Optical Absorption Properties of Three-Dimensional Au Nanoparticle Crystals

Seiichi Sato,* Hiroshi Yao, and Keisaku Kimura
Department of Material Science, Himeji Institute of Technology, 3-2-1 Koto, Kamigori-cho, Ako-gun, Hyogo 678-1297

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Optical absorption properties of Au nanoparticle crystals are studied in the near infrared-to-near ultraviolet region. Although sparsely deposited Au nanoparticles show a small absorption peak at 2.4 eV, the Au nanoparticle crystals show a significantly stronger peak at 1.9 eV. Altering the temperature from room temperature to 77 K brings about very little difference in the intensity and width of the absorption peak. A qualitative model of the electronic polarizability is introduced to explain the observed peak shift as a result of assembling the nanoparticles into the 3D lattices.

A nanoparticle crystal, or a periodic array of quantum dots, is one of the most attractive material for future electronic devices since the electronic structure of a nanoparticle crystal can be tailored by controlling the core size, surface coverage thickness and packing arrangement. Since the discovery of nanoparticle chemical self-assembly in two-dimensional (2D) and three-dimensional (3D) arrays, various nanoparticle crystals, which consist of semiconductors[1–4] or metals,[4–16] have been synthesized.

From an optical point of view, metal nanoparticle crystals are assumed to be artificial dielectrics because conduction electrons in each metal nanoparticle behave as an oscillating system with an eigenfrequency equal to the surface plasmon frequency of the metal.[17] To date, detailed optical properties of 2D metal nanoparticle crystals have been reported: Heath's group has investigated linear reflectance, absorbance and the second-harmonic generation response of 2D Ag nanoparticle crystals, and has shown characteristic properties resulting from dipole coupling between nanoparticles;[3,11,12] Pileni's group has studied absorption and reflectance properties of 2D Ag nanoparticle crystals using polarized light and has found a collective effect due to mutual interactions between nanoparticles.[13] In contrast to the accumulation of optical data of 2D metal nanoparticle crystals, optical properties of 3D metal nanoparticle crystals have not been reported. One reason may be the difficulty in synthesizing enough large sized high-quality 3D metal nanoparticle crystals to study. Recently we have found that Au nanoparticles with surfaces modified by hydrophilic surfactants are good components for 3D nanoparticle crystals. Adjusting the pH[15,16] when an extremely slow growth rate (i.e. equilibrium growth) is enforced, the Au nanocrystals self-assemble into high quality lattice arrangements. In this letter, we would like to report the optical absorption properties of 3D Au nanoparticle crystals.

The preparation method of the Au nanoparticle crystals is essentially the same as that described in detail elsewhere.[15,16] 4.1 ml of an aqueous solution of 0.12 M hydrogen tetrachloroaurate tetrahydrate ($HAu(III)Cl_4{\cdot}4H_2O$) is mixed with 100 ml of methanol containing 1.5 mmol of mercaptosuccinic acid (MSA). Then under vigorous stirring 25 ml of an aqueous solution of sodium borohydride (0.2 M) is added. After the reaction is complete, Au nanocrystals with a MSA modified surface are obtained. The solvent is decanted after centrifugation. Then the samples are washed twice with a 20% (v/v) water-methanol solution by repeating resuspension with a sonicator and recentrifugation. Finally the samples are dialyzed to remove the inorganic (Na, Cl and B) and organic impurities.

In the present study we have prepared two types of samples. One with sparsely deposited Au nanoparticles, and the other with Au nanoparticle crystals. The sparsely deposited Au nanoparticles are prepared by dispersing the Au nanoparticles in distilled water and allowing them to air-dry while the crystallization of the Au nanoparticles is performed by the following procedure. To weaken the repulsive interactions among the nanoparticles, HCl is added to an aqueous suspension containing Au nanoparticles. After adding HCl, the suspension is stored in a closed glass bottle to prevent solvent evaporation. With an appropriate amount of HCl, the Au nanoparticle crystals form at the air/suspension interface in 4–10 days.[15,16] Few Au nanoparticle assemblies are observed to be descended to the bottom of the suspension. The thickness of the Au nanoparticle crystals is controlled by the HCl concentration. In this study, the HCl concentration is 3.6×10^{-1} M.

In our previous studies on Au nanoparticle crystals, we have determined the structure resulting from this procedure.[13,14] The Au nanoparticles form a close-packing arrangement in the 3D nanoparticle crystals. The Au core diameter is 3.5 nm, and the thickness of the surfactants is 0.7 nm. The overall widths and thickness of the nanoparticle crystals are between 1–6 μm and 0.1–1 μm, respectively.

Figure 1 shows the absorption spectra of (a) the sparsely deposited nanoparticles and (b) the nanoparticle crystals at room temperature. In Figure 1a, a small peak is found at 2.4 eV that corresponds with the surface plasmon band of Au particles. Unlike the sparsely deposited nanoparticles, the nanoparticles in a 3D lattice display a strong absorption peak at 1.9 eV (Figure 1b).

The optical absorption data can be explained by using the classical theory of electronic polarizability. By assuming that Au nanoparticles are artificial atoms in the Thomson model,[17] the number of valence electrons corresponds to the number of conduction electrons, N_v, in an Au core. The number of conduction electrons can be calculated by the following equation: $N_v = (4/3)\pi R^3 n_{Au}$, where R is the radius of the Au core and n_{Au} is the conduction electron density of bulk Au. Assuming that the artificial atoms are simple harmonic oscillators with the eigenfrequency, ω_s, the dielectric function of the crystal consisting of the artificial atoms is[18]

$$\mathcal{E}(\omega) = 1 + \frac{n_a N_v e^2/\mathcal{E}_0 m_o}{\omega_s^2 - (n_a N_v e^2/3\mathcal{E}_0 m_o) - \omega^2 + i\Gamma\omega}, \qquad (1)$$

where n_a is the number density of the artificial atoms in a crystal, m_o is the optical mass, and Γ is the damping factor. The number density, n_a, is set to the value that nanoparticles form closest-

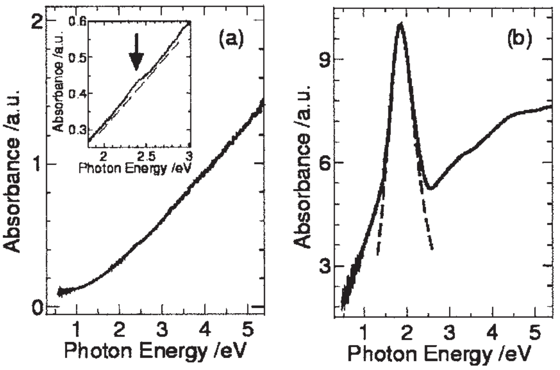

Figure 1. Optical absorption spectra: (a) the sparsely deposited Au nanoparticles, and (b) the Au nanoparticle crystals. The inset in the figure (a) is the magnification of the spectrum. The dashed curve in the figure (b) is the imaginary part of eq 1 fitted to the experimental spectrum.

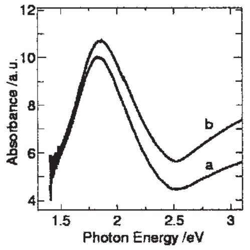

Figure 2. Optical absorption spectra of the Au nanoparticle crystals measured at (a) room temperature and (b) 77 K.

packing arrangements. On the assumption that Drude electrons behave as oscillators in artificial atoms of the Thomson model, the value of ω_s corresponds to the surface plasmon frequency of individual nanoparticles.[17] Using $\hbar\omega_s = 2.4$ eV, the experimental peak shift from 2.4 to 1.9 eV is explained by setting optical mass, m_o, to $2.5m_e$ (m_e: mass of free electrons). The calculated curve is fitted into the experimental peak as shown in Figure 1b. To fit the peak width, the damping factor Γ is set to $1.4 \times 10^{15}\ \mathrm{s}^{-1}$. The mean free path, l, of the conduction electrons is estimated to be about 1 nm by $\Gamma = v_F/l$, where v_F is the Fermi velocity of Au. Since the order of the obtained mean free path corresponds to the radius of Au cores, it is plausible to assume that oscillations of conduction electrons occur in individual nanoparticles and not over some nanoparticles. This conjecture is reasonable in our system because our surface modifier is a good insulator and there is a high potential barrier at Au core/surfactant interface that prevents conduction electrons from moving out of Au cores.

The absorption spectrum of the Au nanoparticle crystals at 77 K is shown in Figure 2. Unlike periodical arrays of molecules,[19] lowering the temperature is not likely to cause a significant change in the spectrum. The negligible change of the peak shape indicates that the mean free path of conduction electrons is not altered. This result is consistent with the above hypothesis that the oscillation of conduction electrons is restricted to Au cores due to the high potential barriers at core/surfactant interfaces.

In summary, optical absorption spectra of Au nanoparticle crystals were measured at room temperature and at liquid nitrogen temperature. The nanoparticle crystals showed a strong peak at 1.9 eV, whereas the sparsely deposited nanoparticles showed a small peak at 2.4 eV. The peak energy and the width of the nanoparticle crystals were independent of the temperature. The observed absorption spectra were evaluated using a classical theory of electronic polarizability. By fitting the calculated curve to an experimental spectrum, the optical mass and the damping factor were estimated to be $2.5m_e$ (m_e: mass of free electrons) and $1.4 \times 10^{15}\ \mathrm{s}^{-1}$, respectively.

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