Nanoparticles

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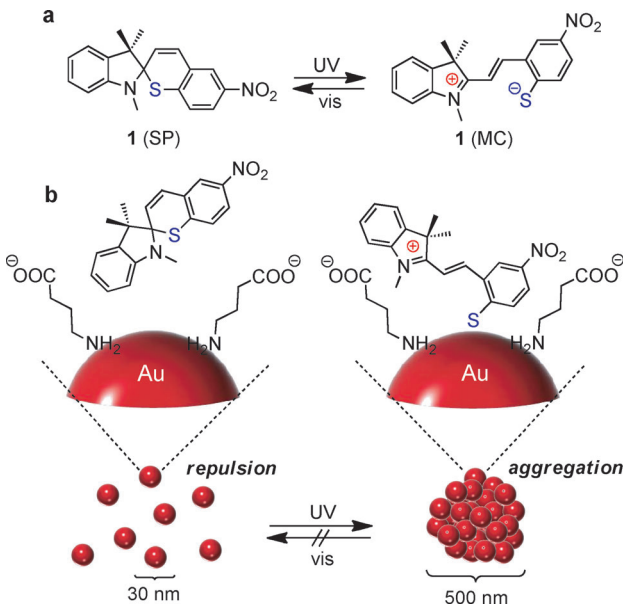
Light-Triggered Self-Assembly of Gold Nanoparticles Based on Photoisomerization of Spirothiopyran**

Yasuhiro Shiraishi, Kazuya Tanaka, Eri Shirakawa, Yoshitsune Sugano, Satoshi Ichikawa, Shunsuke Tanaka, and Takayuki Hirai*

Gold nanoparticles (AuNPs) are unique building blocks with sophisticated optical,[1] electronic,[2] and chemical[3] properties that differ dramatically from those of the bulk metal. They have potential for cancer diagnosis and therapy on account of their surface plasmon resonance (SPR) enhanced light scattering and absorption properties.[4] Owing to their high surface-to-volume ratio and high surface energy, AuNPs exhibit unusual catalytic[5] and photocatalytic activities[6,7] as well as electronic properties.[8] These properties are strongly size-dependent;[9] therefore, accurate size control of AuNPs is a challenge for advanced processing of AuNPs.

Self-assembly of AuNPs is one powerful method for the size control, a simple and low-cost method to produce ensembles of AuNPs in a controllable manner.[10–12] Light-triggered methods have been studied extensively[13–24] because light is non-invasive and can be delivered instantaneously to a precise location. All of the early reported methods employ AuNPs modified with covalently bound photoresponsive molecules. These AuNPs, when left in the dark, are well dispersed in solvents because of the electrostatic repulsion between AuNPs. Photoactivation of the surface molecules promotes several reactions, such as isomerization of azobenzenes,[13–21] dimerization of thymine,[22,23] and coupling of aldehyde with amine moieties.[24] These reactions change the surface polarity, surface electronic charge, or particle geometry, promoting aggregation of the AuNPs. All of these methods, however, suffer from a fundamental problem: AuNPs need to be modified with an excess amount of photoresponsive molecules in advance, and many of these molecules are left unused for particle aggregation. The design of a new method, which avoids the preparation of surface-modified AuNPs and only attaches the minimum amount of molecules to the surface for aggregation, is necessary for rapid and simple processing of AuNPs.

Herein we report a simple method for the light-triggered self-assembly of AuNPs, which does not require the preparation of AuNPs modified with photoresponsive molecules and promotes aggregation with only the minimum amount of the molecules. We use spirothiopyran (**1**), a sulfur-containing spiropyran dye which has photochromic properties, as an initiator for aggregation (Scheme 1a). As shown in Scheme 1b, **1**, when dissolved in aqueous solution with AuNPs,



Scheme 1. a) Photoisomerization of spirothiopyran and b) mechanism for light-induced aggregation of AuNPs.

exists as a spirocyclic (SP) form and scarcely associates with AuNPs. UV irradiation promotes photoisomerization of **1** and produces spirocycle-opened merocyanine (MC) form. Its thiolate moiety becomes bonded to the AuNPs surface. This changes the electronic charge of AuNPs surface and triggers aggregation. This simple system successfully produces aggregates of AuNPs with tunable sizes and narrow size distributions.

Compound **1** was obtained, by condensation of 5-nitrosalicylaldehyde with *N*,*N*-dimethylthiocarbamoyl chloride and subsequent condensation with 1,3,3-trimethyl-2-methyleneindoline, as a yellow solid (overall yield: 63%).[25,26] The purity of **1** was confirmed by ^{1}H, ^{13}C NMR spectroscopy and

[*] Dr. Y. Shiraishi, K. Tanaka, E. Shirakawa, Dr. Y. Sugano, Prof. T. Hirai
Research Center for Solar Energy Chemistry and Division of Chemical Engineering, Graduate School of Engineering Science, Osaka University
Toyonaka 560-8531 (Japan)
E-mail: shiraish@cheng.es.osaka-u.ac.jp
Dr. S. Ichikawa
Institute for NanoScience Design, Osaka University (Japan)
Dr. S. Tanaka
Department of Chemical, Energy and Environmental Engineering, Kansai University (Japan)

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EI-MS analysis (Figure S1–S3, Supporting Information). Figure 1 shows the absorption spectra of **1** (20 μM). In the dark, **1** shows almost no absorption at over 450 nm, and the spectrum does not change even when the sample is left for

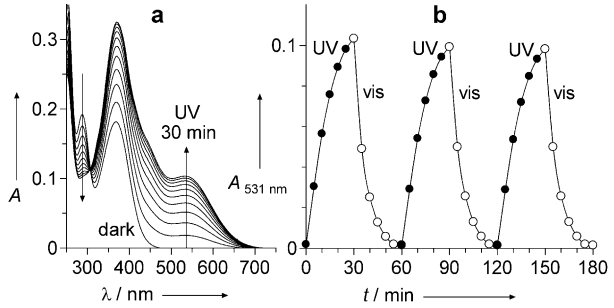

Figure 1. a) Absorption spectra of **1** (20 μM) measured in a buffered water/MeCN mixture (7/3 v/v; HEPES 10 mM, pH 7.0) at 25 °C, under irradiation of 280 nm light. b) Change in 531 nm absorbance by sequential UV–visible light irradiation.

12 h, indicating that **1** exists as a SP form (Scheme 1 a) and scarcely undergo thermal isomerization.[27] Irradiation of the solution with 280 nm light, however, creates a distinctive absorption at 531 nm, assigned to the spirocycle-opened MC form. As shown in Figure S4 (Supporting Information), irradiation of the solution with 530 nm light reverts the spectrum back to that for SP form. As shown in Figure 1 b, sequential UV/Vis light irradiation of the solution promotes repeated spectral change. These data suggest that **1** undergoes reversible SP⇄MC isomerization by UV/Vis irradiation (Scheme 1 a).

AuNPs were simply prepared according to a literature procedure,[28] by the reduction of $HAuCl_4$ with trisodium citrate in water and γ-aminobutyric acid (GABA), a surface protecting agent. Figure 2 shows the absorption spectra of AuNPs stabilized with GABA. As shown by the green line, the solution exhibits a strong SPR band arising from the AuNPs at 527 nm. As shown by the red line, stirring the solution with **1** (5 μM) in the dark for 12 h scarcely changes the

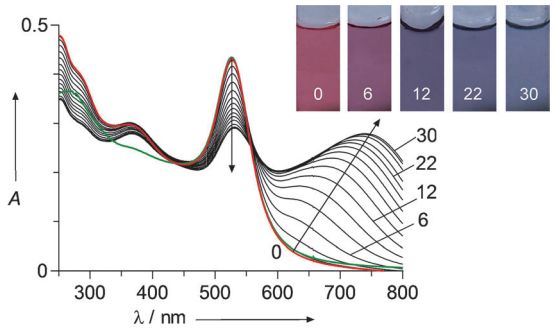

Figure 2. Absorption spectra of AuNPs (0.12 nM) stabilized with 4.8 mM GABA in a buffered water/MeCN mixture (2 mL; 7/3 v/v; HEPES 10 mM, pH 7.0), green: after stirring without **1** in the dark for 1 h, red: after stirring with **1** (5 μM) in the dark for 12 h, and black: after stirring with **1** (5 μM) under irradiation of 280 nm light. The numbers denote the irradiation time (min). Inset: photos of the solution at the indicated times.

SPR band, although a band assigned to the SP form of **1** appears at 369 nm. As shown in Figure 3 a, the transmission electron microscopy (TEM) image of the sample shows highly

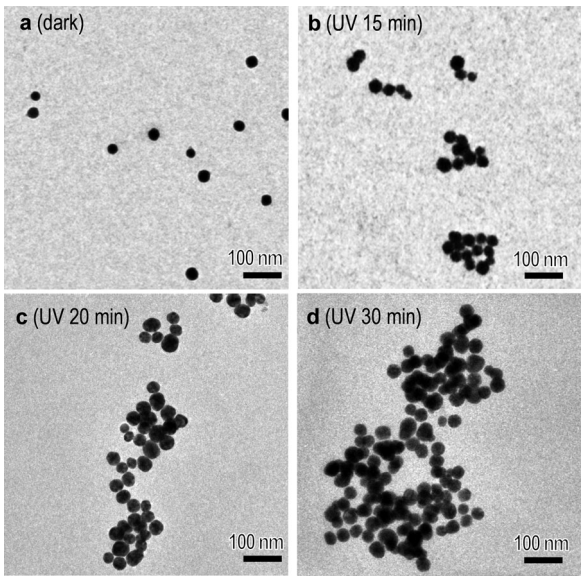

Figure 3. TEM images of AuNPs (0.12 nM) stabilized with 4.8 mM GABA in a buffered water/MeCN mixture (7/3 v/v; pH 7.0), measured a) after stirring with **1** (5 μM) in the dark for 60 min, and after stirring with **1** (5 μM) under 280 nm irradiation for b) 15, c) 20 and d) 30 min. TEM observations were carried out after the sample grid was dipped into the respective solutions and dried in vacuo.

dispersed AuNPs with an average diameter of approximately 30 nm. In contrast, as shown by the black line in Figure 2, irradiation of the solution with 280 nm light decreases the SPR band and creates red-shifted band at over 600 nm, assigned to the interparticle-coupled plasmon excitons of aggregated AuNPs.[29] TEM observation (Figure 3 b–d) indeed shows the formation of aggregated AuNPs and the size of the aggregates increases with photo-irradiation time. As shown in Figure S5 (Supporting Information), UV irradiation of an AuNPs solution without **1** shows almost no spectral change. In addition, the solution containing aggregated AuNPs obtained after UV irradiation in the presence of **1**, when left in the dark for 12 h, scarcely promotes further aggregation. These findings suggest that photoactivation of **1** triggers aggregation of AuNPs.

Figure 4 shows the change in hydrodynamic diameter of AuNPs with photoirradiation time, determined by a dynamic laser scattering analysis. As shown in Figure 4 b (black), the size of aggregates increases from 30 to 500 nm with photo-irradiation time, and the aggregates maintain narrow size distribution with the standard deviation being less than 25 %. This result suggests that the method successfully creates aggregates with tunable sizes and narrow size distributions. It is also noted that the aggregation can be precisely controlled by on–off switching of UV irradiation. Figure 5 shows the change in the 740 nm absorbance of the AuNPs solution during the repeated on–off sequence of UV irradiation. Turning off the light completely suppresses the absorbance

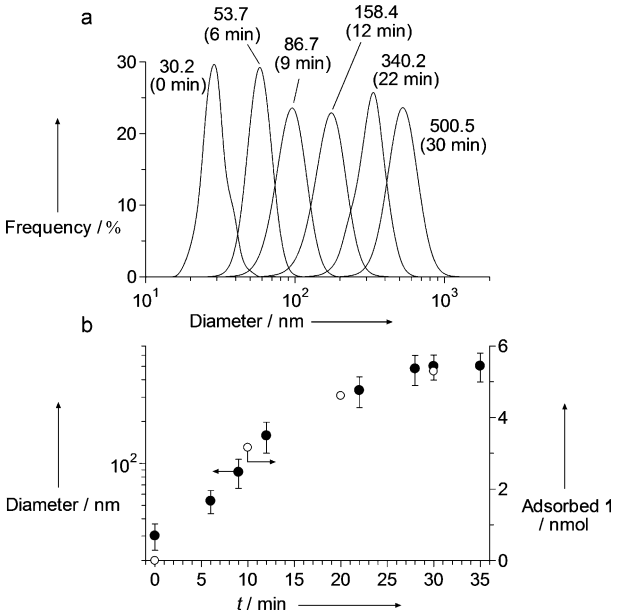

Figure 4. a) Time-dependent change in hydrodynamic diameter of aggregates for AuNPs stabilized with 4.8 mM GABA, during 280 nm light irradiation in the presence of **1** (5 μM: 10 nmol). b) Change in average diameter (black) of aggregates and amount of **1** (white) adsorbed on AuNPs. The adsorbed amount of **1** was determined by absorption spectra of the supernatant obtained after centrifugation of respective samples.

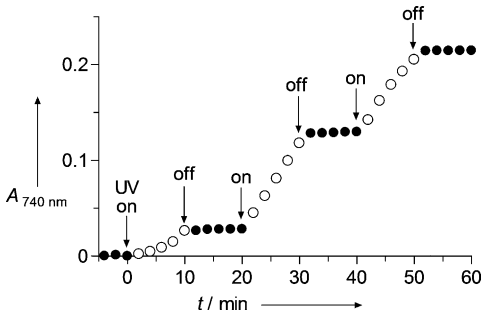

Figure 5. Change in 740 nm absorbance of the solution containing AuNPs (0.12 nM) stabilized with 4.8 mM GABA, during repeated on-off sequence of UV irradiation in the presence of **1** (5 μM).

increase, indicating that on–off switching of UV light precisely controls aggregation.

The mechanism for the light-induced aggregation of AuNPs with **1** is explained in Scheme 1. In the dark, AuNPs are well dispersed in solution owing to the electrostatic repulsion of AuNPs by negatively charged carboxylic acid groups (-COO^-) of the surface-attached GABA molecules. Thus, the SP form of **1** scarcely associates with the AuNPs surface. In contrast, UV irradiation promotes SP→MC isomerization of **1**. The thiolate moiety (-S^-) of the MC form is strongly adsorbed onto the AuNPs surface by the covalent Au–S binding.[30] The positive charge on the indole moiety of the adsorbed MC form neutralizes the negative charge of the carboxylic acid groups of GABA. This decreases the electrostatic repulsion between AuNPs and triggers their aggregation.

The adsorption of the MC form of **1** onto the AuNPs surface by the covalent Au–S bonding is confirmed by X-ray photoelectron spectroscopy (XPS). Figure 6 shows the XPS

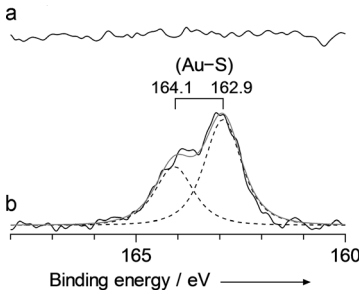

Figure 6. XPS spectrum (S 2p region) of AuNPs (0.12 nM) stabilized with 4.8 mM GABA, recovered by centrifugation a) after stirring with **1** (5 μM) in the dark for 60 min and b) after stirring with **1** (5 μM) under 280 nm irradiation for 30 min; gray: theoretical curve, broken lines: deconvoluted spectra.

results for S 2p region of AuNPs. The AuNPs recovered after stirring with **1** in the dark do not show any signals (Figure 6a). In contrast, the AuNPs recovered after UV irradiation with **1** show characteristic S 2p1/2 and 2p3/2 peaks at 162.9 and 164.1 eV, respectively, with the ratio of their peak areas being 2:1 (Figure 6b), indicative of a thiolate moiety bound to AuNPs surface.[31] These suggest that the photoformed MC form of **1** is adsorbed onto the AuNPs surface by covalent Au–S bonding, whereas the SP form of **1** is not adsorbed. The covalent Au–S bonding is further confirmed by visible light irradiation of aggregates. As shown in Figure S6 (Supporting Information), irradiation of the aggregates with 530 nm light does not promote any change in the absorption spectra, although the free MC form of **1** undergoes reversion to the SP form (Figure S4, Supporting Information). This result suggests that the thiolate moiety of the MC form of **1** is stabilized by the Au–S bonding and does not undergo reversion to the SP form even under visible light irradiation. As shown in Figure 4b (white), the amount of **1** adsorbed onto the AuNPs surface increases with irradiation time, which is consistent with the increase in the size of aggregate. This finding clearly indicates that adsorption of MC form of **1** onto the AuNPs surface indeed triggers aggregation.

The adsorption of the MC form of **1** onto the AuNPs surface leaves a positively charged indole moiety (Scheme 1b). These moieties neutralize the negative charge of carboxylic acid groups on the AuNPs surface, promoting aggregation. This situation is confirmed by the potential of zero charge (PZC)[32] for AuNPs. Figure 7 shows the acid–base titration curves for AuNPs measured in a water/MeCN mixture by the addition of HCl, where the titration curve for the blank solution is depicted by the dotted line. As shown by curve (a), the PZC of AuNPs stabilized with GABA is 6.0, indicating that the AuNPs surface is indeed charged negatively due to the carboxylic acid groups of GABA. As shown by curve (b), the PZC of AuNPs obtained after stirring with

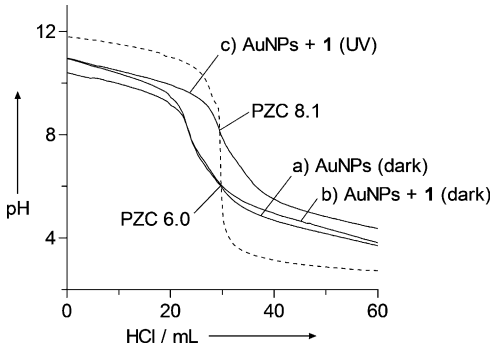

Figure 7. Acid–base titration curves for AuNPs (0.12 nM) stabilized with 4.8 mM GABA, obtained a) after stirring without **1** in the dark for 60 min, b) after stirring with **1** (5 μM) in the dark for 60 min, and c) after stirring with **1** (5 μM) under UV irradiation for 30 min.

1 in the dark is similar (6.0). In contrast, as shown by curve (c) in Figure 7, the AuNPs obtained after stirring with **1** under UV irradiation show a higher PZC (8.1). This result indicates that the negative charge on the AuNPs surface is neutralized by the positive charge of the indole moiety on the adsorbed MC form of **1**. This decreases the electrostatic repulsion between AuNPs[33] and triggers the aggregation of AuNPs.

It is noted that the aggregation rate of AuNPs strongly depends on several factors, such as 1) the amount of **1**, 2) the intensity of incident UV light, 3) the amount of GABA, and 4) the ionic strength of the solution. As shown in Figure S7 (Supporting Information), UV irradiation of an AuNPs solution containing lower amounts of **1** shows a decreased aggregation rate. In addition, as shown in Figure S8, the decrease in incident light intensity also decreases the aggregation rate. Decreases in both the amount of **1** and the light intensity produces lower amounts of the MC form. This suppresses adsorption of the MC form of **1** onto the AuNPs surface, resulting in lower aggregation rate of AuNPs. Furthermore, as shown in Figure S9, AuNPs stabilized with a larger amount of GABA require a longer time for aggregation. This is because a larger amount of the MC form of **1** must be adsorbed onto the AuNPs surface to neutralize the correspondingly larger amount of carboxylic acid groups. In contrast, as shown in Figure S10, the increase in ionic strength of the solution accelerates the aggregation rate of AuNPs. This is because the increased ionic strength reduces the thickness of the electric double layer around the AuNPs and strengthens interaction between AuNPs.[34]

In conclusion, we found a simple method for the light-triggered self-assembly of AuNPs based on the photoisomerization of spirothiopyran (**1**). UV irradiation of **1** dissolved in an aqueous solution containing AuNPs stabilized with GABA, a common surface protecting agent, successfully promotes aggregation of the AuNPs. Photoisomerization of **1** promotes covalent binding of its thiolate moiety onto the AuNPs surface. This binding neutralizes the surface negative charge of the AuNPs and promotes aggregation. This simple method avoids the tedious preparation of surface-modified AuNPs and creates AuNPs aggregate with tunable size (30–500 nm) and narrow size distribution (standard deviation under 25%). The basic concept presented herein, based on the photoisomerization of spirothiopyran, may contribute to the design of a more efficient method for light-induced self-assembly of metal nanoparticles and may open a new strategy for the rapid and simple processing of AuNPs.

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