

Rapid Formation of Silver Shells on Gold Nanorods in a Micellar Solution of Hexadecyltrimethylammonium Chloride

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Rapid chemical reduction of silver ions forming silver shells on gold nanorods was realized in a micellar solution of hexadecyltrimethylammonium chloride. It was shown that the stable bilayers of hexadecyltrimethylammonium bromide on gold surfaces contributed to retard the chemical reduction of silver ions on the gold surfaces.

Gold nanorods (GNRs) are rod-shaped gold nanoparticles which are obtainable in micellar solutions of hexadecyltrimethylammonium bromide (CTAB).^{1,2} The GNRs show double surface plasmon (SP) bands which are assignable to transverse and longitudinal SP oscillations in visible and near-infrared (near-IR) regions, respectively.³ Featuring these unique optical properties, various applications of GNRs have been reported.^{2,4}

Silver shells formed on gold nanoparticles provide an effective means to tune the spectroscopic properties of those: the silver shells shifted the SP bands of gold nanoparticles into a shorter wavelength region.⁵ The first paper describing silver shells on GNRs was reported by Ah et al.,⁶ in which they coated GNRs with silver shells through the reduction of silver ions using hydroxylamine hydrochloride as a reducing agent. Liu and Guyot-Sionnest also prepared silver shells on GNRs using citrate or poly(vinylpyrrolidone) as a passivating agent⁷ and ascorbic acid as a reducing agent. Chang and co-workers studied the microscopic and spectroscopic changes of core-shell particles induced by pH changes.^{8,9} Song et al. indicated that the silver shells formed on the GNRs occurred via epitaxial growth on the gold surfaces.¹⁰ All these works were performed in CTAB solutions. The stabilities of colloidal dispersions of GNRs and core-shell nanorods originated from the CTAB bilayers that were formed on GNR surfaces.¹¹ We found that the formation of silver shells in colloidal solutions of hexadecyltrimethylammonium chloride (CTAC) was much faster than that in a CTAB solution. In this paper, we discuss the chemical reduction of silver ions at the surface of the GNRs coated with CTAC molecules.

GNRs were prepared based on a photochemical method¹² in a joint research project between Mitsubishi Materials Corp. and Dai-Nippon-Toryo Co., Ltd. The mean sizes of the GNRs in the longitudinal and transverse directions were 51 ± 7 and 9.7 ± 1.1 nm, respectively. CTAB and CTAC were purchased from Tokyo Kasei and used without further purification. CTAB solution (80 mM) and CTAC solution (80 mM) were mixed with variations of volume ratios at CTAC:CTAB = 0:100, 25:75, 50:50, 75:25, and 100:0. These micellar solutions were noted as CTAC-0, CTAC-25, CTAC-50, CTAC-75, and CTAC-100, respectively.

An as-prepared GNR solution was centrifuged at $8000 \times g$ for 10 min, and the supernatant was removed. The precipitates

were redispersed in one of the CTAC-0–100 solutions. The concentration of gold atoms in the redispersed GNR solutions was adjusted to 0.039 mM. In one of the redispersed GNR solutions (22 mL), 1.0 mL of silver nitrate (10 mM), 2.0 mL of ascorbic acid (100 mM), and 0.4 mL of sodium hydroxide (NaOH) solution (500 mM) were sequentially added during circulation over a period of one minute; the resultant GNR solutions were noted as GNR/CTAC-0–100. The final concentrations of GNRs, silver ions, and ascorbic acid were 0.034 (Au atom), 0.39, and 7.9 mM, respectively. The final pH of the reaction solutions was 5.9. All the procedures were carried out at 30 °C. The spectral changes of each solution were monitored by sampling a small portion of the reaction solutions in a thin optical cell (optical path length: 1 mm). A spectrophotometer (JASCO V-570) was used to obtain the extinction spectra of the reaction solutions.

Figure 1 shows the extinction spectra of GNR/CTAC-100 and GNR/CTAC-0 solutions before the addition of ascorbic acid solution (dotted lines) and after the addition of NaOH solution (solid lines, 5, 10, 20, 30, 40, 50, 60, 120, 180, 240, and 300 min). Spectral changes of GNR/CTAC-25, -50, and -75 are shown in the Supporting Information.¹⁷ Before the addition of ascorbic acid solution (dotted lines), the solutions indicated longitudinal SP bands of GNRs at around 900 nm. Addition of the NaOH solutions initiated the chemical reactions. Figure 1a shows the spectral changes of the GNRs/CTAC-100 solution, in which no CTAB was present. Soon after the addition of the NaOH solution, the longitudinal SP band at around 900 nm disappeared, and a new band around 550 nm was observed 5 min after the addition of NaOH solution. This spectral change was assigned to silver shell formation that drastically changed the SP oscillation of GNRs.^{6–10} Within 10 min, the spectral changes ceased and the final spectra showed two bands at 400 and 520 nm. These two bands were consistent with the SP bands of the Au–Ag core-shell nanorods.^{6–10} In the absence of CTAC (in CTAB, Figure 1b), the spectral changes were very slow; however, the spectrum after 300 min also showed double peaks.

Figure 2 shows the changes of peak wavelength of the SP

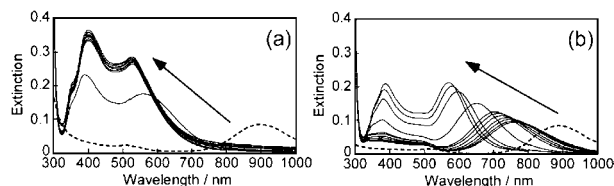


Figure 1. Extinction spectra of GNR/CTAC-100 (a) and GNR/CTAC-0 (b) before addition of ascorbic acid solution (dotted lines) and after the addition of NaOH solution (solid lines). Spectra were obtained at 5, 10, 20, 30, 40, 50, 60, 120, 180, 240, and 300 min after the addition of NaOH solution.

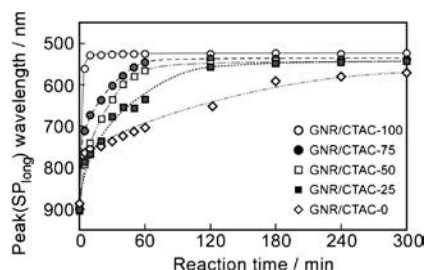


Figure 2. Time courses of the peak positions of SP bands located in the longer wavelength region. (○) GNR/CTAC-100, (●) GNR/CTAC-75, (□) GNR/CTAC-50, (■) GNR/CTAC-25, and (◇) GNR/CTAC-0.

bands in the longer wavelength region after the addition of NaOH solution. At time zero, the peak positions corresponded to those of the longitudinal SP bands of the GNRs. The GNR/CTAC-100 solution showed a very fast rise and reached a plateau within 10 min. The GNR/CTAC-25, -50, and -75 solutions showed a slower rise depending on the contents of CTAB. In the absence of CTAC (CTAC-0: 100% micellar CTAB solution), the reactions continued, even at 300 min after the addition of a NaOH solution. It was clearly shown that the presence of CTAB in the reaction solutions retarded the formation of silver shells.

TEM images of the nanoparticles (Figure 3) indicated boat-shaped Ag shells were formed on GNRs. This was the same as reported in a previous paper.^{8–10} In Figure 3b (GNR/CTAC-0), a few core-shell particles were observed, because the reaction continued even after 300 min. However, the resultant shells in the absence of CTAC were also boat-shaped. Thus, CTAC accelerated the reaction speeds of the silver-shell formation but did not intensively affect the shape of the shells (TEM images of core-shell particles formed in the other solutions were shown in the Supporting Information.).

Waters et al. reported strong adsorption of bromides on gold surfaces.¹³ In the case of CTAB layers, the counter cations of the bromide ions were hexadecyltrimethylammonium ions (CTA⁺). The CTA⁺ molecules probably formed densely-packed and static monolayers on gold surfaces, and on the CTAB monolayer, second CTAB layers would be formed through hydrophobic interaction with the methylene chains.¹¹ The stable and densely packed CTAB bilayer contributed to the stabilization of the colloidal dispersion of GNRs and probably suppressed the chemical reduction of silver ions on the surface of the GNRs. On the other hand, the chloride ions interacted with the gold surfaces in very different way from that of bromide.^{14–16} For example, yields of GNRs decreased with an increase of CTAC concentration in reaction solutions.¹⁵ Kawasaki et al. reported that the adsorption

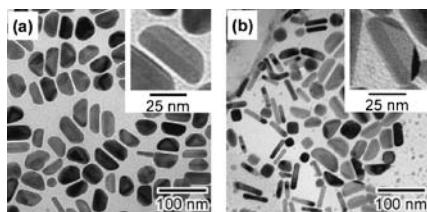


Figure 3. TEM images of core-shell particles at 300 min after the addition of NaOH. (a) GNR/CTAC-100 and (b) GNR/CTAC-0.

affinity of CTA⁺ chloride on gold surfaces was weaker than that of CTA⁺ bromide.¹⁶ At the present stage of this work, there is no quantitative data revealing the properties of CTAC layers on nanorod surfaces; however, the previous papers^{14–16} and our experimental results indicated that CTAC layers on gold surfaces are more dynamic and loosely packed than CTAB layers. The rapid formation of silver shells on GNRs probably originated from the dynamic and loosely packed properties of the CTAC layers on nanorod surfaces.

A further tuning of the experimental conditions is expected to improve the homogeneity of the silver shells and size distribution of core-shell nanorods. Ag-shell formation in a micellar CTAC solution will be a new standard to obtain homogeneous core-shell nanoparticles in practical quality and quantity.

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- 17 Supporting Information is also available electronically on the CSJ-Journal Web site, <http://www.csj.jp/journals/chem-lett/index.html>.