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Research Article

Synthesis and Characterization of Copper Nanoparticles by Chemical Reduction Method

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Abstract: This research paper is aimed to prepare copper nanoparticles easily and inexpensively at low temperature without the use of inert atmosphere. Copper nanoparticles have been synthesized by using chemical reduction method, this is a simple and effective. In this method, copper sulfate pentahydrate is used as a precursor; starch is used as a capping agent; ascorbic acid is used as a reducing agent; sodium hydroxide is used as a reagent to make reduction reaction faster and control pH of the solution. The whole procedure is taken at the boiling temperature using hot plate, and needs to be stirred continuously at this temperature. Once the reaction in the solution has completed for some periods of time, stop heating and let the solution cool and settle for a night to get copper nanoparticles precipitates which will be collected by filtration later. The outcomes of the particles are tested by using XRD (X-ray diffraction) and SEM (Scanning Electron Microscope) to know their particle sizes, composition and morphology. Copper nanoparticles have been fabricated by chemical reduction method which have diameter range from 14nm to 55nm. Structural analysis, the resulted diameter size revealed the face center cubic (FCC) Structure of copper nanoparticles.
Keywords: Copper nanoparticles, chemical reduction method, copper sulfate pentahydrate, XRD and SEM.

I. Introduction

Nanoparticles are particles having size ranges of 1-100nm with a surrounding interfacial layer, which is an integral part of nanoscale matter, affecting all of its properties. The interfacial nanoparticles consist of ions, inorganic and organic molecules. Organic molecules coating inorganic nanoparticles are known as stabilizers, capping and surface ligands, or passivating agents [1].

In nanotechnology, ultrafine particles are the same as nanoparticles between 1-100nm size ranges; fine particles are between 100-2,500nm; coarse particles are of 2,500 and 10,000 size ranges [3]. Nanoscale materials have unique optical, electronic, or mechanical properties [7]. Many materials such as gold, silver, magnesium, titanium and copper can be prepared into nanoscale particles by using various methods. Among them, copper nanoparticles are popular due to their low-cost and unique properties [4].

Copper nanoparticles display unique characteristics including catalytic and antifungal/antibacterial activities that are not observed in commercial copper. First of all, copper nanoparticles demonstrate a very strong catalytic activity, a property that can be attributed to their large catalytic surface area. With the small size and great porosity, the nanoparticles are able to achieve a higher reaction yield and a shorter reaction time when utilized as reagents in organic and organometallic synthesis [2].

A copper nanoparticle is a copper based particle 1 to 100nm in size [8]. Copper nanoparticles received much attention due to its high electrical conductivity, high melting point, low electrochemical migration behavior and low cost. Copper is a Block D, Period 4 element, which other colors [5]. Copper nanoparticles are very popular in biomedical field and act as antibacterial agent than any other nanomaterials. The antimicrobial activity is induced by their close interaction with microbial membranes and their metal ions released in solutions [10].

Figure 1. Copper Nanoparticles [6]

II. Materials and Methods

2.1 Samples Collection

Raw materials that are used during the whole procedure are copper sulfate pentahydrate ($CuSO_4.5H_2O$), starch $(C_6H_{10}O_5)_n$, ascorbic acid ($C_6H_8O_6$) and sodium hydroxide (NaOH).

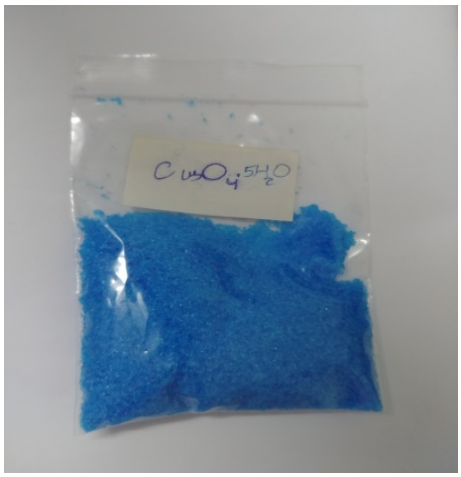

Figure 2. Copper Sulfate Pentahydrate

2.2 Chemical Reduction Method

Although there are numerous methods to prepare copper nanoparticles, chemical reduction method is popular and commonly used since the earlier centuries due to its effortless procedure. Chemical reduction method and microemulsion route were used for the first time to synthesize gold metal, and they have been used to reduce other less noble metals such as copper by using mainly copper salts (sulfates, nitrates, and chlorides) and reducing agents (sodium borohydride, isopropyl alcohol, ascorbic acid, and hydrazine) and, sometimes, by using stabilizing agents (polyvinyl pyrrolidone and polyethylene glycol). Green chemical

synthesis by using novel Ginkgo biloba Linn leaves is a successful option to obtain stable spherical copper nanoparticles about 15–20nm [10].

In the reduction method Cu (II) salts can be reduced by a variety of reducing agents, for instance: hydrazine, ascorbic acid, hypophosphite or sodium borohydride and polyol. These reducing agents are used to produce copper nanoparticles with controlled size and morphology.

2.3 Synthesis and Characterization of Copper Nanoparticles

The four-step preparation scheme for copper nanoparticles starts with dissolving copper (II) sulfate pentahydrate salt, $CuSO_4.5H_2O$ (0.1M), in deionized water to obtain a blue solution. Next, starch (1.2%) is dissolved in boiling water and added to the aqueous solution containing the copper salt while vigorously stirring. In this step, the solution changed from clear blue to deep blue. In the third step, ascorbic acid (0.2M) is dissolved in water and added to the synthesis solution. Finally, sodium hydroxide (1M) solution is prepared and added to the solution under continuous rapid stirring. Color change occurred in the aqueous phase from deep blue to green. The appearance of this color indicated that the reduction reaction has started. The mixture was further stirred rapidly for around 2 hours at 80^oC, to allow the reaction to complete. After heating the solution, the solution is allowed to cool and settle overnight. Then, the precipitates are filtered by decantation, centrifuged and washed with deionized water and ethanol for three times. The resulted particles are dried at room temperature and stored in a glass bottle.

2.3.1 Solutions Mixing and Stirring Condition

Firstly, 120ml of 1.2% starch solution of cloudy color which is put in a burette is slowly added into 250ml of 0.1M copper sulfate solution of clear blue color which is put in a beaker of 1000ml. These first two solutions are needed to stir rapidly and thoroughly by using overhead machine with 900rpm at least; so that starch can be able to capture the small crystals of copper particles which are resulted from dissociation in the solution as it acts as a capping agent in the procedure. And then, 50ml of 0.2M ascorbic acid (VC) solution of colorless which is put in a burette is slowly added into the pre-mixed solution of copper sulfate and starch in a manner of one droplet addition in a second so that it can reduce the particle size well in the solution as it is already used as a reducing agent. All these solution have to be stirred at 900rpm or a bit more.

The solution of these three reagents needs to be stirred vigorously by using overhead machine at least 900rpm. The next step is that 30ml of 1M sodium hydroxide (NaOH) solution is added by drop-wise manner into the above solution under continuously stirring and heating at 80^oC for 2 hours. During the procedure, the solution color slowly changes from blue to green of final solution. It can be obvious that the solution color changes whenever sodium hydroxide solution is added into it. After the reaction has completed, let the solution cool at room temperature and settle for a night in order to get the precipitates.

2.3.2 Particles Separation and Storage Condition

At first, after settling, solution has to be filtrated by decantation, and then it has to be centrifuged with 9,000rpm for 30 minutes to separate particles and liquid by layer. The liquid needs to be test with pH meter or paper whether it reaches neutral level or not. Later, the particles under the test tube is pulled out by adding small amount of deionized water and washing needs to be done for 30 minutes without any heat. When the solution reaches neutral level or pH 7, the last washing with ethanol is done to remove impurities in the solution.

After filtration, there is moisture in the precipitates, and so, they have to be dried in a desiccator at room temperature. After drying for a few days, the dry particles are stored in an air tight bottle to avoid oxidation because copper nanoparticles tend to oxides easily even at room temperature.

III. Results and Discussion

Typical copper deposition is obtained in a 0.1M copper sulphate solution by reduction process. It can be found that copper starts to deposit after the reaction in the solution has completed at low temperature. The rate of growth is controlled by the addition of reducing agent like ascorbic acid, and the stability of copper particles is controlled by the addition of capping agent like starch. The formation of particle deposits is facilitated by adding each solution of reagents into the precursor solution and stirring them vigorously at lower temperature.

The X-ray diffraction pattern of the copper powder is shown in figure 3. The signature of copper was observed in peaks that are very sharp due to the high nanocrystalline nature of copper.

In figure 3, the peaks in red lines show copper nanoparticles presence and the peaks in blue lines describe other oxide minerals. The three distinct peaks 2θ values 43.2, 51.3, and 75.2 deg corresponding to the planes of (111), (200), and (220) are, observed according to (JCPDS, copper file No. 04–0836). This confirmed that the resultant particles were (FCC) Cu and average particle size of less than 25nm is obtained from the following equations.

In this study, for particle size calculation, considering the peak at degrees, average particle size has been estimated by using Debye-Scherrer formula;

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

Where 'λ' is wave length of X-Ray (0.1541 nm), 'β' is FWHM (full width at half maximum), 'θ' is the diffraction angle and 'D' is particle diameter size. The calculated particle size details are in Table 1.

For calculation of d-spacing, Bragg's Law is used to calculate the value of d (the interplanar spacing between the atoms) $2d\sin\theta = n\lambda$

$$d = \frac{\lambda}{2\sin\theta} \quad (n=1)$$

Wavelength λ = 1.5418Å is for copper (Cu). Simple peak indexing can be calculated from theta values. Table 2 show the calculation of d-spacing in detail. Table 3 shows the comparison of the experimental and theoretical results. The calculation of particle sizes is shown in Table 4.

Table 1. Simple Peak Indexing

Peak Position (2θ)	1000x $Sin^2\theta$	1000x $Sin^2\theta$ /51	Reflection	Remarks
43.2	136	3	(1 1 1)	$1^2+1^2+1^2=3$
51.3	187	4	(2 0 0)	$2^2+0^2+0^2=4$
75.2	372	8	(2 2 0)	$2^3+2^2+0^2=8$

Table 2. Peak Indexing from Interplanar Spacing

2θ	D	$1000/d^2$	$(1000/d^2) / 77.32$	hkl
43.2	2.09	228.93	2.96	111
51.3	1.78	315.62	4.08	200
75.2	1.26	629.88	8.15	220

Table 3. Experimental and Standard Diffraction Angles of Copper Specimen

Experimental diffraction angle [2θ in degrees]	Standard diffraction angle [2θ in degrees] JCPDS Copper: 04-0836
43.2	43.297
51.3	50.433
75.2	74.130

Table 4. The Grain Size of Copper Nanopowder

2θ of the intense peak (deg)	hkl	θ of the intense peak (deg)	FWHM of intense peak (β) radians	Size of the particle (D) nm	d-spacing nm
43.2	(1 1 1)	21.6	0.0059	25.265	0.209
51.3	(2 0 0)	25.65	0.0066	23.296	0.178
75.2	(2 2 0)	37.6	0.0070	24.991	0.126

SEM analysis is used to study the surface morphology of synthesized nanoparticles. Surface morphology of the copper nanoparticles are described in figure 4.

SEM images demonstrate that the prepared copper and some oxide nanoparticles are spherical shape. Depending on temperature arrangements that are used during the whole procedure, the morphologies of resulted copper nanoparticles will be found to be changed in the following figures.

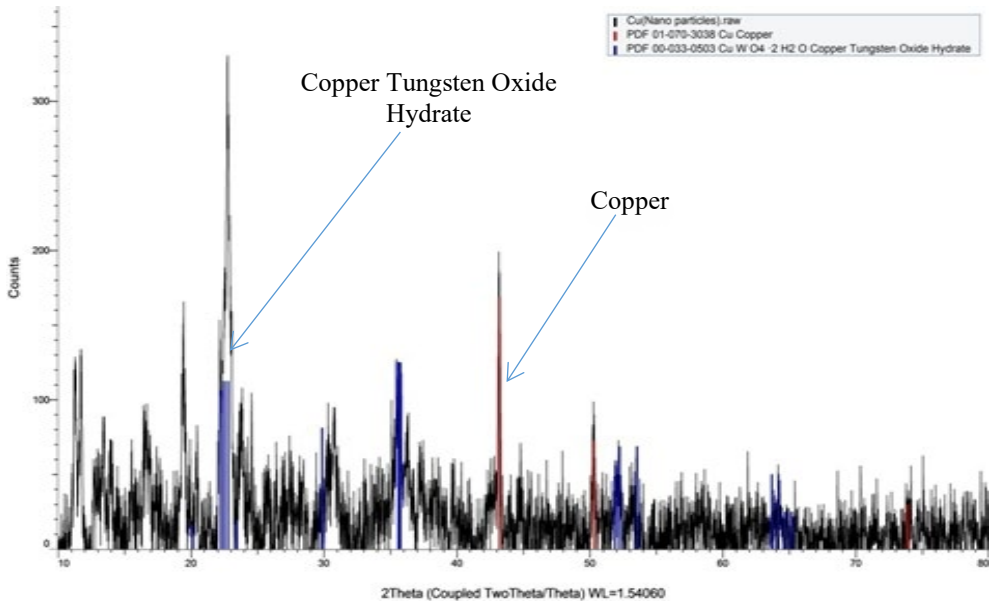

Figure 3. XRD Characterization of Copper and Other Oxide Mineral

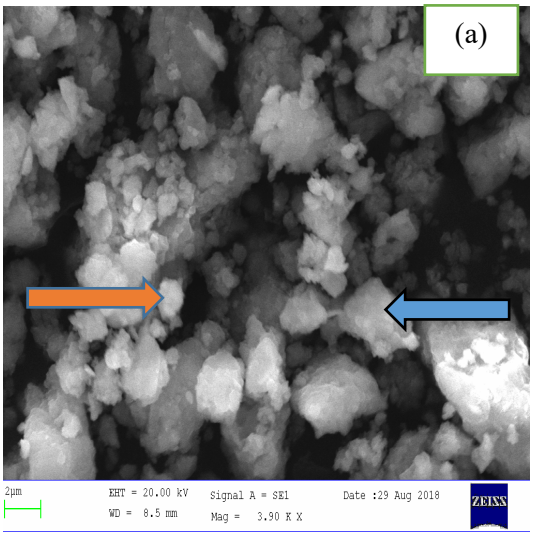

Figure 4 (a). SEM Image of Copper Powder

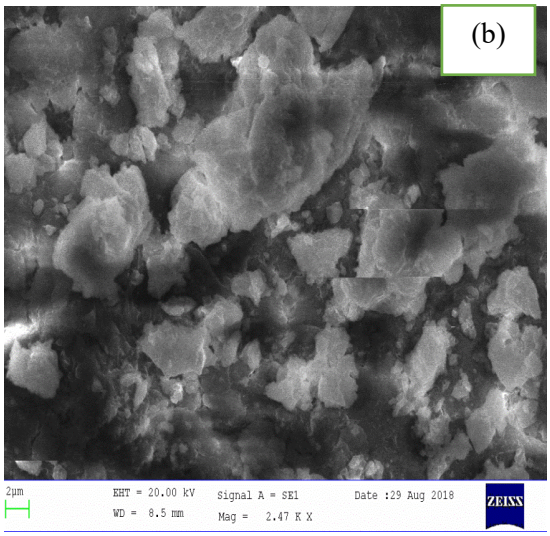

Figure 4 (b). SEM Image of Copper Powder

The image (a) describes SEM image of copper and other oxide minerals that are performed at 80°C and are spherical in shape. Copper oxides minerals are described by the red arrow and copper nanoparticles are described by the blue arrow. The image (b) describes SEM image of oxide minerals that are performed above 80°C and the particles presence are mostly copper oxides which are in flake like structure.

IV Conclusion

In this study work, using precursor salt like copper sulfate pentahydrate, capping agent like starch, reducing agent like ascorbic acid and pH controller like sodium hydroxide during the whole procedure. XRD and SEM are used to find out the characteristics of the resulted copper nanoparticles. XRD analysis shows that copper nanoparticles have FCC structure and are less than 25nm in diameter. SEM analysis shows morphology of copper nanoparticles. According to SEM images, copper nanoparticles are found as spherical in shape. In this paper, a simple, fast and effective chemical reduction method to synthesize copper nanoparticles is introduced. This method provides a clean, eco-friendly and nontoxic and efficient route for the synthesis of nanoparticles with tunable particle size, at room temperature conditions without using any additive. Copper nanoparticles are very popular in biomedical science and various medical applications. So, their uses can be more advantageous in these applications and they can give more benefits.

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Conflicts of interest: The authors declare no conflicts of interest.

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