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Preparation of CuO nanoparticles by microwave irradiation

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Abstract

CuO nanoparticles with an average size of ca. 4 nm have been successfully prepared by microwave irradiation, using copper (II) acetate and sodium hydroxide as the starting materials and ethanol as the solvent. The CuO nanoparticles are characterized by using techniques such as X-ray powder diffraction, transmission electron microscopy, selected area electron diffraction, X-ray photoelectron spectroscopy and UV–Visible absorption spectroscopy. The as-prepared CuO nanoparticles have regular shape, narrow size distribution and high purity. The band gap is estimated to be 2.43 eV according to the results of the optical measurements of the CuO nanoparticles.

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1. Introduction

Nanocrystalline semiconductor particles have drawn considerable interest in recent years because of their special properties such as a large surface-to-volume ratio, increased activity, special electronic properties and unique optical properties as compared to those of the bulk materials [1,2]. The oxides of transition metals are an important class of semiconductors, which have applications in magnetic storage media, solar energy transformation, electronics and catalysis [3–12]. Among the oxides of transition metals, CuO has attracted much attention because it is the basis of several

high- T_c superconductors. CuO is a semiconducting compound with a narrow band gap and used for photoconductive and photothermal applications [13]. However, up to now, the reports on the preparation and characterization of nanocrystalline CuO are relatively few to some other transition metal oxides such as zinc oxide, titanium dioxide, tin dioxide and iron oxide. Some methods for the preparation of nanocrystalline CuO have been reported recently such as the sonochemical method [14], sol–gel technique [15], one-step solid state reaction method at room temperature [16], electrochemical method [17], thermal decomposition of precursors [18], and co-implantation of metal and oxygen ions [19], and so on.

Microwaves are electromagnetic waves containing electric and magnetic field components. It is well known that the interaction of dielectric

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materials, liquids or solids, with microwaves leads to what is generally known as dielectric heating. Electric dipoles present in such materials respond to the applied electric field. In liquids, this constant reorientation leads to the friction between molecules, which subsequently generates heat [20]. Claimed effects of microwave irradiation include thermal effects and non-thermal effects. Microwave irradiation as a heating method has found a number of applications in chemistry. The microwave synthesis, which is generally quite fast, simple and efficient in energy, has been developed and is widely used in various fields such as molecular sieve preparation, radiopharmaceuticals, the preparation of inorganic complexes and oxide, organic reactions, plasma chemistry, analytical chemistry and catalysis [21]. The applications of microwave irradiation in the preparation of nanoparticles have been reported in recent years [22–30]. Microwave irradiation has shown very rapid growth in its application to material science due to its unique reaction effects such as rapid volumetric heating and the consequent dramatic increase in reaction rates, etc. Compared with the conventional methods, the microwave synthesis has the advantages of short reaction time, small particle size, narrow particle size distribution and high purity.

In this paper, we report a novel method for the preparation of monoclinic CuO nanoparticles by microwave irradiation. It is found to be a fast, convenient, mild, energy-efficient and environmentally friendly route to produce CuO nanoparticles in only one step. The product has regular shape, small size, narrow size distribution and high purity.

2. Experimental section

2.1. Materials

$\text{Cu}(\text{CH}_3\text{COO})_2$ and NaOH of analytical purity were purchased from Shanghai Chemical Reagent Factory (China). Absolute ethanol of analytical purity was purchased from Nanjing Chemical Reagent Factory (China). Polyethylene glycol-19000 (PEG) was purchased from Tianjing Third

Reagent Factory (China). All the reagents were used without further purification. Distilled water was used in our experiments.

2.2. Instruments

A microwave oven with 650 W power (Sanle general electric corp. Nanjing, China) was used. A refluxing system was connected with the microwave oven.

Powder XRD measurements were performed on a Shimadzu XD-3A X-ray diffractometer at a scanning rate of $4^\circ/\text{min}$ in the 2θ range from 15° to 60° , with graphite monochromatized $\text{Cu K}\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$) and nickel filter. TEM images and SAED pictures were recorded on a JEOL-JEM 200CX transmission electron microscope, using an accelerating voltage of 200 kV. The samples used for TEM observations were prepared by dispersing some products in ethanol followed by ultrasonic vibration for 30 min, then placing a drop of the dispersion onto a copper grid coated with a layer of amorphous carbon. Further evidence for the purity of CuO was obtained by the X-ray photoelectron spectra (XPS) of the product. The XPS patterns were recorded on an ESCALAB MK II X-ray photoelectron spectrometer by using non-monochromatized $\text{Mg K}\alpha$ X-ray as the excitation source and choosing C1s (284.6 eV) as the reference line. A Shimadzu UV-3100 photospectrometer was used to record the UV-Visible absorption spectra of the as-prepared particles.

2.3. Preparation of CuO nanoparticles

In a typical procedure, 25 ml ethanolic solution of 0.2 M $\text{Cu}(\text{CH}_3\text{COO})_2$ was mixed with 25 ml ethanolic solution containing 0.01 mol NaOH in a round-bottom flask. Then 0.5 g PEG-19000 was dissolved in the stock solution. The mixture was placed in the microwave reflux system and the reaction was carried out under ambient air for 10 min. The microwave oven followed a working cycle of 6 s on and 24 s off (20% power) and altogether the on/off heating procedure was repeated 20 times. Then a great amount of dark-brown precipitate occurred. After cooling to room

temperature, the precipitate was centrifuged, washed with distilled water, absolute ethanol and acetone in sequence and dried in air at room temperature. The final products were collected for characterizations.

3. Results and discussions

3.1. XRD analysis

The XRD pattern (Fig. 1) of the product obtained is identical to the single-phase CuO with a monoclinic structure. The intensities and positions of the peaks are in good agreement with literature values [31]. No peaks of impurity are found in the XRD pattern. The broadening of the peaks indicates that the crystal size is small. The average size of the CuO nanoparticles is estimated to be ca. 4 nm according to the Debye–Scherrer formula [32].

3.2. TEM and SAED measurements

The size and morphology of the product are analyzed by transmission electron microscopy (TEM). The TEM image (Fig. 2a) reveals that the product consists of spherical particles with a regular morphology and narrow size distribution. The size of the particles observed in the TEM image is in the range of 3–5 nm, which is in good agreement with that estimated by Debye–Scherrer

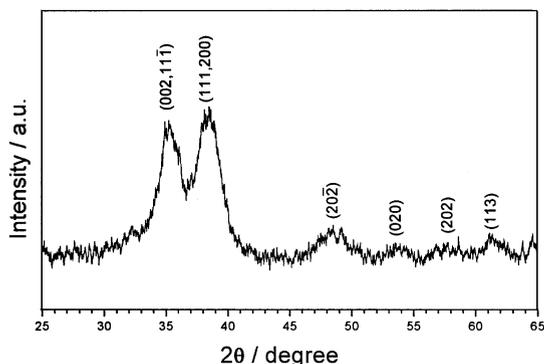


Fig. 1. Powder X-ray diffraction pattern of the as-prepared CuO nanoparticles.

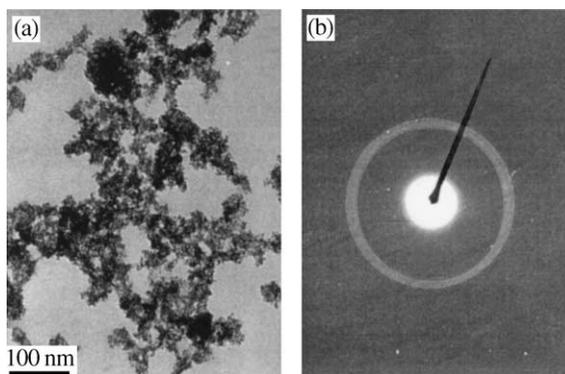


Fig. 2. (a) TEM and (b) electron diffraction pattern of the as-prepared CuO nanoparticles.

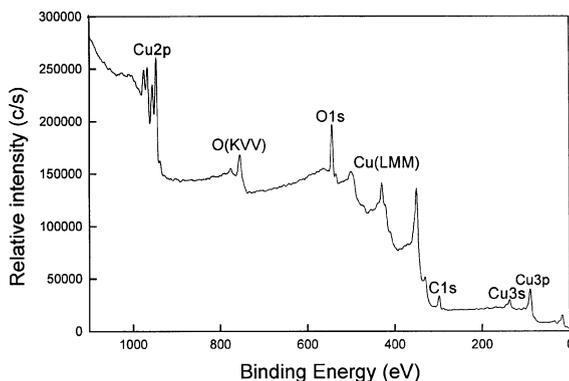


Fig. 3. Wide X-ray photoelectron spectrum of the as-prepared CuO nanoparticles.

formula from the XRD pattern. The SAED image (Fig. 2b) shows that the particles are well crystallized. The two diffraction rings on the picture correspond to $(111, 00\bar{2})$ and $(111, 200)$, respectively, which is in accordance with $(111, 00\bar{2})$ and $(111, 200)$ peaks in the XRD pattern.

3.3. XPS measurements

The wide XPS picture of the product is shown in Fig. 3. The C1s peak lies at 297.0 eV, which should be corrected to 284.6 eV. All the other peaks are corrected accordingly. No peaks of other elements except C, Cu and O were observed in the picture, indicating the high purity of the product.

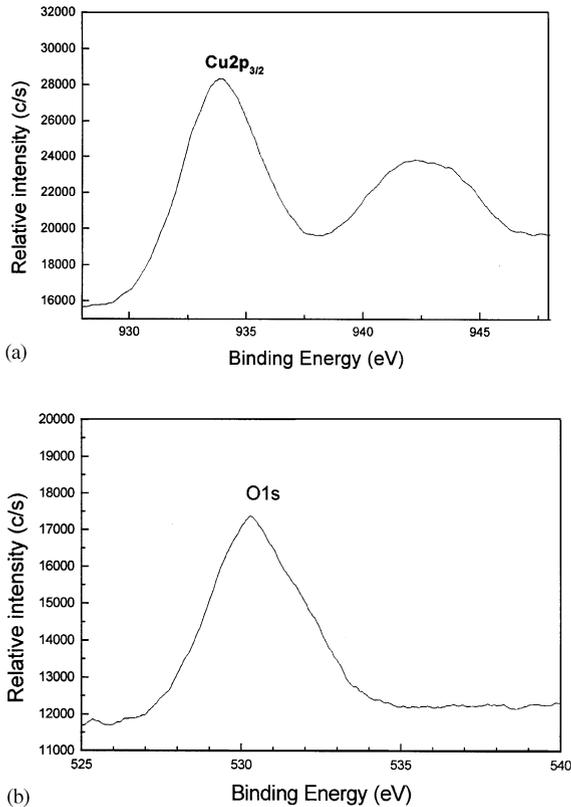


Fig. 4. High-resolution XPS spectra taken for the Cu and O region of the as-prepared CuO nanoparticles: (a) Cu_{2p} and (b) O_{1s}.

In the high-resolution XPS spectra (Fig. 4) of the as-prepared CuO nanoparticles, the Cu_{2p} peak lies at 933.6 eV with a satellite feature located at a higher binding energy by about 8.2 eV, and the broad peak that lies at 530.8 eV is assigned to O_{1s}. The results are in agreement with the literature [16]. The atomic ratio of Cu:O calculated on the basis of Cu_{2p} and O_{1s} spectra is approximately equal to 3:4, which shows that the surface of the product is rich in O.

3.4. Optical properties

We have carried out the UV–Visible absorption spectrum of the product in order to resolve the excitonic or interband transitions of CuO nanoparticles. UV–Visible absorption spectrum (Fig. 5a) of the as-prepared CuO nanoparticles

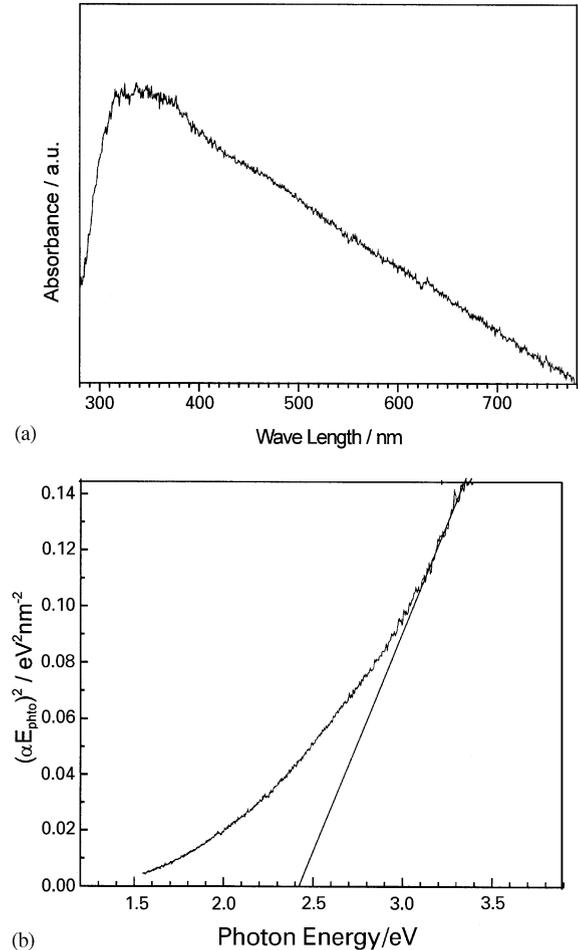


Fig. 5. (a) The UV–Visible absorption spectrum of CuO nanoparticles dispersed in ethanol solution; (b) plots of $(\alpha E_{\text{phot}})^2$ vs. E_{phot} for direct transitions.

dispersed in ethanol solution (the concentration is 0.1187 mg/ml) shows a broad absorption peak whose center is at about 340 nm. The CuO nanoparticles were well dispersed in ethanol to form a transparent solution by ultrasonic vibration for 20 min. An estimate of the optical band gap is obtained using the following equation for a semiconductor:

$$\alpha(\nu) = A(h\nu/2 - E_g)^{m/2},$$

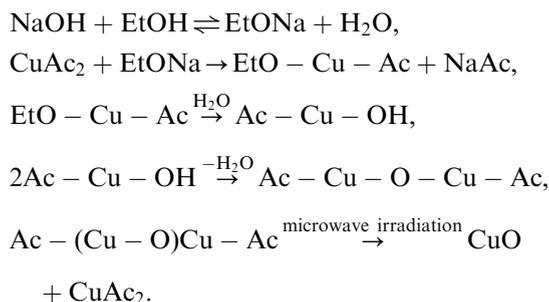
where A is a constant, α is the absorption coefficient and m equals 1 for a direct transition.

The energy intercept of a plot of $(\alpha E_{\text{phot}})^2$ vs. E_{phot} yields E_g for a direct transition (Fig. 5b) [33]. The band gap of the as-prepared CuO nanoparticles is calculated to be 2.43 eV from the UV–Visible absorption spectrum, which is larger than the reported value for bulk CuO ($E_g = 1.85$ eV) [34]. Light absorption leads to an electron in the conduction band and a positive hole in the valence band. In small particles they are confined to potential wells of small lateral dimension and the energy difference between the position of the conduction band and a free electron, which leads to a quantization of their energy levels. The phenomena arise when the size of the particles becomes comparable to the de Broglie wavelength of a charge carrier. The increase in the band gap of the as-prepared CuO nanoparticles is indicative of quantum size effects [35].

3.5. Discussions

In the literature, a few examples of the preparation of the nanocrystalline transition metal oxides by microwave synthesis have been reported [28,29]. The mechanism for the formation of transition metal oxides is the hydrolysis of metal salts in aqueous solution driven by microwave irradiation. In our method, we used absolute ethanol as the solvent. The mechanism for the formation of CuO nanoparticles is totally different from the hydrolysis mechanism that has been reported. There are two interesting features in this method: one is the use of copper acetate as a starting material and the other is the use of EtOH as solvent. Ito Seishiro and his co-workers have reported a method for the preparation of uniform nanocrystalline ZnO particles though the reaction of zinc acetylacetonate with 2-equivalent NaOH in EtOH at 75–76°C [36]. They also proposed a probable reaction mechanism for the formation of ZnO nanoparticles based on further research on the details of the reaction process [37]. We think that the mechanism for the formation of CuO nanoparticles in our method may be similar to that proposed by Ito Seishiro and his co-workers, except that metal acetate was used as a starting material instead of acetylacetonate complex. The probable mechanism may be summarized as

below:



First, small amounts of EtONa and H₂O were generated from the equilibrium reaction of NaOH and EtOH. Then a part of Ac[−] was subject to nucleophilic attack by EtO[−], which produced the intermediate CuAcEtO. Hydrolysis of CuAcEtO yielded another intermediate CuAcOH. Cu–O–Cu bonds were formed by dehydration–condensation of CuAcOH, which was followed by a decomposition process leading to formation of CuO nanoparticles under microwave irradiation.

We have tried to prepare CuO nanoparticles using some other solvents such as *N,N*-dimethylformamide and ethylenediamine as well. We also tried to prepare CuO nanoparticles in aqueous solution using complexing agents such as EDTA, sodium citrate and TEA to prevent the formation of Cu(OH)₂ precipitates before being exposed to microwave irradiation. However, in all these experiments, we failed to obtain pure single phase of CuO. The products we obtained were mixtures of monoclinic CuO and some other unknown products. We also attempted to use some other copper salts such as CuSO₄ and Cu(NO₃)₂ as starting materials, but we did not succeed to obtain CuO either. So we may draw the conclusion that CuAc₂ should be chosen as the starting material, but the details of the effects of Ac[−] on the formation of CuO nanoparticles still remain unknown. Further research works are needed to be done to investigate the details of the mechanism for the formation of the CuO nanoparticles in this system.

In our experiment, PEG was used as the dispersant. If PEG was not added, the CuO nanoparticles agglomerated to form some quadrate aggregates of over 200 nm as observed in the

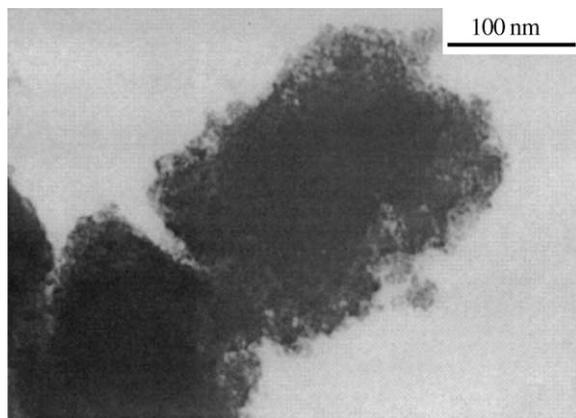


Fig. 6. TEM image of the CuO nanoparticles prepared in the absence of PEG.

TEM image (Fig. 6). These can be explained by the stabilization effect of the surface caused by PEG. The existence of PEG can reduce the Gibb's free energy of the surface of the CuO nanoparticles. As a result, it can prevent the grains from merging into larger ones.

Microwave irradiation played a very important role in the formation of CuO nanoparticles. Microwave not only provided the energy for the formation of the final product, but also greatly accelerated the nucleation of the CuO and depressed the straightforward growth of newborn CuO due to the intense friction and collisions of the molecules created by the microwave irradiation. The formation of uniform nanosized particles demands a uniform growth environment, and microwave heating affords this. With microwave irradiation of reactants in polar solvents, temperature and concentration gradients can be avoided, providing a uniform environment for the nucleation. As a result, the as-prepared CuO nanoparticles are of small size and narrow size distribution.

4. Conclusions

Nanocrystalline CuO particles with a monoclinic structure have been prepared successfully by a novel method using microwave irradiation. It is a simple and efficient method to produce CuO

nanoparticles with regular shape, small size, narrow size distribution and high purity. We can foresee the upscaling of the process to form large quantities of nanosized CuO particles, which have wide applications in various fields such as photonics, catalysis and biosensors.

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