The effect of Au amount on size uniformity of self-assembled Au nanoparticles

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Abstract. The self-assembled fabrication of nanostructure, a dreaming approach in the area of fabrication engineering, is the ultimate goal of this research. A finding was proved through previous research that the size of the self-assembled gold nanoparticles could be controlled with the mole ratio between AuCl4− and thiol. In this study, the moles of Au were fixed, only the moles of thiol were adjusted. Five different mole ratios of Au/S with their effect on size uniformity were investigated. The mole ratios were 1:1/16, 1:1/8, 1:1, 1:8, 1:16, respectively. The size distributions of the gold nanoparticles were analyzed by Mac-View analysis software. HR-TEM was used to derive images of self-assembled gold nanoparticles. The result reached was also the higher the mole ratio between AuCl4− and thiol the bigger the self-assembled gold nanoparticles. Under the condition of moles of Au fixed, the most homogeneous nanoparticles in size distribution derived with the mole ratio of 1:1/8 between AuCl4− and thiol. The obtained nanoparticles could be used, for example, in uniform surface nanofabrication, leading to the fabrication of ordered array of quantum dots.

Keywords: nanoparticles, self-assembly, mole ratio, AuCl4−, thiol, HR-TEM, nano-structure, array of quantum dots

Introduction

The size of self-assembled gold nanoparticles could be controlled by the molar ratio between Au and thiol is proved by past experimental results [1]. In the past experiments, we control the molar ratio between Au and thiol, but we don’t discuss the influence of the concentration of each one. In this study, we fix the Au amount, and adjust the moles of thiol to observe the change.

The self-assembly of gold nanoparticles with colloidal gold solution has been developed for years. To put on as a gold marker in all kinds of microscopy applications was one of the reasons for its development. The particle size ranged between 0.85-64nm by various methods. Leff, et al., discovered that the surfactant concentration is the key factor for the self-assembly of gold nanoparticles when particle size reached the nano scale, about 1.5-20 nm [2]. The synthesis of nanoparticles in a two-phase liquid system was developed by Brust, et al. The colloidal Au particles, enclosed by alkanethiol of various kinds, were stabilized in colloidal gold solutions with various pH values [3].

The Au nanoparticles formed by surfactant-assisted synthesis protocol were guaranteed when surfactant alkanethiol was used. The self-assembled nano-thin film was formed based on the generation of SH-terminated particle surfaces, which would offer the possibility to anchor nanoparticles to each other and form the thin film [4-5]. The colloidal gold solution was added into water. A thin film based on the colloidal gold nanoparticles was formed at the interface between the air and water.

There was another finding that the size of the self-assembled gold nanoparticles could be controlled with the mole ratio between AuCl4− and thiol. In general, the mole ratio between AuCl4− and thiol is higher; the gold nanoparticles are bigger. The finding was proved through past experiments. In the past experiments, to quantify the relationship of the size of the self-assembled gold nanoparticles and the mole ratio between AuCl4− and thiol was the endeavor contributed. Four different molar ratios of Au/S used in the reactions that included 1:64, 1:32, 1:16, 1:4, 1:1, 3:1, 5:1, 8:1, respectively. The conclusion was proved. It is the higher the mole ratio between AuCl4− and thiol, the bigger the self-assembled gold nanoparticles.
In this paper, the moles of Au were fixed, only the moles of thiol were adjusted. Five different mole ratios of Au/S with their effect on size uniformity were investigated. The mole ratios were 1:1/16, 1:1/8, 1:1, 1:8, 1:16, respectively.

**Experiment**

The self-assembly process for nanoparticles is described as following. Two kinds of solutions were concocted the golden salt (HAuCl\(_4\) · 3H\(_2\)O) in water and phase transfer reagent (N(C\(_8\)H\(_{17}\))\(_4\)Br) in organic solvent. Due to the inability in dissolving to each other, a two-layer solution was formed when they were mixed together. On the other hand, the surfactant alkanethiol (C\(_{12}\)H\(_{25}\)SH) was dissolved in toluene to form a solution with the concentration of 0.167M. Solution of reducing agent (NaBH\(_4\)) in water was formed with the concentration of 0.4018M. These two solutions, C\(_{12}\)H\(_{25}\)SH and NaBH\(_4\), were then added into the two-layer solution and agitated for 12 hours. After the agitation, the two phase solution was then underwent a thermal annealing process by refluxing at ~125°C in silicon oil bath ~12 hours. The top part of the solution toluene phase which is called colloidal solution was separated and enriched to a volume of 5ml under a heating process in a vacuum environment. 350ml of alcohol was added into the enriched 5ml solution. After cooling down in an environment of -18°C for several hours, the gold nanoparticles were formed.

To quantify the relationship of the size of the self-assembled gold nanoparticles and the mole ratio between AuCl\(_4\) and thiol was the endeavor contributed. Four different mole ratios of Au/SH used in the reactions that included 1:1, 3:1, 5:1, 8:1, respectively. Experimental results supported the qualitative description that is the higher the mole ratio between AuCl\(_4\) and thiol the bigger the self-assembled gold nanoparticles [6].

In this study, the moles of Au were fixed, only the moles of thiol were adjusted. Five different mole ratios of Au/S with their effect on size uniformity were investigated. The mole ratios were 1/16, 1/8, 1:1, 1:8, 1:16, respectively. The size distributions of the gold nanoparticles were analyzed by Mac-View analysis software. HR-TEM was used to derive images of self-assembled gold nanoparticles.

**Result and Discussion**

The same fabrication process was done with different mole ratios between AuCl\(_4\) and thiol. The change on the particle size due to the mole ratio adjustment was evident. Self-assembled nanoparticles were photographed by the HR-TEM, High-Resolution Transmission Electron Microscope. Figure 1 (a) ~1 (d) show HR-TEM micrographs of thiol-capped gold nanoparticles dispersed in ethanol and synthesized by the mole ratio between AuCl\(_4\) and thiol of 1, 3, 5, and 8, respectively. Each figure is 600,000 times. Figure 2 is the electronic diffraction image derived by HR-TEM to show the crystal structure. Corresponding electronic diffraction demonstrated some spotty ring patterns as shown in Figure 2 (a) and 2 (b) indicating well-defined crystalline lattices, the analysis were carry out with Au/S mole ratio in 1:1; (a) is gold nanoparticles dispersed in ethanol solution and (b) is gold nanoparticles dispersed in toluene solution.

The moles of Au were fixed, only the moles of thiol were adjusted. Five different mole ratios of Au/S with their effect on size uniformity were investigated. The mole ratios were 1/16, 1/8, 1, 8, and 16, respectively. Figure 3 (a) ~3 (e) show HR-TEM micrographs of gold nano-thin films which are by the mole ratio between AuCl\(_4\) and thiol of 1/16, 1/8, 1, 8, and 16, respectively. Each figure is 600,000 times.

The size distribution was analyzed by the software Mac-View based on the HR-TEM image. For each image, 100 particles were picked in random and done on the statistical analysis of the particle size distribution. Figure 4 (a) ~4 (e) is the size histogram derived by analyzing HR-TEM micrograph of Figure 3 (a) ~3 (e) at least for 90 particles. The size distributions are 2.81±0.416nm, 2.83±0.413nm, 2.85±0.433nm, 4.97±0.523nm, 8.79±2.546nm, respectively.
Conclusion

Through the HR-TEM images and size distributions of the gold nanoparticles were analyzed by Mac-View analysis software. A conclusion could be drawn. The result reached was also the higher the mole ratio between AuCl₄⁻ and thiol the bigger the self-assembled gold nanoparticles. Under the condition of moles of Au fixed, the most homogeneous nanoparticles in size distribution derived with the mole ratio of 1:1/8 between AuCl₄⁻ and thiol. The obtained nanoparticles could be used, for example, in uniform surface nanofabrication, leading to the fabrication of ordered array of quantum dots.

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Figure 1 (a)–(d) show HR-TEM micrographs of thiol-capped gold nanoparticles dispersed in ethanol and synthesized by the mole ratio between AuCl₄⁻ and thiol of 1, 3, 5, and 8, respectively. Each figure is 600,000 times.

Figure 2 is the electronic diffraction image derived by HR-TEM to show the crystal structure.
Figure 3 (a) ~3 (e) show HR-TEM micrographs of gold nano-thin films which are by the mole ratio between AuCl$_4^-$ and thiol of 1/16, 1/8, 1, 8, and 16, respectively. Each figure is 600,000 times.

Figure 4 (a) ~4 (e) is the size histogram derived by analyzing HR-TEM micrograph of Figure 3 (a) ~3 (e) at least for 90 particles.