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ORIGINAL CONTRIBUTION

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Template functions of particle monolayers on hydrophobic solid substrates

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Abstract The template function of cationic particle monolayers bearing quaternary ammonium groups on their surfaces towards anionic colloids was investigated in this paper. Monodispersed cationic polymer particles having quaternary ammonium groups were self-organized on octadecylated glass plates through hydrophobic interaction. The morphology of the resulting particle monolayers was changed by tuning hydrophilic–hydrophobic balance of particles to fabricate aggregated type and dispersed type of particle monolayers. Gold and silver colloids were selectively deposited onto the particle monolayers through electrostatic interaction. The deposited gold and silver colloids on particle monolayers showed plasmon absorbance. Fluorescent silica colloids were also selectively deposited on particle monolayers to permit fluorescence labeling of the particle monolayers. Cationic particle monolayers fabricated on hydrophobic solid octadecylated were found to effectively work as templates for the deposition of above mentioned inorganic colloids.

Keywords Cationic particle · Hydrophobic solid substrates · Particle monolayer · Selective deposition · Plasmon absorbance

Introduction

Polymer particles with various functions are promised materials as individuals or assemblies. Recently, bottom-up technology with such particles in two and three dimensions has received much attention as production technology of new materials and devices. Fabrication of particle assemblies in two dimensions, especially, has many potential applications such as lithographic masks [1], antireflection surfaces [2], sensors [3], microlens arrays [4, 5], and surface modification of solid substrates [6, 7]. The monolayer formation of various colloids utilizing solvent evaporation method [8], Langmuir–Blodgett method [9], electrophoretic deposition method [10], and methods through chemical reaction and interaction [11, 12] has been investigated.

On the other hand, hybrid particles having metal colloids on their surface have been prepared [13–16]. Such hybrid particles have attracted considerable interest because these hybrids exhibit wide applications as active catalysts in various chemical reactions such as hydrogenation and hydrogenolysis. However, to our knowledge, the hybridization of self-organized particles on substrates has not been reported yet. In the previous paper, we reported the self-organization of cationic polymer particles bearing sulfonium and quaternary ammonium groups on hydrophobic solid substrates through hydrophobic interaction and fabricated the particle monolayers of close-packed structure with a relatively regular particle interval by tuning hydrophilic–hydrophobic balance of particles and controlling temperature [17–21]. In this work, we demonstrate that cationic particle monolayers bearing quaternary ammonium groups on their surfaces work as an effective template for selective deposition of inorganic colloids. As shown in Fig. 1, cationic polymer particles were self-organized on alkylated glass plates treated with *n*-octadecyltriethoxysilane through hydrophobic interaction, followed by the deposition of inorganic colloids (gold, silver, and fluores-

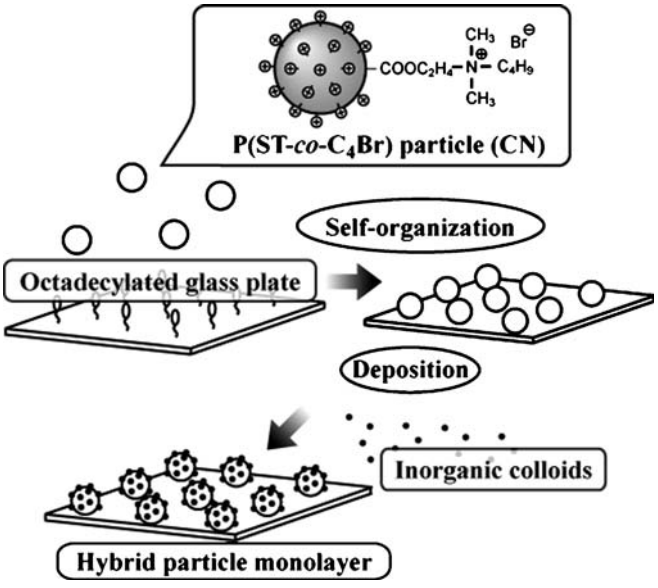

Fig. 1 Schematic representation of fabrication of hybrid particle monolayers on octadecylated glass plates

cent silica colloids) through electrostatic interaction. We used the particle monolayers as templates for selective deposition of inorganic colloids and investigated their characteristics.

Experimental

Materials and methods

Styrene (ST) was purified by distillation under reduced pressure in a nitrogen atmosphere. Water-soluble, cationic monomer, methacryloyloxyethylbutyldimethylammonium bromide (C_4Br), was prepared by the reaction of 2-(dimethylamino)ethyl methacrylate with *n*-bromobutane in acetone and purified by recrystallization. 2,2′-Azobis(2-amidinopropane) dihydrochloride (V-50) was used as radical initiator for the emulsifier-free emulsion copolymerization. Glass plates (10×26×1.0 mm) used in this study were cleaned with boiling HNO_3 solution for 1 h, washed with water, and dried in vacuum at 100 °C. *n*-Octadecyltriethoxysilane, Triton X-100, tetraethyl orthosilicate (TEOS), and tris(2,2′-bipyridyl)dichlororuthenium (II) (Ru(bpy)) were obtained from Tokyo Kasei Kogyo N/400 Potassium poly(vinyl sulfate) solution (N/400 PVSK) was used with a dilution to N/20000. Water was distilled and deionized by a Millipore system before use. All reagents were purchased from Wako Pure Chemical Industries, unless otherwise noted.

Synthesis and characterization of cationic polymer particles Emulsifier-free emulsion copolymerization of ST with a water-soluble, cationic monomer, C_4Br, was carried out in 500 ml three-necked, round-bottomed flask equipped with reflux condenser, nitrogen inlet, and mechanical stirrer. The stirring speed was maintained at 200 rpm. The flask was initially charged with ST (320 mmol), C_4Br (0.32, 3.2 mmol), and deionized water (140 g). The contents of the flask were stirred and flushed with nitrogen for about 45 min. Radical initiator, V-50 (3.2 mmol), dissolved in deionized water (20 g) was added into the flask and then the flask was immersed in a water bath thermostated at 60 °C for 12 h. The resulting latex was purified by centrifugation at 12,000 rpm for 30 min and washed with deionized water several times. The number average diameter, D_n, and the coefficient of variation, C_v, were determined using a scanning electron microscopy (SEM) (JEOL, JSM-5310). A colloid titration method was employed to determine the surface charge density of polymer particles [22]. The purified latex dispersion of cationic polymer particles was titrated with N/20000 PVSK solution using toluidine blue as indicator. The charge density on the particle surface was expressed as equivalent mole of charge groups per unit area. Characteristics of the resulting cationic polymer particles were summarized in Table 1.

Preparation of octadecylated glass plates Freshly prepared glass plates were reacted with *n*-octadecyltriethoxysilane (4.0 g) in purified toluene solution (200 ml) at 110 °C for 24 h, followed by washing with methanol and drying in vacuum. Surface characterization of octadecylated glass plates was carried out by contact angle measurements (ERMA, goniometer type, model G-I) of deionized water.

Self-organization of polymer particles on octadecylated glass plates Self-organization experiments were conducted as follows: octadecylated glass plates were immersed into latex dispersion (0.025 wt%) for 24 h, taken out of the dispersion, and washed in water by ultrasonic irradiation of 18 W at 42 kHz oscillation frequency for 5 min to remove weakly and/or physically adsorbed particles. The morphology of particle monolayers was examined by SEM.

Preparation of inorganic colloids Gold and silver colloids were prepared according to the procedures reported by Frens and Lee groups, respectively. Gold ion solutions were prepared using $HAuCl_4$ (4.8×10^{-2} wt%, 200 ml) and trisodium citrate dihydrate (1 wt%, 20 ml) [23]. Silver ion solutions were prepared using $AgNO_3$ (1.8×10^{-2} wt%, 200 ml) and trisodium citrate dihydrate (1.5 wt%, 40 ml) [24]. Each solution was heated at 100 °C for 1 h, and the resulting gold and silver colloids were used as prepared. Fluorescent silica colloids were prepared in water-in-oil microemulsion using Triton X-100 as surfactant using the method reported by Bagwe et al. [25]. The procedure consisted of mixing 8.85 g of Triton X-100, 8 ml of hexanol, 37.5 ml of cyclohexane, followed by addition of

Table 1 Characteristics of CN particles produced by emulsifier-free emulsion copolymerization[a]

Latex code	C_4Br (mol%) to ST	Yield (%)		Particle size[b]		Surface charge density[c]	A_p[d]
		Latex	Coagulum	D_n (nm)	C_v (%)	(μeq/m^2)	(A^2)
CN-0.1	0.1	96.9	1.8	336	3.1	1.33	125
CN-1.0	1.0	98.6	1.4	203	2.4	1.62	103

[a]Styrene, 320 mmol; V-50, 3.2 mmol; water, 160 g; temperature, 60 °C, stirring rate, 200 rpm; 12 h
[b]Determined by SEM. D_n Number average diameter, C_v coefficient of variation of particle size distribution
[c]Determined by colloid titration
[d]Occupied area by a charged group

2 ml of water, 400 μl of 0.1 M Ru(bpy) dye, 500 μl of TEOS, and 300 μl of NH_4OH. The reaction mixture was stirred for 24 h, followed by addition of ethanol to break the microemulsion and the particles were collected. The particles were washed twice with ethanol and then with water. The solution of silica colloids was evaporated and dried in vacuum for 24 h. Finally, silica colloids were redispersed in water and the colloidal solution was dialyzed before use.

Deposition of inorganic colloids onto particle monolayers (fabrication of hybrid particle monolayers) The cationic particle monolayers formed on octadecylated glass plates were immersed into each inorganic colloidal solution for 24 h at 25 °C, followed by washing with water. The morphologies of hybrid particle monolayers were observed by a field emission scanning electron microscope (FESEM) (JEOL, JSM 6330F). The hybrid particle monolayers were also characterized by UV and fluorescence spectroscopies. In the fluorescence measurements, the fluorescence intensity at the wavelength near 600 nm was examined for the excitation at 450 nm.

Results and discussion

Characteristics of cationic polymer particles

At first, the cationic polymer particles having quaternary ammonium groups on their surfaces were prepared to fabricate particle monolayers which were used as template for the deposition of inorganic colloids. The cationic polymer particles bearing quaternary ammonium groups were chosen in the present study to investigate the effect of kind of charge on the self-organization instead of those having sulfonium groups. Cationic polymer particles having different surface charge densities were used to get insight into the effect of hydrophilic–hydrophobic balance of particles on the self-organization.

The characteristics of the resulting cationic polymer particles are listed in Table 1. Two kinds of monodisperse, cationic particles having different diameters and surface charge densities were obtained in high yields by varying the amount of C_4Br (mol%) to ST in feed. As expected, the size and the surface charge density of CN-1.0 particle are smaller and higher, respectively, compared with those of CN-0.1 particle. With an increase of a water-soluble comonomer in emulsifier-free emulsion copolymerization, the number of particles nucleated would increase and, hence, the amount of ST supplied to the particle nuclei decreases, resulting in the decrease of particle diameter [26]. The cationic charges on CN particle surfaces would stem from initiator (V-50) fragments and water-soluble comonomer (C_4Br) units. Two kinds of particles in Table 1 were prepared at the same initiator concentration in feed and, hence, the higher surface charge density of CN-1.0 particle is due to the higher feed concentration of C_4Br. Thus, the surface charge density can be controlled by varying the molar ratio of water-soluble comonomer to water-insoluble monomer as a main component for emulsifier-free emulsion polymerization, though the particle size changes concurrently. Because cationic surface charges are hydrophilic groups, CN-1.0 particle should be more hydrophilic than CN-0.1 particle.

Self-organization of cationic polymer particles on octadecylated glass plate

Yamaguchi et al. reported that the cationic polymer particles bearing sulfonium groups on their surfaces self-organized on hydrophobic solid substrates to form dispersed or aggregated type of particle monolayers dependent on the hydrophobicity of substrates [18–20]. Furthermore, we have found that the surface coverage of particle monolayers decreased and the morphology changes from aggregated type to dispersed type with an increase of the particle surface charge density for the self-organization of cationic polymer particles having quaternary ammonium groups. The dispersed type of particle monolayers having a relatively regular particle distance was obtained by tuning the self-organization temperature [21].

Figure 2 shows SEM photographs of CN particle monolayers formed, when *n*-octadecylated glass plates exhibiting an average contact angle of 96.4 ° for water were immersed into CN latex dispersions of 0.025 wt% for 24 h under the different conditions. More hydrophobic CN-0.1 particles form aggregated type of particle monolayer in

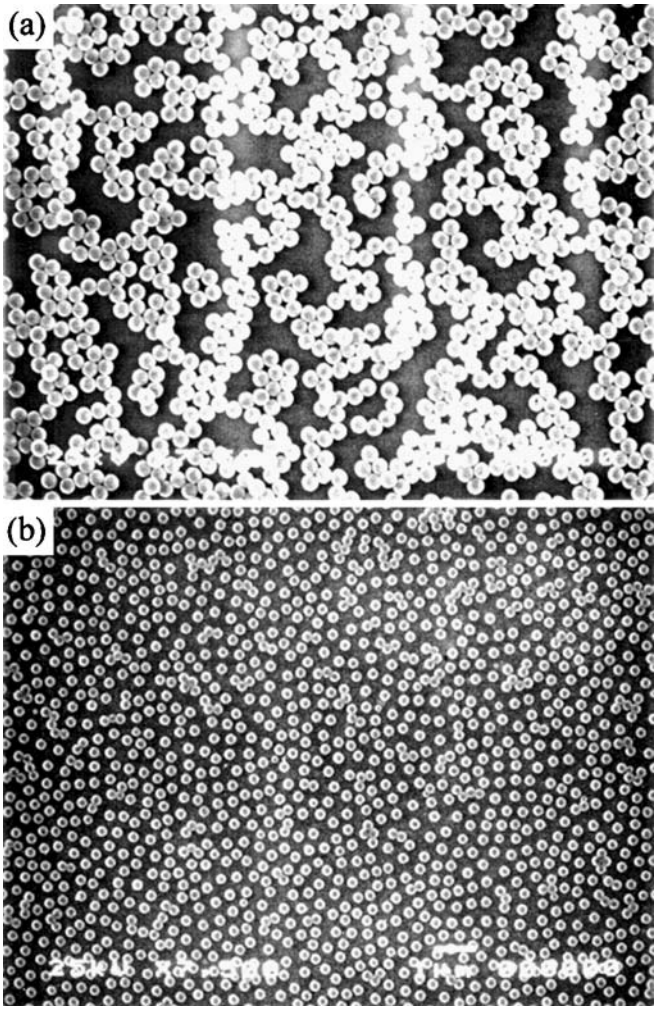

Fig. 2 Scanning electron microscope (SEM) photographs of **a** aggregated type and **b** dispersed type of particle monolayers on octadecylated glass plates. **a** Self-organized in 10 mM NaCl at 25 °C and **b** self-organized at 60 °C at latex concentration of 0.025 wt%

NaCl solution (10 mM) (Fig. 2a) and less hydrophobic CN-1.0 particles self-organized into dispersed type of particle monolayer at 60 °C (Fig. 2b). In latex dispersions containing eletrolytes, the particle electric double layer is compressed. As the result, the electrostatic repulsion between particles on the substrates becomes weaker and more closely packed, aggregated type of particle monolayers are formed. When the self-organization was conducted on octadecylated glass plates for at 25 °C, CN particles self-organized into aggregated type of particle monolayers. However, the self-organization at higher temperature (60 °C) yields dispersed type of particle monolayers having a relatively regular particle distance, as shown in Fig. 2b, together with the increase in the surface coverage. Debye length of particles would increase at higher temperature [27], resulting in increased stronger electrostatic repulsion between particles which lead to the formation of dispersed type of particle monolayers. The increase in the surface coverage at higher temperature might be ascribed to the increase in the particle collision frequency against substrates caused by more active Brownian motion. Thus, the morphology of particle monolayers greatly varies with the ionic strength of media and the self-organization temperature as well as hydrophilic–hydrophobic balance of particles.

Selective deposition of inorganic colloids on CN particle monolayers (fabrication of hybrid particle monolayers)

Particle monolayers fabricated on octadecylated glass plates, described above, have cationic charges on the particle surfaces and, hence, the monolayers may work as templates for negatively charged inorganic colloids to afford organic–inorganic hybrid particle monolayers. In this study, the deposition of gold, silver, and silica colloids was investigated to examine the template function of particle monolayers.

Wine red gold colloid solution has plasmon absorbance at 530 nm. The zeta potential in 1 mM NaCl solution was −26.7 mV, which come from trisodium citrate on the colloid surface used as reducting agent for the preparation of gold colloids [23]. The cationic particle monolayers shown in Fig. 2 were used as templates for the deposition of gold colloids. The particle monolayers were immersed into 2.4×10^{-2} wt% gold colloid solutions for 24 h at 25 °C and FESEM photographs of the resulting hybrid particle monolayers formed for aggregated and dispersed types of particle monolayers are shown in Fig. 3. It can be seen that gold colloids are selectively and uniformly deposited on the particle monolayers. The presence of gold colloids on the CN particle monolayers was also investigated by UV spectroscopy for the hybrid particle monolayers shown in Fig. 3b. Figure 4 clearly shows plasmon absorbance for the hybrid particle monolayers near the wavelength where the gold colloids exhibit plasmon absorbance. In addition, plasmon absorbance of hybrid particle monolayers is observed at 516 nm slightly lower than 530 nm for gold colloid solution, which would be caused by the change of surrounding environment of gold colloids. Furthermore, increased background for the hybrid particle monolayers would be brought by light scattering on the deposited gold colloids. Thus, gold colloids are readily deposited by immersing cationic particle monolayers into gold colloid solution to form hybrid particle monolayers, indicating that the cationic charges on particle monolayers effectively can work towards anionic gold colloids.

Next, the deposition of silver colloids and fluorescent silica colloids onto particle monolayers was examined. The cationic particle monolayers were immersed into 9×10^{-3} wt% silver colloid solution or 1×10^{-1} wt% fluorescent silica colloid solution for 24 h at 25 °C. Yellow green silver colloid solution has plasmon absorbance at 425 nm and the

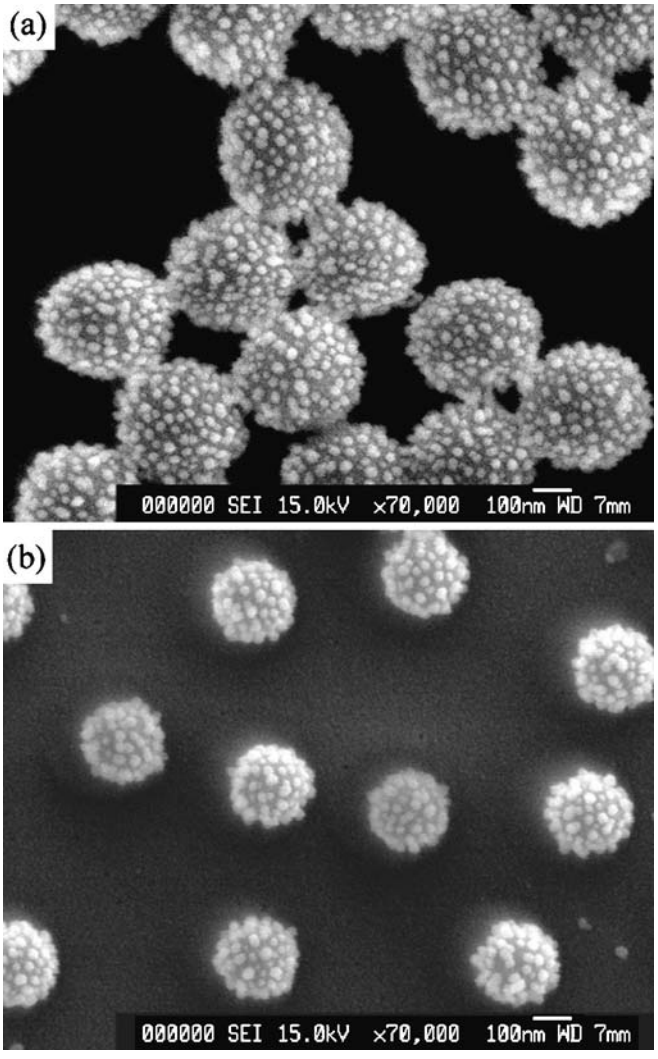

Fig. 3 Field emission scanning electron microscope (FESEM) photographs of **a** CN-0.1 and **b** CN-1.0 particle monolayers containing gold colloids on octadecylated glass plates. Particle monolayers shown in Fig. 2**a** and 2**b** were used as template. Deposition of gold colloids: [colloid], 2.4×10^{-2} wt%; temperature, 25 °C; time, 24 h

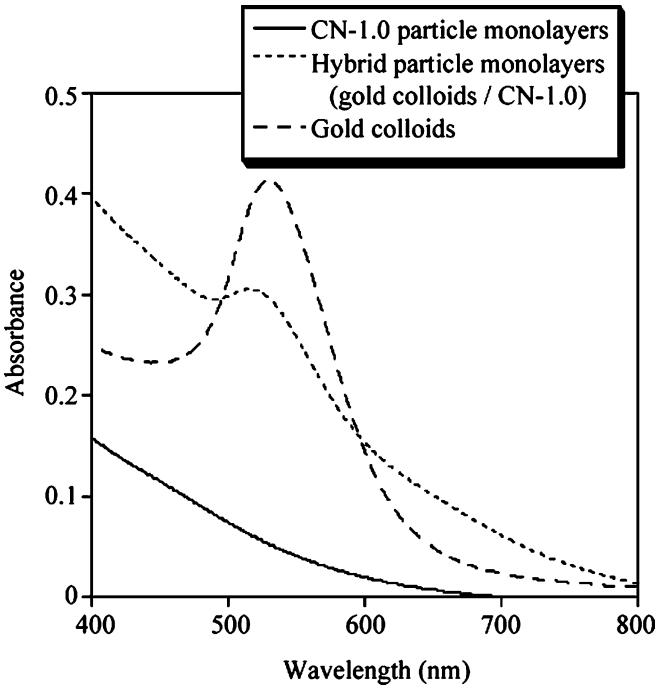

Fig. 4 UV-spectra of hybrid particle monolayers of CN-1.0 particles and gold colloids on octadecylated glass plates. Hybrid particle monolayer shown in Fig. 3**b** was used

zeta potential in 1 mM NaCl solution was −6.6 mV, considerably lower than that for gold colloids in absolute value. The zeta potential of fluorescent silica colloid in 1 mM NaCl solution was −14.0 mV. Figure 5 shows FESEM photographs of the resulting hybrid particle monolayers having silver colloids and fluorescent silica colloids. These colloids can be observed to be also selectively deposited on particle monolayers. However, the deposition of silver colloids is not uniform and less in contrast with that of gold colloids, which might result from lower zeta potential of silver colloids in absolute value. Figure 6 shows the UV spectra of hybrid particle monolayers with silver colloids. Silver colloids on the particle monolayers in Fig. 5a look like being aggregated, but the peak of plasmon absorbance for hybrid particle monolayers is observed at 410 nm slightly lower than that for silver colloid solution, though the reason is unclear at present. As can be seen in Fig 5b, silica colloids are well deposited onto cationic particle monolayers. Fluorescent dye-doped silica colloids were used to spectroscopically confirm the presence of silica colloids on hybrid particle monolayers. Figure 7 shows fluorescence spectra of hybrid particle monolayers formed using fluorescent silica colloids. Ru(bpy) exhibits a peak at 603 nm, which shifts to 586 nm on being incorporated inside silica colloids [25]. When exposed to excitation at 450 nm, the intensity at 586 nm greatly increases through the deposition of fluorescent silica colloids, indicating that particle monolayers are well labeled with fluorescent silica colloids. Thus, the particle monolayers fabricated using cationic particles with quaternary ammonium groups can be used as good templates for selective deposition of anionically charged colloids. This demonstrates that cationic charges of particle monolayers on octadecylated glass plates work well towards anionic charges.

In summary, the cationic particle monolayers fabricated in the present study effectively worked as templates for selective deposition of negatively charged, inorganic colloids such as gold, silver, and fluorescent silica colloids. The resulting hybrid particle monolayers had plasmon absorbance and fluorescent luminescence. In the present study, we have found that cationic polymer particles having quaternary ammonium groups on their surfaces also well self-organize on polymer films such as polystyrene, poly

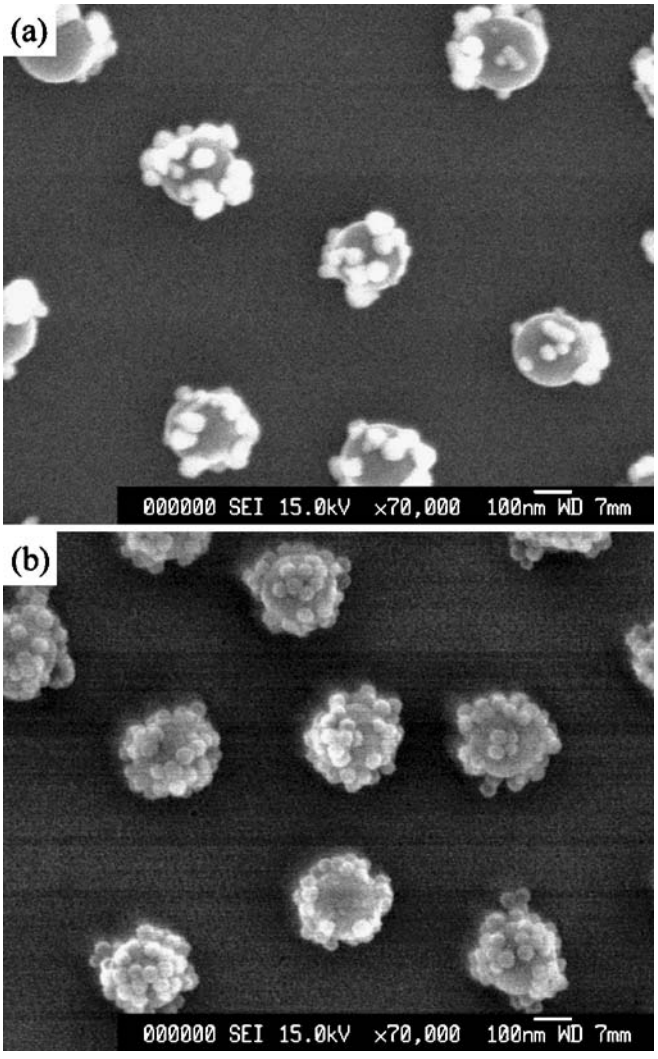

Fig. 5 FESEM photographs of CN-1.0 particle monolayers containing **a** silver colloids or **b** fluorescence silica colloids on octadecylated glass plates. Particle monolayer shown in Fig. 2**b** was used as template. Deposition of inorganic colloids: [silver colloid], 9×10^{-3} wt%; [fluorescent silica colloid], 1×10^{-1} wt%; temperature, 25 °C; time, 24 h

(ethylene terephthalate) and polycarbonate to form particle monolayers. Therefore, the results obtained in this study suggest that inorganic colloids having no interaction with polymer films can be effectively deposited through cationic particle monolayers on the films by the method described in this paper. This template technique using cationic particle monolayers would be useful as the surface modification of hydrophobic solid substrates. Furthermore, it may be applied to the fabrication for new materials such as catalysts and electroconductive materials.

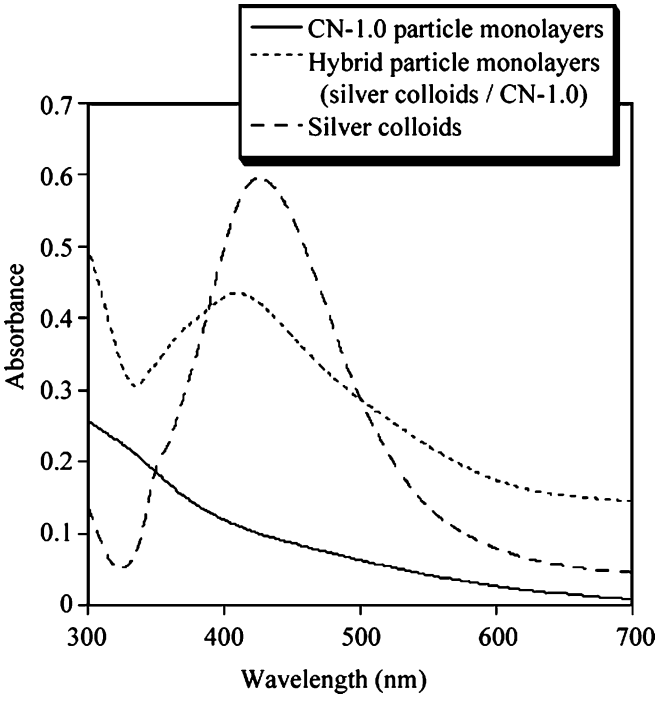

Fig. 6 UV-spectra of hybrid particle monolayers of CN-1.0 particles and silver colloids on octadecylated glass plates. Hybrid particle monolayer shown in Fig. 5**a** was used

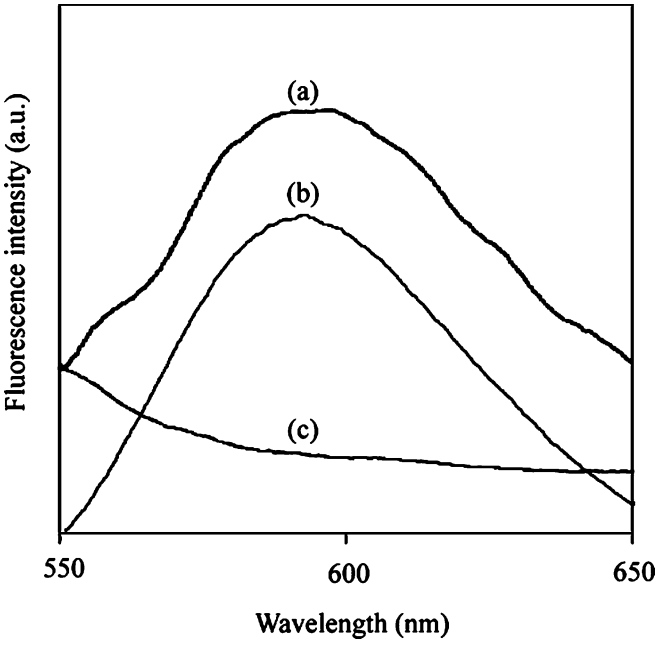

Fig. 7 Fluorescnece spectra of hybrid particle monolayers of CN-1.0 particles and fluorescent silica colloids on octadecylated glass plates. Hybrid particle monolayer shown in Fig. 5**b** was used. **a** Hybrid particle monolayer (fluorescent silica colloids), **b** fluorescent silica colloids, and **c** CN-1.0 particle monolayer

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