Photocurrent Generation by Surface Plasmon Excitation *via* Electron Transfer Quenching of Excited Porphyrins Linked Covalently to a Gold Film Electrode

Akito Ishida,* Yoshiteru Sakata, and Tetsuro Majima*
The Institute of Scientific and Industrial Research, Osaka University, Mihogaoka 8-1, Ibaraki 567

(Received December 8, 1997; CL-970928)

Photocurrent was generated by surface plasmon excitation upon a porphyrin-modified gold film electrode using p-polarized light at 632.8 nm light in which electron transfer occurred from the excited porphyrin linked covalently to the gold electrode to a quencher such as molecular oxygen and methyl viologen in an aqueous solution.

Surface plasmon (SP) is surface charge density wave generated by coupling of the plasma oscillation of a metal with the incident light at the resonance angle.[1] SP induces strong electromagnetic field on the metal surface known as the characteristic filed enhancement effect.[1,2] We have reported the fluorescence properties of a porphyrin covalently linked to a gold surface (Au-S$(CH_2)_{10}$CONH-Por, Por = *p*-(tris(*p*-tolyl)-porphyrinyl)phenyl) using SP as a novel excitation source.[3,4] In this paper, we report on electron transfer reaction from the SP-excited porphyrin to a quencher such as molecular oxygen and methyl viologen in an aqueous solution on the basis of photocurrent measurements.

A gold film was prepared on a 15×15×15 mm^3 BK-7 right-angle prism as reported previously.[3] SPs were generated on a gold surface by an attenuated total reflection (ATR) method using a Kretschmann-Raether's configuration (Figure 1).[5] At the ATR minimum denoted as SP resonance angle (θ_R), SPs were most effectively generated on the opposite side of the gold film.[1] Sharp and broad ATR minima were observed with θ_R at 43.6° and 71.9° in air and water with the refractive index n= 1.000 and 1.362, respectively (Figure 2), which are approximately equal to the reported values.[6] Since the resonance conditions are sharply dependent on the refractive index of the medium, the θ_R in water was significantly larger than that in air. After the modification of the gold film with -S$(CH_2)_{10}$CONH-Por, the θ_R shifted to 43.9° and 72.2° in air and water, respectively. The shifts are attributable to the change in the refractive index of a dielectric substrate attached on the gold surface and demonstrates that the porphyrin chromophore with a long alkyl chain is covalently linked to the gold surface.[7]

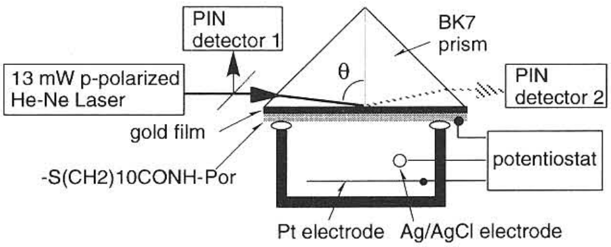

Figure 1. Experimental configuration of simultaneous measurements of photocurrent and ATR minimum.

Electrochemical measurements were carried out in an oxygen-saturated 0.1 mol dm^{-3} aqueous solution of Na_2SO_4 at 26 °C using the modified gold film as a working electrode, an Ag/AgCl reference electrode, a platinum counter electrode, and a potentiostat as shown in Figure 1. The θ_R shifted to 73.3° in the electrolyte solution because of the larger refractive index of the solution than in water. When SP excitation of the modified gold film was started with p-polarized 632.8 nm light from a 13 mW He-Ne laser at the incident angle (θ) of 73° without application of the bias voltage, a cathodic current of 1.12 μA was observed and it decreased exponentially to reach a constant current of 700 nA at approximately 30 s later as shown in Figure 3. The constant current varied in the range 200-700 nA depending on θ as shown in Figure 2. Photocurrent was measured to be negligibly small (<1 nA) in a control experiment using a bare gold film with the SP excitation. The results indicate that the photocurrent generation is due to the SP excitation of -S$(CH_2)_{10}$CONH-Por on the gold surface. It is noteworthy that only the small photocurrent of 160 nA was observed upon direct photoirradiation of the modified electrode with the same light as shown in Figure 3. The considerably large photocurrent by the SP excitation as compared with the direct photoirradiation indicates that the photocurrent generation proceeds effectively through the generation of SP and excitation of the porphyrin chromophore attached on the gold surface.

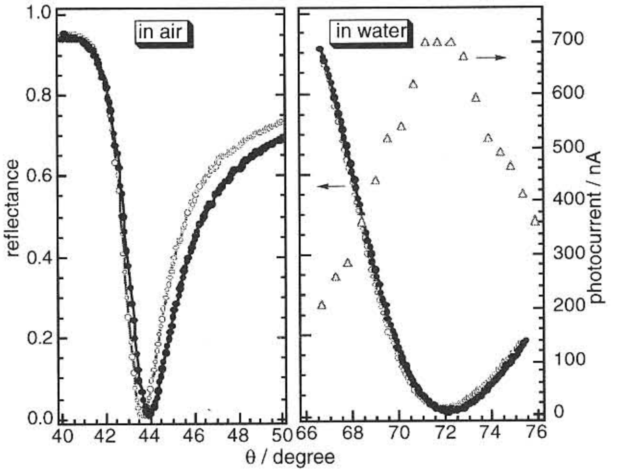

Figure 2. SPR reflectivity curves for the gold film on a BK-7 right angle prism (open circle) and that modified by -S$(CH_2)_{10}$CONH-Por (closed circle) in air (left) and water (right) and dependence of the photocurrent on the incident angle (right, open triangle).

The photocurrent decreased by argon bubbling of the solution and the initial photocurrent was almost recovered by successive oxygen bubbling. The result suggests that the singlet excited porphyrin ($^1Por^*$) is quenched by molecular oxygen *via* electron transfer to give a radical cation of the porphyrin ($Por^{\bullet +}$) and superoxide ($O_2^{\bullet -}$) or reduction products of molecular oxygen.

When superoxide formation is assumed, free energy change in the electron transfer quenching of $^1Por^*$ by molecular oxygen was calculated to be -39 kJ mol^{-1} based on the excitation energy of $^1Por^*$ (E_S=185 kJ mol^{-1})[8] and the oxidation potential of Por (1.24 V vs NHE),[9] and the one electron reduction potential of molecular oxygen (-0.28 V vs NHE).[10] Two electron reduction of molecular oxygen giving H_2O_2 (-0.15 V vs NHE)[10] is also suggested as the quenching process of $^1Por^*$, since it is energetically more preferable than the one electron reduction.

The constant photocurrent is probably due to the bimolecular quenching of $^1Por^*$ with 3.5 ns of lifetime[3,4] by molecular oxygen. Since the concentration of molecular oxygen is only 1.27 mmol dm^{-3} in an oxygen saturated aqueous solution,[11] $^1Por^*$ is partly quenched by molecular oxygen.

In order to quench $^1Por^*$ effectively, methyl viologen (MV^{2+}) was added as an electron acceptor. The increase of the initial and constant currents were observed with an increase of the concentration of MV^{2+} as shown in Figure 3. The initial peak current of 1.66 μA was obtained in the presence of 40 mmol dm^{-3} of MV^{2+}. The results indicate that the electron transfer quenching occurred to give $MV^{\bullet+}$ and $Por^{\bullet+}$. The free energy change in the electron transfer quenching of $^1Por^*$ by MV^{2+} was calculated to be -22.0 kJ mol^{-1} on the basis of the reduction potential of MV^{2+} (-0.45 V vs NHE).[12-14] Since the concentration of MV^{2+} is much higher than that of molecular oxygen and the free energy change is sufficiently exothermic, $^1Por^*$ is quenched more effectively by MV^{2+} than by molecular oxygen.

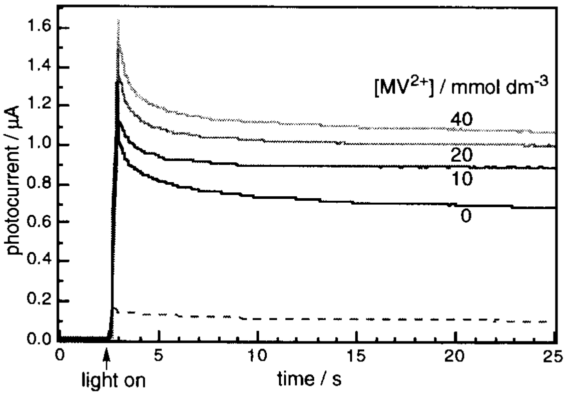

Figure 3. Time profiles of the photocurrent of $-S(CH_2)_{10}$-CONH-Por film on a gold surface in oxygen saturated 0.1 mol dm^{-3} aqueous solution of Na_2SO_4 upon the SP excitation at θ = 73° in the absence and presence of 10, 20, and 40 mmol dm^{-3} of MV^{2+} at 26°C. The dashed line is a time profile of the photocurrent upon the direct photoirradiation in the absence of MV^{2+}.

The present work is the first example showing that the SP excitation can be used as a unique and effective excitation source to cause the bimolecular reaction of $^1Por^*$ covalently linked to the gold surface *via* electron transfer to generate photocurrent. The irradiation area of 6.0 mm^2 allows us to calculate the initial peak current per area to be 27 μA cm^{-2}. We are currently studying the photocurrent generation by the SP excitation using other gold film electrodes modified by $-S(CH_2)_nCONH$-Por and a mixture of $-S(CH_2)_{10}CONH$-Por and $-S(CH_2)_nCH_3$ to improve the photocurrent behavior.

This work is partly supported by a Grant-in Aid for Scientific Research (No. 08650979 and 09279224 to A.I.; No. 09238234, 09226223, and 09875209 to T.M.) from the Ministry of Education, Science, Sports and Culture of Japan, and by Research Area of "Fields and Reactions", Precursory Research for Embryonic Science and Technology, Japan Science and Technology Corporation (A.I.), and NEDO (A.I.).

References and Notes

1 H. Raether, "*Surface Plasmons on Smooth and Rough Surfaces and on Gratings*," ed by G. Höhler, Springer-Verlag, Berlin (1988), Vol. 111, p 4.

2 H. Kano and S. Kawata, *Opt. Lett.*, **21**, 1848 (1996).

3 A. Ishida, Y. Sakata, and T. Majima, *Chem. Commun.*, in press (1998).

4 The fluorescence maxima of Au-$S(CH_2)_{10}CONH$-Por were observed at 655 and 720 nm. The decay showed multi-exponential components of which the major and minor components had lifetimes of 500 ps (67%) and 3.5 ns (33%), respectively. The excitation spectrum was different from the absorption spectrum. The intensity ratio between the $Q_x(1,0)$-band and Soret band, I_Q/I_S= 4.0 was significantly larger than that of the absorption spectrum (0.06).

5 E. Kretschmann, *Z. Phys.*, **241**, 313 (1971).

6 X. Sun, S. Shiokawa, and Y. Masui, *Jpn. J. Appl. Phys.*, **28**, 1725 (1989).

7 The thickness of the $-S(CH_2)_{10}CONH$-Por layer was estimated to be approximately 2 nm from the shift of θ_R in air and the skeleton of $-S(CH_2)_{10}CONH$-Por has a linear conformation perpendicularly to the gold surface.

8 M. Gouterman and G. E. Khalil, *J. Mol. Spectrosc.*, **53**, 88 (1974).

9 A. Wolberg and J. Manassen, *J. Am. Chem. Soc.*, **92**, 2982 (1970).

10 A. J. Bard, R. Rarsons, and J. Jordan, "*Standard Potentials in Aqueous Solution*," Marcel Dekker, New York (1985).

11 "Oxygen and Ozone," ed by R. Battino, Pergamon Press, Oxford (1981), Vol. 7, p 519.

12 W. R. Heineman, T. P. DeAngelis and J. F. Goelz, *Anal. Chem.*, **47**, 1364 (1975).

13 M. Ito and T. Kuwana, *J. Electroanal. Chem.*, **32**, 415 (1971).

14 The free energy change for the triplet excited Por (E_T=140 kJ mol^{-1} [ref. 8]) was calculated to be 23.0 kJ mol^{-1} and endoergonic. Accordingly, the triplet excited Por seems to be hardly responsible to the electron transfer quenching even if it forms with a longer lifetime.