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SYNTHESIS, CHARACTERIZATIONS, AND GAS SENSING APPLICATION OF COPPER (II) OXIDE NANOPARTICLES BY CHEMICAL PRECIPITATION METHOD

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***Abstract*:**
The development of nanotechnology and the production of nanomaterials has revolutionised science and technology. Nanoparticles link molecular and bulk states of matter, expressing size-dependent physical and chemical properties. CuO-NPs were synthesised using a chemical precipitation process including copper (II) chloride dihydrate and sodium hydroxide. Nanoparticles were analysed using X-ray Diffraction (XRD), SEM, EDX, and FT-IR spectroscopy. XRD and EDX spectra revealed high purity, crystalline, and nano-sized CuO-NPs. SEM images revealed spherical nanoparticles with a tendency to aggregate. FT-IR analysis confirmed copper-oxygen interactions in the nanoparticles. CuO has good H2S gas sensing properties in the 300-400°C temperature range. Sensitivity increases with gas concentration, but temperature has only a minimal effect. H2S sensing was done using thick screen-printed films. CuO thick films were shown to be sensitive to H2S gas. Copper oxide films were found to be 87% sensitive to H2S when exposed to gas. A concentration of 100 ppm at ambient temperature (400°C). The prepared films demonstrated good responsiveness and recovery time.

Keywords: Nanoparticles, CuO, Chemical precipitation method, Gas sensing

1. Introduction:

Nanoparticles, both metallic and non-metallic, have a wide range of applications. Metal nanoparticles have numerous applications in physics, chemistry, materials science, and industry [1-3]. Semiconducting metal oxides such as CuO, In_2O_3, TiO_2, NiO, and ZnO, as well as their composites with carbon-based materials such as carbon nanotubes, graphene oxide, graphene, and heterostructures (n-type and p-type semiconductors), are being studied for their technologically significant features. Cupric oxide (CuO) is employed in a wide range of applications, including gas sensors. [4]. The nanoparticles have attractive features that differ fundamentally from their bulk condition [5]. Gas-sensing metal oxide semiconductors are incredible because of possible alterations in morphological and structural content to enhance the sensing property [6-8]. Hydrogen sulphide has a low odour threshold, detectable at quantities below 1 ppm in air. As the gas concentration increases, it emits a distinct rotten egg odour that can be detected up to 30 ppm. Above this level, the gas is described to be sickeningly sweet. Odour levels up to about 100 ppm.

At concentrations above 100 ppm, the gas can temporarily disable the olfactory neurons in the nose, causing a loss of smell [9-12]. Cu_2O has a cubic crystal structure, while CuO has a monoclinic structure. In nanotechnology, single-phase CuO is recommended for most applications because it contains the most stable oxide phase. It commonly occurs as a p-type semiconductor with a narrow bandgap of 1.2 eV [13,14].

This study aimed to synthesise nanosized copper oxide powder and analyse its properties, including crystallite size, shape, microstructure, composition, and interactions with other CuO-NP species. This study synthesised CuO-NPs via chemical precipitation and annealing at 200˚C, 300˚C, and 400˚C and study of H_2S gas sensing properties of CuO-NP.

2. Experimental Details

2.1 Materials:

Copper (II) chloride dihydrate, Sodium hydroxide pellets, and ethanol were purchased from SD Fine, India. Analytical research grade chemicals were used in the experiment and they were used without further purification. Distilled water was used throughout the experiment for preparing solutions and washing purposes.

2.3 Synthesis of CuO-NPs:

To synthesise CuO-NPs via chemical precipitation, a conventional technique was used [15]. During the CuO-NPs synthesis, 4 g of copper (II) chloride dehydrate was first dissolved in 150 ml of ethanol, followed by 2 g of sodium hydroxide pellet in 50 ml of ethanol. At room temperature, sodium hydroxide solution was added drop by drop to copper (II) chloride dihydrate solution while being stirred constantly. As the reaction progressed, the solution's colour changed from green to bluish green, then to black. The dark precipitate was copper hydroxide. Fig.1 The precipitate was filtered using a centrifuge. To remove the sodium chloride salt solution, wash with ethanol and deionized water. The precipitate was then dried at approximately 50˚C in a drier. The dry sample was annealed at temperatures at 200˚C, 300˚C, and 400˚C temperatures. The annealed sample was then ground into powdered nanoparticles. The power sample was utilised to characterise CuO nanoparticles.

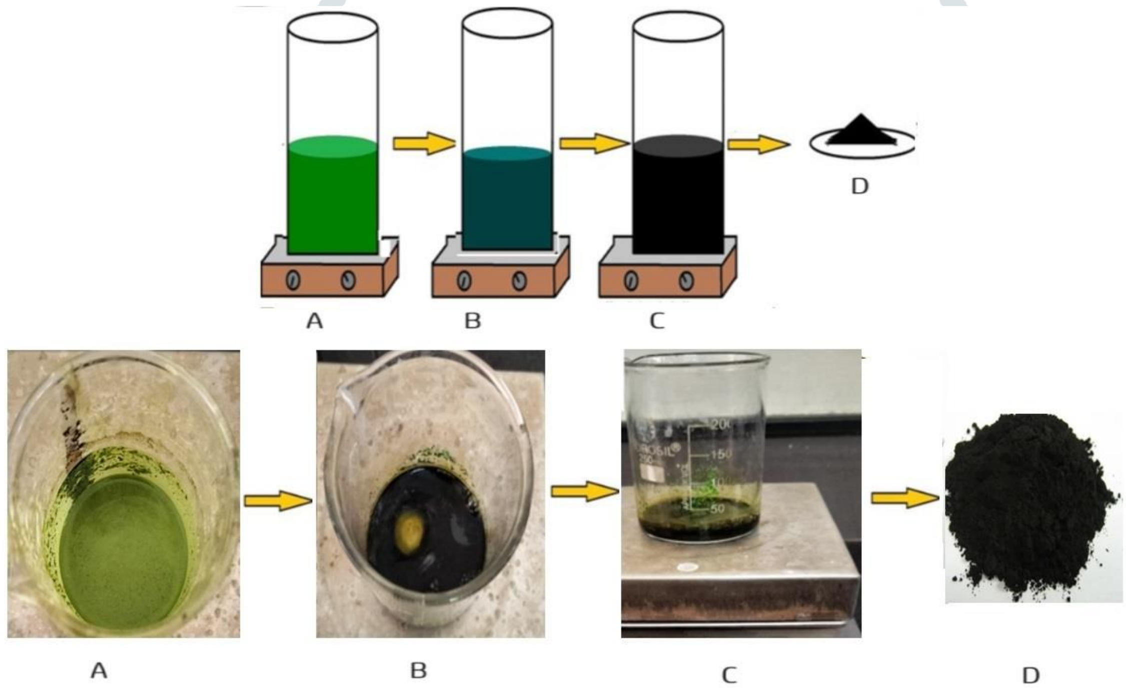


Fig.1 solution colour changed from green (A) to bluish green (B), then to black (C) to form CuO-NPs (D).

3 Characterizations:

3.1 X-ray diffraction (XRD):

Fig. 2 shows the X-ray diffraction pattern of a thick CuO layer. XRD investigation indicates that CuO nanoparticles are monoclinic. (JCPDS card no. 48-1548). The sharpness of peaks shows that CuO NPs are highly crystalline. a, b and c are the lattice constants, d is the inter planer spacing, β is the interfacial angle and h, k, l are the Miller indices. The obtained lattice parameters are a = 4.683 Å, b = 3.427 Å, c = 5.136 Å, $\alpha = 90^0$, $\beta = 99.50^0$ and $\gamma = 90^0$ are in good match with the reported CuO The crystalline size of CuO nanoparticles calculated using FWHM of from most intense XRD peak using Scherrer's formula[16]. Crystallite size for CuO NPs is found to be 27 nm.

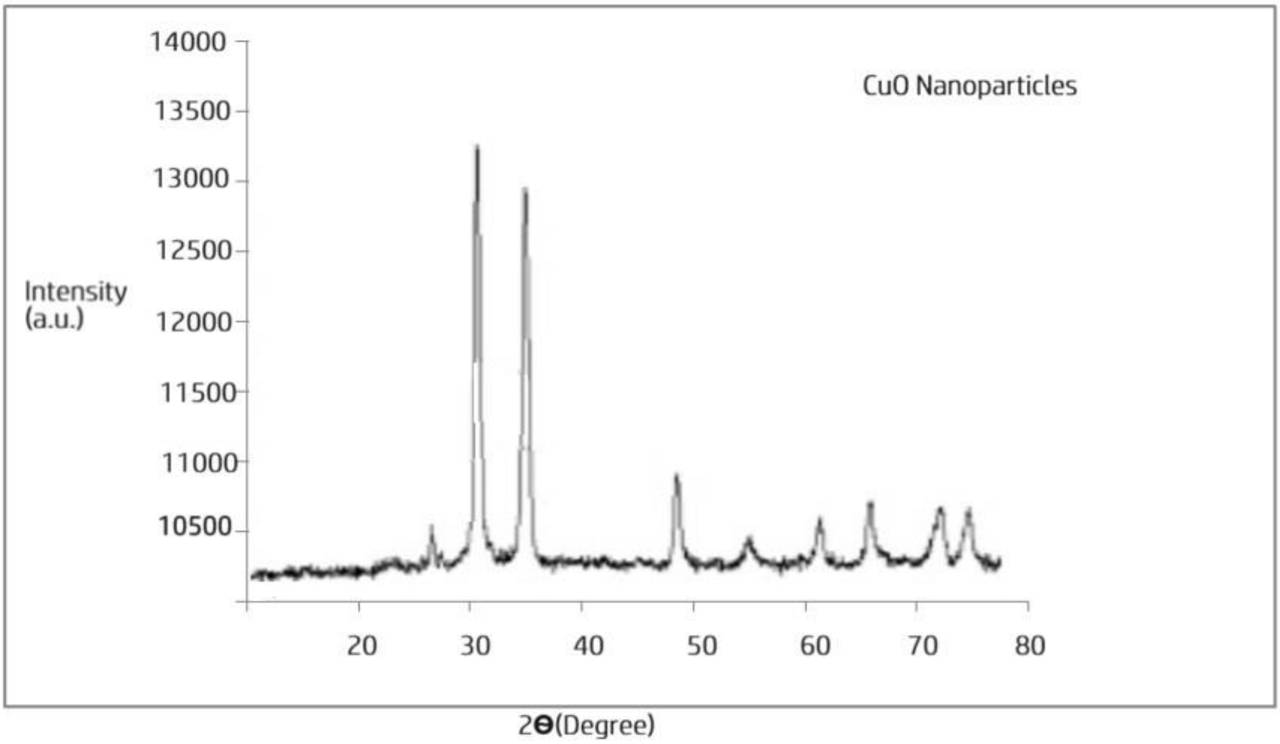
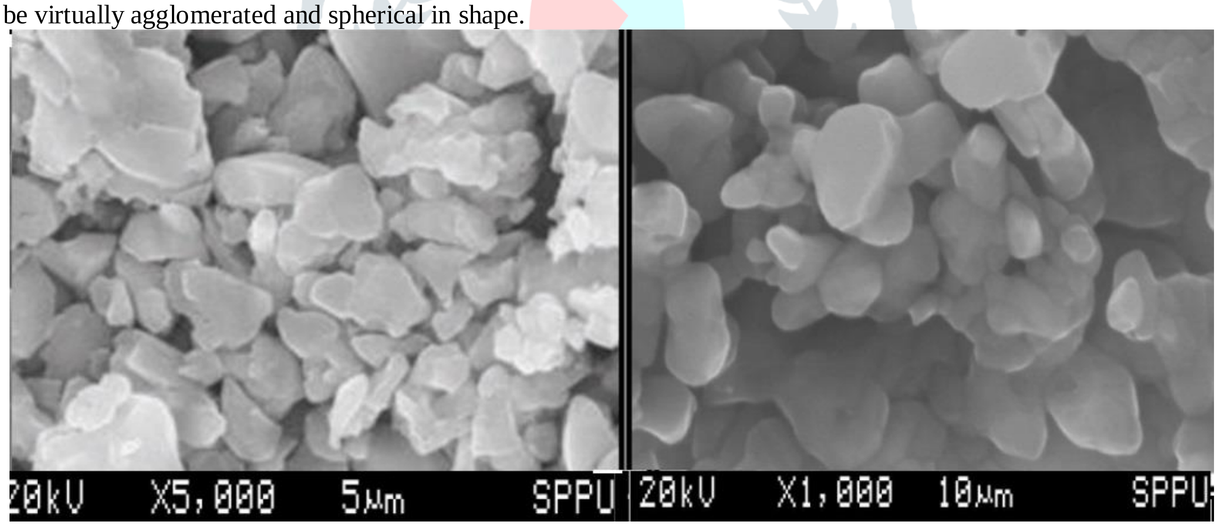


Fig 2- Shows the XRD pattern of CuO-NP

3.2 Scanning Electron Microscope(SEM):

The SEM image in Fig. 4 reveals the surface morphology of CuO nanoparticles, with high magnification allowing for detailed examination. It demonstrates a uniform dispersion of the CuO spherical particles that were synthesised. CuO nanoparticles were found to be virtually agglomerated and spherical in shape.



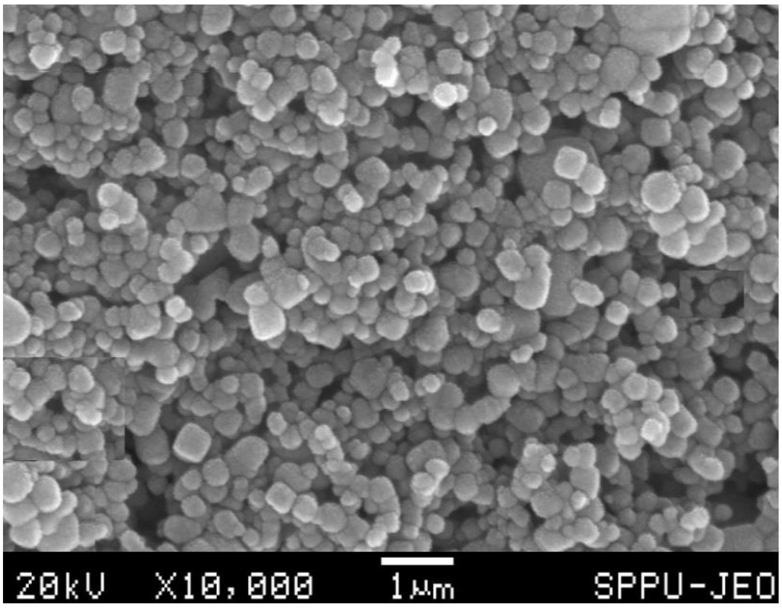


Fig.4 Scanning Electron Microscope(SEM) of CuO nanoparticles

3.3 EDAX spectrum

The EDAX spectra of synthesised CuO nanoparticles shows only the indicated elements, such as Cu and O, indicating the samples are free of contaminants.Fig.5

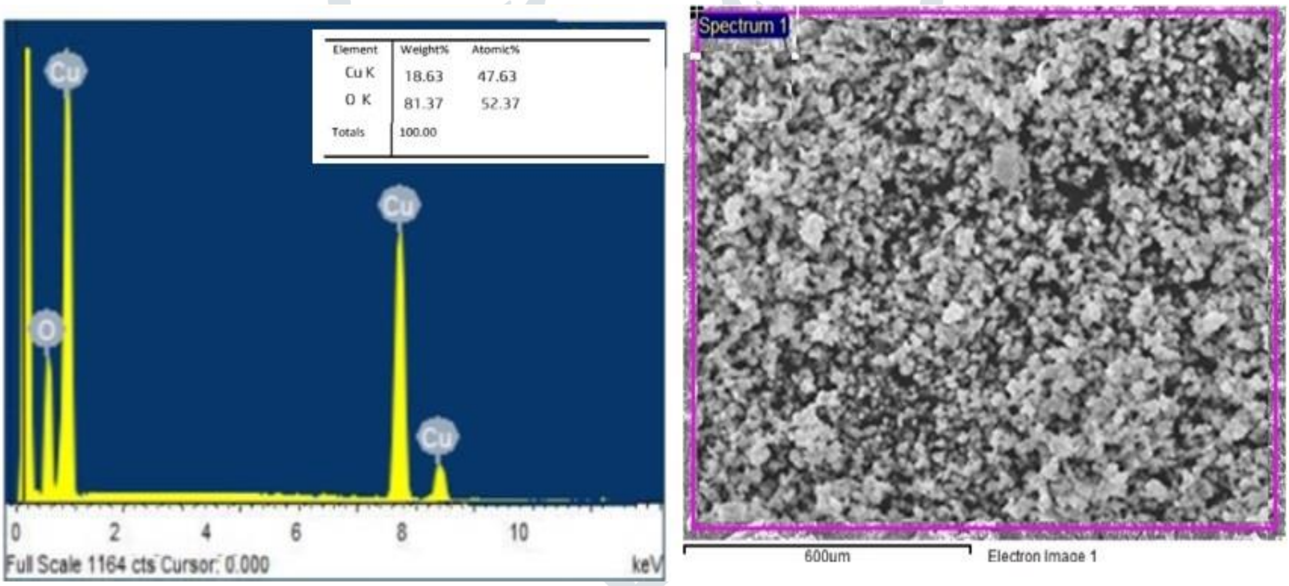


Fig. 5 The EDAX spectra of synthesised CuO nanoparticles

3.4 FT-IR:

FT-IR is useful for identifying functional groups and substances based on their energy absorption over different ranges. FT-IR is utilised as most compounds absorb light in the infrared region of the electromagnetic spectrum.

CuO-NP were analysed using FT-IR at room temperature to determine their chemical composition and validate the production of CuO. Results were recorded in the 400-4000 cm^{-1} range. The FT-IR spectra of CuO-NP are presented in Fig. 6.

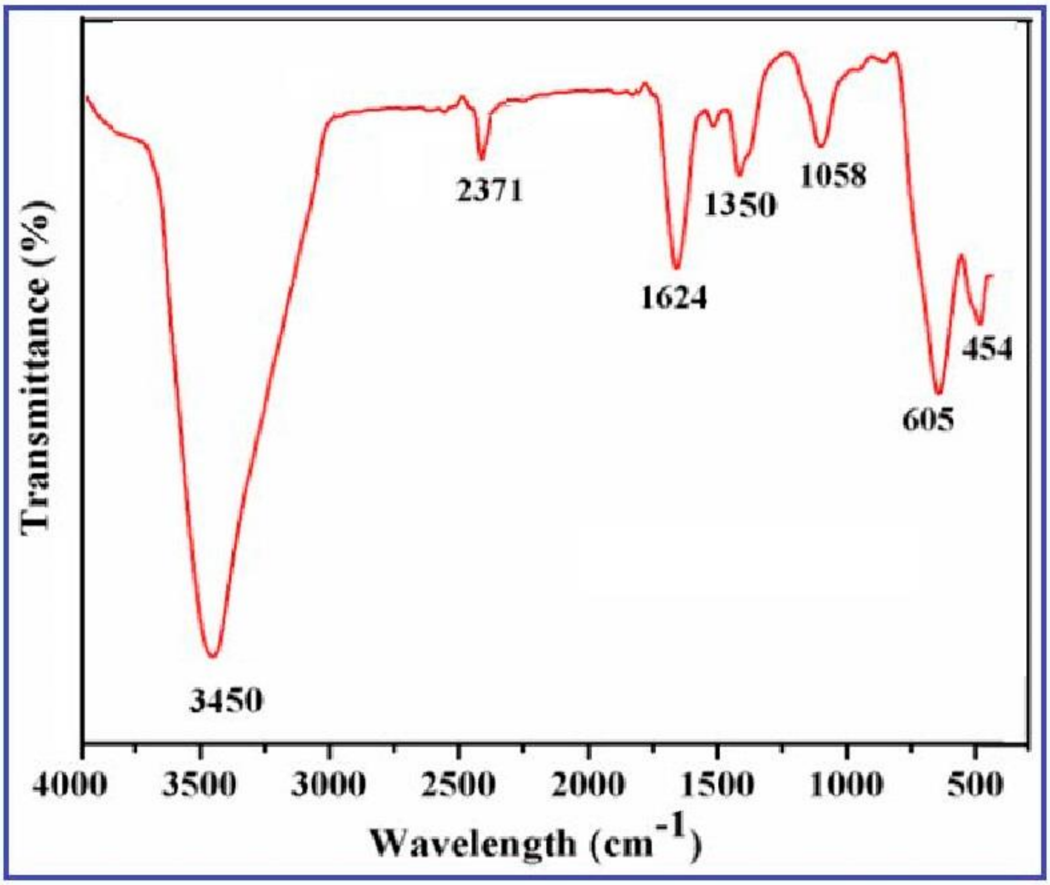


Fig. 6 FT-IR of CuO-NP

4 Gas Sensing applications

4.1 CuO thick film sensor fabrication by screen printing technology

The thick films of CuO thick film sensor were prepared by screen printing technique. The ratio of CuO nanoparticles to organic binders was kept constant as 70:30 (Inorganic to organic ratio). Initially 0.7 g of CuO nanoparticles was grinded in mortar pestle for 30 min by addition of ethyl cellulose (EC) to make homogeneous mixing of CuO and ethyl cellulose. After the homogeneous mixing between these two materials, butyl carbitol acetate (BCA) solution was added. The BCA was added till the mixture appears to be homogeneous paste then applied on previously cut glass substrate having dimensions of 3 cm × 1.5 cm. By utilizing the paste nearly 10 thick films were prepared. The thick films then dried under IR lamp for 25 min. The film sensors then fired in muffle furnace for 3 h at 450 °C. The fabricated thick film sensors were utilized for further gas sensing study and characterization.

4.2 Gas sensing properties

The H_2S gas reaction was found to be greatest at room temperature at 100 ppm. CuO thick films respond 88% to H_2S gas at ambient temperature. The CuO film was stabilized at an operating temperature for 10 minutes before being exposed to H_2S. The stabilized resistance was then measured as Ra. After exposing the film to H_2S gas, the altered resistance was measured as Rg. H_2S reduces gas. It reacts with oxygen ions on the film's surface. Reducing the film improves the quantity of free carriers. The resistance of the film increases with diminishing gas.[17]

Conclusion

This study synthesised CuO nanoparticles using the chemical precipitation method. Nanoparticle structure and shape were characterised using XRD and SEM methods. CuO morphology is monoclinic, resulting in short nanotubes. The crystal size of CuO calculated by Scherer formula is 27 nm. SEM images revealed a uniform distribution of spherical CuO nanoparticles. Screen printing was used to create thick CuO films. Copper oxide thick films that have been prepared exhibit semiconductor behaviour. XRD, SEM, EDAX, and FT-IR tests demonstrate that produced copper oxide nanoparticles have a typical Cu-O stretch. CuO films show possibility as gas sensors for H_2S at room temperature and low ppm levels.

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