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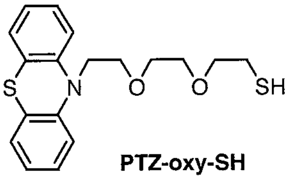
Self-assembled spherical aggregates of gold nanoparticles and their network ensembles mediated by metal ion recognition

T. GOTO, H. FUJIHARA
Department of Applied Chemistry and Molecular Engineering Institute, Kinki University, Kowakae, Higashi-Osaka 577-8502, Japan
E-mail: h-fuji@apch.kindai.ac.jp

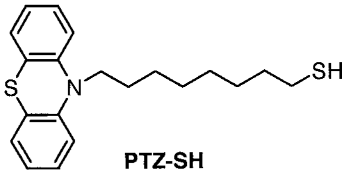
The study of noble metal nanoparticles has been an extremely active area in recent years because of their unique electronic, optical, and catalytic properties [1–5]. Specifically, considerable current interest has been focused on the development of the methods for assembling metal nanoparticles into organized nanoparticle superstructures, because the assembly of nanostructured materials is an important goal in materials chemistry for application in electronic devices. For example, the construction for gold nanoparticle aggregates from relatively small gold nanoparticles (2–10 nm diameter in size) has been accomplished using dithiols [6] as covalent link molecule and DNA [7] as non-covalent method, i.e., such molecular templates have been used to assemble metal nanoparticles into two- and three-dimensional macroscopic structures. More recently, the large-scale assembly of gold nanoparticles was performed by employing a polymer containing hydrogen bonding site as a molecular template [8]. In contrast, much less attention has been paid on the self-assembly of nanoparticles into large-scale nanoparticle aggregates without use of molecular template and their network ensembles.

Here we describe the preparation and transmission electron microscopy (TEM) characterization of new gold nanoparticles stabilized directly by the monolayers of the ether-substituted alkanethiol (PTZ-oxy-Au nanoparticles) and the alkanethiol (PTZ-Au nanoparticles) containing phenothiazine (PTZ) as an electron donor and a redox-active group, and the assembly of large-scale nanoparticle aggregates mediated by metal ion recognition of the PTZ-oxy-Au nanoparticles. The system described herein was designed bearing the following information in mind: (1) The protective ligand of PTZ-oxy-Au nanoparticles is designed to have two functional groups, a PTZ unit and an oligoethyleneoxy linkage, the former inducing the interaction between the ligands and the latter serving to bind metal ion. (2) Self-assembled monolayers with oligoethylene glycols on flat gold electrode are able to bind metal ions [9]. (3) Metal ion recognition of the oxy-interchain of the PTZ-oxy-Au nanoparticles may afford the assembly of nanoparticles. (4) No clear-cut example of difference between alkyl chain as hydrophobic spacer and oxy-alkyl chain as hydrophilic spacer in the particle shape of gold nanoparticles has been hitherto reported.

Phenothiazine ω-functionalized oligoethyleneoxythiolate and alkanethiolate-stabilized gold nanoparticles (PTZ-oxy-Au and PTZ-Au) were prepared using PTZ-oxy-alkylthiol (PTZ-oxy-SH) and PTZ-alkylthiol (PTZ-SH) as a protective ligand; the synthesis of these thiols will be reported elsewhere. The synthesis of PTZ-oxy-Au nanoparticles is as follows: To a vigorously stirred solution of tetraoctylammonium bromide (1.09 g, 2 mmol) in 40 mL of toluene was added $HAuCl_4 \cdot 4H_2O$ (185 mg, 0.45 mmol) in 15 mL of deionized water. The thiol, PTZ-oxy-SH (144 mg, 0.42 mmol), was added, and the resulting solution was stirred for 20 min at room temperature. The solution was then vigorously stirred and $NaBH_4$ (189 mg, 5 mmol) in 13 mL of deionized water was added. The mixture was stirred for 3 h at room temperature. After stirring the organic phase was evaporated to 5 mL *in vacuo* and mixed with EtOH (200 mL). The resulting precipitate was collected by filtration and washed serially with EtOH. PTZ-oxy-Au nanoparticles obtained were very stable and soluble in toluene, CH_2Cl_2, $CHCl_3$, and tetrahydrofuran. PTZ-Au nanoparticles and octanethiol-stabilized gold nanoparticles were also prepared by the same method as PTZ-oxy-Au nanoparticles.



PTZ-oxy-SH



PTZ-SH

The UV-vis spectrum of the PTZ-oxy-Au nanoparticle solution in CH_2Cl_2 exhibited a plasmon resonance at ∼510 nm and characteristic peaks due to phenothiazine unit at 315 and 250 nm. PTZ-Au nanoparticles showed the similar UV-vis spectrum. The electrochemical properties were studied by cyclic voltammetry. The cyclic voltammogram of PTZ-oxy-Au nanoparticles in CH_2Cl_2-0.1 M Bu_4NClO_4 at a glassy carbon electrode showed the reversible redox peak at $E_{1/2} = +0.50$ V (vs. Ag/0.1 M $AgNO_3$). While the reversible oxidation potential of PTZ-Au nanoparticles was $E_{1/2} = +0.46$ V. Thus, the difference between

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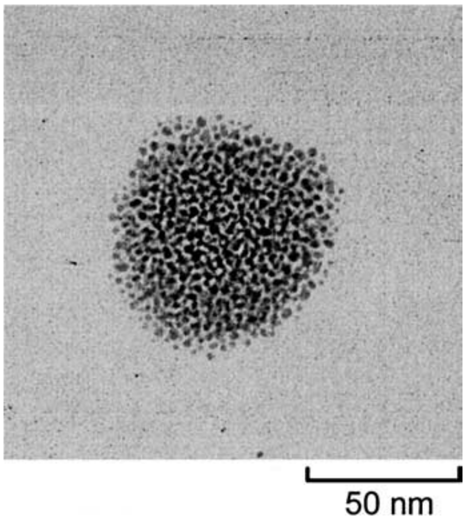

Figure 1 TEM micrograph of PTZ-oxy-Au nanoparticles.

the oxy-alkyl chain and the alkyl chain in their redox behaviors was found.

The size, shape, and dispersity of PTZ-oxy-Au and PTZ-Au nanoparticles can readily be determined with transmission electron microscopy (TEM). Interestingly, Fig. 1 is a TEM micrograph of a large spherical nanoparticle aggregate with diameter of ca. 75 nm which self-assembled when a drop of a dilute solution of PTZ-oxy-Au nanoparticles in $CHCl_3$-CH_3CN [1 mg in a mixture of $CHCl_3$ (4 mL) and CH_3CN (2 mL)] was placed on a TEM grid and allowed to evaporate. The same co-solvent of $CHCl_3$-CH_3CN was used for the addition of $NaClO_4$ to PTZ-oxy-Au nanoparticles (*vide infra*), since sodium perchlorate can be dissolved in $CHCl_3$-CH_3CN. The mean diameter of the individual nanoparticles of PTZ-oxy-Au nanoparticles is about 2–4 nm. In contrast, the TEM image of a sample of PTZ-Au nanoparticles that was prepared by spreading a drop of a $CHCl_3$ dispersion (0.1 mg/mL) on the TEM grid, reveals the formation of dispersed particles with diameter of $\sim$ same size 2.1 ± 0.4 nm (Fig. 2). Analogously, the TEM micrograph of octanethiol-stabilized gold nanoparticles showed the dispersed particles with core size of 3.2 ± 0.7 nm.

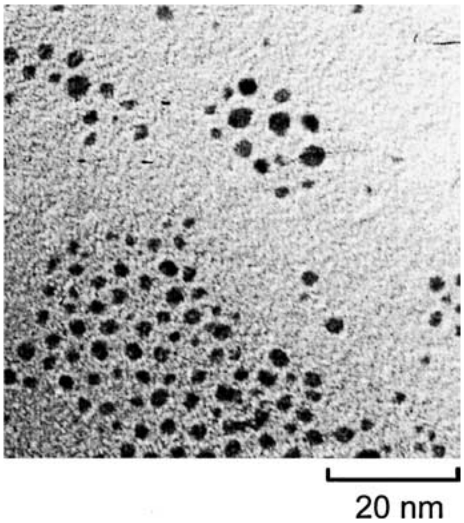

Figure 2 TEM micrograph of PTZ-Au nanoparticles.

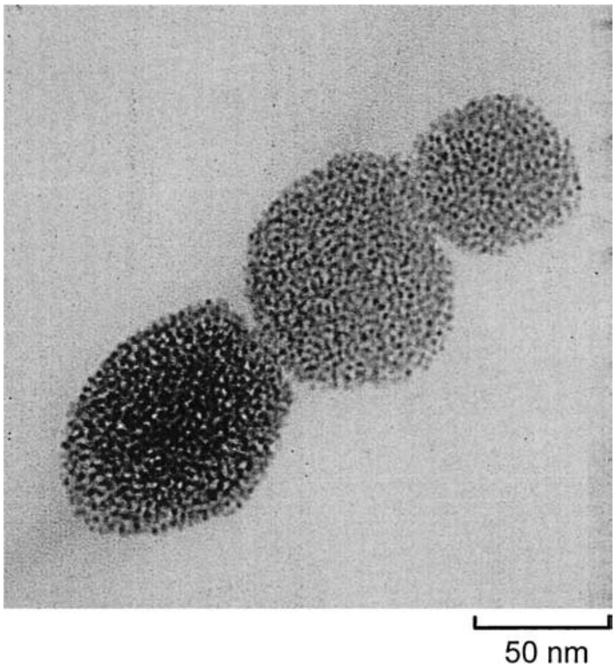

Figure 3 TEM micrograph of PTZ-oxy-Au nanoparticles in the presence of $NaClO_4$.

More significantly, the spherical aggregates of PTZ-oxy Au nanoparticles assembled into the nanoparticle network upon addition of alkali metal ion. Typically, PTZ-oxy-Au nanoparticles (1 mg) and $NaClO_4$ (1 mg) were dissolved in a mixture of $CHCl_3$ (4 mL) and CH_3CN (2 mL), and a drop of the resulting dispersion was placed on a TEM grid. Its TEM micrograph shows the formation of spherical aggregates network (Fig. 3). However, the shape of octanethiol-stabilized Au nanoparticles and PTZ-Au nanoparticles did not change by addition of alkali metal ion. This intriguing large-scale ordering organization of PTZ-oxy-Au nanoparticles can be rationally explained in terms of metal ion recognition by intermonolayer with oligoethyleneoxy linkage (Fig. 4). Although a number of studies for the organization from relatively small gold nanoparticles using molecular templates have been reported, only limitted information of the assembly of large spherical aggregates without use of molecular template is known.

In summary, PTZ-oxy-Au nanoparticles self-assemble into spherical aggregates as evidenced from the TEM characterization. The novel assembly for the spherical aggregates of PTZ-oxy-Au nanoparticles was induced by metal ion recognition of intermonolayer with oligoethyleneoxy units. This finding suggests the possibility of the fabricating multiscale assembled aggregates without use of molecular template. In contrast, such intriguing behaviors were not observed

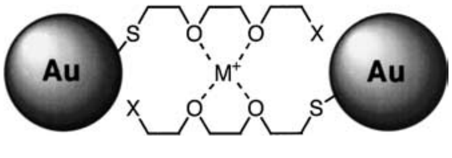

Figure 4 Proposed schematic illustration for metal ion recognition of PTZ-oxy-Au nanoparticles.

in octanethiol-stabilized gold nanoparticles. This work represents a general strategy for the creation of multiscale self-organized materials.

Acknowledgments

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