The use of biodegradable polymers for the stabilization of copper nanoparticles synthesized by chemical reduction method

ALI OLAD*, MAHNAZ ALIPOUR and RAHIMEH NOSRATI

Polymer Composite Research Laboratory, Department of Applied Chemistry, Faculty of Chemistry, University of Tabriz, 5166614776 Tabriz, Iran

*Author for correspondence (a.olad@yahoo.com)

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Abstract. Copper nanoparticles were synthesized by a convenient and rapid chemical reduction method in ambient condition using $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ as a precursor, hydrazine hydrate as reducing agent and deionized water as solvent. The product was characterized by X-ray diffraction (XRD) patterns, field emission scanning electron microscopy, Fourier transform infrared spectroscopy and UV–Vis spectroscopy. However, agglomerated copper nanoparticles were obtained by this chemical reduction method. Hence, the effects of three polymers of polyvinyl pyrrolidone, polyethylene glycol (PEG) and starch as stabilizers on the size and size distribution of Cu nanoparticles were investigated. According to the results, smallest copper nanoparticles (30–50 nm) with a narrow size distribution were obtained using PEG as the stabilizing polymer. Zero-valent copper nanoparticles with high purity were obtained by this method and there was no peak related to the oxidized impurities such as CuO and Cu_2O in the XRD and UV–Vis studies, both in the presence and in the absence of stabilizer. On the other hand, by this method, zero-valent copper nanoparticles were obtained in the absence of any anti-oxidant agent and any inert gas flow. The effects of synthesis parameters including initial concentration of precursor, polymer concentration and the reaction temperature on the size and size distribution of copper nanoparticles were investigated using the UV–Vis analysis to determine the optimum synthesis conditions.

Keywords. Copper nanoparticle; chemical reduction; agglomeration; stabilizer; polymer.

1. Introduction

During recent decades, metallic nanoparticles have gained special attention because of their unique properties and specific applications, which are usually different from those of their bulk materials [1–3]. Among various metal nanoparticles, copper nanoparticles have attracted wide attention for their low cost and many great physical and chemical attributes such as high electrical conductivity and chemical activity [4,5]. One of the important features of copper nanoparticles is their localized surface plasmon resonance peaks in the visible light region that are used for their optical characterization [6]. Copper nanoparticles have an important and a fundamental role in many applications in various fields, for example in catalysts, conductive inks, irreversible humidity indicators and electronic systems [7–10]. There are numerous recognized methods for the synthesis of Cu nanoparticles, such as reverse micelles, laser irradiation method, microemulsion techniques, electrolysis, sonochemical reduction and chemical reduction [11–20]. Among the various techniques, chemical reduction method is the most commonly used route for the synthesis of Cu nanoparticles because of its superior features such as an easy process, high efficiency, high quality products, simple and finite equipment and simple control method [21,22].

Since the copper oxide phases are more stable than copper metal phases, the copper nanoparticles, synthesized in ambient condition, naturally have surface oxide layers. Moreover, in the absence of a suitable stabilizer, copper nanoparticles tend to aggregate after the formation. The use of some protective agents, such as organic ligands and polymers, could prevent these problems [23–25].

Starch, polyethylene glycol (PEG) and polyvinyl pyrrolidone (PVP) are three polymers whose stabilizing behaviour role has been proved [26–28]. Starch is the most commonly used carbohydrate consisting of a large number of glucose units linked by glycosidic bonds. Starch has unique properties such as biodegradability, low cost and renewability and can be regenerated from carbon dioxide and water by photosynthesis in plants. Stabilization of copper nanoparticles occurs through the interactions between Cu nanoparticles and available free hydroxyl groups of starch particles [29]. PEG, $\text{HO}-(\text{CH}_2\text{CH}_2\text{O})_n-\text{H}$, is a hydrophilic polymer, easily soluble in water and many organic solvents; it is available in a variety of molecular weights from 200 to tens of thousands. Aqueous PEG solutions have low toxicity and biodegradability [30]. PEG, with metal ions, forms stable complexes through interactions between metal ions and the hydroxyl groups on the surface of PEG particles, which leads to the formation of stabilized metal nanoparticles with smaller

dimensions [31]. PVP is a biodegradable and water soluble polymer [32]. PVP molecules coordinate to copper ions through their polar groups (oxygen and nitrogen), leading to the formation of complexes and surrounding of copper particles, which prevent them from agglomeration [33].

The aim of this study is the preparation and characterization of pure Cu nanoparticles using $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and the strong reducing agent hydrazine hydrate (HH) by a convenient and rapid chemical reduction method. Three polymers of PVP, PEG and starch were used as stabilizing agents and size controllers to prevent the aggregation of Cu nanoparticles. The effects of operating parameters were also studied by UV-Vis analysis to determine the optimum synthesis conditions, such as initial concentration of precursor, polymer concentration and the reaction temperature.

2. Experimental

2.1 Reagents and materials

Copper (II) nitrate trihydrate $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ($M = 241.60 \text{ g mol}^{-1}$), HH $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ ($M = 50.06 \text{ g mol}^{-1}$), PEG 4000 ($M = 4000 \text{ g mol}^{-1}$), PVP ($M = 25000\text{--}30000 \text{ g mol}^{-1}$) and starch were of analytical grade and purchased from Merck Chemicals (Germany). Ethanol was obtained from Jahan Alcohol Teb Co., Iran. Deionized water was used in all the experiments. All chemical reagents were used as received without any further purification.

2.2 Synthesis of stabilized copper nanoparticles

$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (1 g) was dissolved in 10 ml deionized water to obtain a blue colour solution. For stabilization of the synthesized copper nanoparticles, 10 ml of aqueous 1% (w/v) PEG, PVP or starch solution was added to the above solution separately. $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ solution (23 ml) was added dropwise to the stirring solution and the colour changed from blue to yellow, indicating the reduction of Cu (II) to metallic zero-valent Cu. Gradually by the formation of precipitates the solution colour changed to reddish brown, indicating the formation of copper nanoparticles. The resulting mixture was stirred thoroughly for about 10 min. Final volume of the solution was increased up to 70 ml using deionized water and the solution was placed in a closed vessel in an oil bath at 120°C temperature for 2 h. Finally, the mixture was cooled to room temperature and centrifuged at 1000 rpm. The supernatant liquids were discarded and a reddish brown precipitate was obtained. The precipitate was washed with ethanol, at least two times, to remove the impurities and the unreacted precursors. After drying for 2 h at 80°C in an oven, the red-brown powder was collected.

Pure copper nanoparticles were also synthesized, by an identical method but without the use of polymer stabilizers, to investigate the effect of stabilizing polymers on the size and agglomeration of obtained copper nanoparticles.

For the investigation and optimization of the initial concentration of Cu precursor on the size and size distribution of Cu nanoparticles, five experiments with different concentrations of Cu precursor (21, 31, 41, 51 and 61 mmol l^{-1}) were performed without adding any stabilizing agent into the reaction solution. All parameters were fixed during the experiments, except the initial concentration of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$. Also, for the investigation and optimization of the temperature of reaction on the size and size distribution of Cu nanoparticles, five experiments with different reaction temperatures of 80, 100, 120, 140 and 160°C were performed without adding any stabilizing agent into the reaction solution. All parameters were fixed during the experiments except the temperature of reaction. For the investigation of the stabilizer concentration effect on the size and size distribution of Cu nanoparticles, four experiments with different PEG (the best stabilizer investigated in this work) concentrations of 0.5, 1.0, 1.5 and 2% w/v were performed.

2.3 Characterization

UV-Vis absorption spectroscopy of synthesized samples was studied using a double-beam spectrophotometer (Shimadzu UV-Vis 1700 Pharma Spectrophotometer) in the wavelength range of 190–1100 nm. Particle size and shape of prepared copper nanoparticles were obtained using a Tescan, MIRA3 field emission scanning electron microscope (FESEM). X-ray diffraction (XRD) patterns were also recorded using a Siemens D500 X-ray diffractometer to confirm phase and purity of the produced nanoparticles. Fourier transform infrared (FTIR) spectra of synthesized samples were recorded using a Bruker Tensor 27 spectrophotometer between 500 and 4000 cm^{-1} . Size distribution of particles was determined using Manual microstructure Distance Measurement software (Nahamin Pardazan Asia Co., Iran). Particle diameter size data were collected from SEM images.

3. Results and discussion

3.1 XRD analysis

To investigate the structure of the produced copper nanoparticles, the analysis of XRD patterns was employed. The XRD patterns of Cu nanoparticles, stabilized with different polymers as well as the non-stabilized Cu nanoparticles, have been shown in figure 1. Figure 1a shows the XRD patterns of non-stabilized Cu nanoparticles attributed to the sample prepared without using any stabilizing agent. Three reflection peaks can be seen at 2θ values of 43.358° , 50.486° and 74.098° corresponding to the (111), (200) and (220) Miller indices of copper metal, respectively. The peaks are very sharp due to the high nano-crystalline nature of obtained copper. The results have compliance with the standard powder diffraction data of copper metal (JCPDS, File No. 04-0836). The XRD patterns analysis confirms that the synthesized copper nanoparticles

Figure 1. XRD patterns of (a) non-stabilized Cu nanoparticles, and stabilized Cu nanoparticles using (b) PVP, (c) starch and (d) PEG polymers.

have face-centred cubic (FCC) structure [34]. Also, other phases such as Cu_2O and CuO were not observed. The average size of Cu crystals estimated using the Debye–Scherrer formula is about 20 nm. Equation (1) shows the Debye–Scherrer equation:

$$D = \frac{0.9\lambda}{\beta \cos \theta}, \quad (1)$$

where D is the average size of Cu crystals, λ the wavelength of X-ray (0.1541 nm), β the full-width at half-maximum and θ is the diffraction angle [34].

Figure 1b, c and d displays the XRD patterns of Cu nanoparticles stabilized with PVP, starch and PEG, respectively. The XRD patterns of stabilized copper nanoparticles show the same characteristic peaks of non-stabilized Cu nanoparticles, which confirms the formation of copper metals. The average size of PVP-stabilized Cu nanoparticles crystals, starch-stabilized Cu nanoparticles crystals and PEG-stabilized Cu nanoparticles crystals, calculated using the Debye–Scherrer equation, was 16, 15 and 13 nm, respectively. The peaks are very strong and sharp due to the high nano-crystalline nature of the obtained copper metal [35]; hence, PEG, starch and PVP are efficient stabilizers that lead to the production of smaller copper nanoparticles without impurities.

3.2 UV–Vis spectroscopic analysis

The UV–Vis spectra of stabilized and non-stabilized copper nanoparticles were recorded and analysed to investigate the effect of stabilization on the light absorption characteristics of Cu nanoparticles. Figure 2 shows the UV–Vis spectra of non-stabilized Cu nanoparticles as well as stabilized Cu nanoparticles with different polymers. The UV–Vis spectra of pure stabilizers were also investigated. Figure 2a shows the UV–Vis spectra of pure stabilizers with the λ_{max} values

Figure 2. UV–Vis absorption spectra of (a) pure polymer stabilizers and (b) non-stabilized Cu nanoparticles and Cu nanoparticles stabilized with PVP, starch and PEG.

in UV region. UV–Vis absorption spectra of non-stabilized Cu nanoparticles show the characteristic plasmon absorption band at 600 nm (figure 2b). The surface plasmon resonance (SPR) band for copper nanoparticles has been reported to be in the range of 500–600 nm [36]. With the use of PVP, starch and PEG as stabilizing agents, the characteristic plasmon absorption band of synthesized Cu nanoparticles shifted to lower wavelengths and appeared at 590, 586 and 571 nm, respectively. The results of recent studies show that the blue-shift in SPR band position confirms the formation of smaller nanoparticles [37]. Also, narrower and sharper peaks are indicative of more uniform particle size distribution of nanoparticles [38]. Hence, according to figure 2b, the polymer-stabilized Cu nanoparticles have smaller particle size with respect to the non-stabilized Cu nanoparticles. Also, PEG has the best effect on the stabilization of copper nanoparticles and yields the smallest nanoparticles with the most uniform size distribution. Starch and PVP yield bigger copper nanoparticles.

Since the pure polymer stabilizers do not absorb visible light, they do not have any effect on the λ_{max} values of stabilized Cu nanoparticles.

3.3 Morphological studies

A FESEM was used to investigate the morphology, size and the agglomeration of prepared copper nanoparticles. Figure 3a shows the FESEM images of spherical non-stabilized copper nanoparticles at two different magnifications. As can be seen in figure 3a, the synthesized non-stabilized copper nanoparticles have non-uniform size and shape, which can be related to the agglomeration of copper units and irregular growth of crystal beads during the synthesis process. Size distribution of non-stabilized copper nanoparticles is shown in figure 3e, which indicates that most copper nanoparticles are in the size range of 100–400 nm. FESEM images of Cu nanoparticles stabilized with PVP, starch and PEG at two different magnifications have been shown in figure 3b, c and d, respectively. Also, the respective size distributions of Cu samples are shown in figure 3f, g and h, correspondingly. Results showed that the smallest Cu nanoparticles and the most suitable size distribution of nanoparticles with the average particle size of 30–50 nm were obtained using PEG as the stabilizing polymer, while the average particle size of the Cu nanoparticles stabilized with starch and PVP is 50–70 and 70–100 nm, respectively.

3.4 FTIR studies

To examine the interactions between the stabilizing agents and Cu nanoparticles, FTIR spectra of stabilizing polymers and polymer-stabilized Cu nanoparticles were recorded (figure 4). Curve *a* in figure 4 presents FTIR spectra of PVP and PVP-stabilized copper nanoparticles. For pure PVP the broad peak observed at 3444 cm^{-1} corresponds to the stretching vibration of O–H group of adsorbed water on the surface of the polymer. The peaks at 1660 and 1374 cm^{-1} are related to C=O stretching vibration and out of ring C–H bonds, respectively. Another important peak at 1288 cm^{-1} is attributed to the stretching vibrations of C–N bond; also, the double peak observed at 1428 and 1461 cm^{-1} is related to the CH_2 groups in the pyrrole ring. In the FTIR spectrum of PVP-stabilized Cu nanoparticles, the peak of the C=O bond shifted from 1660 cm^{-1} of pure PVP to a lower wavenumber of 1574 cm^{-1} , which is due to the interactions between the carbonyl group of PVP and copper nanoparticles.

The FTIR spectra of starch and starch-stabilized copper nanoparticles are shown in figure 4b. For pure starch, the peaks in the range of 670 – 1000 and 1300 – 1420 cm^{-1} are attributed to the bending vibration and stretching vibration of C–H bonds, respectively. The two absorption peaks at 1655 and 1163 cm^{-1} are related to bending vibrations of C–H and stretching vibrations of C–O bonds, respectively. The peaks observed at 2925 and 3276 cm^{-1} are related to O–H stretching vibrations. Also, the weak C–O stretching at 985.9 cm^{-1} is a characteristic of ether functional moiety. Almost all the peaks presented in the FTIR spectra of pure starch are observed in the FTIR spectrum of starch-stabilized Cu nanoparticles, with a red-shift. One of the absorption peaks related to O–H

stretching vibration at 2925 cm^{-1} in the FTIR spectrum of pure starch has disappeared in the FTIR spectrum of starch-stabilized Cu nanoparticles and another peak at 3276 cm^{-1} has shifted to lower wavenumbers. These dramatic differences may be due to the formation of a thin layer of starch around the Cu nanoparticles due to interaction of starch with copper nanoparticles through the hydrogen bonds.

The FTIR spectra of PEG and PEG-stabilized copper nanoparticles are shown in figure 4c. For pure PEG, the strong peak, observed at 2887 cm^{-1} , is related to C–H stretching vibrations. The peak at 1112 cm^{-1} is assigned to C–O stretching vibrations. The two absorption peaks at 1346 and 1468 cm^{-1} wavenumbers are attributed to the C–H bending vibrations of the $-\text{CH}_2$ and $-\text{CH}_3$ groups, respectively. Comparing FTIR spectra of pure PEG with that of PEG-stabilized copper nanoparticles shows that interactions between PEG and copper nanoparticles have caused significant changes in the position and intensity of peaks of pure PEG.

3.5 Effect of synthesis parameters on the size and size distribution of Cu nanoparticles

3.5a Effect of initial concentration of Cu precursor $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$: Nucleation and growth are two main processes that occur during the formation of copper nanoparticles. To obtain smaller nanoparticles, it is necessary that the nucleation rate be faster than growth rate. Hence, finding the optimum initial concentration of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ as precursor of Cu nanoparticles is very important [39]. For the investigation and optimization of the effect of initial concentration of Cu precursor on size and size distribution of Cu nanoparticles, several experiments were performed. All parameters were fixed during the experiments except the initial concentration of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$. Also, a series of same experiments were performed without adding any stabilizing agent into the reaction solution. The UV–Vis spectra of prepared Cu nanoparticles were used to investigate the effect of initial concentration of Cu precursor on the size and size distribution of obtained Cu nanoparticles (figure 5). According to the UV–Vis spectra for the five samples prepared by five different concentrations of Cu precursor, it is observed that with increasing initial concentration of Cu precursor from 21 to 41 mmol l^{-1} , the λ_{max} values of UV–Vis spectra decrease from 605 to 600 nm , which indicates a decrease in size of the prepared Cu nanoparticles. Also, it can be seen that for concentrations higher than 41 mmol l^{-1} , despite the increase in absorption intensity, maximum absorption wavelength shows a significant increase due to the agglomeration and aggregation of copper nanoparticles because when the precursor concentration exceeds a certain amount, a large number of nuclei are formed and aggregate. In other words, concentrations higher than 41 mmol l^{-1} of Cu precursor cause aggregation and larger Cu nanoparticles so that the related λ_{max} value is bigger wavelength [40]. Therefore, it was found that the optimal initial concentration of Cu^{2+} is 41 mmol l^{-1} .

Figure 3. FESEM micrographs of (a) non-stabilized Cu nanoparticles and Cu nanoparticles stabilized with (b) PVP, (c) starch and (d) PEG with low and high magnifications, and the diameter size distribution of (e) non-stabilized Cu nanoparticles and Cu nanoparticles stabilized with (f) PVP, (g) starch and (h) PEG.

3.5b Effect of reaction temperature: The synthesis temperature of nanoparticles is one of the most important parameters that affects the size and size distribution of metal nanoparticles. We investigated the preparation of copper nanoparticles at different reaction temperatures. Figure 6 shows the UV–Vis spectra of non-stabilized Cu nanoparticles prepared at

different reaction temperatures. In metal preparation reaction systems, the effect of reaction temperature on the rate of formation of initial nuclei is much larger than that on the growth rate of crystals. Therefore, with increasing reaction temperature, the nucleation rate becomes larger than growth speed and smaller nanoparticles are obtained; however, when the

Figure 4. FTIR spectra of (a) pure PVP and PVP-stabilized Cu nanoparticles, (b) pure starch and starch-stabilized Cu nanoparticles and (c) pure PEG and PEG-stabilized Cu nanoparticles.

Figure 5. UV-Vis absorption spectra of non-stabilized Cu nanoparticles prepared with different concentrations of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ precursor.

temperature is higher than a certain level, the surface activity of nuclei increases strongly, which causes the nuclei to collide and join together. Joining together of nuclei results in increasing particle size and increasing λ_{max} . At temperatures lower than an optimum temperature, nucleation rate decreases and λ_{max} value is increased again. Hence, finding

Figure 6. UV-Vis absorption spectra of non-stabilized Cu nanoparticles prepared at different reaction temperatures.

the optimum temperature during the synthesis process is very important. At the optimum temperature, the purity of the product is increased and oxidation of nanoparticles is reduced [40].

Figure 6 shows UV-Vis spectra of Cu nanoparticles prepared at different temperatures. According to the results, the peak observed at the preparation temperature of 120°C is

Figure 7. UV-Vis absorption spectra of PEG-stabilized Cu nanoparticles prepared in the presence of PEG stabilizer at different concentrations.

sharper and at lower wavelength than those of the other peaks, which indicates the preparation of small size Cu nanoparticles with more uniform size distribution in this condition.

3.5c Effect of concentration of polymer stabilizer: The Cu nuclei tend to agglomerate in the synthesis process to reduce the total energy level. This gathering could result from van der Waals attractive forces between the crystals, which must be inhibited or limited [41]. The presence of polymer chains as stabilizing agents prevents produced nanoparticles from excessive agglomeration by the creation of steric repulsion and improves the dispersion of nanoparticles.

We studied the effect of PEG concentration on the size of the Cu nanoparticles by comparing the UV-Vis spectra of colloidal dispersion of PEG-stabilized Cu nanoparticles in distilled water. PEG at three concentrations in water (0.5, 1 and 1.5% w/v) was used as the stabilizing agent in the preparation of Cu nanoparticles and UV-Vis spectra of obtained Cu samples have been shown in figure 7. The results showed that by increasing the polymer concentration, $\lambda_{\max}$ of related obtained Cu nanoparticles in UV-Vis spectra is shifted to lower wavelengths. Figure 7 clearly shows that for sample with 0.5% PEG, $\lambda_{\max}$ is obtained around 597 nm, while for samples with 1 and 1.5% PEG concentration, the related $\lambda_{\max}$ values are 585 and 571 nm, respectively. Also, in this study, no surface plasmon peak was observed for PEG-stabilized copper nanoparticles with concentration of 2% and higher, which is due to the formation of nanoparticles too small in scale (smaller than 5 nm), probably [27].

4. Conclusions

In summary, pure Cu nanoparticles were synthesized by a convenient and rapid chemical reduction method and characterized by analysis of XRD, UV-Vis, FTIR and SEM techniques. The copper nanoparticles were synthesized in the presence of stabilizing polymers of PVP, PEG and starch. The efficacy of polymers in the prevention of excessive

aggregation of Cu nanoparticles was confirmed by SEM, UV-Vis, FTIR and XRD analysis. According to the results, the smallest particles and the most suitable size distribution of nanoparticles were obtained using PEG as the stabilizing polymer. Zero-valent copper nanoparticles with high purity were obtained in this work and there is no peak related to the oxidized impurities such as CuO and Cu₂O in the XRD and UV-Vis studies, both in the presence and in the absence of stabilizing polymer. Also, zero-valent copper nanoparticles were obtained in the absence of any anti-oxidant agent or inert gas flow. In the second part of the study, the effects of operating parameters were studied by UV-Vis analysis to determine the optimum values of synthesis conditions, including initial concentration of Cu precursor, polymer concentration and the reaction temperature. The optimum concentrations of Cu(NO₃)₂·3H₂O and stabilizing polymer were obtained as 41 mmol l⁻¹ and 1.5% (w/v), respectively, and the optimum reaction temperature was determined to be 120°C.

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