Single-crystalline Gold Nanodisks Prepared by the Shape Transformation under UV Irradiation from Nanoparticles Protected with Discotic Liquid Crystalline Ligands

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In this paper, we investigated a convenient shape transformation of gold nanoparticles to nanodisks by UV irradiation in chloroform with the aid of protective agents carrying a triphenylene moiety, which absorbs UV energy and plays a role as a mask in directing the deposition of gold atoms at aspecific position.

The properties of anisotropic nanomaterials have raised a tremendous interest compared with conventional spherical nanoparticles. We have been developing methods to prepare anisotropic metal nanomaterials with the aid of organic protective agents,[1] adsorbents,[2] and solvent polarity.[3–5] Among various geometries, gold and silver nanodisks are recently intensely studied, especially with respect to optical properties.[6] Existing methods to produce gold nanodisks include use of ultraviolet (UV) reducing,[7] colloidal lithography,[8] seed-growth,[9] electrochemical preparation,[10] and specific adsorption of halide ions.[11] According to our best knowledge, no report appears yet to prepare gold nanodisks by UV irradiation of nanoparticles.

Our new approach is to transform gold nanoparticles into nanodisks in chloroform solution by UV irradiation. There are three critical strategies in the present study. First is to introduce a light-absorbing aromatic functional group on the gold nanoparticle surface, which may efficiently transfer absorbed energy to the nanoparticles.[12] We employed triphenylene disulfide as protecting agent of the nanoparticles.[4,5] Second is to use chloroform as a solvent, which provides a chemical environment for dissolution and deposition of gold nanoparticles.[13] Third is to form single-crystalline gold nanodisks, presumably with the aid of triphenylene ligand: deposition of gold ion restricted in a specific position because of triphenylene molecule with discotic liquid crystalline properties on gold nanoparticles densely packed by π–π interaction to prevent deposition like a mask.[14]

In order to estimate the role of the ligand on transformation of nanocrystals under irradiation, we prepared two kinds of gold nanoparticles (AuTP and AuDT) with different protective agents, 8-[3-methoxy-6,7,10,11-tetrakis(pentyloxytriphenylen-2-yloxy)]octanyl disulfide (TPD) and dodecanethiol (DT) (Scheme S1)[20], by modified Brust method.[15] These two kinds of nanoparticles were dissolved into chloroform at a concentration of 10^{-5} g/mL. Thus prepared gold nanoparticle solutions placed in quartz cells were irradiated by UV lamp (254 nm) for 12 h in a dark box. Samples obtained after the irradiation in chloroform are denoted as AuTP-UV and AuDT-UV.

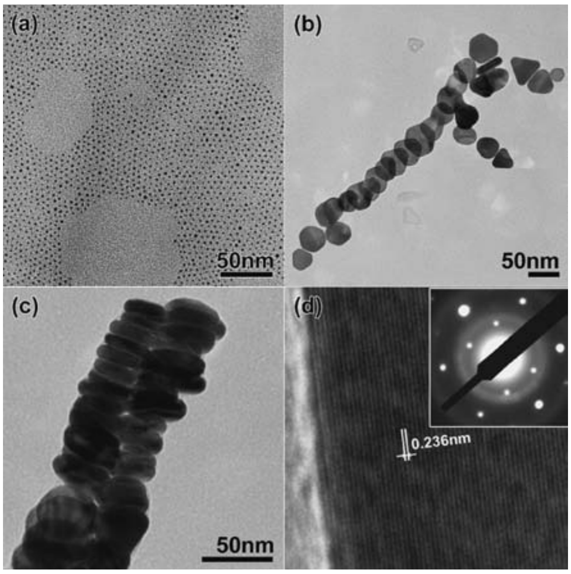

Figure 1. (a) TEM image of AuTP as prepared; (b) and (c) are the TEM images of AuTP-UV parallel and perpendicular to TEM grids, respectively; (d) high-resolution TEM image of AuTP-UV on top view. Inset shows the selected area electron diffraction pattern of nanodisk (d) on top view.

We use TEM to characterize the gold nanoparticle before and after UV irradiation. The average diameters are 3.7 ± 0.8 and 2.5 ± 0.4 nm for AuDT (Figure S1)[20] and AuTP (Figure 1a), respectively. AuTP converted to nanodisks with diameter and thickness of ca. 40 and 10 nm, respectively, which appear parallel (Figure 1b) and perpendicular (Figure 1c) to the carbon-supported substrate or tilt each other. High-resolution TEM (HRTEM) images of AuTP-UV indicate that the nanodisk is in the single-crystalline state (Figure 1d). The selected area electron diffraction (SAED) spots (Figure 1d inset) could be indexed based on the face-centered cubic (*fcc*) structure of gold crystal and showed a {111} facet on flat surfaces. The lattice spacing between the {111} planes, 0.236 nm, is also in agreement with that of bulk gold crystal. We treated AuDT under similar UV irradiation conditions. AuDT-UV increased in diameter to 10 nm without significant change in shape (Figure S1).

We also monitored the change in emission spectra. In order to exclude the effects of TPD monomers on emission spectra, AuTP-UV was thoroughly purified by precipitation using chloroform and sufficient methanol. The precipitate was collected by a centrifuge and redissolve into chloroform. As shown in Figure 2 an emission peak of the fluorescence spectra appears at 382 and 467 nm for AuTP and AuTP-UV, respectively. It is worth noting that in our previous work,[4,5] the different π-electron overlapping of triphenylene leads to different emission peaks: staggered and eclipsed forms for inter- and intraparticle stacking (438 and 460 nm, respectively).[16] The fluorescence spectrum of AuTP-UV in Figure 2 indicates triphenylenes on AuTP-UV have intraparticle stacking with eclipsed overlap.

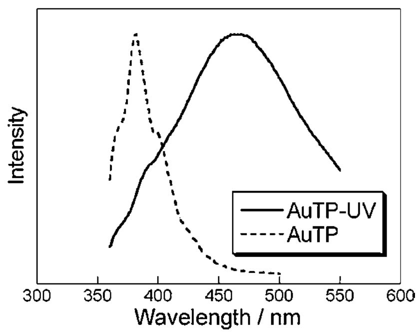

Figure 2. Fluorescence spectra of AuTP (dotted line) and AuTP-UV (solid line). The excited wavelength is 345 nm.

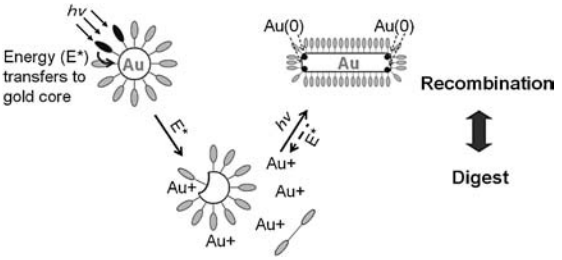

Figure 3. Plausible mechanism for AuTP under UV irradiation in chloroform.

As reported by Baibarac et al.,[13] gold metal can dissolve in chloroform to form AuCl under UV irradiation. In order to investigate the stability of AuTP in chloroform without irradiation, a chloroform solution of AuTP was put into a light-proof box for 2 weeks. TEM observation of aged solution indicates no change in the shape of nanoparticles (Figure S5).[20] Thus, the AuTP is stable in chloroform without irradiation. Furthermore, triphenylenes serve as photoresponsive ligands to transfer photon energy to the gold core.[12] That is, triphenylenes sensitize the changes of shape of gold nanoparticles under UV irradiation.

Recently, mechanisms have been discussed for transforming from gold nanoparticles to nanodisks. Chen's group has proposed that orientationally attached gold nanoparticles are important precursors for systems using a temple of surfactant and liquid crystals.[17] Wang and Imae reported a transformation process based on unstable aggregates of gold nanoparticles, which gradually change to nanodisks in an energetically more stable state.[18] However, a decisive mechanism has not yet been clarified. Figure 3 schematically shows the most plausible mechanism for the present system compatible with all results. Compared with the absorbance of light by gold core, the triphenylene on gold nanoparticles efficiently absorbs UV energy, resulting in acceleration to dissolve nanoparticles as Au ion after the absorbed energy transfers to gold core.[12] Au ion is easily reduced to Au atom under UV irradiation[7,19] which accumulats on gold surfaces by a recombination process. For AuDT, such growth proceeds without selectivity. On the other hand, for AuTP, reduced Au atoms from nanodisks by selected deposition because of the strong π–π interaction between triphenylene moieties, which behave like a mask for deposition. Furthermore, such a specific path on gold crystal facet {111} may be preferential because of favorable stability.[18]

In conclusion, monodispersed gold nanoparticles stabilized by TPD have been prepared by modified Brust method. The nanoparticle, AuTP, can be converted to single-crystalline nanodisks under UV irradiation in chloroform. This method opens a new way to a convenient shape transformation of nanocrystals with the aid of protective agents and a solvent system of chloroform by UV energy.

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20 **Electronic Supplementary Information (ESI)**: Synthesis method, TEM images, UV–vis spectra of AuDT, and ^{1}H NMR spectra of TPD, AuTP and AuTP-UV are available at http://www.csj.jp/journals/chem-lett/index.html.

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