

Synthesis and spectroscopic properties of silver:dye composite nanoparticles with a double-shell structure

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Noble metal nanoparticles (NPs), such as Au, Ag and Cu NPs, are currently one of the most attractive nanomaterials. They have a wide variety of applications including catalysis, printable conductor, antibacterial agent, and so on. In particular, there has been a large interest in the optical and spectroscopic properties because of the ability to couple with the electromagnetic wave in the visible or near-infrared region, called localized surface plasmon resonance (LSPR). The LSPRs induce a large extinction of light and generate the enhanced electromagnetic fields in the vicinity of the metal surfaces. More importantly, the enhanced fields lead to several intriguing phenomena such as surface-enhanced Raman scattering (SERS), enhanced photoluminescence (PL), and enhanced Förster resonance energy transfer. Manipulating and controlling the surface-enhanced effects are therefore considered to be an essential issue for the development in the area of imaging, diagnostics, photonics, plasmonics, etc.

Cyanine dye J-aggregates (JAs), a kind of molecular assemblies, have been known to form on the solid surfaces, LB films, etc., and have several interesting spectroscopic properties which cannot be observed in the form of monomer. For example, they show a sharp absorption band (J-band) red-shifted with respect to the monomer band and the resonance fluorescence with a small Stokes shift. Those properties have been extensively studied for many years and explained in terms of the delocalization of Frenkel exciton, resulting from the strong coupling between transition dipole moments of dyes.

Considering the unique properties of the surface plasmon and exciton, it is reasonable to expect that the hybrid materials composed of the noble metal NPs and the JAs exhibit certain novel properties useful for the optical or optoelectronic materials. In this sense, our group has been interested in such hybrid systems [1-3].

In this study, to examine the spectroscopic properties of the exciton–plasmon hybrid systems, we have synthesized double-shell-type composite NPs, consisting of the following three components; spherical Ag core, spacer layer (inner shell), and cyanine dye JA layer (outer shell) (see Figure 1a). The spacer layer is made of the self-assembled monolayer of *N, N, N*-trimethyl(11-mercaptoundecyl)ammonium chloride (TMA) and plays a significant role in the formation of JA shell. Two kinds of cyanine dyes, 3,3'-disulfopropyl-5,5'-dichloro-thiacyanine sodium salt (TC) and 3,3'-disulfopropyl-5,5'-dichloro-oxacyanine triethylammonium salt (OC) (Figure 1b) were used as an ingredient of the JA shell. In Figure 2, the absorption spectra of colloidal solution containing Ag/TMA/TC and Ag/TMA/OC composite NPs are shown. The spectrum of the Ag/TMA/TC NPs (Figure 2a) is characterized by two peaks at 398 nm and 470 nm. The former peak can be ascribed to the LSPR band of Ag NPs, and the latter peak to the J-band of TC JAs, supporting the ability of TMA layer to facilitate the J-aggregation. On the other hand, the spectrum of the Ag/TMA/OC NPs (Figure 2b) shows an anomalous “dip” at 409 nm, instead of a “peak” of OC J-band ($\lambda_{J,OC} = 410$ nm [4]). The appearance of the dip-type absorption suggests the presence of a strong *exciton–plasmon coupling* between the Ag NP core and the OC JA shell.

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References:

- [1] N. Kometani, M. Tsubonishi, T. Fujita, K. Asami, Y. Yonezawa, *Langmuir*, **17** (2001) 578.
 [2] A. Yoshida, N. Kometani, Y. Yonezawa, *Colloids Surf., A*, **313/314** (2008) 581.
 [3] A. Yoshida, Y. Yonezawa, N. Kometani, *Langmuir*, **25** (2009) 6683.
 [4] K. Tani et al. *J. Photochem. Photobiol., A*, **199** (2008) 150.

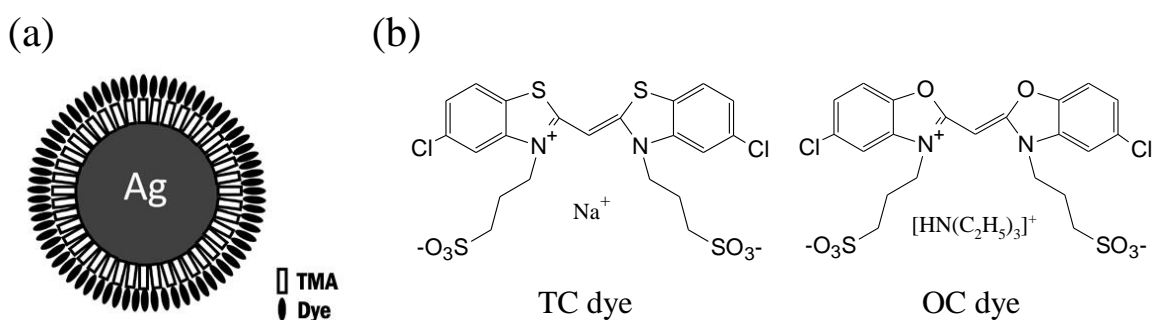
Figures:

Figure 1. (a) Schematic illustration of an Ag/TMA/Dye composite NP. (b) Molecular structure of the cyanine dyes used in this study.

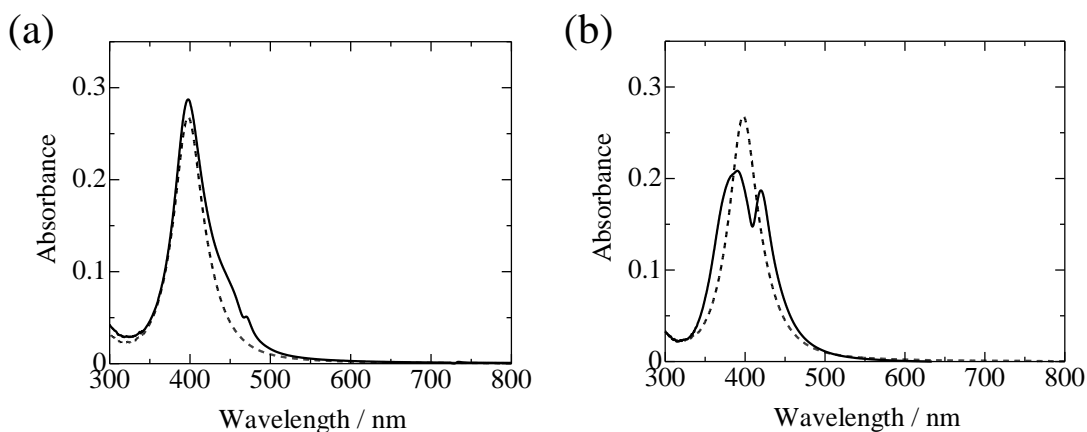


Figure 2. Absorption spectra of colloidal solutions containing (a) Ag/TMA/TC NPs and (b) Ag/TMA/OC NPs. The spectra depicted in broken line in each spectrum correspond to the Ag/TMA NPs (without dye layer).