Selected Paper

Synthesis of Au Nanoparticles in the Interlayer Space of a Layered Titanate Intercalated with 2-Aminoethanethiol

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The intercalation compound of a layered titanate with 2-aminoethanethiol was synthesized to prepare and support Au nanoparticles with morphology replicated by two-dimensional nanospace. The morphology of the formed Au nanoparticles was revealed to be plate, and the thickness and diameter of the platy particles varied with the added amount of Au source; less than 0.7 nm and ca. 6.8 nm, less than 0.9 nm and ca. 6.5 nm, and less than 0.9–1.0 nm and ca. 5.7 nm at molar Au/SH ratios of 0.5, 1.5, and 2.0 respectively. Platy Au nanoparticle-supported layered titanate (Au/SH ratio of 0.5) was thermally stable up to 180 °C in air and 160 °C in helium, respectively.

Au nanoparticles have attracted a wide range of scientific and practical interests partly due to their morphology dependent useful properties.[1] The preparation of Au nanoparticles in heterogeneous systems has extensively been investigated to control their morphologies and properties. The preparation and properties of Au nanoparticle supported solids have also been investigated,[2] while the morphological control of Au nanoparticles on supports is still difficult compared with that achieved with nanoparticles synthesized from homogenous solutions. Among possible templates and supports of Au nanoparticles such as surfactant assemblies and polymers, inorganic nanoporous solids such as surfactant-templated mesoporous materials are unique due to defined and stable nanostructures. The formation of Au nanoparticles with morphologies replicated by one-dimensional nanostructures of mesoporous silicas (wire) has been reported.[3] Recently, we have reported the synthesis of Au nanoparticles in the interlayer space of a layered silicate modified with alkanethiol groups, (3-mercaptopropyl)-trimethoxysilane (MPS), where platy Au nanoparticles formed by replicating the two-dimensional nanospace and the plates were bound to the silicate via thiol groups.[4] Since various layered solids with different compositions and properties are available, the extension of the reported strategy to other layered solids is worth performing to exploit the applications of this system.

In this article, a layered titanate was used as a host to prepare Au nanoparticles. The synthesis and properties of Au nanoparticles supported on titania has been investigated; the oxidation of CO at low temperature for Au nanoparticle (ca. 5 nm spherical and/or hemispherical)-supported titania particulates synthesized from homogenous solutions of Au and titania sources[2b] and visible light-induced charge separation for a titania film loaded with pre-synthesized Au nanoparticles (ca. 50 nm spherical)[5] have been reported. These successes motivated us to prepare Au nanoparticles in the interlayer of a titania based layered solid. In order to bind Au nanoparticles to the interlayer space of the layered titanate, 2-aminoethanethiol (AET) was used as a linker. It has been reported that AET was intercalated into a layered titanium phosphate by interactions between the amino group of AET and the phosphate sheet and the intercalation compound adsorbed heavy and noble metal ions from water through thiol–metal ion interactions.[6]

Experimental

Reagents and Materials. A layered titanate, $K_{0.73}Ti_{1.73}Li_{0.27}O_4$, was synthesized according to the literature.[7] The raw materials, titanium dioxide (rutile), and alkali metal carbonates (≧99.9%), were purchased from Rare Metallic, Co. and used as received. Octadecyltrimethoxysilane (C_{18}TMS, >85%) and 2-aminoethanethiol (AET) hydrochloride (>95%) were purchased from Tokyo Chem. Ind. Co., Ltd. and used as received. $HAuCl_4 \cdot 3H_2O$ (98%) and $NaBH_4$ (≧98%) were purchased from Sigma-Aldrich and Kanto Chemical Co., Inc., respectively and use as received.

Preparation of Aminoethanethiol-Intercalated Titanate. Before cation-exchange reaction between $K_{0.73}Ti_{1.73}Li_{0.27}O_4$ and AET, the particle surface of the titanate was modified with C_{18}TMS to avoid precipitation of Au nanoparticles on the particle surface;[4] $K_{0.73}Ti_{1.73}Li_{0.27}O_4$ (1.5 g) was dispersed in a solution of C_{18}TMS (1.0 mL) in toluene (50 mL) and the mixture was concentrated at 80 °C under 40 hPa for 2 h. The intercalation of AET was carried out by a reaction between an aqueous solution (200 mL) of AET hydrochloride and C_{18}TMS-modified $K_{0.73}Ti_{1.73}Li_{0.27}O_4$ (0.20 g; molar AET/K ratio was 2.0) at room temperature for 12 h and then the reaction was repeated. The product was separated by centrifugation (4000 rpm, 20 min), washed with water, and dried under P_2O_5. The intercalation compound thus obtained is abbreviated as AET–TLO. The preparation of an intercalation compound of the titanate, where the particle surface is not modified with C_{18}TMS, was carried out in a manner similar to that used for the preparation of AET–TLO.

Preparation of Au Nanoparticle-Immobilized Titanate. $HAuCl_4 \cdot 3H_2O$ (97.2, 293.0, or 389.0 mg, equivalent to a molar

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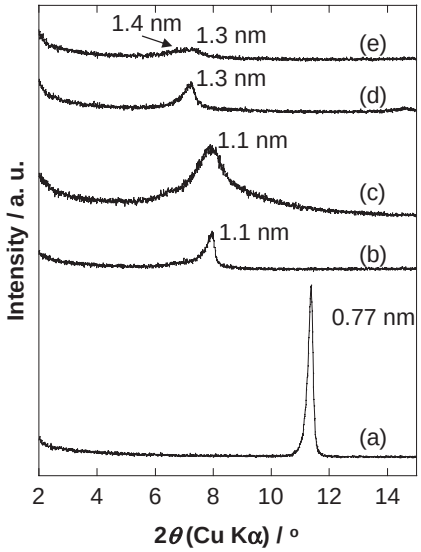

Figure 1. X-ray diffraction patterns of (a) $K_{0.73}Ti_{1.73}Li_{0.27}O_4$, (b) AET–TLO, (c) 0.5AuAET–TLO, (d) 1.5AuAET–TLO, and (e) 2.0AuAET–TLO.

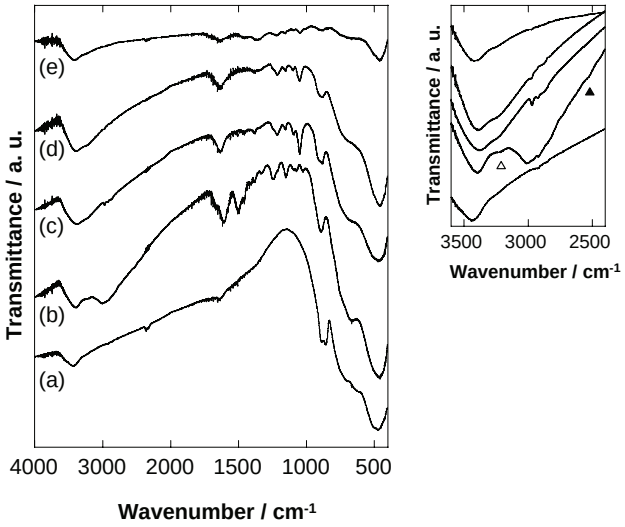

Figure 2. FT-IR spectra of (a) $K_{0.73}Ti_{1.73}Li_{0.27}O_4$, (b) AET–TLO, (c) 0.5AuAET–TLO, (d) 1.5AuAET–TLO, and (e) 2.0AuAET–TLO. Inset shows the expanded spectra in the range of 2400–3600 cm^{-1}.

Au/SH ratio of 0.5, 1.5, or 2.0) was added to a suspension of AET–TLO (100 mg) in ethanol (80 mL) and the mixture was stirred for 7 days at room temperature. The precipitate obtained by evaporating the solvent was re-dispersed in ethanol (80 mL) and the suspension thus obtained was added to a solution of $NaBH_4$ (63.4, 190.2, or 253.6 mg, equivalent to a molar Na/Au ratio of 7.0) in ethanol (15, 45, or 60 mL) and the mixture was stirred for 1 day. After removal by decantation of particles containing Au which formed outside the titanate particles, the product was separated by centrifugation (4000 rpm, 20 min) and dried under reduced pressure. The product is abbreviated as *x*AuAET–TLO, where *x* denotes the molar Au/SH ratio, 0.5, 1.5, or 2.0).

Characterization. X-ray diffraction (XRD) patterns of products were recorded on a Rigaku RAD IB powder diffractometer equipped with monochromatic Cu Kα radiation operated at 20 mA and 40 kV. Infrared spectra of KBr disks were recorded on a Shimadzu FT-8200 Fourier-transform infrared spectrophotometer at a resolution of 1.0 cm^{-1}. Thermogravimetric and differential thermal analysis curves were recorded on a Rigaku TG8120 at a heating rate of 10 °C min^{-1} under air using α-Al_2O_3 as standard material. Transmission electron micrography (TEM) was performed on a JEOL JEM-100CX transmission electron microscope.

Results and Discussion

Formation of AET-Intercalated Titanate. Figure 1 shows the XRD pattern of AET–TLO together with that of $K_{0.73}Ti_{1.73}Li_{0.27}O_4$. The basal spacing of AET–TLO was 1.1 nm, which was an increase from that of $K_{0.73}Ti_{1.73}Li_{0.27}O_4$ (0.77 nm). In the IR spectrum of AET–TLO, in addition to absorption bands due to CH stretching vibration at around 2900 cm^{-1}, those ascribable to NH_3^+ and SH stretching vibrations were observed at 3220 and 2568 cm^{-1}, respectively (Figure 2). These results indicate the successful intercalation of AET into $K_{0.73}Ti_{1.73}Li_{0.27}O_4$ by the electrostatic interactions between NH_3^+ groups and the negatively charged titanate sheet. The amount of adsorbed AET was calculated from the thermogravimetric curve of AET–TLO (Figure 5a) to be 0.68 groups per $Ti_{1.73}Li_{0.27}O_4$ unit cell, suggesting that AET reacted with potassium ion quantitatively. The basal spacing (1.1 nm) and composition (0.72 groups per $Ti_{1.73}Li_{0.27}O_4$ unit cell) of AET-intercalated $K_{0.73}Ti_{1.73}Li_{0.27}O_4$, whose particle surface was not modified with C_{18}TMS, were similar to those of AET–TLO. The access of AET into the interlayer space of the titanate was hardly suppressed even after the hydrophobic modification of the particle surface.

From the composition of AET–TLO (0.68 groups per $Ti_{1.73}Li_{0.27}O_4$ unit cell) and the available surface area of $K_{0.73}Ti_{1.73}Li_{0.27}O_4$, 0.23 nm^2 per $Ti_{1.73}Li_{0.27}O_4$ unit cell ($=2ac = 2 \times 0.38 \times 0.30\,nm^2$, where a and c are the lattice parameters of the titanate[8]), the distance between the adjacent AET was calculated to be 0.58 nm ($(0.23/0.0.68)^{1/2}$) assuming that AET takes hexagonal closest packing.[9] Accordingly, in light of the gallery height (0.7 nm, determined by subtracting the thickness of a titanate sheet (ca. 0.4 nm)[10] from the observed basal spacing of AET–TLO, 1.1 nm) and the size of AET ($0.4 \times 0.4 \times 0.7\,nm^3$), the adsorbed AET is thought to form a bilayer or an interdigitated monolayer arrangement in the interlayer space. The packing density of alkanethiol groups in AET–TLO is comparable to that in layered silicate modified with MPS, where the distance between the adjacent MPS is estimated to be 0.64 nm and the bilayer or the interdigitated monolayer arrangement of MPS in the interlayer space of the silicate was proposed.[4] AET–TLO was a possible template and support for the preparation and immobilization of platy Au nanoparticles.

Formation of Au Nanoparticle-Immobilized Layered Titanate. Figure 3b shows the UV–vis–near infrared spectrum of 0.5AuAET–TLO, in which the absorption band from 800 to 1400 nm due to the longitudinal surface plasmon band of Au particles with platy morphologies[11] was observed. From the TEM image of 0.5AuAET–TLO, taking the gallery height of 0.5AuAET–TLO (0.7 nm, calculated by subtracting the thickness of the titanate sheet from the observed basal spacing of 0.5AuAET–TLO, 1.1 nm (Figure 1c)) into consideration, the morphology of the formed Au in the interlayer space of

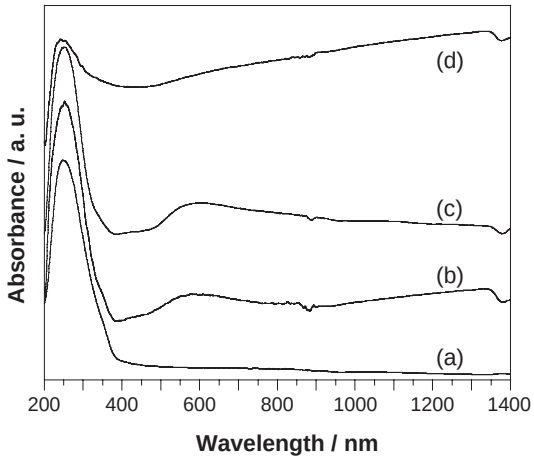

Figure 3. Diffuse reflectance UV–vis–NIR spectrum of (a) AET–TLO, (b) 0.5AuAET–TLO, (c) 1.5AuAET–TLO, and (d) 2.0AuAET–TLO.

AET–TLO is a disc or polygonal plate with a thickness of less than 0.7 nm and an average lateral size of 6.8 nm (Figure 4a), which was replicated by two-dimensional interlayer nanospace. Similar results for the formation of platy Au nanoparticles were obtained for the MPS system,[4] showing that the thiol group of AET intercalated in layered solids can be used to bind Au nanoparticles to interlayer surfaces, as that of MPS can. Au particles were thought to form also at the particle surface of the titanate (aggregated particles with the size of several tens of nm observed in the TEM images).

Increase in the added amount of $HAuCl_4 \cdot 3H_2O$ resulted in increase of the thickness and decrease of the diameter of Au plates, which was revealed by the XRD patterns (Figures 1d and 1e; gallery height of 0.9 and 0.9–1.0 nm) and TEM images (Figures 4b and 4c; the average diameter of 6.5 and 5.7 nm) of 1.5AuAET–TLO and 2.0AuAET–TLO, respectively. In the MPS-modified layered silicate system, only the diameter of the Au plates increased with increase in the added amount of Au source.[4] AET, which interacts electrostatically with the interlayer surface, is thought to deintercalate during Au plate formation, creating space for the Au plate to grow more. The UV–vis–near infrared spectra of Au nanoparticle immobilized titanate varied with the morphology of the formed Au nanoparticles. Both longitudinal absorption in the near infrared region and transverse absorption at 500–600 nm have been known to shift toward longer wavelength regions and the ratio of the intensity of the longitudinal to transverse adsorption bands has been known to increase with increase in the length/diameter ratio of Au rods.[12] Such systematic variation in UV–vis–near infrared spectra was not observed for the present system. It is thought that the presence of Au nanoparticles on the particle surface of the titanate affects plasmon adsorption leading to this observation. The change of reflective index around the intercalated Au nanoparticles by desorption of AET with the increase of added $HAuCl_4$ may another factor.

The adsorbed AET in 0.5AuAET–TLO was thermally stable up to 180 °C in air (Figure 5b) and 160 °C in helium (data not shown), respectively, indicating the formed Au nanoparticles are stably bound to the interlayer surface below these temperatures. Figure 4d depicts a TEM image of 0.5AuAET–TLO

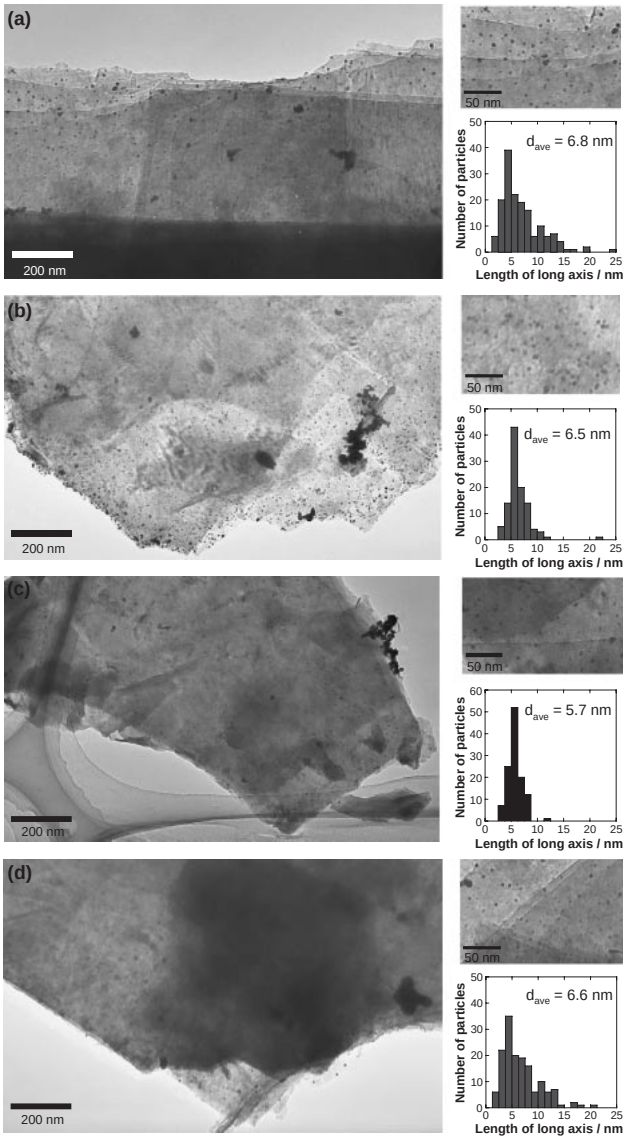

Figure 4. TEM images of (a) 0.5AuAET–TLO, (b) 1.5AuAET–TLO, (c) 2.0AuAET–TLO, and (d) (a) heated at 150 °C in helium. Inset shows the size distribution of Au nanoparticles and the magnified TEM image.

heated at 150 °C in helium, showing that the diameter of Au nanoparticles in 0.5AuAET–TLO did not change with heating. These results suggest that the present Au nanoparticle-immobilized layered titanates are a possible catalyst for the oxidation of CO; for example, catalytic experiments were performed for Au nanoparticle-supported TiO_2 at 10–65 °C[2b] and for Pt nanoparticle-supported mesoporous silica at 15–150 °C.[13]

Conclusion

We have synthesized an intercalation compound of a layered titanate with 2-aminoethanethiol and revealed that platy Au nanoparticles formed in the interlayer space of the thiol-functionalized layered titanate. The thickness and diameter of the plates changed with variation in the added amount of Au source. These results showed the application of 2-aminoethanethiol-intercalated layered titanates as a possible support of platy Au nanoparticles.

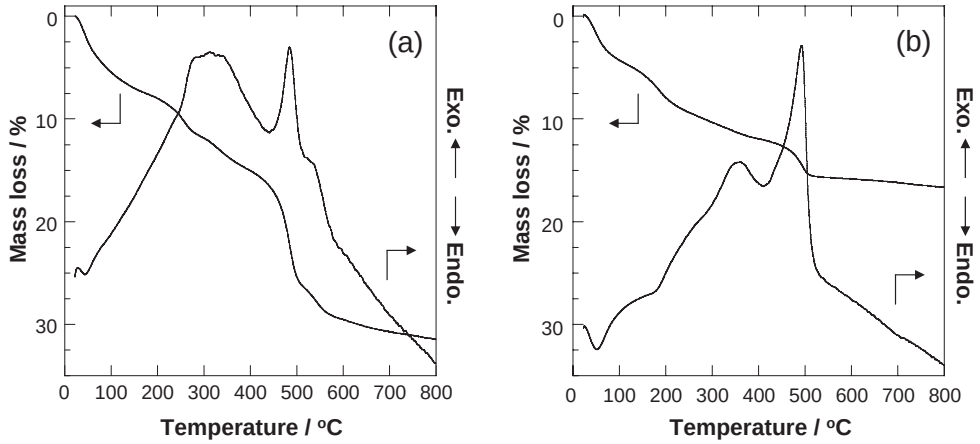

Figure 5. Thermogravimetric-differential thermal analytical curves recorded in air of (a) AET–TLO and (b) 0.5AuAET–TLO.

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