Polyol mediated synthesis & characterization of Cu nanoparticles: Effect of 1-hexadecylamine as stabilizing agent

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Abstract: - A facile method of preparing well-dispersed copper nanoparticles by polyol method, using 1-hexadecylamine as a protecting agent in ambient atmosphere, has been developed. Polyol mediated preparation of nanoparticles is one of the widely used methods that enables controlling the size and shape of nanoparticles. It is demonstrated that 1-hexadecylamine used as stabilizing agent during polyol mediated synthesis presents uniform, spherical and small sized copper nanoparticles than the commonly use PVP stabilizer. Higher alkylamine/Cu molar ratio leads to production of spherical and smaller copper nanoparticles. Palladium and gold prepared using alkylamine show uniform and small nanoparticles suggesting the efficiency of long chain alkylamine as capping agents. The nanoparticles showed a self-assembling on the alkylamine template.

Key Words: - **C**opper nanoparticles, Polyol synthesis, Stabilizer, 1-Hexadecylamine, poly vinylpyrrolidone (PVP)

1 Introduction

Nanoparticles have unique physical and chemical properties different from bulk materials due to drastic reduction of particle size. Nowadays, researches on synthesis of metal nanoparticles are largely studied due to their special properties. Among various metal particles, copper nanoparticles have attracted considerable attention because of its unique catalytic, optical and electrical conducting properties [1,2]. Several methods have been developed for the preparation of copper nanoparticles, including thermal reduction, sono-chemical reduction, metal vapor synthesis, chemical reduction, vacuum vapor deposition, radiation methods, microemulsion techniques and laser ablation [1-4]. Most of the mentioned methods use an oxygen-free environment to synthesize copper as it easily oxidizes in air. Although chemical reduction of copper salts in aqueous systems presents a fast reaction rate, it related with agglomeration effect. In this way, the preparation of copper nanoparticles avoiding these drawbacks is a challenge in this research field.

The polyol process is one of widely applied technique using non-aqueous liquid (polyol) as a solvent and reducing agent for nanoparticle preparation [4]. The use of non-aqueous solvents has an advantage of minimizing surface oxidation and agglomeration. Polyol mediated nanoparticles synthesis allows flexibility controlling the size and shape of nanoparticles. This method can also be applied during large-scale nanoparticle production. In this process, stabilizing agents are employed in order prevent the nanoparticle from agglomeration, oxidation or precipitation of the particles. In addition, stabilizing agent determines the shape, size and uniformity of the resulting nanoparticles, related with the PVP/M^{2+} molar ratio. The most widely used polymer includes poly-vinylpyrrolidone, (PVP). Recently Zhu et al. [5] show this effect, preparing well-dispersed nanoparticles with controllable shapes (rods, needles, etc) adjusting the composition of the reaction system. Other synthesis parameter that is able to determine shape and size of the nanoparticle is the type stabilizing agent [6,7,8]. There has been few quantity of work based on the use of long-chain alkylamine as stabilizing agents during polyol synthesis. The alkylamines are commonly employed as capping and phase-transfering agents in phase-transfer synthesis of nanoparticles. V. Tzitzios et. al. depicted that the use of mixtures of Oleic acid and oleyl amine during polyol synthesis of hexagonal close-packed Ni particles favors higher solubility of the nanoparticles in non-polar solvent [9]. Shen et al. successfully synthesized the alkylamine capped gold nanoparticles by ethanol (polar) reduction under microwave irradiation [3]. In the same way Fe, Co and Ni nanoparticles were prepared using dodecylamine as stabilizing agents by microwave

assisted polyol synthesis[10].

2 Problem Formulation

The synthesis of copper nanoparticles is associated with drawbacks like instability of the particles against oxidation and agglomeration. Polyol based method showed promising results in recent studies. However, the distribution of particle size obtained using the commonly used PVP are large for further application in fields like catalysis. Long chain alkylamines, which has proved to be efficient during phase-transfer nanoparticle synthesis, can be employed in polyol process. These compounds can form stable amine complex with transition metals, which result in small and stable nanoparticles. Following this idea, this work study the use long chain alkylamine as stabilizing agent in polyol method in order to obtain copper nanoparticles which are stable against oxidation and agglomeration.

3 Problem Solution

3.1. Experimental

3.1.1. Synthesis of Copper Nanoparticles

Copper nanoparticles were synthesized following polyol method, using long chain alkyl amine as protecting agent. Analytically pure $Cu(NO_3)_2.2H_2O$, hexyldecyl amine and ethylene glycol were used as the starting materials without further purification. In a typical synthesis procedure, 100 ml of 0.05 M ethylene glycol solution of $Cu(NO_3)_2.2H_2O$ was mixed with an appropriate amount of hexadecylamine (alkylamine) in a round-bottom flask equipped with a magnetic stirrer, refluxing device, thermometer and argon purging source. The alkylamine mixture was mixed thoroughly at 60°C to achieve a complete homogeneous solution. The mixture was then heated rapidly to 160°C with Argon bubbling. The previous transparent blue solution rapidly turned into green turbid, then to brown solution of CuO, which later changed into an intense red mixture of Cu_2O. After long time of reaction, the mixture started to turn into black turbid. Finally, the solution was cooled rapidly to room temperature. The copper nanoparticles were separated by centrifugation, washed several times with ethanol, and dried under Ar atmosphere. The resulting Copper nanoparticles were stable even for several weeks in ambient atmosphere. Following this procedure copper nanoparticle was synthesized with Cu/Alkylamine molar ratio of three, two and 1. Two samples were prepared at different time of reaction (16th and 24th h) from the amine mixture for further characterization. For comparison Poly (vinylpyrrolidone),PVP,(K30, Mw≈44,000–4,000) stabilized copper nanoparticles were also prepared in a similar way with Cu/PVP molar ratio of 1. Similar procedure was followed to prepare alkylamine capped palladium and gold nanoparticles at 60°C for 5 hour.

3.1.2 Nanoparticles characterization

The oxidation state and crystallinity of the copper nanoparticles were investigated using X-ray diffraction, Siemens D5000 diffractometer (Bragg-Bentano for focusing geometry and vertical θ-θ goniometer) fitted with a grazing incident (ω: 0.52º) attachment for thin film analysis and scintillation counter as a detector. The samples were dispersed on Si (510) sample holder. The angular 2θ-diffraction range was between 20º and 70º. The data were collected with an angular step of 0.03º at 5 s per step and sample rotation. The phases were identified using the JCPDS files.

Uv-Vis spectra of ethanol solution alkylamine capped copper nanoparticles were carried out at ambient temperature using UV-Vis spectrophotometer by scanning wavelengths between 200-820 nm.

TEM operated at 100 kV (JEOL JEM-2000EX II) was taken to analyze the morphology and dispersion of nanoparticles. Samples were dispersed in alcohol/toluene mixture bath and a drop of suspension was poured onto a holey carbon-coated grid and dried completely before the measurements were taken.

3.2. Results

The color of the nanoparticles usually can explain the oxidation states of the respective nanoparticles. The solution of the copper nanoparticles synthesized using PVP as stabilizing agent present an intense rose color (characteristic of bulk material in metallic state), whereas the solution of the particles prepared with the amine show brown-black color. The XRD profile of different copper nanoparticles prepared are shown in Figure 1. In a typical polyol synthesis of copper nanoparticles, alkyl amine as stabilizing agent was studied. As shown in the figure at 16th hour of reaction, the polyol is composed of both metallic copper and copper(I) oxide species.

Nevertheless, at a longer time of reaction (24h) the polyol is able to reduce all the copper ions to the metallic state. Figure 1 also shows the XRD profile of pure copper nanoparticles prepared using PVP as stabilizing agents. In both cases, copper nanoparticles with face-centered cubic (fcc) crystal structure were synthesized after 24 hours of polyol reduction.

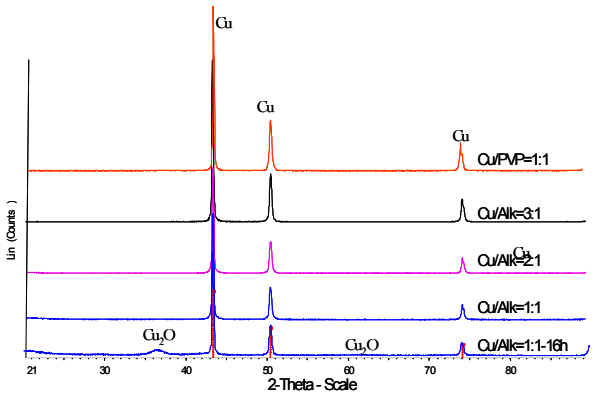

Fig 1. XRD profile of copper nanoparticles stabilized using alkylamine and PVP

Alkylamine capped copper nanoparticles showed a two main UV-absorption peak at around 290nm and 410nm respectively as shown in Fig 2. The first absorption peak can be assigned to small separated Cu nanoparticle complexes as Aslam et al reported [9].The second absorption peak (410nm) could represent absorption of copper nanoparticles. The typical surface plasmon resonance for Copper nanoparticles is at around 600nm. The blue shift of the absorption edge for the prepared copper nanoparticles (480nm) relative to that of bulk copper could suggest the existence small Cu nanoparticles.

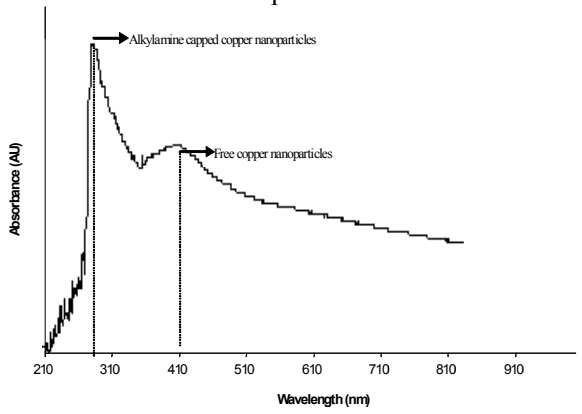

Fig 2. UV-Vis spectra of alkylamine capped copper nanoparticles

TEM results confirm the difference in the particle size related with the stabilizing agent employed during the polyol synthesis method. PVP capped copper result large average particle size of around 300nm, whereas the alkylamine is related with smaller particle size of 8nm as shown in Figure 3. PVP stabilized particles present a wide range of size between 100-1000 nm, larger than in the alkylamine stabilized particles with a range between 6-20nm. The stabilizing agent also affected in the shape configuration. The use of PVP leads to polyhedron (spherical, rods and hexagonal) copper nanoparticles while alkylamine leads to spherical shape. In general, it is demonstrated that the performance of alkylamine exceeds that of the commonly used polymer (PVP) in producing small, uniform and stable copper nanoparticles.

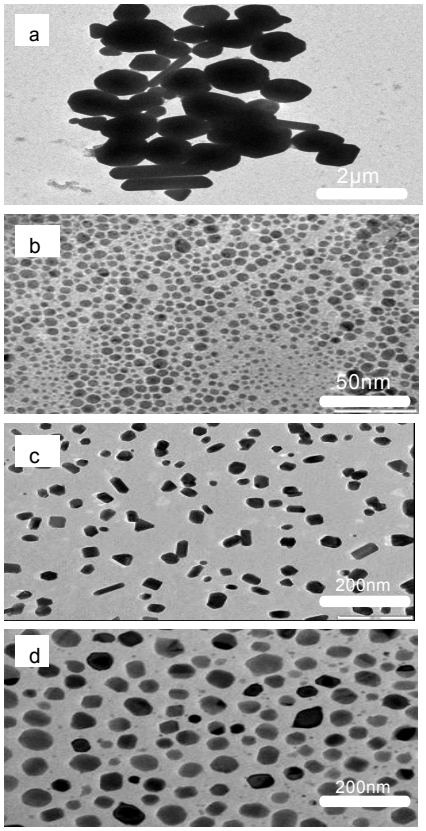

Fig. 3 TEM images of Cu nanoparticle samples (a) PVP -Cu (b)Alk/Cu 1:1 (C)Alk/Cu 1:2 (d)Alk/Cu 1:3

TEM images of copper metal nanoparticles with different alkylamine/Cu molar ratios are shown in fig 3b, 3c and 3d. When the molar

ratio of alkylamine to copper was 1:1, 1:2 and 1:3 the average diameters recorded were 8nm, 20nm, 40nm respectively. This demonstrates the use of high concentration of alkylamine protect the nanoparticles from agglomeration and particle growth. In the process, the copper nanoparticle could coordinate with 1-hexadecylamine with the amine extension while the long alkyl chain sterically inhibits further particle growth and agglomeration. Varying Alkylamine/Cu molar ratio similarly affects the shape the nanoparticle. Spherical copper nanoparticles can be obtained for alkyamine/Cu molar ratio of 1:1. Rods and polyhedrons were observed for nanoparticles with Alkylamine/Cu molar ratio of 1:1 and 1:3 respectively. Palladium and gold nanoparticles prepared using the same procedure presents particle size of 4nm and 15nm respectively as shown in Fig 3. These particles are characterized by a uniform particle size and shape distribution. Moreover, self-assemble of Pd and Au nanoparticles was possible on 1-hexadecylamine template.

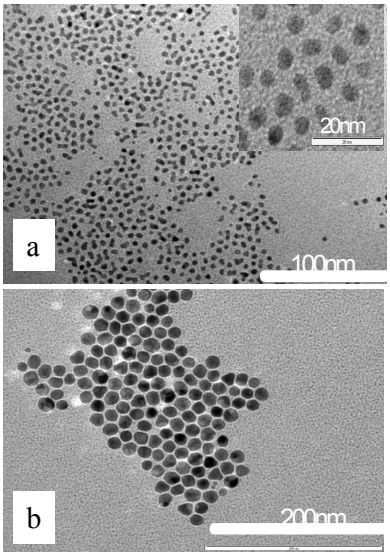

Fig 3 TEM pictures of palladium (a) and gold (b) nanoparticles prepared using alkylamine as capping agent.

4 Conclusion

We have successfully developed a method to synthesize well-distributed small size copper nanoparticles. It has been demonstrated that uniform, nanosized, spherical copper nanoparticles were using 1-hexadecylamine as protective agents in polyol method. XRD characterization depicted that copper ions are transformed to metallic copper within 24 hour of reaction. TEM results showed smaller average particle size (8nm) using the alkylamine as protecting agent than when PVP was employed (300nm). High molar ratios of alkylamine/copper favor production of small and spherical copper nanoparticles. Palladium and Gold prepared in similar way showed self-assembly property.

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