Synthesis of Copper (II) Oxide (CuO) Nanoparticles and Its Application as Gas Sensor

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Abstract

Copper sulfate was used as a precursor to prepare CuO nanoparticles in reverse micelles (o/w microemulsion). This is a technique which allows the preparation of ultrafine metal oxide nanoparticles within the size ranging from 50 to 60 nm. The preparation of copper (II) oxide nano particles was investigated in the inverse microemulsion system. Therefore, the nucleation of metal particles proceeds in the water capsules of the microemulsion. Tween 80 was added as surfactant. The products were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The study provides a simple and efficient route to synthesize CuO nanoparticles at room temperature.

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Introduction

Preparation and application of nanosized materials are significant scientific and industrial interests [1–3], due to their unique or improved properties, which are primarily determined by size, composition and structure. These properties are, strongly related to the synthetic processes. Numerous solution techniques, for example, pulsed laser ablation [4], vacuum vapor deposition [5], pulsed wire discharge [6] and mechanical milling [7] are physical techniques while, microemulsion techniques [9], sonochemical [10], electrochemical [11], microwave assisted [12] and hydrothermal methods [13] are chemical approaches for the synthesis of nanoparticles. Biological or biosynthesis techniques are also considered as chemical methods [14].

One of the techniques developed is the use of reverse micelles or water in oil microemulsions of surfactants as nanoreactors. The nanometer sized aqueous cores of the reverse micelles provide an appropriate stabilized environment to produce nanoparticles with fairly uniform size, through the necessary chemical reactions within the core. In addition, the surfactant layer acts as a steric stabilizer to inhibit the aggregation of nanoparticles formed, and keep them dispersed.

A large variety of nanoparticles have been prepared ever since the invention of technique by Boutonnet *et al*. A comprehensive account of this water-in-oil microemulsion technique can be obtained in reviews by Eastoe and Warne and Pileni.

Some advantages of using the microemulsion to synthesize nanoparticles are given below:
(a) At room-temperature and pressure, nanoparticles of a large number of materials can be prepared.

(b) This technique does not require any special equipment.
(c) It is possible to control the size and morphology of the particles formed.
(d) It can be utilized for carrying out all the precipitation reactions that are known, to obtain particles in homogeneous solution.

In the present study, a simple and original method for the synthesis of nanosized CuO by sol-gel technique in nano and micro micelles is described. The morphology, crystallographic structure, surface properties and size of CuO particles are characterized by means of transmission electron microscope (TEM), scanning electron microscope (SEM) and X-ray diffraction (XRD) which will give much valuable information about these materials. Copper oxide nanoparticles have been of considerable interest due to the role of CuO in catalysis, in high-Tc superconductors [15–18], and in gas sensors [19–21]. Copper (II) oxide is an important industrial material with many properties such as electrical, optical and so on. CuO has been widely used, such as magnetic ceramics, gas sensors, electrode materials, solar cells, hydrogen storage materials and photocatalysis [22–27]. The detection of hazardous gases such as CO and NO_2 has attracted great interest in order to reduce environmental pollution over the past decades [28]. Among the hazardous gases, nitrogen oxides (combination of NO and NO_2) were one of the most harmful gases to the human body [29]. Up to now, intense efforts have been made to detect nitrogen oxides by sensor materials including carbon nanotubes [30], conducting polymers [31] and metal oxide semiconductors (such as In_2O_3, WO_3, V_2O_5, TiO_2 and SnO) [32–36]. More recently, the composites of copper oxides and n-type metal oxides such as

CuO/SnO$_2$ and CuO/ZnO have been studied as gas sensors to detect H$_2$S, H$_2$ and CO gas [37–40].

For example, Li's group reported that mono dispersed CuO nanospheres had good sensitivity and selectivity to some flammable gases [41]. In this paper, we report on the synthesis of CuO particles and plates and their sensitive properties for NO$_2$ and alcohol. The results showed that the as synthesized CuO particles and plates are potential in the sensor application for NO$_2$ gas detection. The methods and gas sensor instruments were similar to that reported in our previous literature [42]. The CuO sensor was fabricated by dip-coating the as-prepared CuO particles or plates to the ceramic tube of the sensor body, which was annealed in a muffle stove at 500 °C for 4 h. The as-fabricated sensors were fixed into the gas sensing apparatus and aged at 300°C for 24 h. The sensor settled chamber was kept under the continuous flow of dry air for 30 min before analysis. A given amount of NO$_2$ gas was injected into the chamber by a micro injector, while the alcohol liquid was injected on a heating device part of the apparatus and gasified quickly. The sensitivity could be measured when the detecting gas was mixed homogeneously with the air.

Materials and Methods
Chemicals and apparatus
All materials (CuSO$_4$.7H$_2$O, Tween 80, NaOH) and solvents in high purity were purchased from the Merck and Fluka Chemical Company. All materials were commercial reagent grade and used without further purification. X-ray diffraction was conducted on a Philips Analytical XPERT diffractometer using a Cu Kα radiation (λ = 1.54056 A°) with a MINIPROP detector and operating at 40 kV and 40 mA. Transmission electron microscopy (TEM) was performed with ZeissEM10C-80 KV, operated at 80 KV. Scanning electron microscope (SEM) was performed with a PHILIP XL-30, operated at 30 KV. The purity determination of the substrates and reaction monitoring were accomplished by thin layer chromatography (TLC) on silica gel polygram SILG/UV 254 plates.
Preparation of Copper oxide nanoparticles
Tween 80, CuSO$_4$.7H$_2$O, NaOH, soybean oil and distilled water were used in the experiments. Nanoparticles were synthesized by following steps: 0.80 g of CuSO$_4$.7H$_2$O in water (3 ml) and 6.5% Tween 80 were added into purified soybean oil (80 ml) under mechanical stirrer with 2500 rpm until obtaining a nearly clear emulsion. This solution was referred to as solution A. NaOH (0.45 g) was dissolved into water (2.8 ml) was added into solution A under mechanical stirrer with 2100 rpm for 3.5 h at room temperature and then the reaction mixture was filtrated. The precipitate was washed with absolute water (3 × 600 ml) for 4 times. This material was calcinated in electronic oven at 220°C for 5 h. Surface morphologies of the specimens were observed with a scanning electron microscope (SEM, Philips XL-30). The ordered nano structures of CuO can be further confirmed by transmission electron microscope (TEM, Philips KV-120).The resulting powder X-ray diffraction was conducted on a Philips Analytical XPERT diffractometer using a Cu Kα radiation (λ = 1.54056 °A) with a MINIPROP detector and operating

at 40 kV and 40 mA. X-ray diffraction patterns were recorded between 2θ = 5° and 79° with a step of 0.04° and a time of 0.8 s by step. The crystallographic data of the resulting CuO nano powders were collected by using the PC-APD, Diffraction software.

Results
Figure 1 shows the XRD patterns of CuO powders after calcinations at 200 °C. The nano-sized CuO powders are in amorphous structure. Its average particle size was 53 nm for CuO nanoparticles, calculated through the Scherrer's formula in which D=0.89λ/Bcosθ. D, λ, B and θ were the average particle size, the X-ray wavelength, the angular line width of half maximum intensity and the Bragg's angle, respectively. The phase composition and the structure of obtained samples were examined by X-ray powder diffraction (XRD).

Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM) images of CuO nanoparticles (Figure 2 and 3) indicated an agglomeration of particles, homogeneous and uniform size, with diameters ranging from 50 to 60 nm. The morphology caracterization of the CuO nanoparticles was investigated by SEM and TEM images as shown in Fig. 2 and 3. From obtained images, we can observe a large quantity of uniform nanoparticles (NPs) with an average particle size of 40-60 nm, indicating that our synthesis process is an easy method for the preparation of CuO nanoparticles.

The synthesized nanoparticles show good structure and stability in hydrocarbon solvents against air oxidation.
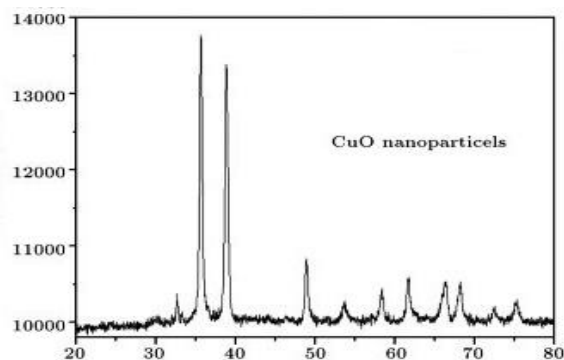

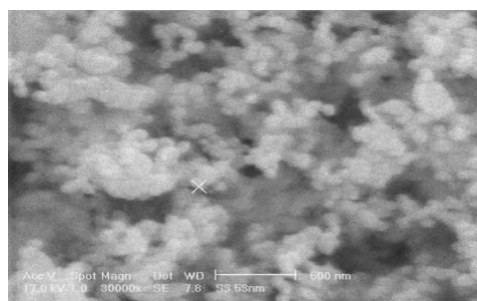**Figure 1:** XRD pattern of the CuO nanoparticles.

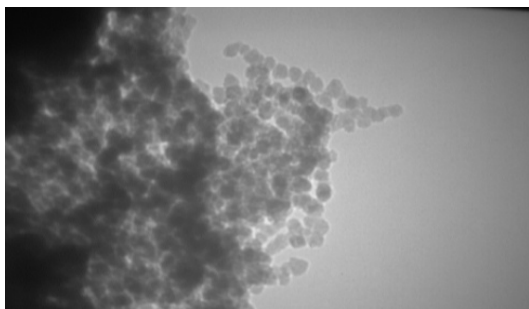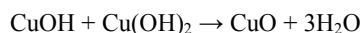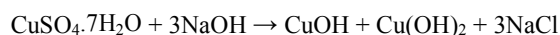**Figure 2**. SEM image of the CuO nanoparticles.

Figure 3. TEM image of the CuO nanoparticles.

Discussion

The synthesis of copper (II) oxide (CuO) nanoparticle was carried out with the concurrent addition of sodium hydroxide and increasing the stirring time, to prevent excessive grain growth and aggregation of nanoparticles. The overall reaction scheme is shown below:

$$CuSO_4.7H_2O + 3NaOH \rightarrow CuOH + Cu(OH)_2 + 3NaCl$$

$$CuOH + Cu(OH)_2 \rightarrow CuO + 3H_2O$$

This is a multi step process that involves the transformation of the salt of metal to an metal hydroxide CuOH and $Cu(OH)_2$ followed by the dehydration to form an oxo-hydroxide intermediate, that will constitute the precursor in the sol-gel process. In this study, when the mixture of $CuSO_4.7H_2O$, soybean oil (containing Tween 80) and water were mixed with mechanical stirrer, water solution was dispersed in the oil phase and Tween 80 assembled at the water/oil interface, acting as the emulsifier for the formation and stabilization of emulsion. The water solution was in the droplets and the oil solution became the continuous phase, hydroxyl groups in the droplets of water emulsion diffused to the water/oil interface, a part of which reacted with $CuSO_4.7H_2O$ to form copper (II) oxide.

Conclusion

In this research, we have described the use of an inorganic phase in water-in-oil from $CuSO_4$ source at room temperature. The nanoparticles with homogeneous size, shape and agglomeration distribution, with diameters ranging from 60 to 460 nm have been characterized by SEM, TEM and XRD. In addition, the easily controllable condition with using low cost copper source is merit to be considered for scaling up by industrial researchers. In the present study the synthesis of nanoparticles can be easily implemented because it is simple and environmentally friendly. The gas sensing properties of CuO nanoparticles to detect NO_2 and alcohol were systematically investigated. The results showed that the as-prepared CuO behaved as p-typed semiconductor. It was found that the suitable operating temperatures for CuO nanoparticles to detect NO_2 and alcohol were about 200 and 350°C, respectively. The sensitivity of CuO plates was better than that of CuO nanoparticles. This research suggested that the low cost CuO plates had potential application to detect NO_2 with low energy consumption due to their good sensing properties and low operating temperature.

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