Optical and Gas Sensing Properties of Cuo Nanoparticles Grown by Spray Pyrolysis of Cupric Nitrate Solution

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***Abstract*—CuO nanoparticles were deposited by spray pyrolysis using aqueous cupric nitrate solution at substrate temperature 473K. The film grown at 473K showed a powder-like, non-oriented polycrystalline structure when they were converted afterwards to CuO by annealing. The X-ray diffraction pattern confirmed the formation of CuO nanoparticles. Transmission electron microscope analysis indicated that the as-synthesized particles are nanoparticles with an average particle size of 6nm. In addition to this, the ultraviolet-visible spectroscopy was employed to the resulting product to study its optical properties. Carbon dioxide gas sensing characteristics such as sensing response, operating temperature, transient response and stability was also reported.**

***Index Terms*—CuO, Spray pyrolysis, Optical properties**

I. Introduction

Copper oxide, a main p-type semiconductor with the band gap 1.2eV, has obtained rising interest due to it has many potential applications such as solar cell, photocatalytic degradation of organic pollutants. Pre-transition-metal oxides are predictable to be quite inert, whereas post transition fairly good for sensing application. It is a versatile material with wide range of optical and electronic application. Now, a day CuO based sensors have attracted much attention as gas sensors because of their chemical sensitivity to gases, high chemical stability, nontoxicity and low cost. Kannaki et al reported the synthesis of CuO nanoparticles from copper sulfate pentahydrate aqueous solution under the low hydrothermal condition at 80 ℃ [1].

One of the exclusive properties of nanoparticles is their high surface area-to-volume ratio, which gives them diverse properties compared with bulk materials that are made from the same materials. Shahmiri et al successfully synthesized the CuO nanosheets in polyvinylpyrrolidone (PVP) via a quick precipitation method [2]. Nemade, *et al.* reported the synthesis of CuO nanoparticles by chemical route and studied optical properties [3]. Liu, *et al*. demonstrate that CuO nanoflower-decorated reduced graphene oxide nanocomposites can be successfully prepared by heating the mixture of Cu salts and GO in the presence of poly [(2-ethyldimethylammonioethyl methacrylate ethyl sulfate)-co-(1-vinylpyrrolidone)] (PQ11) and urea [4]. Wang, *et al.* synthesized CuO flowers and nanorods for the first time by the composite-hydroxide-mediated and the composite-molten-salt method, respectively, with advantages of one-step, ambient pressure, low temperature, template-free and low cost [5].

The various applications of metal oxide are due to the precise chemical, surface and micro structural properties of material. The micro structural and physical properties of metal oxide can be modified by introducing changes into the procedure of its chemical synthesis. Especially for the application of CuO as gas sensors porous microstructure of the materials with controlled pore size is preferred. The sensitivity and response time of CuO based sensors strongly depend on the particle size of the material.

In the present work, we synthesized CuO nanoparticles by spray pyrolysis of cupric nitrate solution. To the best of our knowledge, we report for the first time synthesis of CuO by spray pyrolysis. The prepared sample was characterized through X-ray diffraction (XRD), transmission electron microscopy (TEM) and ultraviolet-visible spectroscopy (UV-VIS). Furthermore, various gas sensing properties of CuO sensor was studied towards the CO_2 gas. The interesting results were observed for the sensor.

II. Experimental

Cupric nitrate ($Cu(NO_3)_2$) used in this work was of analytical grade. CuO nanoparticles were prepared via quick precipitation route using $Cu(NO_3)_2$. In the typical procedure a stock solution of 1M solution of $Cu(NO_3)_2$ was prepared by dissolving suitable quantity in distilled water. The prepared solution was mixed under magnetic stirring for 10min at room temperature. After this step, prepared solution was loaded in chamber of spray pyrolysis, which is made of a capillary tube with an outer diameter of 1mm (inner diameter 0.6mm) and an opening of 1.2mm in diameter (Labtronics, India). The spray was evaporated by a supporting flamelets maintain at 473K. The flow rate was controlled by a flow controller. The product was collected on a SiO_2 substrate.

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The prepared sample was characterized by XRD, TEM and UV-VIS spectroscopy. X-ray diffraction pattern was acquired from Rigaku miniflex-II diffractometer with CuKα radiation in the range 30°-90°. The morphology and grain size of the sample was studied by using TEM (JEOL-1200ex). UV-VIS spectrum was performed on Perkin Elmer UV spectrophotometer in the range 200-400 nm in aqueous solution of CuO nanoparticles.

The prepared film was used as chemiresistive film. For surface resistance measurement, the electrodes of silver were formed on adjacent sides of the film and then it was subjected to heating at 80°C for 15min for drying the silver paint. During this stage, the volatile organic solvent in paints was removed by vaporization.

The electrical resistance was measured by using a voltage drop method. The sensing response was determined from resistance change of chemiresistor/sensor at different concentrations (ppm) and at different temperatures. The heater was fixed on the base plate to heat the sample under test up to required operating temperatures. A Cr-Al thermocouple was used to know the operating temperature. The output of the thermocouple was connected to a digital temperature indicator. Schematic view of the experimental set-up for gas sensing is shown in Fig. 1.

Figure 1. Schematic view of the experimental set-up for gas sensing

The required gas concentration inside system was achieved by injecting a known volume of test gas using a gas-injecting syringe of volume 50ml. The response time of the sensor can be defined as the time needed for its resistance to change from its initial value to 90% of its highest value. Likewise, the recovery time of the sensor can be defined as the time taken for its resistance to be reduced by 90% from its highest value. The response time was determined by injecting required amount of gas in the test chamber keeping the sensor at the room temperature.

III. Results and Discussion

The X-ray diffraction (XRD) pattern of nano-sized CuO is shown in Fig. 2. All the XRD peaks are indexed to the monoclinic crystal system of CuO (JCPDS-45-0937). The crystallite size was calculated by Scherrer equation using prominent peak between 30°-50°; we found that the average CuO crystallite size was 6.2nm [6]. In the XRD pattern, it also seems other peaks observed between 25° and 35° that were indexed to nonstoichiometry on the development of defect structures and the generation of secondary phases.

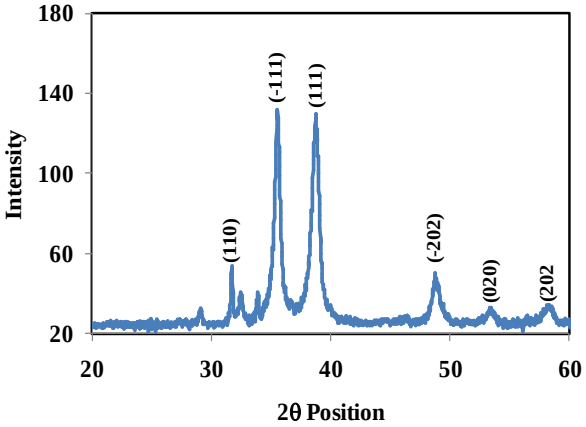

Figure 2. XRD pattern of CuO nanoparticles

The morphology of the synthesized nanomaterial was observed by Transmission Electron Microscopy (TEM). Fig. 3 shows TEM image of as-synthesized CuO nanoparticles. Very small spots that can be distinguished are polycrystals with dimensions about 6 nm or less.

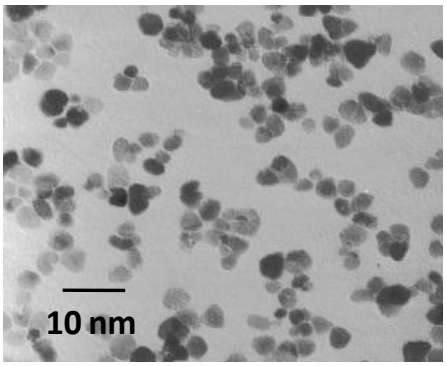

Figure 3. TEM image of as-synthesized CuO nanoparticles

Fig. 4 illustrate the UV-VIS spectrum of CuO film did not exhibit any absorption peak beyond 300 nm. The strong absorption spectrum appeared at 204 nm [7].

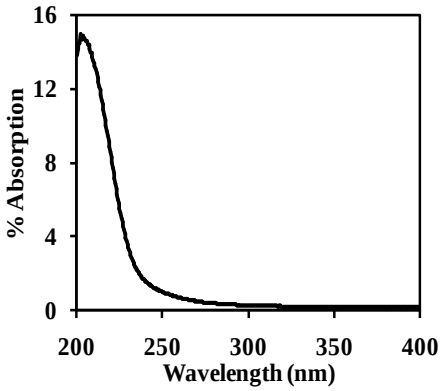

Figure 4. UV-VIS spectrum of CuO nanoparticles recorded between 200-400nm

To determine the optical band gap, mostly researchers use interband transitions model with relation

$$\alpha h\nu = c(h\nu - Eg)^{1/2} \quad (1)$$

where $h\nu$ is photon energy, n is index of refraction, and α is the absorption coefficient. In this approximation, $(\alpha h\nu)^2$ is linear function of $h\nu$. This model is not completely suited to wide band gap materials as the optical absorption band edge is strongly disturbed by a coulombic electron-hole interaction leading to the excitonic effect [8]. The optical band gap of CuO nanoparticles was found to be 5.5eV, displayed in Fig. 5.

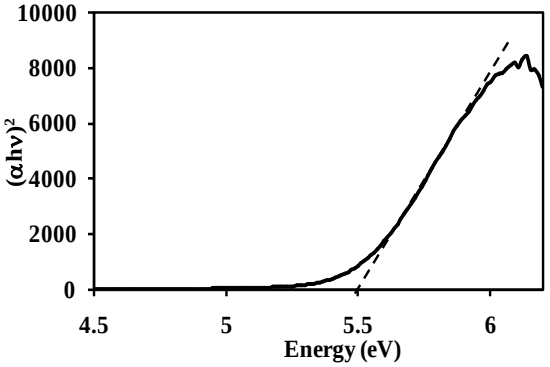

Figure 5. Plot between $(\alpha h\nu)^2$ versus $(h\nu)$ for CuO nanoparticles

The relationship between gas sensing response and CO_2 gas concentration for CuO film is shown in Fig. 6. The sensitivity is defined as [9], S = (Rg-Ra)/Ra, where Ra and Rg are the resistance of sensor in air and the CO_2 gas respectively.

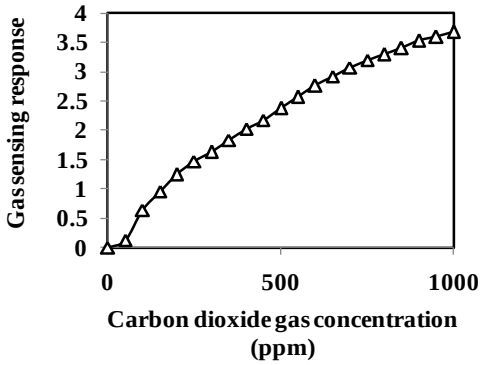

Figure 6. Gas sensing response of CuO film towards CO_2 gas

The resistance of the film was found to be increases linearly with increasing CO_2 concentration up to 1000ppm at room temperature. This shows that the sensor possesses linear sensing response up to 1000ppm of CO_2. This may represents the detection limit of sensor. The saturation effect was not observed up to 1000ppm. The higher value of CO_2 gas sensitivity was found to be 3.5 at 1000ppm.

The gas-sensing mechanism of sensor based on the surface reaction between the adsorbed oxygen ions and the gas species [10-11]. Oxygen may be either physisorbed or chemisorbed as charged species on the surface. The adsorbed oxygen may not engage the active sites, while the chemisorbed oxygen species act as surface acceptors, catching electrons. As CO_2 is an oxidiser gas with electron withdrawing power. When sensor exposed to CO_2 gas then it is chemisorbed on bridging oxygen atoms with the formation of a surface carbonate and increase the resistance of sensor.

Fig. 7 shows the sensing response as a function of temperature to 500ppm CO_2. It is inspected from figure, the response increased up to 423K. This is operating temperature for chemiresistors, which is much lower than the reports mentioned in literature of material science. This is important achievement of present work. The thermal energy at higher temperature is enough to overcome the potential barrier resulted in significant increase in electron concentration for the sensing reaction. The sensing response of semiconductor oxide based gas sensors depends on the rate of the chemical reaction on the surface of the particles and the rate of diffusion of the gas molecules to that surface. At lower temperatures, sensing response is forced by the speed of the chemical reaction, and at higher temperatures it is constrained by the speed of diffusion of gas molecules. At some transitional temperature, the speed values of the two processes become equal, and at that point the chemiresistor response attained its maximum value. The response value starts to decreases beyond 423K. This may be due to desorption of oxygen ions and diffused gas molecules from sensing surface.

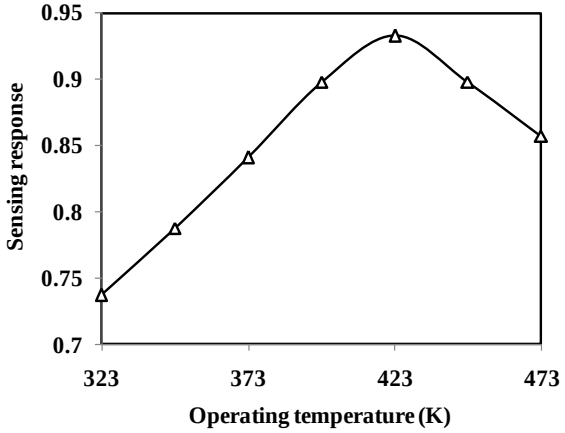

Figure 7. Operating temperature response of CuO sensor

The transient response characteristic of CuO to 500ppm CO_2 is shown in Fig. 8. The fast response around 16s for CO_2 was showed by sensor. Whereas, recovery time was around in 20s.

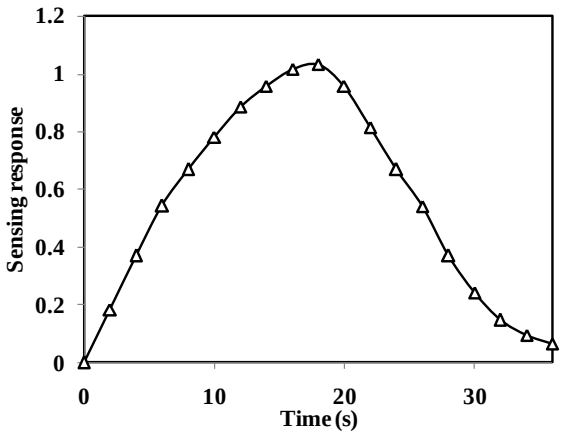

Figure 8. Transient response characteristic of CuO sensor

For stability measurements, sensor responses towards 500ppm CO_2 at room temperature was measured for 30 days and shown in Fig. 9. The chemiresistors possesses nearly constant response to CO_2, indicating the good stability.

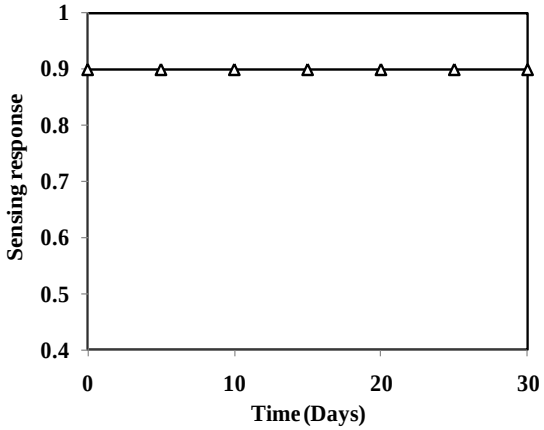

Figure 9. Stability response of CuO sensor

IV. Conclusions

In conclusion of present work, nanoparticles of CuO were successfully synthesized by using a spray pyrolysis technique. An average particle size of the resulting nanoparticles was found to be 6nm. The optical property of the produced nanoparticles was studied by measuring the % absorbance and band gap energy. The optical band gap for as-synthesized CuO nanoparticles was found to be 5.5eV. The spray pyrolysis technique used in this study is a useful and economic technique to prepare CuO nanoparticles. The as prepared CuO sensor film shows good sensing response towards the CO_2 gas. The higher value of sensing response was found to be 3.5 at 1000ppm concentration of CO_2 gas. Similarly, the operating temperature for sensor was found to be 423K at 500ppm. The response time observed for CuO sensor was around 16s, whereas, recovery time was around in 20s showed by sensor.

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