超分子化学的アプローチに基づく厚さ１ nmの革新的金属ナノシート合成

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Novel preparation of ultra-thin metal nanosheets via supramolecular approach

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In this paper, positively charged fluorescent gold nanocluster was successfully prepared for the first time using the shortest cationic thiolate ligand, thiocholine chloride. By introducing oppositely (negatively) charged surfactant to minimize electrostatic repulsion between the thiocholine ligands on the surface of the gold clusters during nucleation, we could obtain non-plasmonic particles, which showed blue emission at around 448 nm. Without the oppositely charged surfactant, on the other hand, only large plasmonic nanoparticles were obtained. Using these positively charged Au clusters in the interface of negatively charged inorganic nanosheets, we now investigate the formation of ultrathin Au nanosheets by supramolecular approaches.

１． Introduction

Nanocluster synthesis is an interesting field of study, and various researchers are aiming at manipulating individual atoms, molecules, or groups of molecules to produce novel hybrid materials with unprecedented structures and properties. A typical example is the synthesis of gold nanoclusters with a non-metallic structure, whose distinctive optical properties are derived from the constituent gold nanoparticles, which generally show surface plasmon resonance at relatively larger diameters (> 3 nm). The optical properties of the gold nanoclusters are hypothesized to originate from the particle core, and they can be altered depending on the attached ligand. Unlike the collective oscillation of conduction electrons in the gold nanoparticle, a single electron transition results in molecule-like absorption and emission from the UV to NIR region in a gold nanocluster. Experimentally, it has been determined that the sharp contrast between the optical properties of the gold nanocluster and gold nanoparticles become observable when the particle size is below 2.4 nm and the gold particles no longer exhibit metallic properties.

In this regard, there are two commonly exploited methods involving the use of anionic and neutral thiol ligands such as alkylthiols, tiopronin, phenylethylthiolate, and thiolate cyclodextrin. However, there is no established method for the synthesis of fluorescent gold nanoclusters by means of conventional chemical reduction using cationic thiols. Such nanoclusters are expected to play a significant role in bioimaging[17] and sensing as cellular proteins show high affinity for positively charged nanocomposites than for neutral and anionic nanocomposites. In particular, quaternary ammonium-terminated thiols have rarely been used for the preparation of gold nanoparticles. Quaternary ammonium groups are always positively charged under any pH conditions. The main limitation of cationic thiolate-protected gold nanoclusters is that the electrostatic repulsion between the cationic ligands on the surface of the nanoparticles hinders the formation of small clusters (< *ca.* 2 nm) during nucleation in solvents. Our objective is the utilization of the shortest cationic thiolate ligand, thiocholine ($HS\text{-}(CH_2)_2\text{-}N(CH_3)_3^+$), to synthesize fluorescent gold nanoclusters. This paper reports the first successful synthesis of positively charged nanoclusters by the conventional chemical reduction method.

２． Results and Discussion

In order to suppress the electrostatic repulsion between thiocholine (TC) ligands on the surface of Au nanoclusters during the nucleation, we added sodium dodecylsulfate (SDS) to form a Au(I)-TC-SDS complex before the reduction, which may neutralize the cation on TC and minimize the repulsion between the TC molecules. To verify this concept, we synthesized Au nanoclusters at Au:TC:SDS molar ratios of 1:3:3, 1:5:5, and 1:7:7. In a typical experiment (1:7:7 mol ratio of $HAuCl_4$:TC:SDS), we dissolved 0.0218 g of TC and 0.0404 g of SDS in 5 mL methanol followed with the addition of (1 mL, 20 mM) $HAuCl_4$ stock aqueous solution. The resulting solution was diluted with 3 mL distilled water and sonicated for 60 minutes until the solution becomes white indicating the

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formation of Au-thiolate complexes. The colour change from yellow to pale yellow/white indicated the reduction of Au(III) to Au(I) by the excess thiol compounds. $NaBH_4$ (1 mL, 20 mM) was then added and the resulting solution was sonicated for another 60 minutes.

We observed the TEM images to determine the particle sizes (Figure left). The sample showing plasmon absorption had particles with diameters larger than 3 nm. The samples that did not exhibit plasmon absorption (Au:TC:SDS = 1:5:5 and 1:7:7), on the other hand, had particles with diameters well below 2 nm, indicating successful Au nanocluster formation. It is difficult to determine the exact diameter of such small clusters (~ 1 nm of diameter) by conventional TEM; however, we observed a clear decreasing trend in the particle size with an increase in the mol ratios of TC and SDS.

Under irradiation at 300 nm, we observed blue fluorescence, as shown in Figure right. The maximum excitation wavelength was around 357 nm, which was in good agreement with that for Au nanoclusters comprising 11 Au atoms and fewer, particularly those reported for Au_4 (~313 nm) and Au_3 (~303 nm), respectively, and for Au_5 (330 nm) and Au_8 (~384 nm). Moreover, the maximum fluorescence wavelength (~448 nm) agreed well with that of the Au_8 cluster (455 nm). Hence, we hypothesized that the observed emission wavelength originates from the Au_8 nanocluster or a Au nanocluster with a similar size.

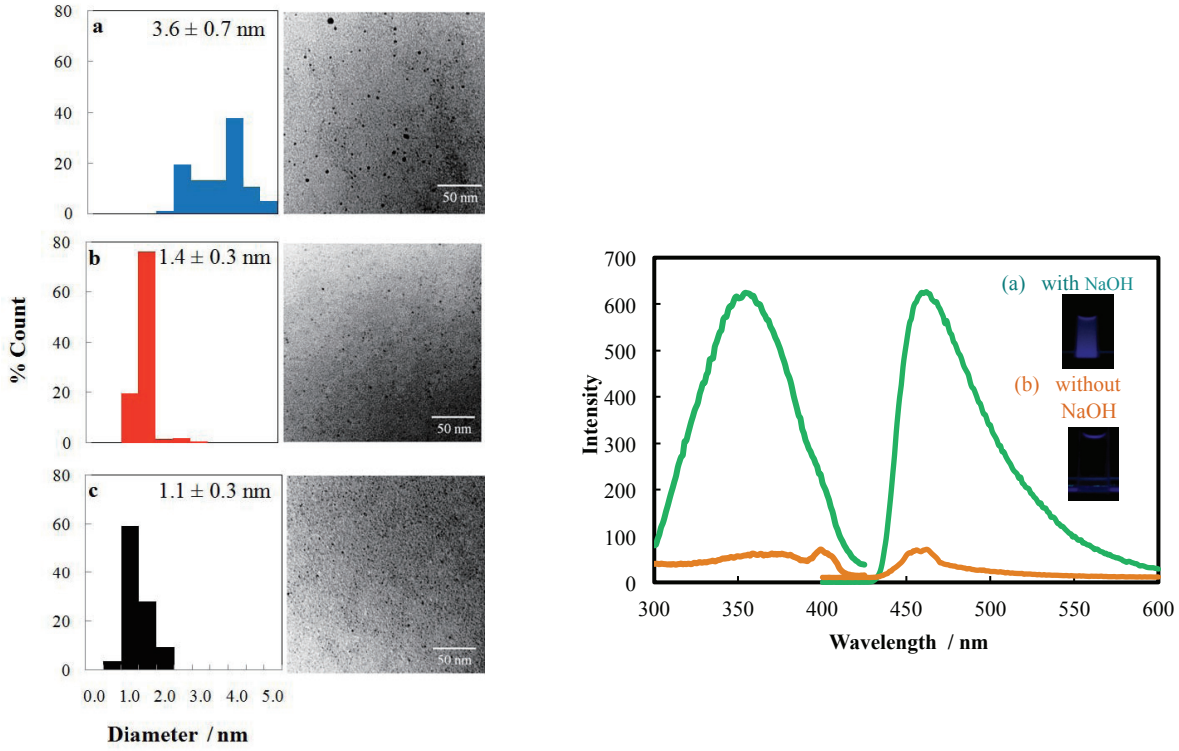

Figure. Left: TEM images and particle size distributions of Au nanoparticles or nanoclusters synthesized at Au:TC:SDS mol ratios of (a) 1:3:3, (b) 1:5:5, and (c) 1:7:7 (mol/mol/mol). Right: Fluorescence emission and excitation spectra of synthesised Au nanoclusters (excitation wavelength = 300 nm, Au:TC:SDS = 1:7:7 (mol/mol/mol)).

３． Future plans

Using these positively charged Au clusters in the interface of negatively charged inorganic nanosheets, we now investigate the formation of ultrathin Au nanosheets by supramolecular approaches. One of anionic charged inorganic nanosheets, saponite type clay minerals are used for the template of Au nanosheet synthesis. By mixing solutions of our positively charged gold clusters and negatively charged clay nanosheets, we will prepare sandwiched structure of gold clusters by 2 clay nanosheets, and then growth them in the regulated nano–space for ultrathin nanosheet preparations.