

Field-Limited Digestive Ripening for Self-Organization of Thiol-Capped Gold Nanoparticles

M.-L. Lin¹, F. Yang², J.S. Peng¹, C.M.Hsu³ and Sanboh Lee¹

¹Department of Materials Science and Engineering, National Tsing Hua University, Hsinchu 30013, Taiwan

²Department of Chemical and Materials Engineering, University of Kentucky, Lexington, KY 40506, USA

³Department of Chemical Engineering, National United University, Miaoli 36003, Taiwan

ABSTRACT

This work investigated the effect of electric field on digestive ripening of gold particles of nanosizes during reflux heating at 130°C. The effect of electric field on the evolution of the particle size and the self-assembly of the formed gold nanoparticles is also examined. Under the action of an electric field, the polydispersed gold nanoparticle with the negative charge reached the state of nearly monodispersity. The electric field caused the increase of the particle size and induced the self-assembly of the nearly monodisperse gold nanoparticles, which is observed under high electric field intensity. The nanostructure of self-assembled gold particle nanostructures is six-fold symmetry. These experimental observations reveal that digestive ripening with the current is a new way for engineering application to control the particle size of metallic nanoparticles.

Keywords: Digestive ripening, gold nanoparticles, electric field

1. Introduction

Digestive ripening is the reverse process of Ostwald ripening [1], in which particles of nanosizes in a polydispersed particle system grow at the expense of large ones to form a nearly monodispersed particle system. Using this process, various nearly monodisperse metallic particles of nanosizes have been prepared. Moreover, the models for self-assembly of gold nanoparticles have been developed. Leff et al. [2] suggested that the size of the thiol-capped gold nanoparticles becomes smaller as more thiol is added by expressing the “surface energy” of a thiol-capped gold particle as a function of the number of gold atoms and the number of thiols. Lee et al. [3] found that there existed stable and mesostable states during digestive ripening of charged nanoparticles. However, they do not show any experimental results to support the assumption of charged nanoparticles, and there is no report on the examination of the effect of electric field on digestive ripening of metallic particles of nanosizes. This work is focused on investigating the effect of electric field on digestive ripening of gold particles of nanosizes during reflux heating. The effect of electric field on the evolution of the particle size and the self-assembly of the formed gold nanoparticles is also examined.

2. Experimental detail

NaBH₄ aqueous solution of 9.4 M was first prepared by dissolving the powder of sodium borohydride (Thermo Fisher Scientific Taiwan Co., Taipei, Taiwan) in DI water, and a micelle solution of 0.025 M was formed by dissolving 156 mg DDAB (didodecyldimethylammonium bromide, Sigma-Aldrich Co., St. Louis, Missouri) in 15 mL toluene. Gold chloride of 51 mg (Sigma-Aldrich Co., St. Louis, Missouri) was then dissolved in the micelle solution and followed by sonication for 15 min. 54 μL of the NaBH₄ aqueous solution was added to the colloid, and the solution was stirred for 15 min. After the reduction of gold ions by NaBH₄, 5 mL of the prepared solution was transferred to a 50 mL vial, and 0.4 mL (0.36 g) of dodecanethiol was added with stirring for 1 min. 15 mL of ethanol was added, and the solution was shaken vigorously in order to remove the excess DDAB, dodecanethiol, and other reaction side products. The solution was left undisturbedly overnight to let gold particles precipitate. The clear top solution was then decanted, and the bottom precipitate was dried in vacuum. The precipitate was re-dissolved in 18 mL toluene with the addition of an extra amount of 0.74 g dodecanethiol to form a gold colloid.

A liquid cell of rectangular prism was made of quartz with two parallel copper electrodes being attached to the outer surfaces of the rectangular prism, respectively. The distance between two parallel inner surfaces was 13 mm. The liquid cell with the electrodes was immersed in an oil bath, which was filled with silicon oil. A thermocouple was placed in the oil bath to monitor and control the temperature, and a cooling system was used to make uniform distribution of temperature around the liquid cell. To avoid possible dielectric breakdown in the oil bath, only electric voltages of 6, 8, and 10 kV were applied during the reflux heating at 130 °C.

A drop of the gold colloids prepared by the reflux heating, which was taken near either the anode or the cathode, was deposited on a carbon-coated copper grid of 300 meshes (Ted Pella, INC., Pedding, CA) by a dropper. The copper grid was placed on a filter paper which could rapidly wick up the excess solvent and help the particles spread uniformly over the grid area. The gold nanoparticles deposited on the copper grid were dried in vacuum at 70 °C for at least one day in order to evaporate the residual solvent. TEM images were taken by Hitachi H-7500 transmission electron microscope (Hitachi, Ltd, Tokyo,

Japan) at a magnification of 100 kX. The images were analyzed by the software, Scion Image (NIH, Bethesda, MD).

3. RESULTS AND DISCUSSION

The reflux heating of the gold colloid at 130 °C was performed under the action of electric fields of 0, 0.363, 0.484, 0.605 MV/m. Figure 1 shows the typical TEM images of the gold nanoparticles with different heating times. No coagulation and coalescence of gold nanoparticles are observed. Gold nanoparticles with two different sizes were observed after the reflux heating of 48 h. To examine the size evolution of the gold nanoparticles, the TEM images were analyzed. The temporal evolution of the size distribution of the gold nanoparticles is depicted in Fig. 2. Without the action of an electric field, the gold colloid become nearly monodisperse around 5.20 nm after the reflux heating of 8.5 h at 130 °C and became bi-disperse after prolonged heating of 48 h. The presence of the bi-disperse distribution is qualitatively in accord with the prediction given by Lee et al. [10]. At high temperatures, there likely exist a stable state and a mesostable state with different particle sizes, respectively. The reflux heating increases the thermal energy of gold ions and helps gold ions move in the solution to reach the mesostable state. Figure 3 shows typical TEM images of the gold nanoparticles near both electrodes under the action of an electric field of 0.605 MV/m. The electric field caused the size change of the thiol-capped gold nanoparticles near both electrodes.

Figures 4a and 4b show the size distribution of the gold nanoparticles for different heating times under the action of an electric field of 0.605 MV/m. The gold nanoparticles near the anode became nearly monodisperse around 6.33 nm after the reflux heating of 7 h, while it needed about 11 h of the reflux heating for the gold nanoparticles near the cathode to become nearly monodisperse around 6.78 nm. The electric field accelerated the digestive ripening of the gold nanoparticles near the anode and slowed down the digestive ripening of the gold nanoparticles near the cathode; it also altered the particle size corresponding to the nearly monodispersed particle system. In addition, bi-disperse distribution of the gold colloid appeared near the anode after the reflux heating of 11 h, and no bi-disperse distribution appeared near the cathode with the reflux heating up to 13 h. With the action of an electric field, it is expected that bi-disperse distribution of the gold colloid would appear near the cathode after the reflux heating more than 48 h. The electric field caused the gold colloid near the anode to achieve the bi-disperse state much faster than without an electric field. Note that the electrodes were attached to the outer surfaces of the liquid cell made of quartz, and there was no deposition of gold nanoparticles on the surfaces of the quartz walls and no transfer of electric charges.

Table 1 shows the effect of electric field on the time to reach a nearly monodispersed gold nanoparticle system with the reflux heating at 130 °C and the corresponding particle size. The electric field caused the increase of the particle size for the nearly monodispersed gold nanoparticle system, independent of the polarity of electrode. Such behavior likely was due to the increase of the system internal energy when subjected to an electric field, which changes the particle size at the stable state. The particle size for the nearly monodispersed gold nanoparticle system started to increase with increasing the field intensity for the field intensity less than or equal to 0.484 MV/m, while it decreased for an electric field of 0.605 MV/m. The mechanism for the decrease of the particle size for the nearly monodispersed gold nanoparticle system under the action of an electric field of high field intensity is unclear.

Generally, negatively charged nanoparticles will move to anode and positively charged nanoparticles to cathode under the action of an electric field. However, there exists ionic atmosphere around each gold nanoparticle in the gold colloid due to the attachment of the thiol-ligands, which limits the motion of the gold nanoparticles. Without the action of an electric field, the distributions of ionic atmosphere and the thiol-ligands are symmetric. The gold colloid is uniform and homogeneous. The distance between gold nanoparticles is statistically same, which is a function of the concentrations of gold nanoparticles and dodecanethiol. Relatively uniform distribution of the gold nanoparticles was observed, as reported by Lin et al. [4]. In an electric field, the thiol-ligands attached to the gold nanoparticles will move with the gold nanoparticles towards the anode, which forms a region of the thiol-ligands with high concentration. As pointed out by Lin et al. [5], the size evolution of the gold nanoparticles is dependent on the concentration of the thiol-ligands (dodecanethiol). The more of the thiol-ligands, the faster is for a gold colloid to become nearly monodisperse. From the results given in Table 1, one can conclude that, under the action of an electric field of larger than or equal to 0.484 MV/m, the thiol-capped gold nanoparticles moved to the anode to increase the concentration of the gold nanoparticles and the thiol-ligands. The thiol-capped gold nanoparticles carried negative charges, which was also observed by Chandrasekharan and Kamat [6]. Comparing to the gold colloid without the action of an electric field, space-charges layers were formed near the electrodes to counterbalance the electric field. Near the anode, the increase in the concentration of the gold nanoparticles led to the decrease of the distance between gold nanoparticles and the increase of the concentration of the thiol-ligands. Less time was needed for the gold colloid near the anode to reach the nearly monodisperse state, in accord with the observation by Lin et al. [14] in studying the effect of the amount of dodecanethiol on the digestive ripening of gold nanoparticles. Near the cathode, the distance between gold nanoparticles was larger than that without the action of an electric field due to the decrease of the concentration of the

gold nanoparticles and the thiol-ligands, which limited the digestive ripening of the thiol-capped gold nanoparticles.

4. SUMMARY

In summary, this work studied the effect of an electric field on the digestive ripening of the thiol-capped gold nanoparticles with the reflux heating at 130 °C. Under the action of an electric field, the gold colloid can still reach the stable state of nearly monodispersity. The electric field caused the increase of the particle size for the nearly monodispersed gold nanoparticle system, independent of the polarity of electrodes. The electric field decreased the time for the gold colloid to reach the nearly monodispersed gold nanoparticle system near the anode with the field intensity larger than or equal to 0.484 MV/m, while it increased the time to reach the nearly monodispersed gold nanoparticle system near the cathode. All of these results demonstrated the strong field effect on the digestive ripening of the thiol-capped gold nanoparticles through the interaction among electric field, gold particles, and thiol-ligands. The electric field caused the thiol-capped gold nanoparticle towards the anode. The experimental results suggest that the thiol-capped gold nanoparticles carried negative charges. The self-assembly of the gold nanoparticles under the action of an electric field of a high field intensity was observed. The gold nanoparticles tended to form self-assembled nanostructures of six-fold symmetry. The electric field had little effect on the self-assembly of the gold nanoparticles, which is primarily controlled by the interaction of the gold nanoparticles.

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Table 1: Effect of electric field on the particle size of the nearly monodispersed gold nanoparticle system to reach the nearly monodisperse state with the reflux heating at 130 °C

Electric field (MV/m)	Particle size for a nearly monodisperse system (nm)	
	Anode	Cathode
0	~5.20	~5.20
0.363	~5.90	~5.56
0.484	~6.63	~8.71
0.605	~6.33	~6.78

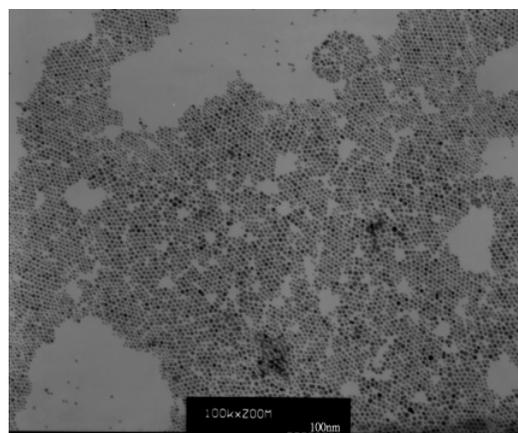


Figure 1: TEM images of the gold nanoparticles without electric field (temperature for reflux heating: 130 °C) with 3 h heating

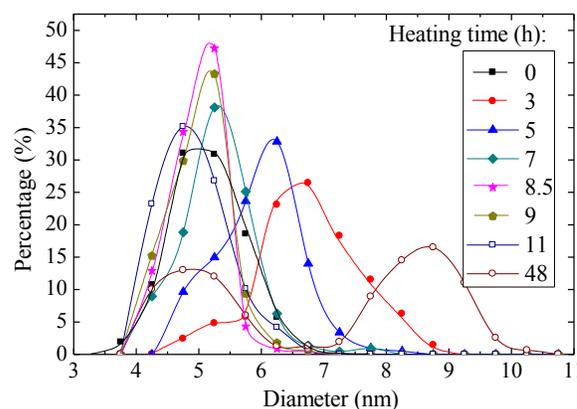


Figure 2: Size distribution of the gold nanoparticles without the action of an electric field for several reflux heating times

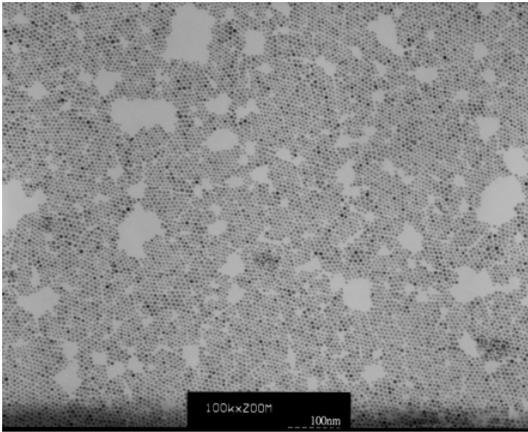


Figure 3(a): TEM images of the gold nanoparticles near an electrode (electric field intensity: 0.605 MV/m; temperature for reflux heating: 130 °C) near anode with 3 h heating

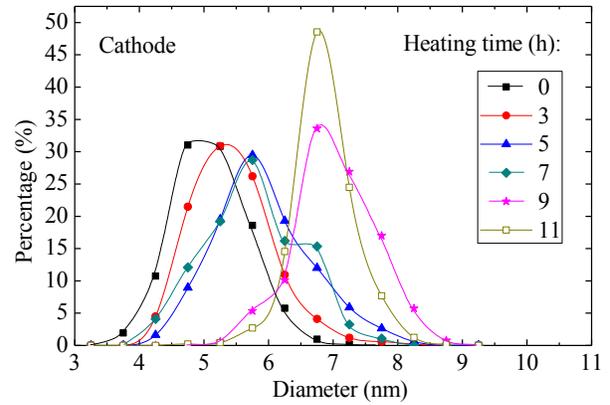


Figure 4(b): Size distribution of the gold nanoparticles near the cathode for several reflux heating times (electric field intensity: 0.605 MV/m)

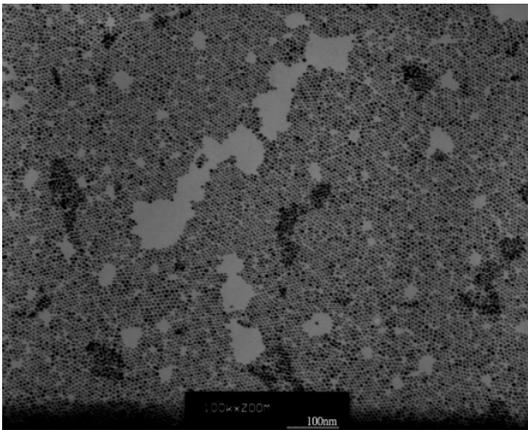


Figure 3(b): TEM images of the gold nanoparticles near an electrode (electric field intensity: 0.605 MV/m; temperature for reflux heating: 130 °C) near cathode with 3 h heating

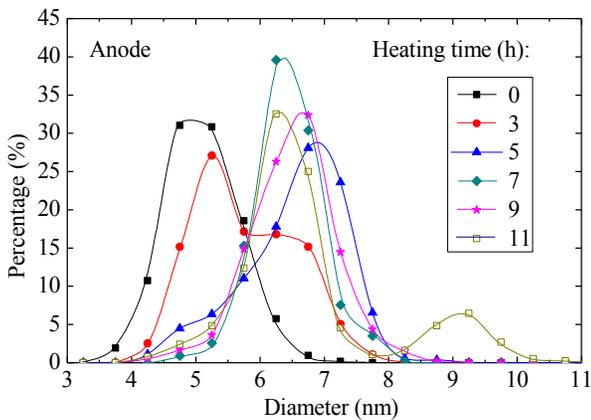


Figure 4(a): Size distribution of the gold nanoparticles near the anode for several reflux heating times (electric field intensity: 0.605 MV/m)