Effects of Localized Plasmon on the Photocurrent Generation from Organic Dye - Gold Nanoparticle Multistructures

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1. Introduction

Gold nanoparticles exhibit strong absorption bands in the visible-near infrared region due to surface plasmon oscillation. This unique optical property has materialized various applications of gold nanoparticles to catalysis, Raman sensors, electronic switches and so on. Surface plasmon resonance (SPR) occurring at the surface of gold (or silver) metal has enabled the enhancement of electronic excitation of molecules immobilized near the surface, as has been verified from fluorescence enhancement (1, 2). In the meantime, SPR has also been successfully applied for the enhancement of photocurrent generation from the self-assembled (3, 4), and Langmuir-Blodgett (LB) (5, 6) monolayers prepared on the gold and silver surfaces, respectively. In those SPR experiments, optical excitation of surface plasmon waves (therefore, immobilized molecules) has been materialized under the attenuated total reflection geometry for a given wavelength using a prism or a grating. As to photocurrent generation, one has to scan the excitation wavelength to obtain a photocurrent action spectrum. Thus, it is very difficult and complicated in instrumentation to obtain the action spectrum so long as the total reflection geometry is applied. Recently, multistructure assemblies consisting of gold nanoparticles and photoresponsive dyes have been fabricated on the electrode, and these modified electrodes generated photocurrents (7, 8). In the present study, we have compared the photocurrent action spectra from monolayers of a thiol dyes prepared on the nanostructured and planar gold electrodes, and have found significant enhancement of photocurrents by LPR.

2. Experimental

Gold nanoparticles were prepared by the reduction of $HAuCl_4$ with citric acid. The mean diameter was 15-20 nm. The gold nanoparticles were immobilized on the above-described gold substrate by the salting-out procedure as described before, and then the thiol dye was self-assembled on the gold surfaces. We have carried out an alternative precedure by alternately self-assembling the thiol dye and the gold nanoparticles. Electrochemical measurements of gold and its modified electrode were carried out using platinum counter and silver (Ag^+/Ag) reference electrodes. Photoelectrochemical measurements were done in acetonitrile in the presence of methylviologen (MV: 5×10^{-3} M) and TBAP(0.1 M).

3. Results and Discussion

Photocurrent responses were compared in some different organic dyes and different preparation conditions of multistructures. First, we have prepared the multistructure by sedimentation of the gold nanoparticles on the elelctrode, and subsequent self-assembling of theh N3 dye. The adsorbed amount of N3 on the nanostructured or the planar gold electrode was evaluated to be 1.5×10^{15} or 1.1×10^{15} molecules/cm^2, from the integration of the reductive waves of N3 in the differential pulse voltammograms of the modified electrodes. Photocurrents were measured in the presence of MV (5×10^{-3} M) under aerobic condition (thus, both MV and oxygen function as sacrificial reducing agents). The action spectrum had a clear peak corresponding to the absorption peak of N3. The ratio of photocurrents between nanostructured and planar electrodes were obtained as a function of wavelength. The SP bands of the colloidal solution of gold nanoparticles appear at ~530 nm. The spectral broadening in the nanostructured electrode has been observed in the case of considerable proximity of gold nanoparticles, and is assignable to a collective particle plasmon oscillation. It is noteworthy that the photocurrent ratio does not stay constant but it increases steeply at longer wavelengths where the onset of steep rise corresponding well with the plasmon band.

Photocurrent action spectra were also measured for the multistructure assemblies prepared by alternate self-assembling, where the porphyrin or the ruthenium complex was used as the dye. In this case, the degree of immobilized gold nanoparticles was quite low and was much less than monolayer level under in the one assembling procedure. Detailed analyses are underway.

As described above, the irradiation angle must be tightly tuned for a given wavelength so long as the SPR method using the planar electrode is applied. This is not the case in this case. LPR must be achieved independently with irradiation angle and wavelength, though the LP-fields are limited (localized) at specified sites in the surface of the spherical metal particle. Also, some important effects such as excited state quenching by gold, molecular orientation and packing, and diffusion of electrolytes and sacrificial reagents in the nanostructure, must be revealed to make the most of LPR on photocurrent generation. Anyway, design of nanostructures with highly-efficient LP-fields as well as selective immobilization of molecules at "hot sites" is basically important for successful applications of LPR.

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