

Self-Assembly of Gold Nanoparticles at the Liquid/Liquid Interface

Kang Yeol Lee and Sang Woo Han*

Nanomaterials Laboratory, Department of Chemistry and Research Institute of Natural Sciences,
Gyeongsang National University, Jinju 660-701, Korea. *E-mail: swhan@gsnu.ac.kr

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The intense research activity in the field of nanoparticles is motivated by the search for new materials in order to further miniaturize electronic devices, as well as by the fundamental question of how molecular electronic properties evolve with increasing size in this intermediate region between molecular and solid-state physics.¹ In this respect, molecularly bridged nanoparticle aggregates have been attracting growing interest.²⁻⁵ The properties of two-dimensional assemblies of metal nanoparticles are controlled by the composition, geometry, and spatial arrangement of the nanoparticle building blocks. Such structures have been used for a variety of important applications in catalysis, photonics, electronics, and biological sensing.⁶ The 2D/3D control over the spatial arrangement of nanoparticles is primarily based on the thiolamphiphilic nature of metal nanoparticles,² hydrogen-bonding interactions,³ the highly specific recognition interaction of antigens/antibodies,⁴ and specific base-pairing interactions between DNA and its complementary strand.⁵

The liquid/liquid interface has also served as a fertile medium for nanoparticle assembly. Recently, Kumar *et al.* have observed that aromatic molecules such as benzene and anthracene present in the organic phase bind strongly with aqueous gold nanoparticles.⁷ This process leads to the immobilization of the gold nanoparticles in the form of a highly localized film at the interface. Most recently, Reincke and co-workers reported that the introduction of ethanol can pull hydrophilic citrate-stabilized Au-nanoparticles into the water/heptane interface, leading to a closely packed monolayer.⁸ Meanwhile, Duan *et al.* directed the assembly of hydrophobic and hydrophilic nanoparticles at water/oil

interfaces by capping the nanoparticles with organic ligands.⁹ These reports demonstrate a promising way to create a 2D arrangement of hydrophobic or hydrophilic nanoparticles at water/oil interfaces.

Based on these previous studies, we have developed a new high-throughput wet chemical method to fabricate 2D array of metal nanoparticles. We found that an appropriate ligand, 4'-aminobenzo-15-crown-5 hydrotetrafluoroborate (**L**) (Figure 1a), can mediate the self-assembly of gold nanoparticles (AuNPs) at the liquid/liquid interface in the form of a stable nanocomposite film.

Experimental Section

HAuCl₄, sodium citrate were purchased from Aldrich. Other chemicals, unless specified, were reagent grade, and triply distilled water (resistivity greater than 18.0 MΩ·cm) was used when preparing aqueous solutions.

The gold sol was prepared by following the literature with difference only in the molar ratio of HAuCl₄ to sodium citrate.¹⁰ Namely, 40 mg of HAuCl₄ was initially dissolved in 90 mL of water, and the solution was heated to boiling. 10.2 mL of aqueous solution of sodium citrate (40 mM) was then added to the HAuCl₄ solution under vigorous stirring, and boiling was continued for *ca.* 15 min. The concentration of gold nanoparticles was calculated to be about 6.3 nM by assuming an average 19.6 nm diameter for all nanoparticles. The ligand **L** was synthesized by referring to the literature procedure.¹¹

AuNPs-**L** nanocomposite films were fabricated as follows. The 5.0 mL of the freshly prepared Au hydrosol was taken in a vial along with 5.0 mL of organic solvents resulting in a biphasic mixture with the colorless organic part and wine-red colored hydrosol. Upon addition of 0.7 mL of 1.00 × 10⁻² M solution of **L** in water to this mixture, a thin film of golden reflectance and blue transmittance is formed immediately at the liquid/liquid interface.

The extinction spectra were recorded with a UV-vis absorption spectrometer (SINCO S-3100). Transmission electron microscopy (TEM) images were obtained with a JEOL JEM-2010 transmission electron microscope operating at 200 kV.

Results and Discussion

Aqueous suspensions of AuNPs with average diameter of

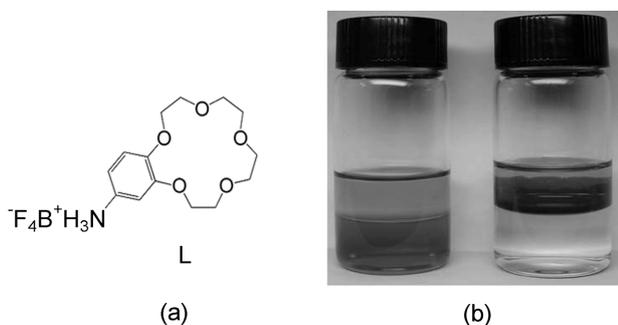


Figure 1. (a) Organic ligand **L**. (b) Left: an aqueous gold sol (wine-red) covered with diethyl ether (colorless), right: after the addition of aqueous solution of **L** to the sol, a gold nanocrystal layer is formed at the water/diethyl ether interface.

19.6 ± 3.7 nm were prepared by citrate reduction method as described above. The freshly prepared gold hydrosol was taken in a vial along with diethyl ether resulting in a biphasic mixture with the colorless organic part on top and wine-red colored hydrosol below (Figure 1b, left). Upon addition of aqueous solution of **L** to this mixture, a thin film of golden reflectance and blue transmittance is formed immediately at the water/oil interface (Figure 1b, right). This interfacial entrapment of AuNPs may be accelerated by gentle shaking. The gold hydrosol was now colorless, indicating transfer of the AuNPs to the interface. This metallic luster results from the electronic coupling of AuNPs, suggesting the formation of closely packed nanoparticle thin films.¹² The UV-vis spectra demonstrate that no AuNPs exist in water or are transferred into the diethyl ether phase. In fact, we also achieved interfacial entrapment and self-assembly of AuNPs at the various water/oil interfaces in which organic phases are chloroform, dichloromethane, ethyl acetate, and *n*-hexane. The interfacial film of nanoparticles could be transferred to a mica substrate and carbon-coated TEM grids as a Langmuir-Blodgett (LB) film, and then studied by UV-vis spectroscopy and TEM, respectively.

The UV-vis spectrum recorded from the AuNPs-**L** film on mica is shown in Figure 2 (dashed curve). For comparison, UV-vis spectrum recorded from the as-prepared aqueous gold sol solution is also shown in Figure 2 (solid curve). All of the spectra exhibit bands due to the surface plasmon. One can clearly notice that the transverse plasmon component observed at 525 nm in the spectrum of aqueous Au sol almost completely disappears and a noticeably red-shifted and broad plasmon resonance peak occurs at 730 nm in the case of the AuNPs film. This result indicates an extended assembly of nanoparticles in the AuNPs-**L** composite film.¹²

A typical TEM image of the composite film is presented in Figure 3. At low magnification (data not shown), it was observed that the grid was uniformly covered with

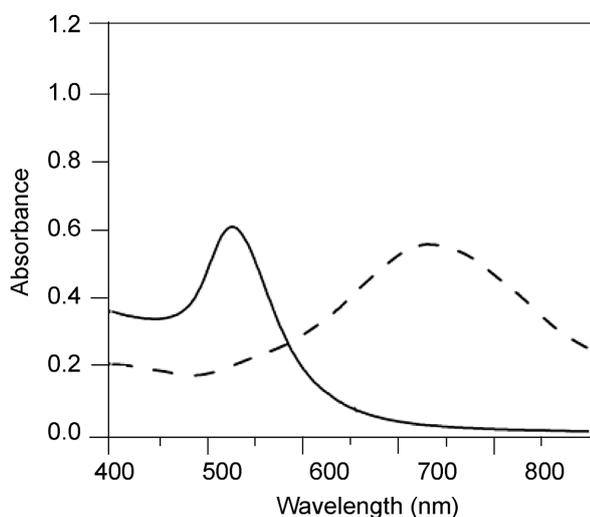


Figure 2. UV-vis spectra recorded from the AuNPs-**L** film on mica (dashed curve), and the as-prepared aqueous Au sol solution (solid curve).

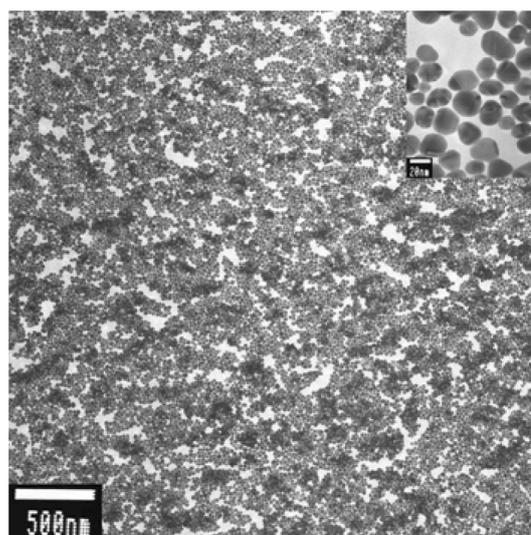


Figure 3. TEM image of the AuNPs-**L** film. The enlarged image is shown in the inset.

extremely large domains of the AuNPs without any apparent disruption in the close-packed assembly of the nanoparticles. The higher magnification image reveals very regular in plane packing of the AuNPs (Figure 3). While some degree of sintering of the particles appears to have occurred, the particles in the 2-D assembly are to a large extent well separated from one another. As observed by Reincke and co-workers⁸ and Duan *et al.*,⁹ domains of close-packed AuNPs coexist with small voids. However, the relative amounts of voids are distinctly smaller in the present work, indicating more efficiency of our method for fabricating the monolayers of nanoparticles. Enlarged images (inset of Figure 3) reveal further that the particles are not in direct contact with each other, and are consistent with the assumption of layers of ligand molecules covering each gold particle and hence leading to an inter-particle spacing of 1-2 nm. Many earlier studies have demonstrated the very regular, hexagonal arrangement of silica-coated gold nanoparticles¹³ as well as CdSe quantum dots.¹⁴ Even though we observe a very regular edge-edge separation of the gold nanoparticles in the nanoparticles film over large distances, there is clearly lack of periodicity in the ordering of the particles observed in earlier studies.¹³ While the exact reason for this difference is not known, we speculate that it could be due to the fact that the gold nanoparticles of this study are not very monodisperse (*ca.* 20% standard deviation) and it is known that this level of polydispersity does not lead to good two-dimensional ordering.

All the above experimental results show that the crown ether derivative, **L**, can direct the assembly of AuNPs to form the stable monolayer of nanoparticles at water/oil interface through a specific interaction between **L** and the surface of AuNPs. The nature of the ligand-surface interaction is believed to be covalent. In fact, amine or protonated amine groups bind very strongly to gold nanoparticles by this interaction.¹⁵ The mechanism of film formation at the

liquid/liquid interface can be ascribed to the above specific interaction and an intrinsic property of ligand. When using interfaces between water/oil fluids to trap sub- or micrometer-sized particles, besides the particle diameter, the interfacial entrapment is mainly determined by the surface wettability of the particle with the water/oil interface.¹⁶ When a particle is hydrophilic or hydrophobic it is localized totally within the water or oil phase, respectively. On the other hand, when the particle surface has an intermediate wettability, the particle prefers to reside at the interface. Recent studies on phase transfer of aqueous AuNPs show that by using single long-chain alkylamines, one may transfer carboxylic acid derivatized AuNPs onto water/oil interfaces.¹⁷ Wei and co-workers have observed interfacial attachment of the AuNPs capped with a resorcinarene ligand.¹⁸ These reports suggest that interfacial entrapment and self-assembly of nanoparticles might be realized by appropriate hydrophobic coating. We have confirmed that the capping with **L** should drive nanoparticles to reside and self-assemble at water/oil interfaces. The choice of this ligand was encouraged by the characteristic wettability of crown ether group. Namely, oxygen atoms of crown ethers are highly flexible, allowing them to exhibit either a hydrophilic or hydrophobic exterior. Therefore, crown ethers have remarkable hydrophilicity and lipophilicity.¹⁹ Owing to this amphiphilic nature of the ligand, the AuNPs coated with **L** can be stabilized at the water/oil interface, results in the formation of stable nanocomposite films.

Conclusions

We have shown that the crown ether derivative can mediate the transfer of gold nanoparticles in water solution to water/oil interface, results in directing the self-assembly of nanoparticles in the form of a novel nanocomposite film. The interfacial film of nanoparticles could be transferred to various solid substrates. The experimental results indicate the formation of nanoparticles monolayers at water/oil interfaces. Our work is an important step towards interfacial entrapment and self-assembly of nanoparticles for efficient creation of 2D nanostructures. These types of materials may be used in developing catalysts, sensors, and nanoelectronic devices. Currently, we are attempting to synthesize other composite films by using specific interactions between

suitable organic or inorganic ligands and various nanoparticles.

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