Preparation of Au Nanoparticles in the Interlayer Space of a Layered Alkali Silicate Modified with Alkylthiol Groups

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The preparation of Au nanoparticles in heterogeneous systems has been conducted in order to control the nanoparticles' morphology and the properties of the nanoparticles.[1] The preparation and the properties of the nanoparticle-supported solids have also been investigated actively,[2] whereas it is still difficult to control the nanoparticles' morphology on solid supports. Inorganic nanoporous solids such as mesoporous materials and layered materials are possible templates and supports for nanoparticles because of the defined and stable nanostructures if compared with organic systems such as surfactant assemblies and polymers. There are a few reports on the preparation of Au nanoparticles in mesoporous silica, in which the nanoparticles with morphologies replicated by the one-dimensional nanostructures such as wire are synthesized.[3]

The two-dimensional interlayer space of layered materials seems to be a unique template for the preparation of Au nanoparticles, possibly nanosheet or plate, although there are few reports on the preparation in layered materials (a layered double hydroxide[4a] and a perovskite titanate[4b]); the formation of the nanoparticles with morphologies replicated by the two-dimensional interlayer space has not been achieved yet. Layered materials with variable reactivities are available and the modification of the interlayer space is also possible, so that the study on Au nanoparticle formation is worth further investigation. In this communication, we report the preparation of Au nanoparticles in the interlayer space of a layered alkali silicate, octosilicate,[5] modified with alkylthiol groups that are known to interact with Au.

The modification of the interlayer space of octosilicate (Na-oct), which was prepared according to the reported method,[6] with alkylthiol groups was conducted via the silylation of Na-oct with 3-mercaptopropyltrimethoxysilane (MPS) using the dodecyltrimethylammonium-exchanged form (C_{12}TMA-oct) as the intermediate.[7] This procedure has often been used for the interlayer silylation of layered alkali silicates.[8] In the present study, the particle surface of Na-oct was modified with another silane coupling reagent that does not possess thiol group, *n*-octadecyltrimethoxysilane (C_{18}TMS), to avoid the formation of Au particles on the particle surface (the C_{18}TMS-modified Na-oct was abbreviated as C_{18}TMS−Na-oct),[7] as schematically shown in Figure 1. The preparation of Au nanoparticles in the interlayer space of the mercaptopropylsilylated derivative (MPS-oct) was conducted by the reaction between $HAuCl_4{\cdot}3H_2O$, the MPS-oct ethanol suspension, and $NaBH_4$.[9] The Au-incorporated derivative thus obtained was abbreviated as AuMPS-oct.

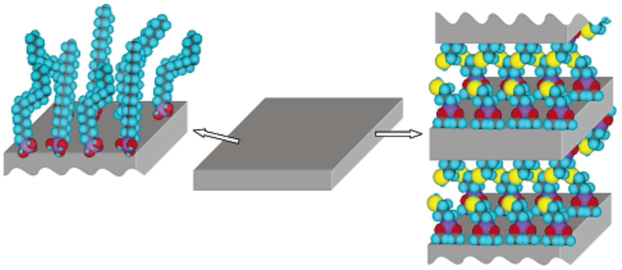

Figure 1. Schematic presentation of the selective silylation at the particle surface of Na-oct with C_{18}TMS and at the interlayer surface with MPS. Color assignment of organosilyl groups: blue, hydrogen; gray, carbon; red, oxygen; purple, silicon; and yellow, sulfur.

The XRD pattern of C_{18}TMS−Na-oct is shown in Figure 2 together with that of raw Na-oct. The basal spacing of Na-oct, 1.1 nm, did not change upon the reaction with C_{18}TMS. The IR spectrum of C_{18}TMS−Na-oct showed the presence of C_{18}TMS in the product (Figure 3a). From the

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(7) The silylation at the particle surface of Na-oct was conducted by mixing Na-oct (1.0 g) in a C_{18}TMS (2.0 mL) toluene (50 mL) solution and stirring the mixture for 1 day at 100 °C. The product was separated by centrifugation and washed with acetone. C_{12}TMA-oct was prepared by cation-exchange reaction between C_{18}TMS−Na-oct (0.80 g) and a 0.1 M aqueous solution (160 mL) of dodecyltrimethylammonium chloride for 1 week at room temperature. The product was separated by centrifugation and washed with ethanol. The interlayer silylation was conducted by dispersing C_{12}TMA-oct (0.50 g) in an MPS (25 g) toluene (20 mL) solution and stirring the mixture for 8 days at 80 °C under N_2. The product was separated by centrifugation and washed with acetone.
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(9) $HAuCl_4{\cdot}3H_2O$ (0.5 Au:SH molar ratio (equivalent to 11 % as Au)) was added to the MPS-oct ethanol suspension, which was prepared by dispersing MPS-oct (100 mg) in ethanol (80 mL) followed by ultrasonication for 3 hours and subsequent stirring for 1 hour;[10] the mixture was then stirred for 7 days at room temperature. The yellow precipitate obtained by evaporating the solvent was redispersed in ethanol (80 mL), and the yellow suspension thus obtained was then mixed with $NaBH_4$ ethanol (18.6 mL) solution (7 Na:Au molar ratio).[11] The color of the mixture turned to blackish purple immediately after $NaBH_4$ was added and finally to dusty purple after it was stirred for 1 day. After the removal of particles containing the Au that formed outside MPS-oct particles (black precipitate, see Figure 5c) by decantation, the product was separated by centrifugation and dried under reduced pressure.

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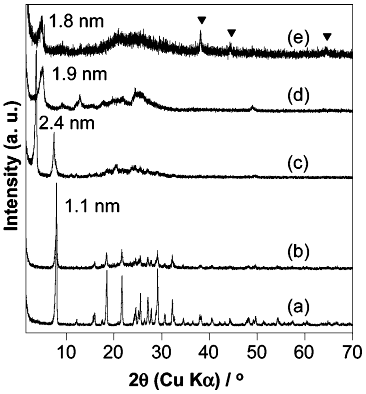

Figure 2. XRD patterns of (a) Na-oct, (b) C_{18}TMS−Na- oct, (c) C_{12}TMA-oct, (d) MPS-oct, and (e) AuMPS-oct. Triangles denote diffraction peaks due to Au.

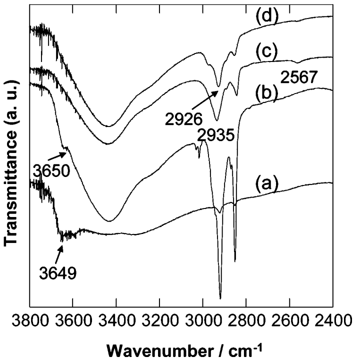

Figure 3. IR spectra of (a) C_{18}TMS−Na-oct, (b) C_{12}TMA-oct, (c) MPS-oct, and (d) AuMPS-oct.

TG-DTA curves of C_{18}TMS−Na-oct, the amount of the attached C_{18}TMS was determined to be 3 mass % (see the Supporting Information). Moreover, C_{18}TMS−Na-oct dispersed in toluene. These results confirm the modification of Na-oct with C_{18}TMS only at the particle surface.

Figures 2c and 3b depict the XRD pattern and the IR spectrum of C_{12}TMA-oct, respectively. The basal spacing was 2.4 nm, and the IR spectrum showed the absorption bands characteristic to C_{12}TMA such as C−H stretching vibration at around 2900 cm^{-1}. These results are consistent with those reported for the dodecyltrimethylammonium-exchanged forms of Na-oct,[6,12] indicating the successful intercalation of C_{12}TMA even after the organic modification of the particle surface of Na-oct. From the elemental analysis and the TG analysis results (C, 22.1 mass %; N, 1.7 mass %; SiO_2, 73.3 mass %), the amount of the adsorbed C_{12}TMA was determined to be 1.2 groups per Si_8O_{17}.[13] This value was smaller that those (1.6 or 1.4 groups per Si_8O_{17}) reported for the dodecyltrimethylammonium-exchanged forms described above.[6,12]

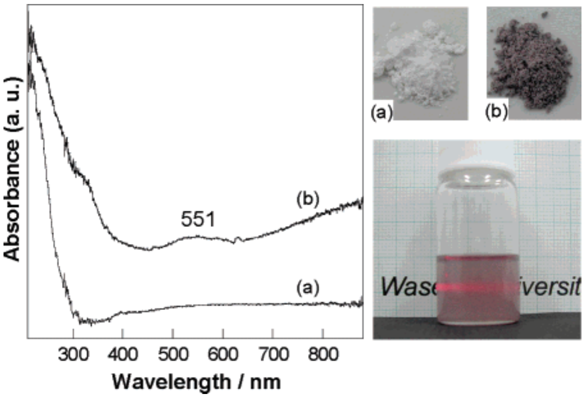

Figure 4. Diffuse reflectance UV−vis spectra of (a) MPS-oct and (b) AuMPS-oct. Inset shows photographs of the corresponding powders and the AuMPS-oct ethanol suspension.

The XRD pattern of MPS-oct is shown in Figure 2d. The basal spacing decreased to 1.9 nm from 2.4 nm for C_{12}TMA-oct. In the IR spectrum (Figure 3), the absorption bands due to MPS such as S−H stretching vibration at 2567 cm^{-1} appeared and the absorption band due to the interlayer SiO−H stretching vibration at 3650 cm^{-1} disappeared upon the silylation. These results confirm the attachment of MPS on the interlayer surface through Si−O−Si covalent bonds. From the elemental analysis and the TG analysis results (C, 8.6 mass %; N, 0.12 mass %; SiO_2, 75.6 mass %), the amount of the attached MPS was determined to be 1.3 groups per Si_8O_{17}.[13] The absence of N in the product shows that all of the C_{12}TMA were deintercalated during the silylation. If the packing of MPS is a hexagonal closest packing, the distance between adjacent MPS attached on the surface was calculated from the composition of MPS-oct and the lattice constants of Na-oct ($a = b = 0.73$ nm)[14] to be $(0.73 \times 0.73 / 1.3)^{1/2} = 0.64$ nm. This value was smaller than that (0.74 nm) between adjacent silanol groups seen in the structure of Na-oct,[14] suggesting that all the interlayer silanol groups were reacted with MPS. The high surface coverage with organosilyl groups is known to facilitate the swelling in organic solvents[10,15] and thus thought to make the intercalation of Au precursors effective. The basal spacing of MPS-oct increased to 2.2 nm from 1.9 nm upon the swelling with ethanol.

The formation of Au nanoparticles in the interlayer space of MPS-oct was indicated both by the IR and the UV−vis spectra. The IR spectrum of AuMPS-oct showed that the intensity of the absorption band due to S−H stretching vibration was weakened as a result of the complexation of thiol groups with Au[16] (Figure 3d). In the UV−vis spectrum, the absorption band centered at ca. 550 nm, which is ascribable to the surface plasmon resonance of Au nanoparticles, was observed (Figure 4b). The SEM image of AuMPS-oct is shown in Figure 5b together with that (Figure 5a) of MPS-oct. The surface morphology of AuMPS-oct was identical to that of MPS-oct. It is worth mentioning that Au particles with a submicrometer size did not form on the particle surface as shown by the SEM image. The modification at the particle surface of Na-oct with C_{18}TMS and that at the interlayer surface with MPS, as schematically shown in Figure 1, led to the formation of Au nanoparticles in the

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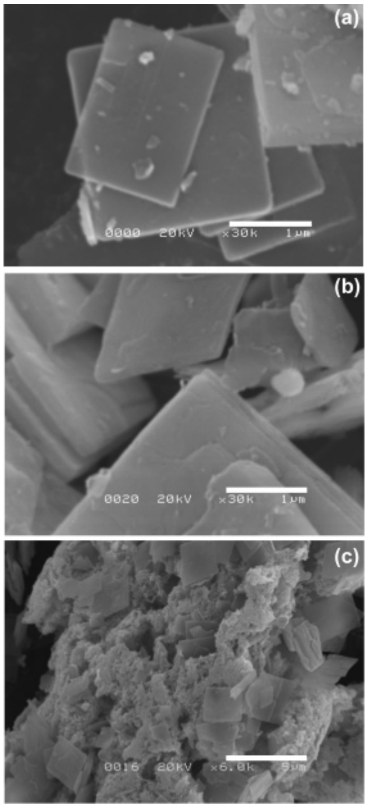

Figure 5. SEM images of (a) MPS-oct and AuMPS-oct (b) without and (c) with Au that formed outside MPS-oct particles. Scale bar: 1 μm for (a) and (b), 5 μm for (c).

interlayer space and not on the particle surface. The Au particles that formed outside MPS-oct particles (Figure 5c) were effectively removed by decantation.[9] The basal spacing of AuMPS-oct (1.8 nm) was smaller compared with that (1.9 nm) of MPS-oct (parts d and e of Figure 2), which is explained by the conformational change of the attached MPS upon the formation of Au nanoparticles. The absorption band due to C−H asymmetric stretching vibration at around 2930 cm^{-1}, which is sensitive to the conformational change of alkyl chains,[17] shifted to a lower-frequency region, indicating the conformational change of propyl chain to a more ordered (all-trans) conformation (parts c and d of Figure 3).

Taking the gallery height (1.1 nm, which was calculated by subtracting the silicate sheet thickness, 0.74 nm,[5] from the basal spacing, 1.8 nm) into account, we believe the morphology of the formed Au in the interlayer space of MPS-oct to be disc or polygonal plate with a thickness of less than 1 nm and an average lateral size of 4.8 nm (Figure 6). The platy morphology is suggested also by the UV−vis spectrum (Figure 4b). The absorption band from visible light region to 1400 nm was observed, which is ascribable to the longitudinal surface plasom band of Au nanopartices with anistropic morphologies (plate and rod).[18,19] The absorption band observed at ca. 550 nm is ascribable to the transverse surface plasmon band[18] or the localized surface plasmon resonance[19] of Au nanoparticles with anisotropic morphologies. Thus, it is thought that the two-dimensional interlayer space directed the formation of the platy nanoparticles.

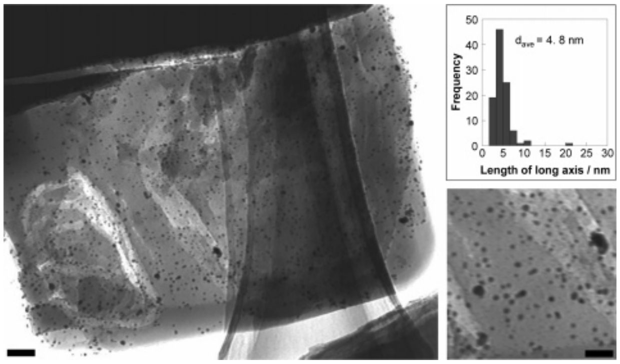

Figure 6. TEM image of AuMPS-oct. Scale bar: 50 nm. Inset shows the size distribution of Au nanoparticles and the magnified TEM image (scale bar: 25 nm).

Au plates with a diameter of ca. 140 nm and a thickness of ca. 8 nm were synthesized using ca. 5.2 nm Au spherical particles as seeds[18b] and those with a controlled diameter from a few hundred nanometers to longer than 10 μm were synthesized in a lamellarly ordered surfactant assembly.[20] The diameter and thickness of the presently formed Au plates were smaller than the previous plates. The diameter of Au nanoparticles in the interlayer space increased by changing the amount of the added $HAuCl_4$ (see the Supporting Information). As shown in the inset of Figure 4, AuMPS-oct dispersed in organic solvents such as ethanol and chloroform to form stable suspensions. This character is useful for device fabrication.

In summary, we have successfully synthesized Au nanoparticles in the interlayer space of the mercaptopropylsilylated octosilicate. The morphology of the formed Au nanoparticle was characterized to be plate, which was replicated by the two-dimensional interlayer space. The present result suggests that the present strategy is applicable to a wide variety of interlayer hydroxyl-group-bearing layered materials with different nanostructures and compositions.

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Supporting Information Available: The TG-DTA curves of $C_{18}TMS-Na$-oct and the TEM image of the product prepared with an increased amount of $HAuCl_4$. This material is available free of charge via the Internet at http://pubs.acs.org.

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