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A convenient alcohothermal approach for low temperature synthesis of CuO nanoparticles

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Abstract

A convenient alcohothermal route to prepare cupric oxide nanoparticles using copper acetate as the starting material was successfully developed. The influence of reaction temperature on the formation of CuO nanoparticles was investigated. The yield was as high as 100% when the alcohothermal synthesis was carried at 110°C. The particle sizes of the CuO nanoparticles can be controlled to be between ~3 and 9 nm simply by varying the reaction temperature. The possible formation mechanism of CuO nanoparticles via the alcohothermal method is discussed. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

In recent years, copper oxide has attracted increasingly interests for both fundamental and practical reasons. It has shown to be an industrially important material that can be widely used in applications such as gas sensors, magnetic storage media, solar energy transformation, semiconductors and catalysis [1–4]. With the decrease in the crystal size, nanosized copper oxides may exhibit unique properties which can be significantly different from those of their bulk counterparts, for example, the large interfacial areas, homogeneity and highly reactive surfaces, unusual optical, electrical, and catalytic properties, etc. As a result, it is always desirable that physical and chemical characteristics can be controlled by tuning the grain size of the CuO particles in practical applications.

In the past decades, much effort has been made toward the synthesis and characterization of nanosized transition metal oxide particles. Among all transition metal oxides that have been investigated, much less work has been devoted to the preparation and characterization of CuO nanoparticles. It is well known that copper oxides can be conventionally obtained by the thermal decomposition of copper salts in solid state, for instance, the nitrates, hydroxides or sometimes the hydroxysalts obtained from the direct deposition method [5]. This simple method allows the preparation of the tenorite copper oxide in large amounts. However, it is too difficult to control

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the grain size of the resulting copper oxide particles through this method. Several new synthetic approaches have been developed in the aim to achieve the preparation of nano-sized CuO particles. Recently, Vorobyova et al. [6] prepared a stable colloidal solution of copper(II) oxide (6 nm) in octane by an interphase synthesis at interaction of copper(II) oleate and sodium hydroxide dissolved in octane and water, respectively. This method is too elaborate and may not be appropriate for preparation of CuO nanoparticles in large amounts. More recently, a novel sonochemical method has been successfully developed by Kumar et al. [7] to prepare the copper oxide nanoparticles (~6 nm) in various organic solvents such as DMF. Using copper acetate as starting material, this method only affords the formation of CuO in a very low yield; moreover, the highly expensive ultrasonic equipment (a high-intensity ultrasonic horn) is required in this preparation process.

Solvothermal process has been shown to be a powerful technique for generating novel materials with interesting properties. Particularly, the solvothermal technique provides the alternative approach that allows the economical synthesis of fundamentally important well-defined nanometer-sized materials at mild conditions. To our knowledge, this new synthetic technique has not been applied in the synthesis of transition metal oxides such as copper oxide.

The present work is focused on the synthesis and characterization of nanometer-sized CuO particles prepared by a solvothermal method. In this work, we report a simple synthetic approach for the preparation of CuO nanoparticles through an alcohothermal process using copper acetate as starting materials at mild conditions. Two influential parameters, including the reaction temperature and reaction time on the alcohothermal process, were investigated. The structural and morphological characterization of the as-prepared CuO nanoparticles were carried out by means of transmission electron microscopy (TEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy. The results show that CuO nanoparticles can be obtained at a yield of as high as ~100%. It is also found that the particle sizes of the CuO nanoparticles can be controlled in the range of 3–9 nm simply by varying the reaction temperature.

2. Experimental

2.1. Sample preparation

Fifty milliliters of copper acetate ($Cu(OAc)_2$) alcoholic solution (0.05 M) were put into a Teflon liner stainless steel autoclave of 60-ml capacity. The autoclave was then put into an oven and kept constantly under autogeneous pressure at varied temperatures (±1°C, controlled by the oven) for 20 h. A representative sample was prepared at temperature of 110°C (S2). For comparison, the varied preparation temperature at 90°C (S1), 130°C (S3), 150°C (S4), and 180°C (S5) were also carried out. After the reaction, the autoclave was cooled to room temperature naturally. The product was recovered by centrifugation, then the product was washed two times in distilled water and three times in ethanol, and then vacuum dried at room temperature. A black powder product was finally obtained. The purity of the product was analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES), and no more than 100 ppm of any purity was detected.

2.2. XRD, TEM and XPS studies

X-ray diffraction patterns of the CuO nanoparticles were recorded using nickel filtered Cu Kα radiation on a Bruker D8 Advance diffractometer (Bruker, Germany). The feature micrographs were obtained using a Hitachi H600 high resolution transmission electron microscope, with the voltage applied to measurements being 20 kV. The average grain size of the samples was measured and determined by TEM and XRD. The X-ray photoelectron spectroscopy (XPS) experiments were carried out on a Perkin-Elmer PHI 5000C ESCA system using Al Kα radiation (1486.6 eV). The spectrometer was operated at the resolution of about 1 eV.

3. Results and discussions

Stable CuO nanoparticles, having size as small as 3–9 nm, have been successfully synthesized using a novel synthetic route by alcohothermal processing of the copper acetate at temperatures below 150°C. Fig. 1 shows the XRD patterns of the as-prepared samples obtained at various reaction temperatures. The

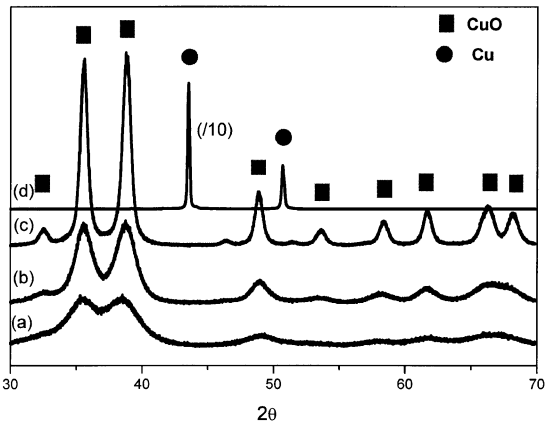

Fig. 1. X-ray diffraction patterns of the samples prepared using the alcohothermal route at different temperatures: (a) 90°C; (b) 110°C; (c) 150°C; and (d) 180°C.

samples prepared at different reaction temperatures of 90°C, 110°C, 130°C, 150°C and 180°C are referred as S1, S2, S3, S4 and S5, respectively. As shown in Fig. 1a, the broad diffraction bands from the sample S1 are characteristic of nanoparticles with a low crystallinity. The XRD pattern is identical to that of pure CuO, without signals from $Cu(OAc)_2$, Cu_2O, or other precursor compounds, indicating the formation of high purity single-phase CuO with a monoclinic structure. The mean crystalline size of the sample S1, estimated from Sherrer formula, is about 2.9 nm. Increasing the reaction temperature in the alcohothermal synthesis results in the observation of the intensification and sharpening of the diffraction peaks for the samples of S2 (110°C) and S4 (150°C) in Fig. 1b and c. This shows that the size of the CuO grains has grown and the crystal quality has been improved. Using Sherrer formula, the estimated average grain sizes for sample S2, S3 (not shown in Fig. 1), and S4 were ~3.4 nm, 4.2 nm and 8.9 nm, respectively. The present XRD data demonstrate clearly the growth in size of the CuO nanoparticles as a function of the reaction temperature. The results clearly show that the particle size of the CuO nanoparticles can be controlled simply by the variation of the alcohothermal reaction temperature.

When the alcohothermal reaction was carried out at a higher temperature of 180°C, remarkable changes in the XRD pattern for sample S5 was observed in Fig. 1d. Obviously, all characteristic diffraction peaks corresponding to that of CuO has now disappeared. Meanwhile, only two sharp diffraction peaks characteristic of metallic copper could be found for sample S5, indicating the formation of metallic copper instead of the production of larger CuO nanoparticles under higher reaction temperature in the alcohothermal synthesis. This interest finding demonstrates that at a high reaction temperature (> 180°C), the oxide state of Cu(II) was readily reduced to elemental Cu(0) by the organic solvent of ethanol, which was in good accordance with the experimental facts as reported by other researchers [8].

A typical TEM image of the CuO nanoparticles alcohothermally prepared at 150°C is presented in Fig. 2, showing that the samples are composed of non-aggregated spherical particles. The average particle diameters based on the TEM analysis were found to be approximately ~11 nm for sample S4, which was in good agreement with the result of XRD results. Note that the XRD technique appears to slightly underestimate the particle size in the present case.

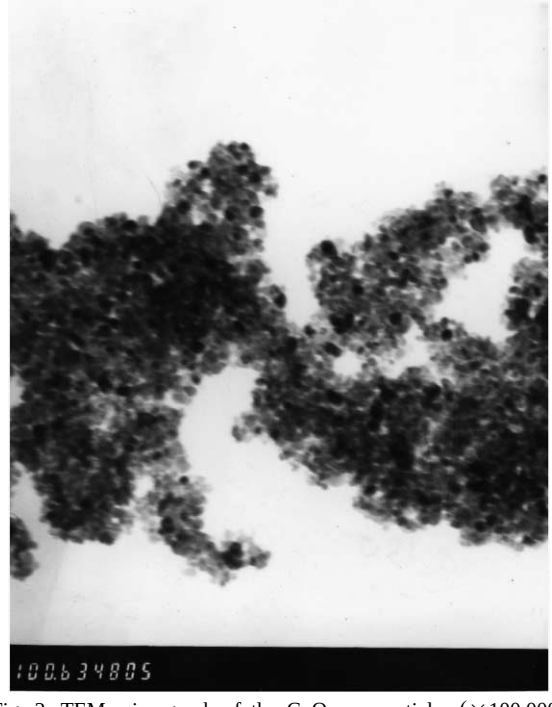

Fig. 2. TEM micrograph of the CuO nanoparticles (×100,000) prepared by the alcohothermal method at 150°C.

XPS is a powerful technique for surface compositional studies of the nano-materials. XPS survey scans did not show any impurity in all as-prepared samples, which further confirmed the high purity nature for the alcohothermally derived CuO nanoparticles. Fig. 3 exhibits the Cu $2p_{3/2}$ spectra for CuO nanoparticles prepared at 90°C, 110°C and 150°C, respectively. For comparison, the Cu 2p XPS level for CuO bulk powder is also presented in Fig. 3d. In general, XPS core lines are much broader for CuO nanoparticles. It is well known that large number of atoms reside on the surfaces of nanoparticle, leading to wider peaks (large full width at half maximum) in photoemission spectra.

As shown in Fig. 3a, the Cu^{2+} peak for sample S1 lies at 935.2 eV, with two shake-up satellites at about 7.2 and 9.8 eV higher in binding energy than that of the main peak. The existence of strong satellite features for Cu 2p rules out the possibility of presence of Cu_2O phase [9]. Thus, the XPS results clearly proved that the sample is composed of CuO. The main Cu $2p_{3/2}$ features for samples S2 and S4 are shown in Fig. 3b and c, respectively. A subtle increase in binding energy has been observed in the main Cu $2p_{3/2}$ peak, with decrease in size. This observation may be attributed to the size effect associated with the present alcohothermally derived CuO nanoparticles.

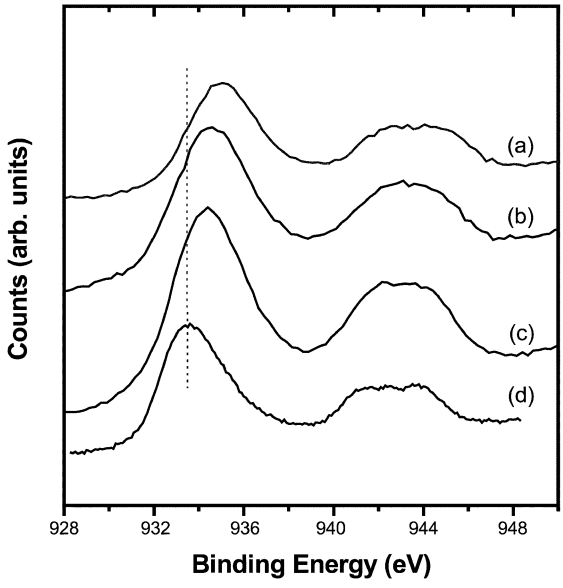

Fig. 3. X-ray photoelectron spectroscopic Cu $2p_{3/2}$ level of CuO nanoparticles prepared at different temperatures: (a) 90°C; (b) 110°C; (c) 150°C; and (d) CuO bulk powder.

Apparently, the present alcohothermal route may be extended to the synthesis of other fundamentally important nano-sized transition metal oxides such as ZnO, etc. This method is attractive since it offers simple way to obtain oxide nanoparticles with variable mean diameters. Moreover, this new synthesis route allows the attainment of a very high product yield under mild reaction conditions. In the present paper, we have successfully demonstrated that CuO nanoparticles having size between ~ 2 and 6 nm could be synthesized using the alcohothermal route. In our case, the reaction temperature is a very important factor that should be considered in the alcohothermal synthesis of CuO nanoparticles. We have found that when the synthesis temperature was below 90°C, the formation rate of CuO was very slow and the reaction is not complete. For example, the yield is only about 30% after reaction for 20 h when reaction was performed at 90°C. On the other hand, if the temperature was raised to above 180°C, the reducing alcohol would readily reduced the Cu(II) to metallic copper nanoparticles with a relatively large size of 54.1 nm.

At reaction temperatures between 110°C and 150°C, the alcohothermal reaction to the CuO nanoparticles is complete, as can be evidenced by the colorless of the mother liquid after the alcohothermal synthesis reaction. It should be noted that the present reaction could be taken as the alcohothermally assisted "decomposition" of copper acetate to CuO in presence of ethanol alcohol. Considering the present reaction temperature for the formation of CuO is considerably lower than that for the directly thermal decomposition of copper acetate to CuO in air [10], the role of the organic solvent of ethanol is of critically importance for the present low temperature decomposition of $Cu(OAc)_2$ to CuO. Under alcohothermal conditions, the esterification reaction is readily occurred between $(OAc)^-$ and ethanol. In fact, we do have detected the formation of ethyl acetate in the reacted solvents by a GC with FID detector. As a result, the thermal "decomposition" of copper acetate to CuO could proceed at a much lower temperature under alcohothermal conditions.

4. Conclusions

In summary, copper oxide nanoparticles have been successfully prepared from copper acetate with a yield of as high as 100% by a novel alcohothermal technique at a low temperature. The as-prepared high purity CuO nanoparticles were investigated using combined techniques of XRD, TEM, and XPS. The results show that the formation of CuO nanoparticles from acetate precursors is complete and the particle sizes of the CuO nanoparticles can be controlled to be between ~ 3 and 9 nm simply by varying the reaction temperature.

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