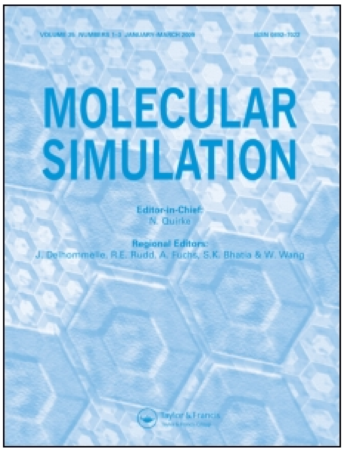

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Gold Nanoparticles Surface-confined by Hybrid Self-Assembled Monolayers of Dendrimer and Dodecanethiol

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Gold Nanoparticles Surface-confined by Hybrid Self-Assembled Monolayers of Dendrimer and Dodecanethiol

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Gold nanoparticles surface-confined by hybrid self-assembled monolayers (SAMs) were synthesized by replacement of dendrimer-passivated nanoparticles by dodecanethiol. Transmission electron microscopy, small-angle X-ray scattering (SAXS), infrared absorption spectroscopy, ^{1}H NMR and elemental analysis were performed to characterize hybrid-layer-passivated nanoparticles. The hybrid particles were separated into domains of small and large spheres. This indicates that the replacement may be dependent on the particle size.

Keywords: Dendrimer; Poly(amido amine) dendrimer; Dodecanethiol; Gold nanoparticle; Self-assembled monolayer; UV–vis absorption

INTRODUCTION

Metal nanoparticles are of great interest today because of their unusual optical, electrical, catalytic and other properties [1–7]. Homogeneous alkanethiol self-assembled monolayers (SAMs) have been used in the synthesis of stable hydrophobic nanoparticles [8–13]. The potential of hybrid SAMs [10–12] is superior to the homogeneous ones. For example, a mixed SAM generates microscopic domains of different functionality. It is, therefore, of our interest to develop systems where nanoparticles are stabilized by hybrid monolayers of fascinating molecules such as dendritic polymers [14–18] and surfactants [19].

Dendrimers are regularly-branched polymers possessing a very high concentration of surface functional groups [14–18,20–22]. Their solubility and SAM-forming ability are strongly influenced by the nature of the terminal functionalities. The dendrimers terminated by thiol, amine and hydroxyl groups are used in stabilization of water-soluble nanoparticles [7,23–25]. Recently, the complete surface modification of dendrimers accomplished by spontaneous acid-base self-assembly has been reported [24]. The dendrimer-encapsulated and doped guests (such as Pd nanoparticles and methyl orange, respectively) could be easily shuttled between hydrophobic and hydrophilic phases by adjusting the pH of the aqueous phase.

In contrast to the reversible process described above, we report an irreversible transfer of gold nanoparticle from aqueous to organic solvent without changing the solution pH and particle size or shape. The water-soluble fourth generation poly(amido amine) (G4 PAMAM) dendrimer-protected gold nanoparticle is transferred into water-immiscible medium by the formation of hybrid-layer with alkanethiol. This is the first report of such hybrid-layer formation onto the gold nanoparticle surface. The hybrid-layer of dendrimer and alkanethiol is conceptually, structurally and chemically very similar to the membrane/protein composite found in nature [26] and the thiol-dendrimer hybrid SAM on gold substrate [10,11,27,28]. Varying the quantity of thiol added for the replacement reaction will

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change the composition of the dendrimer–alkanethiol mixed monolayer.

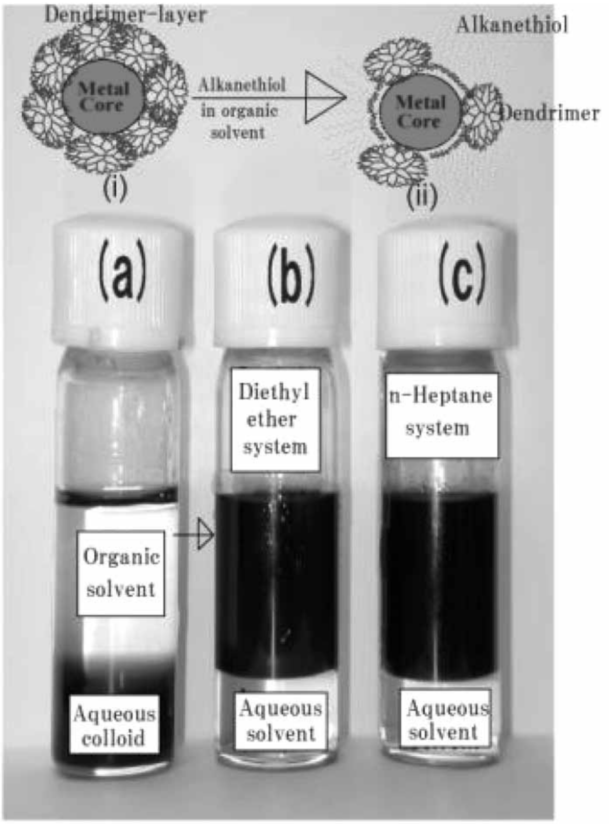

FIGURE 1 A real-time photograph of aqueous (colored) solution with transparent water-immiscible dodecanethiol solution before stirring (a) and after stirring for 10–15 h (b and c). Cartoon of nanoparticles (i) before and (ii) after stirring is illustrated in the upper part of the photograph.

EXPERIMENTAL

We preferred the 1 : 10 ratio for the Au atom–terminal amine group of dendrimer to prepare the colloid. The synthesis procedure is similar to that reported in literatures [29]. Briefly, 10 cm^3 of aqueous 10 mM $NaAuCl_4$ solution, 2.22 g (1.56×10^{-5} mole dendrimer) of methanol solution of dendrimer (10 wt%), and 5 cm^3 of methanol were mixed together to produce a reaction mixture. Five cubic centimeter of aqueous 200 mM $NaBH_4$ solution was added slowly to the stirred reaction mixture to form very stable brown colloid of dendrimer-passivated gold nanoparticles.

Five cubic centimeter of colloid dispersion and 5 cm^3 of *n*-heptane or diethyl ether solution of dodecanethiol (0.85 or 1.7 mM) were kept together in a glass vessel. The mixture was vigorously stirred, until the aqueous phase decolors completely. A complete color transfer from aqueous to organic layer was observed after 10–15 h stirring, as shown in Fig. 1. The organic phase was collected and washed by water–MeOH (2 : 1) mixture for several times to eliminate the dissolved free G4 PAMAM (if any) in organic phase. The particles were precipitated by the addition of ethanol. Then solid product was isolated as a blackish-brown and very sticky material in which both G4 PAMAM and dodecanethiol were adsorbed onto gold nanoparticle surface. The product, hybrid-layered gold nanoparticle, forms a stable dispersion in water-insoluble solvent. The hybrid-layer was formed onto the particle surface through the ligand replacement reaction.

CHARACTERIZATION AND DISCUSSION

The bright field TEM (Hitachi H-800) of nanoparticles passivated by (a) G4 PAMAM and (b) hybrid-layer are shown in Fig. 2. The photographs show that all the particles are almost spherical. The particle size analysis on a photograph of Fig. 2(a) reveals that particles are 5.1 ± 1.4 nm in size and did not agglomerate during the preparation of TEM specimen, that is, the drying of a thin film of nanoparticle dispersion. The average diameter of dendrimer-passivated colloidal particles remains unchanged during hybrid-layer formation.

The photograph of the hybrid-layer-passivated particles (Fig. 2 (b)) shows a distinct tendency to microphase-separate into domains of small and large spheres, that is, an approximately bimodal ensemble of particles. The domain of small particles exhibits the long-ranged 2D hexagonal packing [30,31]. These results indicate that the formation of the amphiphilic hybrid layer after the partial replacement of hydrophilic ligand by the hydrophobic one induces the close-packing and segregating properties [30–33]. The replacement by dodecanethiol may depend on the particle size. Then the hybrid-layer protected particles with similar degree of replacement induce the segregation into the close-packed monodispersed phase. The large particle domain shows less close-packed 2D hexagonal array of particles.

Right-hand-side of the Fig. 2 shows small-angle X-ray scattering (SAXS, Rigaku SAX-LPB) of (a) dendrimer- and (b) hybrid-layer-protected gold nanoparticles. The SAXS of the dendrimer-protected nanoparticles presents a broad scattering peak at $Q = 0.083\,\text{Å}^{-1}$ corresponding to the reflection of (10) plane with a Bragg's lattice parameter [34,35] α of 87 Å. On the other hand, a spectrum of hybrid-layer-protected particles shows two peaks at $Q = 0.097$ and $0.127\,\text{Å}^{-1}$. Both peaks correspond to the reflections of (10) with $\alpha = 99$ and 57 Å, respectively. These two α values support the segregation of particles into domains with different degrees

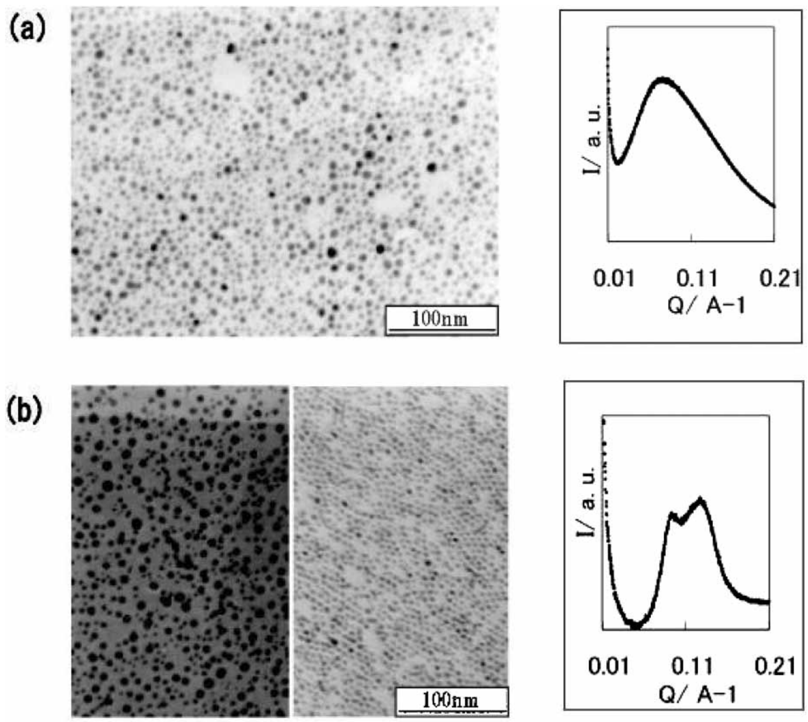

FIGURE 2 TEM micrographs of deposition on carbon-coated copper grids (left) and small-angle X-ray scattering spectra of cast-films on Capton-films (right). (a) G4 PAMAM dendrimer-protected gold nanoparticles; (b) hybrid-layer-protected gold nanoparticles.

of replacement by dodecanethiol, as concluded from the TEM photograph (Fig.2b).

Figure 3 shows Fourier-transformed infrared (FT-IR) absorption spectra [36] (BIO-RAD FTS 575C) of the (a) free dodecanethiol [37–39], (b and c) hybrid-layer-protected gold nanoparticles and (d) free G4 PAMAM dendrimer. The bands at 3276 and 3069 cm^{-1} in Fig. 3(b–d) are assigned to the amide A and B (NH stretching vibration modes), respectively, of dendrimer. The positions of these bands are not influenced by the formation of the mixed monolayer on particle surfaces. The characteristic bands assigned to amide I and II are at 1655 and 1555 cm^{-1}, respectively. The band position of amide I seems to be invariant, while the amide II band shifts slightly to the higher wavenumber (to 1559 cm^{-1}) with respect to the adsorption. All these amide bands broaden and weaken in the hybrid-layer-protected particles, indicating the lower density of the dendrimer in the mixed monolayer.

The absorption bands due to CH_2 antisymmetric and symmetric stretching vibration modes at 2939 and 2829 cm^{-1} of dendrimer are superimposed to the same bands of dodecanethiol in the hybrid-layer-protected particles. It is suggested from the band positions at 2919 and 2850 cm^{-1} in spectra of Fig. 3(b,c) that the alkyl chains of dodecanethiol are extended with ordered conformation in the hybrid-layer-protected particles [37–39]. The CH_2 twisting, rocking and wagging bands between 1350–1100 cm^{-1} in Fig. 3(b,c) are very similar to those of the free thiol in Fig. 3(a) but slightly different from free dendrimer.

Figure 3(b,c) compares the IR absorption spectra of hybrid-layer-protected particles prepared at Au–thiol, 2.5 : 1 and 5 : 1, respectively. The intensities of all amide bands (A, B, I and II) decrease with the increasing thiol content. On the other hand, the spectra gain more thiol characteristics at higher thiol content. These results suggest that the composition of hybrid-layer depends on the concentration of alkanethiol.

We used ^{1}H NMR spectra (Bruker ARX 400) for the characterization of hybrid monolayer on metal nanoparticles. A spectrum obtained in $C_6D_5CD_3$ for hybrid-layer-protected particles (prepared in Au-thiol, 2.5 : 1) reveals two resonances at chemical shift δ 0.8–0.9 and 1.2–1.6 ppm, but no free alkanethiol (δ 2.2–2.5 ppm for C_α atom) [40,41] was detected. These observations suggest that all thiol species are attached to the surface of the nanoparticle via the sulfur atom. However, no resonance for G4 PAMAM dendrimer was observed in ^{1}H NMR spectra at the range of 2.5–3.5 ppm. This fact indicates that either the G4 PAMAM dendrimer molecules are completely collapsed due to the chemisorption or the nonsolvent effect of the nonpolar solvent restricts the segmental motions.

To determine the mixed layer composition of hybrid-layer-protected particles prepared at

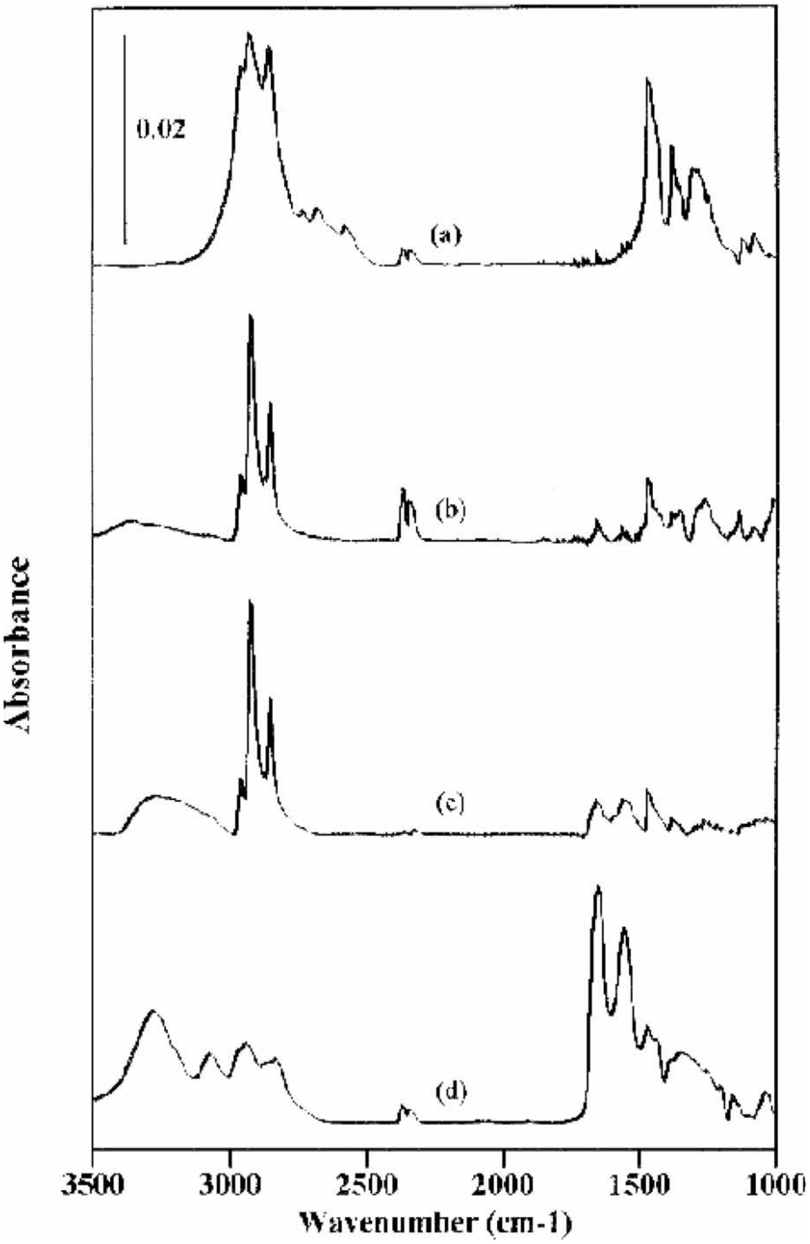

FIGURE 3 Comparison of the FT-IR spectra. (a) free dodecanethiol; (b and c) hybrid-layer-protected gold nanoparticles (Au–thiol = 2.5 : 1 and 5 : 1, respectively); (d) free G4 PAMAM dendrimer.

Au–thiol (2.5 : 1), we took the help of C, H and N elemental analysis (Perkin Elmer PE 2400). The analysis result of $C = 15.2$, $H = 2.3$ and $N = 2.7$ wt % reveals that the mixed layer consists of ~83 dodecanethiol molecules per dendrimer molecule i.e. the ratio of the thiol to terminal amine group of dendrimer is 5 : 4. Then the total organic content of hybrid-layer-protected particle is ~23 wt % with G4 PAMAM–dodecanethiol, 11 : 13 (weight ratio). This result was supported by the thermogravimetric and differential thermal analysis (Seiko TG/DTA 6200), where the total organic content was ~21 wt %.

CONCLUSION

In conclusion, the formation of the hybrid monolayer is very feasible by the partial replacement of surface-confined dendrimer onto the gold particle surface. Such replacement indicates that the interaction of gold particle surface with amine terminal groups of the dendrimer is weaker than that with thiol. The change of the hydrophilic particle surface to the amphiphilic one induces the segregation into the close-packed monodispersed phases. These hybrid-layer-protected nanoparticles will stimulate the field of basic sciences and applications to chemical sensing, catalysis, separation, etc.

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