Luminescence Enhancement of Ruthenium Complexes in Polymer Nanosheet by Surface Plasmon Resonance of Metal Nanoparticle

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The luminescence properties of tris(2,2′-bipyridine) ruthenium complex ($Ru(bpy)_3{}^{2+}$) incorporated into polymer Langmuir–Blodgett (LB) films (polymer nanosheets) excited by localized surface plasmon on metal nanoparticles are described. It was clearly demonstrated that the luminescence intensity of $Ru(bpy)_3{}^{2+}$ was changed by the distance from the localized surface plasmon on the nanoparticle. The enhancement of luminescence by silver nanoparticle and the quenching of luminescence by gold nanoparticle were observed.

Surface plasmon resonance (SPR) has attracted much attention because of high potential of photonics and electronics application.[1] For example, very large enhancements of fluorescence and Raman scattering have been observed on metal surfaces.[2–5] Local electromagnetic fields are found to increase by more than 3 orders of magnitude at the metal surfaces. Previously, we have found that photocurrent generation based on the polymer LB monolayer containing $Ru(bpy)_3{}^{2+}$ on a silver electrode excited by SPR was enhanced largely compared with far field light irradiation.[6] The SPR generation on metal thin film occurs at a critical incident angle of excitation beam, however, SPR generation on metal nanoparticles requires no special incident angle condition. By far field light irradiation on metal particle, effective SPR occurs on the surface. Recently, we have found that the regular adsorption of metal nanoparticle occurs on a template of polymer nanosheet of (poly(*N*-dodecylacrylamide-*co*-*N*-2-(2-(2-aminoethoxy)ethoxy)ethylacrylamide).[7,8] The arrangement of metal nanoparticle on a well-defined nanostructure is of interest, because noble metal particle has a lot of fascinating features, such as quantum size effect, localized surface plasmon, photocatalytic reaction, etc. It is expected to build up tailored array of nanoparticle on polymer nanosheet containing $Ru(bpy)_3{}^{2+}$ for the exploitation of the photocurrent enhancement phenomena by SPR reported in previous work, based on adsorption of metal nanoparticle on the template of polymer nanosheet. In this paper, the luminescence behavior of $Ru(bpy)_3{}^{2+}$ incorporated into polymer nanosheet excited by SPR on metal nanoparticles is investigated. Since the thickness of poly(*N*-dodecylacrylamide) (pDDA) monolayer is reported to be 1.72 nm,[9] the deposition of the number of pDDA nanosheet can tailor the distance between the $Ru(bpy)_3{}^{2+}$ layer and gold or silver nanoparticle arrays (Figure 1). The luminescence intensity was investigated as a function of the well-defined separation distance between $Ru(bpy)_3{}^{2+}$ monolayer and metal nanoparticle array.

Poly(*N*-dodecylacrylamide-*co*-*N*-2-(2-(2-aminoethoxy)ethoxy)ethylacrylamide) (p(DDA/DADOO)), and $Ru(bpy)_3{}^{2+}$ copolymer (p(DDA/Ru)) were synthesized according to the literature (Figure 1).[6,10] The nanoassembled system for the measurement of luminescence behavior was prepared as follows; bilayers of p(DDA/Ru) nanosheets were transferred on a quartz substrate by LB method, pDDA homopolymer nanosheet with a fixed number of layers was transferred onto the p(DDA/Ru) layers, and then the substrates were overcoated with bilayers of p(DDA/DADOO) nanosheets, finally the substrate was immersed into aqueous metal nanoparticle solution for the adsorption of nanoparticle (Figure 1). Gold (30 nm in averaged diameter) and silver (60 nm in averaged diameter) nanoparticles prepared by citrate reduction method were employed.[8] The resulting nanoassemblies were excited by a He-Cd laser beam (441.6 nm, IK5451R-E, Kinmon Electric Co., Ltd.). The luminescence intensity was monitored by a photodiode array (USB2000-FLG, Ocean Optics) as a function of the number of pDDA monolayer.

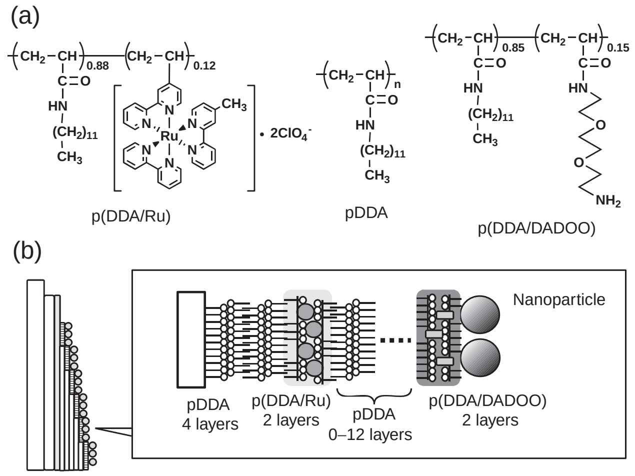

Figure 1. (a) Chemical structure of p(DDA/DADOO), p(DDA/Ru), and pDDA, and (b) a schematic of sample structure.

Figure 2 shows absorption spectra for gold and silver nanoparticles immobilized on the polymer nanosheets. The surface coverage of each nanoparticle was 40 and 35% determined from SEM image. In both cases, the nanoparticles are uniformly distributed on the polymer nanosheets as reported previously.[8] There is a broad absorption band around 600 nm for gold nanoparticle array, whereas the absorption band is appeared at 400 nm in the case of silver nanoparticle array. $Ru(bpy)_3{}^{2+}$ has a strong and broad absorption band around 460 nm due to MLCT absorption band. Besides, a strong emission band appeares at 610 nm (Figure 2). It is interesting that the luminescence behavior of $Ru(bpy)_3{}^{2+}$ on the metal nanoparticle array is drastically changed depending on gold or silver. As shown in Figure 3, the luminescence of $Ru(bpy)_3{}^{2+}$ is effectively

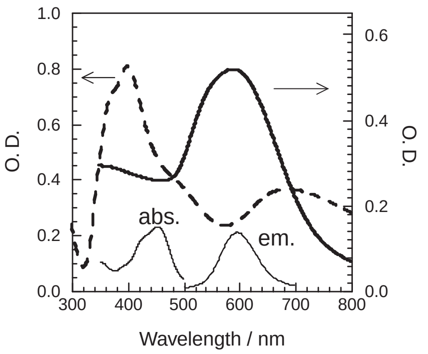

Figure 2. UV–vis absorption spectra of gold (solid line) and silver (dashed line) nanoparticles immobilized on p(DDA/DADOO) nanosheets. Absorption and luminescence spectra (arbitrary unit) of p(DDA/Ru) nanosheets are also shown in the figure.

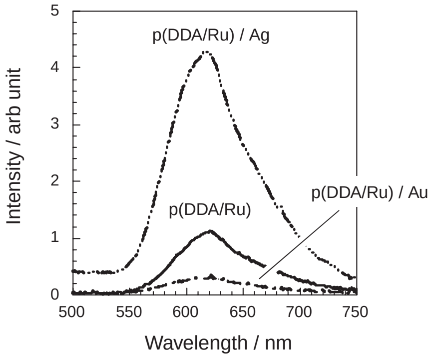

Figure 3. Luminescence spectra of two-layer p(DDA/Ru) nanosheets with silver and gold nanoparticle arrays. As a comparison, luminescence spectrum of two-layer p(DDA/Ru) nanosheets is given in the figure. No pDDA layer was used as a spacer.

quenched by gold nanoparticle array. On the other hand, the luminescence is remarkably enhanced by silver nanoparticle array. The gold nanoparticle is working as quencher, while the excitation of $Ru(bpy)_3^{2+}$ on the silver nanoparticle is enhanced. The luminescence intensity increases four times as large as that without silver nanoparticle and the enhancement factor will be improved by optimization of the silver nanoparticle's size, the amount of the immobilized silver nanoparticle, and the layer structure.

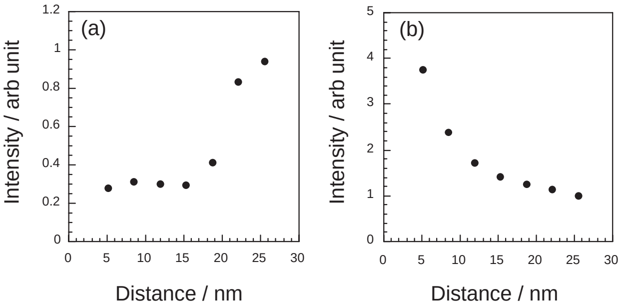

Figure 4. Luminescence intensity of two-layer p(DDA/Ru) nanosheets as a function of separation distance from metal nanoparticle arrays (a) gold, and (b) silver.

As a mechanism for luminescence decrease by the presence of gold nanoparticle, the emission quenching via electron transfer or energy transfer to gold nanoparticle can be considered. In the present study, the luminescence intensity change occurs at the separation distance larger than 20 nm (Figure 4). This implies that the luminescence quenching caused by electron transfer is not likely in this case, since the electron-transfer quenching occurs at short-range length. The absorption band of the gold nanoparticle overlaps with the emission band of the $Ru(bpy)_3^{2+}$, and energy transfer from excited $Ru(bpy)_3^{2+}$ to gold naoparticles is possible to occur at the long-range distance (≈10 nm). On the other hand, an increase in the luminescence by approaching of silver nanoparticle is apparently caused by energy transfer from the surface plasmon electromagnetic field produced on the nanoparticle. The quantitative analysis is now in progress.

In conclusion, the luminescence properties of $Ru(bpy)_3^{2+}$ under surface plasmon excitation was investigated as a function of separation distance between $Ru(bpy)_3^{2+}$ and metal nanoparticles array. The hybrid nanostructure was constructed with "bottom up" approach mainly based on the Langmuir–Blodgett technique. The separation distance was well defined at the nanometer scale using pDDA monolayer with 1.72 nm thickness as a ruler. The efficient luminescence enhancement was achieved in the case of localized surface plasmon resonance generated at the silver nanoparticle surface, indicating that the luminescence enhancement strongly depends on spectroscopic properties of the luminophore. As a future work to exploit the surface plasmon electromagnetic field occurred at the metal nanoparticle surface, controlling the dye molecule and metal nanoparticle ordering with flexible spacer at the range of ≈10 nm will open up a new avenue of photonic and/or electronic application based on both luminescence quenching and enhancement mechanism.

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References

1 J. R. Lakowicz, *Anal. Biochem.*, **337**, 171 (2005).
2 T. Huang and R. W. Murray, *Langmuir*, **18**, 7077 (2002).
3 "Surface Enhanced Raman Scattering," ed. by R. K. Chan and T. E. Furtak, Plenum, New York (1982).
4 S. Pan and L. J. Rothberg, *J. Am. Chem. Soc.*, **127**, 6087 (2005).
5 P. Das and H. Metiu, *J. Phys. Chem.*, **89**, 4680 (1985).
6 N. Fukuda, M. Mitsuishi, A. Aoki, and T. Miyashita, *J. Phys. Chem. B*, **106**, 7048 (2002).
7 H. Tanaka, M. Mitsuishi, and T. Miyashita, *Langmuir*, **19**, 3103 (2003).
8 M. Mitsuishi, H. Tanaka, and T. Miyashita, *Trans. Mater. Res. Soc. Jpn.*, in press.
9 T. Miyashita, Y. Mizuta, and M. Matsuda, *Brit. Polym. J.*, **22**, 327 (1990).
10 Y. Kado, A. Aoki, and T. Miyashita, *J. Mater. Sci.*, **37**, 4839 (2002).

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