Aggregation of Gold Nanoparticles with Cysteine in Aqueous Solutions Measured by Absorption Spectroscopy

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Introduction. Generally, the aggregation of gold nanoparticles in aqueous solutions leads to a color change from red to blue. It comes from the coupling of surface plasmon resonance of neighboring nanoparticles in the aggregates. The formation of a covalent bond, Au–S, on gold surfaces is also known and therefore the surface is easily modified. The purpose of the present study is to clarify the characteristics of aggregation of gold nanoparticles by a biological compound possessing a thiol group, cysteine (isoelectric point, 5.05), and to examine the aggregate size in the solutions by optical microscopy and filtration technique.

Experimental. A gold nanoparticle solution was prepared by the reduction of AuCl₄⁻ with sodium citrate and was diluted. The maximum absorption wavelength of the prepared gold nanoparticle solution was 520 nm, from which its average size was calculated to be about 15 nm. The pH of the gold nanoparticle solution was adjusted to 3 – 7 and then a cysteine solution was added. The final concentrations of gold nanoparticle and cysteine were 1.0×10⁻⁴ – 2.0×10⁻⁴ mol L⁻¹ (gold atom concentration) and 1.0×10⁻⁴ – 4.0×10⁻⁴ mol L⁻¹, respectively. After the reactions, the solutions were observed with an optical microscope with transmitted light or filtrated with membrane filters with various pore sizes.

Results and Discussion. Figure 1 shows the absorption spectrum change of the mixture of gold nanoparticles and cysteine. After the mixing, a red-shift as well as a broadening of the absorption peak was observed. This led to a color change from red to violet. The red-shift and absorbance at the longer wavelength increased with the elapse of time. The red-shift and color change indicated that the gold nanoparticles were aggregated in the solutions. Under the same conditions, the reaction of the gold nanoparticles with other amino acids, glycine, serine, tryptophan, histidine, were examined but no changes of the absorption spectra were observed. These facts mean that the thiol group of cysteine is bound to the gold nanoparticle surface.

Original gold nanoparticles have some negative surface charges due to the adsorption of anions, Cl⁻ or citrate, and they were not aggregated. When cysteine was bound to the gold nanoparticle surface, the electrostatic repulsion was reduced and the aggregation proceeded. From the maximum absorption wavelength of the aggregates, the size was estimated to be less than 100 nm. However, larger aggregates, such as 1 μm, were observed by optical microscope observation as shown in Figure 2. The filtration with the membrane filters also indicated that the aggregate size was larger than 500 nm. These facts mean that a part of aggregate exhibits the absorption spectrum.

Figure 1. Absorption spectra of 2.0×10⁻⁴ mol L⁻¹ gold nanoparticle solution with 2.0×10⁻⁴ mol L⁻¹ cysteine at pH 5. Path length, 1.0 cm.

Figure 2. Optical microscope image of gold nanoparticles with cysteine in the aqueous solution. Gold nanoparticle 2.0×10⁻⁴ mol L⁻¹, cysteine, 2.0×10⁻⁴ mol L⁻¹, pH 5, reaction time 120 min.