CHAPTER 5
SYNTHESIS AND CHARACTERIZATION
OF NANO COPPER OXIDE PARTICLES

5.1 INTRODUCTION

Nano particles exhibit attracting size dependent optical, electrical, chemical and magnetic properties compared to their parent bulk material. The possible reasons for the enhancement of the properties (Cao 2004) may be due to, large fraction of surface atoms, high surface energy, spatial confinement and reduced imperfections. Because of their smaller size, the nano materials have large surface area to volume ratio, which provides room for millions of atoms present in the surface resulting in surface dependent material properties. Nano copper oxide particle was found to be a better choice to use it as an additive with the lubricant since it exhibits good anti-wear and anti-friction properties over the TiO$_2$ and Nano diamond particles (Wu et al 2007).

This chapter focuses on synthesizing the nano CuO particle by chemical reduction process. The XRD, PSD, Zeta potential and SEM testes have been used to characterize the morphology of the prepared nano particle.

5.2 SYNTHESIS OF COPPER OXIDE NANOPARTICLES

The nano CuO particles were synthesized by simple aqueous precipitation method (Amrut S Lanje et al 2010). The chemical compounds which have been used in the experiment belong to an analytical reagent grade (AR). Copper acetate monohydrate Cu (CH$_3$COO)$_2$ H$_2$O and acetic acid
glacial were purchased from Nice Chemical and Merck, India used without further treatments as shown in Figure 5.1. Sodium hydroxide NaOH (pellets) was purchased from Rankem, India and Deionized water was used throughout the experiment.

![Figure 5.1 Ingredients used in the synthesis of Copper oxide nano particle](image)

Figure 5.1 Ingredients used in the synthesis of Copper oxide nano particle

The detailed step by step procedure used for synthesis of nano-CuO particle is explained below,

- First aqueous solution of copper acetate (0.02 mol) was prepared along with deionized water in a round bottomed flask as shown in Figure 5.2. The solution appears blue in colour. Then 1 mL glacial acetic acid was added to the above aqueous solution and it was heated up to a temperature of 65°C for the period of 30 minutes with constant stirring using a magnetic stirrer as shown in Figure 5.2.
About 0.4 g of NaOH pellets were added to the above heated solution till pH reaches to 7. The large amount of black precipitate formation was observed (Figure 5.3) and the solution was kept in atmosphere to cool down to reach room temperature, so that the black precipitate settles down at the bottom of the flask as shown in Figure 5.4.

Prepared sample was centrifuged at 5000 rpm for 10 min and washed 3-4 times with deionized water as shown in Figure 5.5. In the first wash, pale blue colour precipitate was observed and that supernatant solution was then discarded carefully.

The obtained precipitate was dried in air for 24 hours to get the nano-CuO particles.

The entire chemical reaction process happened in the aqueous precipitation process has been written as,

\[
\text{Cu(CH}_3\text{COO)}_2 + 2\text{NaOH} \rightarrow \text{CuO} + 2\text{Na(CH}_3\text{COO)} + \text{H}_2\text{O}
\]

![Figure 5.2 Mixing of copper acetate and glacial acid in deionized water by continuous heating and stirring using magnetic stirrer](image-url)
Figure 5.3 Formation of black precipitate by the reaction of NaOH

Figure 5.4 Settled black precipitate on the bottom of flask
5.3 CHARACTERIZATION TECHNIQUES

5.3.1 X-Ray Diffraction (XRD) Test

As a non-destructive testing technique, x-ray diffraction is a powerful tool for the analysis of a crystalline structure. X-ray has wavelengths comparable to the crystalline lattice constants. Thus it can be used for the accurate measurement of lattice parameter, crystallite size and lattice strain etc.

X-ray diffraction of the synthesized powder samples were performed using the diffractometer. The X-ray powder diffraction (XRD) was performed on an X’Pert Philips diffractometer using Cu K-alpha radiation (λ = 1.5405 Å), operating at 40 kV and 30 mA. The X-ray intensity was measured over a scan range from 4° to 90° with the scan speed of 10 deg/min.

The detailed analysis of the XRD and the assignments of various reflections have been shown in Table 5.1. The detailed report have been attached in the Appendix 1.
Table 5.1 XRD results - Strongest three peaks of sample

<table>
<thead>
<tr>
<th>No.</th>
<th>Peak number</th>
<th>2θ (deg)</th>
<th>d(Å)</th>
<th>FWHM (deg)</th>
<th>Intensity (Counts)</th>
<th>Integrated Int (Counts)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7</td>
<td>38.6631</td>
<td>2.32695</td>
<td>1.44770</td>
<td>576</td>
<td>9061</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>35.4477</td>
<td>2.53031</td>
<td>1.42890</td>
<td>481</td>
<td>7977</td>
</tr>
<tr>
<td>3</td>
<td>21</td>
<td>66.0000</td>
<td>1.41433</td>
<td>1.54540</td>
<td>164</td>
<td>2286</td>
</tr>
</tbody>
</table>

From this study the peak average particle size has been estimated by using Debye-Scherrer formula (Amrut S Lanje et al 2010)

\[ D = \frac{0.9\lambda}{\beta \cos \theta} \]  \hspace{1cm} (5.1)

Where \( \lambda \) is the wavelength of X-Ray (0.15406 nm),
\( \beta \) is FWHM (full width at half maximum),
\( \theta \) is the diffraction angle and ‘D’ is the particle size diameter.

By using equation (5.1), the average size of the particle was found to be, \( D = 5.82 \) nm. The resultant particle size (D) calculated using equation (5.1) was 6-7nm and verified later using a particle size analyzer.

Figure 5.6 represents the XRD pattern of the typical sample. The peaks observed on the XRD pattern can be indexed to that of monoclinic CuO according to the JCPDS file No. 05-661. There was only Cu and O elements existing in the XRD pattern.
5.3.2 Particle Size Distribution (PSD) Test

The particle size in nano meter range and dispersion stability of ultrafine particles in nano fluids was measured by Nano zeta sizer (Model: Nano ZS90, Malvern). The sample was prepared by dispersing small amount of ultrafine particles in deionized water with constant ultrasonication and magnetic stirring for 30 minutes each. Then the sample was kept in a sample holder with the help of a syringe and analysed in the equipment.

The results of PSD test were shown in Figure 5.7 and Table 5.2. The PSD by volume shows that almost all particles in suspension were in the range of 100-1000 nm. The maximum was reached for 323.4 nm. Due to the agglomeration of the nano-particle (Chattopadhyay & Patel 2012), the results of PSD appears in the above mentioned range. The detailed report has been attached in the Appendix 1. Ultra-sonication process was applied to deagglomerate the particles. However, sonication time was not sufficient to break up most of the agglomerates. Power of the ultrasonic mixer may also have had an impact on the PSD. Any instability of the suspension might have
come from the particle’s size which is not sufficient to deagglomeration by sonication.

Table 5.2 PSD results - peak values of CuO

<table>
<thead>
<tr>
<th>Peak</th>
<th>Size (d in nm)</th>
<th>% intensity</th>
<th>Width</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak 1</td>
<td>323.4</td>
<td>89.0</td>
<td>185.7</td>
</tr>
<tr>
<td>Peak 2</td>
<td>4645</td>
<td>8.1</td>
<td>810.8</td>
</tr>
<tr>
<td>Peak 3</td>
<td>32.15</td>
<td>2.9</td>
<td>7.037</td>
</tr>
</tbody>
</table>

Figure 5.7 PSD of prepared CuO in water dispersant

5.3.3 Scanning Electron Microscopy (SEM) Study

The SEM micrographs of the received CuO nanoparticles have been obtained to study the morphology of the particles. The images were taken in both secondary electron (SE) and back scattered electron (BSE) mode according to requirement. Microscopic studies were used to examine the morphology, particle size and microstructure. The SEM images were taken using JEOL 6390 scanning electron microscope (SEM) equipped with an energy dispersive X-ray (EDX) detector of Oxford data reference system.
Micrographs were taken at suitable accelerating voltages for the best possible resolution using the secondary electron imaging.

Figure 5.8 shows the SEM images of the synthesized nano-CuO sample. The general morphologies of synthesised nano-CuO were observed with large number of CuO nanosphere agglomerates with a uniform size as in Figure 5.8. An individual sphere-like nanostructure is shown in Figure 5.9 which demonstrates that the CuO nanostructures with sphere-like shapes are composed of many interconnected sheet-ball like crystallites structure. It has also been observed that the particles were composed of agglomerated random shape particles.

Figure 5.8 SEM image of nano-CuO particle at magnification of 2000 x
5.3.4 Zeta Potential Analysis

The magnitude of the electrostatic charge or charge repulsion/attraction was found to be the critical factor in affecting the stability of the dispersion. Zeta potential test has been used to measure such magnitude. Figure 5.10 shows the variation of Zeta Potential with intensity. The maximum count has been observed at the magnitude of 27.1 mV. The positive value of zeta potential suggested that the copper oxide particles were positive particles and moderately stable. The positive nature of zeta potential prevents the particles coming together. Due to this nature, a good dispersion stability can be obtained in CuO nanoparticles and particle attains stable condition over the time. A detailed report has been attached in the appendix-1.
5.4 OLEIC ACID TREATMENT OF CuO NANOPARTICLES

Generally nanoparticles tend to agglomerate and form as a large particles, because of their strong chemical activity and adsorption affinity. These particles were dispersed in base media primarily by an ultrasonication. Then the particles were coated with Tween 20 surfactant in the laboratory.

Tween 20 (contains maximum of oleic acid) and ethanol have been mixed and heated to 70°C for 3 hours with continuous stirring in the magnetic stirrer as shown in Figure 5.11. The required amount of nano particles have been added along with the prepared solution. This combination forms the precipitation of nano-CuO particles as shown in Figure 5.12. The formed precipitates were rinsed thoroughly with ethanol using filter paper. The aggregated particles have been separated from dispersion by centrifugation at 5000 rpm for 15 minutes. This has produced a surfactant coated nano-CuO particles.
Referring to Mustafa Akbulut (2011), it is known that the surfactant coated nano particles have better lubricating property than other particles. The bare metal and metal oxides particles have strong Van der Walls forces which attracts the hydrocarbon and thus forms aggregation (Min et al 2008). While coating the surfactant over the nano-CuO particles, it prevents the agglomeration. Besides, the coating protects the original particle not to contact the other shearing body. This also prevents both direct metal transfer and cold weld between the shearing surfaces. Also the coating over the particle provides a smoother exterior surface than the interior. This synergic combination provides a rigid shape and greasy like surface.
5.5 SUMMARY OF RESULTS

The copper oxide nano particles have been synthesized by aqueous precipitation chemical method. XRD results reported that the monolithic CuO particle of average size 6-7 nm have been produced from the process. Since the particles have the higher cohesive forces, the agglomerates have been formed and verified in the PSD test. It has been suggested to use ultrasonication to deagglomerate the particle. The positively charged nano-CuO particles have shown better results in Zeta potential test and this seems to be appropriate for dispersion within the lubricant. The formation of surfactant coating over the metallic nano-CuO particle have been carried out by oleic acid treatment under sonication. The smooth and slippery surfaces have been formed over the surfactant treated nano-CuO particles which provides a friction free motion between the adjacent layers of the lubricant during shearing.

Nano fluid is a novel lubricant prepared by dispersing nano meter sized solid particle in a conventional lubricant to increase anti-friction and anti-wear performance. The surface modified nano-CuO particles have to be dispersed into lubricant to prepare the nano-fluid. The methodology of dispersion and tribological performance of the nano-fluid have been explained in the following chapter.