GREEN SYNTHESIS OF COPPER OXIDE NANOPARTICLES

Nguyen Ngoc Hanh, Vo Huu Thao

University of Technology, VNU-HCM

(Manuscript Received on May 13th, 2011, Manuscript Revised November 01st, 2011)

ABSTRACT: *Nanoparticles of metal and metallic oxides have become a very active research area in the field of material chemistry. The surface effect is mainly responsible for deviation of the properties of nano-materials from that of the bulk. Nanosize copper oxide was synthesized by hydrolysis of copper salts in basic medium using biodegradable non-ionic polymer polyethylene glycol (PEG) as surface active agent The X-ray powder diffraction patterns (XRD) present typical peaks of copper oxides formed. The transmission electron microscopy (TEM) and scanning electron microscopy (SEM) images determined the shape and the nanosizes of the particles of about 10-30nm. The results exhibited the role of intermediate nanosize copper hydroxide species on the formation of copper oxide nanoparticles. The influence of synthesis temperature, reaction time, calcination temperature, etc. was studied.*

Key words: *green synthesis.*

1. INTRODUCTION

In recent years, copper oxide has been interested in fundamental research as well as in various applications. It has been widely used as industrial materials such as gas sensor, magnetic storage, solar energy converter, inorganic dyes… In the field of adsorption and catalysis, CuO is a traditional oxidation catalyst for treatment of carbon monoxide in gas phase in place of precious metals. Carbon monoxide, emitted from many industrial processes and transportation activities, is considered as an important class of air pollutions. Catalytic oxidation is an efficient way to convert CO to CO_2 at rather low temperature. As particle size reduced from micrometer to nanometer the physical properties, such as electrical conductivity, stiffness, acive surface, chemical activity, biological properties could unpredictably change.. Antibacterial effect of metallic nanoparticles has ever known as result of their nanosize and great surface/volume ratio. These characteristics permit them to easily access the bacterial membranes along with electronic effects. Furthermore the CuO nanoparticles could combine with the polymers or cover on other surfaces without difficulty. This feature increases their antibacterial effect [1-5]. Some methods have been suggested for the preparation of CuO nanoparticles: sonochemical decomposition in water in presence of DMF, alcoholthermal, electrochemical synthesis, reaction in solid phase, microemulsion, reduction reaction, sol-gel route,…[7–9]. CuO nanoparticles with an average size of about. 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 [6]. Most of the pathways suggested for the synthesis of CuO nanoparticles involve organic solvents and environmentally malignant chemicals. Organic solvents are particularly problematic, because many are toxic and not easily degraded in the environment. Environmentally friendly chemical syntheses use alternative solvents such as ionic liquids, liquid and supercritical carbon dioxide, and water. Water is particularly attractive because it is inexpensive and environmentally benign. Poly(ethylene glycol) (PEG) is one of the most extensively studied bio-polymers due to its biocompatibility and its good solubility in both organic solvents and water [10]. In this work we focused on the sol-gel synthesis of CuO nanoparticles via a green pathway using non-ionic low molecular biodegradable polyethyleneglycol *(*PEG*)* in water. It was also found that the presence of PEG dispersant and its content have great effects on the shape and size of nanocopper oxides...[11-13]. The influence of reaction chemical compositions, drying temperature and calcination temperatures on morphology and structure of CuO nanoparticle as well as its intermediate copper hydroxide was studied.

2. EXPERIMENTAL

2.1. Reagents and instruments

Hydrated copper (II) sulphate and NaOH of analytic grade purity were purchased from Shanghai Shaoyun Co. Absolute ethanol of analytical purity was purchased from Nanjing Chemical Reagent Factory (China). Polyethylene glycol (PEG) with molecular mass of 400 Da was purchased from Aldrich. All the reagents were used without further purification.

The structure of synthesized nanoparticles was characterized on a Siemen D5000 X-ray powder diffractometer (XRD), using Cu Kα radiation (l = 1.5406 Å), the operation voltage and current were 40 kV and 60 mA, respectively, with the rate of 1.0 ^{o}C/min. The morphology of nanoparticles was observed on a JEOL-JSM-6500F (FESEM) with Schottky emitter of acceleration potential of 2 kV. The surface morphology was performed on a Transmission Electron Microscope (TEM) (JEM-1400, JEOL, Japan), operating at an acceleration voltage of 200 kV; for these observations, the sample was prepared by dropping the CuO nanoparticles ethanol dispersion on carbon-coated Cu grids.

2.2. Preparation of CuO nanoparticles

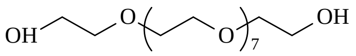
The reaction was processed in a thermostat. The temperature was adjusted in the range of 10 to 30^{o}C, and distilled water was used as medium in the bath. The solution of $CuSO_4.5H_2O$ with a given ratio (x_1) with NaOH was added into the round-bottom flask set in the thermostat in 4h. A quantity of PEG 400 surfactant of given ratios (x_2)with $CuSO_4$ and the solution of NaOH were respectively added into the flask under violent mixing.The reaction time was maintained in about 40 minutes. The precipitate was then centrifuged, washed once with distilled water, then three times with absolute ethanol. The intermediate product was characterised by XRD patterns and TEM image before drying in air at room temperature or various temperatures in oven. The final products were collected for other characterizations as XRD, SEM, TEM images… The influence of chemical composition (x_1, x_2), reaction temperature and drying condition (time, temperature) on CuO particle size was studied.

3. RESULTS AND DISCUSSION

In basic medium copper sulphate quickly converts into its hydroxide form and then the copper oxide obtained after drying as the following reaction equations:

$$CuSO_4 + 2NaOH \rightarrow Cu(OH)_2 + Na_2SO_4$$

$$Cu(OH)_2 \rightarrow CuO + H_2O$$

In other words, the sol-gel route for synthesis of nano CuO composed of two stages: formation of copper hydroxides and then dehydration of hydroxides to form final product. It is evident that the nanosize of CuO particles mainly depended upon the intermediate copper hydroxides $Cu(OH)_2$. In aqueous medium, the ionic repulsion forces produced due to adsorption on their surface make the nanosized particles separated. Therefore the surfactant supported stabilization of the nanoparticles has been demonstrated to be one of the most effectual method. Acting as a steric stabilizer to inhibit aggregation, the surfactant play an important role in altering nanoparticle's shape, size and other surface properties to different extent depending upon their molecular structure, i.e., nature of head group, length of hydrophobic tail and type of counterions. The termination of the nanoparticle growth is controlled by the diffusion and the attached rates of surfactants on the nanoparticle surface. The PEG with structure  has been found suitable for this stabilization [13].

The XRD patterns of the intermediate and final products obtained are identical to the single-phases with monoclinic structures (space group C2/c) of Cu $(OH)_2$ and CuO, respectively (Fig.1). The intensities and positions of the peaks are in good agreement with literature values [11]. No peaks of impurity are found in the XRD patterns. The broadening of the peaks indicated that the crystal size is small. The average crystalline diameter (d_{CuO}) of the particles could be estimated from this broadening of corresponding X-ray spectral peaks by the Debye-Scherrer's formula $d=0.89\lambda/b\cos\theta$, where d is the crystallite size, λ the wavelength of the X-ray radiation (CuKα = 0.15418 nm), b the line width at half-maximum height after subtraction of broadening caused by equipment, and θ is the diffraction angle. Here we chose the XRD spectra of (100) and (111) plane to estimate their crystallite size and then average them out in order to decrease the error of the system.

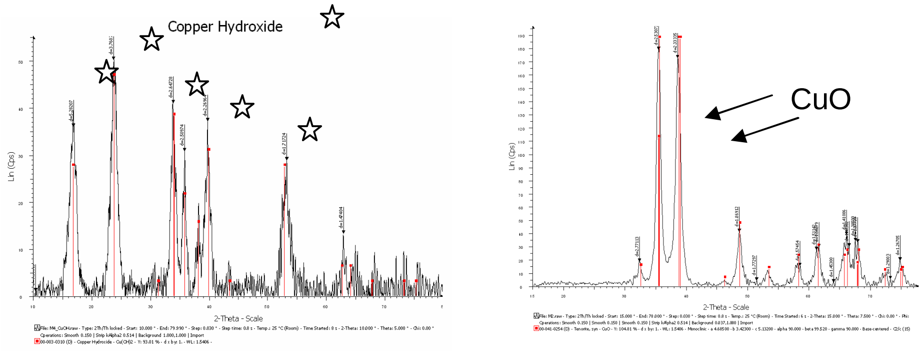


Fig. 1 . XRD patterns of $Cu(OH)_2$ (left) and CuO (right) obtained by drying

The size and morphology of the products were analyzed by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). The TEM image (Fig. 2a) reveals that the product consists of spherical particles with a regular morphology and narrow size distribution. Typical TEM image of the as-prepared $Cu(OH)_2$ nanoparticles is presented in Fig. 2, showing that the intermediate product was composed of nanofibers of 500ppm length. The effect of aging or heating could make good conversion of $Cu(OH)_2$ nanofibers into CuO nanoparticles. The size of the CuO particles observed in the SEM image (Fig.3) is in the range of 15–25 nm, which is in agreement with that estimated by Scherrer equation from the XRD pattern.

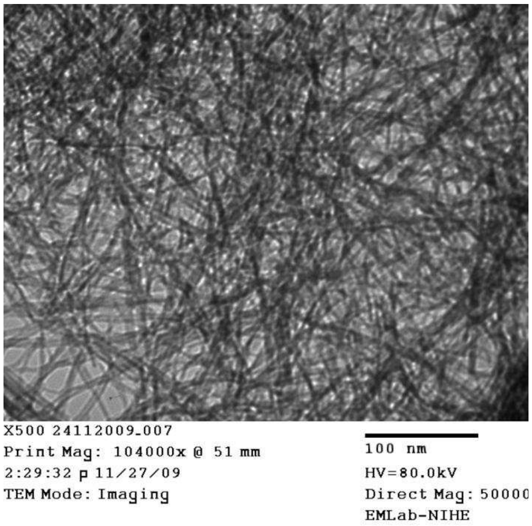


Fig.2. TEM image of $Cu(OH)_2$

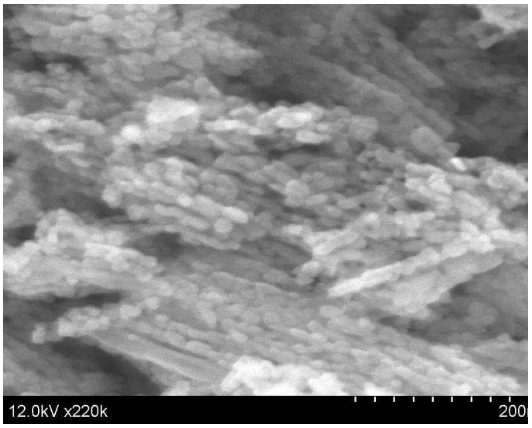


Fig.3. SEM image of CuO

We have tried to prepare CuO nanoparticles in changing chemical compositions of initial reaction mixture. As shown in Table 1, in experiments at 30^{o}C with the amount of PEG slightly increasing (increasing x_2), the estimated size of the obtained CuO particles rested between 13-17nm. The NaOH content (x_1) required an optimum value for CuO nanosize. In order to investigate the suitable conditions such as reaction temperature and treating condition of $Cu(OH)_2$ we took the composition of sample 1 (Fig.4) as our study object in the following discussion.

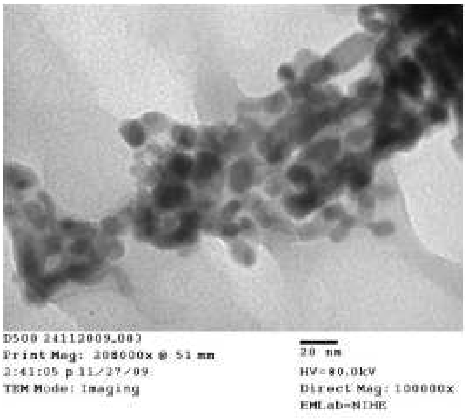


Fig.4.TEM images of CuO (sample 1)

Table 1. Influence of chemical compositions on CuO nanosize

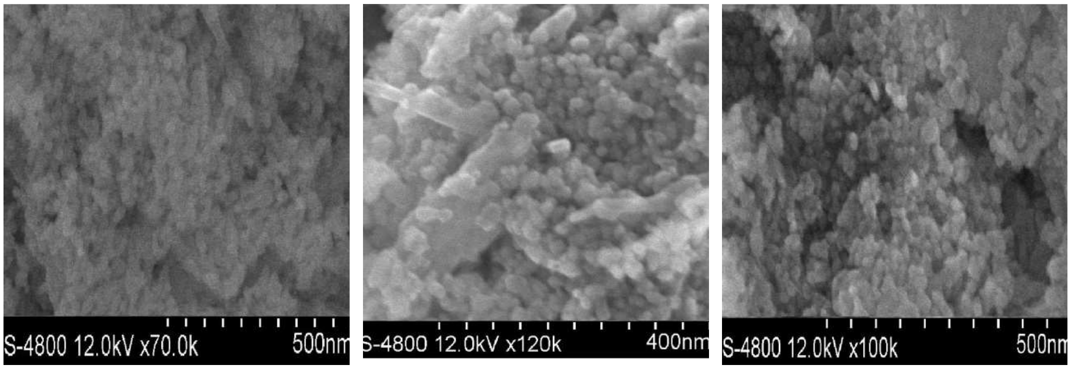
Sample	x_1	x_2	d_{XRD} (nm)
1	3	1.25	15
2	3	0.75	14
3	3	1.75	17
4	3.5	1.25	18
5	4	1.25	19
6	2.5	1.25	plate

The reaction temperature plays an important role in the formation of highly dispersed $Cu(OH)_2$ nano species. This is possible because the nucleation and growth rate were low at mild reaction condition, which leads to aggregation of $Cu(OH)_2$ crystals. On the contrary, if the NaOH solution was added into the system, the higher temperature caused higher reaction rates, which might cause large amounts of nuclei to form in a short time, and the aggregation of crystals was inhibited. In these experiments, we chose various temperatures (10-20-30^{o}C) for the reaction process. It has been obsersed that the ambient temperature seemed more effectual way to obtain well dispersed system (Table 2 and Figure 5)

Table 2. Influence of reaction temperature on CuO size

No	T (^{o}C)	d_{XRD}(nm)
1	10	18
2	20	16
3	30	14

*[NaOH] =3[$CuSO_4$] ; [PEG]=1.25 $CuSO_4$], drying at 300^{o}C in 3h



(a) (b) (c)

Fig 5. SEM images of CuO in various reaction temperature (a) 10^{o}C (b) 20^{o}C(c) 30^{o}C

As presented in Table 3, after drying the intermediate products at various conditions: 6h in air, drying at 100^{o}C (2h-12h-20h) in drier and calcinating at 300^{o}C in oven, the presence of $Cu(OH)_2$ and CuO species has clearly been determined (Fig.6). After drying 6h in air an important amount of $Cu(OH)_2$ rested. Drying at 100^{o}C had promoted the better transformation into CuO. It can be found that there was no considerable difference between drying 100^{o}C in 20h and 300^{o}C in 3h (Fig. 6). For convenience we chose the treatment at 300^{o}C in 3h to have complete conversion of $Cu(OH)_2$

Table 3. Influence of drying condition on CuO particle size

No	Drying condition	Final product	d $_{XRD}$ (nm)
1	in air, ambient	$Cu(OH)_2$, CuO	17
2	100^{o}C, 2h	$Cu(OH)_{2,}$ CuO	18
3	100^{o}C,12h	$Cu(OH)_2$(trace),CuO	16
4	100^{o}C, 20h	CuO	18
5	300^{o}C,3h	CuO	16

*[NaOH] =3[$CuSO_4$] ; [PEG]=1.25 $CuSO_4$], T reaction = 30^{o}C

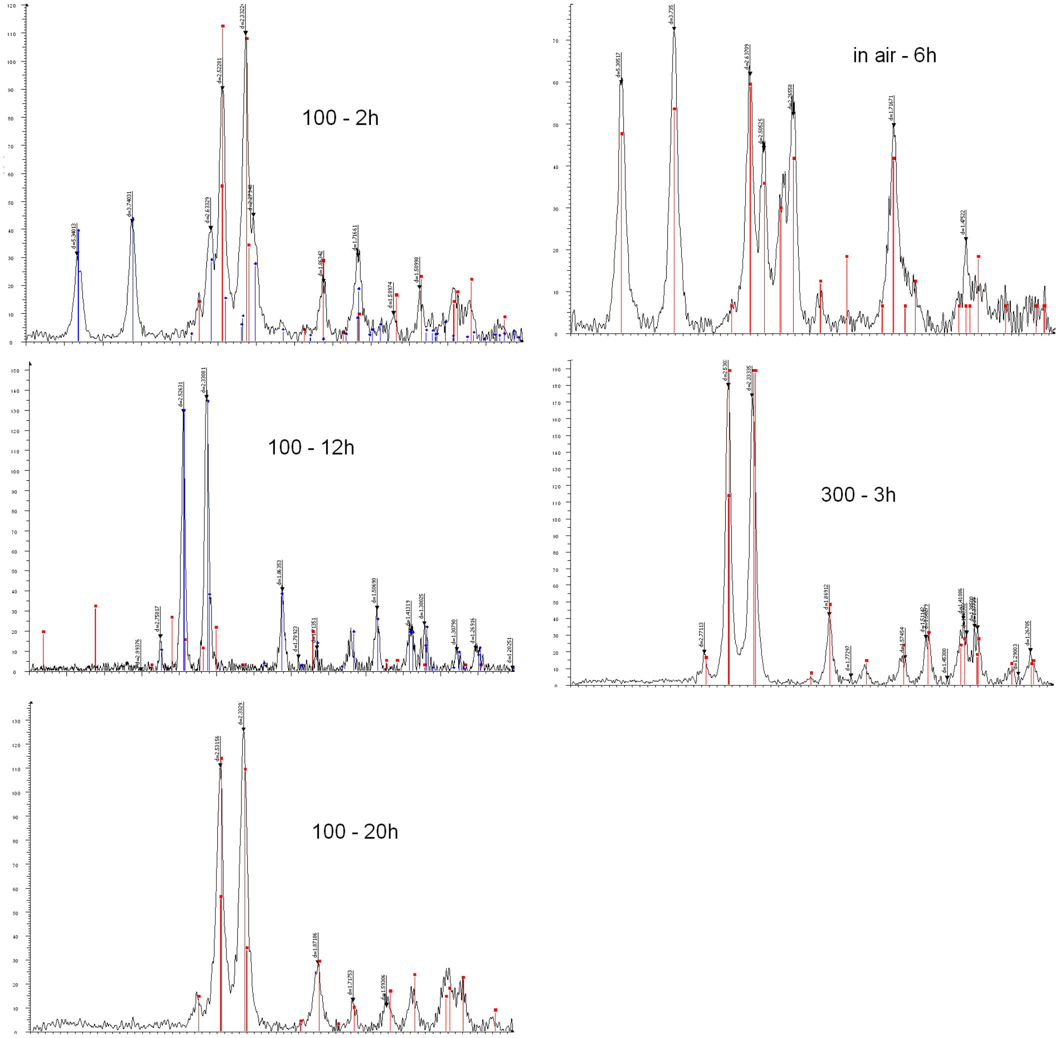
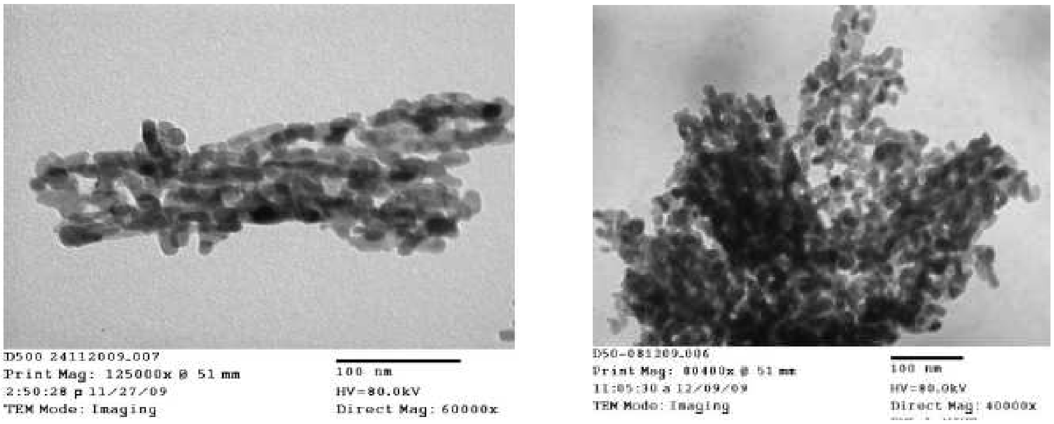


Fig.6. XRD patterns of intermediate products in various condition of treatment of products



(a) (b)

Fig.7. TEM images of CuO samples after treatment (a) 100°C, 20h (b) 300°C, 3h

4. CONCLUSION

Nanocrystalline CuO particles have been prepared successfully by sol-gel method using non-ionic surfactant polyethyleneglycol with suitable chemical composition. It is a unexpensive and efficient method to produce CuO with the size of 15-30 nm. We can foresee the upscaling of the process to form large quantities of CuO nanoparticles, which have wide applications in various fields such as catalysis and biomedicals.

TỔNG HỢP ‘XANH’ NANO OXYT KIM LOẠI ĐỒNG

Nguyễn Ngọc Hạnh, Võ Hữu Thảo
Trường Đại học Bách Khoa, ĐHQG-HCM

TÓM TẮT: *Nano kim loại và oxyt kim loại đang là lĩnh vực nghiên cứu rất được chú ý trong hóa học vật liệu. Hiệu ứng bề mặt của vật liệu nano làm cho các tính chất của chúng khác biệt so với vật liệu dạng khối. Nano oxyt đồng. được tổng hợp bằng cách thủy phân muối đồng trong môi trường kiềm có mặt chất hoạt động bề mặt không ion là polyetylen glycol (PEG) phân hủy sinh học. Nhiễu xạ tia X cho thấy các pic đặc trưng của oxyt đồng hình thành. Các ảnh quan sát trên kính hiển vi điện tử truyền qua (TEM) và kính hiển vi điện tử quét (SEM) xác định hình dạng và kích thước nano của các hạt khoảng 10-30 nm. Kết quả nghiên cứu cho thấy vai trò của sản phẩm trung gian hydroxyt đồng trong việc hình thành các hạt nano oxyt đồng. Ảnh hưởng của nhiệt độ phản ứng, thời gian tổng hợp, nhiệt độ nung,… đã được khảo sát.*

Từ khóa: *Tổng hợp xanh.*

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