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Influence of ligand structure on the stability and oxidation of copper nanoparticles

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Abstract

The stability and oxidation of copper nanoparticles stabilized with various ligands have been studied. Lauric acid-capped copper nanoparticles were prepared by a modified Brust–Schiffrin method. Then, ligand exchange with an excess of different capping agents was performed. Oxidation and stability were studied by UV–vis, XRD, and TEM. Alkanethiols and oleic acid were found to improve air stability. The oxidation resistance of thiol-capped copper nanoparticles was found to increase with the chain length of the thiol. However, excess thiol caused etching of the particles under nitrogen. With oleic acid no etching was observed under nitrogen. After oxidation, no traces of the ligand-exchanged particles were found, suggesting their dissolution due to excess ligand. Oleic acid protected the particles against oxidation better than the tested thiols at large excess (ligand–copper ratio 20:1).

Keywords

Copper nanoparticles; Oxidation; Ligand exchange; Etching; Alkanethiols; Oleic acid; Lauric acid

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1. Introduction

Research on nanoparticles has gathered wide attention during the last decade because of their unusual and size-dependent optical [1], magnetic [2] and [3], electronic [4] and [5], and chemical [6] and [7] properties. To fully utilize these properties, the size and shape must be well controlled. Particularly gold and silver have attracted large interest among metal particles, due to their unique plasmon resonance and high stability. Although metal nanoparticles have been synthesized for a long time by numerous methods, the ground-breaking work of Brust et al. [8] reported a method to prepare gold nanoparticles of specific size capped by alkanethiolate ligands, which can be carried out using standard laboratory equipment. These particles can be isolated, as a waxy powder, and redispersed. Several other preparation methods have been developed. It has been shown that the ligands can be exchanged by adding an excess to the colloidal solution [9] and [10]. This provides a very effective method to functionalize particles of predefined size with desired chemical groups.

The melting point of a nanoparticle is approximately proportional to the inverse of the radius. Thus, it is significantly lowered in small particles, e.g., 1.5 nm gold particles encapsulated in silica have been observed to melt at 380 °C compared to 1086 °C for bulk gold [11]. Additionally, other related properties such as sintering and annealing show similar size dependence. The lowering of the melting point is interesting for conducting inks for printable electronics, since well conducting patterns can be obtained even on heat-sensitive substrates such as paper. While conducting inks containing nanoparticles of noble metals such as silver and gold are commercially available, copper could offer a more affordable alternative with superior properties. However, copper nanoparticles are known to be extremely sensitive to oxygen, and therefore there are several problems related to the stability and oxidation resistance that need to be solved before copper inks become available.

Despite that oxidation resistance is of immense importance in several applications, few studies have been carried out in this area and there are no clear guidelines for how to improve air stability. Both the metal and the type of ligand used to stabilize the nanoparticles are known to significantly affect the oxidation resistance. Proper combinations have been shown to give excellent results; for example, even air stable aluminum particles have been reported [12].

The synthesis of copper nanoparticles has not been as widely explored as that of many other metals due to the easily oxidized nature of copper, which is enhanced in nanoscale structures. Several methods have, however, been presented. Copper nanoparticles have been successfully synthesized, for example, by γ -radiolytic [13], laser irradiation [14], thermal decomposition [15] and [16], thiol-induced reduction in supercritical water [17], reduction in microemulsions [18] and reverse micelles [19], vapor deposition [20], sonoelectrochemical [21], flame spray [22], and chemical reduction [23], [24] and [25] methods. The oxidation state, size, and stability of the particles vary greatly in these syntheses. In general, these particles cannot be exposed to air without extensive oxidation. Yanase and Komiyama [26] examined the mechanism and kinetics of copper nanoparticle oxidation and reduction with UV–vis spectroscopy by recycling glass-supported particles between oxygen and hydrogen atmospheres. They found a fast oxidation process from Cu to CuO_{0.67} and a slow process from CuO_{0.67} to CuO. Huang et al. [27] studied the role of cetyltrimethylammonium bromide (CTAB) in forming hollow Cu₂O nanoparticles and finally ellipsoidal CuO nanoparticles through copper oxidation. On the other hand, Wu and Chen [28] used CTAB as capping ligand when they synthesized small (5.1 nm) Cu nanoparticles, which they reported to be stable in aqueous solution for months. Additionally, there have been reports of copper nanoparticles coated with cuprous or cupric oxide shells when exposed to air [16], [29], [30] and [31]. Chen et al. [32] studied the self-limiting nature of the process. They concluded that at room temperature internal stress caused by an oxide layer on the surface is the reason for self-limiting oxidation. At a slightly higher temperature (323 K) the thermal energy was enough to relax this stress and resulted in faster, nonself-limiting oxidation.

In this work, a series of copper nanoparticles with various ligands were prepared by a modification of the two-phase Brust–Schiffrin method followed by ligand exchange. The particles were then exposed to air and their oxidation was followed by observing changes in their UV–vis spectra, particularly in the plasmon resonance, which is very sensitive to oxidation. The studied ligands were lauric acid, oleic acid, hexanethiol, dodecanethiol, and octadecanethiol.

2. Materials and methods

Copper(II) chloride (CuCl₂·2H₂O, p.a. grade, Merck), lauric acid (>99%>99%, Sigma), tetraoctylammonium bromide (TOAB, 98%, Alfa Aesar), sodium borohydride (NaBH₄, for

synthesis, Merck), 1-hexanethiol (C₆SH, 97%, Alfa Aesar), 1-dodecanethiol (C₁₂SH, >98%, Aldrich), 1-octadecanethiol (C₁₈SH, 95%, Lancaster), and oleic acid (extra pure, Merck) were used as received. Toluene (analytical reagent, Lab-Scan), acetone (analytical reagent, Lab-Scan), and methanol (p.a., Fluka) were used without further purification. All water used was purified by distillation and ion exchanged with a Millipore Milli-Q system. All solutions were purged with nitrogen prior to use. The synthesis and ligand exchange reactions were carried out in a nitrogen box.

Copper nanoparticles were synthesized by a modified Brust–Schiffrin method [8] and [33]. Typically, 30 ml of aqueous CuCl₂ solution (25 mM) was mixed together with 75 ml of lauric acid in toluene (10 mM) and 30 ml of TOAB in toluene (25 mM). The mixture was stirred for 30 min. Then, under heavy stirring, 150 ml of aqueous NaBH₄ (80 mM) was added dropwise. Stirring was continued for 2 h and then the phases were separated.

Ligand-exchange was performed directly in the organic phase obtained from the reduction reaction. A volume of the organic phase was added to a toluene solution of the new ligand. The molar excesses of the new ligand compared to the original ligand were approximately 1, 10, and 20. The ligand mixture was then stirred under nitrogen for 3 days.

The UV–vis spectra were recorded with Varian Cary 50 Conc spectrometer from 300 to 1000 nm. The samples were prepared by diluting 200 µl of the nanoparticle solution in 2 ml of toluene. The sample was mixed between measurements to ensure uniform conditions in the oxidation studies. Since both the intensity and the wavelength of the plasmon absorption band of metallic nanoparticles depend on particle size and the surrounding media, a quantitative analysis of the kinetics involved would require detailed knowledge of particle size and extent of oxidation. However, for the purpose of this paper the absorption intensity at the plasmon peak was followed to obtain information on the extent of oxidation.

Transmission electron microscopy (TEM) was used to study the size of the particles. The samples were prepared by placing a drop of ligand-exchange solution on Formvar/carbon-coated copper grids (Electron Microscopy Sciences) and drying it in air. The TEM measurements were done with a Tecnai 12 instrument operating at a 120 kV accelerating voltage. The size distribution was analyzed by manually measuring particle diameters from TEM pictures. Approximately 200 particles were analyzed.

The oxidation products were determined with XRD measurements performed with a Philips MPD 1880 diffractometer and CuK α radiation ($\lambda=0.1542$ nm). The samples were prepared from the ligand-exchanged solutions by precipitating the nanoparticles with methanol. The mixture was then taken out of the nitrogen cabinet and filtered. The precipitates were washed with methanol and acetone and then dried in air. The spectra were taken directly from the sample on the filter paper. The spectrum of the filter paper was reduced from the intensity readings.

3. Results and discussion

3.1. Brust–Schiffrin synthesis and oxidation of lauric acid-protected nanoparticles

The aqueous copper chloride solution was mixed with toluene containing TOAB and lauric acid in the initial stages of the synthesis. The aqueous phase remained light blue and organic phase colorless, indicating that no significant phase transfer of copper to the organic phase had occurred. In this respect the synthesis differs significantly from the Brust–Schiffrin synthesis of gold particles, where the aqueous [AuCl $_4$] $^-$ ion is exchanged against the less lipophilic Br $^-$. In the system considered here, Cu $^{2+}$ cannot replace the strongly associated proton from lauric acid, and is hence not transferred to the organic phase. When NaBH $_4$ solution was added, the organic phase turned from colorless to yellow and then black, while the aqueous phase lost its blue color. The role of TOAB as a possible phase transfer catalyst is not clear; however, if omitted a black precipitate resulted. Thus, TOAB is important for the stabilization of the colloid. After stirring for 2 h, the organic phase had changed color from black to dark red. The dark red color of copper nanoparticles is due to the plasmon band in the 560–570 nm range [34]. The UV–vis spectrum taken from the organic phase expectedly showed a peak at 570 nm (Fig. 1). Similar results were obtained when synthesis was tried with hexanoic acid, octanoic acid, and oleic acid.

Fig. 1. UV-vis spectra of lauric acid-capped copper nanoparticle colloids at different times after exposure to air. The particles were aged for 3 days in toluene solution under nitrogen.

If stirring was continued under nitrogen overnight, the color of the organic phase turned to yellow and some precipitation occurred. This was attributed to the oxidation of the particles induced by the reaction products in the aqueous phase. The pH of the aqueous phase was ~ 11 , which was unexpected since protons are released in the reduction. A TEM image of the resulting particles is shown in Fig. 2. The particle diameter was approximately 3.3 ± 0.7 nm. If the synthesis was carried out with ligands other than carboxylic acids, the resulting particles were either unstable or too small to exhibit a plasmon band. This was one of the main reasons for carrying out the synthesis with lauric acid. The tested ligands were hexanethiol, dodecanethiol, trioctylphosphine, trioctylphosphine oxide, and perfluorated dodecanoic acid.

Fig. 2. TEM image of lauric acid-capped copper nanoparticles. The particle size was 3.3 ± 0.7 nm.

The effect of exposure to air on the UV–vis spectrum of the lauric acid-protected copper nanoparticles is shown in Fig. 1. Immediately after exposure, the intensity of the surface plasmon peak starts to weaken and a red shift is observed. After 10 min there was practically no sign of the plasmon left. The color of the solution turned from red to black in 30 s, then light yellow, and finally colorless after 1 day. No visible precipitation occurred during 2 days. The effect of oxygen on the plasmon absorbance of copper nanoparticles has been observed before both in simulations [34] and experiments [26] and [35] and can be explained by oxidation layers formed on the particle. It is known that the surface plasmon peak broadens and its intensity decreases when the diameter of the nanoparticle is decreased below 3 nm [34]. In the particle size range considered here, the size of metallic copper core decreases below this limit as oxide layers start to form on the surface. While the plasmon peak disappeared, diffraction peaks in the XRD spectrum (Fig. 3) corresponding to metallic copper were observed at 2θ values of 43.3° , 50.5° , and 74.2° and cuprous oxide peaks at 36.4° and 61.4° . The cuprous oxide diffraction corresponding to the (2 0 0) Miller index at 42.3° is masked by the stronger copper peak at 43.3° . It is clear that some metallic copper remains in the core of the particles while the surface is oxidized to Cu_2O .

Fig. 3. XRD spectrum of oxidized lauric acid-capped copper nanoparticles.

3.2. Ligand exchange and etching

While a large range of ligands were tried for ligand exchange, including hexanethiol, dodecanethiol, octadecanethiol, trioctylphosphine, triphenylphosphine, trioctylphosphine oxide, perfluorated lauric acid, oleic acid, didodecylamine, trioctyl aluminum, and a mixture of dodecanethiol and trioctylphosphine, the following results cover only the thiols and oleic acid, as only these resulted in increased air stability. The other ligands precipitated the nanoparticles (perfluorated lauric acid and the mixture of dodecanethiol and trioctylphosphine) or showed identical behavior to lauric acid (trioctylphosphine, triphenylphosphine, trioctylphosphine oxide, didodecylamine, trioctyl aluminum). The latter may indicate that no exchange occurred, resulting from weaker adsorption than that of lauric acid.

The wavelength and the absorption intensity of the original lauric acid-capped nanoparticles and the ligand-exchanged nanoparticles before air exposure are presented in Table 1. The first samples were taken and prepared after 3 days of mixing with the new ligand. It can be seen that the effects of the three thiols are similar: the plasmon peak shifts to higher wavelengths from 556 nm to over 560 nm. This can be explained by the strong bond formed between the sulfur atom and the copper surface [36] and [37]. Oxide surface layers have been shown to red shift the copper plasmon peak wavelength [34] and a copper thiolate layer is expected to have the same effect. It has previously been shown that when gold nanoparticles were prepared with capping molecules containing both

a thiol group and a carboxylic group, adsorption occurred through the thiol groups [38], indicating that thiol adsorption is more favorable than carboxylic acid on gold nanoparticles. The ligand exchange reactions carried out here indicate that the thiol group also substitutes the carboxylic acid group on copper nanoparticles.

Table 1. The position of Cu(0) surface plasmon in UV-vis spectrum after ligand-exchange. Immediately after the synthesis the plasmon has absorbance of 0.738 A.U. and it is located at 557 nm.

ligand and excess	3 days		5 days		8 days	
	abs / A.U.	λ / nm	abs / A.U.	λ / nm	abs / A.U.	λ / nm
lauric acid						
N/A	0.665	556			0.641	563
C6SH						
1x	0.632	561			0.573	564
10x	0.481	561	0.441	561		
20x	0.440	564				
C12SH						
1x	0.665	563			0.582	566
10x	0.543	561	0.515	559		
20x	0.511	561				
C18SH						
1x	0.696	565			0.610	568
10x	0.593	561	0.529	561		
20x	0.530	561				
oleic acid						
1x	0.667	556			0.662	555
10x	0.665	566	0.669	568		
20x	0.702	563				

As the excess of the thiol is increased, the absorption intensity decreases more notably but the wavelength of the plasmon resonance remains approximately constant. Also, the carbon chain length of the thiol affects the absorption intensity; the decrease in intensity is larger for shorter chain lengths. As these observations were made under nitrogen atmosphere, and therefore no oxidation due to oxygen was possible, they could indicate etching of the copper nanoparticles in thiol-containing solutions. Similarly, etching of gold particles by thiols has been reported [39] and [40]. Additionally, similar trends were observed for the chain length and concentration of the thiol. The thiol excess has an increasing effect beyond the 1/1 ratio of thiol/Cu (Table 1) and etching does not seem to stop after 1 day, contrary to what has been found for gold nanoparticles. This suggests that an ordered and stable thiol–metal structure does not form on copper nanoparticles as it does with gold nanoparticles.

In the case of oleic acid the effect of the ligand is quite different. When the amount of oleic acid is the same as lauric acid, there is no observable difference in the plasmon peaks. This is explained by the similar magnitude of the adsorption energies since the only differences are in the structure of the carbon tails, while the head groups remain the same. When the excess is increased to 1:10 and 1:20, the wavelength of the plasmon peak shifts to over 560 nm from 556 nm at excess of 1:1. When the metal to ligand ratio is 1:20, the decrease in absorption intensity with time is less than that for the original lauric acid-stabilized particles after the same time (Table 1). These good stabilizing properties of oleic acid have been previously observed for iron oxide particles [41]. Thus, contrary to thiols, it seems that oleic acid does not induce etching of the copper particles.

3.3. Oxidation of ligand-exchanged nanoparticles

The stability of the nanoparticle solutions against air exposure was examined next. The spectra of octadecanethiol and oleic acid-protected nanoparticles at ligand to metal ratios of 1:1 and 20:1 after exposure to air are shown in Fig. 4. For all cases, the surface plasmon decreases in intensity and a red shift is observed, indicating that oxidation is taking place. The spectra for a thiol excess of 20 shows an increasing peak at ~310 nm. This peak is clearly visible only at excesses of 10 and 20 with all thiols, which emphasizes the destabilizing effect of the thiol excess. Peaks at these wavelengths have been attributed to copper oligomers of few atoms [42]; however, many other

absorption bands appear in this region. Since this peak is observed only in the presence of oxygen, it is suggested that it is linked to an oxidation product of copper, when excess thiol is present.

Fig. 4. Evolution of UV-vis spectra of ligand-exchanged copper nanoparticles after air exposure. (A) C18SH (ligand/metal ratio 1/1), (B) C18SH (20/1), (C) oleic acid (1/1), (D) oleic acid (20/1).

Oleic acid-capped copper nanoparticles show a wide peak at ~ 350 nm, which has been connected to Cu-O-Cu structures [43]. The intensity of this peak decreases over time and a wide absorbance band emerges at 650–700 nm after some 20 min in air. This has been assigned to Cu^{2+} in CuO [44] and [45]. Additionally, the color of the colloids changed with time; oleic acid-stabilized copper nanoparticle solutions became blue, thiol-stabilized solutions light yellow, and lauric acid-stabilized colorless after a day in ambient air. The colors indicate that different oxidation products are formed.

XRD measurements were taken from the oxidized particles to resolve the products formed. These measurements were performed 4 weeks after the introduction of oxygen to the samples. Neither copper, cuprous oxide, cupric oxide, or copper sulfide peaks were found for thiol and oleic acid-protected particles. Additionally, no particles were observed with transmission electron microscopy of oleic acid and thiol-exchanged particles. While the original lauric acid-capped particles were visible in TEM and had crystalline copper cores (XRD), the lack of particles in the TEM micrographs and crystalline structures suggests dissolution of the particles in the presence of these ligands and oxygen.

In Fig. 5 the plasmon peak intensities for the three thiols and oleic acid are presented as a function of time for different ligand excesses. The absorbance is given relative to the absorbance at the beginning of air exposure. The curve for lauric acid-capped nanoparticles is included for reference in each figure. It is immediately clear that thiol-capped copper nanoparticles are more oxidation resilient than those capped with lauric acid. Even though thiols do not block oxidation completely, there is a marked improvement of stability compared to lauric acid. Since the only difference between lauric acid and dodecanethiol is the head group, the increased oxidation resistance must result from the strong adsorption of the thiol head group on the copper surface that hinders oxidation by blocking preferential reaction sites for oxygen.

Fig. 5. Surface plasmon absorbance of ligand-exchanged Cu(0) nanoparticles with different ligands and excesses. The absorbance is presented relative to the absorbance at the beginning of oxidation. Absorbance reading has been taken at the peak of plasmon absorbance at any time and not at a fixed wavelength. (A) C6SH, (B) C12SH, (C) C18SH, (D) oleic acid. (●) Lauric acid-capped nanoparticles, (■) ligand/metal ratio 1/1, (▲) 10/1, (◆) 20/1.

The oxidation resistance increases as the carbon chain lengthens. This is explained by the well-ordered carbon tail layer of the longer alkanethiols blocking oxygen [24]. It is also noteworthy that the oxidation proceeds approximately at the same rate at any excess, indicating that there is no need for a large excess of thiols. Thus, it appears that the Cu-S bond is strong enough to fully replace lauric acid and saturate the surface at lower concentrations. Additionally, the plasmon absorbance decreases more rapidly with larger excess at longer time scales, evidencing the

accelerated effect due to etching. Additionally, the increased monolayer stability of longer chain ligands favorably decreases etching.

The oxidation of oleic acid-stabilized particles is rather different. Stabilization increases steadily with increasing excess. With a 1:1 molar ratio there is only a minor increase in stability compared to lauric acid. When the excess is 10, oxidation at time scales shorter than 5 min is suppressed. At an excess of 20, oxidation is prevented also at longer time scales. It has previously been shown that the double bond in the oleyl chain is vital to the stabilization of nanoparticle colloids [41]. In this case, it seems that the oleyl chain is also effective against oxidation.

In Fig. 6, the UV-vis spectra of the particles stabilized by the different ligands are compared. Clearly, oleic acid-stabilized particles have the best resistance to oxidation at high ligand excess. The weaker performance of thiol-stabilized particles can be explained by continuous etching, which makes the surface of the particle unstable. Additionally, there have been reports that thiol adsorption reconstructs copper surfaces, which could make them more vulnerable to oxidation [37]. As for thiols, it is clear that a longer carbon chain gives better protection against oxygen.

Fig. 6. Surface plasmon absorbance of ligand-exchanged Cu(0) nanoparticles with different ligands and excesses. The absorbance is presented relative to the absorbance at the beginning of the experiment. The absorbance intensity has been taken at the peak of plasmon absorbance. (A) Ligand/metal ratio 1/1, (B) 10/1, (C) 20/1. (■) C6SH, (▲) C12SH, (◆) C18SH, (▼) oleic acid.

4. Summary

The oxidation stability of copper nanoparticles capped by different ligands has been studied. The particles were synthesized under nitrogen by a modified Brust–Schiffrin method, using lauric acid as a capping agent. The particles were approximately 3.3 nm in diameter. Then successful ligand exchange was carried out at ligand to Cu ratios of 1:1, 10:1, and 20:1, with C6SH, C12SH, C18SH and oleic acid. Experimental results indicate that both thiols and oleic acid are capable of replacing the lauric acid ligand. Additionally, in the absence of oxygen the particles appeared to be etched

by thiols. The etching rate increased with decreasing thiol chain length. After oxidation, ligand-exchanged particles were not detected by TEM or XRD, suggesting dissolution of these particles, while the original lauric acid-capped particles were spherical with crystalline copper cores.

Thiols were found to improve oxidation resistance already at a ratio of 1:1. The stability was not found to increase with increasing concentration. The oxidation resistance improved with increasing chain length. Oleic acid was found to marginally increase oxidation resistance at low excess; however, the oxidation resistance improved with increasing excess. At a ligand to Cu ratio of 20:1 oleic acid-capped particles were clearly superior to thiol-stabilized particles.

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