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Synthesis of Copper Nanoparticles in Aqueous Ambient Using Dismutation Reaction

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The present study has investigated the synthesis of copper nanoparticles via copper dismutation reaction in an aqueous solution and ambient conditions. Copper (II) chloride hydrate ($CuCl_2.2H_2O$), sodium oleate (SO), sodium chloride (NaCl) and ethylene diamine (EN) have been used as copper (I, II) ions source, surfactant, chloride ions supplier and ligand, respectively. Also, an amount of hydrochloric acid (HCl) was used as a multiplier for reaction rate. To perform copper dismutation reaction in the aqueous solution, the copper (I)–chloride complexes were first prepared from $CuCl_2.2H_2O$ at a high concentration of chloride solution. Then, sodium oleate was added to solution as a size modifier. The reaction proceeded through the addition of ethylenediamine as a ligand to the solution. The crystalline structure, size, and morphology of the copper nanoparticles were characterized using X-ray diffraction (XRD), transmission electron microscopy (TEM), and scanning electron microscopy (SEM) techniques, respectively. According to the analyses, the synthesized particles are less than 20 nanometers in size and spherical in shape.

Keywords: Dismutation; Comproportionation; TEM; SEM; Copper nanoparticles

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1. Introduction

Reports on the various methods for synthesis of nanoparticles have shown the growing importance attached to the synthesis of metal nanoparticles in the recent literature. Metal nanoparticles have numerous industrial and scientific applications and are used for qualifying materials and instrument properties, improving human health etc. In this context, copper nanoparticles are commonly applied and many researchers have stressed the emphasis of copper nanoparticles properties, applications and synthesis.

Previous studies on the thermal conductivity and viscosity of copper nanoparticles in fluids have shown an increase in the aforementioned properties versus the normal fluids. The measurements of some Cu suspensions indicate that the nanoparticle diameter, volume fraction, and bulk temperature have a considerable impact on the effective thermal conductivity of these nanofluids (1, 2). It has been reported that copper nanoparticles show good catalytic activity both as homogeneous and heterogeneous catalytic hydroxylation of phenol by hydrogen peroxide to dihydroxybenzenes (3-5). Copper nanopaste and atmospheric-pressure plasma (APP) sintering is highly adoptable for mass production of printable and flexible electronic devices at low cost. The Cu patterns sintered at 250 W for 40 min showed the lowest electrical resistivity of 21.06 μΩ cm, which is around 12.61 times less than the bulk Cu (6). Copper nanoparticles show also antimicrobial activity. In this case, the starch-stabilized copper nanoparticles exhibited interesting antibacterial activity with both gram positive and gram negative bacteria at micro molar concentrations (7). The copper nanoparticles have lethal effects against Escherichia coli, B. subtilis and S. aureus microorganism (8, 9). Moreover, Copper nanoparticles are promising for application in cancer cell battling (10).

Laser ablation, a physical process, is used to synthesize metal (copper and so on) nanoparticles in arbitrary fluids directly (11). Another synthesis method is wire explosion. In this method a thin copper wire is exploded by passing high current through it. In wire explosion technique, average diameter of particles depends on the applied pressure (12). The synthesis of copper nanoparticles using reverse micelles in organic solvents has also been reported. Sodium bis(2-ethylhexyl)sulfosuccinate (AOT), for instance, is an important process to create reverse micelle in this

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procedure (13). Furthermore, Polyol (14), thermal decomposition (15), solvothermal (16) and sonochemical reduction(17) are used to synthesize copper nanoparticles.

In the present study, the synthesis of copper nanoparticles using dismutation reaction has been reported. This process is simple and fast in operation. Some other advantages of this method are: synthesis under mild temperature, no need for protection against oxygen, accessibility and cost efficiency. The reference number should be on the right-top of relevant contents.

2. Experimental

2.1 Materials and instruments

All materials have analytic purity and were purchased from Merck. Applied apparatus are TEM (Zeiss, Germany, model: em10c), XRD (INEL, France, EQuinox), SEM (China, KYKY-EM3200 SN: 0792).

2.2 Experiment

In the first stage of the reaction, 5 g of $CuCl_2.2H_2O$ was dissolved in 25 mL distilled water resulting in a light blue solution due to the formation of $[Cu(H_2O)_6]^{2+}$ complex. Then 4 g of sodium chloride and 0.25 ml hydrochloric acid 37% were added to the solution. Under vigorous stirring and heating, 0.5 g metal copper ($Cu_{(s)}$) was added into the mixture simultaneously. Addition of metallic Cu leads to the comproportionation process between $Cu_{(s)}$ and $Cu^{2+}_{(aq)}$ (reaction 1). After continuous stirring and heating up to 56˚C for about 20 min all $Cu_{(s)}$ is oxidized to Cu(I) ions (copper(I)–Chloride complexes) and disappeared in the reaction pot, as a result of copper comproportionation reaction (reaction1) (18).

$$Cu_{(s)} + Cu^{2+}_{(aq)} - \text{Chloride complexes} \xrightarrow{\text{heat}} 2Cu(I) - \text{ Chloride complexes} \quad (1)$$

The color of solution at this stage, turned to dark-brown due to the formation of copper (I)–chloride complexes. At this time 1 ml of sodium oleate 10% w/w was injected into the reaction dish. After two minutes of stirring, the solution was cooled down to about 40˚C. In the next stage, 7 ml EN was slowly introduced into the solution with constant stirring. Due to the formation of intense complexes between EN and $Cu^{2+}_{(aq)}$ ions dismutation reaction took place through the following reaction (19).

$$2Cu(I) - \text{Chloride complexes} + 2EN \rightarrow Cu_{(S)} + Cu(EN)_2^{2+} \quad (2)$$

Subsequently, copper nanoparticles (nano- $Cu_{(s)}$) were produced and precipitated at the bottom of the reaction flasks. At the end of the process, copper nanoparticles were filtered and washed several times by ethanol and distillated water, respectively. Then, the obtained product was conveniently filtered off, washed with distilled water, dried and stored in ambient conditions.

3. Results and discussion

3.1 Reaction properties

To perform copper dismutation reaction in the aqueous solution Cu^+ ions must be prepared in the solution, firstly. But, Cu^+ ions are not stable in aqueous solutions and instantly oxidized to Cu^{2+} ions (18). Therefore a great value of chloride ions was added into the solution for stabilize Cu^+ ions. In fact the formation of strong complexes between Cu^+ and the chloride ions caused to stabilize Cu^+ ions(20). A problem to directly prepare of Cu^+ is very low solubility of Cu (I) salts in aqueous solutions; i.e. CuI and CuCl are not enough soluble in aqueous medium. So, here $CuCl_2.2H_2O$ was used as a precursor to prepare Cu^+ ions. In an aqueous solutions, the $CuCl_2.2H_2O$ copper(II)– chloride complexes in the presence of sufficient chloride ions may have variety of forms; e.g. $CuCl^{1-}_{3(aq)}$, $CuCl^{2-}_{4(aq)}$, $CuCl^{3-}_{5(aq)}$and $CuCl^{3-}_{6(aq)}$ (21). Most of these complexes were reduced to $Cu^+_{(aq)}$ through the redox reaction (with comproportionation reaction) (18). The $Cu^+_{(aq)}$ ions in chlorine aqueous solution are in the form of copper(I)–chloride complexes ($CuCl_{(aq)}$, $CuCl^-_{2(aq)}$, $CuCl^{2-}_{3\,(aq)}$ and $CuCl^{3-}_4$) (20, 22).Sequentially, upon adding EN, the formation of another strong complex between EN and Cu^{2+} ($Cu(EN)_2$) forced the dismutation reaction (eq.2), which lead to the synthesis of Cu nanoparticles.

As mentioned previously the type of chloride ions source has significant effect on the particles size. For example the particles size is in the micrometer scales when only NaCl was used as chloride ions source (Figure 1). In the other hands, simultaneously using HCl and NaCl leads to production of smaller particles which their size is in the range of 100 to 1000 nm (Figure 2).

The previous experiments showed using NaCl and little amount of HCl are important to reduce the particles size. So, the particle size could be controlled simply by varying the experimental conditions. In the present study using proper proportion of NaCl and HCl as well as sodium oleate caused to considerable decrease in the particles size. Without coating of sodium oleate on the particles, due to the increase in the large ratio of surface area to volume, the attractive force between the nanoparticles will increase, and growth of the nanoparticles will take place.

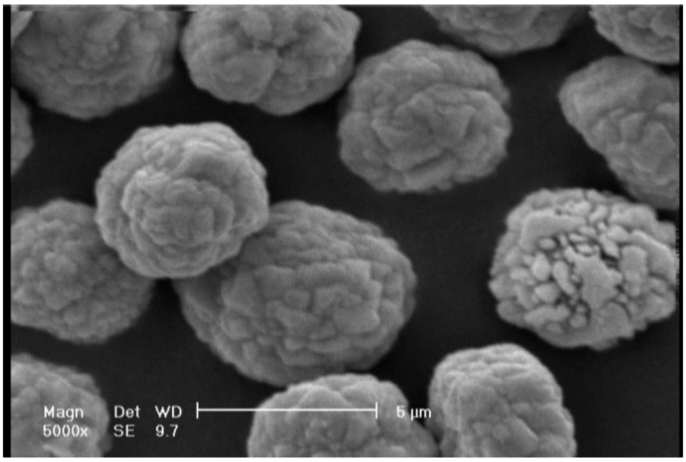

Figure 1. SEM image of particles synthesized by using only NaCl as Chloride ions source.

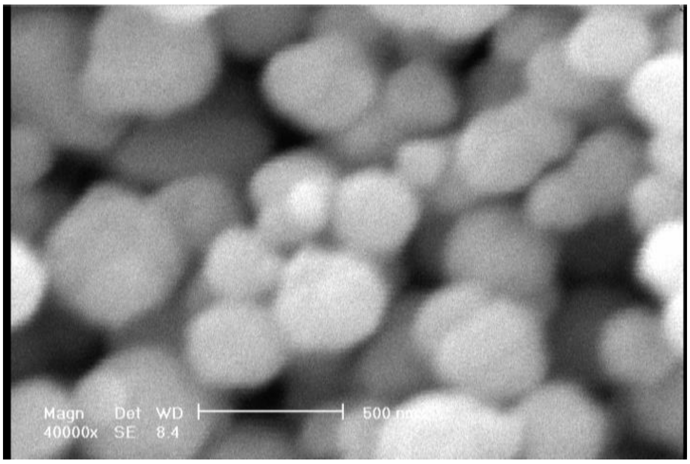

Figure 2. SEM image of particles synthesized by simultaneously using NaCl and HCl as Chloride ions source.

In this synthesis process due to the three side reactions (reaction 3, 4 and 5), (23) which consume the oxygen dissolved in the solution, no care was taken to keep away from oxidation through synthesis of these nano-particles.

$$Cu_{(s)} + \frac{1}{4}O_2 + H^+ + Cl^- \leftrightarrow CuCl_{aq} + \frac{1}{2}H_2O \quad (3)$$

$$Cu_{(s)} + \frac{1}{4}O_2 + H^+ + 2Cl^- \leftrightarrow CuCl_2^{1-} + \frac{1}{2}H_2O \quad (4)$$

$$Cu_{(s)} + \frac{1}{4}O_2 + H^+ + 3Cl^- \leftrightarrow CuCl_3^{2-} + \frac{1}{2}H_2O \quad (5)$$

Also, the color of the solution has changed three times depending on the type of the formed species in the solution. The copper (II)-chloride complexes changed the color of solution to green. However, after the formation of copper (I)–chloride complexes, the color changed into dark brown. Upon the addition of the ethylenediamine into the solution, the violet color appeared due to the $Cu\,(EN)_2$ complex.

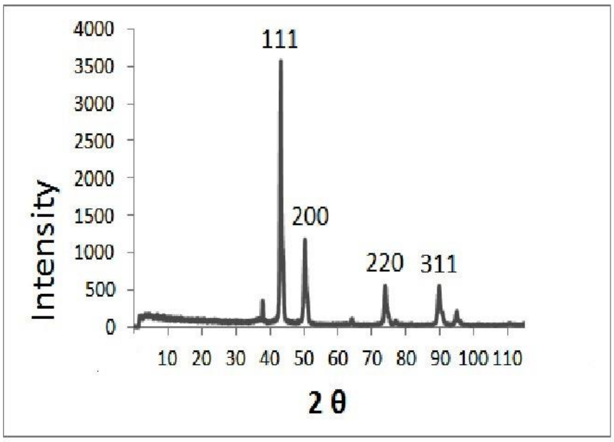

Figure 3. XRD pattern of the sample

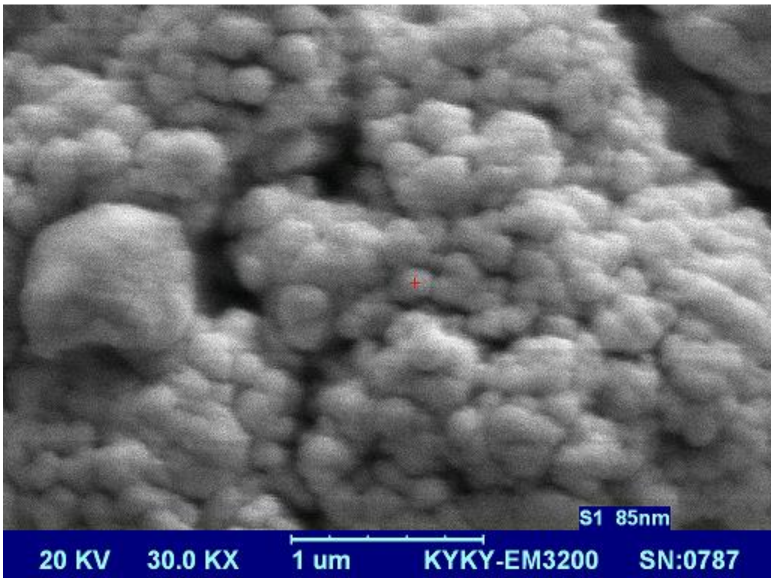

Figure 4. SEM image of the sample.

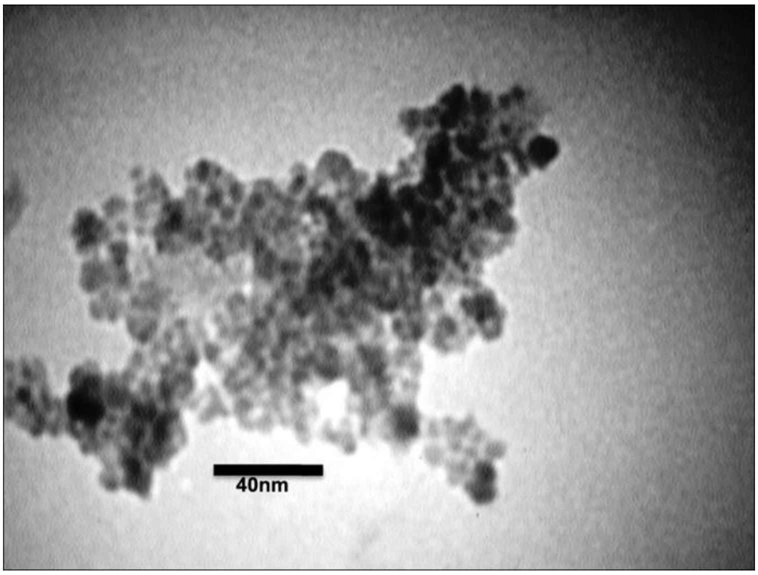

Figure 5.TEM image of the sample

Figure 3 shows the X-ray diffraction pattern recorded for the copper nanoparticles stored for about 30 days in ambient condition. The sharp peaks of the XRD pattern indicate the crystalline structure. The peaks at 43.192°, 50.2430°, 74.9064° and 89.6530° correspond to the Miller indices (111), (200), (220) and (311), respectively, which prove the face centered cubic (fcc) structure of the copper. It is clear from XRD pattern of the Cu particles which there is no sign for presence of other forms of copper compound like copper oxide (I, II).

Figure 4 shows the SEM image of copper nanoparticles. It is clear from this image that the particles are in agglomerated form. Due to the agglomeration the particles look much bigger than their real size. The TEM image of the particles is presented in Figure 5. This image shows the size of the spherical particles is less than 20 nm.

4. Conclusions

In the present study, Cu nanoparticles have been synthesized from copper dismutation reaction as a chemical process. Copper comproportionation occurred before dismutation in the reaction dish. As the results show, copper (II) cations in an acidic aqueous phase were converted to the copper (I) cations via electron exchange between $\mathrm{Cu}^{2+}_{(aq)}$ and $\mathrm{Cu}_{(s)}$. After preparation of copper (I)–chloride complexes ions, they were transformed to $\mathrm{Cu(EN)_2}$ complexes and Cu nanoparticles by addition of EN as a basic ligand. The proposed method offers a simple and non-expensive approach to produce the metallic Cu nanoparticles in large-scale fabrication in aqueous media. The XRD and TEM analyses shows that copper nanoparticles have FCC structure and are less than 20 nm in diameter. The method is also promising for the synthesis of other multi valance metal nanoparticles.

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