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Effect of temperature and time on morphology of CuO nanoparticle during synthesis

ABSTRACT

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In the past decades, many methods have been developed to synthesize zero-dimensional nanoparticles, quasi-one-dimensional (1D) CuO nanostructures, such as metal organic deposition technique, microwave irradiation, sol-gel-like dip technique, reverse micelle-assisted route, chemical method, and simple template free solution route. Among those synthesis methods, hydrothermal and chemical reaction methods are of particular interest because they are safe and environmental-friendly synthesis. By use of nonionic surfactant polyethylene glycol (PEG), the clew CuO nanostructure with the diameter of about 4 μm was prepared at 150°C for 11 hr. As the temperature increased to 160°C for 11 hr, the gear wheel CuO nanostructure with the diameter of about 70 nm was made. Furthermore, two other temperatures (180 and 200) are utilized for 20 hr to produce nanowire. The product was characterized by powder X-Ray diffraction, and scanning electron microscopy SEM showed the various shapes of CuO nanostructures, including clew, gearwheel, and nanowire bundles.

Keywords: Nanostructure; Hydrothermal; Nanowires; Novel shape.

INTRODUCTION

Micro- and nanostructures with well-defined shape and inner structure have attracted great interests due to their novel properties and diverging applications [1, 2]. Self-assembly driven by various interactions, such as surface tension, capillary effects, electric and magnetic forces, and hydrophobic interactions, is an effective strategy for forming versatile "soft" nanocrystal-assembly motifs [5,6]. Copper oxide nanoparticles have been of considerable interest due to the role of CuO in heterogeneous catalysis, in high-T_c superconductors in heat exchangers, lithium ion electrode materials, and in gas sensors. There have been various methods to prepare ultrafine CuO, such as sol-gel, precipitation-stripping method, solid-state reaction and alkoxide-based synthesis [9].

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However, there has been limited work on copper oxide nanowires and nanorods [11,12]. One-dimensional nanostructure materials are currently the focus of considerable interest, because they often possess unique chemical, mechanical and physical properties, and may prove to be key components in the next generation of nano-optical and electronic devices [14]. Recent studies indicate that CuO can exist in three different magnetic phases. The p-type semiconductor of copper oxide (CuO), demonstrating a thin band gap (1.85 eV), is a significant practical material used in catalysis, gas sensors and photovoltaic cells [15]. In this work, clew, gear wheel and narowire bundles CuO nanostructure have been selectively prepared by hydrothermal in the presence of a structure-directing surfactant of the polyethylene glycol (PEG) just through simply changing the growth time and temperature. The approach of hydrothermal is demonstrated to be a convenient route to produce CuO nanostructures [16].

EXPERIMENTAL

Synthesis process

The chemical materials which were used in this experiment were all commercial and available. And all of the chemical reagents were analytical grade and used without any further purification in this experiment. $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{CO}_3$ and polyethylene glycol (PEG), were respectively, dissolved in demineral water to form 0.25 M $\text{Cu}(\text{NO}_3)_2$ solution, 0.5 M $(\text{NH}_4)_2\text{CO}_3$ solution and 0.25 % PEG solution. 25 ml of 0.25 M $\text{Cu}(\text{NO}_3)_2$ solution was slowly dropped into 30 ml of 0.5 M $(\text{NH}_4)_2\text{CO}_3$ with high speed stirring to obtain a precipitate. Then it was transferred into Teflon-lined stainless steel autoclave of 200 ml capacity. The autoclave was maintained at 150, 160, 180 and 200 °C for 11, 11, 20, and 20 hr and then cooled down in room temperature. The precipitate was filtered and rinsed repeatedly with distilled water to remove the contaminants such as surfactants and then dried at 75 °C for 1 hr.

Characterizations

The composition of the sample were examined by a Unisantix XMD 300, X-ray diffract meter and analytical Xpert PRO X-ray diffraction

($\lambda=0.17890$ nm). 2θ range used was from 20-70 in steps of 0.02 with a count time of 1 s. XRD patterns of the sample obtained with different reaction condition are shown in Figures 1-4. The formation of crystalline CuO nanostructures was confirmed by the use of XRD. Figures 1-4 shows XRD spectrum of different shaped CuO nanostructures. All the diffraction peaks can be indexed to the monoclinic phase of CuO (S.G. C2/c; with lattice constants of $a = 4.682\text{\AA}$, $b = 3.423\text{\AA}$, $c = 5.127\text{\AA}$, and $\beta = 99.468^\circ$). The broadening of all recorded peaks in the spectrum indicates the presence of nanoscale crystallites. No other impurities were detected by XRD analysis, indicating the phase purity of CuO rectangular shaped nanostructures.

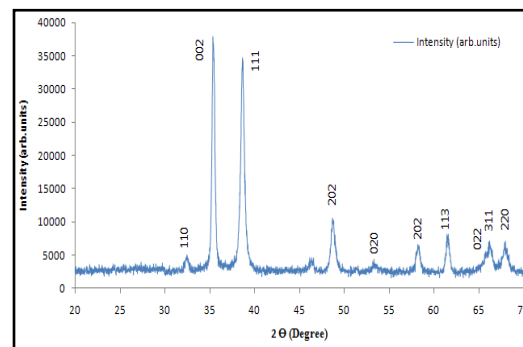


Fig. 1. XRD Pattern of product 150 °C

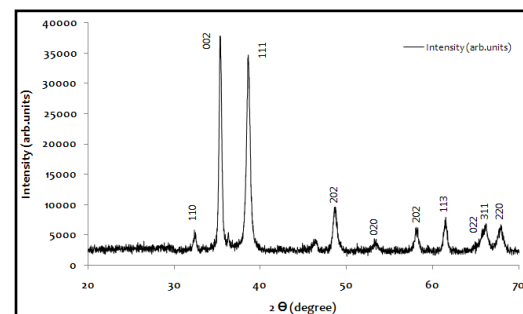


Fig. 2. XRD Pattern of product 160 °C

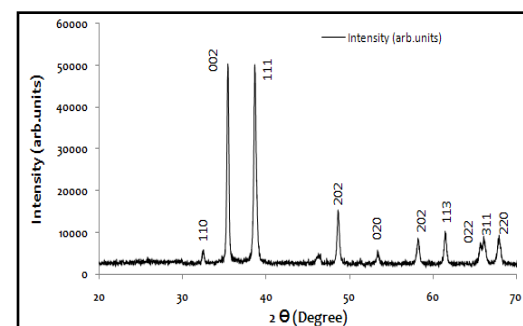


Fig. 3. XRD Pattern of product 180 °C

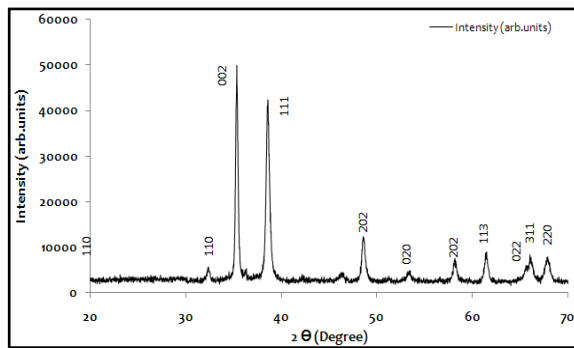


Fig. 4. XRD Pattern of product 200 °C

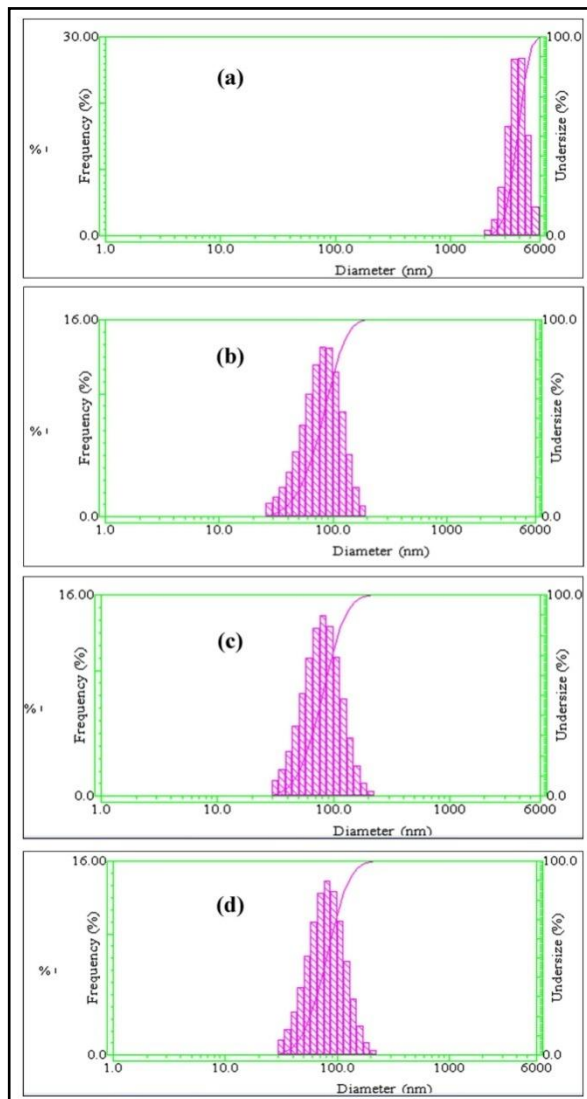


Fig. 5. Particle size analyzer of products a: (150° C), b: (160°C),c:(180°C), d:(200° C)

Figure 6 shows the SEM images which are illustrated CuO nanostructure under four reaction conditions. Under 150 ° C for 11 hr, the structure holds together like clews, as shown in Figure 6a, the diameter of that is around 3.8 μm. When increasing the temperature to 160 ° c for 10 hr CuO nanostructure stretched more like gear wheels and the diameter is around 70 nm (Figure 6b). The crystalline sizes of the CuO-NPs were determined by means of an X-ray line-broadening method using the Scherrer equation: $D=(k\lambda/\beta hkl \cos\theta)$.

Where D is the particle size in nanometers, λ is the wavelength of the radiation (1.54056 Å for CuK α radiation), k is a constant equal to 0.94, βhkl is the peak width at half-maximum intensity and θ is the peak position. The (102) plane was chosen to calculate the crystalline size (either plane can be used for this purpose).

The values of d – the distances between adjacent crystal planes (hkl) – were calculated from the Bragg equation, $\lambda=2d \sin\theta$. The lattice constants a, b and c; the inter planar angles, the angle ϕ between the planes (h1k1l1) of spacingd1 and the plane (h2k2l2) of spacingd2; and V, the primary cell volumes, were calculated from the Lattice Geometry equation.

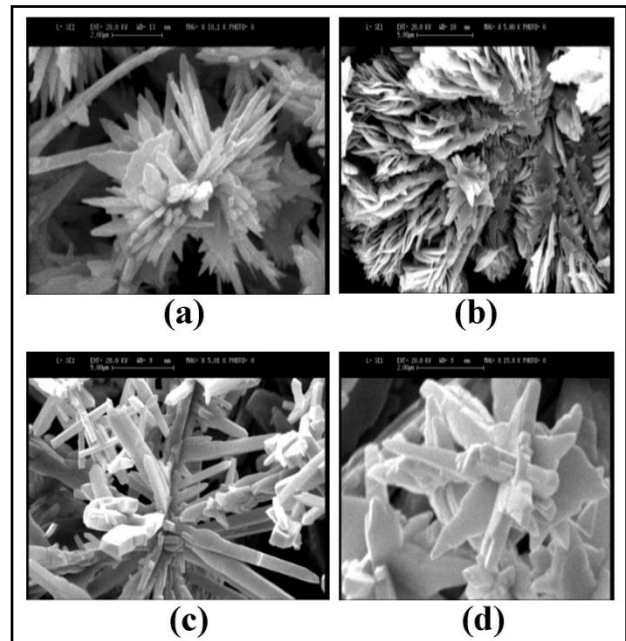


Fig. 6. SEM image of the CuO nanostructure synthesized in different condition (a)150° C for 11 hr; (b)160 °C for 11 hr; (c)180°C for 20 hr; (d)200°C for 20hr

Unit cell representation of CuO

Figure 7 shows a schematic representation of a monoclinic CuO unit cell in 1 * 1 * 1 format. Java Structure Viewer (Version 1.08lite for Windows) and VRML-View (Version 3.0 for Windows) [53,54] programs were used to model this crystalline structure. The structural parameters and atomic coordinates obtained from the Rietveld refinement were used in these programs. As it can be seen in Figure 7, CuO unit cell presents the copper atoms coordinated to four oxygens in a planar square configuration.

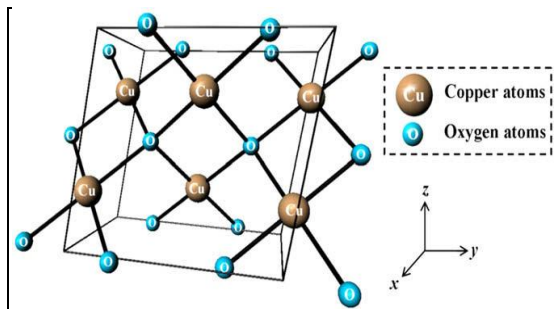


Fig. 7. Schematic representation of a monoclinic CuO unit cell

RESULTS AND DISCUSSION

The reaction temperature is one of the important factors that directly influence the products' components and shapes. In addition, the precursor is broken up into CuO crystal cores by heating. Then the growth of CuO nanostructures was influenced greatly by the temperature. At lower temperature, the crystal was apt to grow into bulk for precursor's incomplete breakup and low crystallization. The breakup of the precursors and the growth of CuO were all accelerated with increasing temperature. At higher temperature, the thermal movement of the molecular in the elements for growth speeded up and then quickened the growth of the crystal cores, because the nanocrystals tended to orient the crystal lattice's to growth direction. An experimental formula can describe the above relation rightly as follows:

$$\frac{d \ln V}{dT} = \frac{C}{RT^2}$$

Where V was the growth velocity, C and R were constant and gas constant. If the temperature is high enough, the crystal's growth will quicken in all directions. Therefore, the crystal was tending to grow into spherical or sphere-like structure and even cubic crystal. In summary, the suitable temperature for the growth of CuO nanowire was from 150 to 200°C.

As for the growth mechanism of CuO nanostructure, the role of surfactant should be taken into consideration. As it is known, PEG is a sort of nonionic surfactant and its molecular formula is H-(O-CH₂-CH₂)_n-OH. Its monomer was apt to exist with chain structures in the water, which made CuO growing along the chain direction possible. The chain structure of the PEG induced the CuO grew into quasi-1D nanostructure to a certain extent.

CONCLUSION

As it is mentioned the temperature and time directly influence on the morphology of CuO nanostructure of clew gear wheel and nanowire bundle respectively. At least it is hoped that this aqueous solution synthetic route can be applied as a general method for the preparation of other oxide nanostructures.

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