Fabrication of Submillimeter-sized Gold Plates from Thermal Decomposition of $HAuCl_4$ in Two-component Ionic Liquids

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We first report the fabrication of submillimeter-sized Au plates (up to about 1 mm in size) through the simple thermal decomposition of $HAuCl_4$ in two-component ionic liquids of 1-butyl-3-methylimidazolium hexafluorophosphate (C4ImPF6) and 1-octyl-3-methylimidazolium hexafluorophosphate (C8ImPF6), which were about ten times larger sizes than those from the single-component ionic liquid of the either.

Over the past few decades, a considerable number of studies have been conducted on metal-nanostructured materials owing to their unique physical and chemical properties that strongly depend on their size and shape.[1] Thus, the concern with the size- or shape-controlled fabrication of metal nanoparticles,[2,3] such as rods,[4] wires,[5] plates,[6] and branched multipods,[7] has been growing. Gold (Au) plates are of particular interest because of their potential applications of electrochemistry and producing new nanodevices.[8,9] Some groups have reported the fabrications of two-dimensional gold nanostructures, called Au nano- or microplates in the size range from 50 nm to 100 μm.[9] However, there have been few studies that tried to fabricate millimeter-scale Au plates with nanolevel thickness, even though such extremely large crystals could be useful in microelectronic systems and the understanding the mechanism of shape-controlled growth from the nanometer to the millimeter scale. Recently, Li et al. reported high-yield production of Au plates with several ten micrometer-scale size and the thickness of 50 nm in microwave heating of $HAuCl_4$ in an ionic liquid, 1-butyl-3-methylimidazolium tetrafluoroborate.[10] It was suggested that the two-dimensional polymeric layer in the ionic liquid could act as the template structure for the formation of Au nanoplates.

Here, we report for the first time the formation of submillimeter-sized Au plates through the simple thermal decomposition of $HAuCl_4$ in two-component ionic liquids of 1-butyl-3-methylimidazolium hexafluorophosphates (C4ImPF6) and 1-octyl-3-methylimidazolium hexafluorophosphates (C8ImPF6). It is considered that the preferential adsorption of amphiphilic molecules from solutions onto different crystal faces influences the growth of nanometals into various shapes and sizes by controlling the growth rates. The adsorption of ionic liquids onto Au surfaces, which depends on the composition of ionic liquid mixture, should contribute to the formation of Au plates.

In a typical fabrication of submillimeter-sized Au plates, $HAuCl_4 \cdot 3H_2O$ (100 mg/mL) was dissolved in 1:1 mixture of C4ImPF6 and C8ImPF6 (5 mL). The extremely large size Au plates were obtained by a slow reduction of gold precursor with a gradual growth of Au plates in mixed ionic liquids by electrically heated plate at 220 °C for 2 h to give a golden precipitate, which was collected, washed with ethanol, and dried under air stream. Similar process was employed for the preparation of Au plates in a single component ionic liquid, except that the different heating temperatures were used for the C4ImPF6 (270 °C) and the C8ImPF6 (210 °C).

We have found high-yield production of submillimeter-sized Au plates (up to about 1 mm in size, see Graphical Abstract) through the thermal decomposition of $HAuCl_4$ in the two-component ionic liquids of C4ImPF6 and C8ImPF6. Figure 1 shows the typical microscope image of submillimeter-sized Au plates. The sizes of Au plates mainly range from 50 to 900 μm in the micrometer-scale (see the histogram of Figure 1), which were about ten times larger sizes than those from the single-component ionic liquid (up to ca. 80 μm in size for C4ImPF6 and up to ca. 30 μm in size for C8ImPF6). The AFM image showed that the plate thickness is very thin to be in the range of 10–50 nm (approximately 10 nm for the sample in Figure 1c).

The FE-SEM images indicated that the products are mainly Au plates with regular shapes (equilateral triangular, hexagonal, and truncated triangular shapes), coexisting with a few polyhedral particles with submicrometer dimensions (Figures 2a and 2b). The FE-SEM images also confirmed some of Au plates with

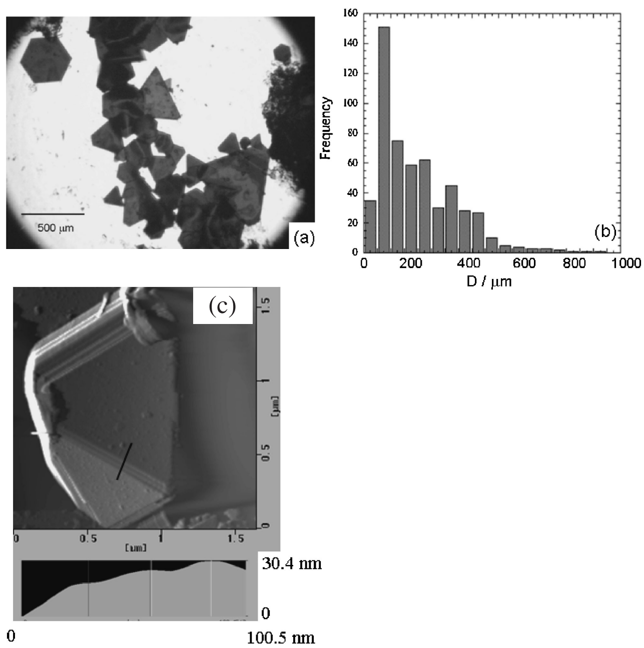

Figure 1. (a) Optical microscopy image of Au plates through thermal decomposition of $HAuCl_4$ in mixed ionic liquids of C4ImPF6 and C8ImPF6. (b) The size histogram of Au plates, and (c) the cross-sectional profile along the line of three layers of Au plates in the deflection AFM image.

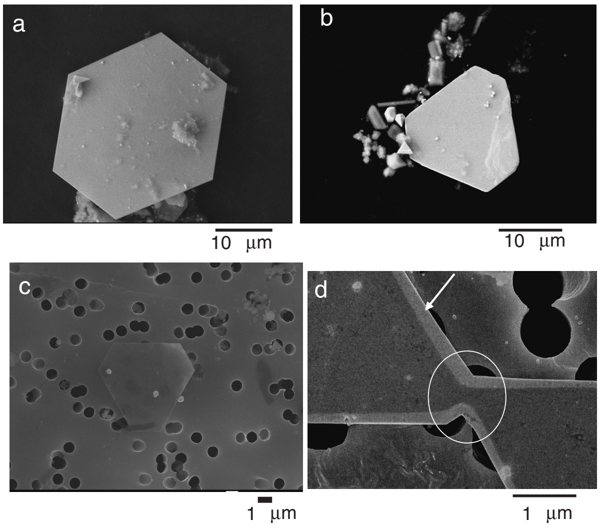

Figure 2. FE-SEM images of gold plates obtained by thermal decomposition of $HAuCl_4$ in the two-component ionic liquids of C4ImPF6 and C8ImPF6. (a), (b) Drops of ethanol dispersion of nanoplates were deposited on carbon tape. (c), (d) Samples were washed over a Pt-coated membrane filter.

very thin thickness from the transparent image (Figure 2c).[11] Energy-dispersive X-ray (EDX) analysis demonstrated that the resulting plate-like materials are composed of Au metals (Figure S1).[11] The SEM image shows lateral faces of triangular Au plates that are not perpendicular to the substrate (as shown in an arrow in Figure 2d). It has been reported that Au plates are primarily dominated by {111} facets.[9] It appears that Au plates are dominated by {111} as flat nanocrystals, probably truncated by {111} faces or {100} faces. It is worth noting that Au plates also could attach to other surface of Au plates, resulting in the rearrangement of faces of Au plates (a white circle in Figure 2d).

The ionic liquid molecules adsorbed on the Au plates were examined by surface-assisted laser desorption/ionization-mass spectrometry(SALDI-MS). The SALDI-MS analysis indicates that $C4Im^+$ with shorter alkyl chain lengths has the higher ion intensities than that of $C8Im^+$ in the mass spectrum, and the relative intensity of $C4Im^+$ (m/z 139) to $C8Im^+$ (m/z 195) was about 2 (Figure 3), suggesting that the preferential adsorption of C4ImPF6 on {111} facets of Au plates occurs during the plate growth. The stabilized effect of {111} face of Au plates in the mixed ionic liquid may be favorable to produce the extremely large size Au plates, compared to the single adsorbed layer of the ionic liquid. One minor peak at m/z 83 is attributed to a fragment ion after loss of an alkyl chain.

It should be noted that the thermal decomposition of $HAuCl_4$ in ionic liquids at high temperatures is an important parameter in producing Au plates in the ionic liquid. For example, we performed the reduction of $HAuCl_4$ in C4ImPF6 via photochemical reduction or hydrazine reduction at room temperature, but Au microplates were not formed in these routes. The photochemical reduction yielded spherical nanoparticles as main products, coexisting few rod and triangular nanoparticles, while hydrazine reduction produced Au aggregates of spherical particles (Figure S2).[11] In addition, our experiments showed if the solution of $HAuCl_4$ in the mixed ionic liquid was heated by microwave heating (300 W), Au plates with several ten

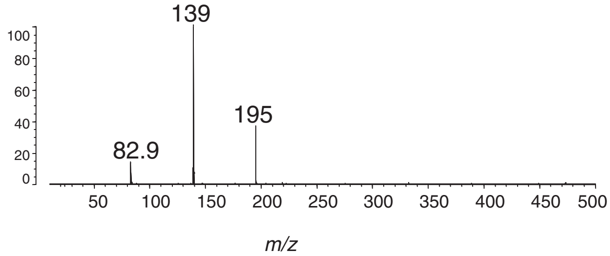

Figure 3. SALDI-TOF mass spectra obtained from the adsorbed ionic liquids (C4ImPF6 and C8ImPF6) on the Au plates in a positive mode.

micrometer-scale size were formed rapidly within five minutes. The slow reduction of gold precursors by a thermal heating may contribute to a slow rate of the plate growth and hence the formation of submillimeter-sized Au plates.

In conclusion, submillimeter-sized Au plates have been successfully prepared by the simple thermal decomposition of $HAuCl_4$ in two-component ionic liquids of C4ImPF6 and C8ImPF6. The present route is very simple and has high-yield production of Au plates. It can be estimated that this method can be extended to the fabrication of other metal plates in ionic liquids.

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11 Supporting Information is available on the CSJ-Journal website; http://www.csj.jp/journals/chem-lett/.

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