Two-dimensional Aggregates of Gold Nanorods Prepared at a Hexane-Water Interface in the Presence of Additional Amphiphilic Molecules

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Two-dimensional (2D) aggregates of gold nanorods (NRs) were prepared at a liquid-liquid interface by addition of acetonitrile to phase-separated solutions of hexane and a colloidal NR solution. The 2D-aggregates were transferred onto hydrophilic glass substrates by using vertical dipping. In the absence of additional surface-capping agents, the NRs formed densely-packed 2D-aggregates at the interface. Additional amphiphilic molecules, namely phosphatidylcholine in acetonitrile and didodecyldimethylammonium bromide in the hexane phase, give a loosely-packed 2D-aggregates showing two surface plasmon bands that correspond to those of isolated NRs.

Key words: gold nanorod, monoparticle film, two-dimensional aggregation, phosphatidylcholine

1. INTRODUCTION

Self-assemblies of metal/semiconductor nanoparticles at an interface [1, 2] have been attractive research targets over the past decade, due to their unique properties depending on nanoscale periodic structures. The two-dimensional (2D) assemblies of the nanoparticles are required for sensing [3, 4] and electronic [5-7] applications. A number of strategies have been adopted to assemble nanoparticles at liquid-solid/air interfaces. Some such methods include organization of nanoparticles via simple solvent evaporation on a solid-surface [5, 8-11], attachment onto chemically modified solid-surfaces via covalent interactions [3, 4], and the Langmuir-Blodgett (LB) techniques at air-liquid interfaces [7, 12, 13]. Each technique can control the alignment of the nanoparticles in its own ways; the reversible metal-insulator transitions of silver nanoparticles at an air-liquid interface are a typical example proving that the nanoscale periodic structures control the macroscopic characteristics of the nanoparticle-assemblies [7].

Recently, it has been reported that rod-shaped gold nanoparticles (gold nanorods, NRs) can be organized as 2D-assemblies on a solid substrate by the solvent evaporation [11] and the LB method [13]. Anisotropic features of the NRs assemblies gave very interesting alignment and packing structures depending on solvent, electrolytes, and surface conditions of NRs. In our previous paper, we prepared 2D-aggregates of NRs at a hexane-water interface that could be transferred onto a glass substrate as monoparticle films [14]; however, the degree of packing and homogeneity of the films could not be controlled. In this study, we have tried to establish a new technique to control the packing structures of the 2D-aggregates at the interface by using additional amphiphilic molecules that are expected as additional capping agents for NR.

2. EXPERIMENTAL SECTION

Colloidal NRs were supplied by the Central Research Institute NAKA Research Center of Mitsubishi Materials Corporation. The NRs were prepared by the combined method of chemical reduction and photoirradiation [15]. The NRs solution was centrifuged at once just before the film preparation to decrease the concentration of hexadecyltrimethylammonium bromide (CTAB) that was indispensable to NR synthesis. The aspect ratio of the NRs was about 6 (11×65 nm). An absorption spectrum of the NR solution showed two absorption peaks that are assignable to transverse (520 nm) and longitudinal (~900 nm) modes of surface plasmon (SP) oscillations (Fig. 1).

The gold NR films were prepared by the following procedure that is similar to the method described in the literatures [14, 16, 17]. Briefly, the aqueous colloidal solution of NRs (20 mL, 0.3 ~ 1.2 mM (Au atoms)) and hexane (10 mL) were added in a vial to form a hexane-water interface. Ten mL of acetonitrile was vigorously injected into the colloidal solution. The addition of acetonitrile changed the reddish color of the colloidal solution into transparent, and produced a film of the NRs at the liquid-liquid interface. The film was transferred onto a glass plate (~1 × 4 cm) by vertical lifting from the bottoms of the vial through the film [14].

A spectrophotometer (JASCO V-570) that equipped integrating sphere was used to have absorption spectra. Monitor light was focused in a small area (~ 2 × 2 mm) on a substrate that was fixed in front of the integrating sphere. A scanning electron microscopy (SEM, Hitachi S-5000) was used to investigate the shape and distribution of the NRs in the films. Absorption spectra of the monoparticle films at the liquid-liquid interface were obtained by a multichannel spectrophotometer equipped an optical fiber (Ocean Optics, SD1024DWX). White light of a halogen lamp, which runs through the

interface from the bottom to the top of the vessel, was focused at one end of the optical fiber.

3. RESULTS AND DISCUSSION

Fig. 2 shows absorption spectra [A] and a macroscopic photograph [B] of the NRs films on glass substrates. The absorption spectra showed a very broad SP band that was very different from as-prepared NRs solution (Fig. 1). The spectra were assignable to aggregates of NRs [18]. Absorbance of the NRs films increased with an increase of the NRs concentration in the water phase; however, these spectral profiles were almost independent to the NRs concentrations. This indicated that the NRs form aggregates on the substrate; plasmon-plasmon coupling interactions between the NRs diminish and broaden the SP bands [14, 18]. Thus, the degree of the aggregation was independent to the NRs concentrations in the water phase. The macroscopic photograph (Fig. 2[B]) shows that the NRs films were inhomogeneous in the cases of the NRs concentrations are 0.6 (e) and 0.3 mM (f).

Fig. 3 is a typical scanning electron microscopic (SEM) image of the NRs film formed by using 1.2 mM of NRs solution, which corresponded to Fig. 2(a, d). It is notable that three-dimensional stacking structures are not frequently observed in the image; the NRs form a 2D
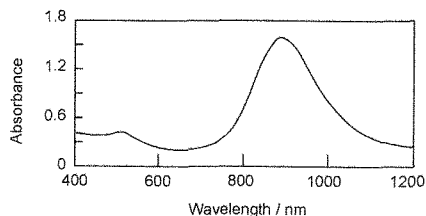

Fig. 1. Absorption spectrum of the twice-centrifuged NRs solution (1.2 mM (Au atoms)). Thin optical cell was used to have the spectrum (1 mm).
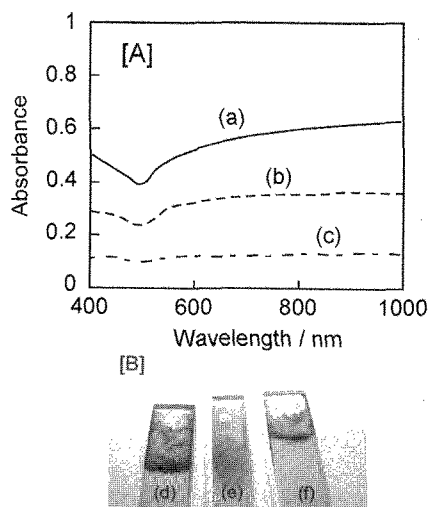

Fig. 2. Absorption spectra [A] and the macroscopic photograph [B] of the NRs films on the glass substrates. Concentrations of NRs in the water phase (a, d) 1.2, (b, e) 0.6, (c, f) 0.3 mM (Au atoms). The rectangle shown in (e) approximately presents the area where the absorption spectra (b) are obtained.

packed structure. In the cases of 0.6 and 0.3 mM of NRs solutions, degrees of the 2D packing were similar to that of Fig. 3 (data is not shown). This was consistent with the profiles of the spectra in Fig. 2(a-c). It is plausible that the addition of the acetonitrile decreases the repulsive interaction between the NRs, and results in formation of densely-packed 2D-aggregates at the hexane-water interface.

Fig. 4 shows absorption spectra [A] and a macroscopic photograph [B] of NRs films that were prepared in the presence of additional capping-agents in the hexane phase. Concentration of the NRs in the water phase was 0.3 mM, which corresponded to the case of the Fig. 2(c) and (f). When dodecanethiol (DT) was dissolved in the hexane phase, the NRs film showed the same spectrum (a) with that in the absence of the additional capping-agents (Fig. 2). Thus, the DT did not suppress the formation of NRs aggregates at the hexane-water interface. The absorption spectra of the NRs films prepared by using didodecyldimethyl-ammonium bromide (DDAB, (b)) and hexadecanethiol (HD, (c)) showed smaller absorbance than that of
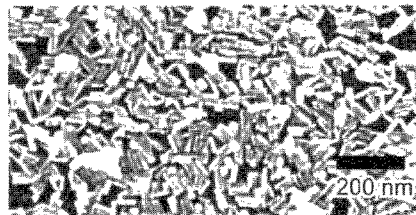

Fig. 3. SEM image of the NRs film prepared in absence of additional capping agents. Experimental conditions were same conditions with that of Fig. 2(a, d). Concentration of the NRs in the water phase was 1.2 mM (Au atoms).
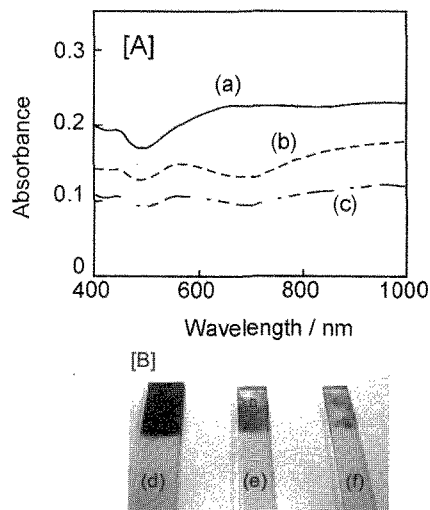

Fig. 4. Absorption spectra [A] and the macroscopic photograph [B] of the NRs films on the glass substrates, that were prepared by using the hexane phases containing dodecanethiol (DT) (a, d), didodecyldimethylammonium bromide (DDAB) (b, e), and hexadecanethiol (HT) (c, f). Concentration of the NRs in water and the additional capping-agents in hexane were 0.3 and 1 mM, respectively.

DT (a). This is due to non-stoichiometric transfer of the NRs films from the interface onto the substrates. It was observed that much amount of the NRs at the interface was retained at the interface after the dipping. Because the thiol compounds did not dissolve in the water phase, the thiol compounds probably adsorb at the interface, and affects the properties of the NRs films at the interface. Thus, as shown in the macroscopic photograph (Fig. 4[B]), the DT and HT in the hexane phase ((d), (f)) did not improve the homogeneity of the NRs films. The thiol molecules were not suitable to disperse the NRs isolatedly at the interface.

On the other hands, the NRs film prepared by using the DDAB-containing hexane phase (DDAB-NRs film), Fig. 4(e), is homogeneous at the beginning part of the dipping (down side of the substrate). In addition, the DDAB-NRs film showed an absorption band corresponding to the transverse SP mode could be observed at around 570 nm (Fig. 4(b)). The absorption band implies that the NRs were not completely isolated each other in the DDAB-NRs film, but the interactions between the NRs were not so strong to diminish the SP bands of NRs. The DDAB molecules having double methylene chains may contribute as filler between the NRs.[19]
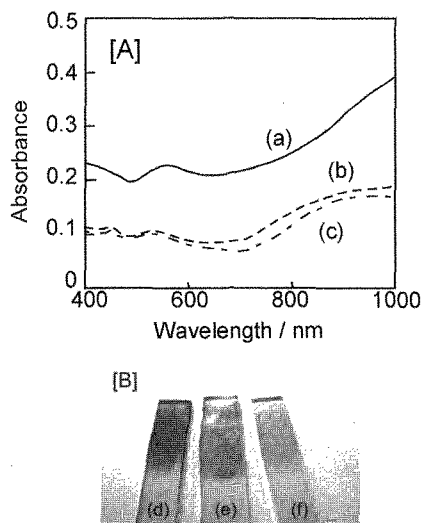

Fig. 5. Absorption spectra [A] and the macroscopic photograph [B] of the NRs films on the glass substrates, that were prepared by using the acetonitrile solution of PC (1mM). Concentrations of NRs in the water phase (a, d) 1.2, (b, e) 0.6, (c, f) 0.3 mM (Au atoms).
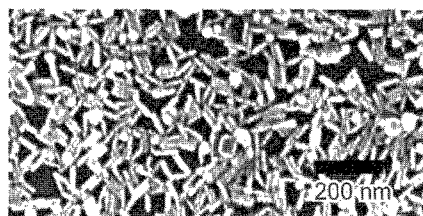

Fig. 6. SEM image of the NRs film prepared by using the PC-acetonitrile solution. Experimental conditions were same conditions with that of Fig. 2(a, d). Concentration of the NRs in the water phase was1.2 mM (Au atoms).

Phosphatidylcholine (PC), which was a typical phospholipid, was added in the acetonitrile as an additional capping-agent (PC-acetonitrile solution). Fig. 5 shows absorption spectra [A] and a macroscopic photograph [B] of the NRs films prepared by using the PC-acetonitrile solution (PC-NRs films). The transverse SP band at around 570 nm and onset of the longitudinal SP bands (~900 nm) can be clearly observed in the spectra. This indicates that the degree of the aggregation was different from that in the absence of the additional surfactants (Fig. 2[A]). The PC molecules also contributed as filler between the NRs. The PC-NRs films showed their longitudinal SP bands in longer wavelength region than 900 nm; in contrast, the as-prepared NRs showed their longitudinal SP band at around 900 nm (Fig. 1). This shift probably comes from the coupling interactions of the SP oscillations [17]. It is probable that weaker interactions than that in the case of Fig. 2 shift the longitudinal bands in the longer wavelength region. The macroscopic photograph [B] showed that the homogeneities of these NRs films are similar to that of DDAB-NRs film (Fig. 4(e)). Thus, the PC in the acetonitrile is another effective surfactant to improve the homogeneity of the NRs films.

Fig. 6 is a SEM image of the PC-NRs film prepared by using 1.2 mM of the NRs solution. It is shown that density of the NRs is smaller than that of Fig. 3. Thus, the two SEM images, Figs. 3 and 6, indicate that the spectral profiles of the NRs films depend on the mean distance between the NRs.

Absorption spectra of the monoparticle films at the water-hexane interface are shown in Fig. 7. Because of the limitation of the detectable wavelength region of the multichannel spectrophotometer used for this experiments, we could not evaluate the spectra of longitudinal SP bands in the near IR regions longer than 800 nm; however, the spectra are enough to discuss the transverse SP bands that also prove the conditions of aggregation of the NRs at the interface. In the absence of the additional stabilizing-agents [A], no SP band could be seen in the spectra. The profiles of the absorption
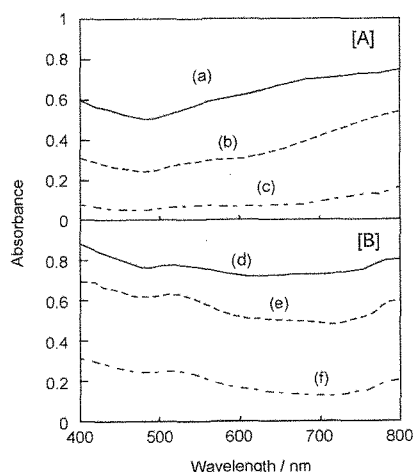

Fig. 7. Absorption spectra of the NRs film at the hexane-water interface in the absence of additional capping agents [A], and of the PC-NRs film [B]. Concentrations of NRs in the water phase (a, d) 1.2, (b, e) 0.6, (c, f) 0.3 mM (Au atoms).

spectra were almost independent to the NRs concentration in the water phase. This indicates that the NRs form 2D-aggregates at the interface, irretrievable of the NRs concentrations. The NRs aggregates forms densely packed structures to diminish the SP bands, probably due to the strong interactions between the NRs after the acetonitrile injection. Fig. 7[B] shows absorption spectra of the NRs films in the presence of the PC in acetonitrile. Transverse SP bands at around 525 nm could be seen in every spectrum. This indicated that the NRs were isolated each other. The PC was effective to suppress formation of the densely packed 2D-aggregates at the interface. These results were consistent with that of the NRs films on the glass substrates. Thus, it is probable that the NRs films at the interface were transferred onto the glass substrates without remarkable reconstruction of the 2D-aggregates.

The reason why the NRs adsorb at the hexane-water interface after the addition of the acetonitrile is not quantitatively clear at present stage; however, qualitatively, deformation of CTAB bi-layers, which are formed on NRs [20, 21], is a trigger of the specific adsorption of the NRs. In the absence of the hexane phase, addition of the acetonitrile into the NRs solution results in formation of 2D-aggregates in the solution. The hexane-water interface probably gives the two-dimensional field that is favorable for the adsorption of NRs. The characteristics of the interface must depend on molecular assemblies at the interface and compositions of the liquids.

Our experimental data strongly suggests that the additional surfactants probably change the characteristics of the interface as well as the molecular assemblies on the surface of the NRs. To have constant transfer of the NR film from the hexane-water interface onto a substrate, the film must flow constantly to the substrate during the withdrawing of the substrate. If a rigid film would be formed at the interface, the film transfer will be occurred only at the beginning of the withdrawing (that is the case of DT and HT in Fig. 4). When the NRs film just around the withdrawing substrate has been transferred onto a glass, no more NRs film would be provided. If a NRs film would be flexible and expandable at the interface, the film can be transferred continuously onto the substrate. Thus, homogeneity of a transferred film probably depends on flexibility of a NRs film, which reflects how the NRs can move around at the hexane-water interface. Probably because the DDAB in hexane phase and PC in acetonitrile provided repulsive interaction between the NRs, the amphiphiles were effective to give flexible and expandable films at the interface. This gave the homogeneous NRs films on the substrates.

In summary, control of the packing structure or density of the 2D-aggregates of the NRs has been achieved by the additional capping-agents. The thiol compounds (DT and HD) in hexane phase were not preferable to have homogeneous films. The DDAB in hexane phase and the PC in acetonitrile were effective to suppress densely-packed aggregation and enhance the homogeneity of the NRs films. We would like to go on to thermodynamic analysis of the hexane-water interface. It will be important to prove the mechanism of the formation of the 2D-aggregates at the hexane-water

interface, and give guidelines how can we control the properties of the aggregates more precisely.

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