

Photocurrent enhancement in a porphyrin-gold nanoparticle nanostructure assisted by localized plasmon excitation

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The nanostructured assembly of porphyrin and gold nanoparticles exhibits distinct enhancement of photocurrents from porphyrin in the longer wavelength region, where the localized plasmon resonance was responsible.

Surface plasmon resonance (SPR) that occurs at the surface of gold (or silver) metal has substantially enhanced the electronic excitation of surface-anchored molecules, as has been verified from the enhancements of fluorescence^{1–8} and photocurrent signals.^{9–12} Thus, SPR can offer tremendous advantages in the spectroscopic sensitivity. However, as to the SPR method reported so far, optical excitation of surface plasmon waves, relevant to the excitation of surface-anchored molecules, has been carried out under the attenuated total reflection geometry using a planar surface, as shown in Fig. 1a.^{1–12} Thus, the optical alignment should be tightly adjusted for a given wavelength. This leads to complicated and troublesome experimental procedures in order to obtain SPR signals as the function of a given wavelength. In fact, the photocurrent enhancement was measured only at a specified wavelength.^{9–12}

Surface plasmon on the surfaces of gold (or silver) nanoparticles has made it possible to extremely enhance the sensitivity in the Raman scattering spectroscopy as a surface-enhanced Raman scattering (SERS) phenomenon.^{13–16} Such an enhancement in optical events must extend the applications of surface plasmon

in various spectroscopies. The primary importance for these applications is skillful design and tailor-made fabrication of gold (or silver) metal nanostructures.

As to gold nanostructures, bottom-up approaches using gold nanoparticles have been applied by using bifunctional linker molecules.¹⁷ Recently, multistructure assemblies consisting of gold nanoparticles and photoresponsive dyes have been fabricated on the electrode by electrostatic interactions¹⁸ and gold–sulfur self-assembling approaches,¹⁹ and these modified electrodes gave appreciably larger photocurrents as compared with the corresponding dye-modified planar electrodes. However, the photocurrent enhancement was simply due to the increased number of immobilized molecules based on nanostructuring of electrodes, and no appreciable effects of localized plasmon have been verified yet.

Recently, Willner *et al.* constructed multistructure assemblies of gold nanoparticles (diameter 2.3 nm) and CdS (5 nm) nanoparticles on the planar gold surface, and proposed the photoelectrochemical charging effect of the gold nanoparticles based on LPR.²⁰ As to localized plasmon resonance (LPR), gold nanoparticles whose diameters are several to several tenths of nanometres show distinct absorption bands based on LPR in the visible to near-infrared region. Thus, their multistructures are expected to enhance the electronic excitation of surface-anchored molecules by localized field of surface plasmon, leading enhanced electron-transfer (that is, photocurrent) events, more efficiently in far-red to near-infrared region. Furthermore, a noteworthy advantage of using the LPR-responsible gold nanoparticles is that it is not necessary to adjust the incident angle of the irradiation light in every excitation wavelength because localized plasmon itself is independent of the incident angle, as illustrated in Fig. 1b. Therefore, the use of gold nanoparticles with diameters of several to several tenths of nanometres as the electrodes for photocurrent generation from surface-immobilized molecules are expected to offer substantial advantages over the planar electrode system in terms of enhancement in molecular excitation over a wide wavelength region as well as easiness in the experimental optical geometry.

From these viewpoints, we have fabricated in this study the self-assembled monolayer of porphyrin on the surface of LPR-responsible (diameter 14 ± 1 nm) gold-nanoparticle film that was generated at a liquid/liquid interface at the level of the nanoparticle layer and then was transferred onto the surface of a planar gold electrode. Significant enhancement of photocurrents ascribing to porphyrin excitation was observed where the absorption band due to LPR of the gold nanoparticles distinctly appeared. It is strongly

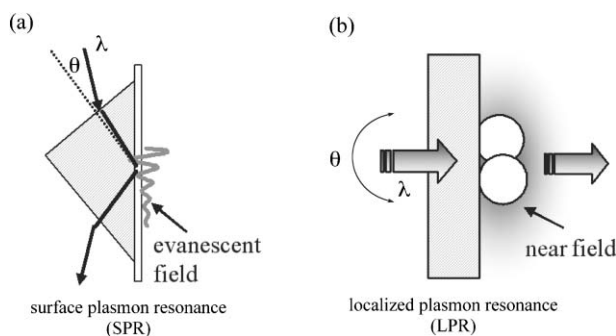


Fig. 1 Illustrated outline of (a) surface plasmon resonance and (b) localized plasmon resonance.

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suggested that the photocurrent enhancement is ascribed to the effect of increased excitation of porphyrin by the electric field of localized plasmon.

The colloidal solution of gold nanoparticles (**AuP**) was prepared by the reduction of HAuCl_4 with citric acid as described previously,¹⁹ and the mean diameter was 14 ± 1 nm. Preparation of gold nanoparticle film at the liquid/liquid interface has also been reported before.²¹ Namely, the liquid/liquid interface of the aqueous colloidal solution of **AuP** (20 ml) and hexane (10 ml) was formed in a vial (ϕ 30 mm), where an indium–tin-oxide (ITO) electrode was placed at its bottom. Then, methanol (10 ml) was poured into the solution at once; it resulted in the instantaneous change of color of the aqueous phase from wine-red to light pink and at the same time produced a liquid-like film of **AuP** at the liquid/liquid interface, as was verified from the appearance of a gold color at the interface. Then, this liquid-like film was transferred onto the surface of the ITO electrode, by carefully and slantingly lifting the electrode with a pair of tweezers, as if the liquid-like film was scooped up from the solution. Since the transferred nanoparticle film was still drenched with water, no substantial cracks were seen after slow drying in air. Accordingly, we have obtained the multistructured electrode with the gold nanoparticles as: ITO/**AuP**. Meanwhile, a planar gold electrode was prepared by vacuum deposition of gold onto the ITO electrode as: ITO/**Au**.

A disulfide derivative of porphyrin (Fig. 2a, **[Po]₂**) was synthesized in our laboratory. Self-assembled monolayers (SAMs) of **Po** on the ITO/**AuP** and ITO/**Au** electrodes were prepared by immersing the electrodes into a CH_2Cl_2 solution of **[Po]₂** (5×10^{-4} M (= mol dm⁻³)) for five days, to obtain **Po**-modified electrodes as: ITO/**AuP/Po** and ITO/**Au/Po**, respectively. The coverages of **Po** on multistructured and planar electrodes were 7.1×10^{-11} and 2.2×10^{-11} mol cm⁻², respectively.²² The

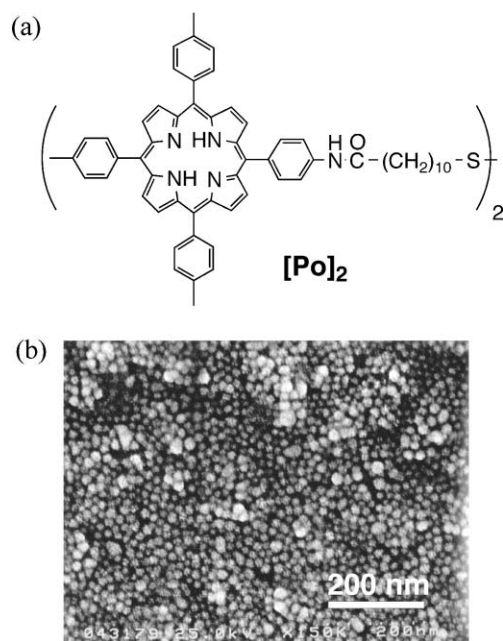


Fig. 2 (a) Formulae of a disulfide derivative of porphyrin **[Po]₂**, (b) SEM image of ITO/**AuP/Po**: **Po**-gold nanoparticle assembly fabricated on the surface of ITO electrode.

Po-modified electrodes, ITO/**AuP/Po** and ITO/**Au/Po**, were stored in the dark.

Fig. 2b shows the scanning electron micrograph (SEM) image of the ITO/**AuP/Po**. As can be seen from the SEM image, the gold nanoparticles are deposited on the ITO electrode at roughly the level of the monolayer. No appreciable cracks were found in the film. Slight fusion of particles is observed, though the reason is not apparent at this stage.

Photocurrents from ITO/**AuP/Po** and ITO/**Au/Po** were measured in an aqueous 0.1 M NaClO_4 solution under aerobic conditions at room temperature, using a three-electrode photoelectrochemical cell (modified electrode as working, Ag/AgCl electrode as reference and platinum electrode as counter). The monochromated light from the Xe lamp irradiated the modified electrode. Stable and static photocurrents were generated in all cases. Photocurrents were detected by a potentiostat.

Fig. 3a shows photocurrent action spectra of ITO/**AuP/Po** and ITO/**Au/Po** at $E = 0$ V vs. Ag/AgCl , together with the absorption spectrum of **Po** in CH_2Cl_2 ; the photocurrents were evaluated at the irradiation power of 1 mW cm^{-2} . The action spectra show clear peaks whose positions are well correlated with the absorption peaks of **Po**. The ITO/**AuP** as well as the ITO/**Au** electrodes, in the absence of porphyrin, showed no appreciable photocurrents under the present conditions. Therefore, the photocurrent generation ascribing from LPR and SPR excitation of gold itself is negligible in this study. Note, however, that the photocurrent intensities of ITO/**AuP/Po** at longer wavelengths are relatively larger as compared with those of ITO/**Au/Po**.

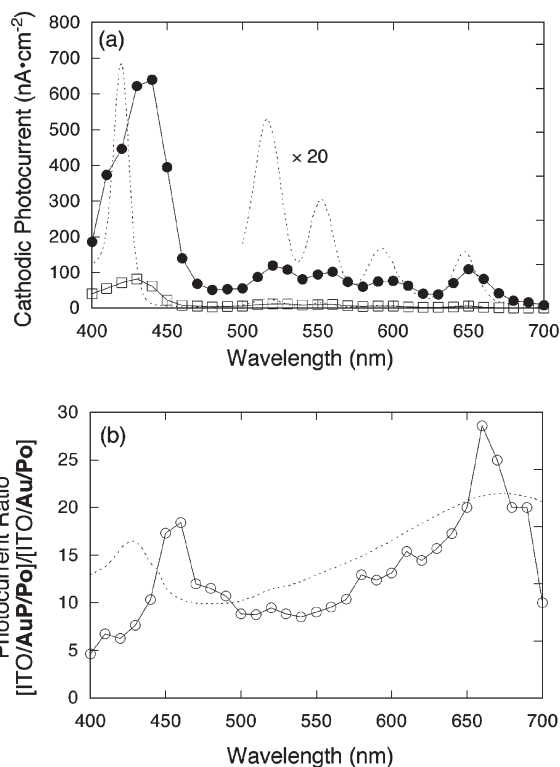


Fig. 3 (a) Photocurrent action spectra of ITO/**AuP/Po** (●), ITO/**Au/Po** (□), and absorption spectrum of **[Po]₂** in CH_2Cl_2 (···). (b) Photocurrent ratios of ITO/**AuP/Po** to ITO/**Au/Po** (○), and transmission absorption spectrum of ITO/**AuP/Po** (···).

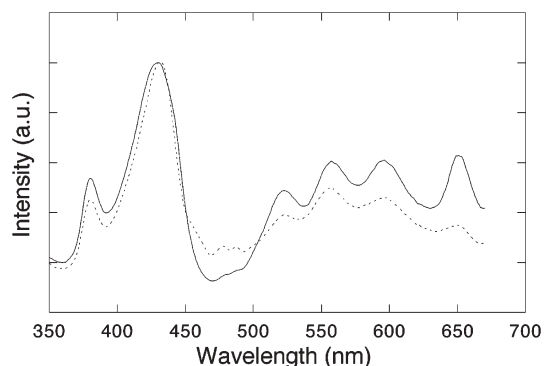


Fig. 4 Fluorescence excitation spectra of ITO/AuP/Po (—) and ITO/Au/Po (···).

In order to verify the effects of a localized plasmon field, we have taken the photocurrent ratios of ITO/AuP/Po to ITO/Au/Po, as shown in Fig. 3b. If the photocurrent from the ITO/AuP/Po electrode is generated only by simple photoexcitation of immobilized **Po** molecules, the photocurrent ratio should be the ratio of immobilized **Po** molecules between ITO/AuP and ITO/Au electrodes (3.2), and thus it should be independent of the irradiation wavelength. However, it is clear that the photocurrent ratio is increasing in the longer wavelength region where the broad plasmon band of the multistructured assembly of gold nanoparticles appears in the ~ 500 – ~ 700 nm region. It is not clear at this time why the photocurrent ratios show a peak around 460 nm. Detailed studies are underway.

Fig. 4 shows fluorescence excitation spectra of the two **Po**-modified electrodes ($\lambda_{\text{em}} = 730$ nm). The fluorescence intensity was very low, maybe one of the reasons for this is due to quenching of the porphyrin excited states by gold. Therefore, the signals from ITO/AuP/Po and ITO/Au/Po at 430 nm were normalized in order to clarify the relative intensity between the two. It is clear that the fluorescence is certainly larger relatively for the ITO/AuP/Po around the broad plasmon band shown in Fig. 3b. These observations clearly show that the photocurrents from the ITO/AuP/Po electrode in the wavelength region longer than ~ 500 nm, where the surface plasmon oscillation of gold nanoparticle assembly is responsible, were enhanced by the enhanced field of localized plasmon.

In conclusion, we have first verified the significant enhancement of photocurrents from the self-assembled monolayer of **Po** in a wide wavelength region, by immobilizing it on the surfaces of LPR-responsible gold nanoparticles. The degree of enhancement must depend on the size, shape, and aggregated (or aligned) condition of gold nanoparticles, and further improvement is now in progress.

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- 22 The determination of the coverages of **Po** molecules on the ITO/AuP/Po and ITO/Au/Po electrodes was spectroscopically difficult due to low absorbance and considerable broadening of the Soret band of **Po**. Thus, we have evaluated the coverage by using the exchange reaction of immobilized **Po** with *n*-dodecylmercaptane (DT), by immersing the **Po**-modified electrode into a CH_2Cl_2 solution of DT (1×10^{-3} M) for 1 day. After removal of the electrode, the absorption spectrum of the solution containing detached **Po** was measured and analyzed by comparing with the absorption spectrum of **Po** in solution. DT has no absorptivity in the visible region.