Morphological Transformation of Ultrathin Gold Nanosheets to Rounded Nanotapes in the Photomediated Reduction Process

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Photoreduction of $AuCl_4^-$ ions in the presence of *o*-phthalaldehyde (*o*-PA) in water provides ultrathin gold nanosheets which show surprising morphological changes to saw-edged nanosheets, multipored sheets, and rounded nanotapes depending on the reaction temperature.

Gold nanocrystals are receiving much attention owing to their unique properties that vary depending on size and shape.[1] Until now, synthetic methods for spherical nanoparticles,[1,2] one-dimensional (1D) nanorods,[3] and 2D nanosheets[4–7] have been accumulated. However, most synthetic methods are limited to producing specific nanostructures. In order to systematically control their nanostructures, morphological transformation of plain nanostructures to more unique nanostructures (i.e., tadpoles[8] and branched nanocrystals[9]) needs to be developed.

We describe herein a novel photoreduction process to synthesize gold nanocrystals by employing *o*-phthalaldehyde (*o*-PA) as reducing agent. The reduction of silver ions by aldehyde is popularly known as silver mirror reaction, but its application to gold is limited to the formation of nanoparticles in alkaline Weimarn sol.[10] As far as we are aware, there have been no reports on the use of aromatic aldehydes to synthesize gold nanocrystals. We expected that reducing ability of aromatic aldehydes would be enhanced by photoexcitation of their π–π^* absorption bands, providing an opportunity to reduce tetrachloroaurate ($AuCl_4^-$) ions. The photomediated synthetic process at varied temperatures would allow variable control on the reaction condition.

An aqueous solution of hydrogen tetrachloroaurate ($HAuCl_4$) (0.5 mM, 3 mL) was mixed with equimolar aqueous solution of *o*-PA (0.5 mM, 3 mL) at room temperature. This aqueous mixture showed no color changes even after a few days. On the other hand, when the mixture was illuminated vertically with a superhigh-pressure mercury lamp for 30 min (Ushio, UI-501C, $\lambda > 300$ nm, light intensity: $I_{310\text{–}390} = 55\,\mathrm{mW\,cm^{-2}}$, temperature at 20 °C), the pale yellow color of $AuCl_4^-$ was gradually changed to opaque orange (Figure S1a).[13] Apparently, reduction of $AuCl_4^-$ ions is triggered by photoirradiation. Interestingly, the photoirradiated solution exhibited blue-violet color when it is looked through the light (Figure S1b).[13] The observed color difference in the reflection light and transmission light indicates the presence of developed nanocrystals in the aqueous dispersion. The products were collected by filtration on polycarbonate membrane filters (Advantec, pore size 0.1 μm), washed with large quantity of pure water and then dried in vacuo. The products were redispersible in water by ultrasonication (Branson 2510J-DTH, 125 W, 1 min).

Scanning electron micrographs (SEM) of obtained nanocrystals are shown in Figure 1a. Ultrathin nanosheets with the size of several hundred nm and thickness of 5–30 nm are seen, together with spherical nanoparticles (diameter, ca. 50–200 nm). The apparent ratio of nanosheet to nanoparticle is roughly estimated to be ca. 6:4 (by solid content). The coexistence of both nanostructures is understandable, since surface stabilizers such as surfactants or polymers are not contained in the present reaction system. However it is noteworthy that the observed thickness of nanosheets is less than those produced by the other methods (above 40 nm).[5] Transmission electron micrograph of nanosheets is shown in Figure 1b, together with an electron diffraction (ED) pattern. The observed ED pattern consists of hexagonal symmetry pattern spots corresponding to the lattice spacing of 1.44 Å, originating from {220} planes of the face-centered cubic (fcc) gold single crystal. The presence of spots corresponding to 2.5 Å spacing is also noticeable, which have been assigned to 1/3{422} typically observed for atomically flat single-crystalline gold nanosheets.[7]

To investigate thermal morphological changes, photoreduction experiments were conducted at varied temperatures. In these experiments, light intensity was lowered to $17\,\mathrm{mW\,cm^{-2}}$, under which condition yields of nonspherical nanocrystals appeared to increase at higher temperatures. Figure 2 shows UV–vis–NIR spectra of gold nanocrystals obtained by the photoillumination of aqueous $HAuCl_4$/*o*-PA at various temperatures. At 20 °C, a broad absorption band ranging from 480 nm to the near-infrared (NIR) region was observed, with a maximum at 586 nm (Figure 2a). The observed broad plasmon resonance peak is consistent with the coexistence of nanoparticles and nanosheets.[11] On the other hand, when photoillumination was conducted at 40 °C, absorption peak intensity around at 1100 nm showed increase, and it became dominant at 60 °C (Figures 2b and 2c).

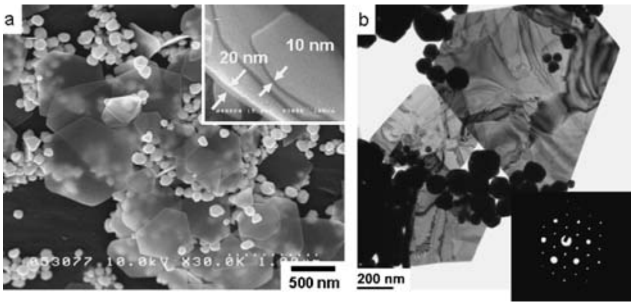

Figure 1. (a) SEM images and (b) TEM images of gold nanosheets obtained by photoirradiation of aqueous $HAuCl_4$/*o*-PA at 20 °C ($I_{310\text{–}390}$, $55\,\mathrm{mW\,cm^{-2}}$). Inset (b) is an electron diffraction pattern of a single nanosheet.

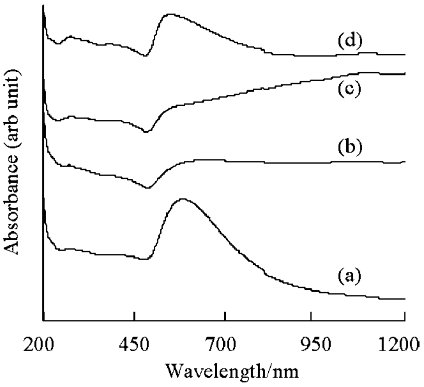

Figure 2. UV–vis–NIR spectra of gold nanocrystals redispersed in water. Aqueous mixtures of $HAuCl_4$ and *o*-PA were photoirradiated at varied temperatures. (a) 20 °C (nanosheets and nanoparticles), (b) 40 °C, (c) 60 °C, (d) 80 °C. Illumination light intensity and period, $I_{310\text{–}390} = 17\,\mathrm{mW\,cm^{-2}}$ for 30 min. Heating of aqueous mixtures without photoillumination causes no spectral changes.

At 80 °C, spectral intensity at NIR region was decreased, and a major peak was observed at 553 nm (Figure 2d). These observations indicate that morphology of gold nanocrystals is changed depending on the reaction temperature.

Figure 3 shows SEM images of nanocrystals obtained at these different temperatures. At 20 °C, both of nanosheets and nanoparticles were obtained, as described previously. On the other hand, photoreduction at 40 °C gave nanosheets with rough and saw-edged structures (Figure 3b). Interestingly, rounded nanosheets were observed at 60 °C, which have triangle, hexagonal, or round-shaped pores of ca. 20–50 nm in diameter (Figure 3c). Dominance of such nanosheet structures is consistent with the large absorption intensities extended to the NIR region (Figures 2b and 2c). Interestingly, these pored nanosheets were converted to rounded nanotapes or tadpole-like structures at 80 °C (Figure 3d, thickness, ca. 50 nm). The plasmon absorption observed for these nanotapes is similar to those reported for tadpole[8] and belt-like nanocrystals.[12]

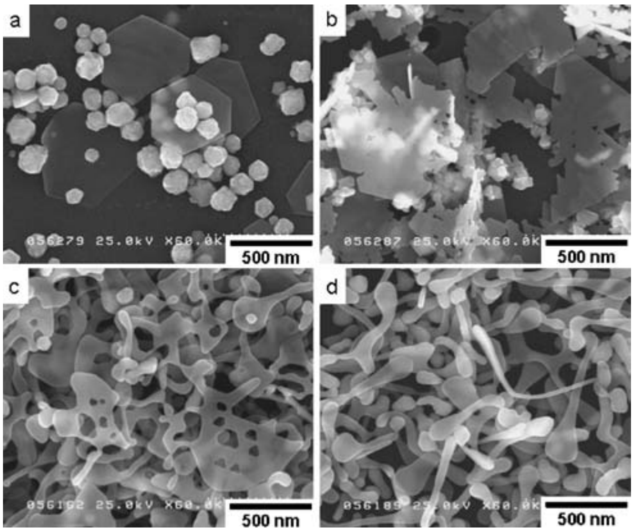

Figure 3. SEM pictures of gold nanocrystals prepared by photoirradiation of aqueous mixtures of $HAuCl_4$ and *o*-PA at varied temperatures. (a) 20 °C, nanosheets and nanoparticles, (b) 40 °C, saw-edged nanosheets, (c) 60 °C, multipored nanosheets, (d) 80 °C, rounded tadpole-like nanotapes. Substrate, membrane filter.

These observations clearly show that *o*-PA-assisted photoreduction of $AuCl_4^-$ ions provides surprising thermal morphological transformation to anisotropic gold nanostructures. Though currently the photoreaction mechanism is not clear, it is probable that photoexcited *o*-PA molecules reduce $AuCl_4^-$ ions and that they are oxidized to products such as *o*-phthalic acids. *o*-PA and phthalic acids would be weakly adsorbed on the surface of growing gold nanocrystals, as these molecules are not contained in the sample after washing with pure water (as checked by FT-IR). The absence of strongly bound molecules such as alkane thiols may facilitate the aggregation and coalescence of photogenerated nuclei and nanocrystals into rounded nanotapes or tadpole-like structures. We also presume that plasmonic excitation of gold nanocrystals at higher temperatures may be also responsible for the observed morphological transformation and smooth surface curvature, which would require enhanced dynamic rearrangement of surface gold atoms.

In conclusion, a new photomediated reduction route to varied gold nanocrystals: ultrathin nanosheets, pored nanosheets, and round nanotapes, is developed by using *o*-PA as photomediated reducing agents. To date, effect of reaction temperatures on the fabrication of gold nanocrystals have been reported.[4] However, morphological transformation of gold nanocrystals into heteromorphic structures as described in this study has been unprecedented. The present fabrication method is simple, and by employing varied aromatic aldehydes, it may provide access to the unexplored heteromorphic nanostructures.

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13 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.