Thiacrownether-mediated Size-controlled Assembly of Gold Nanoparticles

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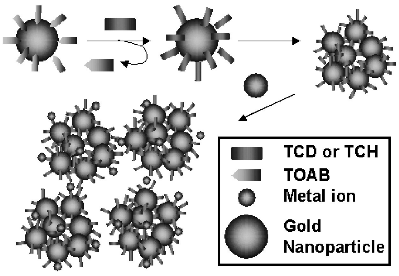
Thiacrownether-mediated self-assembly of Au nanoparticles produced a larger sized aggregation of which grain size was controlled by the relative concentration and the structure of thiacrownethers. The thiacrownethers at the surface of self-assembled nanoparticles have further complexation ability to some metal ions, which can be used to build new metal/semiconductor–metal ion nanocomposite materials.

Monolayer-protected metal and semiconductor nanoparticles are of great interest as nanomaterials and building blocks of nanodevices because of their unique optical, electric, magnetic, and catalytic behaviors.[1,2] In addition to the synthetic efforts to control the size, composition, and shape of nanoparticles,[3–5] there are increasing research activities to arrange and organize individual nanoparticles in controlled fashion to larger dimension by self-assembly.[6–8] This self-assembly process involves mutual interactions such as covalent, biospecific, van der Waals, electrostatic, hydrogen bonding, metal–ligand coordination, and host–guest interaction between the components of monolayer content of nanoparticles with or without external regulator or template.[9]

In this communication, we describe thiacrownether-mediated self-assembly of gold nanoparticles. Alkanethiols are best known ligands for gold nanoparticles owing to the simple synthesis and stability of thiol-derivatized gold nanoparticles.[1,2] Recently, dialkyl disulfides and sulfides were also found as an efficient passivating agent for gold nanoparticles, and a multidentate sulfide has been utilized as an interparticle linking agent in reversible self-assembly of gold nanoparticles.[10,11] We report here that thiacrownether, a cyclic sulfide compound, assembles individual gold nanoparticles into larger domain size in a controlled manner, depending on the concentration and structure of thiacrownethers. Furthermore, thiacrownethers are known to bind selectively some heavy metal ions,[12] which allows further transformation of these thiacrownether-mediated self-assembled gold nanoparticles into new metal–metal ion nanocomposites.

Two representative thiacrownethers, 1,4,7,10-tetrathiacyclododecane (TCD) and 1,5,9,13-tetrathiacyclohexadecane (TCH), which have ethylene and propylene linkage between sulfide, respectively, were taken for self-assembly of gold nanoparticles. Because of the relatively weak ligating ability of sulfides, gold nanoparticles protected by labile tetraoctyammonium bromide (TOAB)[13] were synthesized and used for the assembly. The average diameter of individual TOAB-stabilized gold nanoparticles measured by transmission electron microscopy (TEM) was 4.2 ± 1.5 nm (see Figure 1a). When the toluene solution of TOAB-stabilized gold nanoparticle was treated with the toluene solution of TCD or TCH, the solution color originating from the well-known surface plasmon resonance changed from red to purple, indicating the formation of larger sized aggregation of the gold nanoparticles (Scheme 1).[6] The assembled structure was composed of many spherical grains of about 45-nm size, where the single grain consists of several dozens of individual gold nanoparticles (see Figure 1). The assembly process was in situ monitored by UV–vis spectroscopy at various concentrations of TCD and TCH (see Figure 2). Obviously, the self-assembly process of the gold nanoparticles by thiacrownether depends on both the structure of thiacrownethers and the relative feeding ratio of thiacrownethers to the gold nanoparticles. When the gold nanoparticle solution ($\sim 0.3\,\mu M$) was treated with 50 or $5\,\mu M$ solution of the thiacrownethers, the absorption maximum slowly shifted to 647 nm in addition of TCD or shifted to 570 nm within 20 min after addition of TCH. The molar absorption coefficient was slightly reduced (see Figure 2a) or unchanged (see Figure 2b). The mixed purple solution was optically clear and no precipitation was observed even after 7 days. When thiacrownether containing solutions of $0.5\,\mu M$ were used, TCH slowly mediated the self-assembly process (see Figure 2d), but no spectroscopic change was observed with TCD even after 1 day (see Figure 2c).



Scheme 1. Schematic self-assembly process by thiacrownether and further complexation with metal ions.

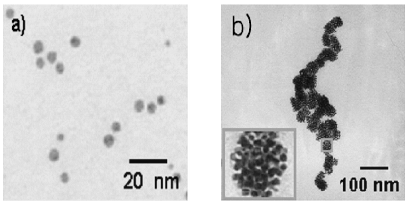


Figure 1. TEM images of (a) TOAB-stabilized individual gold nanoparticles ($0.3\,\mu M$ in toluene) and (b) Assembled structure by TCH ($5\,\mu M$ in toluene). The inset in (b) is 10 times magnification to show individual grains.

Two thiacrownethers (TCD and TCH) induce slightly different assembly pattern elucidated by TEM images. While usual oxygen-bearing crownether prefers “endodentate” conformation, sulfur-bearing thiacrownether is known to prefer “exodentate” conformation because of longer C–S distance (1.8 Å) than

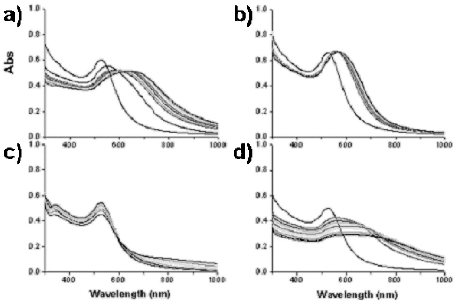


Figure 2. UV–vis spectra during the self-assembly process of TOAB-stabilized gold nanoparticle (0.3 μM) with thiacrownethers in toluene at room temperature. The leftmost in each spectrum is TOAB-stabilized gold nanoparticle and the rightmost is spectrum after 3 h. The scan interval between each curve is 20 min. The concentration of thiacrownethers is as follows. (a) TCD, 50, (b) TCH, 50, (c) TCD, 0.5, (d) TCH, 0.5 μM.

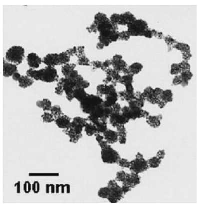


Figure 3. TEM image after metal ion complexation of the self-assembled Au nanoparticles with 50 μM of TCD (metal ion: 50 μM of $HAuCl_4$ (Au^{3+})).

C–O distance (1.4 Å).[14] This exodentate conformation of thiacrownether is essential for the self-assembly process because endodentate conformation can only afford the complexation with a metal cation and this *endo*-binding process is energetically unfavorable owing to the slight repulsive interaction between 4 neighboring sulfurs. Therefore, a gold nanoparticle of which size is much larger than single metal ion, assembles with another nanoparticle by "exodentate" thiacrownether as a bridge.

In addition, the grain size of each assembled structure is dependent on the concentration of thiacrownether in the case of TCH. The average diameter of each grain measured from TEM (30, 45, 63 nm with TCH of 50, 5, 0.5 μM) is reversely and linearly dependent on the log value of relative quantity of thiacrownether to Au nanoparticle. When the concentration of bridge molecules (thiacrownether) is lowered, the less abundant nucleation sites are formed, resulting in a larger sized grain. But in the case of TCD, lowering the concentration of TCD hampered the assembly process, presumably because of the different size and kinetics of TCD compared to TCH.

The self-assembled gold nanoparticles have numerous thiacrownethers at the surface (Scheme 1). These thiacrownethers at periphery can further bind other metal cations according to the characteristic binding nature of thiacrownethers. When the assembled purple toluene solution (50 μM TCD) was treated with 50 μM aqueous solution of $HAuCl_4(Au^{3+})$, precipitation occurred immediately, resulting in the larger sized continuous aggregations in TEM analysis (see Figure 3). The above result clearly shows that the metal cations act as another new bridge between the each assembled structure.

In summary, thiacrownether-mediated self-assembly of Au nanoparticles has been demonstrated. The morphology and grain size of the aggregates can be controlled by the relative concentration and the structure of thiacrownethers. The self-assembled nanoparticles were soluble and stable in organic solvents. This assembly protocol can be applied to other nanoparticle systems with different composition and symmetry. Furthermore, the thiacrownethers at the surface of self-assembled nanoparticles have complexation ability to some metal ions, which opens a way to build new metal/semiconductor–metal ion nanocomposite materials.

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