Enhancement of an Anodic Photocurrent for Polymer Langmuir–Blodgett Monolayer Containing Tris(2,2'-bipyridine)ruthenium Complex by Surface Plasmon Excitation

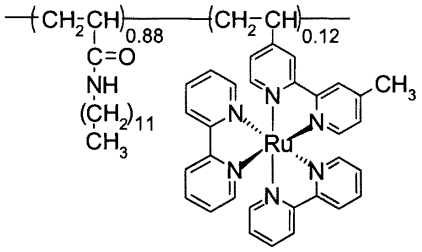
Nobuko Fukuda, Masaya Mitsuishi, Atsushi Aoki, and Tokuji Miyashita*
Institute for Chemical Reaction Science, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577

(Received January 17, 2001; CL-010050)

An anodic photocurrent due to photoinduced electron transfer between excited $Ru(bpy)_3^{2+}$ and triethanolamine was remarkably enhanced by light irradiation using the surface plasmon resonance on a silver electrode which was modified by amphiphilic copolymer Langmuir–Blodgett monolayer containing $Ru(bpy)_3^{2+}$ compared with irradiation of transmitted light.

Tris(2,2'-bipyridine)ruthenium complex, $Ru(bpy)_3^{2+}$ is one of the most attractive materials for use as a sensitizer in photoelectric conversion devices, and a number of photoelectrochemical cells using $Ru(bpy)_3^{2+}$ have been designed and characterized.[1–6] We have previously reported the generation of an anodic photocurrent by visible light irradiation of an amphiphilic polymer Langmuir–Blodgett (LB) films containing $Ru(bpy)_3^{2+}$ derivatives in the presence of ArSH or triethanolamine as sacrificial electron donors.[7–9] The anodic photocurrent was increased by the use of electrolyte solutions containing a high concentration of donors, use of high power light sources, and hetero-deposition on polymer LB films of an $Ru(bpy)_3^{2+}$ derivative and ferrocene as an electron donor.[9,10]

In order to exploit these interesting materials more effectively, it is important not only to consider relationships between the functional groups but also to develop a photocurrent generation system including the nano-assemblies as a whole. In this study, we investigated the induction of a strong enhancement of the electromagnetic field at a metal surface by light excitation of surface plasmons.[11] When surface plasmons are excited, the electromagnetic field at the metal surface is remarkably enhanced, as calculated using Fresnel's theory.[12–14] We attempted to measure an anodic photocurrent generated by photoinduced electron transfer between excited $Ru(bpy)_3^{2+}$ in an *N*-dodecylacrylamide (DDA) copolymer containing $Ru(bpy)_3^{2+}$ (p(DDA-Ru)) and triethanolamine in an electrolyte solution, using surface plasmon excitation by visible blue light.



p(DDA-Ru)

p(DDA-Ru) was prepared as described elsewhere.[8] The counter chloride anion was replaced with more hydrophobic perchlorate anion by pouring the reaction mixture into a large excess of NH_4ClO_4 methanol solution. A silver electrode was prepared as follows. A high-refractive-index glass (LaSFn8: n = 1.86 at 441.5 nm) was used as the substrate and was made hydrophobic with octyltrichlorosilane. Two-metal layers, chromium and silver, were thermally deposited on the substrate under vacuum. The copolymer monolayer was prepared by spreading, from a chloroform solution, onto the pure water subphase at 15 °C in a Langmuir trough. The condensed monolayer was transferred onto the silver electrode at 30 mN m^{-1} by a vertical dipping method. The electrode was coupled with a prism (LaSFn17: n = 1.91 at 441.5 nm) by matching oil in Kretschmann-configuration.[15] The photocurrent measurement was carried out by using a photoelectrochemical three-electrode cell at 0.0 V (vs SCE) combined with a surface plasmon spectrometer (Figure 1).[11] The cell was mounted on a goniometer controlled by a personal computer. A linearly polarized helium–cadmium laser at 441.5 nm was used as the incident beam. Silver electrodes modified with p(DDA-Ru) monolayer, SCE, and platinum were used as a working electrode, a reference electrode, and a counter electrode, respectively. $NaClO_4$ aqueous solution containing 0.6 M triethanolamine was used as an electrolyte solution. N_2 gas was flowed in the electrolyte solution for 10 min before measurement of photocurrent. This system allowed for simultaneous recording of reflectivity and photocurrent.

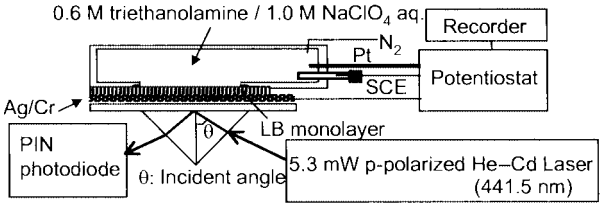


Figure 1. Schematic illustration of photocurrent measurement system combined with surface plasmon spectrometer.

Figure 2 shows angle-dependent reflectivities for the bare silver electrode and p(DDA-Ru) monolayer located in the electrolyte solution. In most cases, a linearly polarized helium–neon laser has been used as the excitation source, because of the larger absolute value of the real part of the dielectric constant in the metal layer at relatively long wavelengths such as 632.8 nm. Both of our reflectivity curves, however, indicate that the surface plasmon mode can be excited at angles of approximately 68.20° and 72.00°, for the bare silver and p(DDA-Ru) monolayer, respectively, even by the fairly blue light (441.5 nm). The dielectric constant and thickness of each layer were precisely determined by comparison between the experimental data and theoretical curves calculated using Fresnel's equation (Table 1). The imaginary part of the dielectric constant of p(DDA-Ru) corresponds to the fact that the

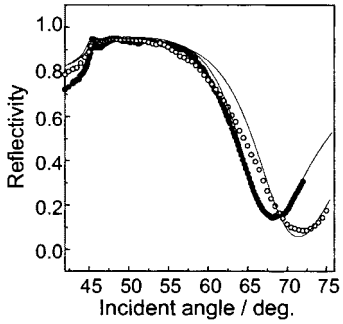


Figure 2. Angle dependent reflectivities for the bare silver (closed circle) and p(DDA-Ru) monolayer (open circle) in an electrolyte solution using p-polarized light at 441.5 nm. The solid lines are Fresnel fits.

Table 1. The dielectric constant and film thickness for each layer determined from Fresnel fits

Layer	ε'	ε''	Thickness
Cr	−12.0	+12.1	1.0 nm
Ag	−5.98	+0.38	36.7 nm
p(DDA-Ru)	+2.90	+0.30	2.0 nm

copolymer has an absorption band at 441.5 nm. This is the reason why the plot of p(DDA-Ru) monolayer reflectivity shown in Figure 2 has a deeper "dip" than that of the bare silver electrode. The intensity of the electromagnetic field at the surface reaches its maximum at the angle with lowest reflectivity. The magnitude of the enhancement is given by the ratio of the field intensity of the surface plasmons to the incoming field intensity in the glass substrate for p-polarized light.[12] The maximum enhancement of the electric field intensity, as calculated using the parameters listed in Table 1, is expected to be approximately 26.

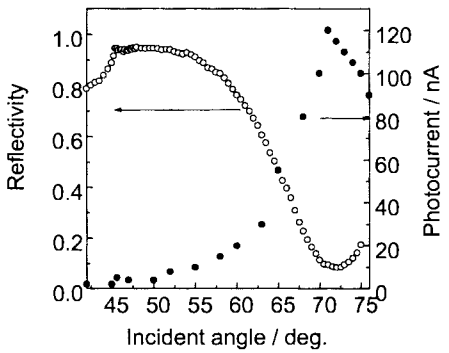


Figure 3. Photocurrent (closed circle) and reflectivity (open circle) curves for p(DDA-Ru) monolayer in an electrolyte solution using p-polarized light at 441.5 nm as a function of incident angle.

The effect of the surface plasmon field enhancement can be clearly seen in the angular dependence of reflectivity and photocurrent of the p(DDA-Ru) monolayer (Figure 3). Below a critical angle (θ_c), the incident light which excites the $Ru(bpy)_3^{2+}$ moiety is in transmitted light mode, and an anodic photocurrent of 2 nA is generated. The incident light is totally reflected at θ_c, and the evanescent waves excite the $Ru(bpy)_3^{2+}$ moiety, resulting in an increase in the photocurrent of 5 nA. Above θ_c, no direct excitation of $Ru(bpy)_3^{2+}$ occurs, and the photocurrent drastically increases until it reaches a maximum value of 120 nA at 71.00°. This maximum current is larger with those measured at 42.00° and θ_c by a factor of 60 and 24, respectively. The photocurrent then decreases as the incident angle becomes greater. This indicates that the anodic photocurrent due to photoinduced electron transfer between excited $Ru(bpy)_3^{2+}$ and triethanolamine is effectively enhanced by the surface plasmon excitation. That is, the surface electromagnetic field at the metal-dielectric interface increases dramatically as the resonance condition associated with the excitation of the surface plasmon is approached, reaches a maximum as the angle of minimal reflectance is reached, and then decays again.[14] It can thus be concluded that enhancement of the anodic photocurrent is induced by a strong increment of the surface electromagnetic field due to surface plasmon excitation.

In this study, we demonstrated that a strong increase in surface electromagnetic field caused the effective enhancement of anodic photocurrent. We are currently in the process of characterizing in detail the photoelectrochemical and photophysical behavior of the p(DDA-Ru) film-silver interface of silver electrodes modified with p(DDA-Ru) LB films.

This work was partially supported in part by a Grant-in-Aid for Scientific Research (No. 12450342) from the Ministry of Education, Science, Sports, and Culture of Japan.

References

1 I. Bedja, S. Hotchandani, and P. V. Kamat, *J. Phys. Chem.*, **98**, 4133 (1994).
2 K. Yamada, N. Kobayashi, K. Ikeda, R. Hirohashi, and M. Kaneko, *Jpn. J. Appl. Phys.*, **33**, L544 (1994).
3 S. Yamada, H. Kohrogi, and T. Matsuo, *Chem. Lett.*, **1995**, 639.
4 P. V. Kamat, I. Bedja, S. Hotchandani, and L. K. Patterson, *J. Phys. Chem.*, **100**, 4900 (1996).
5 R. Argazzi, C. A. Bignozzi, T. A. Heimer, F. N. Castellano, and G. J. Meyer, *J. Phys. Chem. B*, **101**, 2591 (1997).
6 C. Nasr, P. V. Kamat, and S. Hotchandani, *J. Phys. Chem. B*, **102**, 10047 (1998).
7 T. Taniguchi and T. Miyashita, *Chem. Lett.*, **1997**, 295.
8 T. Miyashita, T. Taniguchi, and Y. Fukasawa, *Chin. J. Polym. Sci.*, **17**, 75 (1999).
9 T. Taniguchi, Y. Fukasawa, and T. Miyashita, *J. Phys. Chem.*, **103**, 1920 (1999).
10 A. Aoki, Y. Abe, and T. Miyashita, *Langmuir*, **15**, 1463 (1999).
11 A. Ishida, Y. Sakata, and T. Majima, *Chem. Lett.*, **1998**, 267.
12 H. Raether, "Surface Plasmons on Smooth and Rough Surfaces and on Gratings," Springer-Verlag, Berlin (1988), Vol. 111, Chap. 2.
13 W. Knoll, *MRS Bull.*, **16**, 29 (1991).
14 T. Liebermann and W. Knoll, *Colloids Surf., A*, **171**, 115 (2000).
15 E. Kretschmann, *Opt. Commun.*, **6**, 185 (1972).