Synthesis and Characterization of Copper Nanoparticles, Using Combination of Two Different Sizes of Balls in Wet Ball Milling

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Abstract

The applications of nanoparticles are in biological Nano sensors, optoelectronics, Nano devices, Nano electronics, information storage, catalysis and Nano fluids which differ significantly from size to size of nanoparticles. But controlling the size and preparation in bulk of nanoparticles eco-friendly is interesting.

This paper reports on preparation of Cu nanoparticles by wet milling using a planetary ball mill, taking the combination of two different sizes of balls. The milled powder is characterized using X-ray diffraction (XRD) and particles size analyzer. Samples have taken at 0, 18, 24, 30 and 40 hours after milling the powder. The crystal sizes of milled powder for different milling times are characterized. By increasing the milling time crystal size decreases. After 40 hours average crystal size of milled powder is 21nm.

Keywords: Copper Nanoparticles, Wet Ball Milling, Combination of Balls

1. Introduction
Nano materials can be defined as those materials which have structured components less than 100nm at least in one dimension [1]. One of the most important application of copper nanoparticles is in Nano fluid due to its higher thermal conductivity in comparison to other materials. For synthesis of nanoparticles there are two approaches, namely, ‘Top-down’ and ‘Bottom-up’, available [1]. Top down approach involves breaking of bulk solid into smaller portions. It includes physical methods like attrition or milling, repeated quenching [1]. Bottom-up approach involves condensation of atoms or molecular entities to build up a nanomaterial [1]. It includes chemical methods like reduction of metal salts [1]. But Top-down process is eco-friendly and in Top-down process, Ball Milling is economically in research point of view. The ball-milling is generally used as a mechanical co-grinding of powders, initially different in nature, up to the preparation of a new powder, homogeneous in composition [2]. The milling is done in cylindrical containers called vials and containing balls. The nature of the milling tools can be as diverse as steel, agate, tungsten carbide etc. [2]. The vials are generally filled under an inert atmosphere to avoid side reactions, since the particles are fractured during the milling process and, therefore, new highly reactive surfaces can react with the surrounding gases [2].

Jorge E et al. [3] have prepared iron (Fe) nanoparticles, taking initial size of average 1-10 μm using vibratory mill (SPEX 8000 mixer), ball size 25.4nm, ball to powder ratio 10:1, ethanol added to 0.05 mL/g of iron powder to prevent the oxidations of particles, at 1800 rpm after 30 hours of milling, final sizes got in the range of 2-4 nm. Mohammad Baghar Rahaei et al. [4] have synthesized...
nanoparticles, taking initial powders of Ti (5 µm) and C (50 µm) using Retsch-planetary ball mill PM 400, ball sizes 20 mm (4 ball) and 14 mm (3 ball), ball to powder ratio 10:1, Stearic acid 2wt% to prevent oxidations of particles, at 300 rpm after 8 hours of milling, average size was 103 nm and after 16 hours of milling average size 16.5 nm. O.K. Tan et al. [5] have synthesized nanoparticles, taking initial powders of ZrO₂ (325 mesh) and Fe₂O₃ (<5 µm) using planetary ball mill (Fritsch Pulverisette-5), ball to powder ratio 20:1, at 200 rpm after 20 hours of milling, average size was <10 nm. T.P. Yadav and O.N. Srivastava [6] have prepared cerium (Ce) nanoparticles, taking initial size of average 5 µm using Attritor ball mill, ball to powder ratio 40:1, at 400 rpm after 30 hours of milling, average size was 10 nm. Musa mutlu Can et al. [7] have synthesized iron (Fe) nanoparticles, taking initial size in the range of 20-40 µm using S100, RETSCH planetary ball mill, Distilled water as a wet medium, ball to powder ratio 8:1, at 300 rpm after 24 hours of milling average size was 23.5 nm and after 48 hours of milling, average size was 33.2 nm. G.R Khayati et al. [8] have synthesized nanoparticles, taking initial mixture of Ag₂O (5-40 µm) and C (10-50 µm) powders, using planetary ball mill, ball to powder ratio 20:1 at 450 rpm after 22 hours of milling, average size was 28 nm. Satya V. Ravikumar et al. [9] have prepared copper(Cu) nanoparticles, taking initial size <450 µm, using Fritsch Pulverisette 5/4 planetary ball mill, ball size 10 mm ,ball to powder ratio 10:1, and toluene is used to prevent the oxidations of particles, at 300 rpm after 30 hours of milling, the average size of particles was 34 nm.

Thus literature survey shows that milling parameters are important factors to particles size and economical point of view. So here we have tried to take a best possible milling parameters to synthesize the nanoparticles as smaller size.

2 Experimental Procedure
2.1 Synthesis of copper nanoparticles

Table 1 The specifications for the milling systems.

<table>
<thead>
<tr>
<th>Mill type</th>
<th>Retsch planetary ball mill PM 100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Milling time</td>
<td>40 hours</td>
</tr>
<tr>
<td>Wet milling medium</td>
<td>Toluene Rectified</td>
</tr>
<tr>
<td>Milling speed</td>
<td>250 rpm</td>
</tr>
</tbody>
</table>

Grinding media:
- Ball and jar material: Tungsten carbide
- Ball size: 5 mm and 3 mm
- Ball weight: 540 g
- Ball to powder ratio: 8:1

Jar dimensions:
- Length: 95 mm
- Diameter: 75 mm

Table 2 Specifications of Cu powder

<table>
<thead>
<tr>
<th>Material</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthesized by</td>
<td>Spectrochem PVT.LTD. Mumbai (india)</td>
</tr>
<tr>
<td>Purity</td>
<td>99.7%</td>
</tr>
<tr>
<td>M.W</td>
<td>63.55</td>
</tr>
<tr>
<td>Density</td>
<td>8900kg/m³</td>
</tr>
<tr>
<td>Size</td>
<td>204 nm</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>385 w/m-k</td>
</tr>
<tr>
<td>Other contents</td>
<td>0.3%</td>
</tr>
</tbody>
</table>

Mechanical milling of the micro sized metal powders was carried out in Retsch Planetary Ball Mill PM-100 with Tungsten carbide vials and balls to prepare ultrafine powders. The starting material (see Table 2) used for milling was elemental Copper particles for preparing ultrafine particles of Copper. Cu ultrafine powder was milled in a vial containing 68.75 gram of powder and 550 gram balls for 40 hours. But samples have taken at 0, 18, 24, 30, and 40 hours. The ball to powder weight ratio was 8:1. Milling was conducted at a speed of 250 rpm in wet medium. About 50 ml of toluene was used to prevent undue oxidation and agglomeration of powder. Tungsten carbide balls of 5 mm and 3 mm diameters in the ratio of 4:1 by weight were used for milling. The specifications of the milling systems are given in Table 1.
2.2.2 Nano Zetasizer

The particle size in nanometre range and dispersion stability of ultrafine particles in nanofluid was measured by Nano zetasizer (Model: Nano ZS, Malvern). The sample was prepared by dispersing small amount of ultrafine particles in base fluid with constant ultra-sonication for 30 minutes. Then the sample was kept in a sample holder with the help of syringe and analysed. The sample was analysed using Zetasizer software.

3. Result and Discussion

3.1 X-Ray Diffraction (XRD) Analysis:

Figure 1 shows the XRD patterns of Cu as a function of milling time. With increasing the milling time the peaks of element decrease in intensity and become broader, suggesting reduction in crystallite size. From initial to final crystal sizes are shown in Table 4.

Table 4 Crystallite size.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystallite Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu initial powder</td>
<td>204</td>
</tr>
<tr>
<td>Cu after 18 hours</td>
<td>54</td>
</tr>
<tr>
<td>Cu after 24 hours</td>
<td>38</td>
</tr>
<tr>
<td>Cu after 30 hours</td>
<td>29</td>
</tr>
<tr>
<td>Cu after 40 hours</td>
<td>21</td>
</tr>
</tbody>
</table>

Figure 1 XRD pattern of Cu powder as a function of milling time

The Table 4 and Figure 1 show that as the milling time increases up to 40 hrs., the crystal size of powder decreases due to fracturing of crystal size.
3.2. SEM Analysis:
SEM images show agglomeration of particles. It is due to ultrafine particles agglomerate in the open atmosphere.

![Figure 2 SEM image at 2µm scale](image)

3.3 Nano Zetasizer Analysis
Figure 3 shows the distribution of copper nanoparticles in the fluid (peanut oil) in the average size of 20.40 nm.

![Figure 3 Distribution of copper nanoparticles in the fluid by intensity](image)

Conclusions
Copper nanoparticles are prepared using wet ball milling. After the study of lot of research papers, different parameters like ball size, combination of ball, ball to powder ratio, rpm and medium of milling have optimized in point of view economically and eco-friendly. Some important points regarding the parameters of ball milling are as follows:

If we take size of balls larger, then impact force between the ball and powder will be more but contacting gaps between the balls will also more and thus size of particles after milling will be more. So ball size should be optimized.

If we take equal size of balls then contact gaps will be more but if we take two different sizes of balls then contacting gaps will be less and thus particles size of powder will get smaller. So it is suggested to take combination of balls.

At high ball to powder ratio, the mean free path of the grinding balls decreases and number of collisions per unit time increases. Consequently more energy is transferred to the powder particles resulting faster milling but it may be chance to cold welding of particles due to raise in temperature. So ball to powder ratio should be also optimized.

To reduce the cold welding, we have to use process control agent. This may solid, liquid or gaseous. If this is liquid then milling is called wet milling. The surface active agent adsorbed on particle surface interface with cold welding and lower the surface tension of the material. Thus a reduction in the surface energy results in the use of shorter time to obtain a particular particle size.

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