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Digestive ripening for self-assembly of thiol-capped gold nanoparticles: the effects of adding dodecanethiol and reflux-heating

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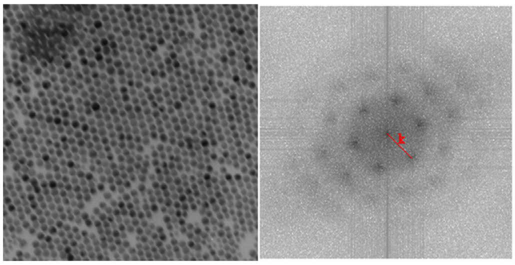
HIGHLIGHTS

- Digestive ripening is used to obtain a mono-dispersed gold nanoparticle system.
- The critical amount of the dodecanethiol is required to obtain gold nanoparticles.
- Reflux heating enhances the transition of poly- to mono-dispersed nanoparticles.
- Gold nanoparticles have the tendency to form nanostructures of six-fold symmetry.

GRAPHICAL ABSTRACT



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ABSTRACT

Digestive ripening is a unique process to prepare a nearly monodispersed nanoparticle system from a polydispersed particle system. A systematical study is performed to investigate the effects of adding an extra amount of dodecanethiol in a gold colloid at room temperature and reflux-heating in a silicone oil bath at 130 °C on the digestive ripening of thiol-capped gold nanoparticles. The experimental results reveal that adding an extra amount of dodecanethiol at room temperature caused the transition of a polydispersed gold nanoparticle system to a nearly monodispersed gold nanoparticle system. The reflux heating is not necessary for preparing a nearly monodispersed gold nanoparticle system. The reflux heating of the gold colloids with an extra amount of dodecanethiol enhances the transition of the polydisperse gold colloids to nearly monodisperse gold colloids. Prolonged heating causes the nearly monodisperse gold colloids to become bi-disperse. It is the combination effect of the reflux heating and the amount of dodecanethiol that determines the digestive ripening of the thiol-capped gold nanoparticles. The self-assembly of the nearly monodisperse gold nanoparticles is observed. The gold nanoparticles have the tendency to form self-assembled nanostructures with six-fold symmetry, and both monodisperse and bi-disperse nanoparticles would have better ordering.

1. Introduction

Metallic particles of nanosizes have attracted great interest in optics, electronics, catalysis, and drug delivery due to unusual chemical and physical properties comparing to the corresponding bulk materials [1,2]. The size effects on material properties are basically controlled by high surface-to-volume ratio [3], quantum effect [4], and electrodynamic interaction [5]. One of the challenges in the applications of metallic nanoparticles is to prepare highly monodisperse metallic nanoparticles. Various techniques have been developed to control the size, shape, and composition of metallic nanoparticles, including laser [6],

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microwave [7], sonochemical techniques [8], and chemical synthesis [9].

Lin et al. [10] found a digestive ripening process to prepare 3D nanocrystal superlattices from a polydisperse colloid through the surface modification of colloidal particles with specific ligands. They demonstrated that the digestive ripening process could narrow the size distribution of gold nanoparticles from an initially polydisperse gold colloid [10] through the temperature-induced size segregation [11]. In contrast to Ostwald ripening [12], which results in an increase of average particle size, the digestive ripening causes the shrink of large particles and the growth of small particles to achieve an equilibrium size at a stable state. Using the digestive ripening process, various metallic nanoparticles have been made. Smetana et al. [12] made Cu–Ag alloying nanoparticles through the digestive ripening. Naoe et al. [13] observed a transition from wormlike to spherical Pa nanocrystals through the digestive ripening. Kalidindi and Jagirdar [14] synthesized Cu@ZnO core–shell nanocomposites through the digestive ripening of Cu and Zn nanoparticles. Zhang et al. [15] prepared monodisperse icosahedral Ag, Au, and Pd nanoparticles with tunable sizes. Combining the digestive ripening with seeding growth, Yang et al. [16] formed monodisperse nanoparticles and core–shell nanoparticles. Cingarapu et al. [17] formed indium nanoparticles under mild conditions. Using the solvated metal atom dispersion and the digestive ripening, Bhaska and Jagirdar [18] synthesized highly monodisperse composite nanoparticles.

Generally, the interaction between the particle surface and surface-active ligands plays an important role in controlling the digestive ripening process. Prasad et al. [19] examined a series of ligands, which were silanes, phosphines, amines, halides, and alkanes, and found that only thiols, amines, silanes, and phosphines are efficient for the digestive ripening. They suggested that the digestive ripening includes three important steps; (1) break large polydisperse colloid into particles of smaller sizes by adding ligands, (2) remove the reaction side-products, and (3) reflux the colloid to get a nearly monodisperse colloid. However, it is unclear if the refluxing is necessary for the digestive ripening. From a thermodynamic viewpoint, the digestive ripening involves atomic migration, which is temperature-dependent. It is expected that the refluxing has an effect on the size evolution of nanoparticles. This work is to investigate the effects of adding dodecanethiol and reflux-heating on the digestive ripening of gold nanoparticles. The self-assembly of the gold nanoparticles formed is also examined and analyzed.

2. Experimental details

2.1. Preparation of gold nanoparticles

The synthesis of thiol-capped gold nanoparticles was prepared by using the procedure similar to the one given by Lin et al. [10]. Fig. 1 shows the schematic of the synthesis of thiol-capped gold colloids. $NaBH_4$ aqueous solution (0.023 g $NaBH_4$ + 0.054 g DI water) 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 sonicated for 15 min, which produced an orange-colored solution. The $NaBH_4$ aqueous solution of 54 μL was added to the colloid, which was stirred for 15 min. After the reduction of gold ions by $NaBH_4$, the solution color became dark-red. The prepared solution of 5 mL was transferred to a 50 mL vial, and 0.4 mL (0.36 g) dodecanethiol was added with stirring for 1 min. The color of the gold colloid became slightly purple. Ethanol of 15 mL was added to the purple solution, and the solution was shook vigorously to remove the excess of DDAB, dodecanethiol, and other reaction side products. The solution (solution A) was left undisturbedly overnight to let gold particles precipitate. Next day, the top-clear solution was decanted, and the precipitate was dried in vacuum. The precipitate was re-dissolved in 18 mL toluene with the addition of dodecanethiol. A series of colloids were prepared with the addition of different extra amounts of dodecanethiol, including 0, 0.22, 0.37, 0.74, 2.22, 4.44, and 6.66 g. The corresponding mole ratios of the dodecanethiol to the gold chloride in the colloids were 10.60, 17.08, 21.49, 32.32, 75.83, 141.19, and 206.43, respectively. These colloids were placed in a silicone oil bath and reflux-heated in an argon atmosphere at atmospheric pressure. The temperature of the silicone oil bath was 130 °C, at which gas bubbles formed in the colloids. This behavior suggests that the corresponding temperature in the colloids was the boiling temperature, 111 °C, of toluene solution.

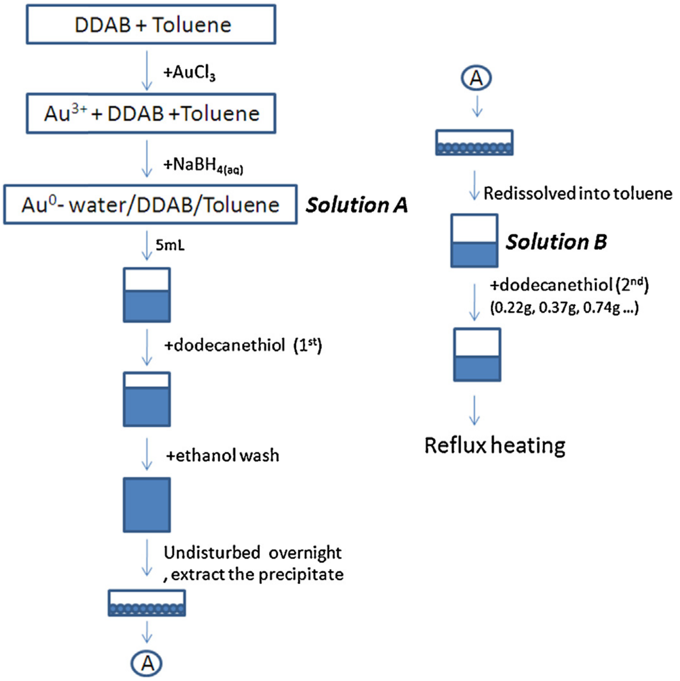

Fig. 1. Schematic of the synthesis of thiol-capped gold colloids.

2.2. TEM characterization

A drop of the colloids was deposited on a carbon-coated copper grid of 300 mesh (Ted Pella, INC., Pedding, CA), using a dropper immediately after preparing the colloids. The drop deposited on the copper grid was dried in vacuum at 70 °C for at least one day before performing the TEM analysis. TEM images were taken by Hitachi H-7500 transmission electron microscope (Hitachi, Ltd, Tokyo, Japan) at a magnification of 100k×. The images were analyzed, using the software, Scion Image (NIH, Bethesda, MD). The size distribution of the gold nanoparticles was independent of the amount of time between the time for the drop deposition and that for the TEM imaging, suggesting that no local sintering was observable for the experimental conditions used.

3. Results and discussion

3.1. Effect of adding dodecanethiol

As mentioned in the experimental section, dodecanethiol was added into the solution twice to examine the effect of adding an