Sonochemical One-Step Synthesis of Surface-Modified Gold Nanoparticles

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1. Introduction

The cavitation of microbubbles produces hydrogen and hydroxyl radicals in aqueous solutions because temperature in a microbubble can rise to 4300 K at 20 kHz sonic oscillation under argon atmosphere. These radicals have been applied to prepare nanoparticles such as gold, silver, and other semiconductor materials. Among these materials, gold nanoparticles (AuNPs) have been focused on because of their own unique optical properties as the labelling tags in solution and the ease of surface functionalization.

Such functionalized AuNPs can be prepared with Brust synthesis or ligand-exchange techniques. In the former case, AuNPs are synthesized directly in the presence of functionalized thiols, but they block the growth of AuNPs and resulting particles are difficult to have a larger diameter than 4 nm. In the latter, one can use AuNPs (diameter > 10 nm) synthesized by the citrate reduction, but stepwise synthesis is required to exchange previous ligands to functionalized molecules. To overcome these problems, a variety of methods for simple and direct synthesis of surface-modified AuNPs with alkyl thiosulfates as ligand precursors have been studied. However, little has been done on direct sonochemical synthesis of AuNPs modified with thiolated molecules on the surface. In this report, one-step modification of AuNPs with sonochemical method is studied and the size distribution and the level of modification are analyzed by TEM and UV-Vis spectroscopy.

2. Experimental

In a test tube glass bottle (20 mL, 27×55 mm), 10 mL of 0.5 mM HAuCl₄ solution and 140 μL of 1-pentanol (98.0 %) (these are purchased from Wako Pure Chemical Ind., Ltd.) were mixed and 2.5 mL of 0.25 mM 3,3´-dithiodipropionic acid solution (Tokyo Chemical Ind. Co., Ltd.) were added (molar ratio of Au/disulfide=8). The bottle was sealed with a cap with Teflon tubes for gas bobbling. After 10 min argon bubbling, the solutions were irradiated with 42 kHz ultrasonic wave for 0 ~ 20 minutes in an ultrasonic bath (1510J-MT, Branson). While irradiation, the reaction bottle were fixed on a plastic cylinder. The water level of the bath was as high as the solution in the bottle, and temperature was maintained at room temperature.

Absorption spectra of the solutions were measured with a UV-Vis spectrophotometer (UV-2550, Shimazu Co., Ltd.) at 1 hour from the start of sonic irradiation. After another 12 hours, absorption spectra were measured again and then, AuNPs were centrifuged for 15 minutes, 5500 rpm and absorption spectra of the supernatant fraction of the sample were measured. Structural characterization of the prepared AuNPs was carried out by JEM-2100XS transmission electron microscope (TEM) with a 200 kV accelerating voltage. Samples for TEM were prepared in parallel with first UV-Vis observation by spreading a drop of diluted AuNPs sol with methanol (1:4, v/v) onto the carbon film on a fine mesh Cu grid (167 mesh) and dried.

Fig. 1 TEM images of the surface modified AuNPs (scale bar = 50 nm). The sonication time was (a) 5 min, (b) 10 min, and (c) 20 min, respectively. (d) is the histogram of NPs diameter.

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3. Result and discussion

Fig. 1 shows TEM images of synthesized AuNPs and their size distribution histograms. The average size of the particles is approximately 16 nm and this result agrees well with UV-Vis spectra. At a sonication time of 5 min, lumpy AuNPs (like Fig. 1a) was decreased which was also confirmed by electron diffraction patterns.

The formation of AuNPs was confirmed with absorption spectra as Fig. 2. The alcohol-assisted sonochemical reduction of tetrachloroaurate proceeds with radical formation of alcohol and its reaction with gold tetrachloroaurate ion:

$$\text{RCH}_2\text{OH} + \cdot\text{OH} \rightarrow \text{R}′\text{CHOH}′ + \text{H}_2\text{O}$$  
(1)

$$3\text{R}′\text{CHOH}′ + \text{AuCl}_4^- \rightarrow 3\text{R}′\text{CHO} + 3\text{H}^+ + \text{Au}^0 + 4\text{Cl}^-$$  
(2)

$$n\text{Au}^0 \rightarrow [\text{Au}_n^0]_n$$  
(3)

Under the presence of disulfide, next reactions also arise simultaneously: reduction of disulfide to thiol and formation of Au(I) coordinated with thiol.

$$\text{RSSR} + 2\text{R}′\text{CHOH}′ \rightarrow 2\text{RSH} + 2\text{R}′\text{CHO}$$  
(4)

$$\text{Au(III)}\text{Cl}_4^- + 3\text{RSH} \rightarrow \text{Au(I)SR} + \text{RSSR} + 3\text{H}^+ + 4\text{Cl}^-$$  
(5)

It is known that Au(I)SR is neutrally charged and forms [Au(I)SR] oligomer, promoting the growth of gold nanoparticles.

Fig. 3 shows the UV-Vis spectra of supernatant fraction of precipitated samples. Absorption around 309 nm is assigned to the band of dπ → pσ transition of Au(I)SR. From the absorbance at 309 nm the residue of Au(I) can be monitored.

From Fig. 2c, the analyzed diameters at 13 hours are larger than those at 1 hour. This suggests that the growth of AuNPs continued even after sonication finished except for the sonication time of 20 min. On the other hand, absorption at 309 nm is clearly decreased in proportion to sonication time (see Fig. 3b). This result suggests that there were two reduction processes in the case of Au/Ligand ratio = 8. During the initial several minutes, the fast reduction of Au ion with alcohol radicals occurred and AuNPs and Au(I)SR oligomer came in. Then slow reduction of Au(I)SR proceeds at the surface of AuNPs after stopping irradiation. Sonication can accelerate the reduction of Au(I)SR dramatically. Concludingly, there is a possibility to control the diameter of surface-modified AuNPs by controlling the amount of remained Au(I)SR with the control of the sonication time.

References