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## ORIGINAL ARTICLE

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# A facile and green synthesis of CuO nanowires by mechanochemical method

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**Abstract :** We report the synthesis of copper oxide nanowires via a facile mechanochemical technique followed by low thermal treatment. The precursors of copper acetate monohydrate and acetamide were employed to grow this one dimensional morphology. The scanning electron microscopy images (SEM) revealed the formation of desired NWs with a diameter range of

19 – 76 nm and lengths of several micrometers. The high quality of the resulting product can draw a useful outlook for industrial mass production of NWs by this way. © Global Scientific Inc.

**Keywords :** Nanocrystalline materials; Green synthesis; Semiconductors; Nanowires; CuO.

## INTRODUCTION

One-dimensional nanoscaled structures such as nanowires (NWs) and nanorods have been known as an important building block of the various nano-systems and nano-devices due to their unique physical and chemical properties<sup>[1]</sup>. Amongst nanostructures, semiconducting metal oxide nanowires are considered as an attractive and applicable group because of their surprising electrical, optical and magnetic properties and potential applications, which are dependent on size of particles. Copper oxide, CuO, is an important p-type semiconducting metal oxide having a narrow optical absorption edge of 1.0 to 1.7 eV, which is widely employed in nano-systems such as magnetic ceramics, electronic devices, hydrogen storage materials, batter-

ies, gas sensors, superconductors, solar cells and catalysts<sup>[2-8]</sup>. Based on wide applications, there is an increasing demand for the synthesis of CuO one dimensional nanostructures such as nanorods and nanowires by using facile, economic and environmentally friendly techniques<sup>[9-11]</sup>. The most of reported methods for the synthesis of CuO nanowires or nanorods are based on the physical thermal oxidation and the chemical methods have been observed, rarely. Amongst applied techniques, a few works have been reported about the synthesis of the special nanostructures by mechanochemical procedure, while this process is an efficient and simple grinding method accompanying a chemical reaction and can be successfully applied in large quantities<sup>[12]</sup>. To the best of our knowledge, the fabrication of CuO nanowires by this method has not been reported, yet.

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In present study, we report the preparation of CuO nanowires by utilizing mechanochemical procedure for the first time. In addition, there are no reports for the synthesis of this nanostructure using organic molecule of acetamide. We designed a simple solid state method for the synthesis of CuO nanowires using copper acetate as the metal source in the presence of acetamide molecules as a driving agent.

## EXPERIMENTAL

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

The reagent materials of copper acetate dihydrate ( $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ ) and acetamide ( $\text{CH}_3\text{CONH}_2$ ) were mixed together with a molar ratio of 1:1 and then were put in a stainless steel milling container (10 mL) with two small stainless steel balls (10 mm in diameter) using a mass ratio of 8:1 ball-to-powder. The grinding

process was carried out in a vibratory Mixer Mill (Retsch MM-400) apparatus at the frequency of 1800 rpm for 30 min at the ambient conditions. The obtained bluish powder was collected and calcined at 350 °C for 2 h in a furnace.

The X-ray diffraction (XRD) pattern was obtained on a PHILIPS PW 1800 diffractometer with monochromatized Cu  $K\alpha$  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  $\text{cm}^{-1}$  using KBr pellets. Scanning electron microscopy (SEM) images obtained on a VEGA\\TESCAN with gold coating. Thermogravimetric analysis (TGA) was carried out on a TA Instruments 931 apparatus with the heating range of room temperature to 800 °C under flowing  $\text{N}_2$  as an inert environment with a flow rate of 10 °C  $\text{min}^{-1}$ . Diffuse reflectance spectrum (DRS) was obtained using UV-Vis spectrophotometer (Shimadzu- MPC – 2200 spectrophotometer).

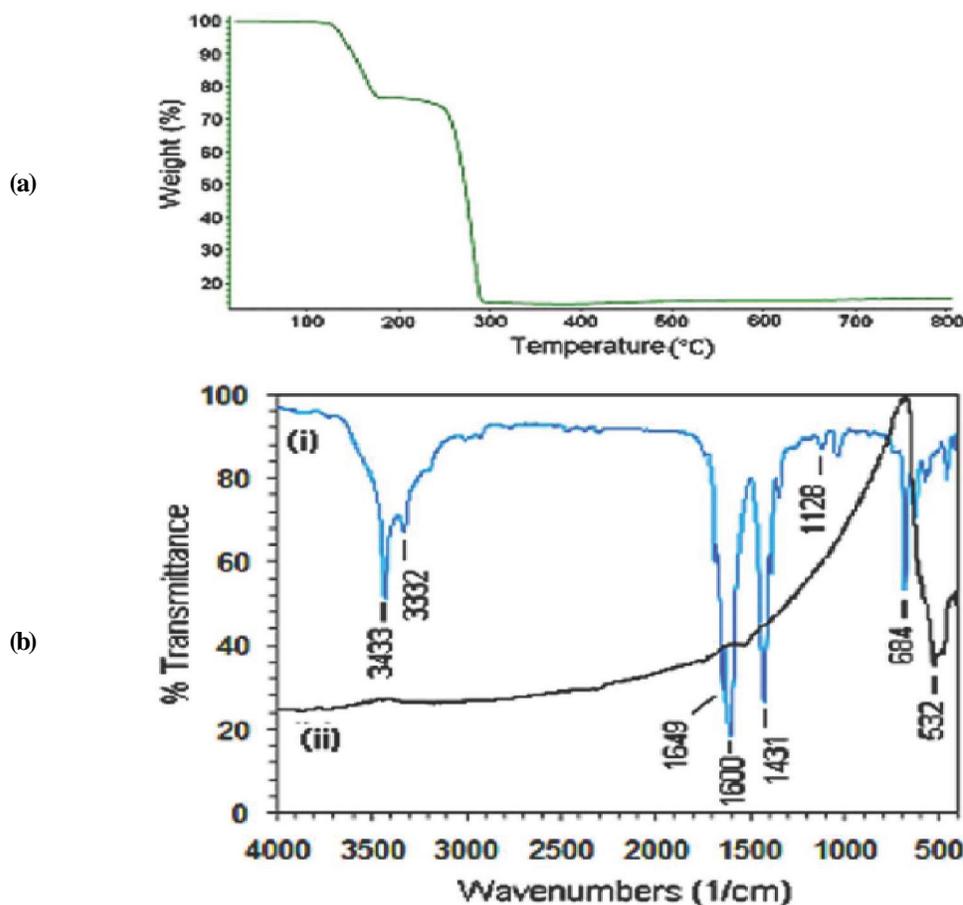


Figure 1 : (a) TGA curve of the precursor and (b) FT-IR spectra of (1b-i) the precursor and (1b-ii) the product after heating at 350 °C for 2 h in air.

## RESULTS AND DISCUSSION

To determine the calcination temperature, the obtained precursor after milling was processed by a TGA. The TGA curve shown in Figure 1a clearly represents two-step pattern of the weight loss at the temperature range of 125–290 °C. A weight loss of 23%, which is rather mild, occurs up to 175 °C that is attributed to the release of the adsorbed water molecules. The weight loss (71%) between 175 and 290 °C occurs with a rapid weight loss rate because of decomposing the organic groups of the prepared precursor. It can be said that the main weight loss is in the second step of weight loss pattern up to 290 °C and then, reaches to a steady level about 300–350 °C. Therefore, the complete decay of organic section and achieving to the inorganic product (calcination temperature) occurs about this temperature.

FT-IR spectra and XRD pattern were planned

to characterize the composition of product. Figure 1b shows the FT-IR spectra of (1b-i) the precursor and (1b-ii) the product after heating at 350 °C for 2 h. The appeared peaks at 3433, 3332, 1649, 1600, 1431, 1128 and 684  $\text{cm}^{-1}$  are related to the stretching vibration frequencies of the functional groups belonging to the precursor (Figure 1b-i)<sup>[13,14]</sup>. As a result of heating treatment, the all of organic sections of the prepared precursor were removed and only one rather broad band at 532  $\text{cm}^{-1}$  remained, which is an evidence for the formation of CuO compound (Figure 1b-ii)<sup>[15]</sup>.

The XRD pattern of product is indexed to a monoclinic phase of CuO in a good according to JCPDS card no. 5-0661 (Figure 1b). The diffraction peaks at  $2\theta$  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),

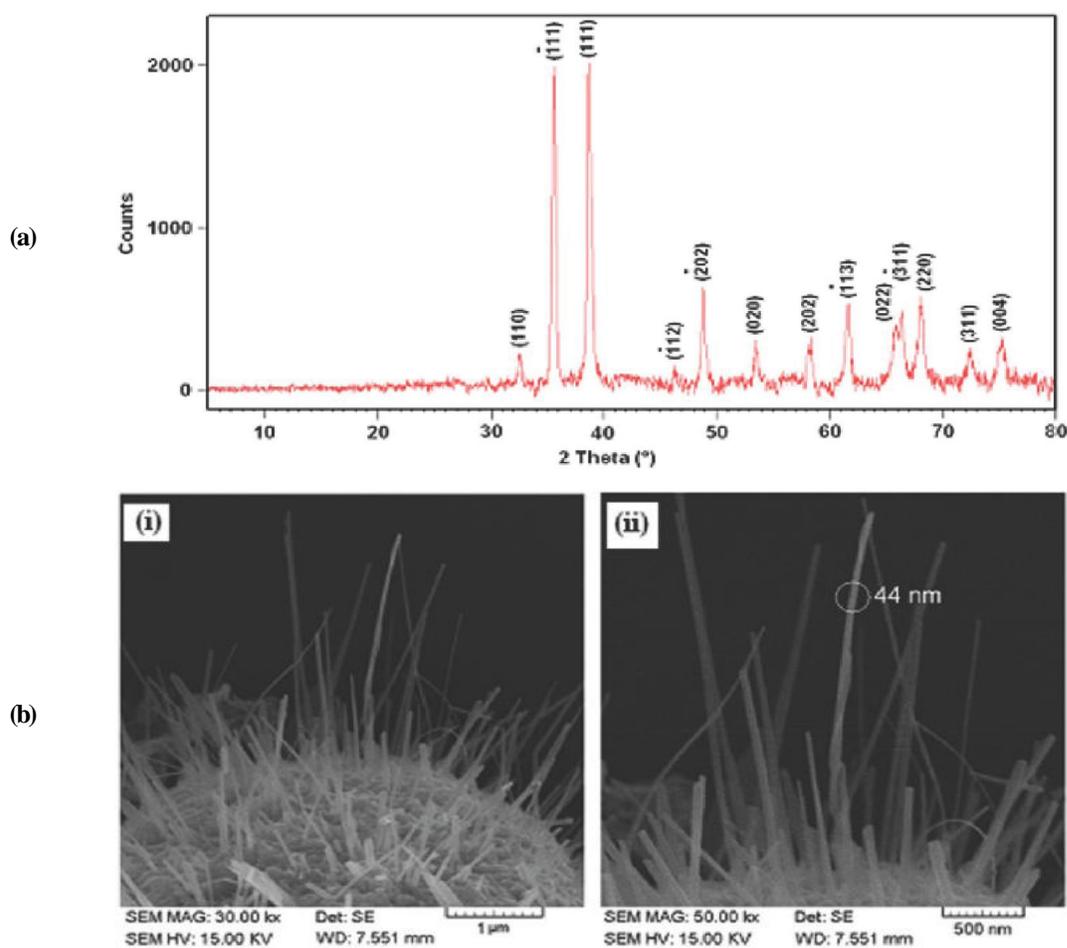


Figure 2 : (a) XRD pattern of the product and (b) SEM images of CuO NWs at (2b-i) low magnification and (2b-ii) high magnification.

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(111), ( $\bar{1}12$ ), ( $\bar{2}02$ ), (020), (202), ( $\bar{1}13$ ), (022), ( $\bar{3}11$ ), (220), (311) and (004) confirm the formation of CuO phase with a high quality and the pure phase. The morphology and size of the product were investigated by SEM images (Figure 2b). Figure 2b reveals the SEM images of the CuO NWs with low magnification (2b-i) and high magnification (2b-ii). These images represent the fine NWs with the diameter of 19 – 76 nm and the length several  $\mu\text{m}$ .

Meanwhile, the optical absorption of the final product was investigated in the wavelength range of 190 – 800 nm (Figure 3a) by DRS of the CuO NWS. The

absorption band gap,  $E_g$ , can be determined by the equation (1)<sup>[16]</sup>.

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

Where,  $h\nu$  is the photo energy,  $\alpha$  is the absorption coefficient,  $\beta$  is a constant relative to the material and  $n$  is either 2 for a direct transition or 1/2 for an indirect transition. To determine the band gap, we have plotted  $(\alpha h\nu)^2$  versus  $h\nu$  curves. According to Figure 3b, the band gap for CuO NWS was found to be 1.65 eV. The observed difference between the calculated band gap and the reported values in the literatures is originated from the size and density of CuO NW<sub>s</sub>.

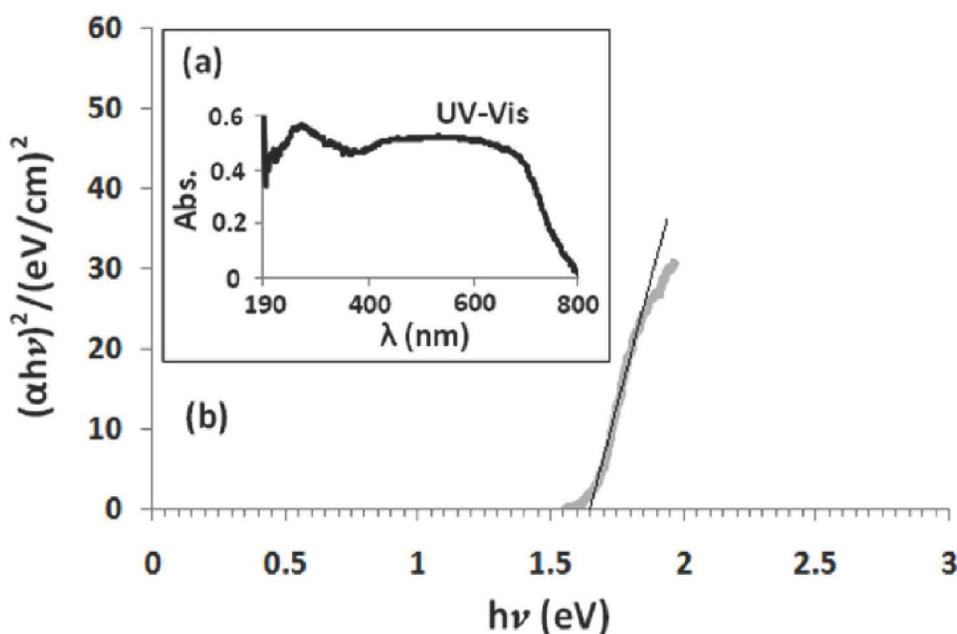


Figure 3 : (a) DRS spectrum and (b) the plot  $(\alpha h\nu)^2$  versus  $h\nu$  curve for CuO NWs.

## CONCLUSIONS

In a summary, the fine CuO nanowires with the diameter of 19 – 76 nm and lengths of several micrometers were successfully synthesized by mechanochemical process using acetamide and copper acetate without any additives, for the first time. The structural analyses of the obtained product revealed a high purity of crystalline phase of CuO NWs having a band gap of 1.65 eV. The synthesis feasibility of the CuO nanowires by mechanochemical method, which is a simple, green and solvent free technique, can be a fitting approach for manufacturing the industrial scale of the various metal oxide nanowires.

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