Ultrasonic-Assisted Chemical Reduction Synthesis and Structural Characterization of Copper Nanoparticles

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Abstract. Copper nanoparticles, due to their special properties, small dimensions and low-cost preparation, have many potential applications such as in optical, electronics, catalysis, sensors, antibacterial agents. In this study, copper nanoparticles were synthesized by chemical reduction method with different conditions in order to investigate the optimum conditions which gave the smallest (particle diameter) dimensions. The synthesis step used copper (II) acetate salt as precursor, ascorbic acid as reducing agent, glycerin and polyvinylpyrrolidone (PVP) as protector and stabilizer. The assistance of ultrasonic was were considered as the significant factor affecting the size of the synthesized particles. The results showed that the copper nanoparticles have been successfully synthesized with the diameter as small as 20-40 nm and the conditions of ultrasonic waves were 48 kHz of frequency, 20 minutes of treated time and 65-70 ºC of temperature. The synthesized copper nanoparticles were characterized by optical absorption spectrum, scanning electron microscopy (SEM), and Fourier Transform Infrared Spectrometry.

INTRODUCTION

Recently, nanoparticles are of great interest for both academia and industry due to their novel physicochemical, magnetic, and optoelectronic properties that are governed by their size, shape, and size distribution [1]. Copper is a 3d transition metal and has some interesting physical and chemical properties such as electrical conductivity, catalytic behavior, good compatibility and antibacterial potency [2]. Therefore, metallic copper nanoparticles are striking materials primarily due to their unique properties, abundancy and low cost compare to other metallic nanomaterials such as gold and silver [3]. Presently there are several approaches to the synthesis of nanoparticles such as physical, chemical and biological methods. Laser ablation [4], vacuum vapor deposition [5], pulsed wire discharge [6] and mechanical milling [7] are examples of physical approaches while thermal decomposition [8], chemical reduction [9] and polyol synthesis [10] are some chemical techniques. Among these processes, chemical reduction is usually preferred, because this method is easy, cost-effective and efficient, and it can control the shape and size of the product obtained by tuning various synthesized factors, for instance the molar ratio of the stabilizer with the precursor salt and the fraction of reducing agent with the precursor salt. In addition, the utilization of ultrasound for materials synthesis has been extensively examined over many years, and is now positioned as one of the most powerful tools in nanostructured materials synthesis [11]. However, there is only a few studies applying the ultrasonic waves in copper nanoparticle synthesis. In this study, a chemical reduction method with the assistance of ultrasonic waves has been proposed to fabricate copper nanoparticles. Copper (II) acetate salt was used as copper precursor. Ascorbic acid, glycerin and polyvinylpyrrolidone work as reducing and protecting agent, which makes the process economical, nontoxic and environment friendly.

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EXPERIMENTS

Reagents

Copper (II) acetate salt ($Cu(CH_3COO)_2.H_2O$) 99.9% from Guangdong Guanghua Sci-Tech JHD (China), glycerin 99.0% from China, ascorbic acid 99.7% from Prolabo (France), polyvinylpyrrolidone (PVP K30) 99.5% from CDH (India) were used for the synthesis of nanoparticle. All of the chemicals were analytical grade and used as purchased without further purification. Deionized water was used throughout the experiments.

Synthesis of Copper Nanoparticles

Copper acetate solution was prepared by dissolving in glycerin and polyvinylpyrrolidone at different mole ratio. The solution was stirred for 30 minutes at 60 – 70 °C. The ascorbic acid solution was prepared by dissolving in glycerin and stirring for 30 minutes.

For the preparation of copper nanoparticles solution, the ascorbic acid was added gently into the copper acetate solution while stirring. The reduction reaction was carried out under ultrasonic wave (Digital Ultrasonic Units TP 680 DH) at different frequency and time.

Characterization

Synthesized samples were studied the optical spectrum using UV-vis absorption spectroscopy (GENESYS 10S UV-Vis) with the wavelength range from 400 nm to 750 nm. Scanning electron microscope (SEM) was used to study the particle size and morphology of the product obtained. Finally, FT-IR spectra (Brucker Tensor 27) was recorded between 400 – 4000 cm^{-1} for the colloidal formation.

RESULTS

Optical Characterization

In the small metal nanoparticles, there is the surface plasmon resonance (SPR) effect which is the absorption of visible electromagnetic waves by the collective oscillation of conduction electrons at the surface [12]. Then, with a simple UV-visible spectrometer, the tracing for the presence of metal nanoparticles becomes possible.

Before using the ultrasonic, the yellow and orange solutions did not show plasmon resonance (Fig. 1a). Upon the effect of ultrasonic waves, a quick increase in the absorbance at low wavelengths occurred that probably indicated the onset of particle formation (light red). The plasmon resonance of the copper nanoparticles appeared at 562 nm when the solution turned red (Fig. 1b). The reaction was allowed to proceed in air. After the end of synthesis, the solution was kept under ambient atmosphere and the oxidation was qualitatively monitored with time by observation its color change (Fig. 1c).

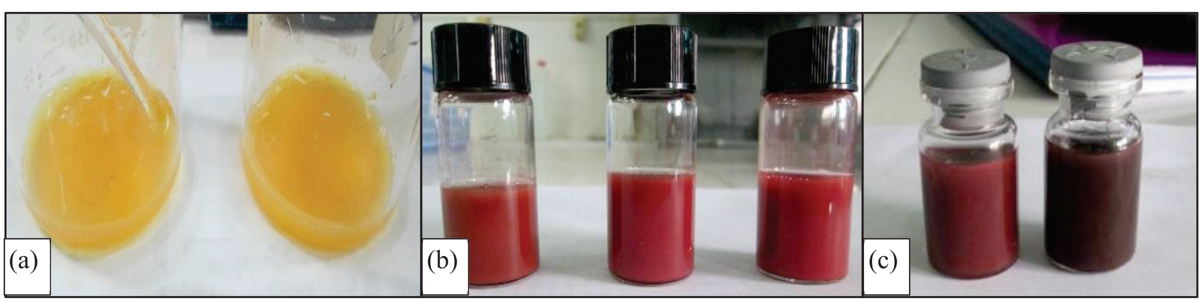

FIGURE 1. The copper particle colloid at different conditions

(a) and (b) Reduction without and with ultrasonic treatment (c) The color change by oxidation in ambient atmosphere

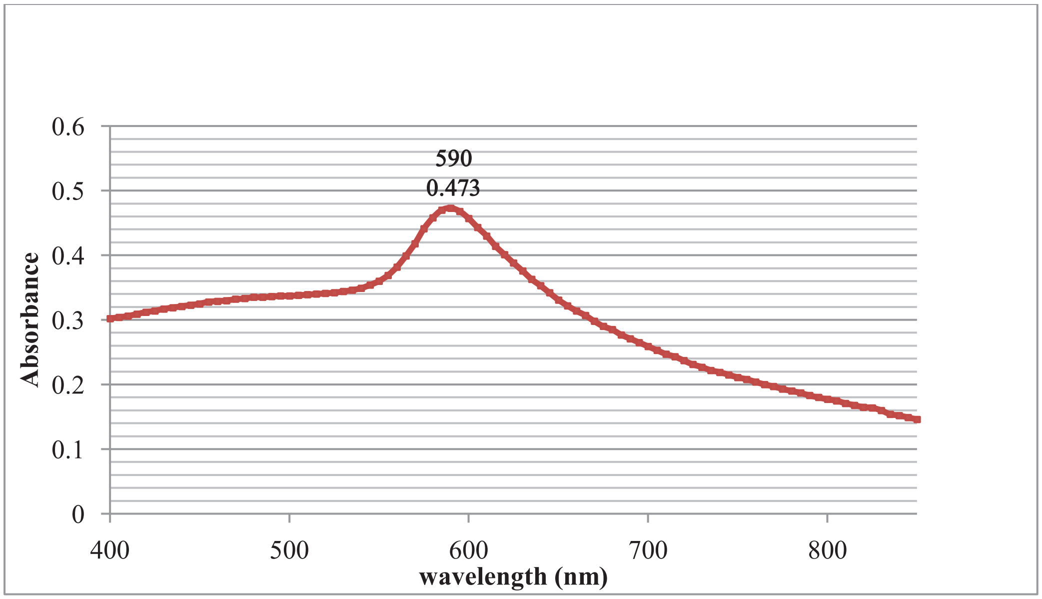

FIGURE 2. The UV-Vis spectrum of obtained sample

The frequency (the absorption maxima or color) and intensity of SPR absorption bands are characteristic of the type of material and are highly sensitive to the size and shape of the nanostructures as well as to their surrounding environments [13, 14]. UV-vis spectra of copper nanoparticles synthesis solution show the peak at 590± 5 nm (Fig. 2) which indicates the formation of copper nanoparticles.

Effect of ultrasonic frequency

The effect of ultrasonic frequency was studied with 3 levels of frequency (40 kHz, 48 kHz and 56 kHz). This parameter is supposed to demonstrate for the energy needed to prevent the copper nanoparticles agglomerating. The samples were prepared as the procedure described above and only variable being the duration of ultrasonic treatment. The results are shown in Fig. 3.

It can be obtained that the results reflected the strongly effect of ultrasonic frequency parameter on the form of copper nanoparticles. The middle frequency might be the suitable value in this case. The absorption was low at 40 kHz and increased when the frequency increased to 48 kHz. However, when continued to increase the frequency to 56 kHz, the absorption decreased. The explanation could be based on the using the lower energy made the lower effect on the chemical reaction rate and also failing to keep the particles far away. In the contrast, the higher frequency could make the higher energy and then the particles could gather to agglomerate. Therefore, the ultrasonic frequency was kept at 48 kHz when study other effects on the copper nanoparticle formation.

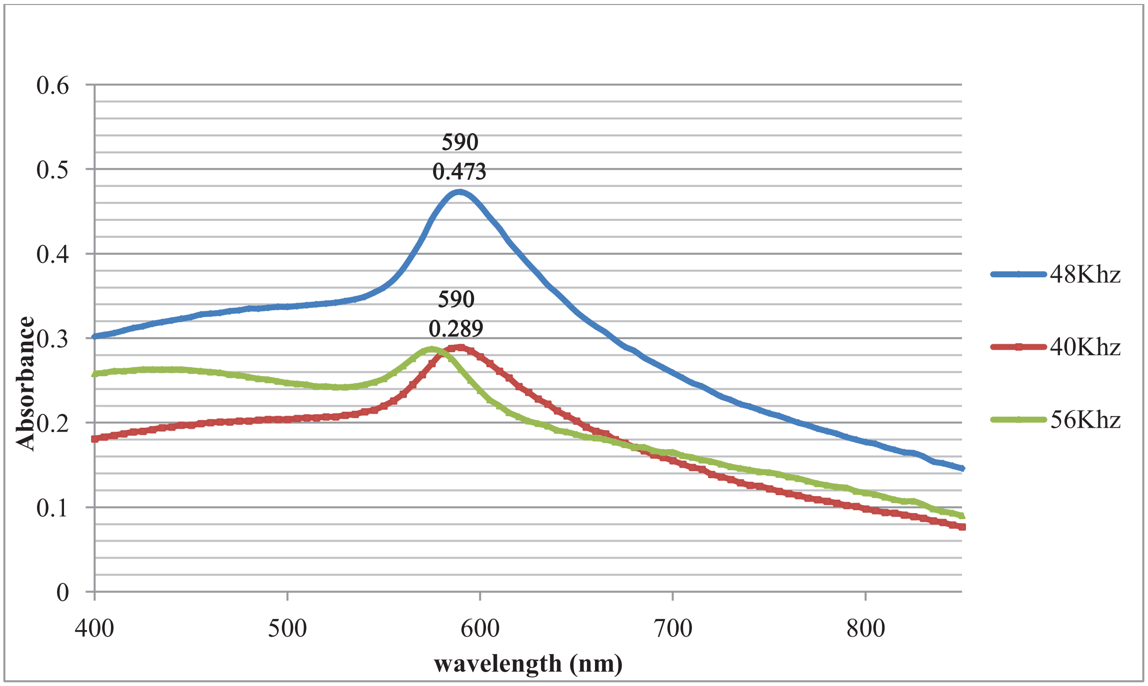

FIGURE 3. The UV-Vis spectra of samples obtained at different ultrasonic frequency

Effect of ultrasonic treatment time

When study the effect of the ultrasonic treatment time, the other parameters were kept at constant such as the ultrasonic frequency is 48 kHz, the molar ratio of acid ascorbic and copper ion is 5, the molar ratio of PVP and copper ion is 5. The treatment time was varied from 0 to 30 minutes with the step of 10 minutes and the results are shown in TABLE 1 and Fig. 4.

The results suggested that the ultrasonic treatment is the important parameter in nanoparticles synthesis. In the sample without the ultrasonic treatment, the nanoparticles could not be appeared. Then, starting the ultrasonic treatment at 10 minutes, and increased the duration time to 20 minutes, 30 minutes, the intensities of the absorption were varied. As can be seen from the Figure 4, at lower time treatment, it was not enough energy to complete the reaction and even if the copper created, the sizes of particles were not at nanosize. In addition, if the treatment time is too long, the copper particles were easily oxidized which was indicated by the darker color of solution.

Therefore, the treatment time is kept at 20 minutes when investigating another effect on the copper nanoparticle formation.

TABLE 1. The effect of ultrasonic treatment time on the absorbance of obtained colloid at 590 nm wavelength

Treatment time, min	Absorbance, a.u.
0	0.026
10	0.379
20	0.473
30	0.407

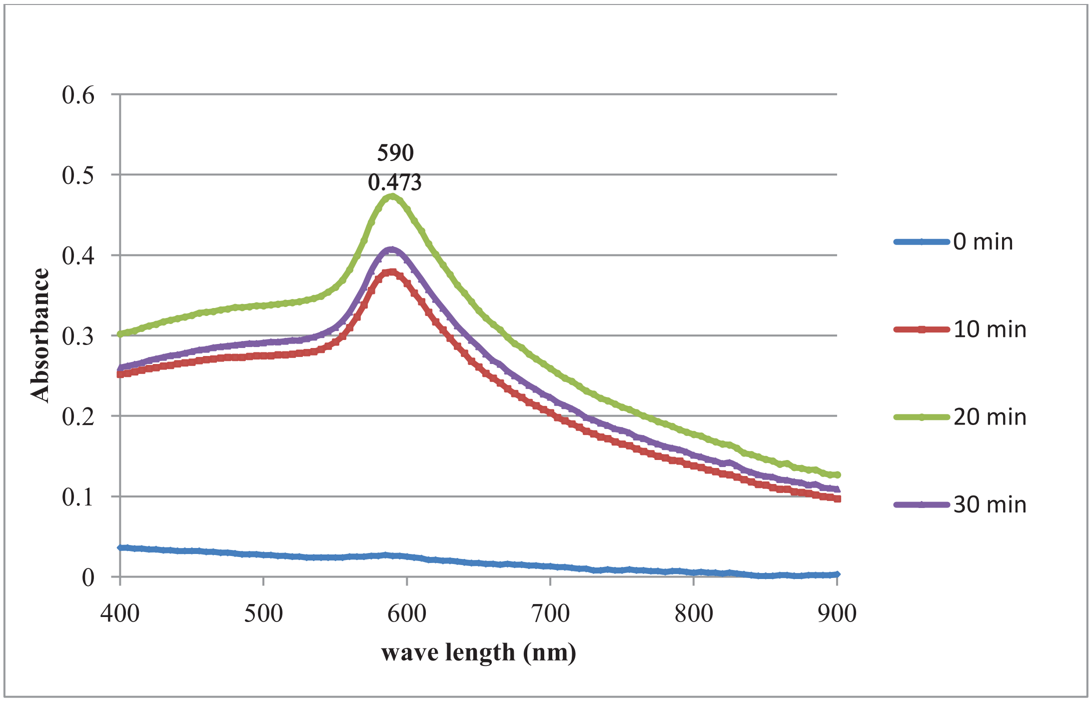

FIGURE 4. The UV-Vis spectra of samples obtained at different ultrasonic treatment time

SEM and FT-IR study

The sample was analyzed using scanning electron microscope to study the morphology and the particle size and the result is shown in Fig. 5. From the result, it can be obtained that the particles are separated and have uniform in size. The particle size is ranging from 20 nm to 40 nm. The 'background material' in the SEM image might be the protectors, PVP and glycerin.

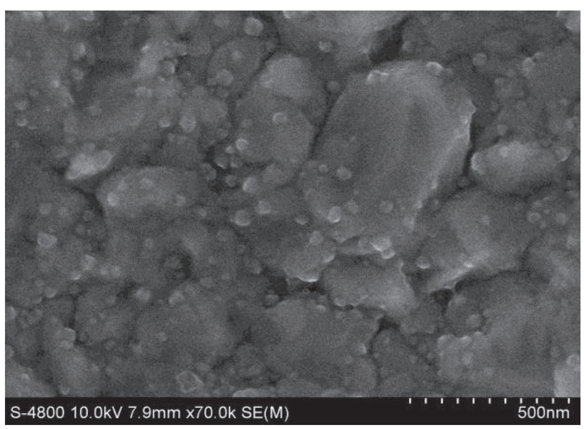

FIGURE 5. SEM images of synthesis nanoparticle copper colloid

FTIR measurement was carried out to identify the possible molecules responsible for capping and reducing agent for the copper nanoparticles synthesized. The result from Fig. 6. shows that the broad bands observed at around 3480 cm^{-1} and 617 cm^{-1} illustrates the stretching frequency of hydroxyl group (OH group) present in the surface of the copper nanoparticle.

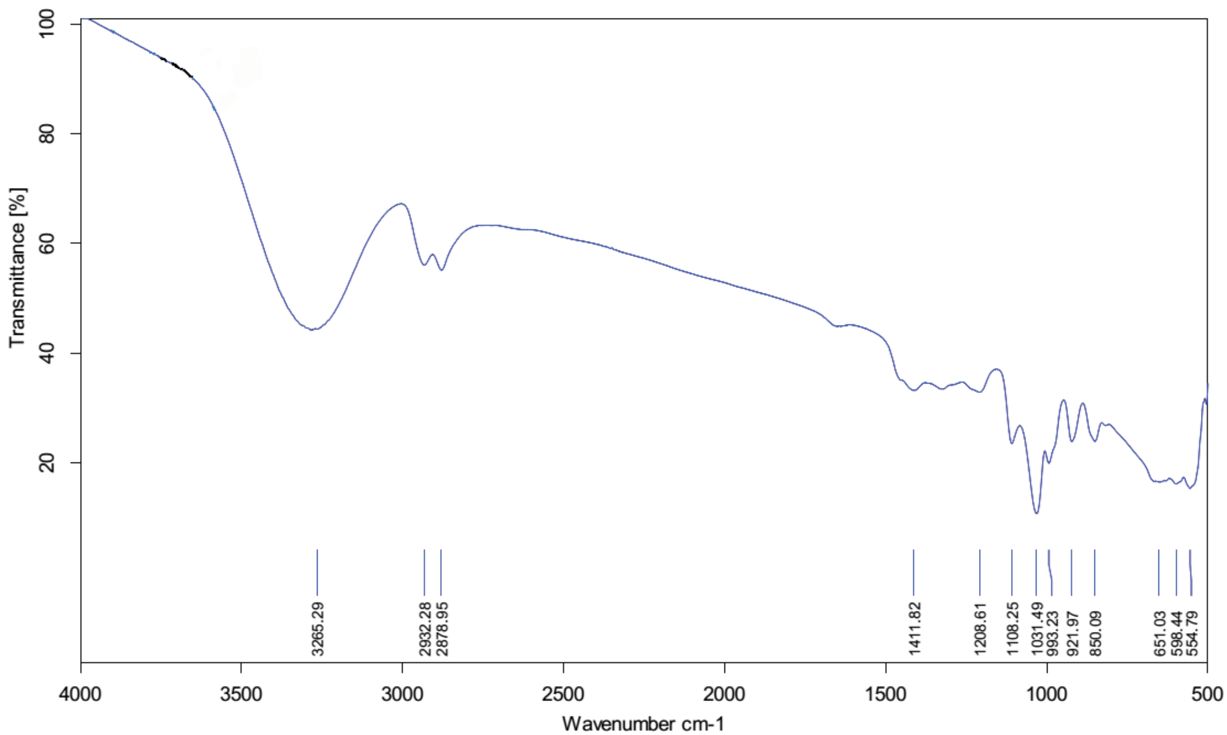

FIGURE 6. FTIR spectra of copper nanoparticles

CONSLUSIONS

The study proposed a simple and promising method to fabricate elemental copper nanoparticles by means of ultrasonic assisted chemical reduction. The optical characterization confirmed the formation of copper nanoparticle by the plasmon resonance at 590 nm. The SEM analysis suggested that the particle size is uniform and in the range from 20 nm to 40 nm. The ultrasonic treatment plays an importance role in the synthesis due to the significant reduction in reaction time to around 20 minutes. The result suggests that the appropriate treatment of ultrasonic wave is at frequency of 48 kHz and processing time of 20 minutes.

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