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Ultrathin Gold Nanosheets Formed by Photoreduction at the Ionic Liquid/Water Interface

Tetsuro Soejima and Nobuo Kimizuka*
Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University,
6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581

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Ultrathin, single-crystalline gold nanosheets with thickness of ca. 10 nm are successfully obtained in water by photoreduction of $Au(OH)_4^-$ ions at the surface of ionic liquid (IL) μ-droplets. The nanosheets produced at the interface are spontaneously extracted into the ionic liquid phase, which effectively prevents the formation of thicker nanoplates.

Nanosized golds are attracting considerable interest in nanotechnology, because of their unique optoelectronic properties which vary depending on the size and shapes.[1] Extensive studies have been devoted to the synthesis of nanoparticles[2] and one-dimensional (1D) nanorods.[3] The anisotropic growth of the latter is achieved by employing rod-like micelles as templates,[3] which allowed control on their aspect ratio. In addition to these classical nanostrucures, two-dimensional (2D) nanoplates are recently emerging as a new family of gold nanomaterials.[4,5] Thermal reduction of $HAuCl_4$ in aqueous block copolymers gave gold nanoplates with the thickness of ca. 100 nm.[4] Au nanoplates with the thickness of ca. 50 nm are formed in water by using *o*-phenylenediamine as reductant.[5] However, these gold nanoplates are fairly thick and there exist no general strategies to synthesize ultrathin gold nanosheets with the thickness regulated at 10 nm level.

In this study, we report the formation of ultrathin gold nanosheets by photoreduction of Au(III) ions at the interface of ionic liquids (ILs) and water. Room-temperature ILs are receiving much attention as environmentally benign solvents for organic and inorganic synthesis, polymerization, extraction, electrochemical applications,[6] and for molecular self-assembly.[7] We have recently proposed the use of ILs for controlled inorganic synthesis, and developed a one-step route to hollow metal oxide microspheres.[8] In this metal oxide system, organic microdroplets in ILs served as a template to direct the sol–gel reaction. Here, microdroplets of ILs in water offer unique interfaces for controlling the thickness of gold nanosheets.

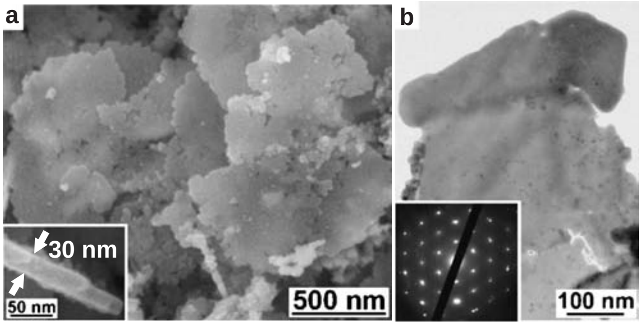

Figure 1. (a) SEM and (b) TEM images of gold nanosheets obtained by illuminating the macroscopic interface formed between $[C_4mim]PF_6$ and aqueous $Au(OH)_4^-$. The inset in (b) shows a corresponding ED pattern.

$[C_4mim]PF_6$ (1-butyl-3-methylimidazolium hexafluorophosphate) was synthesized according to the literature.[9] $HAuCl_4{\cdot}4H_2O$ was dissolved in pure water (concentration, 24.3 mM, pH adjusted to 10.0 by addition of aqueous 1 M NaOH). Au(III) is mostly present as $Au(OH)_4^-$ ions at this pH.[10] In a sample tube, aqueous $HAuCl_4$ (1.0 mL) is layered on 1.0 mL of $[C_4mim]PF_6$ and an interface formed between the layers was illuminated vertically with a superhigh-pressure mercury lamp (Ushio, USH-500D, $\lambda_{ex} > 300$ nm, $I_{300–400} > 20$ mW/cm^2, irradiation time, 20 min.). After photoirradiation, the aqueous layer was removed by pipetting, and acetonitrile was added to the mixture. The reduced products were collected by centrifugation (at 15000 rpm) and were washed repeatedly with acetonitrile and pure water. The samples were dispersed in water and dropped on carbon-coated copper grids, followed by drying in vacuo. Figure 1a shows scanning electron micrographs (SEM). Nanosheets of gold with dimensions above 700 nm and thickness of ca. 30 nm are observed. The nanosheet structures were also confirmed by transmission electron microscopy (TEM, Figure 1b). They are characterized by a uniform contrast, and electron diffraction (ED) of a nanosheet revealed hexagonal spots (Figure 1b inset, detailed analysis shown in Figure S2). These observations indicate that the gold nanosheets are face-centered cubic (fcc) single crystals with an atomically flat (111) surface.

The presence of water/ionic liquid interface is indispensable for the formation of gold nanosheets. When aqueous $HAuCl_4$ solution (24.3 mM; pH, 10) is illuminated with UV light, reduction of Au(III) ions did not occur. At the water/IL interface, $Au(OH)_4^-$ ions would be electrostatically adsorbed on the cationic $[C_4mim]PF_6$ phase. These $Au(OH)_4^-$ ions are not extracted in IL phase even after vigorous mixing, as confirmed by atomic absorption analysis (Shimadzu AA-6700). On the other hand, IL molecules excited by UV light may act as sacrificial electron donors to reduce $Au(OH)_4^-$ ions adsorbed at the interface. Though the photoreduction occurs selectively at the macroscopic water/$[C_4mim]PF_6$ interface, it is suffered from low efficiency arising from the limited contact between two layers. In addition, the thickness of gold nanosheets obtained under the static two-layer condition (ca. 30 nm) still falls short of the intended size-control. It is desirable that the crystal growth along the *c* axis is regulated more finely.

To increase the reaction area, we have employed dynamic mixing conditions and prepared microdroplets of ILs in water. By vigorous mixing of $[C_4mim]PF_6$ (1 mL) and aqueous $HAuCl_4$ (24.3 mM, pH 10, 1 mL), microdroplets of $[C_4mim]PF_6$ with diameter of ca. 10–50 µm were formed in water (Figure S3, The $[C_4mim]PF_6$ phase was stained with Rhodamine B and was observed by fluorescence microscopy.). After UV illumination of the stirred microemulsions for 20 min, the mixture was phase

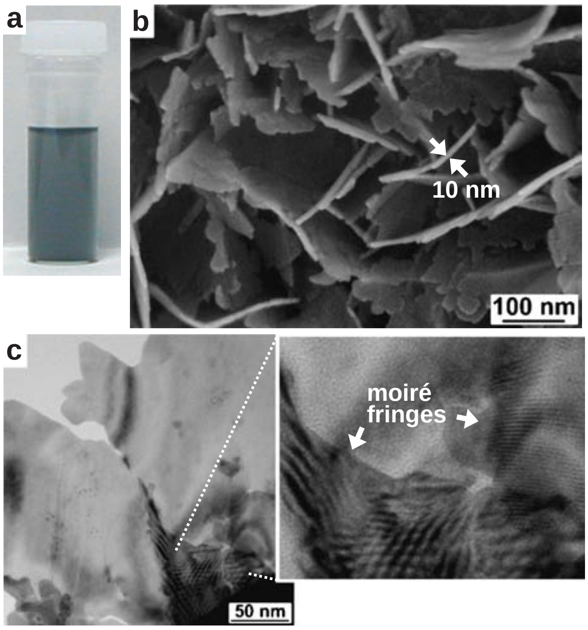

Figure 2. (a) A picture of aqueous dispersion, (b) SEM, and (c) TEM images of ultrathin gold nanosheets. Samples were obtained by photoilluminating mixture of [C_4mim]PF_6 and aqueous $Au(OH)_4{}^-$ under vigorous stirring.

separated into layers of water and [C_4mim]PF_6 upon standing (for ca. 30 s). Interestingly, the IL layer was colored blue, indicating that the photoreduced gold nanosheets are extracted to the IL phase.

The obtained material was collected as described previously and was observed by SEM (Figure 2b). Very interestingly, ultrathin gold nanosheets with thickness of ca. 10 nm are abundantly observed. Aqueous suspensions of these nanosheets displayed broad surface plasmon absorption band ranging from 500 nm to the near-infrared region (Figure 2a, S4). The peak observed around at 800–900 nm is consistent with the formation of gold nanosheets, though it is smoother than those reported for 50-nm-thick gold nanosheets.[5]

To our surprise, in the TEM observation of gold nanosheets, moiré fringes are observed for the overlapped portions (Figure 2c). Such moiré fringes have not been observed for previously reported 2D metal nanoplates probably because of their thicker structures (ca. 40–50 nm).[4,5] These observations confirm that the present ultrathin gold nanosheets are single crystalline with homogeneous thickness.

It is interesting that ultrathin gold nanosheets are facilely synthesized in the IL/water system. We assume that the thickening of nanosheets at the IL/water interfaces is restrained by extraction of nanosheets into the IL microdroplets. The ionic liquid molecules not only provide the reactive interface but also act as surface-stabilizing agents, similarly to the case of TiO_2 microspheres formed in interfacial sol–gel synthesis.[8] The hydrophobized gold nanosheets would be easily extracted to the IL microdroplets, as similarly reported for gold and CdTe nanoparticles.[11] On the other hand, IR spectra of the collected gold nanosheets indicate that the most of IL molecules are rinsed off by repetitive washing with acetonitrile and water (Figure S1), and this is consistent with the observed solubility in water.

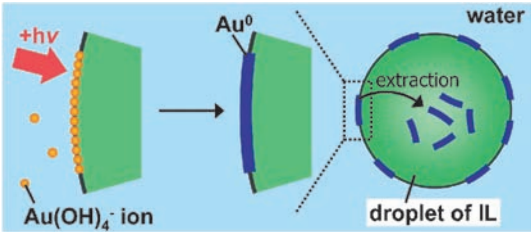

Figure 3. Schematic illustration of the formation of ultrathin gold nanosheets. Photoreduction of Au(III) ions occur at the [C_4min]PF_6/water interface and the formed nanosheets are extracted inside the ILs microdroplet. This extraction process prevents the growth in thickness.

A schematic illustration for the interfacial nanosheet synthesis is shown in Figure 3. The transfer of gold nanosheets from the water/IL interface to microdroplets in the early stage of photoreduction gives a reasonable account for the observed thickness control. IL microdroplets mechanically dispersed in water would experience dynamic equilibrium of fusion and separation by shear forces under vigorous stirring, and this dynamic feature may be responsible for the promoted extraction.

In conclusion, we have developed a novel and practical synthetic route to ultrathin gold nanosheets by the combination of ILs, water and photoillumination. These are the basic elements of green sustainable chemistry and together with the enzymatic synthesis of gold nanoparticles reported recently,[12] colloid chemistry of ILs provides promising routes to the controlled green synthesis of inorganic nanomaterials.

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