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Growth of gold nanorods in gelled surfactant solutions

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Gold nanorods have been actively studied for new nanotechnological materials and industrial applications. It is well known that gold nanorods grow spontaneously in surfactant solutions, and a number of procedures for their preparation have been reported; however, the factors that determine the morphology have not been well understood. In this study, we observed the time series of the growth process of gold nanorods in gelled surfactant solutions by completely stopping the growth reaction. This growth process was compared to that in solution without gelation. The comparison indicates that the self-assembly of surfactant molecules affected the resulting shape, especially the short-axis length, of the nanorods. Small-angle neutron scattering (SANS) experiments revealed that the gelled solutions form lamellar structures, whereas nongelled systems form spherical micelles. On the bases of these results, we present a model showing that the short-axis length of gold nanorods is affected by a decrease in the spontaneous curvature of the outer surfactant layer and/or an increase in the bending modulus of the surfactant membrane neighboring the gold surface.

1. Introduction

A gold nanorod is a one-dimensional crystal of gold, which is among the objects generating the most interest for new nanotechnological materials and industrial applications [1]. It is well known that nanorods grow spontaneously in a cationic surfactant solution; there are three representative kinds of syntheses for these nanorods: electrochemical, photochemical, or seeding [2–7]. The growth mechanisms of gold nanorods have been actively studied [8–15]. For instance, Gao and co-workers [9] focused on the van der Waals stabilization between the hydrophobic tails of surfactant molecules of the bilayer on a gold surface. Perez-Juste and co-workers [10] proposed an electrochemical mechanism by which rod formation is controlled via directional collisions of Au-bound micelles. Seo and co-workers [13] suggested that key factors in anisotropic growth are three-dimensional (3D) decahedral seed structures and the energetic difference of the distinct facets.

Various studies on the kinetics during the growth process have been reported. For example, Jana and co-workers [6] performed a spectroscopic analysis to examine the role of seeds in the formation of particles. Sau and Murphy [7] also reported spectroscopic results revealing that an increase in the short-axis length follows an increase in the long-axis length of nanorods with an aspect ratio of less than 5. Recently, we used transmission electron microscopy (TEM) to observe the time series of the growth process; in this study, growth was experimentally terminated in order to construct a numerical model of the growth process [15]. All the seeding studies noted above have been useful in gaining an understanding of the growth of gold nanorods in surfactant solution without gelation.

However, we have also reported that high-aspect-ratio gold nanorods grow spontaneously, and in high yield, in gelled surfactant solution [16]. Using a mixed aqueous solution of hexadecyltrimethylammonium bromide (HTAB) and octadecyltrimethylammonium bromide (OTAB), we controlled gelation by altering the temperature of the growth solution. The results indicated that there is a close relationship between the gelation of a surfactant solution and the elongation of gold nanorods. However, the time series of the growth process in gelled solution as well as the mechanism by which gelation affects the elongation of gold nanorods remain to be elucidated. In the present study, we experimentally observed the growth process of gold nanorods in gelled surfactant solution. We used an aqueous solution of OTAB as the surfactant solution. We synthesized gold nanorods in surfactant solution with and without gelation (cases A and B), stopped growth at different time intervals, and used scanning electron microscopy (SEM) to compare the transitional morphology. The results confirmed that there is a difference in morphology of nanorods between the two cases at the onset of the gelation. These findings suggested that the

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self-assembly of surfactant molecules at an early stage of growth has a strong effect on the resulting morphology of gold nanorods.

2. Experimental

We controlled the gelation of the surfactant solution by altering the temperature of the solution. For the synthesis of gold nanorods, the initial temperature was set to 40 °C in both cases, i.e., with and without gelation. The resulting temperature for the solution with gelation (case A) was 15 °C and that for the solution without gelation (case B) was 35 °C. The time series for temperature during the growth of the gold nanorods is shown in Fig. 1.

We synthesized gold nanorods using the seeding method. Prior to synthesis, 0.1 M octadecyltrimethylammonium bromide (Wako Pure Chemical Industry) solution was kept at 40 °C, so that the solution would remain completely dissolved. For the preparation of a seed suspension, 1875 μl of the surfactant solution (40 °C), 62.5 μl of 0.01 M tetrachloroauric acid ($HAuCl_4 \cdot 4H_2O$, Nacalai) solution, and 150 μl of 0.01 M sodium borohydride ($NaBH_4$, Nacalai) solution were mixed at 40 °C in this order. With these procedures, the final concentrations of the surfactant, tetrachloroauric acid, and sodium borohydride in a seed solution were 9.0×10^{-2}, 3.0×10^{-4}, and 7.2×10^{-4} M, respectively. As soon as $NaBH_4$ was added, the solution was rapidly mixed for 2 min, and the evolved gas was allowed to escape. The resulting brown suspension of gold seeds was stored at 40 °C for 2 h. For the formation of gold nanorods, 9500 μl of the surfactant solution (40 °C), 400 μl of 0.01 M tetrachloroauric acid solution, and then 64 μl of 0.1 M ascorbic acid ($C_6H_8O_6$, Nacalai) solution were mixed at 40 °C. These procedures yielded a clear solution. The final concentrations of the surfactant, tetrachloroauric acid, and ascorbic acid in a growth solution were 9.5×10^{-2}, 4.0×10^{-4}, and 6.4×10^{-4} M, respectively. Next, 17 μl of the prepared seed suspension was added, and the solution was gently mixed for 10 s. The resulting colorless suspension was stored at 15 °C (case A) or 35 °C (case B). The solutions gradually (~5 min) became dense pink.

To observe the growth process of gold nanorods, we blocked the growth of the nanorods at X min (X = 3, 4, 6, 8, 10, 15, 20, 30, 45, 60) after we added the seed suspension; this was done along with the addition of 500 μl of 1% dodecanethiol–ethanol ($C_{12}H_{25}SH$, Wako Pure Chemical Industries) solution. The growth-stopped suspensions of gold nanorods were characterized by scanning electron microscopy (SEM; Hitachi S-4800T) after centrifugation. At centrifugation, 1400 μl of the resulting suspension was centrifuged at 5000 rpm for 5 min, and the upper transparent portion was removed. The lower portion was redispersed in 700 μl of purified water and centrifuged again at 5000 rpm for 5 min. After the upper transparent portion was removed, the precipitated dense suspension was used to prepare SEM samples. For the SEM samples, 15 μl of the suspension was placed for 1 min on a silicon (Si) substrate with hydrophobic treatment (see Appendix). After excess droplet was removed, the substrate was spin-coated at 5000 rpm for 30 s and was used for SEM observation.

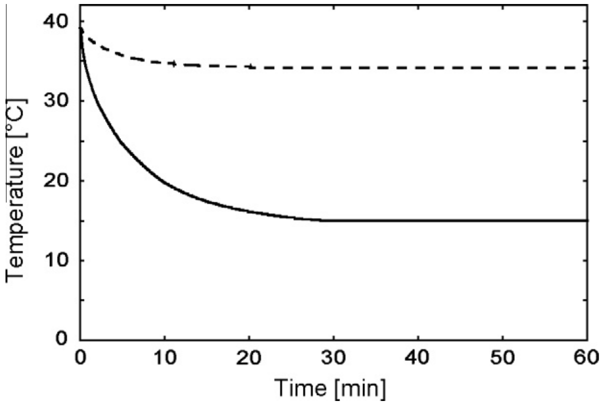

Fig. 1. Time changes in temperature during the growth of gold nanorods in case A (solid line) and case B (dotted line).

To characterize the gelation of the growth solution in both cases A and B, we observed the time change in the transmittance of the surfactant solution. We used the OTAB solution as a sample instead of the suspensions of gold nanorods, as the suspensions gradually exhibited a pink coloration. In previous studies, we confirmed that the growth solution lacking the addition of the seed suspension became a gel in the same manner as the growth solution containing the seed suspension [16]. We set a white-light-emitting diode (LED; NICHIA, NSPW-510BS-bs) in front of the sample and placed a photodiode (EG&G Vactec, VTB8440BH) behind the sample. We estimated transmittance on the basis of the voltage between both edges of the photodiode. The voltage $V(t)$ was obtained by calculating $V(t) = V_0(t) - V_{bg}(t)$, where $V_0(t)$ and $V_{bg}(t)$ are the raw and background values of the voltage, respectively. The background value of the voltage $V_{bg}(t)$ was measured with water kept at the same temperature as that of the sample. Transmittance was normalized from the value $V(t)$ as

$$\text{transmittance} = \frac{V(t) - V_{\text{last}}}{V_{\text{ini}} - V_{\text{last}}},$$

where V_{ini} and V_{last} are the initial and the last values of $V(t)$, respectively.

We also used small-angle neutron scattering (SANS) to observe the self-assembly structure of the surfactant in water in each case. The SANS experiments were performed at SANS-U in JRR-3 M of the Japan Atomic Energy Agency (JAEA), Tokai, Japan [17,18]. An incident neutron beam with a wavelength λ of 0.7 nm ($\Delta\lambda/\lambda = 10\%$) was selected by using a velocity selector. The distances between the sample and the two-dimensional (2D) detector were 2 and 8 m. To investigate the structural difference between cases A and B, the SANS profiles were measured before and after gelation. Since the obtained 2D data were isotropic, they were azimuthally averaged to provide 1D profiles. It should be noted that we used D_2O instead of H_2O as the solvent in order to obtain a strong contrast between the surfactant and the water, as the neutron scattering length density difference of D_2O against OTAB is much larger than that of H_2O. Owing to the deuteration effect, there was a small increase in the transition temperature to the gel phase. Hence, the SANS experiments were performed at 20 and 40 °C for samples corresponding to cases A and B, respectively. To confirm the phase of the surfactants in water, we also measured the sample with H_2O by means of small-angle X-ray scattering (SAXS) at the Photon Factory in High Energy Accelerator Research Organization (KEK), Japan (Supplementary material available). Owing to the small difference in electron density between the water and the surfactant molecules, the profiles observed by SAXS were unclear, even with the use of a synchrotron light source; however, the essential features of the profiles appeared to be the same as those observed with SANS. Therefore, we used the SANS data for the structural analysis of the surfactant in water in both cases A and B.

3. Results

3.1. Growth process of gold nanorods observed by SEM

Fig. 2 shows the time series for the morphology of gold nanorods grown at 15 °C (case A). It can be seen that almost all the nanorods were thin at the beginning of the growth process,