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Sonochemical-Assisted Synthesis of Copper Oxide Nanoparticles and Its Application as Humidity Sensor

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Abstract

Cupric oxide nanostructures were synthesized via a simple reaction between copper nitrate and sodium hydroxide using a sonochemical-assisted method. The synthesized CuO was then characterized using X-ray diffraction, scanning electron microscopy, transmission electron microscopy, Fourier transform infrared, ultraviolet-visible and photoluminescence spectroscopy. Our studies show that the CuO nanostructure can be used as a humidity sensor with a short response time (about 6 sec) and a long recovery time (up to 650 sec). Variation of relative sensor impedance (defined as sensing) at relative humidity of 90% was measured to be about 80, which indicates a high sensing of our designed sensor.

1. Introduction

Moisture affects human comfort as well as many manufacturing processes in industries. The presence of water vapor also influences various physical, chemical and biological processes [1]. Humidity sensors have been used in an increasing number of applications in industrial processing and environmental control devices. Growing demands for controlling water vapor have led to considerable interest in the development of sensing materials [2–6]. Chemical sensors are of great demand in industry and environmental science because

of their low cost and easy fabrications. Humidity measurements in industries are critical because it may affect the business cost of the product and the health and safety of the personnel. Metal oxides are extensively used as gas-sensing materials because of their low cost, high sensitivity and simplicity in fabrication [7]. Nanostructure materials have attracted great attentions in the recent years because of their unique physical properties and applications. Nano-sized metal oxide semiconductors (MOS) have also been generated inexpensively in the recent years. They

have attracted much attention, especially because of their applications in humidity sensing. CuO is an important p-type semiconductor with potential applications in high critical temperature superconductors [8, 9], photovoltaic materials [10], field emission [11] catalysis and gas sensors [12]. In this study, we report a simple synthesis method of CuO nanostructure in order to study its humidity sensing properties.

2. Experimental

2.1. Materials and characterization

Cu(NO$_3$)$_2$ and NaOH were purchased from Merck. X-ray diffraction (XRD) patterns were recorded by a Philips X-ray diffractometer using Ni-filtered Cu K$_\alpha$ radiation (=1.54 Å). A multiwave ultrasonic generator (Bandeline, MS 73, Germany), equipped with a converter/transducer and titanium oscillator, with a maximum power output of 100W, was used for the ultrasonic irradiation. The ultrasonic generator automatically adjusted the power level. The wave amplitude in each experiment was adjusted as needed. Scanning electron microscopy (SEM) images were obtained with LEO instrument model 1455VP. Prior to taking SEM images, the samples were coated by a very thin layer of Pt to make their surface conductor and prevent charge accumulation, and obtaining a better contrast. Fourier transform infrared (FT-IR) spectra were recorded on Galaxy series FTIR5000 spectrophotometer. The electronic spectra of the samples were taken on a JASCO UV–visible scanning spectrometer. Room temperature photoluminescence (PL) was studied using a Perkin Elmer fluorescence instrument.

2.2. Synthesis of CuO nanoparticles

1 g of Cu(NO$_3$)$_2$ was first dissolved in 100 ml of deionized water. 10 ml of NaOH (1M) solution was then added slowly to the solution under applying

ultrasonic waves (30 min, 80 W). A green-blue precipitate was obtained, which confirmed the synthesis of copper hydroxide. The obtained precipitate was then centrifuged and washed with distilled water. The product was then calcinated at 400 °C for two hours. The precipitate color goes from green-blue into black which confirms the production of copper oxide. The sonochemical reactions were carried as shown in Fig. 1.
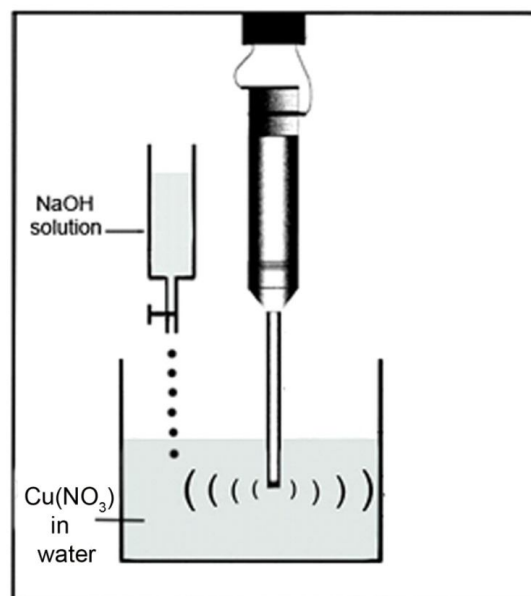

Fig. 1. Schematic diagram for the experimental setup used for the sonochemical reactions.

The synthesized CuO nanostructure material was pressed using a homemade compressor machine and made into some 5 mm disks with a 1 mm thickness. Two semicircle silver thin films were coated on the disk's top surface using electron beam evaporation method. Two pieces of copper wire were then attached to the Ag films using a silver paste. As the Fig. 2a shows, the fabricated sample can be considered as a resistance-capacitor element in an electric circuit.

Prior to the samples sensing measurement, a standard humid chamber was built and its humidity was calibrated using a commercial humidity sensor (Lutron HT3009). In order to check the accuracy of the device as a humidity sensor, the sample was placed as a part of an electric circuit consisting of a 1 MΩ resistance and an impedance analyzer (lock-in amplifier). A power supply with amplitude of 0.1 V was used to apply AC voltages with frequencies of 100, 500, 1000, and 5000 Hz. The circuit impedance was measured using an impedance analyzer (Cassy Lab System, connected to a computer) parallel to the resistance. We define the impedance corresponding to the relative humidity (RH) of 10% as an impedance standard value (Z). The relative impedance of the circuit changes as a function of humidity. The experimental set up for humidity sensing apparatus is illustrated schematically in Fig. 2b.

All the measurements were carried out at room temperature. The response time is defined as the time needs to reach 90% of the final signal for a given RH, while the recovery time is defined as the time takes for the signal to come within 10% of its initial value.

3. Results and discussion

XRD pattern of the as-prepared cupric oxide is shown in Fig. 3. The pattern is indexed as pure CuO with a monoclinic lattice structure (JCPDS 45-0937). SEM and TEM images of CuO nanostructure are illustrated in Fig. 4a and 4b respectively, which show nanoparticles with average diameter of 50 nm.
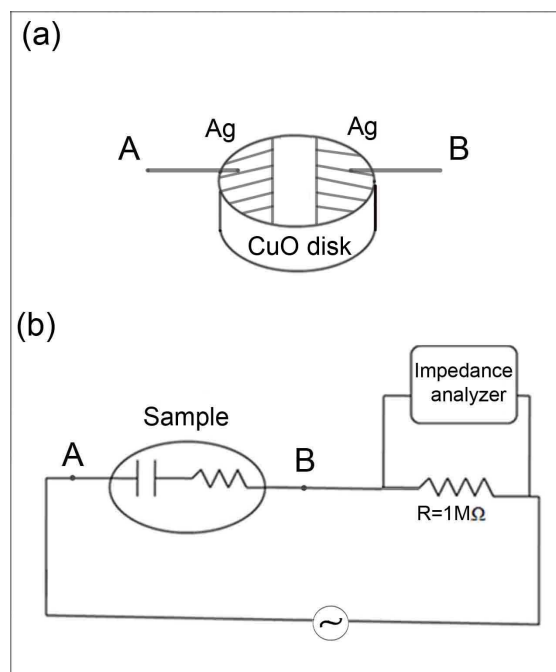

Fig. 2. (a) The schematic diagram, equivalent circuit and (b) experimental setup for measuring the humidity.
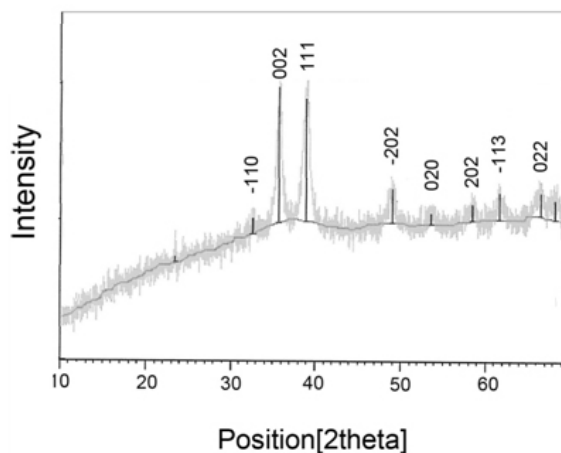

Fig. 3. XRD pattern of the CuO nanostructures.

The UV–vis absorption spectrum of the CuO nanostructure is shown in Fig. 5. The absorption peak of CuO nanostructure at 313 nm exhibits a blue-shift relative to the bulk spectrum of cupric oxide, attributing to the quantum confinement of charge carriers in the nanostructures [13].
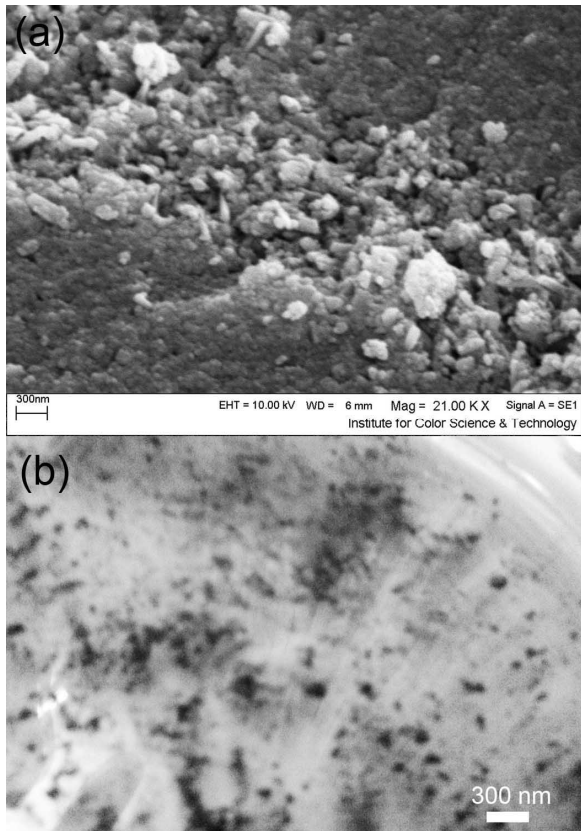
Fig. 4. (a) SEM image (b) TEM image of synthesized cupric oxide nanostructures.

Fig. 5. UV–vis absorption spectrum of CuO nanostructure.

Room temperature photoluminescence of CuO with the excitation wavelength of 394 nm is shown in Fig 6. The PL spectrum consists of one strong peak at 557.8 nm that can be ascribed to a high level transition in CuO nanostructures. This kind of band edge luminescence arises from the recombination of excitons and/or shallowly trapped electron–hole pairs [14].

The FT-IR spectrum of as prepared CuO is shown in Fig. 7. Absorption peaks at 426 cm^{-1} and 501 cm^{-1} are attributed to the Cu-O bonds. The peaks positioned at 1143 and 1447 cm^{-1} are due to the adsorption of nitrate on the CuO surface, while the peak positioned at 3432 cm^{-1} is attributed to the moisture adsorption on the cupric oxide surface.
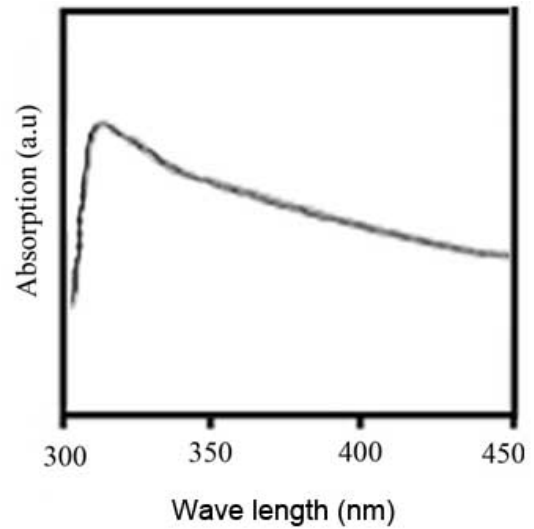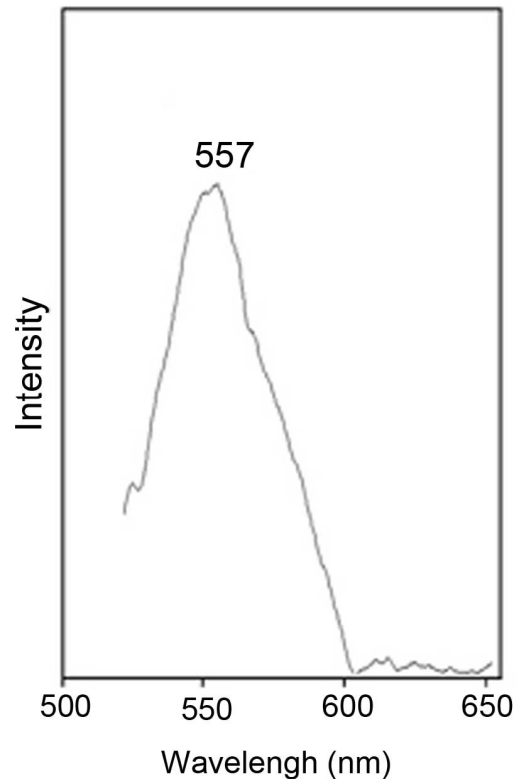

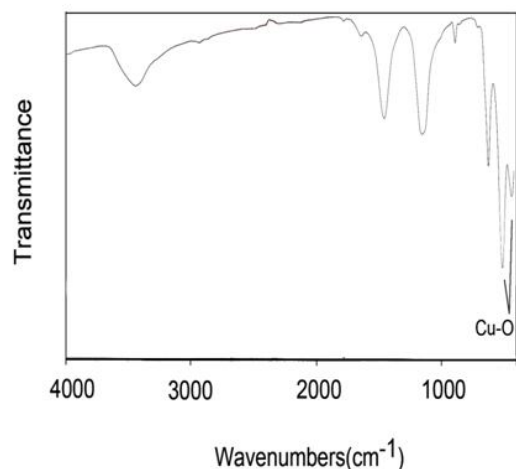**Fig. 6.** Room temperature photoluminescence spectrum of cupric oxide nanostructure.

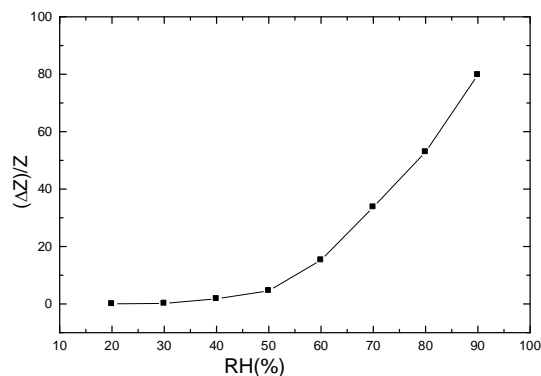**Fig. 7**. FT-IR spectrum of cupric oxide nanostructure.

Fig. 8. Variation of sensitivity as a function of RH for a CuO sensor at frequency of 100 Hz.

Fig. 8 shows the relative variation of circuit impedance as a function of RH at the frequency of 100 Hz. As the graph shows changing the relative impedance increases slowly at the RHs of 20 to 50 percent, then it grows dramatically at the RHs of up to 90%.

The variations of circuit impedance as a function of RH (in semi-logarithmic scale) for four different frequencies are drawn in Fig. 9. The results indicate; at the low RHs, the CuO sensor has the highest sensitivity at the frequency of 100Hz, while at the high

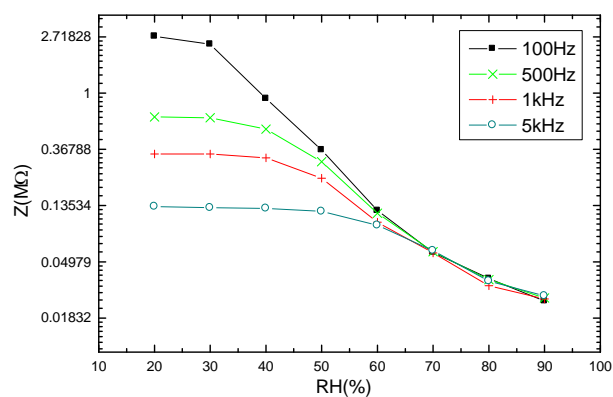RHs (bigger than 65%), the sensitivity is independent of the applied frequency.

Fig. 9. Variation of impedance as a function of relative humidity (in logarithmic scale) of a typical sensor based on CuO.

It is well known that adsorption of water vapor on the CuO surface leads to change of the electric circuit impedance. The higher porosity in CuO surface, the more water molecules being adsorbed by the surface and the higher sensitivity of humidity sensor is achieved.

The conductivity of cupric oxide is due to protonation and deprotonation of surface hydrolysis [1]. On the other hand the adsorption of moisture through ceramic oxide surfaces can be understood as follows: adsorption of moisture affects the protonic conduction on the surface and conductivity varies with the amount of water being adsorbed [15, 16]. At the low humidities, conduction is due to proton hopping between hydroxyl ions on the first layer of chemisorbed water, while at higher the humidities, protons hop between physisorbed molecules with a Grotthus chain reaction mechanism [17].

4. Conclusion

We have successfully synthesized cupric oxide nanostructures via a simple reaction between copper

nitrate and sodium hydroxide using sonochemical method. The samples were characterized using XRD, SEM, TEM, FT-IR, UV-vis and PL spectroscopy. The synthesized CuO was employed as an electric element in an R-C circuit. Our results show that changing the relative impedance increases slowly at the relative humidities of 20 to 50 percent, and then it grows dramatically at the RHs of up to 90%. The results also indicate that the CuO sensor has the highest sensitivity at the frequency of 100Hz, while at high RHs (bigger than 65%), the sensitivity is independent of the applied frequency.

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