Heterodimeric particle assemblies: Preparation of anisotropically connected spherical silica particles *via* surface-bound gold nanoparticles†

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Assemblies of heterodimeric particles were prepared through selective coupling of two kinds of spherical silica particles of different sizes by connection with gold nanoparticles attached anisotropically to the particles.

Two-dimensional and three-dimensional colloid-crystal materials are of great interest owing to their possible applications, *e.g.* optical devices, and are often fabricated by self-assembling of monodispersed spherical particles.[1,2] The ordered arrangement of particles in colloid crystals is based on either cubic close-packing (*fcc*) or hexagonal close-packing (*hcp*) of particles. Therefore, the packing density of colloid crystals can not be changed unless particles have anisotropy to connect each other; if the particles have surface sites, *e.g.*, in tetrahedral directions, a colloid crystal with a diamond-like structure[3] can be fabricated. Similar complex structures of colloidal aggregates have been fabricated *via* template-assisted methodology.[4] However, template-assisted procedures generally require as many templates as product particle assemblies.

Several methods for modifying surfaces of spherical particles anisotropically have been reported.[5] A frequently employed strategy is a two-dimensional one in which a two-dimensional monolayer arrangement of particles is prepared at gas–liquid, liquid–liquid or liquid–solid interfaces followed by modification of a part of the particle surfaces facing one of the two phases.[6–10] There are two problems in this two-dimensional strategy. One is that only particles of side-to-side bilateral characters are obtained, and the other is that the amount of anisotropic particles obtained by an operation is limited to the area of interfaces and, therefore, a large-scale apparatus is required for the mass production of anisotropically modified particles.

A three-dimensional method that can introduce anisotropy to a large number of particles has been reported by Ikeda *et al.*[11] They used a small amount of water to make dry silica particles aggregated through capillary force and modified only the outer surfaces of the particle aggregates to produce "phase boundary catalyst particles" having both hydrophilic and hydrophobic surfaces on each particle. Although this method provides a way for fabrication of anisotropically modified particles in relatively large amount when compared with the above-mentioned two-dimensional methods, the thus-obtained particles have still only side-to-side bilateral characters and no further extension to the other modes of anisotropic modification is expected.

In the present study, therefore, we tried to prepare anisotropically connected spherical silica-particle assemblies *via* surface-bound gold nanoparticles (AuNPs) through a newly developed multistep three-dimensional method, which can be applied to a wide range of anisotropic particle-surface modifications and particle-assembly preparations. As an example, we show here the production of the simplest anisotropic particle assembly of "heterodimer". Preparation of such heterodimeric particle assemblies has been reported as preparation of snowman-like or dumbbell-like particles.[12–14] Different from those reported procedures, the present method includes connection of micrometer or submicrometer particles with AuNPs as a coupler.

Scheme 1 shows a diagram of the procedure for the preparation of heterodimeric particle assemblies. An outline is as follows. First, three kinds of silica particles of small size (*s*-SIO), medium size (*m*-SIO) and large size (*l*-SIO) are prepared or purchased from a commercial source. The surface of *s*-SIO is modified with a thiol group (–SH) and the surfaces of *m*-SIO and *l*-SIO are modified with an amino group (–NH_2) using silylation agents, 3-mercaptopropyltrimethoxysilane and 3-aminopropyltriethoxysilane, respectively. The NH_2-modified *l*-SIO is covered with AuNPs by reaction with colloidal AuNPs (Au–NH_2–*l*-SIO). Then Au–NH_2–*l*-SIO is reacted with a large number of SH–*s*-SIO particles to obtain an "intermediate aggregate", followed by treatment with a sodium hydroxide (NaOH) solution to break the linkage between *l*-SIO and AuNP attached to SH–*s*-SIO and to provide "anisotropically gold-nanoparticle-modified silica particles". Finally, the anisotropically modified silica particles are mixed with a large number of *m*-SIO particles, resulting in the formation of a "heterodimeric particle assembly".

A set of three kinds of monodispersed spherical silica particles with average diameters of *ca.* 220, 480 and 1000 nm were used as *s*-SIO, *m*-SIO and *l*-SIO, respectively, as a standard set in this study. The two kinds of smaller particles were prepared by Stöber's method[15] and *l*-SIO was supplied by Nippon Shokubai (SEAHOSTER KE-P100). An aqueous colloidal solution of citrate-stabilized AuNPs (*ca.* 10 nm) was prepared by the method reported by Frens.[16] The experimental details are given in the Electronic Supplementary Information†.

Fig. 1 shows an SEM image of Au–NH_2–*l*-SIO. On average, *l*-SIO was covered with *ca.* 8000 AuNPs presumably through

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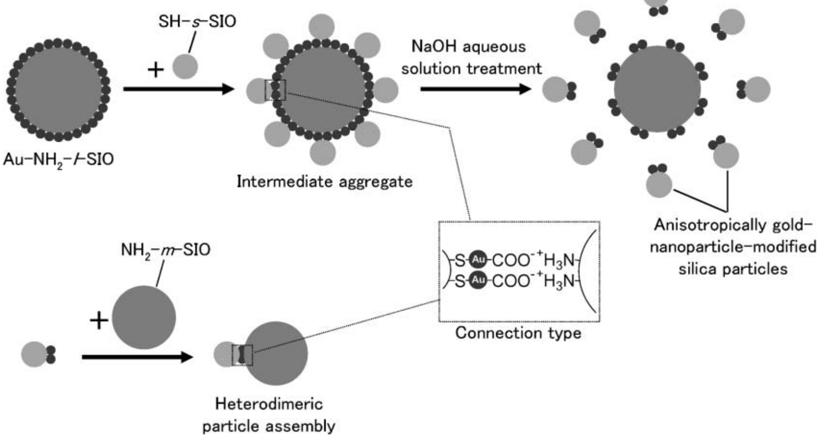

Scheme 1 Diagram of method for preparing heterodimeric particle assemblies.

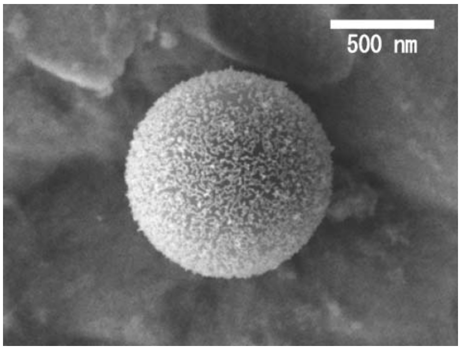

Fig. 1 SEM image of aminoalkylated large silica particle with attached gold nanoparticles (Au–NH$_2$–*l*-SIO).

electrostatic interaction between ammonium ion of the amino-modified *l*-SIO surface and carboxylate ion of surface-absorbed citrate on AuNPs.[17] The surface-attached AuNPs could play a role of a coupler when Au–NH$_2$–*l*-SIO was added to an SH–*s*-SIO suspension.

Fig. 2 shows that the resulting intermediate aggregates were composed of Au–NH$_2$–*l*-SIO with *ca.* 70 surrounding *s*-SIOs. The binding between SH–*s*-SIO and AuNPs attached to *l*-SIO is attributable to well-known sulfur–gold covalent bonds, though the number of intervening AuNPs in each aggregate was not determined at this stage.

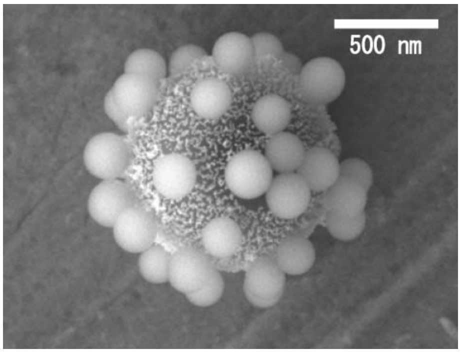

Fig. 2 SEM image of intermediate aggregate.

Fig. 3 shows an SEM image of the anisotropically modified silica particles detached from *l*-SIO by alkaline treatment. It can be clearly seen that one cluster of AuNPs was attached to one *s*-SIO surface. In SEM analysis of more than 200 *s*-SIOs, particles having more than two clusters were not found, suggesting that the anisotropically gold-nanoparticle-modified silica particles could be prepared through the proposed mechanism (Scheme 1). The average proportion of *s*-SIOs with an attached AuNP cluster was *ca.* 30%. Since we could not see AuNP clusters behind *s*-SIOs in the SEM images and since free *s*-SIOs were not completely removed in the process of purification of intermediate aggregates, the selective detachment of anisotropically modified silica particles might proceed efficiently. The average number of AuNPs in their cluster was *ca.* 5 and, therefore, *s*-SIO and *l*-SIO particles were connected *via* 5 AuNPs, on average, in the original aggregates.

In the detachment process, the alkaline treatment might cleave the connection between AuNP and *l*-SIO by reduction of positive charge of ammonium cations, and it was expected that all of the AuNPs, with or without connection to *s*-SIO, would be detached from *l*-SIOs. However, we found that only the AuNPs connected to SH–*s*-SIO were detached by using an aqueous NaOH solution of appropriate concentration, 2 mmol L^{-1}, leaving *l*-SIO still surrounded by AuNPs. Aqueous NaOH solutions of higher (4 mmol L^{-1}) and lower (1 mmol L^{-1}) concentrations caused complete detachment of AuNPs and incomplete detachment of *s*-SIOs from intermediate aggregates.[18]

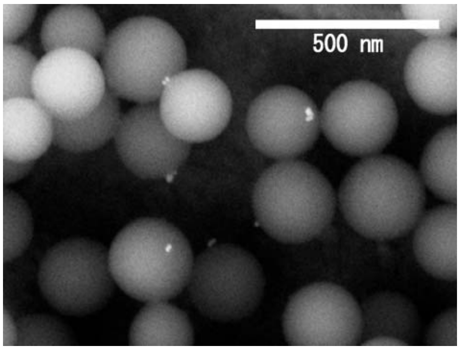

Fig. 3 SEM image of anisotropically gold-nanoparticle-modified silica particles.

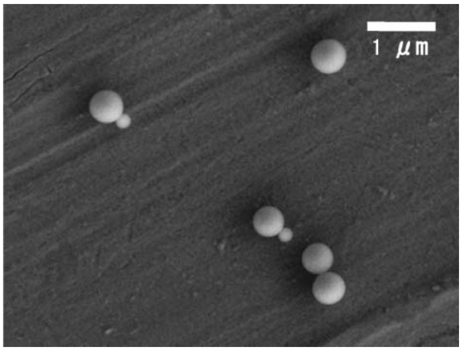

Fig. 4 SEM image of heterodimeric silica particle assemblies.

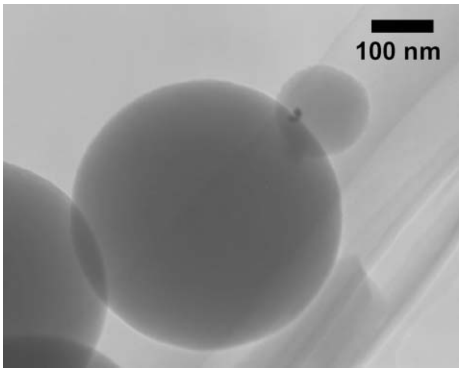

Fig. 5 TEM image of heterodimeric silica particle assembly.

Fig. 4 shows an SEM image of the heterodimeric particle assemblies prepared by the reaction of anisotropically modified silica particles with NH_2–*m*-SIOs. The proportion of *m*-SIOs connected to *s*-SIO, *i.e.*, heterodimeric particle assemblies as a final product, was *ca.* 15%, when calculated for more than 200 *m*-SIO particles in the SEM images. Under the present experimental conditions, the remaining unreacted NH_2–*m*-SIOs used in excess amount could not be removed by centrifugation since their size is not so different from that of the product. In the SEM observation, we could not confirm the possible existence of AuNPs between *m*-SIO and *s*-SIO, and we therefore tried to check this by TEM analyses.

Fig. 5 shows an example of TEM images of the heterodimeric particle assemblies. AuNPs, confirmed by EDS analysis, were observed at the connecting part of the silica particles, being consistent with the proposed structure of a heterodimeric particle assembly, *i.e.*, silica–gold–silica linking. The strength of this silica–gold–silica linkage was examined by ultrasonication. Treatment of the suspension in an ultrasonic bath for 1 min decomposed the heterodimeric particles assemblies almost half. Therefore, in the present experimental conditions, ultrasonication should not be used in the workup processes.

Thus, we have demonstrated an organized procedure for the preparation of heterodimeric particle assemblies through connecting spherical silica particles with AuNPs as a coupler. One of the features of this procedure is that the structure of the final product, particle assemblies, is controlled by the number and position of AuNP clusters on the surface of anisotropically modified particles; in the present case, one cluster was attached to each particle and this was regulated by the structure of the precursor, intermediate aggregates. Structural design of intermediate aggregates can be achieved by, for example, changing the diameter ratio and mixture ratio of starting particles. For example, it is expected that anisotropically modified particles with four AuNP clusters in tetrahedral directions, which can be a precursor for "methane-shaped particle assemblies", would be prepared when relatively small (size ratio of 0.225–0.414) particles modified with a thiol group are mixed with a large number of large particles surrounded by AuNPs followed by detachment of large particles. The present results have opened up a way for fabrication of particle assemblies with desired structure using monodispersed spherical particles made of any material for which the surface can be chemically modified.

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