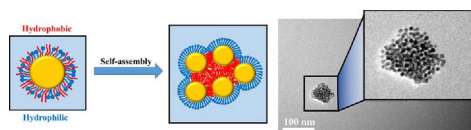# Size control of aggregations via self-assembly of amphiphilic gold nanoparticles

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GRAPHICAL ABSTRACT

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ABSTRACT

A simple and reliable method is described to create aggregated structures of gold nanoparticles (AuNPs) with a tunable size in water. The surface of the AuNPs is covered with mixed monolayers of hydrophobic and hydrophilic ligands, and aggregations of the AuNPs with an irregularly spherical shape are induced by the self-assembly of AuNPs due to hydrophobic and electrostatic interactions. Here, two ligands on the AuNP surface are not fixed but are rearranged for the formation of the AuNP aggregations. The sizes of the aggregations can be easily tuned by varying the molar ratio of the hydrophobic and hydrophilic ligands used. Changes in the sizes of the structures are systematically characterized by transmission electron microscope (TEM) and dynamic light scattering (DLS). A red-shift of the wavelength from UV–vis spectroscopy data and a color change from pale red to pale purple closely related to the surface plasmon resonance of the AuNPs also confirm the aggregation of AuNPs.

1. Introduction

It is well-known that amphiphilic molecules such as surfactants, lipids (two-tailed surfactants) and polymers self-assemble into highly ordered structures such as micelles and vesicles in aqueous solution [1,2]. The main driving forces to induce such structures from amphiphilic molecules are hydrophobic and electrostatic interactions. Given that amphiphilic molecules have hydrophobic (water-hating) hydrocarbon tails and hydrophilic (water-liking) headgroups, the hydrophobic portions tend to be shielded from water while the hydrophilic portions tend to be exposed to water. Thus, in self-assembly systems of amphiphilic molecules, the hydrophobic interactions between hydrophobic tails and the electro-

static interactions between hydrophilic headgroups can play important roles in forming micelles or vesicles. These self-assembled structures have a variety of applications for emulsions, drug delivery, controlled release and bioseperation [3]. Similar to amphiphilic molecules, it has been found that inorganic nanoparticles (NPs) can also form a variety of highly ordered structures, such as well-defined clusters [4,5], spherical vesicles [6,7], cylindrical micelles [8,9], lattices [10] and chains [11]. Although the systems of such highly ordered structures from inorganic NPs are much less well-known than those from amphiphilic molecules, several studies have shown elegant strategies (e.g., by DNA-linking [12,13], multidentate thioethers [14,15] and capillary bridges [16,17]) to form highly ordered structures from inorganic NPs. Such structures cre-

ated by inorganic NPs have been of interest to many researchers given their potential applications in photonics, electronics and sensors depending not only on the shapes of the structures and the properties of the NPs but also the properties of the functional groups on the surfaces of the NPs. Recently, several researchers have also shown that inorganic NPs can have amphiphilic properties by covering the surface of NPs with amphiphilic molecules, resulting in the formation of well-defined structures [6,7,11,18]. Once the surface of such NPs is functionalized with amphiphilic molecules, NPs behave as amphiphilic molecules, forming highly ordered structures such as spherical vesicles, cylindrical micelles and chains by the self-assembly of amphiphilic NPs. Despite several elegant approaches presented thus far to form well-defined structures by NPs as mentioned above, controlling the sizes of the structures, which play important roles in the improvement of applications for optics and electronics and energy capture, remains a significant challenge [19–22]. In this study, we report a simple and reproducible route to form well-defined structures such as irregularly spherical shapes with tunable sizes using gold nanoparticles (AuNPs) in water. The AuNPs have diameters of approximately 6 nm with surface functionalized with mixed monolayers of hydrophobic and hydrophilic ligands via ligand exchange. Given that the surface of the AuNPs has both hydrophobic and hydrophilic ligands, the AuNPs are referred to as amphiphilic AuNPs. The ligand separation behaviors of such amphiphilic AuNPs on the surface under various conditions such as the relative length difference of the ligands and the AuNP size have been studied by several researchers. [23–27] Also, recent theoretical and experimental results have shown that the ligands are not fixed on the surface of AuNPs but can be rearranged dynamically in response to diverse environments [11,28–30]. For instance, once the amphiphilic AuNPs accumulate at the toluene-water interface, the ligands are segregated into two portions, where hydrophobic ligands are oriented toward the toluene side and hydrophilic ligands are oriented toward water. In a similar fashion, the amphiphilic AuNPs also become incorporated into bilayer structures such as vesicles or cell membranes via hydrophobic interactions between hydrophobic ligands on the surface of the AuNPs and the hydrophobic cores of the bilayers. In our system, similar amphiphilic AuNPs functionalized with hydrophobic and hydrophilic ligands were used to create well-defined structures in water. Here, 1-octadecanethiol (ODT) with C-18 and 1-tetradecanethiol (TDT) with C-14 were used as hydrophobic ligands and 11-mercaptoundecanoic acid (MUA), which can be fully deprotonated in water at ~pH 11, was used as a hydrophilic ligand. These amphiphilic AuNPs self-assembled to form aggregations with an irregularly spherical shape. The sizes of the AuNPs aggregations were simply tuned by varying the molar ratio of the hydrophobic and hydrophilic ligands on the surface of the AuNPs. As the molar ratio of the hydrophobic ligand to hydrophilic ligand increases, the average size of the AuNP aggregations increases. In addition, as the length of the hydrophobic ligands increases, fewer hydrophobic ligands on the AuNP surface are required to form the AuNP aggregations. We believe that such aggregations are driven by the self-assembly of AuNPs induced by hydrophobic and electrostatic interactions between neighboring AuNPs in close contact with one another. We also observed a color change of the samples from pale red to pale purple and a red-shift of the wavelength from UV–vis spectroscopy as the sizes of the aggregations increase. This color change and the red-shift of the wavelength can be explained by the delocalization of the surface plasmon of AuNPs, which depends on the structural parameters of

inorganic NPs, such as their size and shape [31–33].

2. Materials and methods

2.1. Materials

1-Octadecanethiol (ODT, 95%), 1-tetradecanethiol (TDT, 98%), gold chloride trihydrate (HAuCl$_4$·3H$_2$O), 11-mercaptoundecanoic acid (MUA, 95%), dodecylamine (DDA, 98%), tetramethylammonium hydroxide (TMAOH, 25 wt%), dichloromethane, toluene, methanol, acetone and Tetra-*n*-butylammonium borohydride (TBAB, 98%) were obtained from Sigma-Aldrich. Didodecyldimethylammonium bromide (DDAB, 98%) was obtained from TCl. Hydrazine monohydrate (25 wt% solution in water) was obtained from KANTO. All chemicals were used without further purification.

2.2. Sample preparation

Gold nanoparticles (AuNPs) were synthesized according to a previous method but with HAuCl$_4$·3H$_2$O instead of AuCl$_3$ [34,35]. Initially, the hydrophobic AuNPs by weakly bound DDA ligands were dispersed in toluene. The surface of the AuNPs was then functionalized with mixed monolayers of 11-mercaptoundecanoic acid (MUA) and 1-octadecanethiol (ODT) or 1-tetradecanethiold (TDT) via ligand exchange. Briefly, 0–2 mL of a 20 mM ODT or TDT solution in toluene was added to 0.5 mL of a 20 mM AuDDA solution and stirred gently for one minute. A subsequent addition was made of 0–2 mL of a 20 mM MUA solution in dichloromethane (DCM), followed by approximately five minutes of stirring at room temperature. After the supernatant was extracted, the functionalized AuMUA/ODT or AuMUA/TDT NPs were washed with toluene, dichloromethane and acetone to remove excess ligands and were then dried with nitrogen. The functionalized AuNPs were subsequently dissolved in 1 mL of deionized water at pH > 11 with the addition of tetramethylammonium hydroxide (TMAOH), followed by sonication for 15–20 min. The samples remained at rest for at least 20 mins after sonication before they were used.

In case of experiments to examine the stability of the AuNP aggregates, the samples remained at rest for 1 min, 10 min, 20 min, 1 day and 30 day after sonication.

2.3. Nanoparticle characterization

Images with a transmission electron microscope (TEM) were taken on JEOL JEM 2100 attached to a high-resolution Gatan-ORIUS SC1000 camera for image collection at a 200 kV acceleration voltage. The samples were prepared by dropping each sample onto a carbon-coated copper grid and drying under ambient conditions or in a freeze-dryer (FDU-1200, Tokyo Rikakikai Co., LTD). Dynamic light scattering (DLS) was conducted on a Malvern Zetasizer Nano ZS90 with an attached 4 mW HeNe gas laser operated at a wavelength of 632.8 nm and a scattering angle of 90°. UV–vis spectra were recorded on a Cary60 UV–vis spectrometer over the wavelength range of 300–800 nm with a quartz cuvette (1 mm path length) and interfaced with Cary Win UV software for data analysis.

3. Results and discussion

3.1. Synthesis of amphiphilic AuNPs

We synthesized amphiphilic AuNPs via a ligand exchange