Journal of Solid State Chemistry **147,** 516–519 (1999)
Article ID jssc.1999.8409, available online at http://www.idealibrary.com on IDEAL®

Preparation and Characterization of CuO Nanocrystals

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Received January 5, 1999; in revised form May 25, 1999; accepted May 27, 1999

Monoclinic CuO nanoparticles were prepared by using a one-step solid state reaction method under ambient conditions. The CuO particles with an average size of 12 nm were pressed into pellets under high pressure. They were studied by X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), transmission electron microscopy (TEM), and Raman spectroscopy. The CuO grains in pellets grow with time at room temperature. The gradual increase in the grain size with time is clearly reflected in their Raman spectra and the XRD results. The correlation between the Raman spectra and the crystal dimension is discussed. © 1999 Academic Press

1. INTRODUCTION

Semiconductor nanocrystals have attracted much attention in recent years because their optical properties can be significantly different from those of their bulk counterparts (1–4). Many studies have been carried out on wide band-gap semiconductor nanocrystals such as CdS, CdSe, ZnS, ZnO, and ZnSe because they have potential applications in optical functional devices, such as optical switches, shutters, and waveguides. CuO is a semiconducting compound with a narrow band-gap that has been studied, together with the other copper oxides, for photothermal and photoconductive applications (5). This material has attracted much interest in the past years, also because it is the basis of several high-Tc superconductors. However, up to now, no systematic study on CuO nanocrystals has been reported.

In this paper we present experiment results on CuO nanocrystals prepared by a one-step reaction method. The samples have been characterized by X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), X-ray diffraction (XRD), and Raman spectroscopy. As XRD is a powerful tool for the study of the structure of materials, it is common to use XRD to determine the crystal structure and to estimate the mean grain size of nano-sized materials. Raman spectra are sensitive, not only to quantum confinement but also to structural characteristics.

2. EXPERIMENTAL

2.1. *Sample Preparation*

The CuO nanoparticles were prepared by one-step solid state reaction under ambient conditions. $CuCl_2 \cdot 2H_2O$ and NaOH in a molar ratio of 2:5 were mixed and ground, and a short induction followed. The color of the mixtures gradually changed from bluish to black, indicating the formation of CuO. After grinding for 30 min, the black product was washed with a ultrasonic wave, then three times in distilled water and twice in alcohol, and then dried in air. The purity of the product was analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES), and no more than 100 ppm of any impurity was detected. The CuO was pressed into pellets of 1 cm in diameter under the pressure of 10 tons for XRD and Raman measurements.

2.2. *XPS, XRD, TEM, and Raman Studies*

XPS measurements were undertaken with a VG ESCALAB MK II with a Mg$K\alpha$ (1253.6 eV) excitation source. The crystal structure and composition of the specimens were analyzed by XRD using a Philips PW 1710 diffractometer equipped with a Cu$K\alpha$ X-ray generator under ambient conditions. The feature micrographs were obtained using a JEM-200CX transmission electron microscope, with the voltage applied to measurements being 160 kV. The average size of the CuO grain was measured and determined by TEM and XRD. For the Raman spectra recorded with 488-nm laser excitation, a micro-Raman system, which was modified by coupling an Olympus microscope to a Spex 1704 spectrometer with a CCD detector,

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was used in the experiment. The power at the sample was estimated to be below 10 mW, and the spectral resolution of the spectrometer is 0.5 cm^{-1}.

3. RESULTS AND DISCUSSION

3.1. XPS Analysis

Figure 1a shows the Cu $2P_{3/2}$ spectrum. The Cu^{2+} peak lies at 933.4 eV, with two shake-up satellites at 7.2 and 9.8 eV higher in binding energy than that of the main peak. As shown in Fig. 1b, the O 1*s* core-level spectrum is broad, and two O 1*s* peaks (marked as I and II) can be resolved by using a curve-fitting procedure. Peak I, at a lower energy of 529.5 eV, is in agreement with O^{2-} in CuO, while Peak II, at a higher energy of 531.6 eV, is attributed to O adsorbed on the surface of CuO particles. Thus, the XPS results proved that the sample is composed of CuO.

3.2. XRD and TEM Results

As shown in Fig. 2a, the XRD pattern from the sample is identical to that of pure CuO, without signals from $CuCl_2$, NaOH, or other precursor compounds, indicating the formation of single-phase CuO with a monoclinic structure. It is interesting to note that the sample in the form of pressed pellets is unstable. At room temperature (RT), after the lapse of a few days, the diffraction peaks from the sample become stronger and sharper, which shows that the size of the CuO grains has grown and the crystal quality has been improved.

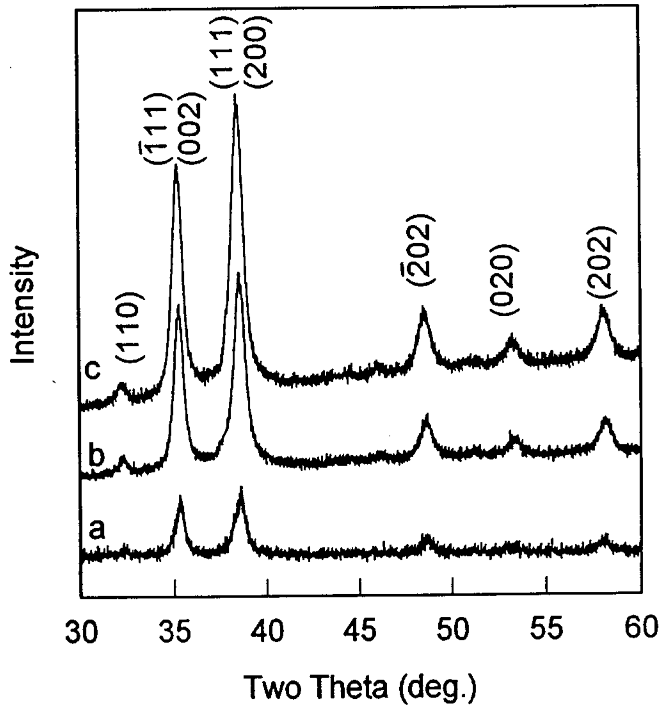

FIG. 2. XRD curves of CuO pellet samples (a) just after pressed, (b) 4 days later, and (c) 15 days later at RT.

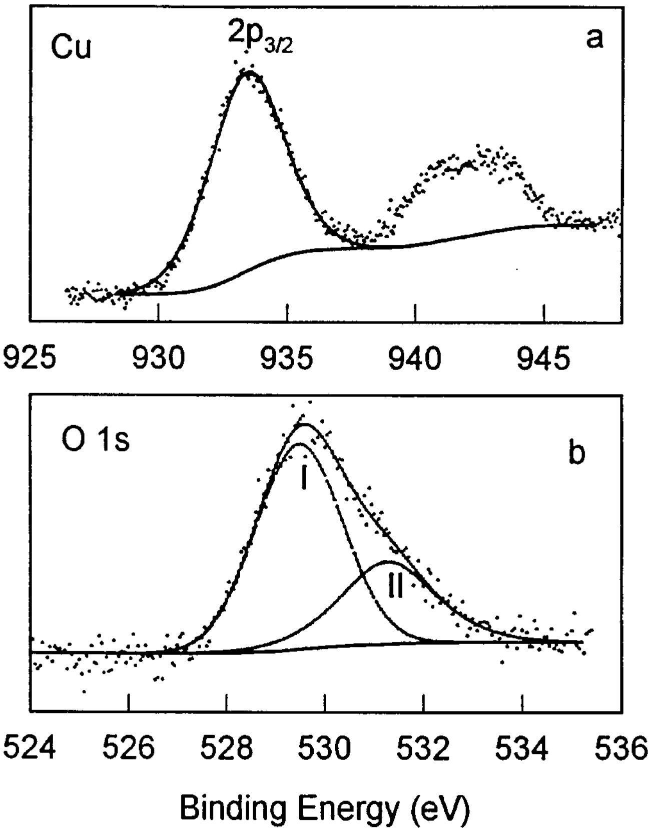

FIG. 1. XPS spectra of (a) Cu 2*p* and (b) O 1*s*.

It is well known that in a substable fluid phase, single atoms or molecules will turn into atoms or molecules of stable grain phase, which will decrease the Gibb's free energy ΔG. If the volume of an atom or molecule of grain is Ω, the interfacial energy between the crystal and the fluid is γ, and the radius of a spherical assembled grain formed in the substable fluid is r, the resultant change in the Gibb's free energy is

$$\Delta G(r) = \frac{4\pi r^3}{3\Omega}\Delta g + 4\pi r^2 \gamma. \qquad [1]$$

If the spherical grain of radius r is composed of n atoms or molecules, ΔG can be expressed as a function of n to give the general expression

$$\Delta G = n\Delta g + A(n)\gamma, \qquad [2]$$

where $A(n)$ is the volume fraction of interface, namely, $A(n) = \eta n^{2/3}$, and η is the form factor which is given by $\eta = (36\pi)^{1/3}\Omega^{2/3}$ for a spherical grain. The free energy can be reduced by merging grains into larger ones. Hence CuO nanoparicles are unstable in nature. However, change in the grain size was found only in the pressed pellets, not in CuO powder from XRD or Raman measurements. The grains in pressed pellets are more closely packed, making them combine more easily into larger ones.

By the width of the XRD diffraction peaks we obtained the following mean sizes of the nanocrystals: 12.1 nm (sample A, immediately after pressing), 15.1 nm (sample B, 4 days at RT after pressing), 16.4 nm (sample C, 15 days at RT after pressing). When a system is far from the equilibrium, it always runs quickly to the equilibrium; when the system is close to the equilibrium, it slows down. The growth of the CuO grains seems to be deferred after 4 days of aging because the system is near the equilibrium. A TEM image of the CuO particles is presented in Fig. 3, showing that the samples are composed of polyhedral nanocrystals.

3.3. *Raman Spectra*

Cupric oxide (CuO) belongs to the C_{2h}^6 space group with two molecules per primitive cell. One can find for the zone center normal modes

$$\Gamma \equiv 4\mathrm{Au} + 5\mathrm{Bu} + \mathrm{Ag} + 2\mathrm{Bg}. \qquad [3]$$

There are three acoustic modes (Au + 2Bu), six infrared active modes (3Au + 3Bu), and three Raman active modes (Ag + 2Bg).

Figure 4 presents the Raman spectra of nanocrystal CuO samples. It can be seen that there are three Raman peaks in sample A, at 282, 332, 618 cm^{-1}, with the second one being weakest and the third being broad. In comparison with the vibrational spectra of a CuO single crystal (6), we can assign the peak at 282 cm^{-1} to the Ag mode and the peaks at 332, 618 cm^{-1} to the Bg modes. When the pellet sample was kept in air for a few days at RT, the Raman peaks become stronger and sharper, and shift slightly to higher frequencies. For example, the peak at 282 cm^{-1} shifts to 285 and 287 cm^{-1}, after 4 and 15 days, respectively, indicating that some change has taken place in the sample, in agreement with the XRD results discussed earlier. In order to observe the pattern more clearly, we annealed the sample in air at 500 and 800°C for 2 h, and their RT Raman spectra are shown in Figs. 4d and 4e, respectively. The Raman peaks become sharper and show a slight blue shift. That is, the red shift and broadening of Raman spectra increase with decrease in grain size. Table 1 presents the experimental results regarding the position and full-width at half maximum (FWHM) of the Raman peaks for different samples.

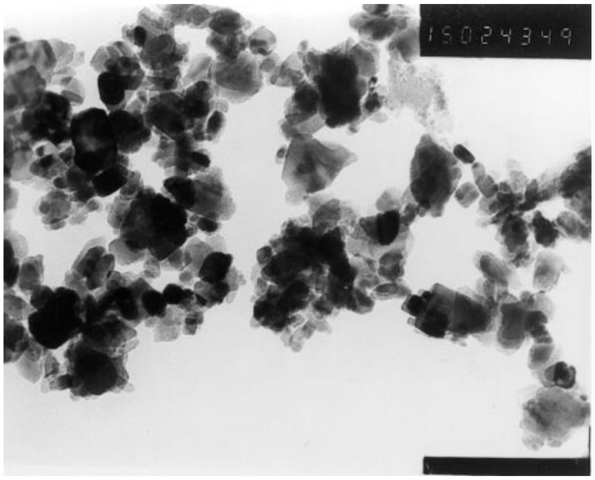

FIG. 3. TEM micrograph of the CuO particles (× 150,000).

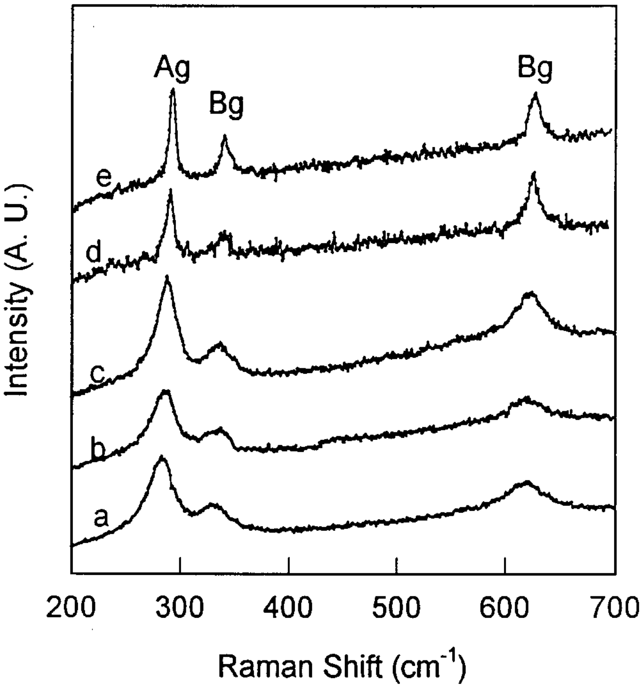

FIG. 4. Raman spectra of CuO pellet samples (a) just after pressed, (b) 4 days later at RT, (c) 15 days later at RT, (d) annealed at 500°C for 2 h, and (e) annealed at 800°C for 2 h.

Confined optical phonons were first discovered in semiconductor superlattices and multiple quantum well structures. For spherical nanocrystals, the first-order Raman intensity $I(\omega)$ is a superposition of weighted Lorentzian contributions over the whole Brilloun zone,

$$I(\omega) = \int \frac{|C(0,k)|^2}{[\omega - \omega(k)^2 + (\Gamma_0/2)^2} d^3k, \qquad [4]$$

where $\omega(k)$ is the phonon dispersion relation, Γ_0 is the natural full linewidth, and $C(0, k)$ is the Fourier coefficient of the phonon confinement function which is often taken as (7)

$$|C(k)|^2 = \exp(-k^2 d^2/16\pi^2), \qquad [5]$$

TABLE 1
Positions and FWHM of Raman Peak for Different Samples: Pressed Pellets (Sample A), 4 and 15 days Later (Samples B and C), and Annealed at 500 and 800°C for 2 h (Samples D and E)

	Ag (cm^{-1})		Bg^1 (cm^{-1})		Bg^2 (cm^{-1})	
Sample	Position	FWHM	Position	FWHM	Position	FWHM
A	282	28	332	19	618	49
B	285	27	334	22	619	45
C	287	22	337	20	622	36
D	292	10	341	17	626	18
E	295	6	342	13	628	15

where d is the average size of nanocrystals. The broadening and the shift of a Raman peak is a result of this integration in Eq. [4] with decreasing grain size. Unfortunately, due to the low symmetry of the CuO lattice and the anisotropic dispersion curves (8), it is very difficult to carry out a detailed analysis using Eq. [4].

4. CONCLUSIONS

By a one-step solid state reaction method, CuO nanoparticles were prepared. XPS and XRD showed that the sample is composed of single-phase CuO with monoclinic structure. The CuO powder sample was stable at room temperature. However, when the powder was pressed into pellets under high pressure, it was unstable. Grains grow with time, which can be manifested by both XRD and Raman spectroscopy. As the grain size increases, Raman peaks shift to higher frequencies and become sharper due to size effects.

ACKNOWLEDGMENTS

This work was partly supported by the National Science and Technology Board (NSTB) of Singapore and the National Science Foundation of China. The authors would like to acknowledge Dr. S. B. Tang for helpful discussions.

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