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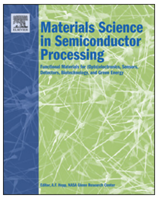

Phase transition of Cu_2O to CuO nanocrystals by selective laser heating

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ABSTRACT

In this paper, we reported the preparation of CuO nanocrystals by microwave irradiation method. With the aid of suitable surfactants, CuO nanoparticles of uniform size and shape were successfully prepared. The as-prepared nano-products were characterized by different techniques such as Xray diffraction (XRD), Raman scattering, scanning electron microscopy (SEM), which all confirmed the good quality of the product. However, Raman spectra showed some peaks, which were attributed to impurity phases such as Cu_2O or $Cu(OH)_2$. Post annealing the samples by laser is a good method to convert these phases into pure CuO. Phase transition was observed *in situ* by Raman spectroscopy. After laser treatment process, Raman spectra of the samples showed that the nano-product is single phase and the crystal quality of CuO nanocrystal was improved clearly.

1. Introduction

Cupric oxide (CuO) is a transition metal oxide semiconductor of monoclinic structure. CuO was well-known for applications in catalyst and thermal conducting fields but recently new potential applications of this material such as high temperature superconductivity, lithium ion batteries, sensors and solar cells [1–6] have renewed a great interest from scientists. Furthermore, many interesting properties of CuO, which are enhanced in nanomaterials, make it a hot topic in different science and engineer fields.

Although great progress has been achieved in preparing different nanostructures of cupric oxide, exploring different approaches to seek for a good method to prepare CuO nanostructures still requires much effort from material scientists. A quick, high throughput process to synthesize nanomaterials of high quality at a large scale not only makes it easier to study the properties of the materials but also paves the way to realize the commercial applications. In this paper, we report the fabrication of CuO nanoparticles by a quick process using microwave irradiation. The product has uniform size and shape as well as good quality, as shown by different characterization techniques: Xray diffraction, Scanning electron and Raman scattering microscopy. The quality of the product can be further improved by post annealing under laser illumination to remove undesired phases from the nanoproduct.

2. Experiment

The detail process to synthesize CuO nanostructures by microwave method could be found elsewhere [7]. Typically, 50 ml of copper acetate (Merk, 99% purity) 0.2 M was continuously magnetic stirred at constant rate. Meanwhile, 50 ml of 0.4 M NaOH in ethanol (Merk, 99% purity) was added dropwise. In case of using surfactants, suitable amount of polyethylence glycol (PEG) or polyvinyl pyrrolidone (PVP) was dissolved into copper salt solution before reaction with sodium hydroxide. The resulting solution was then heated by microwave irradiation in 10 min at microwave power of 80 W to obtain CuO nano product. A dark precipitation was collected at the end of the heating process. The washing process was repeated several times with distilled water and ethanol to obtain pure product. Finally the product was dried to obtain CuO nanopowder or drop-casted on sodalime glass to obtain thin films of nanocrystals for further characterization. Three CuO nanoparticle samples were prepared without surfactant (M1), with PEG (M2) and PVP (M3) as surfactants.

The particle morphologies and structures of the products were investigated by a scanning electron microscope (SEM 1010-JEOL) and X-ray diffractometer (Bruker-AXS D5005). Raman measurements at room temperature were carried out by using Horiba Jobin Yvon spectrometer with several excitation wavelengths: 632.8 nm-line of He-Ne; 514.5 nm-line of Ar ion and 441.6 nm-line of He-Cd laser.

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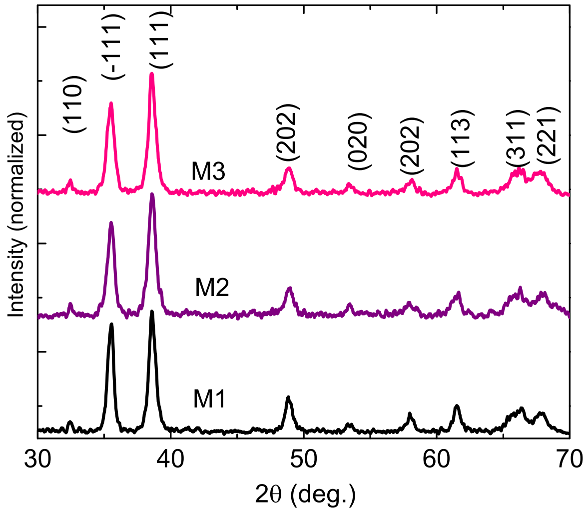

Fig. 1. Xray diffraction patterns of the as-prepared samples.

3. Results and discussion

Xray diffraction patterns of the three samples are shown in Fig. 1. To the limitation of XRD measurement, all of the samples show characteristic peaks of CuO without additional peaks of other phases. Clear peaks in the patterns imply that the crystallinity of the nanoproducts is good. Crystal size estimated by using Debye Sherre formula are 16, 12, 11 nm for the samples prepared without surfactant, with PEG and PVP, respectively.

The influence of surfactants on the morphology of nanoproducts could be observed directly through SEM images of the samples. As can be seen from Fig. 2, particle size is much smaller for the samples prepared with surfactants, especially for sample prepared with PVP. Furthermore, samples prepared with PEG and PVP also show better uniformity in size and shape. The fact that, size of products decreases from around one micron to around one hundred nanometer when using PVP as surfactant, demonstrates the important role of surfactant on the morphology of nanoproduct.

After the nucleation and growth process are completed, the average size of CuO nanoparticles could continue to increase due to agglomeration. As the nanoparticles were agglomerated it is difficult to separate them. In order to obtain product of high quality, it is necessary to stabilize the as-produced nanostructures. There are two main stabilization mechanisms: electrostatic and steric stabilization. While most polymers could only provide steric stabilization, some others show advantages of providing both stabilization mechanisms simultaneously. Many groups had taken advantages of such combination by using certain polymers of high ion density. The ionic nature of the polymer provides the electrostatic repulsion between nanoparticles while the long polymer chain keeps the nanoparticles away from each other by steric effect. Among the polymers of this kind, PVP is one of the most commonly used as it can be dissolved in both polar and nonpolar solvents. The polar amide group in polymeric chain of PVP is readily attached to the surface of nanoparticles to protect them from aggregation by the two stabilization mechanism. The improvement in homogeneity and uniformity of nanoproduct prepared by PVP compared with PEG could be explained by the above understanding on the role of different type of polymer. PEG could mostly provide steric repulsion as it has less ionic nature, which also means that PEG could not produce as strong electrostatic repulsion as PVP.

The following measurements were conducted only on the sample of highest quality (M3). Along with Xray diffraction, Raman spectroscopy, which is a sensitive probe to the local atomic arrangements and vibrations of the materials, has been also widely used to investigate the microstructural nature of the nano-sized materials. Raman scattering also provides useful information about the structures and bonds of materials. In particular for CuO nanomaterial, Raman scattering could help to show the crystallinity of the product or detect the existence of undesired phases such as Cu_2O or $Cu(OH)_2$ at a much lower content compared with limit of detection of Xray diffraction measurement. The space group of CuO is C_{2h}^{6} with two molecules per primitive cell so the zone center Raman active normal modes of CuO are $\Gamma_{RA}=4A_u+5Bu+A_g+2B_g$. Among these vibration modes, there are three acoustic modes (A_u+2B_u), six infrared active modes ($3A_u+3B_g$), and three Raman active modes (A_g+2B_g). Three well known Raman bands of CuO are A_g (296 cm^{-1}), B_{1g} (346 cm^{-1}), and B_{2g} (631 cm^{-1}) [8]. Fig. 3 shows Raman spectra of sample M3, taken with three different excitation wavelengths 623.8, 514.5, 441.6 nm. In these spectra, A_{1g} and B_{1g} modes of CuO agreed well with other reports for CuO bulk material. No peak shift due to phonon confinement effect was observed because particle size did not reach closed enough to the Bohr exciton radius of CuO, which is quite small, and in the range from 6.6 to 28.7 nm [9]. However, an additional peak appeared at around 590 cm^{-1} and convoluted with the B_{2g} peak of CuO to form a broad band.

From theoretical point of view, the occurrence of defects in a crystalline material can break the translational symmetry of the crystal lattice or totally lost material long range order in the extreme case where material is in glassy or amorphous state. Such these changes will lead to variation in Raman selection rules for perfect crystal and could give rise to the appearance/disappearance of some Raman modes. In fact, these changes are rarely observed experimentally because the density of defect is not enough to make a significant perturbation to the vibration properties of materials. However, oxide of copper is an exception as defect induced vibration modes was reported for this material

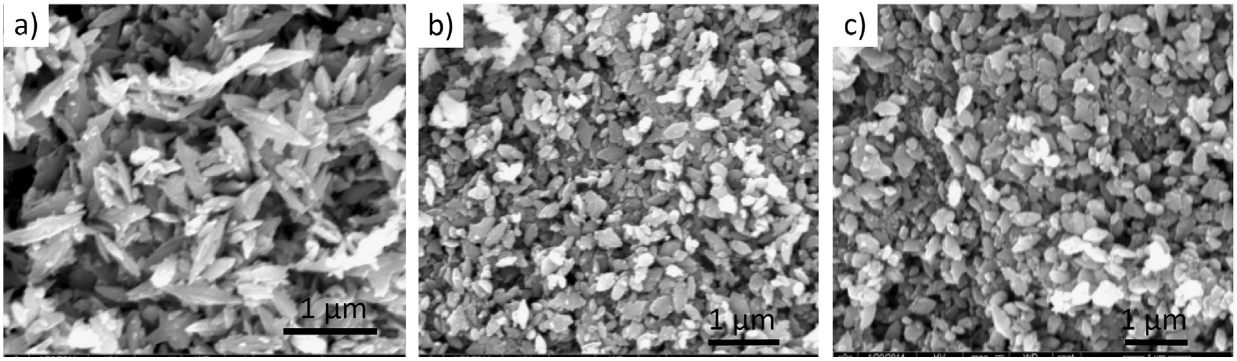

Fig. 2. SEM images of CuO nanostructure samples: (a) M1, (b) M2 and (c) M3.