Sonochemical Synthesis and Characterization of Copper Oxide Nanoparticles

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Abstract

Copper oxide (CuO) nanoparticles were synthesized by a sonochemical process using copper nitrate and sodium hydroxide in the presence of polyvinyl alcohol (PVA) as a starting precursor. The precipitated product was calcined at various temperature ranging from 400-700°C. The physical microstructure and morphology of as-calcined nanoparticles were characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM). From XRD observation, it is evident that the high purity CuO nanoparticles were obtained by this synthesis process. It was additionally revealed that its crystallization and particle size was strongly dependent on the reaction time and calcination temperature.

Keywords: Copper oxide; sonochemical; polyvinyl alcohol

1. Introduction

Ultrasound is the part of the sonic spectrum which ranges from about 20 kHz to 10 MHz and can be roughly subdivided in three main regions: The range from 20 kHz to around 1 MHz is used in sonochemistry. Sonochemistry is typically based on acoustic cavitation phenomenon resulting from the continuous formation, growth and implosive collapse of bubbles in the aqueous solution [1].
When solutions are exposed to strong ultrasound irradiation, sufficient sound energy can drive the formation of novel nanostructures to occur under ultrasonic irradiation [2]. As an important p-type semiconductor metal oxide with a narrow band gap (1.2 eV), copper oxide (CuO) has been extensively studied because of its diverse applications as material for heterogeneous catalysts, gas sensors [3], field emission devices [4], lithium-ion electrode materials [5], dye-sensitized solar cells [6], etc. In recent years, various processing routes have been developed for synthesizing CuO nanoparticles, which include chemical vapor deposition [7], sol–gel process [8], pulsed laser evaporation [9], and hydrothermal technique [10]. More recently, there have been related works employed the potential of sonochemical process to synthesize nanostructures of CuO. Chonghai Deng et.al. [11] reported on the fabrication of hierchical hollow CuO submicrospheres process with the assistant of CH3ON2 in a mix solution. Reza Ranjbar-Karimi et.al. [12] successfully prepared CuO nanoparticles from copper acetate in the presence of PEG. R. Vijaya Kumar et.al. [13] reported on the preparation and characterization of nanocrystalline CuO embedded in poly(vinyl alcohol) and its effect on crystal growth of CuO.

In the present work, the attempt was made to synthesize nanometer-sized CuO particles by the assistance of ultrasonic irradiation in sonochemical process. The effects of calcined temperature and sonication time on its physical properties and microstructure were investigated.

2. Experiment

A stoichiometric amount of copper nitrate trihydrate (Cu2O2N3H20, Sigma-aldrich), and sodium hydroxide anhydrous pellets (NaOH, Carlo erba) in the presence of polyvinyl alcohol (PVA, Sigma-aldrich) was used as starting precursor. NaOH was dissolved in deionized water and the obtained solution (0.5M, 50 mL) was added drop-wise to an aqueous Cu2O2N3H20 solution (0.1 M, 50 mL) for 30 min. Sonication of the solution was performed by a Sonics Model VCX 750 until the completely precipitated product was reached. Finally, the as-precipitated powders were calcined at different temperature range of 400-700°C for 2 hr. Thermo-Gravimetry (TG) of powder was conducted in air with a heating rate of 10°C/ min to investigate thermal behavior of this material. The structural properties and microstructure of copper oxide nanoparticles were characterized by X-ray diffractometer (Panalytical x’Pert Pro MPD) using Cu-Kα radiation, operating at 40 kV and 30 mA and SEM (JEOL JSM-6510), respectively.

3. Results and Discussion

Thermo-Gravimetric and Differential-Thermal Analyses of copper oxide nanoparticles sonicated for 30 min was performed. There are two weight losses in temperature range of 180-250°C and 500-700°C as shown in Fig. 1. The first weight loss is originated from evaporation of polyvinyl alcohol and deionized water in mixed solution. The second weight loss is due to the oxidation of metal copper in air [12,14] resulting to the crystallization of CuO.

![Fig. 1. TG and DTA curves of as-precipitated product sonicated for 30 min.](image)

Figure 2 shows the XRD for the precursor calcined at different temperatures. The noticeable diffraction peaks positioned at 2θ = 35.64°, 37.95°, 38.82°, 48.83°, 53.60° and 58.38° attribute to (110),
(002), (111), (202), (020), and (202) orientation plane of CuO with cubic structure, respectively [11]. There are three observable peaks of (002), (111), (202) orientation for XRD patterns of as-precipitated sample and as-calcined sample at calcined temperature of 400°C to 500°C without other peaks of impurities. This characteristic indicates that good powder of CuO particles can be obtained by only sonochemical process. This feature is also in good agreement to other work [11]. However, for better crystallization accompanying the TG-DTA results, the calcination at higher temperature is necessary. As the calcined temperature elevated to be at the range of 600-700°C, all characteristic peaks of XRD patterns are prominent, suggesting that as-prepared powder have good crystalline structure. Furthermore, the (202), (020) and (202) peaks initially appeared as the calcined temperature reached to 600°C, reflecting to the better crystallinity and higher purity of CuO. This result is in good accordance with the TG-DTA result.

Figure 2. XRD patterns of as-precipitated product and CuO nanoparticles calcined at different temperature.

Figure 3 shows the XRD pattern for the precursor obtained by sonochemical process with different sonication times and calcined at 700°C. It can be observed that all four samples exhibit characteristic XRD peaks which belong to CuO. The effect of the sonochemical reaction times on particle size of CuO was investigated by mean of XRD measurement for different sonochemical reaction time of 10-40 min and calcined at 700°C without changing any other parameters. CuO particles obtained from sonochemical
reaction with reaction time less than 20 min is about 80 nm in their size. Further increase in the reaction
time to 30 min results to significant decrease in their particle size to of 45 nm. This may due to the
sufficient energy supplied to the system by ultrasound after certain reaction period of time, which can
induce the disintegration of nucleation. After extending reaction time reaching 40 min, the particle size
inversely tends to increase. This manner may related to the change of crystallite structure induced by
abundant energy from ultrasound after critical time. No other detection of impurities is observed,
indicating the high purity of as-syntisized products by this method. The Scherrer’s formula expressed in
equation (1) is employed to determine as average crystalline size of CuO:

\[ D = \frac{K\lambda}{\beta \cos \theta}, \]  

where \( D \) is the grain size, \( K \) the shape factor, \( \lambda \) the X-ray wavelength of Cu \( K\alpha \) (0.154 nm), \( \beta \) the full-
width at half maximum (FWHM), and \( \theta \) the Bragg angle. The measured FWHM of (111) orientation peak
and the calculated grain size of the powder samples versus calcined temperature and sonication time are
represented in Figs. 4(a) and (b), respectively.

The calcined temperature plays a key role in the crystallization and particle size of the CuO. Fig. 2.
shows different XRD patterns for the precursor calcined at different temperatures. At the temperature
range of 400-500°C, the crystallization of CuO somewhat improves accompanying slightly increasing
XRD peak intensity. Further increasing calcined temperature up to 700°C, its crystallization drastically
increases and its particle size also increases correspondingly as indicated in Fig. 4(a). This result revealed
by XRD measurement is in harmony with the TG-DTA results.

Fig. 4. FWHM and grain size of CuO nanoparticles versus (a) calcined temperature and (b) sonication time.

The microstructure of as-prepared CuO are shown in Fig. 5. As the calcined temperature was lower
than 600°C, the formation of CuO is incomplete, reflecting to ill-defined microstructure or agglomeration
of as-synthesized products. Further increase in calcined temperature leads to the completeness of
crystallization of CuO, accompanying the well-defined and uniform crystalline particles with particle size
~50–70 nm.
4. Conclusion

In summary, CuO nanoparticles were successfully synthesized by a sonochemical synthesis. The corresponding TG-DTA, XRD, SEM and results suggested that well-defined CuO nanoparticles were obtained by the assistance of ultrasound with the reaction time up to 30 min and calcination at 600–700 °C. The sonicated time and calcined temperature are crucial factors having the drastic effects on the formation and crystallization of CuO nanoparticles.

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References

[3] Jeong Duk Choi.; and Gyeong Man Choi; 2000; Electrical and CO gas sensing properties of layered ZnO–CuO sensor; Sensors Actuator B; 69; 120-122.
[5] Chao Li.; Wei Weia.; Shaoming Fanga.; Huanxin Wanga.; Yong Zhanga.; Yanghai Guia.; and Rongfeng Chenb; 2010; A novel CuO-nanotube /SnO2 composite as the anode material for lithium ion Batteries; Journal of Power Sources; 195; 2939–2944.
[6] Xue Wanga.; Chenguo Hua.; Hong Liu.; Guojun Du.; Xiaoshan He.; and Yi Xi; 2010; Synthesis of CuO nanostructures and their application for nonenzymatic glucose sensing; Sensors Actuator B-Chemical; 144; 220-222.
[7] Mikhail Ottoisson.; and Jan-Otto Carlsson; 1996; Chemical vapour deposition of Cu2O and CuO from CuI and O2 or N2O; Surface and Coatings Technology; 78; 263-273.
[11] Chonghai Deng.; Hanmei Hu.; Xinqing Ge.; Chengiang Han.; Difang Zhao.; and Guoquan Shao.; 2011; One-pot sonochemical fabrication of hierarchical hollow CuO submicrospheres. Ultrasonics Sonochemistry; article in press

Fig. 5. SEM images of CuO nanoparticles calcined at (a) 400°C, (b) 500°C, (c) 600°C, and (d) 700°C.
[12] Reza Ranjbar-Karimi.; Alireza Bazmandegan-Shamili.; AlirezaAslani.; and KarimKaviani; 2010; Sonochemical synthesis, characterization and thermal and optical analysis of CuO nanoparticles; Physical B; 405; 3099-3101

[13] R. Vijaya Kumar.; R. Elgamiel.; Y. Diamant.; and A. Gedanken; 2001; Sonochemical Preparation and Characterization of Nanocrystalline Copper Oxide Embedded in Poly(vinyl alcohol) and Its Effect on Crystal Growth of Copper Oxide; Langmuir; 17; 1406-1410