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Reversible Dispersion and Aggregation of Ag₂S Nanoparticles Capped with Azobenzene-Derivatized Alkanethiols

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Ag₂S nanoparticles (NPs) of 3.1 ± 0.6 , 8.1 ± 1.0 , and 10.2 ± 1.6 nm in diameter capped with a longchain amidoamine derivative (C18AA) were synthesized by a modified Brust method. Ag₂S NPs capped with two types of azobenzene-derivatized alkanethiol differing in chain length (2AM10SH and 8AM5SH) were obtained by the ligand exchange method. The *trans* to *cis* photoisomerization conversion of 2AM10SH and 8AM5SH on Ag₂S NPs dispersed in toluene was above 95%. 2AM10SH-capped Ag₂S NPs of 8.1 nm or more in toluene were found to show reversible dispersion–aggregation behavior under alternating irradiation with UV and visible lights, i.e., Ag₂S NPs capped with *trans*- and *cis*-2AM10SH were in dispersed and aggregated states, respectively. However, Ag₂S NPs of 3.1 nm capped with 2AM10SH and Ag₂S NPs of 8.1 nm capped with 8AM5SH were always in a dispersed state regardless of whether 2AM10SH and 8AM5SH were in the *trans* or *cis* conformation.

Keywords: Reversible, Nanoparticle, Azobenzene, Photoisomerization, Dispersion–Aggregation,

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1. INTRODUCTION

Surface phenomena, including liquid crystal alignment,^{1,2} wettability,³ molecular recognition,^{4–8} and dispersibility,^{9,10} are governed by the atomic constitution of the outermost surface of a material. Therefore, control of the chemical structure of the outermost monomolecular layer of a substrate by light or other external stimuli may allow access to a broad range of new applications. Self-assembled monolayers (SAMs) of azobenzene derivatives are particularly promising candidates for creating films that allow control over their outermost surface. The SAM technique should allow control of molecular order and orientation in films, and photoisomerization of the azobenzene chromophore is reversible, with little degradation even after numerous switching cycles.

There are numerous reports on nanoparticle (NP) dispersion systems and the aggregation behavior of the NPs.^{11–23} However, there are very few on the reversible dispersion–aggregation of NPs driven by changes in pH²⁴ or temperature,²⁵ molecular recognition,²⁶ and photoisomerization of capping molecules.^{27–30} If the conformation of the outermost capping molecules on a NP could be converted by photoisomerization, it would offer the potential to control the dispersibility of NPs in a solvent; that is, a light-controlled dispersion–aggregation system of NPs in a solvent would be fabricated. In a previous report,⁹ we demonstrated the dispersion–aggregation behavior of Au NPs capped with an azobenzene-derivatized alkanesulfide in an apolar solvent under UV and visible lights. The azobenzene sulfide-capped Au NPs were aggregated via photoisomerization of the capping molecule from the *trans* to the *cis* isomer, but did not change from the aggregated to the dispersed state.

Silver sulfide (Ag₂S) is a direct and narrow band-gap semiconductor with good chemical stability and excellent optical properties.^{31–35} Ag₂S nanostructures,^{36–39} are promising materials for developing nano- and atomicscale switching devices with applications in random access memory (RAM), cross bar electronic circuits, and fuel cells or batteries based on ionic conductors and H₂S sensing. In the present work, Ag₂S NPs capped with SAMs of azobenzene-derivatized alkanethiols (Fig. 1) were prepared, and the dispersion–aggregation behavior of the resulting Ag₂S NPs in toluene was investigated by observing the *trans*-to-*cis* isomerization of the thiols under irradiation with UV or visible light.

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Fig. 1. Molecular structures and synthetic routes of azobenzenederivatized alkanethiols (2AM10SH: n = 2 and m = 10, 8AM5SH: n = 8 and m = 5).

2. EXPERIMENTAL DETAILS

2.1. Synthesis of Azobenzene Derivatives

Photochromic 5-[2-methyl-4-(4-ethyl-phenylazo)-phenoxy]decane-1-thiol (2AM10SH) was synthesized according to the scheme in Figure 1.⁹ 5-[2-methyl-4-(4-octylphenylazo)-phenoxy]-pentane-1-thiol (8AM5SH) was synthesized according to a previous paper.⁴⁰

2.1.1. 4-(4-Ethyl-phenylazo)-2-methyl-phenol (2AMOH)

An aqueous solution of 4.13 g (59.9 mmol) of sodium nitrite in 15 mL of water was dropped into 5.41 g (44.6 mmol) of 4-*n*-Ethylaniline in 100 mL of water containing 11 mL (0.13 mol) of 12 N HCl at 0 °C (in an ice bath) for 30 min. The reaction solution was dropped into 14.98 g of *o*-cresol in 150 mL water containing 2.20 g (55.0 mmol) sodium hydroxide at 0 °C for 1 h. After the reaction mixture was neutralized with 1 N HCl, the precipitate was filtered and recrystallized using methanol and water. 2AMOH was obtained as a brownish yellow solid.

2.1.2. [4-(10-Bromo-dodecyloxy)-3-methyl-phenyl]-(4-ethoxy-phenyl)-Diazene (2AM10Br)

Twenty grams (66.7 mmol) of 1,10-Dibromodecane was dropped into 5.00 g (20.8 mmol) of 2AMOH and 10.0 g (72.4 mmol) of potassium carbonate were dissolved in 150 mL of dehydrate acetone and refluxed for 12 h in a nitrogen atmosphere at 60 °C. After the mixture was extracted to chloroform, the chloroform solution was washed with water and evaporated to obtain crude 2AM10Br as orange-colored solid. The crude 2AM10Br was purified by column chromatography using a mixed solvent of chloroform and hexane (1:1). After extract evaporation, 2AM10Br was obtained followed by recrystallization using methanol.

2.1.3. 5-[2-methyl-4-(4-ethyl-phenylazo)-phenoxy]-Decane-1-Thiol (2AM10SH)

A mixture of 3.93 g (8.3 mmol) of 2AM10Br, 1.25 g (17 mmol) of thiourea, and 100 mL of dehydrate ethanol was refluxed for 12 h at 90 °C. After the solvent was evaporated, ethyl acetate was added the residue. The insoluble products were filtered out, and a thiouronium salt was obtained. Next, 3.63 g (8 mmol) of the thiouronium salt and 1.6 g (40 mmol) 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 filtered. The crude filtrate was purified by column chromatography using a mixed solvent of acetone and hexane (1:4). After extract evaporation, 2AM10SH was obtained followed by recrystallization using methanol.

¹H NMR (400 MHz, CDCl₃, TMS) δ : 7.81–7.79 (*d*, 2 H, Ar**H**); 7.78–7.77 (*d*, 1 H, Ar**H**); 7.75 (*s*, 1 H, Ar**H**); 7.32–7.3.1 (*d*, 2 H, Ar**H**); 6.92–6.90 (*d*, 1 H, Ar**H**); 4.06–4.03 (*t*, 2 H, ArOCH₂); 2.73–2.70 (*q*, 2 H, CH₂SH); 2.55–2.49 (*q*, 2 H, ArCH₂CH₃); 2.29 (1 H, ArCH₃); 1.85–1.81 (*q*, 2 H, ArOCH₂CH₂); 1.63–1.59 (*t*, 3 H, ArCH₂CH₃); 1.38–1.35 (*q*, 2 H, CH₂CH₂SH); 1.49–1.26 (*m*, 14 H, -CH₂CH₂–), MS(FAB⁺) *m*/*z*: 413.

2.2. Synthesis of C18AA Capping Ligand

C18AA was synthesized according to a previous paper.^{41–43} Briefly, 10.22 g (0.12 mol) of methyl acrylate was added to 2.0 g (7.12 mmol) of octadecylamine in 15 mL of methanol. The solution was stirred at 40 °C for 3 days and then the solvents and excess methyl acrylate were removed from solution by rotary evaporation. 3-[(2methoxycarbonyl-ethyl)-octadecyl-amino]-propionic acid methyl ester (C18ME) was obtained as a viscous liquid. Yield: 95%. Next, C18ME (3.2 g) and ethylenediamine 17.8 g (0.30 mol) were dissolved in 15 mL of methanol and the mixture was stirred for 1 week at room temperature. Upon removal of the solvent and ethylenediamine by evaporation and freeze-drying, C18AA was obtained as a light yellow solid. The crude solid was recrystallized from a mixed solvent of toluene and methanol. Yield: 90%.

¹H NMR(400 MHz, CDCl₃, TMS): δ 0.88 (*t*, 3 H, CH₃), 1.25 (*br*, 28 H, CH₂), 1.45 (*br*, 4 H, CH₂CH₃, CH₂CH₂CH₂CH₂N), 2.36 (*t*, 4 H, CH₂CH₂O), 2.42 (*t*, 2 H, CH₂N), 2.73 (*t*, 4 H, NCH₂CH₂CO), 2.82 (*t*, 4 H, CH₂NH₂), and 3.29 (*q*, 4 H, NHCH₂) ppm. HRMS: calcd for C18AA (M⁺H⁺) 498.47, found 497.48.

2.3. Preparation and Characterization of Ag₂S NPs

 Ag_2S NPs capped with C18AA were prepared using a method modified from Brust et al.⁴⁴ Ten milliliters of a 7.5 mM aqueous solution of $Na_3Ag(S_2O_3)_2$ were

added to 0.15 mmol of the phase-transfer reagent, $(C_8H_{17})_4$ NBr, dissolved in toluene (15 mL), and the mixture was stirred for 15 min. The toluene phase was subsequently collected and 15 mL of the desired concentration of C18AA in toluene were added. After the solution was stirred for 2 h, 0.075 mmol of sodium borohydride were added. The reaction mixture was vigorously stirred for 24 h. The particle size was controlled by changing the molar ratio of Na₃Ag(S₂O₃)₂ to C18AA ([Na₃Ag(S₂O₃)₂]/[C18AA] = 0.33–3.1).

Ligand exchange of Ag_2S NPs from C18AA to 2AM10SH or 8AM5SH was conducted in the following manner. 2AM10SH or 8AM5SH (0.15 mmol) was added to the Ag_2S NP solution (3.1 mL), and the mixture was stirred for 24 h. The resulting particles were washed twice with a solvent mixture of toluene and ethanol (volume fraction 1:4) to remove the phase transfer catalyst, excess azobenzene derivatives, and reaction byproducts. After washing the NP dispersion twice by centrifugation, the supernatant was colorless, indicating that excess azobenzene derivatives were completely removed.

2.4. Isomerization of Azobenzene Derivatives and UV-Visible Measurements

Trans-to-*cis* isomerization of 2AM10SH and 8AM5SH was carried out by irradiation of either 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 UV of a selected wavelength or visible light, respectively. UV-visible 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 2AM10SH and 8AM5SH at 360 nm. UV-visible spectra were measured immediately in the dark after exposure to UV or visible light.

2.5. TEM and XRD Measurements

Transmission electron microscopy (TEM) samples of Ag_2S NPs capped with C18AA were prepared by placing a drop of the Ag_2S NP dispersion on a 100-mesh carbon-covered copper TEM grid. However, in order to clarify the coagulation behavior of Ag_2S NPs capped with 2AM10SH and 8AM5SH, the copper TEM grid was immersed in a dispersion of the Ag_2S NPs for a few minutes, after which the grid was gently rinsed with toluene. The samples were examined using an H-9500 transmission electron microscope (HITACHI). X-ray powder diffraction (XRD) patterns were recorded at a scanning rate of 4°/min in the 2 θ range of 20–60° using a Rigaku UltimaIV diffractometer with CuK α radiation.

3. RESULTS AND DISCUSSION

3.1. Characterization of Ag₂S NPs

Figure 2 shows the representative XRD pattern of the product prepared under the condition of $[Na_3Ag(S_2O_3)_2]/[C18AA] = 1$. Similar XRD patterns were obtained from other molar ratios of C18AA to $Na_3Ag(S_2O_3)_2$. All peaks except for $2\theta = 39.06$ and 41.62° can be assigned to monoclinic β -Ag₂S with lattice constants of a = 0.42 nm, b = 0.69 nm, and c = 0.79 nm values in agreement with those in JCPDS card 14-72. The peaks at $2\theta = 39.06$ and 41.62° were assigned to (111) and (200) of metallic Ag, respectively. Thus, the product contained small amounts of metallic silver as impurities.

Figure 3 shows the typical TEM micrographs of the resulting Ag_2S NPs. The particle size was strongly affected by the molar ratio of $Na_3Ag(S_2O_3)_2$ to C18AA and increased with increasing molar ratio. Namely, Ag_2S NPs of 3.1 ± 0.6 (Fig. 3(a)), 8.1 ± 1.0 (Fig. 3(b)), and 10.2 ± 1.6 nm (Fig. 3(c)) were obtained for $[Na_3Ag(S_2O_3)_2]/[C18AA] = 0.33$, 1.5, and 1.0, respectively. However, we could not obtain Ag_2S particles larger than 10 nm because the particle size was unchanged at ratios of $[Na_3Ag(S_2O_3)_2]/[C18AA] > 1$. Ag_2S NPs of 20 nm (Fig. 3(d)) were then obtained by heating 10 nm Ag_2S NPs at 150 °C for 15 min.

The effect of changing the ligand from C18AA to 2AM10SH (or 8AM5SH) on the particle size was examined by TEM observations. We could not detect any difference in the particle size or shape between before and after ligand exchange, however, a new peak at 350 nm, which is assigned to the π - π * band of trans-azobenzene, appeared in the UV-vis spectra after the ligand exchange (Fig. 4). Therefore, we concluded that the exchange of ligands on Ag₂S NPs from C18AA to 2AM10SH or 8AM5SH was entirely successful.

3.2. Photoisomerization of 2AM10SH on Ag₂S NPs

Figure 5 shows the UV-vis spectra of 2AM10SH on 8.1 nm Ag_2S NPs dispersed in toluene under irradiation with



Fig. 2. X-ray powder diffraction pattern of the product.

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Fig. 3. TEM images of Ag_2S NPs obtained under the condition of $[Na_3Ag(S_2O_3)_2]/[C18AA] = (a) 0.33$, (b) 0.5 and (c) 1.0. (d) TEM image of Ag_2S NPs prepared by heating the sample (c) at 150 °C for 15 min.

visible and UV lights. The peaks at 350 and 450 nm are assigned to the $\pi-\pi^*$ band of *trans*-azobenzene and the $n-\pi^*$ band of characteristic *cis*-azobenzene, respectively. Note that the peak position of the former band was almost the same as that in the toluene solution, indicating that the 2AM10SH molecules on the Ag₂S NPs do not form H- and J-aggregates. Irradiation with UV light resulted in a significant decrease in the $\pi-\pi^*$ band of the *trans* isomer, and the appearance of $n-\pi^*$ band of *cis* isomer. When visible light was irradiated, the intensity of the $\pi-\pi^*$ band recovered and the $n-\pi^*$ band disappeared. The dependence of the intensity of the $\pi-\pi^*$ band on the irradiation time with alternating UV and visible lights is shown in Figure 6. It is apparent that *trans*-to-*cis* isomerization of 2AM10SH on Ag₂S NPs is completely reversible for numerous cycles.

The *trans*-to-*cis* isomerization conversion of 2AM10SH on Ag₂S NPs was estimated from the decrease in the $\pi-\pi^*$ band intensity to be more than 95%. In general, the conversion rates of azobenzene derivatives with long chains in highly organized films such as self-assembled monolayers (SAMs), LB films, or Langmuir

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monolayers are small. In previous papers,⁹ the conversion of 8AM5SH and di[10-(4-ethoxyphenylazo)-2-methyl-phenoxydecanyl]sulfide, $(2AM10)_2SH$] SAM on flat Au plates were 20–40%, whereas those of SAM on Au NPs were 70–80%. This is due to the large curvature of the NPs, which would ensure sufficient distance between adjacent azobenzene moieties. Thus, the photoisomerization of 2AM10SH on Ag₂S was more efficient than analogous azobenzene derivatives on Au NPs. This improvement in conversion is thought to be due to the lower adsorption density of 2AM10SH on Ag₂S, because 2AM10SH molecules adsorb only on the Ag sites of Ag₂S surface and not on the S sites.

The photo-response behavior of 2AM10SH adsorbed on Ag₂S NPs of different sizes was similar to that on 3.1 nm Ag₂S NPs, as shown in Figure 7. In the case of 20 nm Ag₂S, although the π - π * band intensity was quite low, regular changes in intensity were observed under alternating irradiation of UV and visible lights. Thus, the reversible *trans*-to-*cis* isomerization behavior of 2AM10SH on Ag₂S NPs was found to be independent



Fig. 4. UV-vis spectra of 8.1 nm Ag_2S NPs (a) before and (b) after Scienligand exchange from C18AA to 2AM10SH dispersed in toluene.

of particle size. The low intensity of the $\pi - \pi^*$ band for 20 nm Ag₂S NPs is probably caused by the following effects. The increase of the particle size brings about (i) a decrease in the total amount of 2AM10SH on Ag₂S NPs





Fig. 6. Changes in the intensity of the π - π * band at 350 nm for 8.1 nm Ag₂S NPs with alternating irradiation by UV and visible lights. Irradiation times were 20 and 40 min for UV and visible lights, respectively.

due to the decrease in the total surface area of the NPs, and (ii) a rising of the baseline in a shorter wavelength region of UV-vis spectrum due to a large scattering cross section of light.



Fig. 5. UV-vis spectra of 8.1 nm Ag_2S NPs capped with 2AM10SH dispersed in toluene. The initial state (1) was first irradiated with UV light for 20 min (2). It was subsequently irradiated with visible light for 40 min (3).

Fig. 7. UV-vis spectra of Ag_2S NPs capped with 2AM10SH dispersed in toluene under irradiation with UV (dashed line) and visible (solid line) lights. Particle size: (a) 3.1 nm, (b) 10 nm, and (c) 20 nm.





Fig. 8. TEM images of 8.1 nm Ag_2S NPs capped with 2AM10SH under alternating irradiation with (a and c) visible light for 40 min and (b and d) UV light for 20 min.

3.3. Dispersion-Aggregation Behavior of Ag₂S

Figure 8 shows the TEM images of 8.1 nm Ag_2S NPs capped with 2AM10SH under alternating irradiation with visible and UV lights. Irradiation with UV light resulted in the formation of many aggregates of Ag_2S NPs, whereas the aggregates reverted to the dispersed state by irradiation with visible light. Thus, this result indicated that the dispersion–aggregation states of Ag_2S NPs in toluene can

easily be controlled for many cycles by changing the conformation of 2AM10SH, i.e., by switching between the *trans* and *cis* forms of 2AM10SH.

The stability of the Ag_2S NP dispersion is to some extent determined by the balance of the following factors: the steric interaction between 2AM10SH molecules, van der Waals interaction between the NPs, and affinity between the solvent and 2AM10SH. The aggregation of Ag_2S NPs capped with *cis*-2AM10SH is presumably



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caused by the difference in the functional group of the outermost surface of 2AM10SH-capped Ag_2S NPs. The outermost surfaces of Ag_2S NPs in the *trans* and *cis* forms of 2AM10SH are probably the tail part of the hydrocarbon chain and the azobenzene moiety of 2AM10SH, respectively. Given that the presence of a hydrocarbon chain is considered preferable in terms of Ag_2S NP dispersion in toluene, whereas the azobenzene moiety is likely to have a low affinity for toluene, the Ag_2S NPs capped with *cis*-2AM10SH aggregate. This was consistent with the fact that 8.1 nm Ag_2S NPs capped with *cis*-8AM5SH, which are almost the same size as the Ag_2S NPs capped with 2AM10SH in Figure 8, did not aggregate in toluene

(Fig. 9). The reason for this is that the outermost group, even for Ag_2S NPs capped with *cis*-8AM5SH, is thought to be a hydrocarbon chain rather than the azobenzene moiety because 8AM5SH has a longer terminal hydrocarbon chain than 2AM10SH.

Figure 10 shows the effect of particle size on the aggregation behavior of Ag_2S NPs under irradiation with UV and visible lights. A similar dispersion–aggregation regulation of Ag_2S NPs was effectively accomplished using particle sizes of 10.2 and 20 nm. However, NPs with a smaller size of 3.1 nm always maintained a dispersed state in toluene regardless of whether 2AM10SH was in the *trans* or *cis* conformation. As mentioned above, the



Fig. 10. TEM images of Ag_2S NPs capped with 2AM10SH under irradiations with (b, d and f) UV light for 20 min and (a, c and e) visible light for 40 min. Particle size: (a and b) 3.1 nm, (c and d) 10 nm, and (e and f) 20 nm.

stability of the Ag_2S NP dispersion depends in part on the van der Waals interaction between the NPs. Thus, the strength of the van der Waals interaction between 3.1 nm Ag_2S NPs capped with *cis*-2AM10SH is insufficient to aggregate them, even though the *cis*-2AM10SH molecules have a conformation with a lower affinity for toluene.

4. CONCLUSION

We prepared Ag_2S NPs capped with two kinds of azobenzene-derivatized alkanethiol, 2AM10SH and 8AM5SH, and investigated the dispersion–aggregation behavior of the Ag_2S NPs in toluene. We successfully controlled the reversible aggregation–dispersion behavior for Ag_2S NPs of 8.1 nm or more capped with 2AM10SH by alternating irradiation with UV and visible lights. On the other hand, the dispersions of 8.1 nm Ag_2S NPs capped with 8AM5SH and 3.1 nm Ag_2S NPs capped with 2AM10SH were stable, regardless of whether 8AM5SH was in the *trans* or *cis* conformation.

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