Preparation and Evaluation of CuO Nanoparticles Using the Sol-Gel Method

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Abstract. Nanomaterials have attractive properties. They are employed in different fields of science, such as materials engineering, medicine, the environment and many technological applications. Transition metal oxides, such as CuO, are strong candidates for many scientific applications due to their unique physical and chemical properties. In this research, CuO nanoparticles were prepared using the nonorganic sol-gel technique under controlled conditions. The precursor of the sol-gel process was cupric chloride with NaOH as the stabilising agent. The aqueous solution was altered with two pH values to study their effect on the final precipitate. The prepared CuO nanoparticles were evaluated by XRD, particle size analyser, SEM and visually.

1. Introduction
After more than two decades of research and development in the field of nanoscience, nanotechnology applications still deliver new and unexpected ways to benefit society. A lot of these applications help improve many technological and industrial sectors. Several metals can be considered as potential primary materials for this purpose, but transition metals are the key elements of the future due to their exceptional characteristics and the ease with which they can be economically synthesised, such as via the sol-gel chemical route. The main reason for selecting CuO among other transition metals oxides is its semiconductivity. Semiconductive materials are widely used in electronic and optoelectronic devices, such as electrochemical cells [1], gas sensors [2], magnetic storage devices [3], field emitters [4], high Tc superconductors [5], nanofluids [6] and catalysts [7]. Considering electrical applications, CuO particles in the nano range have a wide bandgap that nearly equals ZnO. CuO nanoparticles can be mixed with highly purified water (CuO-based nanofluid) to significantly enhance energy transfer, such as in coolants and other thermal applications.

The uniqueness of the nanoscale (10–100 nm) is that the material’s aspect ratio or surface-to-volume ratio will be very high, improving many mechanical properties, such as hardness and strength. Furthermore, the material’s particles at the nanoscale will no longer be subjected to regular continuum mechanics laws but rather to quantum mechanics laws.

Several nanomaterial synthesis procedures exist, and they are usually classified as top-down or bottom-up processes depending on the process energy and the starting material conditions [8]. Bottom-up wet chemical methods, such as sol-gel, are considered the most efficient and economical. Some experimental results of the sol-gel method showed CuO nanoparticles in the range of 1–10 nm [9], and the smallest CuO nanoparticle obtained by the electrochemical method was nearly 4 nm. This work aims to prepare and evaluate CuO nanoparticles using the nonorganic sol-gel method and examines the effect of pH value on the properties of the prepared particles.

2. Experimental Procedure
The first step of the nonorganic sol-gel method consisted of preparing an aqueous solution of CuCl2, 2H2O (0.2 M) using deionised water. Then, 4 ml of glacial acetic acid was added to the aqueous solution; it was heated and stirred using a hotplate-stirrer device and then monitored with a digital thermometer and a pH meter, as shown in Figure 1. When the solution temperature reached 100 °C, NaOH pellets were added until the pH value reached 7. During this step, the solution changed gradually to a gel consistency.
chemical reaction was accompanied by a gradual colour change from green to nearly black (Figure 2). The hydrolysis reaction occurred as follows:

\[
\text{CuCl}_2 + 2\text{NaOH} \rightarrow \text{Cu(OH)}_2 + 2\text{NaCl}
\]

The resulting salt was removed by centrifuging and washing the colloid three times with deionised water, and the precipitated Cu(OH)$_2$ particles changed to CuO powder when dried in a furnace at 250 °C. In the second case, the aqueous solution was allowed to exceed the neutral pH value during the addition of NaOH and reached pH 11. The prepared CuO powders were examined by X-ray diffraction (XRD), and a Malvern Zetasizer Nano ZS device and scanning electron microscopy were used for size analysis.

![Figure 1 Instruments used in the sol-gel process](image1.png)

**Figure 1** Instruments used in the sol-gel process

![Figure 2 Precipitation steps of Cu(OH)$_2$ particles](image2.png)

**Figure 2** Precipitation steps of Cu(OH)$_2$ particles (left to right)

### 3. Results and Discussion

#### 3.1 X-ray diffraction test

Figures 3 and 4 show the XRD pattern of the prepared CuO particle samples at pH values 7 and 11, respectively. All of the major peaks showed a monoclinic crystal structure of CuO in comparison with the PDF card no. 00-002-1041 (Figure 5). All of the peaks’ Miller indices were identified. The average grain size was also calculated from Figure 3 using a Debye-Scherrer equation at approximately 60 nm:

\[
d = \frac{K\lambda}{\beta\cos(\theta)}
\]

where $d$ is the average particle size, $K$ is a dimensionless shape factor with an approximate value of 0.9, $\lambda$ is the X-ray wavelength (in this test, it was equal to 0.15406 nm), $\beta$ is the full width at half maximum
(FWHM) of the diffraction peak (in radians) and $\theta$ is the Bragg's angle or diffraction angle of the peak. Figures 3 and 4 also show that the prepared CuO powders have a good purity.

![Figure 3 XRD chart of the prepared CuO powder at pH=7](image_url)

![Figure 4 XRD chart of the prepared CuO powder at pH=11](image_url)

![Figure 5 PDF card no. 00-002-1041](image_url)
3.2 Particle size test
Figures 6 and 7 show the size analysis of the prepared CuO particle samples at pH values 7 and 11, respectively. Figure 6 shows that the CuO particles prepared at pH=7 are mostly 60 to 150 nm in size and 30% are 90 nm. In Figure 7, the CuO particles prepared at pH=11 range from 500 to 1,050 nm in size, and 32% are 955 nm. This test shows that increasing the pH value from 7 to 11 increased the average particles’ size from 90 to 955 nm.

![Figure 6](image1.png) Size distribution of the prepared CuO powder at pH=7

![Figure 7](image2.png) Size distribution of the prepared CuO powder at pH=11

3.3 Scanning electron microscopy test
Figures 8 and 9 include the SEM images of CuO particles prepared at pH values 7 and 11, respectively. Generally, the preparation of these samples caused high agglomeration and bad resolution of the particles on the Al substrate. In Figure 8, the particles were approximately spherical, while the particles prepared at a pH value of 11 were flake-shaped (Figure 9).

![Figure 8](image3.png) SEM micrograph of CuO particles prepared at pH=7
3.4 Visual test

One gram of each CuO nanoparticle type was mixed homogeneously with deionised water to obtain two nanofluids (Figure 10). Visual examination shows a difference in the nanofluids’ colour, as it tends to become darker when the particle size is increased. This is because of the difference in surface energy of particles that react differently with light photons, as explained theoretically by the quantum theory.

4. Conclusion

The main conclusions from this work are that the XRD pattern shows a monoclinic structure of CuO nanoparticles with an average grain size of approximately 60 nm (pH=7). Furthermore, the particle size test shows an increase in the average particle size from 90 nm at pH=7 to 955 nm at pH=11. On the other hand, the particles prepared at pH=7 have a spherical shape, while those prepared at pH=11 are flake-shaped. Finally, a visual examination shows a colour change from brown to black as the average particle size increases from 90 to 955 nm.

5. References

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