Synthesis of Lipophilic Gold Nanosheets by Using Reducing Stabilizers and Their Reversible Transformation between Golden Solid

Rempei Kuwahara,[2] Keita Kuroiwa,[1,2] and Nobuo Kimizuka*[1,2]

[1]*Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University,*
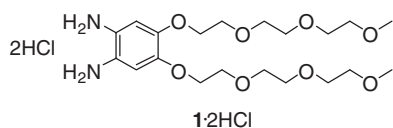*744 Moto-oka, Nishi-ku, Fukuoka 819-0395*
[2]*JST CREST, 744 Moto-oka, Nishi-ku, Fukuoka 819-0395*

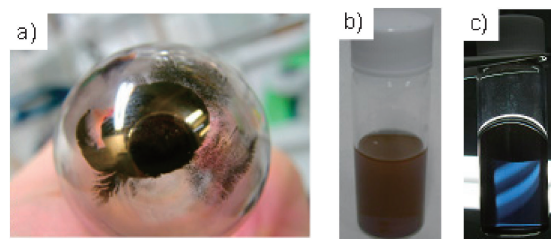(Received November 17, 2009; CL-091018; E-mail: n-kimi@mail.cstm.kyushu-u.ac.jp)

4,5-Dialkylated *o*-phenylenediamine with oligo(ethylene glycol) units is developed as a stabilizer with reducing property. It reduces chloroauric acid in water, giving lipophilic gold nanosheets whose surface is passivated by the quinoid-form ligands generated in situ. These nanosheets show brilliant golden luster in the solid state, whereas they are reversibly dispersible in organic media.

Controlled synthesis of gold nanocrystals has been attracting much attention because of their unique physical and chemical properties which vary depending on their size, shape, and interactions.[1] To date, synthetic methods for gold nanoparticles,[2] nanorods,[3] and nanosheets[4] have been vigorously explored, and several practical routes have been compiled. However, in spite of these efforts, bridging the structural gap between soluble nanocrystals and three-dimensionally accumulated structures has met with limited success.[5] The two extreme electronic structures between a single nanocrystal in solution and bulk assemblies would be controllable if soluble nanocrystals show reversible transformation between these architectures. In this regard, nanosheets passivated by ultrathin molecular layers are interesting building blocks since electronic interactions in their accumulated brick structures are expected to make their optical properties comparable to those of bulk gold. We describe herein a novel one-step route to lipophilic gold nanosheets by using 4,5-dialkylated *o*-phenylenediamine as a reducing stabilizer. These dispersible nanosheets display reversible transformation into golden solid with distinctive metallic luster.

4,5-Dialkyloxy-*o*-phenylenediamine with oligo(ethylene glycol) chains **1** was synthesized (Scheme 1).[6] It was isolated as a hydrochloride (**1**·2HCl). To an aqueous solution of chloroauric acid (TCI, 20 mM, 8 mL), an aqueous dispersion of **1**·2HCl (80 mM, 2 mL) was quickly added at room temperature under vigorous stirring. The color of the solution immediately turned dark red-brown and black precipitates were formed. After 5 min, the supernatant was removed by decantation and the precipitate collected was washed with pure water. After drying under reduced pressure, golden solid with brilliant metallic luster was obtained (Figure 1a). Very interestingly, this golden solid was easily dispersed in chloroform by ultrasonicating for a few seconds (Branson 2510J-DTH, 125 W). The
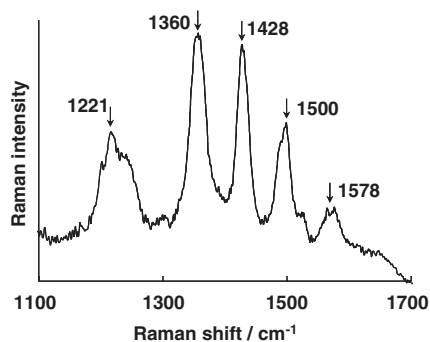

Figure 1. Photographs of Au nanosheets prepared by using **1**·2HCl. (a) Dried nanosheets with golden luster, (b) appearance of chloroform dispersion (reflection color), and (c) the same sample observed in transmitted light.
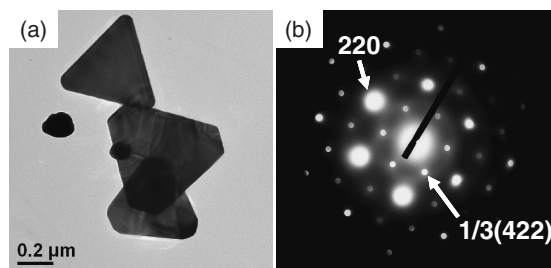
Figure 2. (a) A transmission electron micrograph of Au nanosheets synthesized by using reducing stabilizer **1**·2HCl and (b) its electron diffraction pattern.

opaque orange-colored chloroform dispersion exhibited indigo-purple color when viewed through transmitted light (Figures 1b and 1c). The color difference observed in the reflection and transmission light clearly indicates the presence of developed nanocrystals in the chloroform dispersion.[7]

The purple chloroform dispersion was placed on a carbon-coated copper grid and dried under vacuum. In transmission electron microscopy (TEM, JEOL JEM-2010, acceleration voltage, 120 kV), hexagonal gold nanosheets (length of each side: ca. 200–600 nm, thickness: ca. 10 nm) are seen, together with spherical nanoparicles (Figure 2a, Figures S2 and S3 in Supporting Information[10]). All the nanosheets are oriented parallel with respect to the TEM grid surface. The crystal structure of gold nanosheets was further investigated by selected-area electron diffraction (ED) measurements. The observed ED pattern consists of hexagonal symmetry pattern spots corresponding to the lattice spacing of 1.44 Å, which originates from {220} planes of the face-centered cubic (fcc) gold single crystal (Figure 2b). The presence of spots corresponding to 2.5 Å spacing is also noticeable, which have been assigned to the fcc forbidden 1/3{422} reflections which occur


Scheme 1. Chemical structure of **1**·2HCl.

Figure 3. A Raman spectrum of Au nanosheets ($\lambda_0 = 532\,\text{nm}$).

Figure 4. A schematic illustration of gold nanosheet and its surface molecular layer **1** in the oxidized quinoid form.

due to the presence of (111) stacking fault(s) lying parallel to the (111) surface and extending across the entire planar particle.[8] These observations indicate that the surface of gold nanoplates is indexed as flat (111) planes of face-centered cubic (fcc) lattice, with atomically flat structure.

Extinction spectrum of the chloroform dispersion gave a plasmon peak around at 600 nm (Supporting Information, Figure S1a[10]). In contrast, their golden cast films showed a shoulder peak at 550 nm and a continuous increase in extinction intensity to the near infrared (NIR) region (Figure S1b[10]). The band extending to the NIR is not observable for chloroform dispersions, and it is ascribed to the electronic interactions between gold nanosheets accumulated in the solid. It would be reasonable to assume that such interactions are most facilitated when the nanosheets stack into multilayered brick structures. The conversion between colored chloroform dispersions and golden solids after solvent evaporation was totally reversible and could be repeated many times. It indicates that the surface of nanocrystals is stably passivated by lipophilic stabilizer molecules. To elucidate the molecular structure of lipophilic surface layer, laser Raman spectrometry of gold nanosheets in the solid state was investigated (JASCO NRS-3000). Figure 3 shows a Raman spectrum, in which peaks at 1221, 1360, and $1428\,\text{cm}^{-1}$ are assignable to the stretching modes for C–N, C–N$^+$, and C=N groups, respectively (Figure 3).[9] The peaks at 1500 and $1578\,\text{cm}^{-1}$ are characteristic of the N–H bending and C–C stretching modes of a quinoid ring.[9] These observations indicate that the surface of gold nanosheets is stabilized by **1** in the quinoid form, which are produced by chloroauric acid-oxidation of phenylenediamine compound **1**. A schematic illustration of the quinonoid-form monolayer formed on gold nanosheet is shown in Figure 4.

It is noteworthy that compound **1** displays bimodal functions. First, it acts as a reducing agent for AuCl$_4^-$ ions. Second, oxidized quinoid-form compounds generated by the reaction successively serve as surface stabilizers, which direct the formation of gold nanosheets. The coordinating ability of these quinoid ligands on Au(111) plane would be secured by the presence of two electron donating alkylether groups attached on the quinoid rings. The stabilization of gold nanosheets by the quinoid-form ligand is consistent with the observed reversible transformation between nanosheets dispersed in solution and golden solids formed upon casting the dispersion on solid supports. When the oligo(ethylene glycol) chains of **1** is replaced by normal alkyl chains, single crystalline gold or
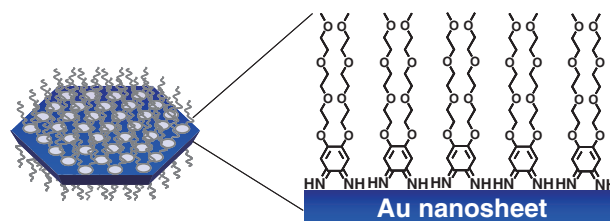
silver nanosheets are also obtainable by biphasic reactions at the water–chloroform interface (Supporting Information[10]). However, in these biphasic reaction systems, the morphology of gold nanosheets observed by TEM is not as regular as those formed by **1**·2HCl. Thus, aqueous phase syntheses of nanosheets by using the water-soluble reducing stabilizer and their dissolution in organic media seem to be a better approach.

In conclusion, soluble gold nanosheets are synthesized in one step by using diologo(ethylene glycol)-chained phenylenediamine as reducing agent, which subsequently serve as surface-passivating molecules in the oxidized quinoid form. Golden-colored multilayered gold nanosheets are obtained upon solvent evaporation, while the solid is reversibly dispersed in chloroform to give nanosheet dispersions. It indicates that the structural integrity of nanosheet structures is maintained in the solid state, as layered brick structures (Figure S3[10]). We envisage that the reversible transformation between soluble nanosheets and golden solid will be applied to develop nanohybrids in which metal nanosheets serve as layered host systems, as exemplified in the Supporting Information.[10]

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