

A study of the behavior of MUA-coated Au colloid in ethanol solution

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A stable gold colloid dispersed in ethanol solution was prepared by coating with MUA. The stability of MUA-gold particles in the ethanol solution was studied using UV-Vis absorption spectra, which were affected by the MUA concentration, water concentration, initial particle size of the gold and heat treatment. A stable MUA-gold colloid in ethanol was obtained when the concentrations of MUA and water were 0.02 mM and 16.7 M, respectively. The small sizes of the gold particles before encapsulation and a low temperature were preferable for the stability of MUA-gold particles in the ethanol solution.

Key words: MUA, Gold colloid, Concentration, Stability, Ethanol.

Introduction

The wet chemical synthesis of small metal and semiconductor particles offers the most economic route for the preparation of nano-structured materials. However, a fundamental difficulty to be overcome is the transfer of these materials out of solution while retaining their size-dependent properties [1-3]. In solution the particles are mobile and will coalesce due to van der Waals forces unless they are protected [4].

In addition, nowadays the metallic nano-particles such as gold and silver are occasionally used under extreme conditions such as optical limiters and three-dimensional optical memories using lasers of high intensity [5-8]. At high light intensities, these are susceptible to damage, leading to photo fragmentation, ligand desorption, etc. To make them stable in extreme conditions, it is necessary to protect them with a more stable and chemically-inert shell such as oxides SiO₂ [9-11] and TiO₂ [12-14]. This type of cover also makes it possible to fabricate materials for special applications. Normally, the oxides used as shell materials were always prepared from an organic precursor solution. So it is significant to study the behavior of metal nano-particles in organic solutions.

In the present study, mercaptoundecanoic acid (MUA) was used as a precipitant and dispersant. As the mercapto group of MUA has a strong affinity with gold, the carboxyl group is considered to face out to the organic dispersing media and helps the dispersion of gold particles [15]. The dependence of various of factors

on the stability of the MUA-gold system such as the MUA concentration, volume percent of water in the dispersing solution and the initial diameter of the Au nano-particles will be discussed.

Experimental

Preparation of MUA-coated Au colloid. A gold colloid (500 ml, 0.5 mM) was prepared by the standard sodium citrate reduction method [16]. In a typical synthesis process, H₂AuCl₄ (120 mg) was dissolved in 500 ml of water and the solution was heated to boiling. A solution of 1 wt% sodium citrate (50 ml) was added to this boiling solution. Boiling was continued for about 1 h. This method produces a stable, deep-red dispersion of Au particles with an average diameter of around 15 nm (Fig. 1).

The mercaptoundecanoic acid (MUA) solution which

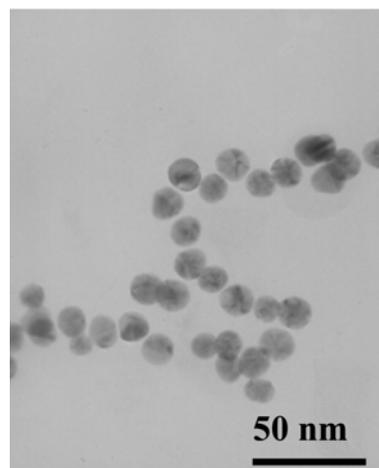


Fig. 1. TEM image of gold colloid synthesized by a sodium citrate reduction method with the average diameter of 15 nm.

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was prepared by dissolution of MUA into 2.5% ammonia solution was then added to the gold colloid and the solution mixture incubated for 2 h [15]. Then the pH value of the solution was adjusted to 3 by adding 1 M HCl to make the MUA-gold particles flocculate. The flocculate was left for one day to sediment. The gold particles collected were centrifuged and washed repeatedly with water. At last, the MUA-coated Au nano-particles were dispersed in 20 ml water, and were re-dispersed by adding about 20 μ l of 28% ammonia solution. Finally, the MUA-gold colloid was transferred into an ethanol solution with different volume percents of water. All the chemicals were ACS grade and were used without further purification.

Characterization

The morphology of the synthesized particles was examined by a transmission electron microscope (JEM-2010, JEOL). The stability and optical property of the MUA-gold nano-particles in the ethanol solution was monitored by a UV-Vis spectroscopy (UV-2550, Shimadzu).

Results and Discussion

Effect of the MUA concentration on the stability of MUA-gold in ethanol solution

The aggregation of the dispersed particles may be

overcome by the addition of suitable polymers. According to the Stokes-Einstein equation [17]:

$$V_s(h) = 2\pi\alpha\phi_s^2\left(\frac{1}{2}-\chi\right)\frac{K_bT}{V}(2\delta-h)^2 \quad (1)$$

where δ is the average thickness of the adsorption layer; ϕ_s is the average segment volume fraction; V is the volume of the solvent molecules; h is the distance between the particles; χ is the Flory parameter, which gives an indication of the compatibility of the polymer and the solvent, the smaller χ , the better the solvent. In a good solvent, $\chi \sim 0$, hence, $V_s(h)$ is positive, and a repulsive steric interaction results. To obtain a stable colloid, no desorption of polymer chains should be expected from the particle surface, which is somewhat incompatible with the Flory parameter; in addition, when the concentration of polymer is too high, the polymer will aggregate in the solvent [17]. Thus, paradoxically, depending on the conditions, the addition of a polymer to colloid dispersions may lead either to stabilization or to aggregation of the particles. So, preferably an optimum amount of polymer should be used to increase the stability of particles in solution.

As shown in Fig. 2(a), the flocculate could almost completely re-disperse in water by adding a minimum amount of ammonia to the ionized MUA. The concentration of MUA had a strong effect on the stability of

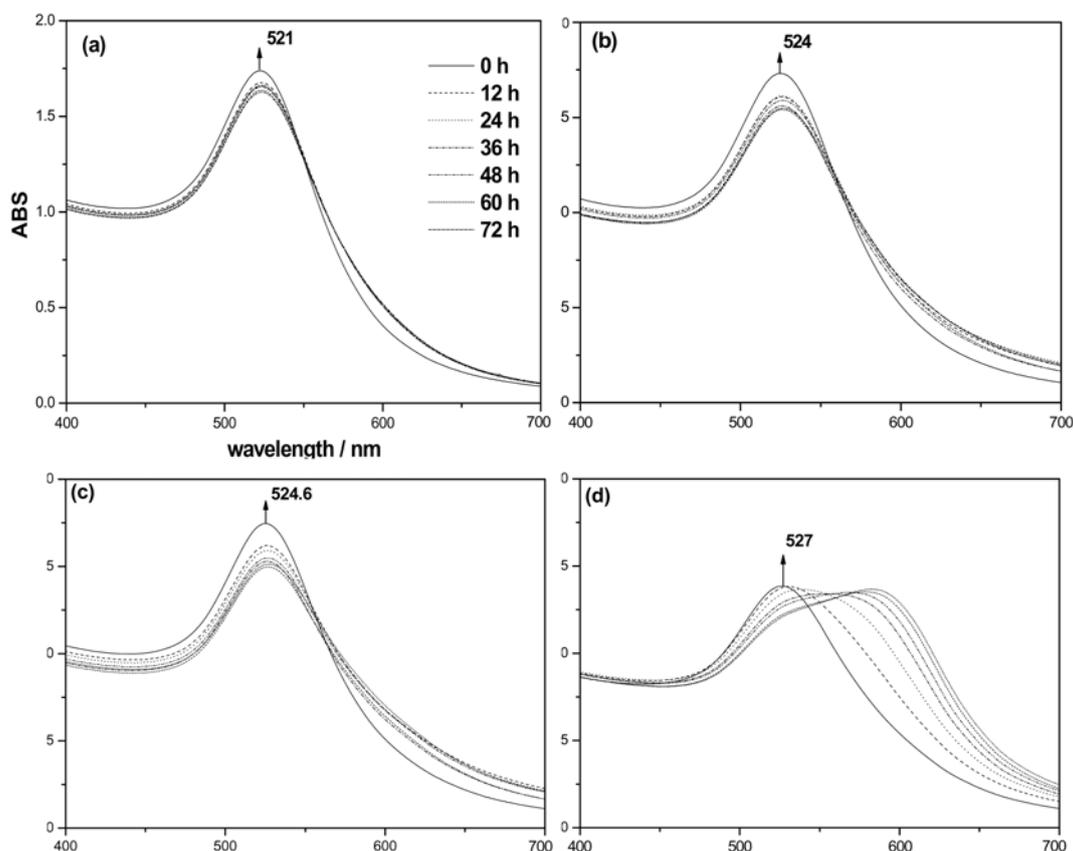


Fig. 2. UV-Vis absorption spectra of MUA-gold colloid with different concentrations of MUA (a) 0.02 mM; (b) 0.05 mM; (c) 0.17 mM; (d) 1.0 mM. The water concentration of all the samples was 16.7 M.

Table 1. Effect of MUA concentration on the stability of MUA-gold colloid incubated for 3 days

MUA Concentration/mM	1.0	0.17	0.05	0.02	0.01	0.005
Peak Location/nm	581.9	527.2	526.1	523.9	*	**

*Partially re-dispersed; **most of the part was not re-dispersed.

the MUA-gold colloid dispersed in the ethanol solution. Aqueous MUA-gold sols obtained from various incubation concentrations were mixed with ethanol and the stability was monitored by the UV-Vis spectrometer. The results are shown in Table 1. During the flocculation, the surface of the MUA-gold is not supposed to change; therefore, the red-shift of the absorption peak is expected due to the aggregation of gold particles. From Fig. 2 we can see that the stability of MUA-gold in the ethanol solution was improved by decreasing the concentration of MUA in the solution. However, since the solubility of MUA is very high in ethanol, the MUA on the surface of the gold may desorb when its concentration is lower than 0.02 mM under the present conditions, despite the strong affinity between the mercapto group and the gold surface.

Effect of aqueous concentration on the stability of MUA-gold particles

The MUA-gold was very stable in various concentrations of aqueous media, on the other hand, although the MUA-gold could be dispersed in ethanol, it was not as stable as in water and the aggregation appeared at the lower H₂O concentration, as shown in Fig. 3. When the H₂O concentration was lower than 5.6 M, the MUA-gold colloid was not stable and aggregated after being kept for 72 h. The absorption peak location of the UV-Vis spectrum red shifted from 521 to 596 nm in company with peak broadening (Fig. 3a). With an increase of the H₂O concentration, the stability of MUA-gold particles dispersed in ethanol increased markedly. When the H₂O concentration reached up to 16.7 M, no aggregation was found even after the MUA-gold colloid incubated for 3 days (Fig. 3c). As a high ionic strength

Table 2. Effect of water concentration on the stability of MUA-gold colloid in ethanol incubated for 3 days

H ₂ O concentration/M	5.6	11.1	16.7
Volume percent of water/%	10	20	30
Peak Location/nm	596.4	527.9	523.9

Table 3. Absorption peak location of Au colloid with different diameters

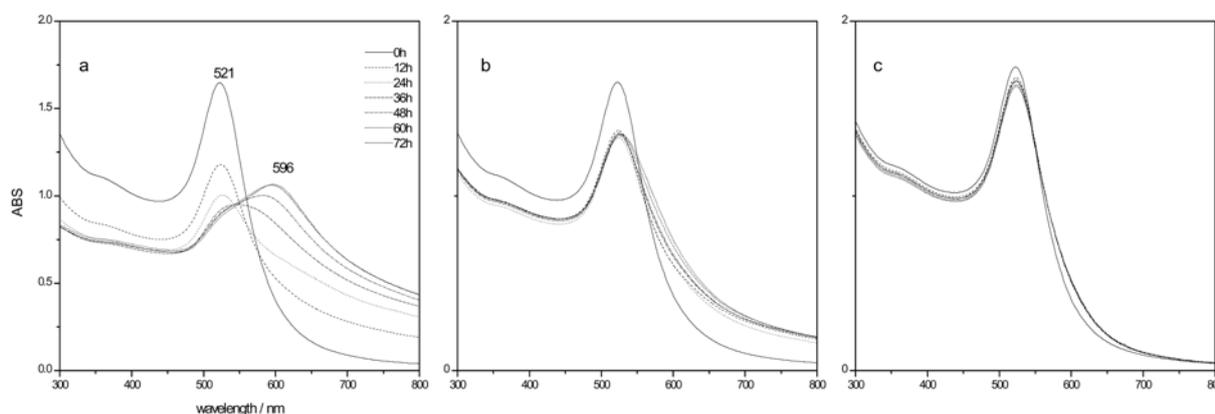
Sample	D0	D1	D2	D3
[KNO ₃]/mM	0	1.0	5.0	10.0
Diameter of gold particles/nm	15	20	30	≥50
Peak location/nm	520	528.7	535.5	546.9

can accelerate the aggregation of nano-particles [18], the low concentration of H₂O induced the aggregation of MUA-gold particles. The peak positions as read from the results of UV-Vis spectra are listed in Table 2.

Effect of particle size of uncoated gold on the stability of MUA-gold

As stated above, a high ionic strength can accelerate the aggregation of nano-particles, the gold particles dispersed in the aqueous solution with different diameters were prepared by adding different amounts of KNO₃ into the aqueous solution (Table 3), the average size of gold particles obtained were 15, 20, 30 and larger than 50 nm (TEM micrographs are not given). The UV-Vis absorption spectra of the gold colloids are seen in Fig. 4.

Then the Au particles with different diameters were coated with MUA, the samples prepared were named MUA-D₀, MUA-D₁, MUA-D₂ and MUA-D₃, and the stabilities of MUA-D_{0,3} colloids in the ethanol solution were studied. Figure 5 shows the UV-Vis absorption spectra of MUA-D_{0,3} colloids. It can be seen that the stability of MUA-gold in the ethanol solution decreased when the gold particle aggregated before being coated with MUA. The MUA-gold has less stability for the bigger gold particles. In Fig. 5b, the MUA-D₁ aggregated apparently after being incubated for 24 h,

**Fig. 3.** UV-Vis absorption spectra of MUA-gold colloid in ethanol solution with different concentrations of water. (a) 5.6 M; (b) 11.1 M; (c) 16.7 M. The MUA concentration of all the colloids was 0.02 mM.

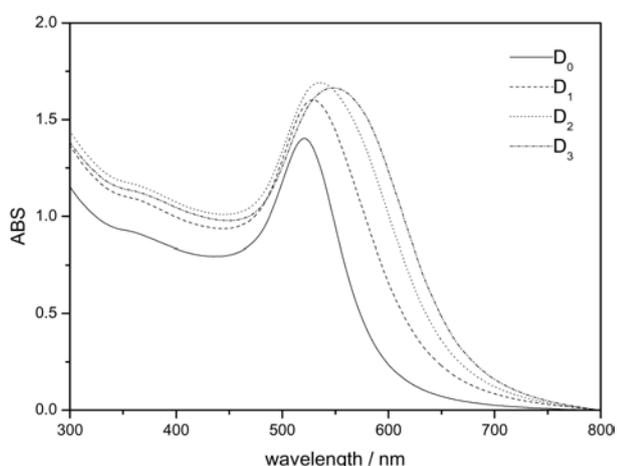


Fig. 4. UV-Vis absorption spectra of gold colloids with different diameters prepared by adding different amounts of KNO_3 . The concentration of KNO_3 is 0 mM (D_0), 1.0 mM (D_1), 5.0 mM (D_2) and 10.0 mM (D_3).

although there was no sediment in the bottom of the bottle. The peak location of the UV-Vis spectrum red shifted from 528 to 567 nm. After the sample was kept for 72 h, some sediment was found in the bottle and the

UV-Vis absorption peak further red shifted. When the average size of the uncoated gold particles reached 30 nm, the stability of the MUA-gold further decreased (Fig. 5c). After the sample MUA- D_2 was incubated for 72 h, the absorption peak red shifted about 70 nm, and more sediment was found than that of the MUA- D_1 sample. When the particle size of the uncoated gold was larger than 50 nm, the MUA- D_2 became unstable (Fig. 5d), some sediment was found after being kept for just 12 h, after being kept for 72 h, most of the MUA- D_3 particles were deposited.

Therefore, it may be concluded from the discussion above that the stability of the gold particles is strongly dependent on the particle size, and the amount of MUA coated onto the gold particles has to be controlled whenever the particle size of gold is changed.

Effect of heat treatment of the gold colloid on the stability of MUA-gold in ethanol solution

To study the effect of heat treatment of the gold colloid on the stability of MUA-gold in the ethanol solution, the MUA solution was added into the gold colloid when heated to 60 °C, and then re-dispersed in

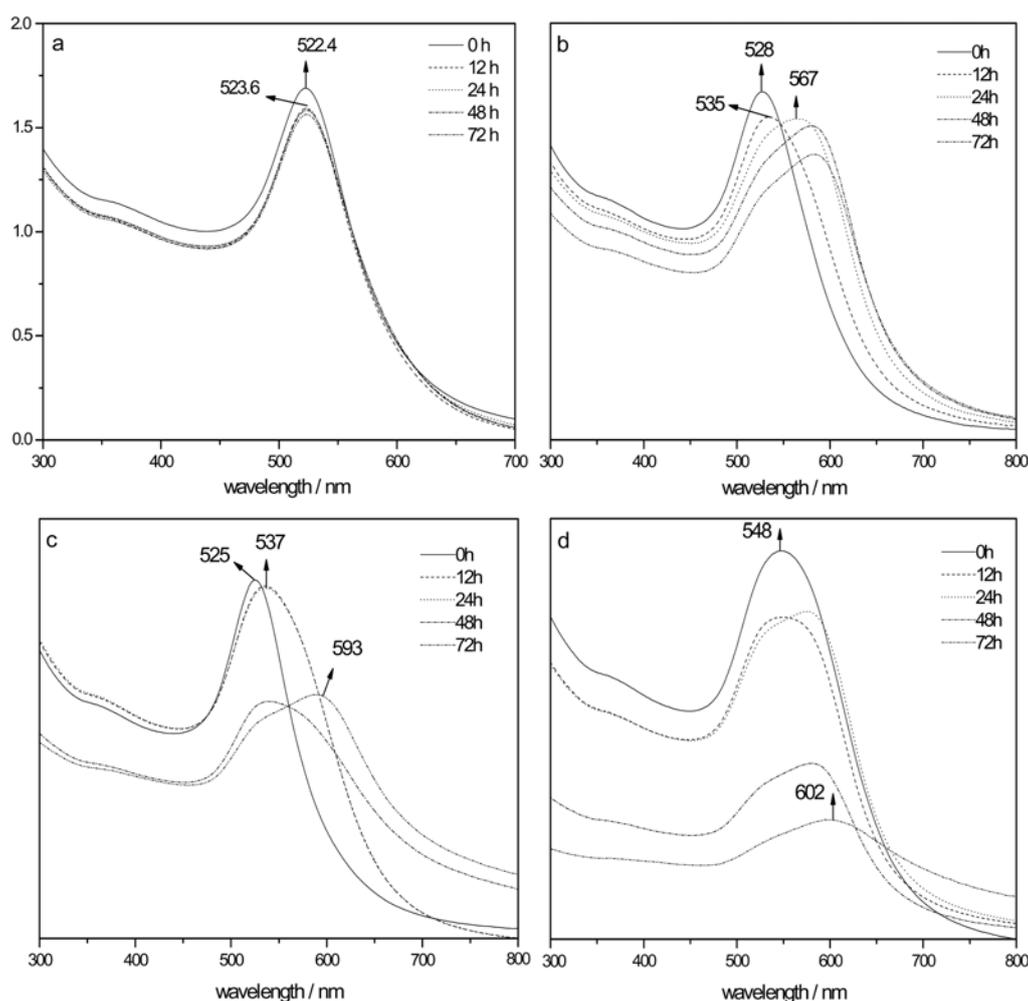


Fig. 5. UV-Vis absorption spectra of D_0 - D_3 coated with MUA and aged for 72 h. a. MUA- D_0 ; b. MUA- D_1 ; c. MUA- D_2 ; d. MUA- D_3 . The concentration of MUA was 0.02 mM, and the water concentration was 16.7 M.

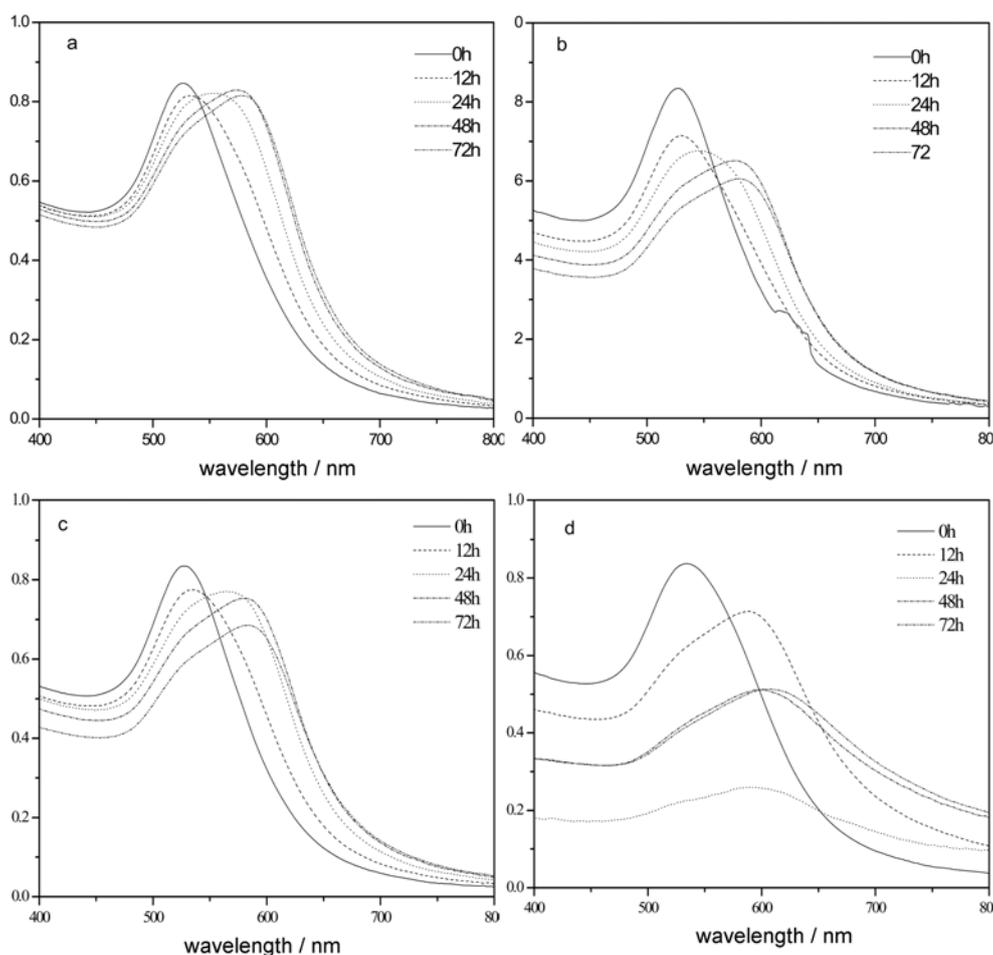


Fig. 6. UV-Vis absorption spectra of MUA-gold colloid where the MUA concentration was (a) 0.02 mM; (b) 0.05 mM; (c) 0.17 mM; (d) 1.0 mM. The MUA was added into the solution at 60 °C and the water concentration of all the samples was 16.7 M.

an ethanol solution at room temperature. Fig. 6 is the UV-Vis absorption spectra of MUA-gold colloids with different concentrations of MUA. We can see from the Fig. 6 that the stability of the MUA-gold in ethanol solution is not satisfied, although increasing the concentration of MUA from 0.02 to 0.05 mM can improve the stability of MUA-gold particles. But when the concentration of MUA was further increased to 1.0 mM, the stability decreased sharply. This phenomenon can be

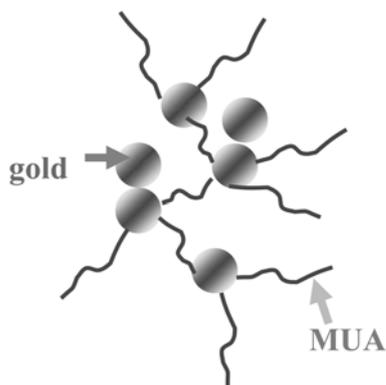


Fig. 7. The scheme of the bridging aggregation of MUA-gold particles in the ethanol solution.

explained in that when the gold colloid is heated to 60 °C, the Brownian motion of gold particles is accelerated, and the frequency of the connection between two gold particles is increased, at this time, when MUA was added into the colloid, the gold particles can not be protected perfectly by MUA, giving rise to bridging aggregation (as shown in Fig. 7). Thus, the stability of MUA-gold in ethanol solution decreased.

In addition, the heat treatment of the gold colloid will also affect the gold particle size, and thus affect the stability of the MUA-gold in the ethanol solution, which has been discussed in 3.3 section.

Conclusions

Mercaptoundecanoic acid (MUA) was employed to obtain a stable gold colloid in an ethanol solution. The stability of the gold colloid was affected by the MUA concentration during incubation, water concentration, the diameter of gold particles before being coated and solution temperature. In order to avoid gold particle aggregation in the ethanol solution, a lower MUA concentration, a higher water concentration and small particles of gold before being coated with MUA were prefer-

able. Desorption occurs when the solution is heated to 60 °C, resulting in a decrease of the stability of MUA-gold particles in the ethanol solution.

Acknowledgments

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