Preparation and Spectroscopic Properties of Silver Nanodisks Covered with J-Aggregate of Cyanine Dye

Tomoo Sato,* Ayako Omura, and Yoshiyuki Kobayashi

Department of Chemistry, Graduate School of Pure and Applied Sciences, University of Tsukuba, Tsukuba 305-8571

Received September 4, 2009

E-mail: tsato@chem.tsukuba.ac.jp

We found a unique spectroscopic property of silver nanodisks covered with J-aggregate. The spectral hole around the position of the J-band was remarkably observed in the surface plasmon band. The origin of the peculiar phenomenon is presumed to be the suppressive interaction between the surface plasmon and Frenkel exciton.

Optics and spectroscopy of molecular aggregates have attracted considerable attention in connection with molecular photonic materials and model systems of light-harvesting.[1,2] J-Aggregate of cyanine dye is a molecular aggregate arranged in brick-stone structure and the spectroscopic properties, such as an extraordinary sharp absorption band (J-band) which is largely red-shifted from monomer band and resonance fluorescence, are characterized by the excitation of the Frenkel exciton.[2] On the other hand, spectroscopic properties of noble metal nanoparticles are characterized by the excitation of the surface plasmon which is the collective oscillation of electrons on the metal surface.[3] If the molecular aggregate and noble metal nanoparticle are located close together, the system would be expected to show new spectroscopic properties and photofunctions originating from the coupling of the exciton and the surface plasmon. Although many studies on the optical properties of noble metal nanoparticles covered with dye such as rhodamine have been done since the 1980s,[4–7] there are not many studies using molecular aggregates, whose spectroscopic properties are characterized by the excitation of the exciton.[8–13]

Previously, we reported that the extinction spectrum of noble metal nanoparticles covered with J-aggregate of cyanine dye is not a simple superposition of the individual spectra of the noble metal nanoparticles and J-aggregate of cyanine dye, and there is a spectral dip in the surface plasmon band around the position of the J-band.[9] We assumed that this phenomenon was related to the interaction of the Frenkel exciton and the surface plasmon. However, the effect was small and not clear in the former paper, in which we used gradually aggregated spherical silver nanoparticles. The reason why the effect was small is presumed that the interaction of the exciton and surface plasmon is not very strong because the directions of the transition dipole moments of the exciton and surface plasmon are not arranged in one direction. Therefore, we predict that this anomalous effect becomes more remarkable by using silver nanodisks. In this case, uniform and large J-aggregate can be formed on a nanodisk with two wide and flat planes which are in parallel to the transition dipole moment of the surface plasmon, and then it is possible to make the exciton and surface plasmon more wide-ranging excitation which means they have larger transition dipole moments. The exciton–surface plasmon interaction would increase because the transition dipole moments of the exciton and surface plasmon become larger and their directions are arranged in one direction. Therefore, we have tried to make silver nanodisks covered with J-aggregate of cyanine dye and examined the extinction spectra.

Experimental

Silver nanodisks were prepared based on a method reported by Brus et al. in 2003.[14] Briefly, to make a suspension of spherical silver nanoparticles, 0.5 mL of ice-cold 25 mM $NaBH_4$ aqueous solution was added to 20.5 mL of a solution containing 9.8 mM sodium citrate and 0.12 mM $AgNO_3$, and the reaction mixture was stirred for 5 min. Then the suspension was kept in the dark for more than 12 h. To make a growth solution, 1 mL of this suspension of silver nanoparticles was added to 9 mL of a solution containing 0.56–1.5 mM sodium citrate and 0.28 mM $AgNO_3$. In order to prepare a suspension of silver nanodisks, the growth solution in the quartz cell (light path length 1 cm) was exposed for 4–7 h with two emission lines (546/577 nm) from a 500 W super high-pressure mercury lamp (Ushio HB-50106AA-A/500 W). The two emission lines were selected by cut off filter Y51 (Asahi techno glass) and the power of the light was 100 mW cm^{-2}. The shape of silver nanodisks was confirmed by transmission electron microscope (JEOL JEM-100CX). Cyanine dye (TCC) shown in Figure 1 was adsorbed on the surface of silver nanodisks by adding 0.1 mL of a solution containing 0.02–0.05 mM TCC and 2–5 mM NaCl or KCl (in 1:1 by volume water and ethanol) to 0.3 mL of the suspension of silver nanodisks. The J-band of TCC is located around $\lambda = 650$–660 nm. The extinction spectra of the TCC adsorbed silver nanodisks were measured with a Shimadzu spectrophotometer (UV-260) without purification. The light path length of the cell used for spectroscopic measurements was usually 2–10 mm, according to the optical density of the solutions. The extinction spectra in the figures have been given as if the cell length for every solution were 10 mm.

Results and Discussion

The change of extinction spectrum of the growth solution by 7 h irradiation is shown in Figure 2. Before irradiation, there is

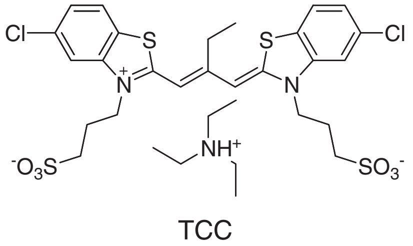

Figure 1. Cyanine dye used in this study.

Published on the web September 2, 2010; doi:10.1246/bcsj.20090235

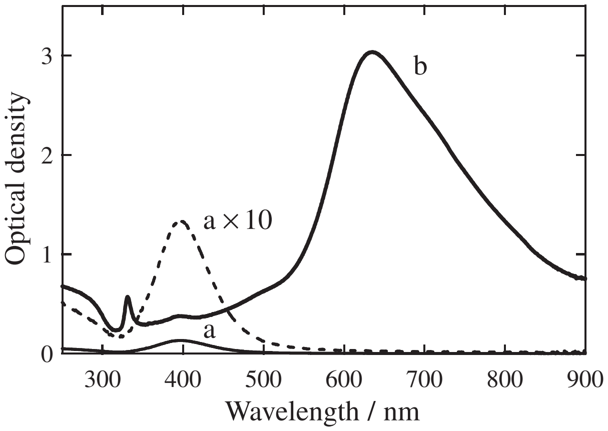

Figure 2. Extinction spectra of growth solution before (a) and after (b) 7 h irradiation. [Ag] = 0.26 mM and [sodium citrate] = 1.5 mM.

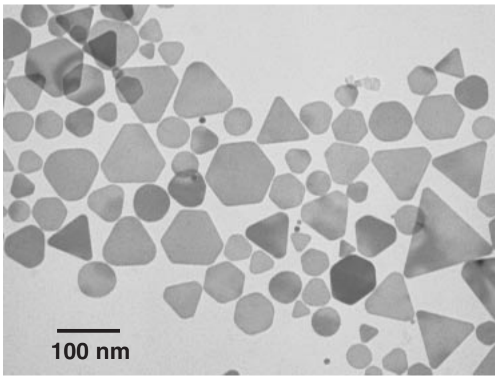

Figure 3. TEM image of silver nanodisks.

an extinction peak at $\lambda = 400$ nm, which is assigned to the surface plasmon band of spherical silver nanoparticles. After irradiation, the extinction peak at $\lambda = 400$ nm was hardly seen, and a strong extinction peak at $\lambda = 635$ nm and a sharp extinction peak at $\lambda = 330$ nm appeared. These extinction bands should be assigned to the surface plasmon extinction of silver nanodisks. The shape and the size of silver nanoparticles were evaluated by transmission electron microscopy (TEM). Silver nanoparticles before irradiation were spherical and 8 nm in average diameter. Silver nanoparticles after irradiation for 7 h were hexagonal or triangle tabular particles as shown in Figure 3. The average diameter was 50 nm and thickness was 5–10 nm. Mirkin and Schatz evaluated the extinction spectrum of the silver triangle pillar (nanoprism), 100 nm in edge length and 16 nm thick, by solving the Maxwell equation.[15] Referring to their results, extinction bands at $\lambda = 635$ nm and $\lambda = 330$ nm are assigned to dipole in plane and quadrupole out of plane, respectively.

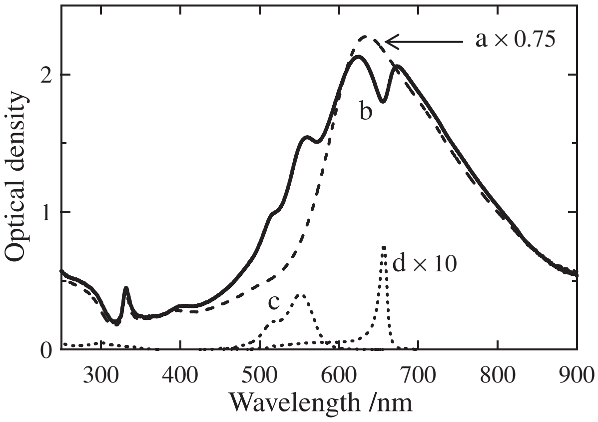

Figure 4. Extinction spectra of suspension of silver nanodisks before (dashed line a) and after (solid line b) adsoption of TCC. (b) [Ag] = 0.2 mM, [TCC] = 0.0075 mM, [NaCl] = 1.3 mM, and [sodium citrate] = 1.1 mM in 7:1 by volume water and ethanol. (c) Absorption spectrum of TCC solution. [TCC] = 0.004 mM, [NaCl] = 1.3 mM, and [sodium citrate] = 1.1 mM in 7:1 by volume water and ethanol. (d) Spectrum of reflection absorbance of J-aggregate monolayer of TCC on the Au(111) covered with cysteamine monolayer.[9] This spectrum is drawn in order to show the approximate position and shape of the J-band of TCC. Because the position of the J-band depend on the aggregational state of TCC, the position of the J-band of TCC on silver nanodisks is not necessarily exactly the same as that shown in this spectum.

The change of the extinction spectrum of the suspension of silver nanodisks by adding a solution of 0.03 mM TCC and 5 mM NaCl is shown in Figure 4. To normalize the concentration of the silver nanodisks, the spectrum before adding the solution was multiplied by 0.75. Considering Lambert–Beer's law, it is generally supposed that the extinction spectrum of silver nanodisks after adsorbing J-aggregate of TCC would be simple superposition of the individual spectra of the nanodisks (dashed line a) and the J-aggregate (dotted line d).[16] Actually, however, an anomalous spectral hole at $\lambda = 655$ nm appeared in the surface plasmon extinction band (solid line b). The anomalous hole is more remarkable than that reported in our previous paper, in which TCC was adsorbed on the gradually aggregated spherical silver nanoparticles. Because of the agreement of the position of the spectral hole and the J-band of TCC aggregate, we infer that the spectral hole is caused by J-aggregate of TCC adsorbed on the silver nanodisks. The origin of the peculiar phenomenon is presumed to be the suppressive interaction of the Frenkel exciton and surface plasmon. On the other hand, a large portion of the extinction peaks at $\lambda = 552$ and 514 nm are assigned to TCC monomer left in the solution without adsorbing on the silver nanodisks, which was confirmed by a spectrophotometric analysis of the centrifuged supernatant of the suspension of the silver nanodisks after adsorption of TCC. In our study, we did not evaluate the spectroscopic interaction between TCC monomer adsorbed on the silver nanodisk and the surface plasmon. Because the extinction band of adsorbed TCC monomer considerably overlaps the extinction band of TCC monomer left in the solution (M_{sol} band). While, in contrast, because the J-band does not overlap the M_{sol} band, it is easy to observe the spectroscopic interaction between the J-aggregate adsorbed on the silver nanodisk and the surface plasmon, even if a large amount of monomer is left in the solution.

Under our experimental conditions, TCC did not form J-aggregate in the solution without silver nanodisks, even in the presence of NaCl (Figure 4 dotted line c). Whereas, even in the presence of the silver nanodisks, TCC did not adsorb and form J-aggregate on the silver nanodisks in the suspension without the chloride ion Cl^-, as a result, the anomalous hole was not observed (Figure S1 in Supporting Information). Therefore, it is safe to say that TCC does adsorb and form J-aggregate only when both the silver nanodisks and Cl^- are present in the TCC solution, and J-aggregate can be formed only by the TCC adsorbed on the silver nanodisks under our conditions. According to detailed studies using silver thin films, which can be regarded as a model system of the silver nanodisk, Cl^- has a very important role for TCC adsorption and J-aggregate formation on the surface of silver.[17,18] The surface of the silver films in water is covered with less ordered OH^- monolayer and the OH^- monolayer can be substitutionally replaced by a well-ordered Cl^- monolayer in solutions containing Cl^-.[17] In our case, at first, the surface of the silver nanodisks is randomly covered with citrate ion $RCOO^-$. As well as OH^-, the $RCOO^-$ can be also substituted for Cl^-,[19] which forms Cl^- monolayer in an orderly manner on the silver nanodisk. TCC adsorption and J-aggregate formation on the silver nanodisks is also thought to be analogous with that on silver thin films.[18] By electrostatic interaction between the cationic chromophore of TCC and the negative surface charge from orderly adsorbed Cl^-, TCC adsorbs orderly on the surface of silver nanodisks in the direction where the chromophore touches the surface of the nanodisks and the sulfopropyl groups are at the outermost surface, and the densely ordered TCC forms two-dimensional J-aggregate monolayer on the surface.

The change of extinction spectrum of the suspension of the ca. 8 nm spherical silver nanoparticles by adding a solution of 0.03 mM TCC and 5 mM NaCl is shown in Figure S2 (Supporting Information). The spectrum change around $\lambda = 650$ nm, which means the formation of J-aggregate, is hardly seen. This is because there is insufficient surface space to form J-aggregate on a small spherical particle. On the other hand, as shown in our previous paper,[9] extinction spectrum of gradually aggregated spherical silver nanoparticles covered with J-aggregate of TCC showed a spectral dip in the surface plasmon band around the position of the J-band. However, the appearance of the dip was not remarkable like the hole shown in Figure 4. Meanwhile, we attempted TCC adsorption in suspensions of silver nanodisks whose polydispersities of size and shape distribution were intentionally larger than that of silver nanodisks shown in Figures 2 and 4. In any case, the observed holes were more remarkable (Figure S3 in Supporting Information) than above-mentioned results for the spherical silver nanoparticle or gradually aggregated spherical silver nanoparticles with TCC. Whether polydispersity is large or small, the superiority of silver nanodisks with large flat surfaces remains the same, although the size and shape distributions of silver nanodisks used for Figures 2–4 in this study were not small. Of course, uniform silver nanodisks are preferable for quantitative investigation of the anomalous phenomenon shown in this study. However, because our main purpose in this report is to show the anomalous phenomenon can be observed more remarkably by using the nanodisks, we used such non-uniform silver nanodisks as they were. Preparation and use of more uniform nanodisks for quantitative study is an issue for the future.

In summary, silver nanodisks were prepared by visible light irradiation to a suspension of spherical silver nanoparticles in the presence of sodium citrate and $AgNO_3$. The typical shape of the nanodisks was tabular triangle or a hexagon, whose size was 50 nm in diameter and 5–10 nm in thickness. By adsorbing J-aggregate of cyanine dye on the surface of the silver nanodisks, a remarkable spectral hole in the surface plasmon band appeared around the position of the J-band. The anomalous hole in the extinction spectrum appears more clearly than that reported in our previous paper.[9] After the first finding of the anomalous phenomenon, some groups have also paid attention to this anomalous phenomenon and studied in various ways.[10–13] The method of using nanodisks is better than that of using spherical particles. We believe that the method shown in this study can contribute to the elucidation of this anomalous phenomenon and the exciton–surface plasmon interaction.

This work was partially supported by a Grant-in-Aid for Scientific Research (C) (No. 16550117) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

Supporting Information

Additional extinction spectra of various suspensions of silver nanodisks and spherical silver nanoparticles with TCC. This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

References

1 D. Möbius, *Adv. Mater.* **1995**, *7*, 437.

2 *J-Aggregates*, ed. by T. Kobayashi, World Scientific, Singapore, **1996**.

3 U. Kreibig, M. Vollmer, *Optical Properties of Metal Clusters*, Springer, Berlin, **1995**.

4 A. M. Glass, P. F. Liao, J. G. Bergman, D. H. Olson, *Opt. Lett.* **1980**, *5*, 368.

5 H. G. Craighead, A. M. Glass, *Opt. Lett.* **1981**, *6*, 248.

6 S. Garoff, D. A. Weitz, T. J. Gramila, C. D. Hanson, *Opt. Lett.* **1981**, *6*, 245.

7 F. R. Aussenegg, A. Leitner, M. E. Lippitsch, H. Reinisch, M. Riegler, *Surf. Sci.* **1987**, *189–190*, 935.

8 T. Orita, T. Sato, Y. Yonezawa, T. Sakaguchi, K. Kadono, K. Ohta, *Mol. Cryst. Liq. Cryst.* **1997**, *294*, 283.

9 T. Sato, F. Tsugawa, T. Tomita, M. Kawasaki, *Chem. Lett.* **2001**, 402.

10 N. Kometani, M. Tsubonishi, T. Fujita, K. Asami, Y. Yonezawa, *Langmuir* **2001**, *17*, 578.

11 J. Hranisavljevic, N. M. Dimitrijevic, G. A. Wurtz, G. P. Wiederrecht, *J. Am. Chem. Soc.* **2002**, *124*, 4536.

12 G. P. Wiederrecht, G. A. Wurtz, J. Hranisavljevic, *Nano Lett.* **2004**, *4*, 2121.

13 T. Uwada, R. Toyota, H. Masuhara, T. Asahi, *J. Phys. Chem. C* **2007**, *111*, 1549.

14 M. Maillard, P. Huang, L. Brus, *Nano Lett.* **2003**, *3*, 1611.

15 R. Jin, Y. Cao, C. A. Mirkin, K. L. Kelly, G. C. Schatz, J. G. Zheng, *Science* **2001**, *294*, 1901.

16 T. Sato, A. Yamamoto, M. Kawasaki, *Chem. Lett.* **2000**, 394.

17 M. Kawasaki, H. Ishii, *J. Imaging Sci. Technol.* **1995**, *39*, 210.

18 M. Kawasaki, H. Inokuma, *J. Phys. Chem. B* **1999**, *103*, 1233.

19 Y. Maruyama, M. Futamata, *Chem. Phys. Lett.* **2007**, *448*, 93.