Control of Interparticle Distance of Au Nanoparticles Capped with Azobenzene-Derivatized Alkanethiols at the Air-Water Interface

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Gold nanoparticles capped with 5-[2-methyl-4-(4-octyl-phenylazo)-phenoxy]-pentane-1-thiol (8AM5SH) were synthesized to study the effects of photo-isomerization of 8AM5SH on the structure of the particle monolayer. Au nanoparticles were synthesized by a modified method of Brust, and the resulting particles were heated at 150 °C for 15 min to obtain Au nanoparticles with a narrow size distribution. A monolayer of the particles was formed at the air-water interface using the Langmuir method. The surface pressure of Au nanoparticles capped with *trans*-8AM5SH is smaller than that for particles capped with *cis*-8AM5SH at the air-water interface. From the surface pressure measurements and TEM observations of the packing structure in the particle monolayer, it was found that the hydrocarbon chain of *trans*-8AM5SH is an interdigitated structure, and the interdigitation is promoted by an increase in the surface pressure.
Key words: Au nanoparticle, Azobenzene derivatives, Thiol, Monolayer

1 INTRODUCTION

Metal nanoparticles have been receiving a great deal of interest in recent years because they present excellent opportunities for applications in various areas such as electro-optic devices, sensors, catalysis and molecular electronics [1,2]. The assembly of nanoparticles into 2-dimensional (2-D) or 3-dimensional (3-D) superstructures allows for the creation of novel materials and devices with potential applications in, for example, optical switches and filters, chemical and biochemical sensors, photoelectronic devices, and templates for ordered microporous materials [3-9]. The Langmuir-Blodgett (LB) technique is the most straightforward approach for the construction of 2-D superlattices using various kinds of electroactive linkers. For instance, Heath et al.[10] utilized the LB technique to prepare ordered 2-D arrays of organically-capped Ag and Au nanocrystals. Pileni et al. [11] utilized colloidal self-organization to prepare 2-D and 3-D superlattices of Ag_2S nanoparticles, the surfaces of which were passivated by a coordinating ligand such as alkanethiol, alkylphoshine or dithiols.

Scheme 1: Schematic illustration of the synthesis route for 8AM5SH

Metal nanoparticles capped with photochromic molecules have the potential for modulation of the interparticle distance by photoisomerization of the chromophore. There are many reports of photoisomerization of chromophore molecules covering nanoparticles dispersed in bulk organic solvents [12-14]. However, there are few studies on photoresponse behaviors of 2-D nanoparticle arrays. In the present work, a 2-D assembly of azobenzene derivative-covered Au nanoparticles was prepared at the air-water interface by the Langmuir technique, and the effects of *trans*-to-*cis* isomerization of the azobenzene derivative on the structure of the particle monolayer, especially the interparticle spacing, has been examined by TEM and surface pressure measurements.
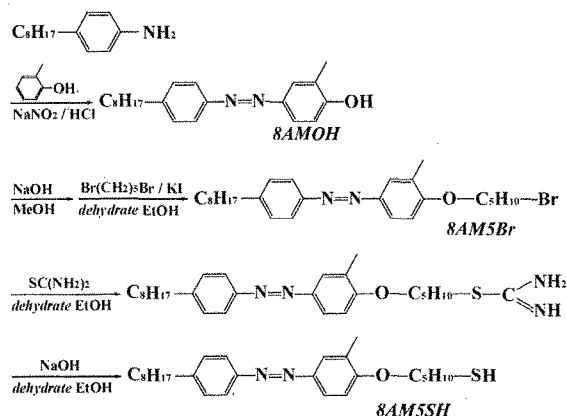
2. EXPERIMENTAL

2.1 Synthesis of 8AM5SH
Photochromic capping molecules of 5-[2-methyl-4-(4-octyl-phenylazo)-phenoxy]-pentane-1-thiol (8AM5SH) were synthesized according to Scheme 1.

2-methyl-4-(4-octyly-phenylazo)-phenol (8AMOH):
An aqueous solution of 2.68 g (38.8 mmol) of sodium nitrite in 10 mL of water was added to 7.14 g (34.8 mmol) of 4-octhyl-phenylamine in 100 mL of water containing 12 mL (0.14 mol) of 12 M HCl at 0~5°C (in an ice bath), and the reaction solution was stirred for 30 min. The reaction solution was added to 3.74 g (35.9 mmol) of o-cresol in 150 mL water containing 1.48 g (37.0 mmol) of sodium hydroxide at 0~5°C. After the mixture was neutralized with 1 M HCl, the precipitate was filtered out and dissolved in chloroform. The residue was removed by filtration, and the solvent was removed from the solution by rotary evaporation. 8AMOH was obtained as a brown solid.

[4-(5-bromo-pentyloxy)-3-metyl-phenyl]-(4-ethoxy-phenyl)-diazene (8AM5Br):

10.1 g (31.1 mmol) of 8AMOH and 1.35 g (33.7 mmol) of sodium hydroxide were dissolved in 600 mL of methanol, and the solution was stirred. On removal of the solvent by evaporation and freeze-drying, an auburn-colored solid was obtained. 11.2 g (32.3 mmol) of 8AMO⁻ Na⁺, 28.1 g (0.122 mol) of 1,5-dibromodecane, and 0.54 g (3.25 mmol) of potassium iodide were dissolved in 100 mL of dehydrate ethanol and refluxed for 8 h in a nitrogen atmosphere at 90 °C. After the mixture was cooled in an ice bath, the precipitate was filtered and dissolved in chloroform. The residue was removed by filtration, and the solvent was evaporated. Crude 8AM5Br was then obtained as an orange-colored solid. The crude 8AM5Br was purified by silica gel column chromatography using a mixed solvent of chloroform and hexane (1:1). After extract evaporation, 8AM5Br was obtained followed by recrystallization using hexane.

5-[2-methyl-4-(4-octyl-phenylazo)-phenoxy]-pentane-1-thiol (8AM5SH):

A mixture of 2.54 g (5.54 mmol) of 8AM10Br, 2.15 g (28.2 mmol) of thiourea, and 80 mL of dehydrate ethanol was refluxed for 12 h under a nitrogen atmosphere at 90°C. The mixture was cooled to room temperature. After the solvent was evaporated, the residue was dissolved in ethyl acetate. The insoluble products were filtered out, and a thiouronium salt was obtained. 4.83 g of the thiouronium salt and 1.11 g (27.8 mM) of sodium hydroxide were dissolved in 100 mL of ethanol and the mixture was refluxed for 12 h at 90°C. The reaction mixture was cooled to room temperature. After the pH of the reaction mixture was changed to 5 by the addition of 1M HCl, the precipitate was filtered. The crude filtrate was purified by column chromatography using a mixed solvent of acetone and hexane (1:4). Evaporation of the extract yielded 8AM5SH.

1HNMR(CDCl₃) δ :7.80-7.74(dx2,4H,ArH); 7.29-7.27(sx2,2H,ArH); 6.91-6.88(d,1H,ArH); 4.05-4.02 (t,2H,ArOCH₂); 2.59-2.54(q,2H,CH₂SH); 2.68-2.64 (t,2H,ArCH₂); 2.29(s,3H,ArCH₃); 1.87-1.80(m,2H, ArOCH₂CH₂);1.72-1.58(m,4H,CH₂CH₂SH,ArCH₂CH₂) ; 1.37-1.27(broad, 12H, CH₂,CH₃); 0.894-0.861(t,3H, CH₃), MS(FAB⁺) m/z:427

2.2 Preparation and characterization of Au nanoparticles

Au nanoparticles capped with 8AM5SH were prepared following a modification of the method of Brust et al. [15]. 15 mL of a 10 mM aqueous solution of HAuCl₄ was added to a 7.5 mM phase-transfer reagent, (C₈H₁₇)₄NBr dissolved in toluene (40 mL), and the mixture was stirred for 10 min. The toluene phase was subsequently collected and 5 mL of a 3mM toluene solution of 8AM5SH was added. After the solution was stirred for 2 h, 2 mL of aqueous sodium borohydride (0.75 M NaBH₄) solution was injected. The reaction mixture was vigorously stirred for 12 h, and the toluene phase was then collected. Au nanoparticles stabilized by 8AM5SH were characterized by transmission electron microscopy (TEM). TEM samples

were prepared by placing a drop of the dispersion on a 400-mesh, carbon-covered, copper TEM grid. The samples were examined using a H-9000 transmission electron microscope (HITACHI). TEM established that the Au nanoparticles had an average diameter of 3 ± 2 nm, as shown in Fig. 1(a).

2.3 Isomerization of 8AM5SH and UV-vis measurements

Trans-to-*cis* isomerization of 8AM5SH was carried out by the irradiation of UV or visible light. Light from a 300 W Xe lamp was passed through either a Toshiba UV-360 or an L-42 optical glass filter to produce selected-wavelength UV or visible light, respectively. UV-vis spectra were obtained using a V-500 spectrophotometer (JASCO). The *trans*-to-*cis* isomerization conversion was estimated from the decrease in the intensity of the π–π* band of 8AM5SH at 350 nm. The intensities of the band at 350 nm were measured after the straight base-line correction between 300 and 430 nm.
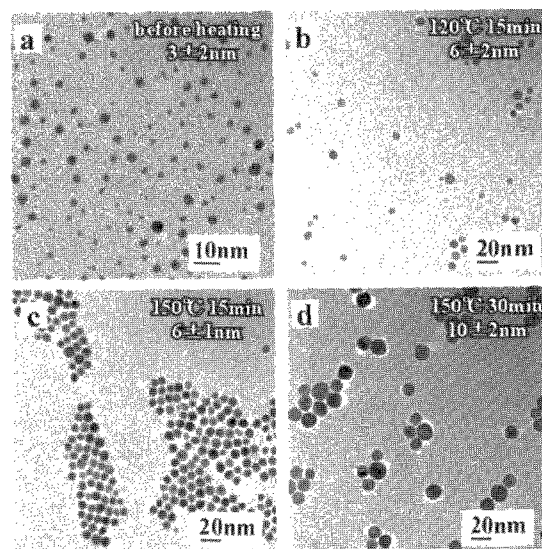

Fig. 1 TEM images of Au nanoparticles capped with 8AM5SH (a) without heating, and with heating under conditions of (b):120°C, 15 min, (c):150°C, 15 min, and (d): 150°C, 30 min.

3. RESULTS AND DISCUSSION

3.1 Preparation of Au nanoparticles with a narrow size distribution

The size distribution of the resulting Au nanoparticles capped with 8AM5SH was quite broad as seen in Fig. 1(a). Monodisperse particles are desirable for determining the interparticle distances. We then used the method of Teranishi et al. [16] to obtain monodisperse Au nanoparticles. The Au nanoparticles shown in Fig. 1(a) were heated at 120 or 150 °C, and the resulting particles were washed three times with a solvent mixture of toluene and methanol (volume fraction 1:1) to remove the phase transfer catalyst, excess 8AM5SH and reaction byproducts. The supernatant solution after washing three

times was colorless, indicating that excess 8AM5SH was completely washed away. Figs. 1(b)-(d) show TEM images of the resulting particles capped with 8AM5SH. It was found that the particles, upon heating at 150°C for 15 min, had a narrow size distribution and a size of 6 ± 1 nm in average diameter. In addition, elemental analysis of the dry sample established the fraction of the organic component by weight to be 22.8% (C; 19%; H; 2.3%, N; 1.5%). From these results, the average surface area occupied by each molecule was estimated to be 0.15 nm². We then used 6 nm Au particles capped with 8AM5SH to conduct the subsequent experiments.

3.2 Photoisomerization of 8AM5SH on Au nanoparticle

Fig. 2 shows the UV-vis spectrum of 8AM5SH on Au nanoparticles dispersed in toluene. The peaks at 350 and 520 nm are the $\pi-\pi^*$ bands of *trans*-azobenzene and surface plasmon bands, respectively [17]. The peak position of the $\pi-\pi^*$ band of 8AM5SH on the Au nanoparticle was almost the same as that in the chloroform solution. This indicates that the 8AM5SH molecules on the Au nanoparticles do not form H-aggregates or J-aggregates [17].

Photoisomerization of 8MA5SH on the Au nanoparticles in toluene was performed by irradiating with UV-light. The dashed line in Fig. 2 shows the UV-vis spectrum after 15 min irradiation of UV light.
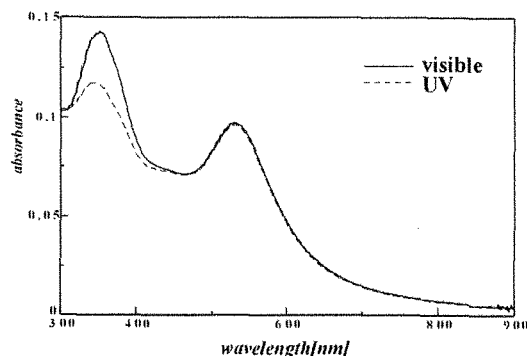

Fig.2 UV-Vis spectra of Au nanoparticles capped with 8AM5SH by irradiation of visible light (solid line) and UV light (dashed line).
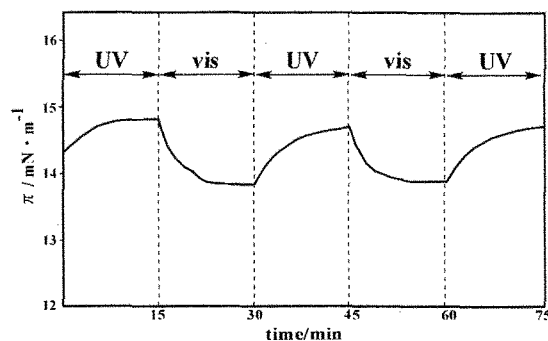

Fig.3 Surface pressure changes for a monolayer of Au nanoparticles capped with 8AM5SH upon alternating irradiation with UV and visible light at the air-water interface.

Note that irradiation with UV light results in relatively decreased $\pi-\pi^*$ band of the *trans* isomer at 350 nm, and the surface plasmon band at 520 nm does not change. Although *cis* isomer has the n-π^* band at about 450 nm, the band intensity is very weak and overlapping of the band with another bands is negligible. These results confirm that UV irradiation causes 8AM5SH to isomerize from the *trans* to the *cis* form, while the dispersion of Au nanoparticles is stable in toluene regardless of UV light irradiation.

From the decrease in the $\pi-\pi^*$ band intensity, the *trans*-to-*cis* isomerization conversion was estimated to be ca. 60% (*trans:cis*=40:60), while that of monodispersed 8AM5SH in toluene or chloroform was 90%. The lower conversion of 8AM5SH on the Au nanoparticle is probably due to the steric hindrance between the 8AM5SH molecules. Interestingly, the conversion fell to 30% when chloroform was used as the dispersion solvent and the conversion was 47% in a mixed solvent of chloroform and toluene (1:1).

3.3 Monolayer of Au particles

A chloroform solution of 8AM5SH-covered Au nanoparticles was spread at the air/water interface to form a monolayer of Au nanoparticles. Photoinduced response of the nanoparticle monolayer was examined by measuring changes in the surface pressure. Fig. 3 shows the changes in the surface pressure of the monolayer under alternating irradiation of UV and visible lights. The surface pressure increased after continuous UV light irradiation, and reverted back to the original pressure upon irradiation of visible light.

We expected a decrease in the surface pressure when 8AM5SH molecules photoisomerize from the *trans* form to the *cis* form, since the cross section of Au nanoparticles covered with *trans*-8AM5SH is larger than that with *cis*-8AM5SH, as shown in Scheme 2(A). There are two possible explanations for the increase in the surface pressure, namely, (i) presence of free 8AM5SH,
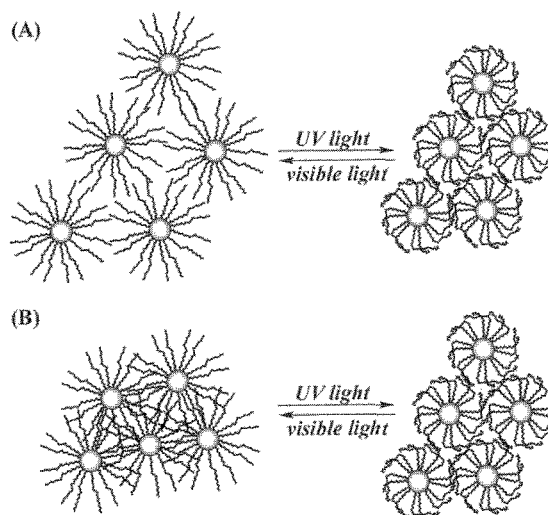
Scheme 2: Schematic illustration of the hydrocarbon chain packing in two-dimensional Au nanoparticles at the air-water interface. (A) Steric exclusion model, (B) interdigitation model of *trans*-8AM5SH.

and (ii) interdigitation of the hydrocarbon chains of *trans*-8AM5SH [Scheme 2(B)].

We can neglect the former possibility. Insoluble monolayers of azobenzene derivatives on water usually show an increase in the surface pressure by the *trans*-to-*cis* isomerization. A monolayer of 8AM5SH molecules on water collapsed below a surface pressure of 7 mN/m, indicating that 8AM5SH did not form a stable monolayer. In addition, we measured the surface pressure area relationship for the Au nanoparticle capped with 8AM5SH with and without the addition of free 8AM5SH and found that there was no difference between the two curves. Thus, if free 8AM5SH molecules exist in the particle monolayer, they do not contribute to changes in the surface pressure.

To confirm the second explanation for increased surface pressure, we examined the packing of Au nanoparticles in the monolayer using TEM. Fig. 4 shows TEM images of the particle monolayers at surface pressures of 10 and 30 mN/m under irradiation of visible light (*trans*-8AM5SH) and UV light (*cis*-8AM5SH). At 10 mN/m, the average interparticle distance was 2.5 nm for the *trans*-8AM5SH and 3.6 nm for the *cis*-8AM5SH. Since the molecular lengths of the *trans*- and *cis*-8AM5SH were 2.7 and 1.8 nm (CPK model), respectively, we concluded that the *trans*-8AM5SH in the particle monolayer should have an interdigitated structure. Furthermore, the interparticle distance for *trans*-8AM5SH decreased with increased surface pressure, while that for *cis*-8AM5SH was independent of the surface pressure. This result indicates that the interdigitation of hydrocarbon chains for *trans*-8AM5SH is promoted by the increase in the surface pressure.
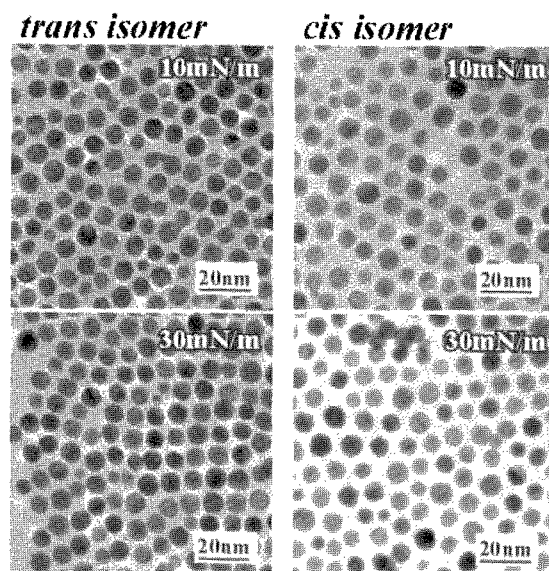
4 CONCLUSIONS

We have prepared Au nanoparticles capped with 8AM5SH with a narrow size distribution. It was demonstrated that 8AM5SH molecules on the particles show reversible isomerization by the irradiation of UV and visible light. We fabricated a 2D assembly of Au nanoparticles covered with 8AM5SH at the air-water interface. The interparticle spacing could be controlled by the photoisomerization of 8AM5SH. Furthermore, it was found that *trans*-8AM5SH on Au nanoparticles is an interdigitated structure, and that the interdigitation of hydrocarbon chains for *trans*-8AM5SH is promoted by an increase in the surface pressure.

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trans isomer **cis isomer**

Fig. 4 TEM images of particle monolayers prepared by the Langmuir-Blodgett method at a surface pressure of 10 and 30 mN/m.