

A green synthesis of copper oxide nanoparticles by mechanochemical method

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ABSTRACT

Copper oxide nanoparticles were successfully synthesized by mechanochemical reaction, which is a green, low cost, solvent free, rapid method and followed by calcining treatment. Copper acetate monohydrate and urea were used as reagents and the resulted precursor was calcined at 500 °C for 2h in air. The scanning electron microscopy (SEM) revealed the formation of nanoparticles with an average size of about 86 nm. The Fourier transform infrared (FT-IR) spectrum and X-ray powder diffraction (XRD) pattern of the product confirmed all of reflections can be indexed to pure phase of CuO with a monoclinic crystal system. The diffuse reflectance spectrum (DRS) showed a band gap of 1.7 eV.

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1. Introduction

Nanostructured materials have stimulated intensive research interest in the recent years due to their unique properties and the potential applications in photonic and nanoelectronics, which are dependent on size of particles¹. Cupric oxide, CuO, is an important *p*-type semiconductor metal oxide with a band gap of 1.0–4.5 eV^{2,3}, which is widely used in nano systems such as high temperature superconductors⁴, magnetic storage media^{1,5}, solar cells^{1,3-9}, hydrogen storage materials⁷, batteries^{1,2,8}, gas sensors¹⁻¹⁰, catalysis^{2-7,9,10}. Up to date, CuO with different morphologies such as nanobelt^{1,8}, nanospindle², nanoring^{2,4}, nanorod^{1,4,6}, nanospherical⁸, nanoribbon^{2,4,9}, nanoparticle^{4, 8}, nanoleaf^{2,11}, nanotube^{4,9,11} and nanowire^{2,4,9, 12, 13} has been successfully synthesized by various techniques, including thermal decomposition¹, chemical vapor deposition^{1,2}, microwave-hydrothermal⁷, sonochemical^{1,2}, solvothermal, hydrothermal process^{1,2,12}, sol-gel², thermal oxidation^{7, 8, 9, 12, 13} methods. One of the approaches to synthesize metal oxide nanostructures is the ball milling or mechanochemical method¹⁴⁻¹⁶. In fact, mechanical milling (MM) is an effective, useful, low cost and a simple technique, which is used to synthesize numerous

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materials including solid solutions, quasicrystalline, nanocrystalline and crystalline materials. This process was developed by Benjamin and his co-workers in 1960s as milling mixing for the first time. Then Mac-Queen described its patent application¹⁷. In this work, we synthesized nanoparticles of CuO with band gap of 1.7 eV by utilizing mechanochemical reaction and then calcination procedure. The obtained precursor was studied by TGA, CHN, ICP and FT-IR spectroscopy. The final product was characterized by FT-IR spectroscopy, XRD and SEM techniques.

2. Results and Discussion

2.1. Structural and morphological study

The composition changes associated with the calcination process were observed by thermal analysis. TGA curve shown in Fig. 1 indicates a several-steps pattern of weight loss in the temperature range 80 – 430 °C. The first weight loss of 2% occurred below the temperature of 100 °C could be attributed to the release of surface adsorbed water. Thenceforth weight loss of 69% observed between 125 and 430 °C may be related to the decomposition of organic groups in the precursor. These composition changes are completed at 430 °C.

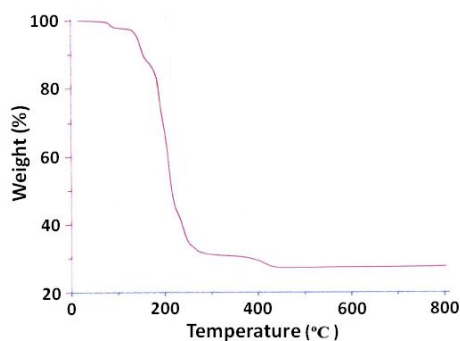


Fig. 1. TGA curve of the precursor

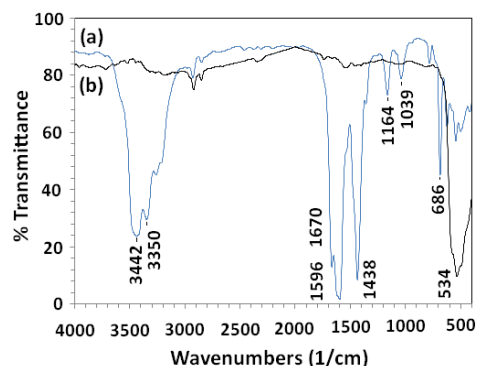
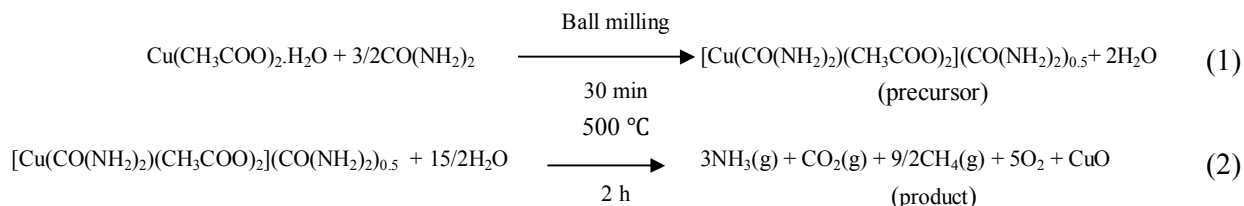


Fig. 2. FT-IR spectra of (a) the precursor and (b) the product after heating at 500 °C for 2 h in air

Fig. 2 shows the FT-IR spectra of (a) the precursor and (b) the product after heating at 500 °C for 2 h in air. The broad double bands at 3442 and 3350 cm^{-1} in Fig. 2-a are related to the N-H anti symmetrical and symmetrical stretching vibrations, respectively, which are in a close agreement with vibrations of the NH_2 group. The overlapping O-H stretching band of H_2O molecules with the NH_2 vibrations led to broaden these bands. The strong peaks at 1670 and 1596 cm^{-1} are assigned to the stretching vibration of the carbonyl groups. In fact, the frequency of the C=O vibrations decreases by the ligand coordination effect of oxygen atom of the amide and acetate groups. The peaks at 1438 cm^{-1} belong to the antisymmetrical bending vibrations of the methyl groups. Also, the observed peaks at 686 cm^{-1} are related to the C-O bending vibrations^{18,19}. As a result of heating, the organic section of precursor was removed and the specified broad band at around 534 cm^{-1} belongs to the Cu-O vibration (Fig. 2-b)²⁰.



Scheme 1. The proposed mechanism for the formation of the product

In addition to FT-IR data, we used elemental analysis, CHN and ICP, in order to confirm the formation of precursor. Anal. Calcd. for : $(\text{CuC}_{5.5}\text{H}_{12}\text{N}_3\text{O}_{5.5})$: C, 24.30; H, 4.42; N, 15.46; Cu, 23.39. Found: C, 23.98; H, 4.44; N, 15.17; Cu: 23.33 (%). These data confirm the suggested molecular formula $[\text{Cu}(\text{CO}(\text{NH}_2)_2)(\text{CH}_3\text{COO})_2](\text{CO}(\text{NH}_2)_2)_{0.5}$ for the precursor.

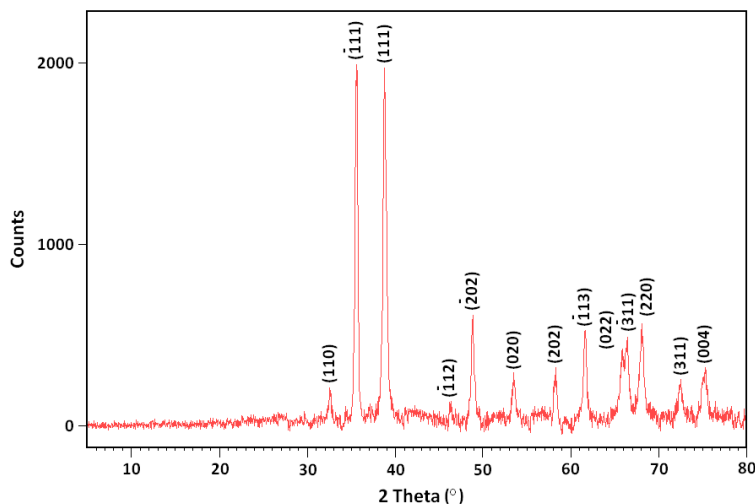


Fig. 3. XRD pattern of the product

According to XRD pattern, as shown in Fig. 3, the diffraction peaks could be indexed to a monoclinic phase of CuO (S.G.: $C2/c$) and the lattice parameters were obtained $a = 4.684$, $b = 3.425$, and $c = 5.129$, and $\beta = 99.47^\circ$ (JCPDS 05-0661). The diffraction peaks at 2θ values of 32.52° , 35.55° , 38.73° , 46.31° , 48.76° , 53.41° , 58.32° , 61.57° , 65.81° , 66.23° , 68.14° , 72.42° and 75.02° matching with the (110), $(\bar{1}11)$, (111), $(\bar{1}12)$, $(\bar{2}02)$, (020), (202), $(\bar{1}13)$, (022), $(\bar{3}11)$, (220), (311) and (004) planes of monoclinic CuO confirmed the formation of CuO compound with excellent crystallinity and no other peaks for impurities. The peak intensities and widths clearly indicate that the sample was highly crystalline in nature.

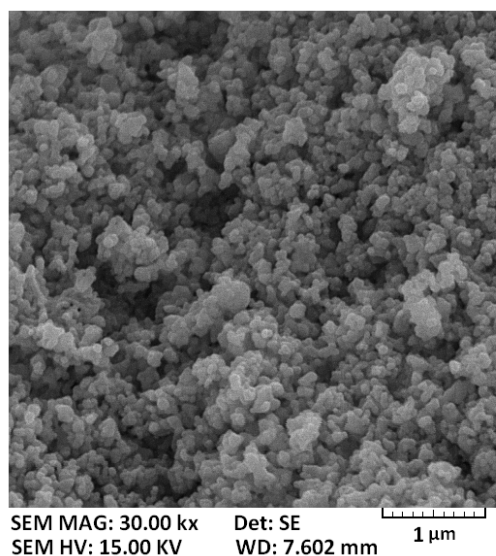


Fig. 4. SEM images of CuO nanoparticles

The morphology and size product were investigated by SEM. Fig. 4 reveals the SEM image of CuO nanoparticles. This image shows the nanoparticles with an average size of about 86 nm.

2.2 The optical property

The optical absorption of the CuO nanoparticles was investigated in the wavelength range of 190 – 800 nm. Fig. 5-a illustrates the DRS of CuO nanoparticles. The absorption band gap E_g , can be determined by the Eq. (1)²¹.

$$(\alpha h\nu)^n = \beta(h\nu - E_g), \quad (1)$$

where, $h\nu$ is the photo energy, α is the absorption coefficient, β is a constant relative to the material and n is either 2 for a direct transition or 1/2 for an indirect transition. We have plotted $(\alpha h\nu)^2$ versus $h\nu$ curves in order to determine the band gap. According to Fig. 5-b, the band gap for CuO nanoparticles was found to be 1.7 eV. It is expected that these CuO nanoparticles can be used as photocatalyst. The observed differences between the calculated band gap and the reported values in the literatures arise from size and density of CuO nanoparticles.

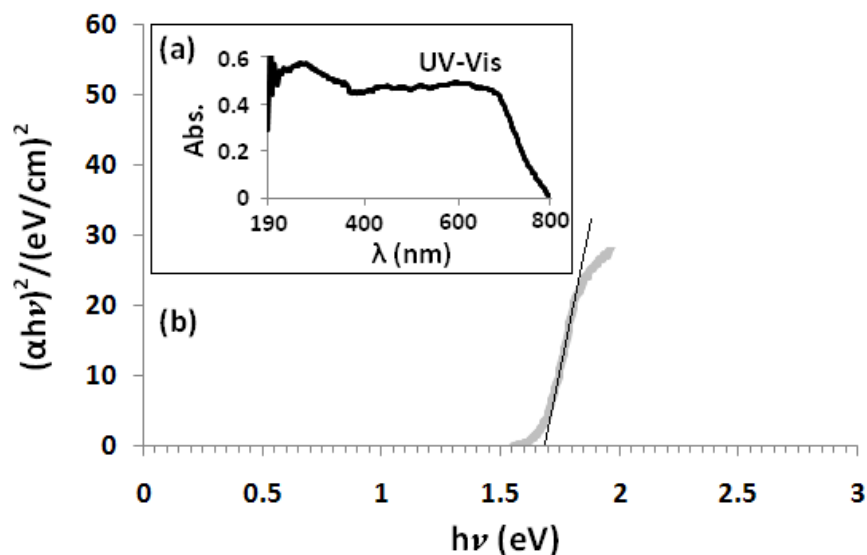


Fig. 5. (a) The Uv-vis diffuse reflectance spectrum in the inset and (b) the plot $(\alpha h\nu)^2$ versus $h\nu$ curves for CuO nanoparticles

3. Conclusions

In summary, the nanoparticles of copper oxide with an average size of about 86 nm and band gap of 1.7eV were prepared by mechanochemical process followed by calcining treatment. The FT-IR spectrum and XRD pattern of the product confirms all of reflections can be indexed to pure phase of CuO with a monoclinic crystal system. Actually, mechanochemical method is performed in solid state and does not involve any organic solvents, it can be applicable for the preparation of various nanomaterials in industry because of simple, low cost and being environmentally. It is expected that these CuO nanoparticles can be used as photocatalyst.

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4. Experimental

4.1. Materials and methods

All chemicals were purchased from Merck Co. and used without further purification. Double distilled water was used in all experiments.

The powder X-ray diffraction (XRD) analysis was done with a PHILIPS PW 1800 diffractometer with monochromatized Cu K α radiation ($\lambda = 1.542 \text{ \AA}$). Fourier transform infrared (FT-IR) spectra were recorded on a Shimadzu-8400S spectrometer in the range of 400–4000 cm^{-1} using KBr pellets. Scanning electron microscopy (SEM) obtained on a VEGA\TESCAN with gold coating. Thermogravimetric analysis (TGA) measurement was carried on a TA Instruments 931 apparatus with a heating rate of 10 $^{\circ}\text{C min}^{-1}$ under nitrogen flow. Elemental analysis was performed by utilizing a Perkin Elmer (model 2400, series 2) CHN microanalyser. The content analyses of copper were performed by the VARIAN VISTA-PRO ICP-OES simultaneous. The diffuse reflectance spectrum (DRS) was recorded on a Shimadzu- MPC – 2200 spectrophotometer.

4.2. General procedure

$\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ and $\text{CO}(\text{NH}_2)_2$ were milled together with a molar ratio of 2:3 and then were put in a stainless steel 10 mL vial containing two small balls of 10 mm diameter by utilizing a mass ratio of 8:1 ball-to-powder. In fact, milling was carried out with Mixer Mill (Retsch MM-400) apparatus at 1800 rpm (30 Hz) for 30 min at room temperature. The resultant bluish substance as precursor was calcinated at 500 $^{\circ}\text{C}$ for 2 h in a furnace. The progress of reaction was monitored by TLC and M.P.

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