

Direct Precipitation Method of Nano-CuO

Mingyu Li, Kefu Ding, Zhihao Li, Zeng Qingxuan

¹State Key Laboratory of Explosion Science and Technology, Beijing Institute of Technology, Beijing 100081, P. R. China

*Corresponding author: Li Mingyu. E-mail: mingyuli@163.com

Abstract: Different reaction conditions were studied through orthogonal experiment and single factor experiment. Using $\text{Cu}(\text{NO}_3)_2$ as the reactant, water-alcohol solution ($\text{H}_2\text{O}:\text{CH}_2\text{CH}_3\text{OH}$ was 3:1) as solvent at 20°C and reaction for 45min could get nano-CuO with good dispersion and uniform size. Different kinds of characterization method were used to characterize the resultant. The average diameter of nano-CuO was 20.38nm after calculated using some relevant formula, the surface area was about 21.988 m^2/g , the pore diameter was about 3.079 nm and the pore volume was 1.349×10^{-1} cc/g . So the method is a feasible, low cost way to industry.

1. Introduction

With small structure units, high specific surface area and unique mechanical, optical, magnetic properties, nanocrystalline materials have become a focus of common attention in the 21st century [1-4]. Among nano materials, nano-CuO has played an important role in catalytic technology, bio-medicine technique, fine chemical industry and other fields and it is likely to have a good future [5, 6]. However, bulk particle is easy to form during the preparation and application losing characteristics of nano materials [7, 8], so the preparation process is very essential. Commonly, solid state reaction method, hydrothermal method, alcohol-thermal method, precipitation method are the methods used in industry and laboratory, recently other methods [9-12] are found such as micro-emulsion method and laser heating gas-evaporation method. Compared with other methods, direct precipitation method has the advantages of simple preparation and low cost, so it can be widely used in industrial production [11].

In the work, different kinds of reactants, temperature, reaction time and ratio of water's volume (V_{water}) and alcohols' volume ($V_{\text{R-OH}}$) were studied through orthogonal experiment and single factor experiment, then the nano-CuO generated was characterized using X-ray diffraction (XRD), fourier transform infrared (FTIR), thermogravimetric analysis (TG), scanning electron microscopy (SEM) and particle surface area measurements to find the best preparation condition. What's more, the diameter, surface area, pore diameter and the pore volume of the CuO generated under best condition were measured and calculated.

2. Experiment

2.1 Materials

Materials included $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{C}_2\text{H}_5\text{OH}$ produced by Beijing chemical plants; $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, Na_2CO_3 produced by Beijing Yili Fine Chemical Co; $\text{C}_4\text{H}_6\text{CuO}_4 \cdot \text{H}_2\text{O}$ by Sinopharm Chemical Reagent Beijing Co. All of the chemicals and reagents used were analytical grade and were used without further purification.

2.2 Equipments

Equipments included an AR2140 electronic balance provided by Ohaus Co. (Shanghai, People's Republic of China), a 81-2 isothermal magnetic agitator provided by Cile Instruments (Shanghai, People's Republic of China), a 80-2 centrifugal precipitator provided by Xinkang Yiliaoqiye Co.(Kangyan, Jiangsu Province, People's Republic of China), a DZF-6020 vacuum drying oven provided by Shanghai Bluepard instrument Co.(Shanghai, People's Republic of China), a stopwatch provided by Jun SD (Shenzhen, Guangdong Province People's Republic of China).

2.3. Experimentalscheme

2.3.1. Precipitation process

Some different kinds of copper salts (CuCl_2 , CuSO_4 , $(\text{CH}_3\text{COO})_2\text{Cu}$ and $\text{Cu}(\text{NO}_3)_2$) were put in the solvent and heated to a certain temperature, then some NaCO_3

solution was added under magnetic stirring condition for a period of time.

2.3.2. Filtration, washing, drying and roasting

Put mixture into centrifuge tubes and centrifuged for a period of time, then washed the precipitate using ethanol twice and put it into vacuum drying oven for 3h at 50 °C to get $\text{Cu}_2(\text{OH})_2\text{CO}_3$ precursor. Heated $\text{Cu}_2(\text{OH})_2\text{CO}_3$ to 400°C for 2h with heating rate $2^\circ\text{C}\cdot\text{min}^{-1}$.

2.4 Characterization

X-ray diffraction (XRD), fourier transform infrared (FTIR), thermogravimetric analysis (TG), scanning

electron microscopy (SEM) and particle surface area measurements were used to analyse chemical composition, structure and properties of the nano-CuO generated.

3. Results and discussions

3.1. Factors influence the experimental process

The volume of $\text{CH}_3\text{CH}_2\text{OH}$ was studied in single factor experiment and then the orthogonal test method was adopted to explore the influences of 4 factors on the products in order to study the factors that influenced nano-CuO. Influence of single factor was given in table 1 and orthogonal factors were given in table 2.

Table 1. Experimental design with single factor

sequence	reactants	temperature	solvent ($\text{CH}_3\text{CH}_2\text{OH} : \text{H}_2\text{O}$)	time
I	CuCl_2	20°C	pure water	15min
II	CuCl_2	20°C	1: 1	15min
III	CuCl_2	20°C	1: 2	15min
IV	CuCl_2	20°C	1: 3	15min

Table 2. Experimental design of orthogonal experiment

sequence	reactants	solvent ($\text{CH}_3\text{CH}_2\text{OH} : \text{H}_2\text{O}$)	temperature	time
1	①(CH_3COO) ₂ Cu	①pure water	①20°C	①15min
2	①(CH_3COO) ₂ Cu	②1:1	②40°C	②30min
3	①(CH_3COO) ₂ Cu	③1:2	③60°C	③45min
4	①(CH_3COO) ₂ Cu	④1:3	④80°C	④60min
5	② CuCl_2	①pure water	②40°C	③45min
6	② CuCl_2	②1:1	①20°C	④60min
7	② CuCl_2	③1:2	④80°C	①15min
8	② CuCl_2	④1:3	③60°C	②30min
9	③ CuSO_4	①pure water	③60°C	④60min
10	③ CuSO_4	②1:1	④80°C	③45min
11	③ CuSO_4	③1:2	①20°C	②30min
12	③ CuSO_4	④1:3	②40°C	①15min
13	④ $\text{Cu}(\text{NO}_3)_2$	①pure water	④80°C	②30min
14	④ $\text{Cu}(\text{NO}_3)_2$	②1:1	③60°C	①15min
15	④ $\text{Cu}(\text{NO}_3)_2$	③1:2	②40°C	④60min
16	④ $\text{Cu}(\text{NO}_3)_2$	④1:3	①20°C	③45min

In experiment above, the concentration of Cu^{2+} is 0.1mol/L, the volume of dispersant that contained $\text{CH}_3\text{CH}_2\text{OH}$ and H_2O is 40 mL. The concentration of precipitant (Na_2CO_3) is 0.1mol/L and the solvent is 40 mL.

3.2. SEM analysis of Nano-CuO

Tested nano-CuO above using Hitachi S-4700 under

operation voltage of 30 kV. Figure 1 was SEM micrographs of nano-CuO under different conditions with one factor changing. (a, b were the micrographs under condition I; c, d were the micrographs under condition II; e, f were the micrographs under condition III; g, h were the micrographs under condition IV). Figure 2 and 3 were SEM micrographs of nano-CuO of orthogonal experiment (micrograph A to P was sequence 1 to 16 respectively).

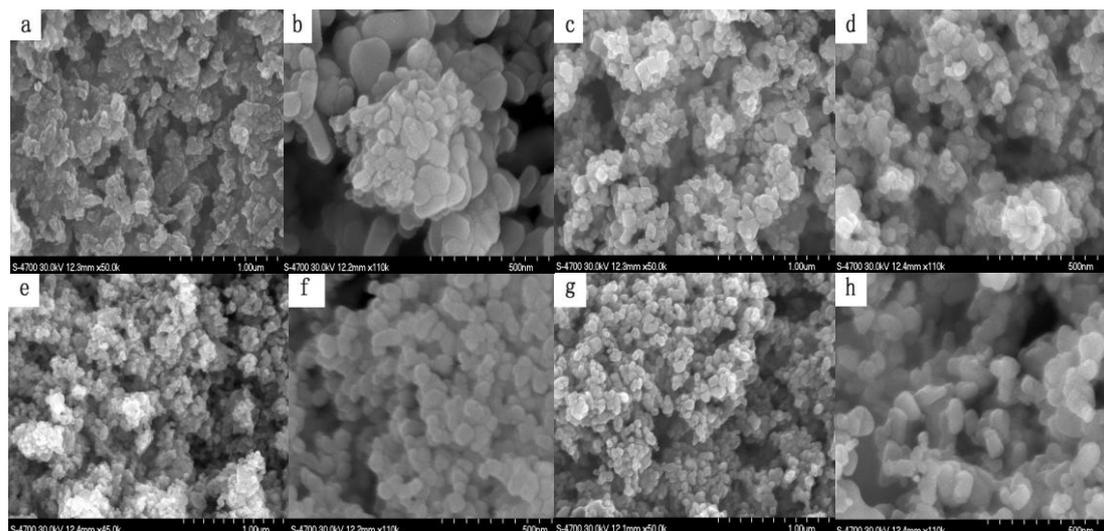


Figure 1. SEM micrographs of Nano-CuO under different conditions (I , II, III and IV)

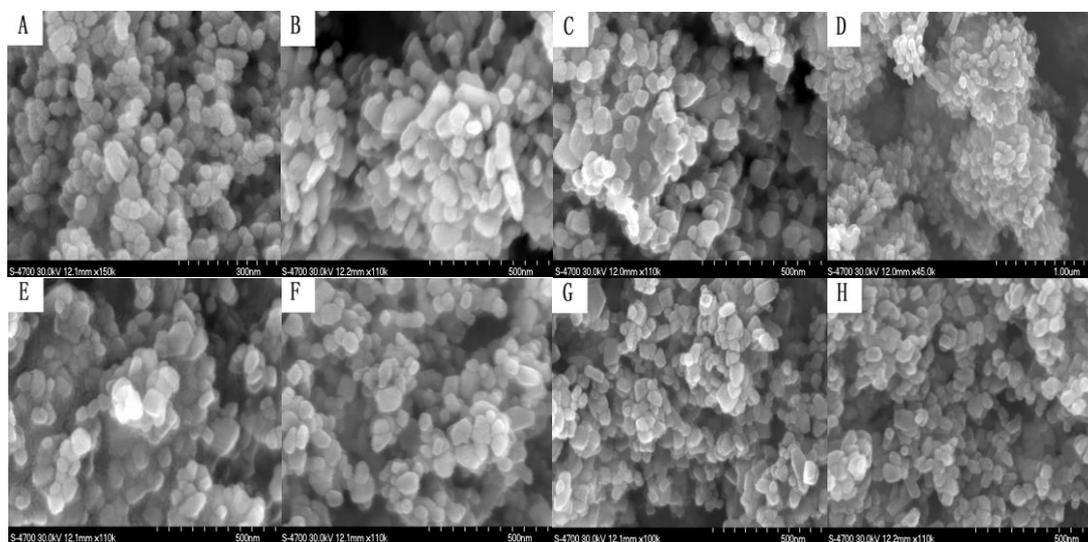


Figure 2. SEM micrographs of Nano-CuO under different conditions (1 to 8)

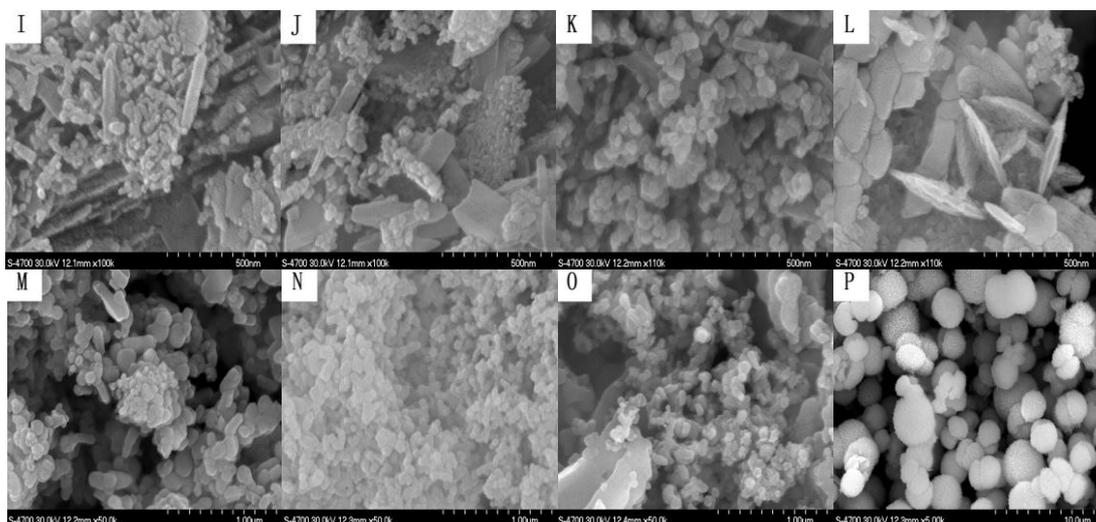


Figure 3. SEM micrographs of Nano-CuO under different conditions (9 to 16)

From the micrographs above, figure A and P that correspond to condition 1 and 16 were best among the figures because the nano-CuO had good dispersion and uniform size. The dispersion of nano-CuO became better when proportion of $\text{CH}_3\text{CH}_2\text{OH}$ increased. Reaction

temperature and reaction time had effect on the reactants' morphology and size, and the nano-CuO generated by CuCl_2 was best. Figure 4 was the micrographs under condition 1 and 16 with different magnifications.

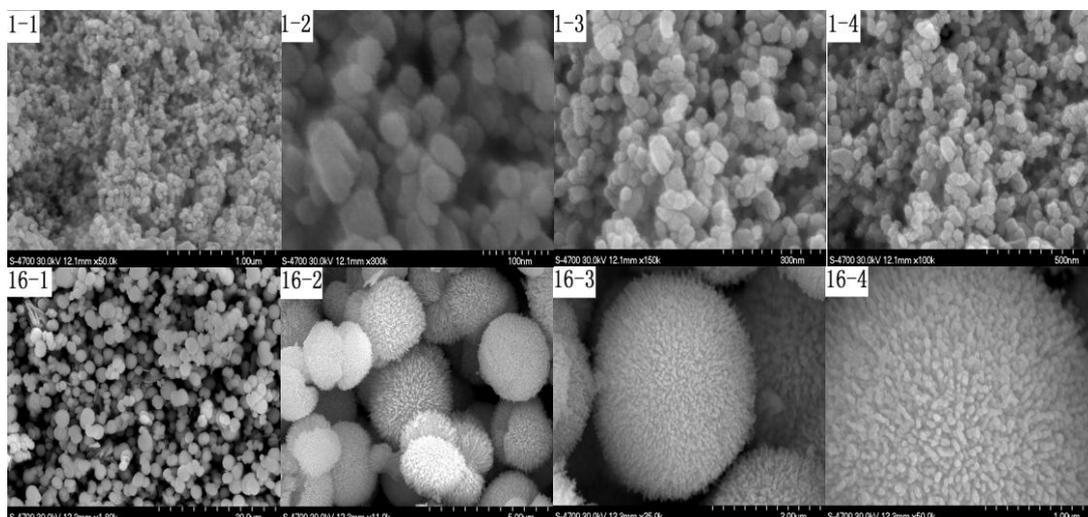


Figure 4. SEM micrographs of nano-CuO with different magnifications under condition 1 and 16

From figure 4, the nano-CuO generated under condition 16 was better than that under condition 1.

3.3. FTIR analysis of nano-CuO

Tested the nano-CuO prepared under condition 16 using FTIR using TENSOR 27. Figure 5 gave the results of final resultant and the precursor.

From figure 5, peaks around 536cm^{-1} for strong bands of the Cu-O stretching vibrations and 582cm^{-1} for strong

bands of the lattice vibration were observed, and peaks of the O-C-O stretching vibrations were found at 1379cm^{-1} and 1481cm^{-1} . Peaks at 839cm^{-1} and 754cm^{-1} for the O-H stretching vibrations were observed as well, and in addition, peak of Cu-OH around 487cm^{-1} was noticed. This observation provides evidence that the final resultant and the precursor were CuO and $\text{Cu}_2(\text{OH})_2\text{CO}_3$ respectively.

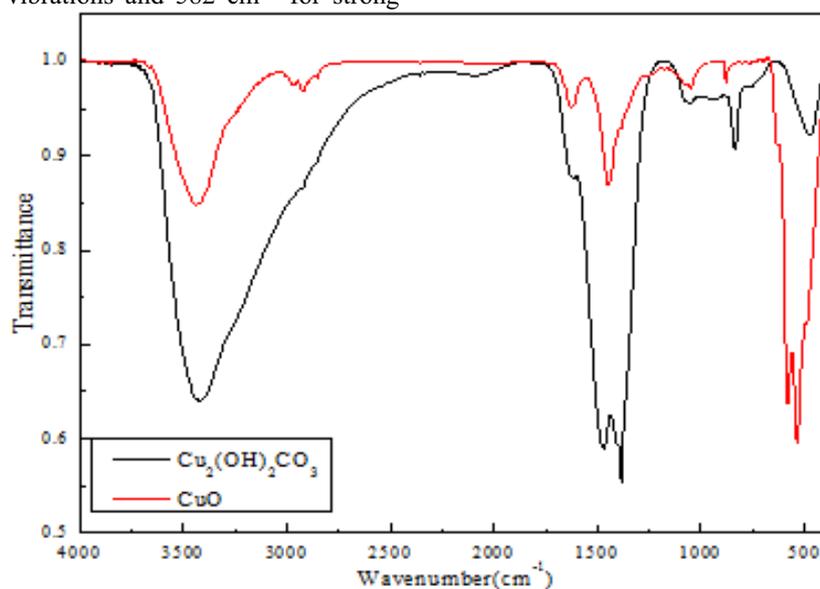


Figure 5. FTIR spectra of $\text{Cu}_2(\text{OH})_2\text{CO}_3$ and CuO under condition 16

3.4. TG and DTG of nano-CuO

Tested nano-CuO above using Seiko TG/DTA 6300 with

temperature varying from $30\text{ }^\circ\text{C}$ to $480\text{ }^\circ\text{C}$ and the heating rate was $5\text{ }^\circ\text{C}/\text{min}$. Figure 6 gave TG and DTG of $\text{Cu}_2(\text{OH})_2\text{CO}_3$ under condition 16.

From figure 6, $\text{Cu}_2(\text{OH})_2\text{CO}_3$ began to decompose

rapidly at about 145°C and the strongest peak of DTG appeared at 327 °C, which meant the fastest decomposition temperature was 327 °C. The mass of $\text{Cu}_2(\text{OH})_2\text{CO}_3$ decreased from 30 °C to 250 °C for free

water's losing and $\text{Cu}(\text{OH})_2$'s decomposing, and the decomposing of CuCO_3 resulted in the rapid decreasing from 250 °C to 340 °C.

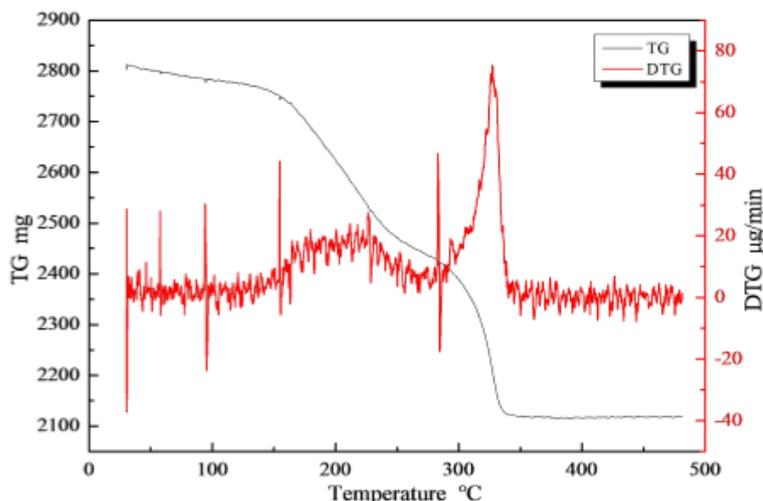


Figure 6. TG and DTG of $\text{Cu}_2(\text{OH})_2\text{CO}_3$ under condition 16.

3.5. XRD analysis

CuO generated under condition 1 and 16 and its precursor were analysed using XRD (laser power 40 kV×40 mA). From figure 7 and 8, characteristic diffraction peaks appeared where 2θ is 14.701°, 17.507°, 24.084°, 31.266° and 35.557°, and compared with JCPDS card, the

material was $\text{Cu}_2(\text{OH})_2\text{CO}_3$. The strongest peak appeared at $2\theta=31.266^\circ$, $d=2.85849\text{nm}$ and the material corresponded to $\text{Cu}_2(\text{OH})_2\text{CO}_3$ crystal plane (020), (021), (022), (-102), (042), (125), (123) and (135), which meant the $\text{Cu}_2(\text{OH})_2\text{CO}_3$ has crystallized completely and its component was single.

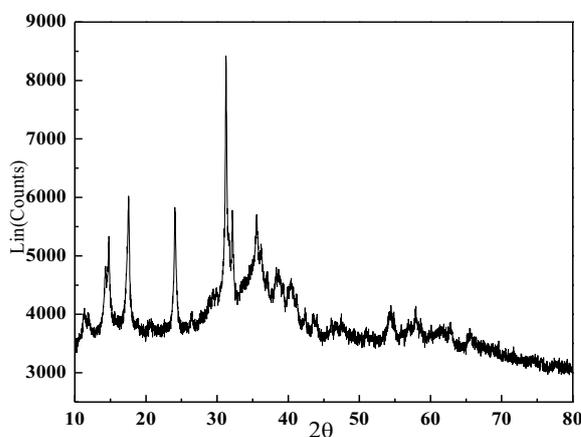


Figure 7. XRD spectrum of precursor under condition 1

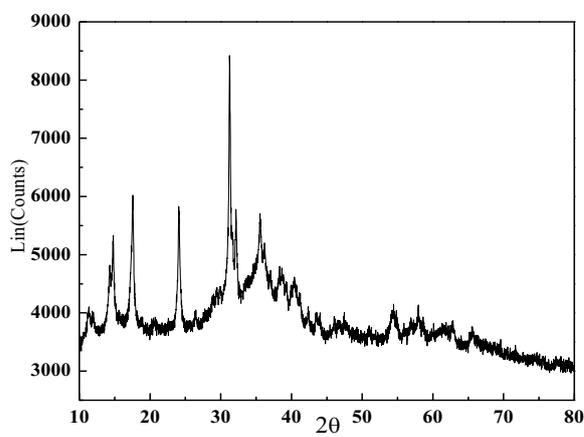


Figure 8. XRD spectrum of nano- CuO under condition 1

From figure 9 and 10, characteristic diffraction peaks appeared where $2\theta=32.65^\circ$, 35.47° , 38.86° , 48.99° , 53.57° , 58.37° , 61.70° , 66.43° , 68.13° , and compared with JCPDS card, the material was CuO , and

the strongest peak appears at $2\theta=35.471^\circ$, $d=2.52872\text{nm}$ and the material corresponded to CuO crystal plane (110), (-111), (111), (-202), (020), (202), (113), (-311) and (220).

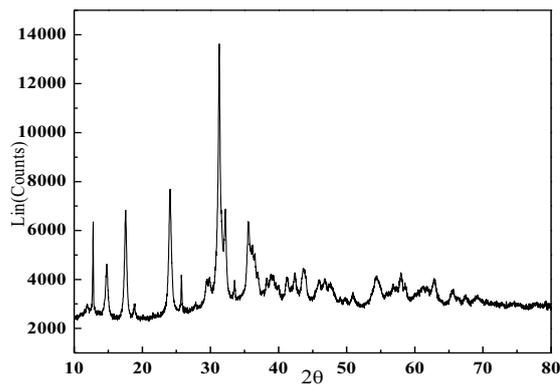


Figure 9. XRD spectrum of precursor under condition 1

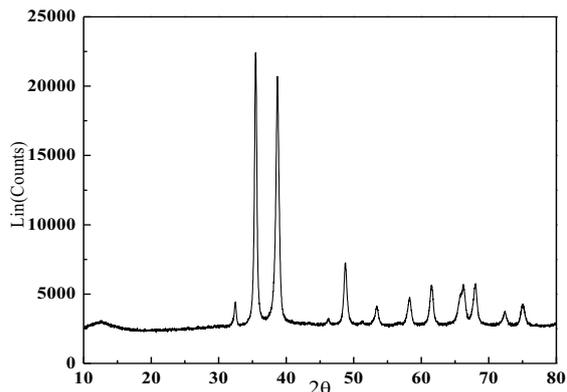


Figure 10. XRD spectrum of nano-CuO under condition 16

Calculated particle size of CuO and Cu₂(OH)₂CO₃ using Deby-Xeror formula as follows:

$$D_c = K\lambda / (\beta \cos\theta) \quad (1)$$

Where D_c is the size of crystal (nm), K is the Xeror constant (to cube particles K=0.94, to spherical particles K=0.89), λ is the wavelength of X-ray (using CuKa

radiation, λ = 1.5406 Å ≈ 0.154 nm), β is full width at half maximum, θ is the diffraction angle of the peak. Particle size of CuO and Cu₂(OH)₂CO₃ under condition 1 and 16 were given in table 3.

Table 3. Particle size of CuO and Cu₂(OH)₂CO₃ under condition 1 and 16

Cu ₂ (OH) ₂ CO ₃	Size (nm)	CuO	Size (nm)
1	27.58	1	16.20
16	85.40	16	20.38

From table 3, materials' diameter became smaller after calcinations and the size of CuO generated using Cu(NO₃)₂ changes more significantly than that of other materials after calcinations.

CuO generated under condition 16 was analysed using NOVA 4200 to get its surface area, average pore diameter and total pore volume. The nitrogen adsorption-desorption curve of nano-CuO under condition 16 was given in figure 11.

3.6. Particle surface area measurements

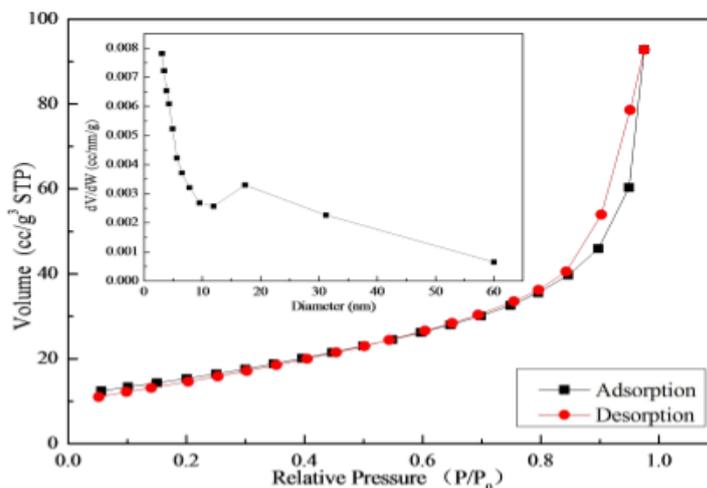


Figure 11. Nitrogen adsorption-desorption curve of nano-CuO under condition 16

After dealing with some procedures, the pore diameter was got, which was about 3.079 nm using BJH method. The surface area is 21.988 m²/g using multipoint BET method and the pore volume was 1.349 × 10⁻¹ cc/g using BJH method.

4. Conclusions

1 Direct precipitation method of nano-CuO using $\text{Cu}(\text{NO}_3)_2$ and Na_2CO_3 is feasible way to industry that is low cost and easy to achieve.

2 After orthogonal test, single factor experiment and characterization, best process conditions are got: reactant is $\text{Cu}(\text{NO}_3)_2$, temperature is 20°C , precipitant's (Na_2CO_3) concentration is 0.1mol/L, $\text{H}_2\text{O}-\text{CH}_3\text{CH}_2\text{OH}$ ratio is 3:1, reaction time is 45min, roasting time is 2h and temperature is 400°C .

3 Nano-CuO generated using best condition above is spherical, uniform and with good dispersivity, the average diameter of nano-CuO is 20.38 nm, the surface area is about 21.988 m/g, the pore diameter was about 3.079 nm and the pore volume was 1.349×10^{-1} cc/g.

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