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The effects of structural transition of surfactant self-assembly on the growth of gold nanroods

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Introduction

It is well known that gold nanorods grow spontaneously in aqueous solution of cationic surfactant. A gold nanorod is one of the fascinating nano-materials, which has several tens of nm in diameter and several hundreds of nm in length. The applications of gold nanorods are actively studied and it is important to control the aspect ratio. As for the high-aspect-ratio gold nanorods, however, the growth mechanism has not been studied enough to control the shape and size precisely.

Recently, we have reported the high yield synthesis of high-aspect-ratio gold nanorods. In the synthesis, we used mixed aqueous solution of cetyltrimethylammonium bromide (CTAB) and stearyltrimethylammonium bromide (STAB), and revealed that the elongation of gold nanorods closely relates to the gelation of surfactant growth solution by the decrease in temperature. In this paper, we studied the relationship between the growth process of high-aspect-ratio gold nanorods and the gelation of surfactant growth solution. Small angle X-ray scattering (SAXS) revealed the microscopic feature of gelation as the structural transition of self-assembly of surfactant molecules from micellar to lamellar.

Results and Discussion

Figure 1 shows the time changes of long-axis length of gold nanorods, which were measured by transmission electron microscopy (TEM) observation. The initial temperature of the growth was 40 °C, and then the samples A and B grew at 15 °C and 35 °C, respectively. By comparing figures 1a and 1b, we can see that the growth of sample B (Fig, 1b) was saturated earlier than that of sample A (Fig. 1a). Besides of the saturation time, the resulting long-axis lengths were quite different. In other words, it is indicated that these differences of the saturation time for growth and the resulting long-axis length should stem from the gelation of growth solution: the structural transition of some kinds of self-assembly of surfactant molecules.

Generally, ionic surfactants have a Krafft temperature, at which the solubility of the surfactant becomes equal to the critical micelle concentration (CMC). Above this temperature, the surfactant solution becomes micelles, while below this temperature, the surfactant solution exhibits the coagel phase: a periodic structure of solid bilayer membranes and water layers between them (so-

called lamellar structure). The Krafft temperature of mixed surfactant ranges from 26 to 38 °C, which correspond to those of CTAB and STAB, respectively. Therefore the gelation observed in this experiment should be attributed to the Krafft transition.

Figure 2 shows the small angle X-ray scattering (SAXS) profiles for the mixed surfactant solution after keeping it at 15 °C over 12 h. The sharp peak appears around 0.036 Å^{-1}. By the above discussion, we can identify the sharp peak as the Bragg peak of the periodic stacking of lamellae in the coagel phase.

It is known that a gold nanorod is covered with a bilayer of surfactant membrane in a growth solution. Thus gold nanorods grow in the aqueous phase in the lamellar structure which is confined in nanometer size space, when the growth solution becomes gel. It means that the observation for the structural change of surfactant self-assembly accompanied with gelation is important for considering the growth mechanism of high-aspect-ratio gold nanorods. Actually, we revealed that the short-axis length of gold nanorods are determined by the curvature of outer layer of surfactant bilayer around gold nanorods[2]. Hence the formation mechanism of gold nanorods will be brought about by deeper understanding of the inner structure of surfactant solutions at a molecular scale.
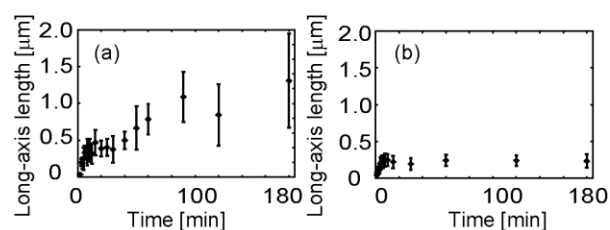

Fig. 1 Time changes of long-axis length of gold nanorods. Copyright American Scientific Publishers.
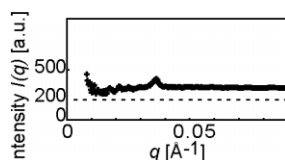

Fig.2 SAXS profiles for the mixed surfactant solution. Copyright American Scientific Publishers.

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