

Two-and Three-dimensional Organization of Gold Nanoparticles

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Abstract— Two- and three-dimensional array of dendrimer-passivated gold nanoparticles was constructed by adsorbing them to hydrophilic surface of arachidic acid Langmuir film from water subphase. Langmuir-Blodgett (LB) films transferred on solid substrate were characterized. Adsorption of hybrid nanoparticles on the LB film was determined by infrared absorption spectroscopy. Atomic force microscopy and transmission electron microscopy supported two- and three-dimensional organization of nanoparticles on the LB films. Surface hydrophilicity of the arachidic acid LB film evaluated by contact angle was not strongly modified by the adsorption of dendrimer-passivated gold nanoparticles.

Keywords— Dendrimer, Langmuir-Blodgett film, nanoparticle, two-dimensional organization, three-dimensional organization

I. INTRODUCTION

Metal nanoparticles are expected the applications for chemical catalysis, photomarker, electron-tracer and so on. The arranging of particles into two- and three-dimensional space will advance the development for the applications to conductive ultra-fine films, nanosensors or micro-devices. Size and surface property of metal particles strongly affect the electric properties, physical adsorption and organization of particles. The trial for controlling the size and polydispersity of particles was carried out for preparing nanometer-sized monodisperse particles [1]. Moreover, for enforcing the dispersion of nanoparticles in medium, nanoparticles were protected by ions, surfactants or polymers.

The preparation of metal particles protected by water-soluble dendrimers gives some advantages. First, water-dispersibility of particles increases. Water-soluble poly(amido amine) (PAMAM) dendrimers with hydrophilic terminals were used for the surface modification of metal nanoparticles [1]. Second, dendrimers have cavities as reservoir for the reaction at the surface of nanoparticles. Titanium dioxide covered by PAMAM dendrimer reacted as photocatalyst doubly in comparison with bare titanium dioxide [2]. In the present work, we report the accumulation of dendrimer-passivated gold nanoparticles.

II. EXPERIMENTAL

Arachidic acid ($\text{CH}_3(\text{CH}_2)_{18}\text{COOH}$) was purchased from

Wako Pure Chemical Industries, Ltd. Fourth generation (G4) amine-terminated PAMAM dendrimer was purchased from Sigma-Aldrich Corporation. Other reagents are of commercial grade.

Dendrimer-passivated gold nanoparticles were prepared as reported before [1]. An aqueous solution of $\text{Na}[\text{AuCl}_4]$ was mixed with a methanol solution of dendrimer at the ratio of $\text{Au}^{3+}:\text{NH}_2$ group (= M : D) = 1 : 10 or 1 : 100. An aqueous solution of reduction agent, NaBH_4 , was slowly added to the mixed solutions while stirring. After added tetrahydrofane (THF), the precipitate was separated by decantation and washed by THF. Dried powder was redispersed in water.

The preparation of LB films was carried out on Nippon Laser & Electronics Lab. Langmuir film of arachidic acid from a chloroform solution (1.0 mg/cm^3) was expanded on water subphase, where dendrimer-passivated gold nanoparticles were dispersed at a concentration of 0.49 or $2.5 \times 10^{-3} \text{ wt } \%$ for particles of M : D = 1 : 10 and 0.2 or $1.0 \times 10^{-3} \text{ wt } \%$ for particles of M : D = 1 : 100. Langmuir films at a surface pressure of 30 mN/m were transferred on freshly cleaved mica substrates (see Scheme 1). Z type LB (LB(Z)) film was prepared by the upstroke of substrate. When Langmuir film was transferred by downstroke on LB(Z) film of arachidic acid, ZX type LB (LB(ZX)) film was obtained.

Contact angle was determined from photographs of water droplets taken using a Nikon digital camera COOLPIX950. Fourier transfer-infrared (FT-IR) absorption spectra were recorded on a Bio-Rad FTS 575C spectrometer using a Harrick reflectance attachment. Atomic force microscopic observation was performed at the tapping mode on a Digital Instruments NanoScope III. Transmission electron microscopic (TEM) photographs were taken on a Hitachi H800 microscope.

III. RESULTS AND DISCUSSION

Figure 1a shows IR reflectance absorption spectra (RAS) of cast, LB(Z) and LB(ZX) films prepared from a chloroform solution of arachidic acid. Three IR spectra resemble each other and display characteristic absorption bands of arachidic acid. However, intensity of LB(ZX) film is double of that of LB(Z) film, indicating the reasonable transfer of Langmuir film to LB film. IR RAS spectra of hybrid nanoparticle-adsorbed arachidic acid LB films are compared with a spectrum of a cast film of dendrimer-passivated nanoparticles at the M : D ratio of 1 : 100 in Figure 1b. Two IR spectra at different particle dispersion concentrations in the Langmuir trough are almost similar, and characteristic absorption bands originating arachidic acid and

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dendrimer coexist in the spectra, supporting the adsorption of hybrid nanoparticles. Similar IR spectroscopic profiles were observed for the hybrid nanoparticle system of M : D ratio = 1 : 10.

AFM images and contact angles of water droplet were examined for cast films and LB films of arachidic acid and hybrid nanoparticle-adsorbed arachidic acid, as given in Figures 2-4 and Table 1. While a cast film of arachidic acid displays arachidic acid domains of 0.5 nm height and <200 nm width, cast films of hybrid nanoparticles do particle domains with 5~10 nm height and 200~400 nm width, although the contact angle of all cast films is less than 20° because of wide area of free hydrophilic mica surface.

While surfaces of LB(Z) and LB(ZX) films of arachidic acid are both very smooth, since Langmuir monolayer of arachidic acid is formed at high density, as reported previously [3]. However, water contact angle is different, depending on hydrophobic surface of LB(Z) film and hydrophilic surface of LB(ZX) film (see scheme 1). Meanwhile hybrid nanoparticle-adsorbed LB(ZX) films are partly covered by terrace. The terrace is commonly of about 4 nm in height and accumulated by second or multi-layer with similar layer thickness. Terrace size and accumulation are stimulated at high particle concentration in the Langmuir trough. In addition, the higher dendrimer content in hybrid nanoparticles seems to affect on the stimulation of two-dimensional array and accumulation, being equivalent to the larger aggregates on the cast film. It should depend on the interaction between amine-terminated dendrimers to promote the two- and three-dimensional ordering. In the event, it can be noted that dendrimer-dendrimer interaction is stronger than dendrimer-arachidic acid interaction. The adsorption of dendrimer-passivated nanoparticles on arachidic acid monolayer is confirmed from water contact angle. The contact angle of hybrid nanoparticle-adsorbed LB(ZX) film slightly decreases with adsorption from concentrated hybrid nanoparticle dispersion.

The adsorption of hybrid nanoparticles and terrace formation was also examined by TEM. In an adsorption film at M : D = 1 : 10, domain texture are almost round, as seen in Figure 5a. However the domains in an adsorption film at M : D = 1 : 100 are somewhat infinite and polydispersity. Moreover, while most of domains are at homogeneous thickness, some of domains are thicker, indicating the formation of multi-layer.

IV. CONCLUSION

The dendrimer-passivated gold nanoparticles in water subphase were adsorbed on Langmuir film of arachidic acid. The nanoparticles formed two-dimensional terrace and three-dimensional accumulation on the film. The formation of terrace and accumulation was promoted with increasing concentration of nanoparticles in the water subphase and for nanoparticles with high dendrimer-passivation. The results are due to the stronger interaction between dendrimers than the interaction between dendrimer and arachidic acid.

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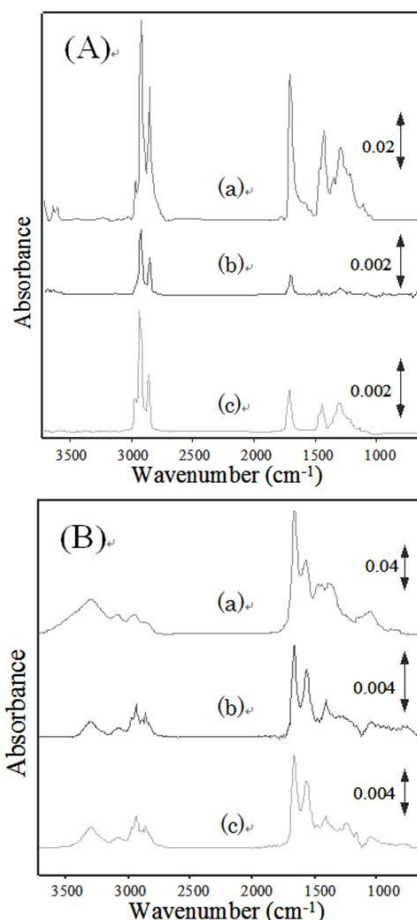


Fig. 1 FT-IR RAS of cast and LB films. (A) arachidic acid (prepared from chloroform solution of 1.0 mg/cm³); (a) cast film, (b) LB(Z) film, (c) LB(ZX) film. (B) dendrimer-passivated gold nanoparticle at M : D = 1 : 100; (a) cast film (prepared from aqueous dispersion of 0.39 mg/cm³, (b) on arachidic acid LB(ZX) film (adsorption on arachidic acid Langmuir monolayer from water subphase of a particle concentration of 0.002 mg/cm³), (c) on arachidic acid LB(ZX) film (adsorption on arachidic acid Langmuir monolayer from water subphase of a particle concentration of 0.01 mg/cm³). LB films were prepared at a surface pressure of 30 mN/m.

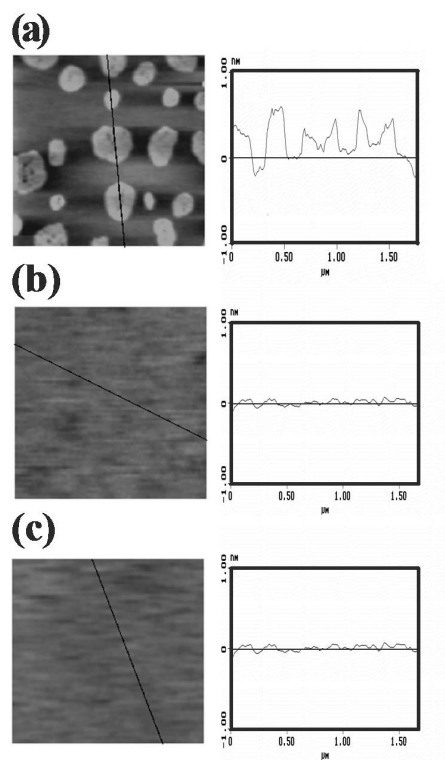
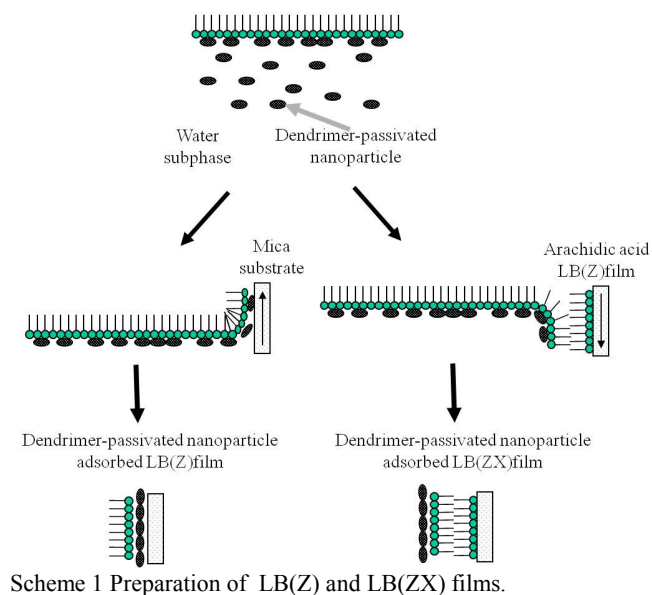


Fig. 2 AFM images and their section analyses of cast and LB films of arachidic acid (prepared from chloroform solution of 1.0

TABLE I
Contact angle of water droplet on cast films and LB films of arachidic acid and hybrid nanoparticle-adsorbed arachidic acid

	Arachidic acid	Hybrid nanoparticle (Au : NH ₂ = 1 : 10)	Hybrid nanoparticle (Au : NH ₂ = 1 : 100)
Cast film	5~10°	10~20°	5~15°
LB(Z) film	90~100°		
LB(ZX) film	50~60°	50~60°a), 40~50°b)	50~60°c), 40~50°d)

a) 0.0049 mg/cm³ dispersion. b) 0.025 mg/cm³ dispersion.

c) 0.002 mg/cm³ dispersion. d) 0.01 mg/cm³ dispersion.

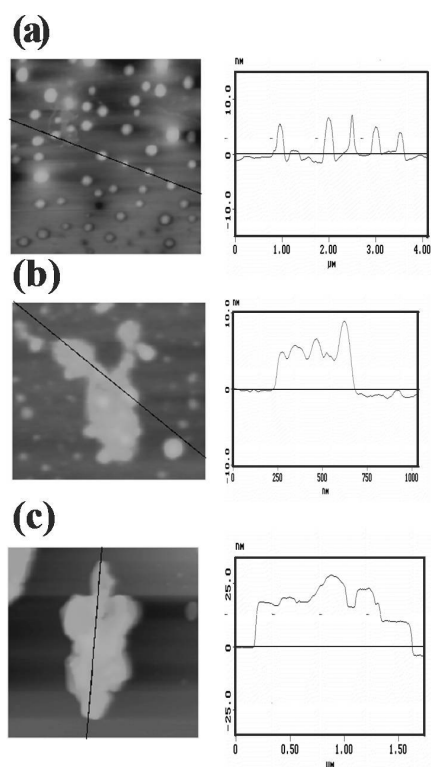


Fig. 3 AFM images and their section analyses of cast and LB films of dendrimer-passivated gold nanoparticle at M : D = 1 : 10; (a) cast film (prepared from aqueous dispersion of 0.98 mg/cm³, (b) on arachidic acid LB(ZX) film (adsorption on arachidic acid Langmuir monolayer from water subphase of a particle concentration of 0.0049 mg/cm³), (c) on arachidic acid LB(ZX) film (adsorption on arachidic acid Langmuir monolayer from water subphase of a particle concentration of 0.025 mg/cm³). LB films were prepared at a surface pressure of 30 mN/m.

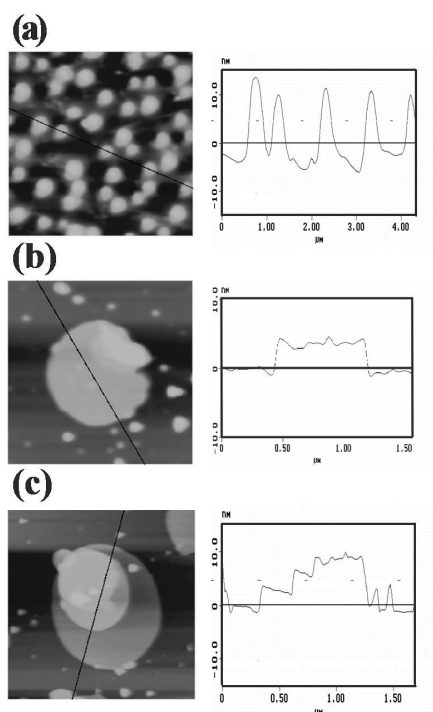


Fig. 4 AFM images and their section analyses of cast and LB films of dendrimer-passivated gold nanoparticle at $M : D = 1 : 100$; (a) cast film (prepared from aqueous dispersion of 0.39 mg/cm^3), (b) on arachidic acid LB(ZX) film (adsorption on arachidic acid Langmuir monolayer from water subphase of a particle concentration of 0.002 mg/cm^3), (c) on arachidic acid LB(ZX) film (adsorption on arachidic acid Langmuir monolayer from water subphase of a particle concentration of 0.01 mg/cm^3). LB films were prepared at a surface pressure of 30 mN/m .

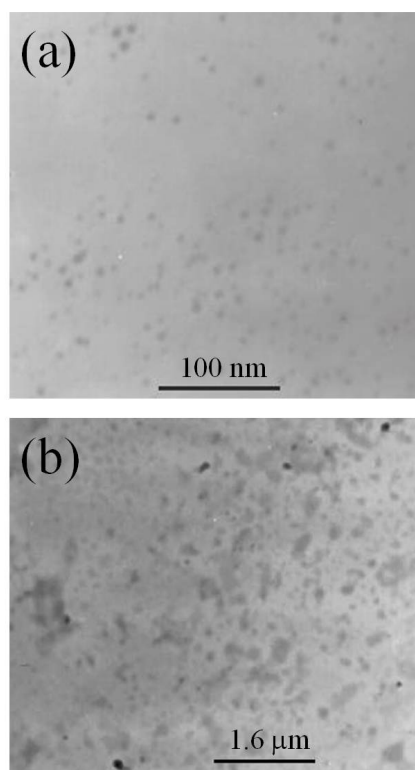


Fig. 5 TEM photographs of LB films of dendrimer-passivated gold nanoparticle. $M : D$: (a) $1 : 10$ (adsorption on arachidic acid Langmuir monolayer from water subphase of a particle concentration of 0.025 mg/cm^3); (b) $1 : 100$ (adsorption on arachidic acid Langmuir monolayer from water subphase of a particle concentration of 0.01 mg/cm^3). LB films were prepared at a surface pressure of 30 mN/m .