Particle Crystals of Surface Modified Gold Nanoparticles Grown from Water

Keisaku Kimura,* Seiichi Sato, and Hiroshi Yao
Department of Material Science, Faculty of Science, Himeji Institute of Technology, Kamigori, Hyogo 678-1297

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Surface modified nanometer-sized gold particles with mercaptosuccinic acid (MSA) are crystallized in the size range of a few micrometer. Two dimensional superlattice was also generated in the same system. The transmission electron microscope images of these superstructures and the reflectance spectrum are reported in comparison with that of bulk sample.

The synthesis of nanometer-size particles with well-defined surfaces is a current interest not only from scientific aspects but also various potential applications to materials science. There are many reports on the surface modifications using thiol, phosphine and nitrogen related compounds. Based on such particles, there has been a significant effort to generate regular assembly using nanoparticles as a building block. The first challenge was done on CdSe quantum dot superlattice by Bawendi et al.[1] followed by the work on gold,[2–4] silver[5–8] and cobalt.[9] In these studies, the solvents used to dissolve the starting nanoparticles are all organic liquids owing to the limitation of modifiers such as alkanethiol or alkylphosphine. Recently we have developed a new synthetic route for water-soluble gold nanoparticles.[10] Application of water-soluble nanoparticles is a new field for crystallization of or self-assembling these particles to organized systems such as 2D (two dimensional) superlattice or 3D crystal array not by weak van der Waals force but by hydrogen bonding and/or ionic interactions. We report here the formation of a 3D-particle crystal of mercaptosuccinic acid (MSA)-modified gold nanoparticles and of a 2D-superlattice from water solution. To our knowledge, this is the first example of a water re-soluble nanoparticle crystal, which dissolves again when dipped in water.

The basic preparation procedure is as follows;[10] 0.5 mmol of $HAuCl_4$ aqueous solution (5 w/v%) was mixed with 1.5 mmol of MSA in 100-mL methanol to give a transparent solution. A freshly prepared 0.2 M aqueous sodium borohydride solution (25 mL cooled in refrigerator in advance) was then added under vigorous stirring. The color of the solution changed dark-brown immediately and then a flocculent dark-brown precipitate was yielded. After further stirring for 1 h, the precipitate was gathered by decantation and centrifugation. The precipitate was washed twice with 20 v/v% water/methanol solution through ultrasonic re-dispersion–centrifugation process, methanol and then with ethanol. Finally, dialysis was applied against distilled water for 1 day. The mean diameter of the particles, determined by a transmission electron microscope (TEM), was 3.5 nm with fwhm of 0.4 nm. From Scherrer's equation for the powdered XRD, the size of particles was estimated to be ca. 3.5 nm. The crystallization took place 4–10 days with hydrochloric acid below pH 2 in a glass bottle giving numerous µm-sized crystal with clear crystal habit (majority triangle with minor rectangular fringe, as shown in Figure 1). The thickness was found by a laser microscope to be in the range of 0.1–1 µm. At pH region higher than pH 2, many 2D-like films formed. Mixing methanol, ethanol and 2-propanol to the solution or addition of electrolytes such as $(NH_4)_2SO_4$ and NH_4Cl to the solution did not give successful crystallization. By starting from the sample with narrow size distribution (~10%), no fractionation process was required for crystallization of nanoparticles.

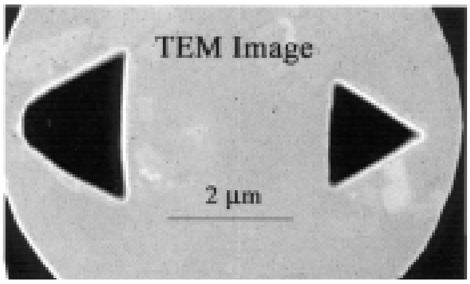

Figure 1. The TEM image of 3D crystals with clear crystal habit.

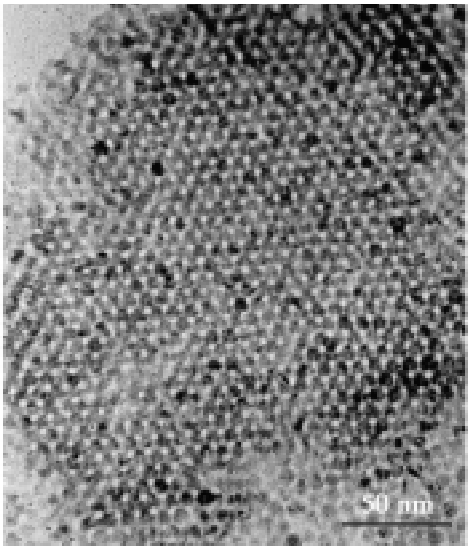

Figure 2. A TEM photograph of two-dimensional lattice of MSA modified gold nanoparticles. From contrast of the image, major part of the lattice seems to comprise of two layers.

Figure 2 shows 2D array of the gold nanoparticles on the carbon reinforced microgrid, in which hexagonal structure is clearly seen. The majority of the array seems to be two layers judged from the contrast of the image. The size of this structure extends to several hundreds nm square. In this figure, the lattice structure is composed of 5-nm particles in size, which does not match the data of size distribution. In other conditions, the lattice consists of 3.5-nm particles. We have observed that many plates, metallic gold in color with clear crystal habit were formed in the interface of air/liquid. In Figure 3, a large plate is broken and the cleavage face is exposed to the solution. A part of the face is contaminated with many extracts deposited from solution in a drying process.

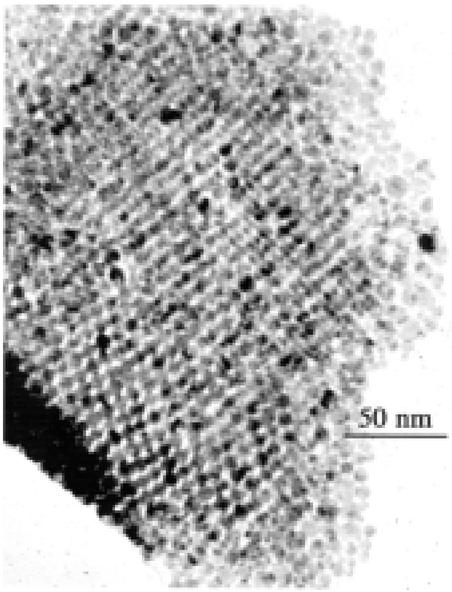

Figure 3. A TEM photograph of 3D crystals with fractured surface.

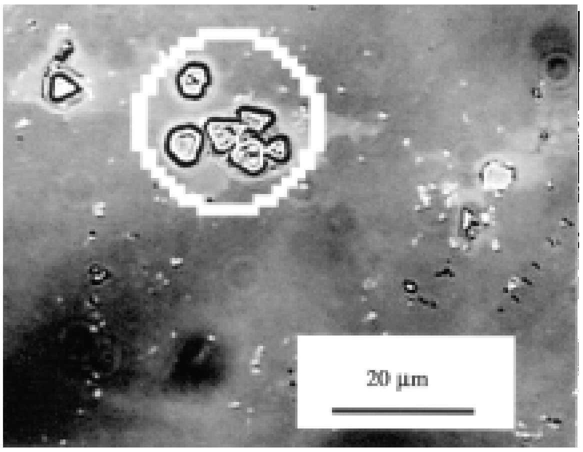

Figure 4. An optical micrograph of crystals. The sample taken for the reflectance spectra is encircled in the figure where six crystals are perceptible.

However, there is no doubt that the plate has a periodic lattice structure. We therefore concluded that the many platelets with a clear crystal-like habit as shown in Figure 1 are a single crystal. Figure 4 shows an optical micrograph of a representative of these crystals on a glass sheet. The color of crystals was metallic gold. We measured a reflectance spectrum of crystals in the encircled region in Figure 4 and shown in Figure 5. The overall features of the reflectance spectrum resemble to that of bulk gold plate. However we note that there is still small difference between bulk sample and particle crystals such as the slight decrease in the reflectance in the long wavelength region and a lack of small hump at around 600 nm. One can simulate the observed reflectance spectrum by assuming two contributions, Drude-type free electrons and inter-band transition. The dielectric constant is a sum of these contributions which is characterized by six parameter sets, free electron relaxation time (bulk value), plasmon frequency (bulk value), dielectric constant of gold, oscillator strength of inter-band transition, resonance frequency, and damping factor abbreviated as τ, ω_p, ε_∞, S_0, ω_1, and Γ_1 in this order. The best fit was obtained with $\tau = 9.3 \times 10^{-15}$ s, $\omega_p = 1.35 \times 10^{16}$ s^{-1}, $\varepsilon_\infty = 7.35$, $S_0 = 1.3$, $\omega_1 = 4.2 \times 10^{15}$ s^{-1}, and $\Gamma_1 = 1.55 \times 10^{15}$ s^{-1}. Using these parameters, the dielectric constants ε_1 and ε_2 are calculated giving qualitatively the same behavior as bulk data.[11] It should be noted that there is only a weak plasmon absorption band for a 3.5-nm single particle used. We also conducted a preliminary experiment on STM and SEM giving a clear image of these particle crystals implying that these crystals are more or less conductive. These peculiar properties are distinct from other thiol-derivatized nanoparticles which show insulating properties.

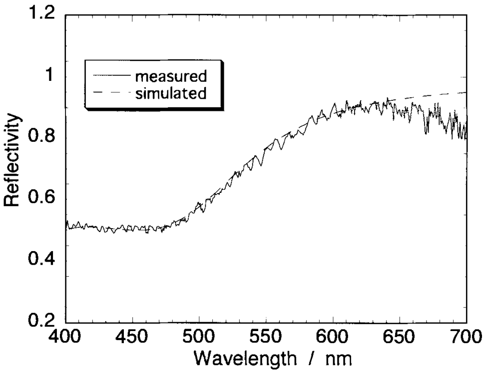

Figure 5. Reflectance spectrum of particles in visible region. A broken line shows the simulation curve.

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