

# Preparation and Optical Absorption Spectra of Dye-Coated Au, Ag, and Au/Ag Colloidal Nanoparticles in Aqueous Solutions and in Alternate Assemblies

Noritsugu Kometani,\* Makoto Tsubonishi, Takeshi Fujita, Kenji Asami, and Yoshiro Yonezawa

Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Sugimoto 3-3-138, Sumiyoshi-ku, Osaka 558-8585, Japan

Received September 13, 2000. In Final Form: November 17, 2000

Au, Ag, and Au/Ag colloidal nanoparticles coated with the J-aggregate of an anionic cyanine dye, 3,3'-disulfopropyl-5,5'-dichlorothiacyanine sodium salt (TC), have been prepared for the first time. The absorption spectrum of TC-coated Au colloidal nanoparticles is not a simple sum of the contributions of colloidal gold and TC but is characterized by an evident absorption dip at the position corresponding to the J-band of TC. These spectral features are reproduced by the simulation based on the Maxwell–Garnett-type treatment of Gao et al. The alternate adsorption technique allowed us to deposit dye-coated Au/Ag composite nanoparticles at the surface of a cationic polymer, poly(diallyldimethylammonium chloride).

## Introduction

Evolution of classical and quantum size effects of organic and inorganic compounds has attracted much attention from scientists in the search for novel materials.<sup>1</sup> Nanoparticles of noble metals are interesting because of the optical properties related to surface plasmon resonance, such as large optical nonlinearity and surface-enhanced Raman scattering (classical size effect).<sup>2–4</sup> On the other hand, considerable attention has been paid on the J-aggregate of cyanine dyes because of its remarkable linear and nonlinear optical properties.<sup>5,6</sup> Dye-coated Au and Ag colloidal nanoparticles are expected to modulate and improve optical properties owing to the electromagnetic interaction between metal core and dye shell, particularly in the case that absorption frequency of dye molecules lies close to the surface plasmon resonance of metal particles. In this context, there have been several works which deal with optical absorption of dye-coated metal particles and island films.<sup>7–10</sup> They have reported that the absorption spectrum of the dye-coated metal particles is not always equal to a simple sum of the contribution of each component. However, no attempts have been made to prepare the colloidal nanoparticles coated with the J-aggregate of cyanine dyes and deposit them on the substrate. In the present Letter, we have prepared colloidal solutions of Au, Ag, and Au/Ag nanoparticles coated with the J-aggregate of anionic cyanine dye, TC. Here, Au/Ag means Au–Ag composite. Furthermore, the layer-by-layer self-assemblies (alternate assemblies) incorporating TC-

coated Au/Ag nanoparticles have been successfully fabricated by the alternate adsorption technique.

## Experimental Section

3,3'-Disulfopropyl-5,5'-dichlorothiacyanine sodium salt (TC) was purchased from the Japanese Research Institute for Photosensitizing Dyes (Okayama). Poly(diallyldimethylammonium chloride) (PDDA) (MW = 40000–50000) was obtained from Aldrich. The chemical structures of TC and PDDA are shown in Figure 1. These materials were used without further purification.

Au, Ag, and Au/Ag colloidal nanoparticles were prepared by the reduction of metallic ions in aqueous solution with freshly prepared NaBH<sub>4</sub> solution in ice-cooled condition.<sup>11</sup> An aqueous solution of 1.5 mM NaBH<sub>4</sub> (30 mL) was cooled with ice and then 1 mM NaAuCl<sub>4</sub> aqueous solution (10 mL) was added to it under vigorous stirring, resulting in the wine-red Au colloidal solution. Similarly, silver colloidal nanoparticles were prepared by pouring 1 mM AgNO<sub>3</sub> solution (10 mL) into 1 mM NaBH<sub>4</sub> solution (30 mL), resulting in the light-brown Ag colloidal solution. To obtain Au/Ag (1:1) nanoparticles, an aqueous solution of the mixture of 0.5 mM NaAuCl<sub>4</sub> and 0.5 mM AgNO<sub>3</sub> (10 mL) was reduced by 1.5 mM NaBH<sub>4</sub> solution (30 mL). The color of Au/Ag colloidal solution was almost the same as that of the Au colloidal solution. The average size of Au, Ag, and Au/Ag colloidal nanoparticles was estimated to be approximately 10 nm by a transmission electron microscope.

Dye-coated colloidal nanoparticles were prepared by adsorbing TC molecules on the surface of metal nanoparticles. This was performed simply by mixing the colloidal solution and TC aqueous solution containing 1 mM KCl. KCl could promote adsorption of TC molecules on the surface. The concentrations of colloidal metal (Au, Ag, or Au/Ag) solution and TC solution were 0.15 mM and  $1 \times 10^{-5}$  M, respectively.

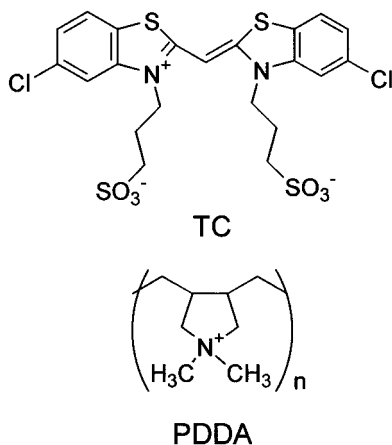
The alternate assembly incorporating TC-coated Au/Ag nanoparticles was fabricated by the simple extension of the method described in ref 12. That is, a clean quartz plate was first immersed in 1.0% w/v PDDA aqueous solution for 30 min to adsorb one PDDA layer. After being carefully rinsed with distilled water, the plate was immersed in the TC-coated Au/Ag colloidal solution for 30 min to adsorb composite nanoparticles on the PDDA monolayer. Multilayer assemblies could be fabricated by repeating the above procedures many times. Absorption spectra of colloidal solutions and alternate assemblies were measured by the V-560 spectrophotometer (JASCO Co.).

\* To whom correspondence should be addressed. Fax: +81-6-6690-2743. E-mail: kometani@a-chem.eng.osaka-cu.ac.jp.

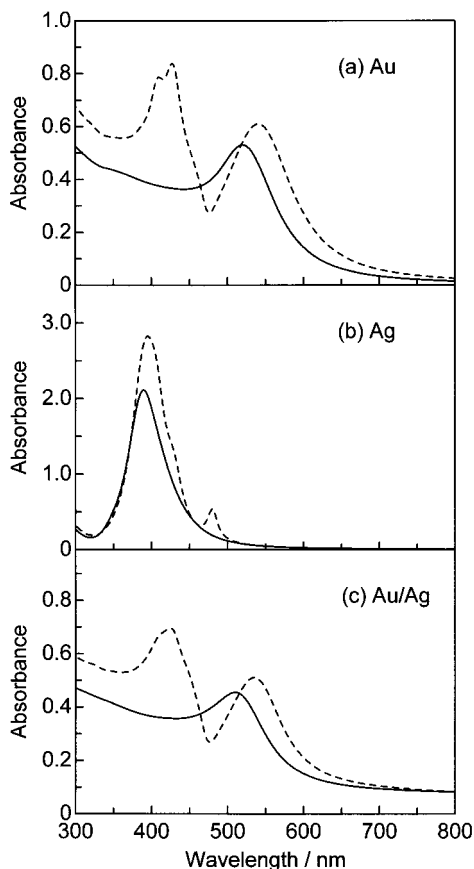
- (1) Link, S.; El-Sayed, M. A. *J. Phys. Chem. B* **1999**, *103*, 8410.
- (2) Sato, T.; Ichikawa, T.; Ito, T.; Yonezawa, Y.; Kadono, K.; Sakaguchi, T.; Miya, M. *Chem. Phys. Lett.* **1995**, *242*, 310.
- (3) Moskovits, M. *Rev. Mod. Phys.* **1985**, *57*, 783.
- (4) Yonezawa, Y.; Miyama, T.; Sato, T. *J. Soc. Photogr. Sci. Technol. Jpn. (Nippon Shashin Gakkaishi)* **1995**, *58*, 109.
- (5) Kobayashi, T., Ed. *The J-Aggregates*; World Scientific: Singapore, 1996.
- (6) Yonezawa, Y. *Recent Res. Dev. Pure Appl. Chem.* **1998**, *2*, 157.
- (7) Glass, A. M.; Liao, P. F.; Bergman, J. G.; Olson, D. H. *Opt. Lett.* **1980**, *5*, 368.
- (8) Garoff, S.; Weitz, D. A.; Gramila, T. J.; Hanson, C. D. *Opt. Lett.* **1981**, *6*, 245.
- (9) Eagen, C. F. *Appl. Opt.* **1981**, *20*, 3035.
- (10) Wang, D.-S.; Kerker, M. *Phys. Rev.* **1982**, *B25*, 2433.

(11) Creighton, J. A.; Blatchford, C. G.; Albrecht, M. G. *J. Chem. Soc., Faraday Trans. 2* **1979**, *75*, 790.

(12) Fukumoto, H.; Yonezawa, Y. *Thin Solid Films* **1998**, *329*, 748.



**Figure 1.** Chemical structures of TC and PDPA.



**Figure 2.** Absorption spectra of (a) Au colloidal solution, (b) Ag colloidal solution, and (c) Au/Ag composite colloidal solution, before (solid lines) and after (dashed lines) adsorbing TC. Light path length = 10 mm.

### Results and Discussion

Figure 2a shows absorption spectra of Au colloidal solution before and after adsorbing TC. A colloidal absorption peak by surface-plasmon resonance appears around  $\lambda = 520$  nm for bare Au colloidal nanoparticles. The absorption spectrum of TC-coated Au colloidal solution is not simply a superposition of Au colloidal solution and TC aqueous solution. A sharp absorption dip at  $\lambda = 475$  nm is remarkable, which coincides in position with the J-band of the TC J-aggregate.<sup>12</sup> We should mention that no J-band is observed in the aqueous solution consisting of  $1 \times 10^{-5}$  M TC and 1 mM KCl. The dip at  $\lambda = 475$  nm strongly suggests that TC molecules are arranged to form the J-aggregate at the surface of Au nanoparticles. Making

reference to the J-aggregate formation of TC in alternate assemblies and Langmuir–Blodgett films,<sup>12</sup> it is plausible that two-dimensional J-aggregate of TC is formed on the surface of Au nanoparticles. The peaks at  $\lambda = 428$  and 409 nm are responsible in position to monomer and dimer bands of TC in aqueous solutions.

The absorption spectra of bare and TC-coated Ag colloidal solution are shown in Figure 2b. A surface-plasmon band appears at  $\lambda = 390$  nm for bare Ag nanoparticles. In contrast to the TC-coated Au colloidal solution, the absorption peak develops at  $\lambda = 475$  nm in the TC-coated Ag colloidal solution. Shorter wavelength peaks ( $\lambda = 409$  nm, 428 nm) are hidden due to the colloidal absorption band of Ag nanoparticles.

Figure 2c shows the absorption spectra of Au/Ag colloidal solutions before and after adsorbing TC. In the absorption spectrum of bare Au/Ag colloidal solution, the surface plasmon band of Ag nanoparticles is not clear and a peak similar to that of a bare Au colloidal solution is blue-shifted to  $\lambda = 510$  nm. Considering the absorption peak of Au/Ag colloidal solution, the formation of a sort of Au/Ag composite structure such as a  $\text{Au}_{\text{core}}/\text{Ag}_{\text{shell}}$  with a very thin Ag layer would be possible.<sup>13,14</sup> An absorption dip at  $\lambda = 475$  nm is evident in the TC-coated Au/Ag nanoparticles. We have examined the dependence of absorption spectrum on the TC concentration, [TC]. The absorption dip appears even at  $[\text{TC}] = 2 \times 10^{-6}$  M for Au/Ag nanoparticles, in contrast to bare Au nanoparticles in which no absorption dip is seen at such low TC concentration. These observations would imply that TC molecules can more easily adsorb on the Au/Ag nanoparticles than on the bare Au nanoparticles.

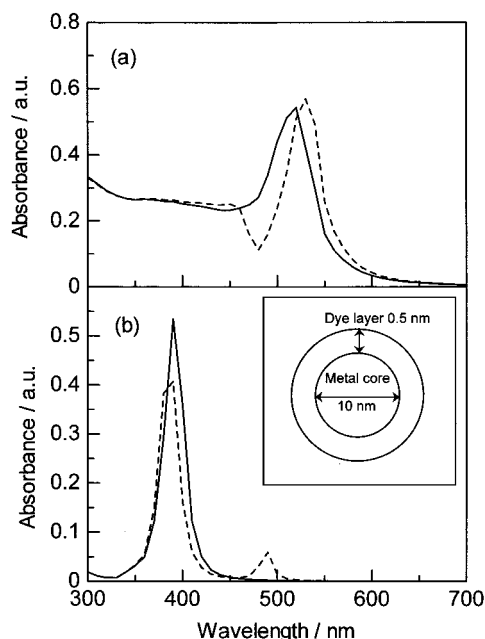
The magnitude of the absorption dip in the TC-coated Au/Ag nanoparticles increases with increasing [TC] from  $2 \times 10^{-6}$  M and is saturated at around  $[\text{TC}] = 6 \times 10^{-6}$  M. Further increase in [TC] causes the development of shorter wavelength bands at around  $\lambda = 428$  and 409 nm. Considering the absorbance of the corresponding bands in parts a and c of Figure 2, these bands around  $\lambda = 428$  and 409 nm are mostly assigned to TC monomer and dimer dissolved in the solution phase.

We have tried to simulate absorption spectra of TC-coated Au and Ag nanoparticles based on Maxwell–Garnett-type treatment of Gao et al.<sup>15</sup> In the calculation, the TC-coated nanoparticle was modeled as a spherical metal core (10 nm in diameter) with the concentric shell of TC dye layer (0.5 nm in thickness) as shown in the inset of Figure 3. The frequency-dependent dielectric constants of Au and Ag are taken from the literature.<sup>16</sup> The dielectric constant of water is  $\epsilon_m = 1.80$ . The dielectric constant of TC layer is estimated by<sup>10</sup>

$$\epsilon_s = 1 + \frac{s}{(\omega_0^2 - \omega^2 - i\omega\tau)} \quad (1)$$

where  $\omega_0 = 3.97 \times 10^{15} \text{ s}^{-1}$  ( $\lambda = 475$  nm),  $s = 1.5 \times 10^{31} \text{ s}^{-2}$ , and  $\tau = 1.0 \times 10^{14} \text{ s}^{-1}$  are chosen so as to reproduce the absorption spectrum of the TC J-aggregate. Simulated absorption spectra of TC-coated Au and Ag colloidal solutions are shown in Figure 3. A qualitative agreement between simulated and observed spectra is quite good. In this calculation, we have set aside remaining TC monomer and dimer absorption bands in Figure 2a. The absorption

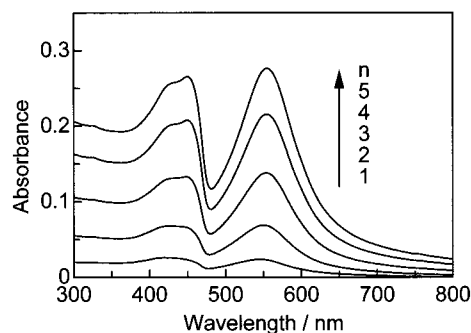
- (13) Morriss, R. H.; Collins, L. F. *J. Chem. Phys.* **1964**, *41*, 3357.  
 (14) Freeman, R. G.; Hommer, M. B.; Grabar, K. C.; Jackson, M. A.; Natan, M. J. *J. Phys. Chem.* **1996**, *100*, 718.  
 (15) Gao, L.; Li, Z.-Y. *J. Appl. Phys.* **2000**, *87*, 1620.  
 (16) Sato, T.; Yonezawa, Y.; Hada, H. *J. Soc. Photogr. Sci. Technol. Jpn. (Nippon Shashin Gakkaishi)* **1988**, *51*, 122.



**Figure 3.** Simulated absorption spectra of (a) Au colloidal solution and (b) Ag colloidal solution before (solid lines) and after (dashed lines) adsorbing TC. The inset illustrates the model of TC-coated nanoparticles assumed in the calculation.

dip for TC-coated Au nanoparticles and the absorption peak for TC-coated Ag nanoparticles are well reproduced in the simulated spectra. These results afford direct evidence that both absorption dip and absorption peak at 475 nm are caused by the J-aggregate of TC in the concentric shell. It is likely that whether the J-band (475 nm) manifests itself as the absorption dip or peak depends on the coupling between surface plasmon of metal core and molecular exciton of dye layer. In this context, we might assume that absorption dip appears when the J-band peak ( $\lambda_{\text{ex}}$ ) lies at a slightly shorter wavelength than the surface plasmon peak ( $\lambda_{\text{SP}}$ ) and that an absorption peak develops when  $\lambda_{\text{ex}}$  is located at a slightly longer wavelength than  $\lambda_{\text{SP}}$ .

Considering possible applications of dye-coated metal nanoparticles for the electronic or optical devices, the fabrication of thin films incorporating them would be important. We have tested the alternate adsorption technique which was proved to be quite useful to fabricate the organized assembly incorporating the J-aggregate of TC.<sup>12</sup> Absorption spectra of the alternate assemblies with different numbers of layers  $n = 1-5$  are shown in Figure 4. As absorption spectra are not significantly different from those in Figure 2c, the size and shape of TC-coated



**Figure 4.** Absorption spectra of alternate assemblies incorporating TC-coated Au/Ag composite nanoparticles for  $n = 1-5$ .

Au/Ag nanoparticles do not suffer serious change during alternate adsorption. The magnitudes of absorption dip ( $\lambda = 475$  nm) and peak ( $\lambda = 552$  nm) are almost linearly increased with increasing  $n$ , implying the completion of layer-by-layer structure. Preliminary results of the atomic force microscopy (AFM) observation indicate the dense and homogeneous adsorption of Au/Ag nanoparticles on the PDDA surface.<sup>17</sup> We have examined the fabrication of alternate assemblies incorporating TC-coated Au nanoparticles and TC-coated Ag nanoparticles. However, it appeared that absorption spectra of alternate assemblies made of them are considerably different from those in parts a and b of Figure 2. In this sense, Au/Ag nanoparticles are superior to Au and Ag ones.

Considering relatively large third-order nonlinear optical susceptibilities of colloidal gold and silver dispersions as well as cyanine dyes and their aggregates,<sup>2,18,19</sup> the combined effects of the Au and Ag nanoparticles coated with the J-aggregate attract much attention. However, no systematic studies have been reported yet, except for limited works.<sup>20,21</sup> In this sense, Au/Ag nanoparticles coated with the J-aggregate of cyanine dyes would be of value as novel linear and nonlinear optical materials, considering fairly strong coupling between metal core and dye shell as evidenced by the spectral change, together with an ease to deposit on the substrate by an alternate adsorption technique.

LA0013190

(17) Kometani, N.; Tosaka, M.; Tsubonishi, M.; Yonezawa, Y. Unpublished data.

(18) Hache, F.; Richard, D.; Flytzanis, C.; Kreibitz, U. *Appl. Phys.* **1988**, *A47*, 347.

(19) Kobayashi, S. *Mol. Cryst. Liq. Cryst.* **1992**, *217*, 77.

(20) Shelkovnikov, V. V.; Zhuravlev, F. A.; Orlova, N. A.; Plekhanov, A. I.; Safonov, V. P. *J. Mater. Chem.* **1995**, *5*, 1331.

(21) Orita, T.; Sato, T.; Yonezawa, Y.; Sakaguchi, T.; Kadono, K.; Ohta, K. *Mol. Cryst. Liq. Cryst.* **1997**, *294*, 283.