

Extraction of Hexadecyltrimethylammonium Bromide from Gold Nanorod Solutions: Adsorption of Gold Nanorods on Anionic Glass Surfaces

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Gold nanorods dispersed in hexadecyltrimethylammonium bromide (CTAB) solutions were extracted with chloroform containing phosphatidylcholine (PC). Triple extractions decreased CTAB concentrations and gave PC-modified nanorods which adsorbed on an anionic glass surface. When more than 8.1 mM CTAB was retained in the nanorod solutions after the extractions, the nanorods dispersed stably without agglomeration. In order to have adsorption of the nanorods on an anionic glass surface, the residual CTAB after extraction should be less than 13.8 mM. Controllable adsorption was obtained between these concentrations.

Key words: gold nanorod, phosphatidylcholine, surface plasmon band, extinction spectra

1. INTRODUCTION

Gold nanorods are rod-shaped gold nanoparticles which show remarkable spectral characteristics [1-4]. Since they have two anisotropic axes, they exhibit two surface plasmon (SP) bands. These bands can be assigned to transverse and longitudinal modes of SP oscillation of free electrons in the nanorods. The transverse SP bands are located in the visible region; in a typical case, they can be found at around ~520 nm. On the other hand, the longitudinal SP bands are found in the near-IR region, and their peak positions and intensities depend on the shape of the nanorods, especially on the aspect ratio (length/diameter) of the nanorods. Theoretical calculations using an ellipsoidal model indicated that at higher aspect ratios nanorods exhibit their longitudinal SP bands in the longer wavelength region; otherwise, the transverse SP bands are not so sensitive to the aspect ratio [3, 4]. Thus, the longitudinal SP bands are sensitive to the dielectric constant (refractive index) of the medium. Consequently, it is expected that the nanorods can be a probe material for sensing the dielectric constant of a medium, using near-IR light [5-7]. Previously, we reported that the longitudinal SP bands of gold nanorods which were fixed on glass substrates by electrostatic interaction showed peak shifts that depended on the medium. That was a preliminary work indicating the potential of gold nanorods as a probe material [8].

Recently, we reported phosphatidylcholine (PC) passivated gold nanorods (PC-NRs) that were designed as a probe material for living cells [9]. The PC-NRs showed a positive zeta-potential and adsorbed on glass substrates that were treated with poly-anionic polymers [10]. It was shown that the adsorbed PC-NRs formed linear assemblies on the anionic glass surfaces [10]; however, the methods for obtaining PC-NRs suitable for adsorption on anionic surfaces have not been optimized

yet. Because gold nanorods were prepared in a micellar solution of hexadecyltrimethylammonium bromide (CTAB), which is a cationic amphiphile, the PC-NRs were prepared by the replacement of CTAB with PC using liquid-liquid extraction (nanorods-aqueous and PC-chloroform solutions) [9, 11]. In this study, we extracted CTAB using different volumes of nanorod and PC-chloroform solutions. Optimal preparation procedures for obtaining nanorods which could adsorb on an anionic surface were examined.

2. EXPERIMENTAL

The gold nanorods were provided from a joint research project of Mitsubishi Materials Corp. and Dai-Nippon-Toryo Co. Ltd. Mean sizes of the nanorods were about 65 and 11 nm in the longitudinal and transverse directions, respectively. The CTAB in the as-prepared nanorods solutions was extracted by PC-chloroform solutions (10 mg/ml) in the same manner as in the previous papers [9, 11]. In the first extraction, 10 or 20 mL of nanorods solution was shaken with 10 mL of PC-chloroform solution. The emulsified solution was kept in a refrigerator (4 °C) until the solution separated into emulsion and water phases. In a typical case, the emulsified solution was kept at 4 °C for 5 days, and then the water phase containing nanorods was collected (Figure 1[A]). The two extraction conditions using 10 and 20 mL of PC-chloroform solution are denoted as "1:1 extraction and 2:1 extraction", respectively. The following double extractions were performed under certain conditions using the same, 1/2, and 1/3 volumes of PC-chloroform solution with the once-extracted nanorod solutions. The last condition is denoted as "3:1 extraction". Because the once-extracted solution did not contain much CTAB, no emulsion was formed in the following extractions. In the second extractions, the phase-separated solutions were stirred

with a spatula, and then kept at 4 °C for 24 hours before collection of the water phases (Figure 1[B]). In the third extractions, the phase-separated solutions were not stirred, but were kept at 4 °C for 24 hours.

We prepared six kinds of triply-extracted nanorod solutions. They are denoted as (first extraction condition)-(second and third extraction conditions)²; for example, (1:1)-(2:1)² indicates that 50 mL of nanorod solution was extracted once with 50 mL of PC-chloroform solution, and then the second and third extractions were performed using half the amount of PC-chloroform solution against the once-extracted nanorod solution. The triply-extracted nanorod solutions were centrifuged once (6,000 ×g, 10 min), and the precipitates were re-dispersed in water. In order to obtain extinction spectra of the nanorod solutions, the solutions were diluted ten times with water. A conventional spectrophotometer (JASCO V-570) was used for the spectroscopy.

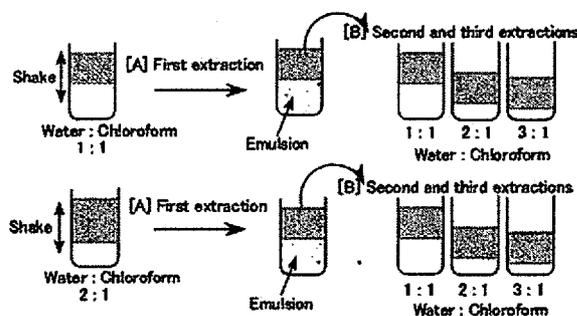


Figure 1. Schematic illustration of the extraction of CTAB into chloroform phases.

Glass substrates were treated with anionic polymer using a layer-by-layer technique [8]. The outermost layer of the glass surface was a poly(styrenesulfonate) layer. The surface-treated substrates were immersed in the centrifuged nanorod solutions for 1, 24, and 72 hours, and then after washing with water, extinction spectra of the substrates were obtained by the spectrophotometer.

3. RESULTS AND DISCUSSION

3.1 Stabilities of colloidal dispersions of the nanorods after the triple extractions

Figure 2 shows the extinction spectra of the gold nanorod solutions extracted with different amounts of PC-chloroform solution. Solid lines show the spectra of as-prepared nanorods passivated with CTAB (a). Dashed (b) and dotted (c) lines are the spectra after the third extractions, and of the re-dispersed solutions after centrifugation, respectively. The spectra in the left column of Figure 2 ([A] and [B]) were obtained from the samples for which the first extraction was a 1:1 extraction. In the right column ([C], [D] and [E]), the first extraction was a 2:1 extraction. In [C], the second and third extractions were 1:1 extractions. In [A] and [D], the second and third extractions were 2:1 extractions. In [B] and [E], the second and third extractions were 3:1 extractions. The extinction spectra of a (1:1)-(1:1)² solution, which should be at the top of the left column, are not shown in Figure 2, because in

that case the nanorods formed aggregates and precipitated after the third extraction.

In the case of the (1:1)-(2:1)² solution [A], the nanorod solution exhibited smaller SP bands after the extraction (b: dashed line), but the full width at half-maximum (FWHM) of the SP band (b) was same with that of as-prepared solution (a). This was assignable to the decrease in the nanorod concentration, due to the formation of a nanorod-containing emulsion. After centrifugation (c: dotted line), the spectrum showed broad and small SP bands. This indicated that the nanorods formed agglomerates after centrifugation [12]. When small amounts of PC-chloroform solution were used for the second and third extractions ((1:1)-(2:1)² [B]), the extinction spectra were not drastically affected after the centrifugation, but the FWHM of the longitudinal SP band (c) was somewhat larger than that of the as-prepared solution (a). In the right column, [C] ((2:1)-(1:1)²) shows the same spectra as [B]. In [D] ((2:1)-(2:1)²) and [E] ((2:1)-(3:1)²) the nanorods after centrifugation showed clear longitudinal SP bands (c) that are unique to well-dispersed gold nanorods.

Under our experimental conditions for the first extractions, 13.4 % and 27.2 % of CTAB was retained in the water phases after the (1:1) and (2:1) extractions, respectively. The CTAB contents in the water phases were determined by the weight of CTAB in the chloroform and emulsion phases. For the second and third extractions, the distribution ratios of CTAB between the water and chloroform phases ($[CTAB]_{chloroform}/[CTAB]_{water}$) were 3.08 and 0.306, respectively. The final concentrations of CTAB after the third extractions are given in Figure 2. It is clear that the residual CTAB in the final solutions contributed to the dispersion of the nanorods; when the concentration of

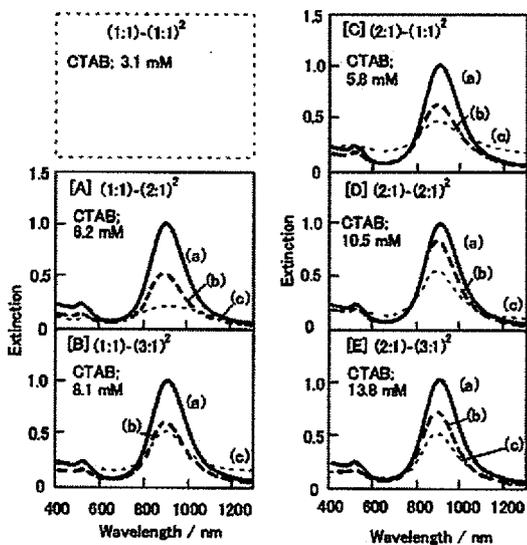


Figure 2. Extinction spectra of the gold nanorod solutions extracted with different amounts of PC-chloroform solution. (a): as-prepared nanorods solution, (b): after three extractions, (c): re-dispersed solution after centrifugation. Extraction conditions: [A] (1:1)-(2:1)²; [B] (1:1)-(3:1)²; [C] (2:1)-(1:1)²; [D] (2:1)-(2:1)²; [E] (2:1)-(3:1)². CTAB concentrations after the third extraction are given.

residual CTAB was smaller than 3 mM, the nanorods formed precipitates after the extraction. When the CTAB concentration was smaller than 8.1 mM, the nanorods formed agglomerates after the centrifugation ([A], [B], and [C]).

3.2 Adsorption of nanorods on anionic glass surfaces

Figure 3 shows extinction spectra of the glass substrates which were immersed in the extracted nanorod solutions for 1 (a), 24 (b), and 72 (c) hours. [A]-[E] indicate the same nanorod solutions as in Figure 2. In every case, the substrates were almost transparent and showed no spots that were ascribable to inhomogeneous adsorption of nanorods. Other than [A], the substrates showed distinct SP bands of gold nanorods in near-IR regions. This shows that the nanorods adsorbed on the glass substrates by immersion of the substrates. In the case of [A], the SP bands were diminished, and flat extinction spectra were observed in the near-IR regions. Those spectra are ascribable to agglomerated nanorods [10, 12]. As shown in Figure 2[A], the nanorods formed small agglomerates in the solution after centrifugation (Figure 2[A], curve (c)). The agglomerated nanorods hardly fixed on a glass substrate as isolated nanorods; rather, they formed larger-sized agglomerates on the glass substrate.

The SP bands in the other cases (Figure 3 [B]-[E]) indicate that 1 hour of immersion (curves (a)) resulted in deposition of nanorods on the substrates. Longer immersion times tended to give larger SP bands; that is, larger numbers of nanorods were fixed on the substrates after longer immersion times. The spectral profiles depend on the immersion time ((a)-(c)) and the extraction procedure ([A]-[E]). In the case of (2:1)-(1:1)² extraction, the SP bands exhibited a slightly broad profile after 1 hour of immersion (curve (a) in Figure 3[C]). After 24 hours of immersion, the substrate exhibited a broad SP band in the near-IR region. In the (1:1)-(3:1)² [B] and (2:1)-(2:1)² [D] extractions, after 1 hour of immersion (a), the substrate showed the same SP bands in the near-IR region as the as-prepared solution. This indicates that the nanorods were fixed independently on the glass substrate. After 24 hours of immersion, the substrates showed red-shifted [B] and broad [D] SP bands in near-IR region (curves (b)). Longer immersion (72 hours) greatly enhanced the extinction in the region where the wavelength was longer than 1000 nm. This indicated that longer immersion resulted in agglomeration of the nanorods on the glass surfaces. On the other hand, for the (2:1)-(3:1)² extraction [E], the typical SP bands of nanorods, which are assignable to well isolated nanorods, were retained even after 72 hours of immersion, and the intensities of the SP bands were much smaller than in the other cases. Thus, when 13.8 mM of CTAB was retained in the nanorod solution after the triple extraction (case [E]), the nanorods could be centrifuged without forming agglomerates (see Figure 1[E]), but adsorption of the nanorods on anionic surfaces was suppressed. This was probably due to the CTAB retained in the centrifuged nanorod solution. The cationic CTAB competitively adsorbed on the anionic glass surfaces, and results in formation of bilayers of CTAB on the glass surfaces. The cationic CTAB molecules on the glass surfaces

interrupt deposition of the nanorods.

The broad SP bands in Figure 3 [B-D] indicate interactions between the SP oscillations of the nanorods fixed on the glass surfaces. The SP band indicated broad profiles in the near-IR region when the extinction was larger than 0.10. By using the extinction coefficient of gold nanorods ($7967 \text{ cm}^{-1} \text{ nanorod}^{-1}$ [13]), the extinction can be used to calculate the surface area occupied by a nanorod. It has been shown that a nanorod occupies about $79,000 \text{ nm}^2$ when the extinction is 0.10. The mean distance from center to center of nanorods was roughly estimated to be 180 nm. Namely, interaction between the SP oscillations was not negligible, when the mean distance of the nanorods from center to center was less than about 180 nm. This is reasonably consistent with theoretical calculations by Gloudenis *et al.* which predicted spectral changes in a pair of gold nanorods depending on the gap distance between the pair of nanorods [12]. Thus, the longer immersion time gave a higher density of nanorod film on the substrates, and then the longitudinal SP bands of the densely deposited nanorods showed broad and flat characteristics in the near-IR region.

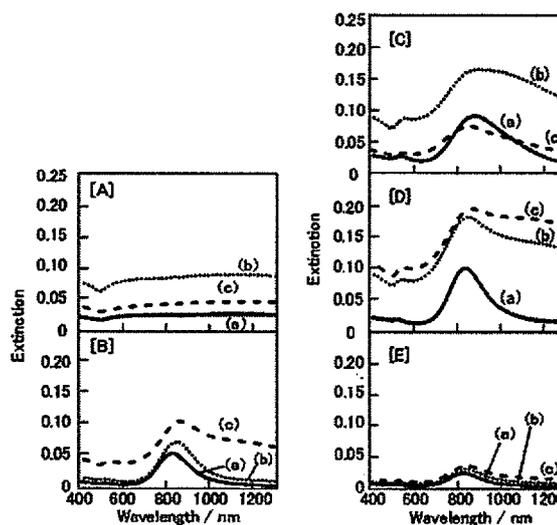


Figure 3. Extinction spectra of the glass substrates which were immersed in the nanorod solutions for 1 (a), 24 (b), and 72 (c) hours. Extraction conditions were the same as in Figure 2.

4. CONCLUSION

Gold nanorod solutions were extracted with PC-chloroform solutions to decrease the CTAB content and to replace CTAB molecules on the nanorod surface with PC. The colloidal stabilities of the nanorods depended on the extraction procedure. When larger amounts of nanorod solution were used for the extractions, well stabilized nanorod solutions were obtained. That was due to the retained CTAB stabilizing the colloidal dispersion of the nanorods. It was shown that the retained CTAB suppresses the adsorption of the nanorods on the anionic glass surfaces. In order to realize controllable adsorption of the nanorods, (2:1)-(2:1)² and (1:1)-(3:1)² extraction procedures are preferable.

5. ACKNOWLEDGEMENT

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- [13] Extinction of a nanorod solution containing 0.3 g/L of gold atoms was about 20. That corresponds to a molar extinction coefficient of 7970. The mean size of the nanorods was about 65 and 11 nm in longitudinal and transverse directions, respectively. This size of nanorod contains about 65,400 gold atoms. Extinction coefficients were evaluated from these data.

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