is considered to be a promising method, which could enhance crystallinity and protect particles from agglomeration [19,20]. In particular, the assistance of microwave irradiation endows the hydrothermal process with shortening reaction time, uniform heating, and energy savings [21–23]. Despite its successes in the direct fabrication of metal oxides nanoparticles, the microwave-assisted hydrothermal approach has seldom used for modifying metal oxides nanoparticles [24].

It has been shown that long-chain Polyethylene glycol (PEG) molecules are an inexpensive and effective nonionic surfactant for the synthesis of various metal oxide nanomaterials, in particular of one-dimensional nanostructures [25–27]. We have previously demonstrated a combined precipitation and microwave hydrothermal synthesis of different shaped CuO nanoparticles [28,29]. However, the exact reaction process and formation mechanism of CuO nanoparticles need to be further investigated. Herein, we further focus on the size and morphology changes of the CuO nanoparticles before and after the microwave hydrothermal treatment. And the influence of experimental parameters including additives and precipitation temperature on the morphology of

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CuO nanoparticles are investigated. Based on these investigations, we make an attempt to develop a microwave hydrothermal modification of CuO nanoparticles. Subsequently, the catalytic activity of the CuO nanoparticles as catalysts is evaluated by the thermal decomposition of ammonium perchlorate (AP). Compared to other reported CuO catalysts [30–32], the unmodified and microwave-modified CuO nanoparticles show promising performance with higher catalytic activity. Meanwhile, the CuO-based gas sensors also exhibit comparable gas sensing performance in the detection of volatile and toxic organic compounds to previous CuO compounds [2,3,9,33].

2. Experimental

2.1. Preparation of CuO nanoparticles

2.1.1. Chemical precipitation for CuO nanoparticles

All the chemical reactants used in our experiment were analytical grade with the exception of PEG-400 (chemical grade) and were used as received without any further purification. The precipitation of the CuO nanoparticles is as follows: a 500 ml three-neck flask was loaded with 2.50 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 10 ml of PEG-400, 10.0 g of urea and 110 ml of deionized water, and heated to 60 °C. A 60 ml of NaOH (5.0 g) aqueous solution was poured into the flask under sonication and mechanic stirring. After 10 min of the growth time, the resultant suspension was cooled to room temperature. The resulting CuO products were directly collected by vacuum filtration and washed with water and ethanol. After dried at room temperature for 48 h, the unmodified CuO products were obtained.

2.1.2. Microwave hydrothermal modification of CuO nanoparticles

Microwave hydrothermal modification was achieved in a commercially available microwave digestion system (model: MicroSYNTH, Milestone S. R. L., Italy), which uses a frequency of 2.45 GHz. In this apparatus, microwave was generated by a magnetron system, and its irradiation power can be adjusted from 0% to 100% of a maximum 1000 W.

Experimentally, the whole suspension of the untreated CuO nanoparticles prepared in Section 2.1.1 was transferred to a 270 mL vessel that was made of poly(tetrafluoroethylene)/tetrafluorometoxil (PTFE/TFM). The vessel was sealed and placed in the programmable microwave system equipped with a magnetic stirrer. The oven was heated to 120 °C within 5 min by microwave irradiation and maintained there for another 15 min. After cooling to room temperature, a brownish-black precipitate was collected as the product by vacuum filtration and washed with water and ethanol. After dried at room temperature for 48 h, the microwave-modified CuO samples were obtained.

2.2. Characterization

The phase purity of the unmodified and microwave-modified samples were characterized on a DX-1000 X-ray diffractometer with the copper $\text{K}\alpha 1$ ($\lambda = 1.54056 \text{ \AA}$) line under an acceleration voltage of 40 kV. Transmission electron microscopy (TEM) images were taken on a Hitachi H-600 with an accelerating voltage of 100 kV. FT-IR spectrum was recorded on a BRUKER EQUINOX55 Infrared Spectrometer in the wave-number region of 400–4000 cm^{-1} . Ultraviolet and visible light (UV-vis) absorption spectrum was performed at room temperature on a Shimadzu UV-2450 spectrometer.

2.3. Measurement of catalytic activity

The catalytic activity of unmodified and microwave-modified CuO nanoparticles was evaluated by thermal decomposition of AP. The experimental procedure is as follows: 2 wt% CuO NCs and 98 wt% AP were carefully grounded for 15 min with a pestle in a mortar. Then, a thermo-gravimetric (TG) analysis technique was applied to determine the thermal decomposition behavior of the mixtures under Nitrogen atmosphere. The amount of the mixture for the TG analysis is about 2 mg. The measurement was performed on an ETZSCH STA 449 PC thermal analyzer with a heating rate of 10 °C min^{-1} .

2.4. Sensor fabrication and measurements

The fabrication and measurement of CuO-based gas sensors was similar to our previous report [28]. ~2 mg of solid CuO powder was dispersed in ethanol in an agate mortar to form a brownish paste. The paste was dip-coated onto an alumina ceramic tube with ~4 mm in length, ~0.8 mm in internal pipe diameter, and ~1.4 mm in external pipe diameter. A pair of gold electrodes (electrode distance 2 mm) had been previously mounted at each end of the ceramic tube before it was coated with the paste. A Ni–Cr wire inserted into the ceramic tube was adopted for the sensor heating. At last, the CuO-based gas sensor was aged at 300 °C for 5 days in the gas testing system to improve the stability of response to the detected gas. Gas sensing performance was carried out on a WS-30A static gas-sensing system (Weisheng Electronics Co., Ltd., Henan, PR China). Sensor response was studied in a sealed PMMA test chamber (18 L) with a gas inlet and outlet.

3. Results and discussion

3.1. X-ray diffraction (XRD) and morphology analysis

Unmodified CuO nanoparticles are synthesized by the precipitation of CuSO_4 with NaOH in the absence/presence of the PEG and urea additives and are symbolized as CuO-A and CuO-C, respectively. After the microwave hydrothermal modification of the CuO-A and CuO-C suspensions, the corresponding CuO samples are denoted as CuO-B and CuO-D, respectively. Powder X-ray diffraction (XRD) patterns confirm that all the unmodified and microwave-modified CuO samples are of monoclinic CuO phase (JCPDS file No. 48-1548 C2/c), as shown in Fig. 1. No peaks from impurity such as $\text{Cu}(\text{OH})_2$ or Cu_2O are observed, indicating the pure phase of the CuO samples. It is observed that the peak intensities of the

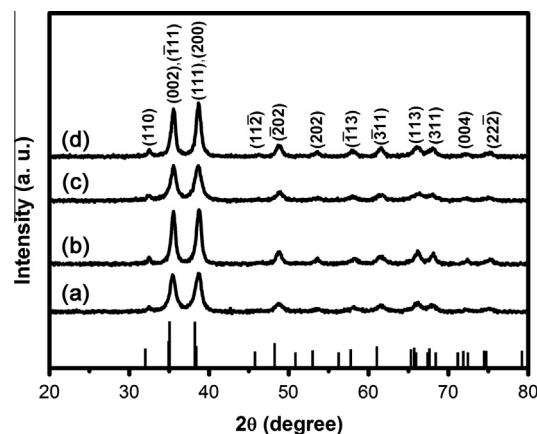


Fig. 1. XRD patterns of the synthesized CuO nanoparticles: (a) CuO-A, (b) CuO-B, (c) CuO-C, and (d) CuO-D.

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