# Gas sensing properties of semiconducting copper oxide nanospheroids

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## ARTICLE INFO

## ABSTRACT

Monosize spheroidal porous particles of copper oxide were produced by controlled calcination of the copper basic carbonate particles, synthesized by the urea-based homogeneous precipitation process. After characterization by various physical methods, such as SEM, XRD, and FTIR, the copper oxide particles were employed for the fabrication of the gas sensor. The latter was made up of a thick film of copper oxide on alumina plate, having printed interdigitated gold electrodes. Electrical properties of the sensor material were evaluated as a function of the temperature, which indicated its semiconductor behavior. On exposing to ammonia gas, the sensor responded in the form of a decrease in electrical resistance in a reproducible manner. Reproducibility in performance was attributed to the use of monodispersed particles of copper oxide in the fabrication of sensor.

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## 1. Introduction

Ammonia gas is extensively used in many chemical industries for the production of useful products. It is harmful to human health and causes chronic lung diseases [1]. A minor leak of ammonia gas in the system may be hazardous to the industrial workers and thus its detection and monitoring are of immense importance in the early stages of the leakage at room temperature in a reproducible manner. In this regard, a number of studies have been conducted, dealing with the development of sensor materials for the detection of ammonia gas at room temperature. Those materials include $Cu_xS$ [2], $In_2O_3$ [3], $TiO_2$ [4], CuBr [5], $Co_3O_4$ [6], ZnO [7], and CuO/ZnO [8], etc. When exposed to ammonia gas, the above-mentioned materials changed their electrical conductivity which gave useful information about their gas sensing properties.

CuO is a p-type semiconductor material with a narrow band gap of 1.4 eV [9] and has been employed as a sensor material for the development of gas sensors, which could detect gases of environmental concern, such as $NO_2$ [10], $H_2S$ [11], ethanol [12], CO [13], and ammonia [14]. It has been noted in these studies that particle morphology of CuO had pronounced effect on their gas sensing behavior. In addition, the morphology of the CuO particles has also been the matter of concern in other advanced applications such as glucose sensing [15], catalysis [16], etc. Hence, scientists have focused on the development of methods and operational strategies for controlling particle morphologies of CuO which include polyol [17], hydrothermal [18], sol–gel [19], thermal oxidation [20], etc. These efforts led to the production of CuO powders, composed of nanoflowers [16], nanowires [20], and nanoribbons [21].

In fact, the dependence of properties of CuO powder on its particle morphology demands the development of a simple process for the production of CuO powder, composed particles of tailored morphology.

In this study, we describe the synthesis & characterization of monodispersed spherical particles of copper basic carbonate, their conversion to copper oxide spheroidal particles by controlled heat treatment, and fabrication of copper oxide sensor for the detection of ammonia gas at different temperatures. To our knowledge, CuO particles of such morphology have not been used for the manufacture of ammonia sensor before.

## 2. Materials and methods

### 2.1. Materials

Analytical grade copper nitrate, urea, ethanol, and ethylene glycol were purchased from Merck and used without further purifications. Pyrex glass vessels were employed for the preparation of solutions and carrying out the reactions. All the solutions were filtered through membrane filters to remove any possible impurities from the solutions.

### 2.2. Copper oxide particles

For this purpose, aqueous solutions composed of urea and copper nitrate in different proportions (molar ratio of copper nitrate to urea was kept in the range of 0.015–0.05) were heated at 85 °C for pre-determined period of time, which converted clear solutions into dispersions of the precipitated particles. The particles were isolated from the liquid phase, dried in the air and then observed with SEM. It was noted that the spheroidal structure formed when the above-

mentioned proportion of the reactant mixture was kept at 0.022. The obtained spheroids were then calcined at 750 °C at the heating rate of 10 °C/min in a programmable furnace (Nebertherm, M7/11), and then characterized by various physical methods, as described below.

## 2.3. Characterization

Fourier transform infrared (FT-IR) spectra were recorded with a spectrophotometer (Shimadzu, IRprestige-21, FTIR-8400). The X-ray diffraction (XRD) profiles were obtained with X-ray diffractometer (XRD, JEOL JDX-3532) using Cu K$_\alpha$ radiations. The XRD generator voltage and current were kept at 40 kV, and 35 mA, respectively. The sample was scanned in the 2θ range of 10–80°. The step angle was 0.05° and scan speed was 0.1° per second. The software, JDX-3500 was used to find out the crystalline phases in the test sample. Similarly, morphology of the as-prepared and calcined particles was evaluated with a scanning electron microscope (SEM: JSM-6490, JEOL). Energy-dispersive X-ray analysis was performed with EDX detector (INCA200/Oxford instruments). All the samples were sputtered with gold for 30 s in Auto Fine Coater (JFC-1600, JEOL) before SEM imaging. The BET surface area was determined by the nitrogen adsorption method by using a Surface Area Analyzer (NOVA 2200e Quantachrome, USA). The metal content of the desired powder samples was determined quantitatively by atomic absorption spectrometry (Analyst 700, Perkin Elmer, USA). The amount of carbonate in the desired powder sample was determined by first dissolving known amount of powder in the weighed amount of nitric acid and then re-weighed nitric acid after the reaction of powder with nitric acid was over. The difference in weight of nitric acid before and after addition of powder was the carbonate content of the dissolved powder. Similarly, for the determination of the base content of the same powder, known quantity of the latter was dissolved in hydrochloric acid and back titrated the excess acid with a standard solution of sodium hydroxide.

## 2.4. Fabrication of gas sensor & gas sensing

In each case, a paste of known amount of copper oxide particles was made with ethylene glycol and then screen printed on 1 cm × 1 cm alumina plate (sensor plate), carrying printed interdigitated gold electrodes. It was dried overnight in the air and then heated to 400 °C at the ramp rate of 2 °C/min with a holding time of 1 h. This operation was performed in order to stabilize the mechanical properties of the printed layer, increasing adhesion of CuO particles with the underlying electrodes, and to remove the vehicle (ethylene glycol) from the sensor material. The thickness of the deposited sensor layer was ~40 μm and the exposed area of about 1 cm$^2$. After attachment of the electrode terminals of the sensor plate to the data acquisition system, the latter was positioned in a specially designed chamber for performing electrical characterization and gas sensing experiments on it. Heating of the sensor chamber was carried out under controlled conditions and temperature was continuously monitored by means of a k-type thermocouple, attached to the data acquisition system. The gas sensing system involved sample gas inlet with valves, flow meter, thermostatically controlled sensor chamber and data acquisition/analysis system. Block diagram of the sensor setup is shown in Fig. 1. Before the ammonia sensing tests, 200 mL/min dry air was allowed to flush the sensor chamber till stabilization of the sensor resistance, which generally took 30 min. After this, the flow was switched to the test gas (dry air mixed with a known amount of ammonia gas) under the same flow rate and temperature, as adopted in the previous procedure. On introduction of the test gas in the chamber, the sensor registered a change in its electrical resistance which was monitored and recorded in a computer through the data acquisition system. Using the same procedures, the sensing experiments were performed in dynamic mode as a function of temperature, ammonia gas concentration, etc.

## 3. Results and discussion

### 3.1. Sensor material

#### 3.1.1. Synthesis of precursors

The particles shown in Fig. 2A were employed as precursors of the sensor material. These particles were obtained by heating aqueous solutions containing an optimized amount of urea and copper nitrate, as mentioned in the caption of the same figure. In fact, the heating process decomposed the dissolved urea and produced hydroxide and carbonate ions in the reactant mixture [22]. These ions reacted with copper ions and produced precipitated particles of copper basic carbonate. It is added that urea-based homogeneous precipitation process has also been used by other researchers for the synthesis of other types of metal basic carbonate particles [23–26].

#### 3.1.2. Characterization

XRD analysis revealed that the particles shown in Fig. 2A were amorphous in nature (XRD, Fig. 2B). Chemical analysis showed that these particles had the composition of copper basic carbonate ($Cu_2(OH)_2CO_3$).
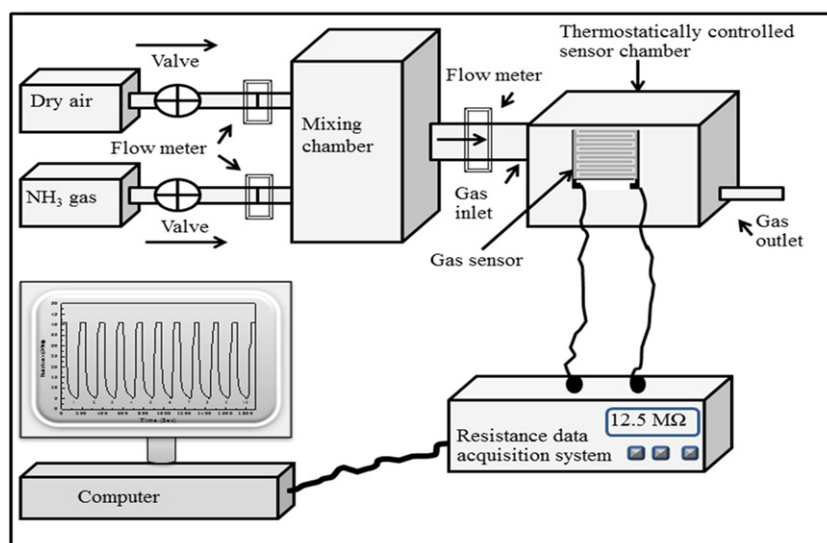


**Fig. 1.** Block diagram of sensor setup.