Supporting Information
for

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

Experimental

Materials:

All chemicals were of reagent-grade and were used without further purification. Ethanol (>99.5%), a 28 wt% solution of ammonia, tetraethyl orthosilicate (TEOS, >95.0%), tetrachloroauric acid tetrahydrate ($HAuCl_4$, 99.9%), trisodium citrate anhydrous (Na-CA, >99%), toluene (>99.5%), methanol (>99.7%), and sodium hydroxide (NaOH, >96.0%) were purchased from Wako Pure Chemical Industries. 3-Aminopropyltriethoxysilane (APTES, >97%) and 3-mercaptopropyltrimethoxysilane (MPTS, >97.0%) were purchased from Tokyo Chemical Industry. Amphoteric ion-exchange resin (Amberlite MB-1) was purchased from ORGANO. Laboratory-grade water with a measured resistivity of >18 MΩ cm was prepared by using a Milli-Q pure water system (WQ501, YAMATO-Millipore).

Preparation of silica particles:

A set of three kinds of monodispersed spherical silica particles with average diameters of ca. 220, 480 and 1000 nm as *s*-SIO, *m*-SIO and *l*-SIO, respectively, as a standard in this study. *l*-SIO was supplied by Nippon Shokubai (SEAHOSTER KE-P100) and the two kinds of smaller particles were prepared by Stöber's method as follows.[15] To an Erlenmeyer flask of 500 mL (or 200 mL) capacity was added 250 mL

(or 100 mL) of mixed solution composed water, ethanol and ammonia. The molar composition of the mixed solution was controlled, depending on the sizes of silica particles. The compositions were water/ethanol/ammonia = 3.75/3.10/0.0625, 3.75/3.10/0.219 for the synthesis of silica particles of ca. 220, 480 nm, respectively. To each of these aqueous solutions, 70 mmol (or 28 mmol) of TEOS was added. The mixture was shaken at rotation rate of 100 rpm using an EYELA MMS-310 reciprocal shaker for 2 h at room temperature, and white products were formed. They were collected by centrifugation, and washed by repeating dispersion-centrifugation cycles in pure ethanol. The final precipitates were dried at 383 K under vacuum. The sizes of these particles were determined by a Shimadzu SALD-7000 laser-diffraction particle size analyzer.

Preparation of aqueous colloidal solution of gold nanoparticles:

An aqueous colloidal solution of citrate-stabilized gold nanoparticles (AuNPs, ca. 10 nm) was prepared by the method reported by Frens.[16] To 750 mL of an aqueous $HAuCl_4$ solution (0.340 g L^{-1}) heated to boiling was added 90 mL of aqueous solution containing Na-CA (38.8 mmol L^{-1}). After the change of color from deep blue to deep red, the solution was boiled for further 30 min. After cooling the solution at room temperature, Amberlite MB-1 (50 mL) was added to remove excess Na-CA. After 1-h treatment, MB-1 was removed using a glass filter.

Surface modification of silica particles with alkylsilylation agents:

To 45 mL of toluene containing 19 mmol of APTES was added 0.45 g of *m*-SIOs or *l*-SIOs. After stirring overnight at room temperature, the solid was collected by

centrifugation, washed with ethanol, and dried at 383 K for 2.5 h under vacuum.

To 45 mL of toluene containing 19 mmol of MPTS was added 0.45 g of *s*-SIOs. After stirring overnight at room temperature, the solid was collected by centrifugation, washed with ethanol, and dried at 383 K for 2.5 h under vacuum.

Preparation of Au-NH_2-*l*-SIOs:

NH_2-modified *l*-SIOs (15 mg) were dispersed in 22.5 mL water and the suspension was added to 21.6 mL of the above-prepared citrate-stabilized colloidal gold solution. After stirring for 6 h at room temperature, Au-NH_2-*l*-SIOs was centrifugally separated from the solution containing unreacted AuNPs and washed with water.

Preparation of intermediate aggregates:

SH-*s*-SIOs (61 mg) were dispersed in 30 mL of methanol and Au-NH_2-*l*-SIOs (10 mg NH_2-*l*-SIOs amount) were dispersed in 15 mL of methanol. The SH-*s*-SIOs suspension was added to the Au-NH_2-*l*-SIOs suspension, and was refluxed for 1 h. After cooling, intermediate aggregates were separated from the suspension containing unreacted SH-*s*-SIOs by centrifugation (1500 rpm, 5 min) and washed with methanol.

Preparation of anisotropically gold-nanoparticle-modified silica particles:

Intermediate aggregates containing 10 mg of NH_2-*l*-SIOs were dispersed in 40 mL of water, and 10 mL of an NaOH aqueous solution (0.01 mol L^{-1}) was added to this suspension slowly. After stirring for 10 min at room temperature, the anisotropic silica particles were collected as a supernatant colloidal solution by centrifugation (2000 rpm, 5 min) and washed with water.

Preparation of heterodimeric particle assemblies:

Anisotropically gold-nanoparticle-modified silica particles (0.5 mg silica amount) were dispersed in 7.5 mL water. The anisotropic silica-particle suspension was added to the NH_2-*m*-SIOs suspension containing 26 mg of particles in 15 mL of water. After stirring overnight at the room temperature, the heterodimeric particle assemblies were separated from the suspension containing unreacted SH-*s*-SIOs by centrifugation (3000 rpm, 5 min) and washed with water.

Characterization:

The morphology of the particles was analyzed using a JEOL JSM-7400F field-emission type scanning electron microscope (FE-SEM) at an acceleration voltage of 4-5 kV and a JEOL JEM-2010F transmission electron microscope (TEM) at an acceleration voltage of 200 kV. Samples for SEM and TEM analyses were prepared by drying a drop of particle suspensions on a copper tape and on a copper grid coated with amorphous carbon membrane, respectively.