Energy Conversion

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Plasmonic Enhancement of Photoinduced Uphill Electron Transfer in a Molecular Monolayer System**

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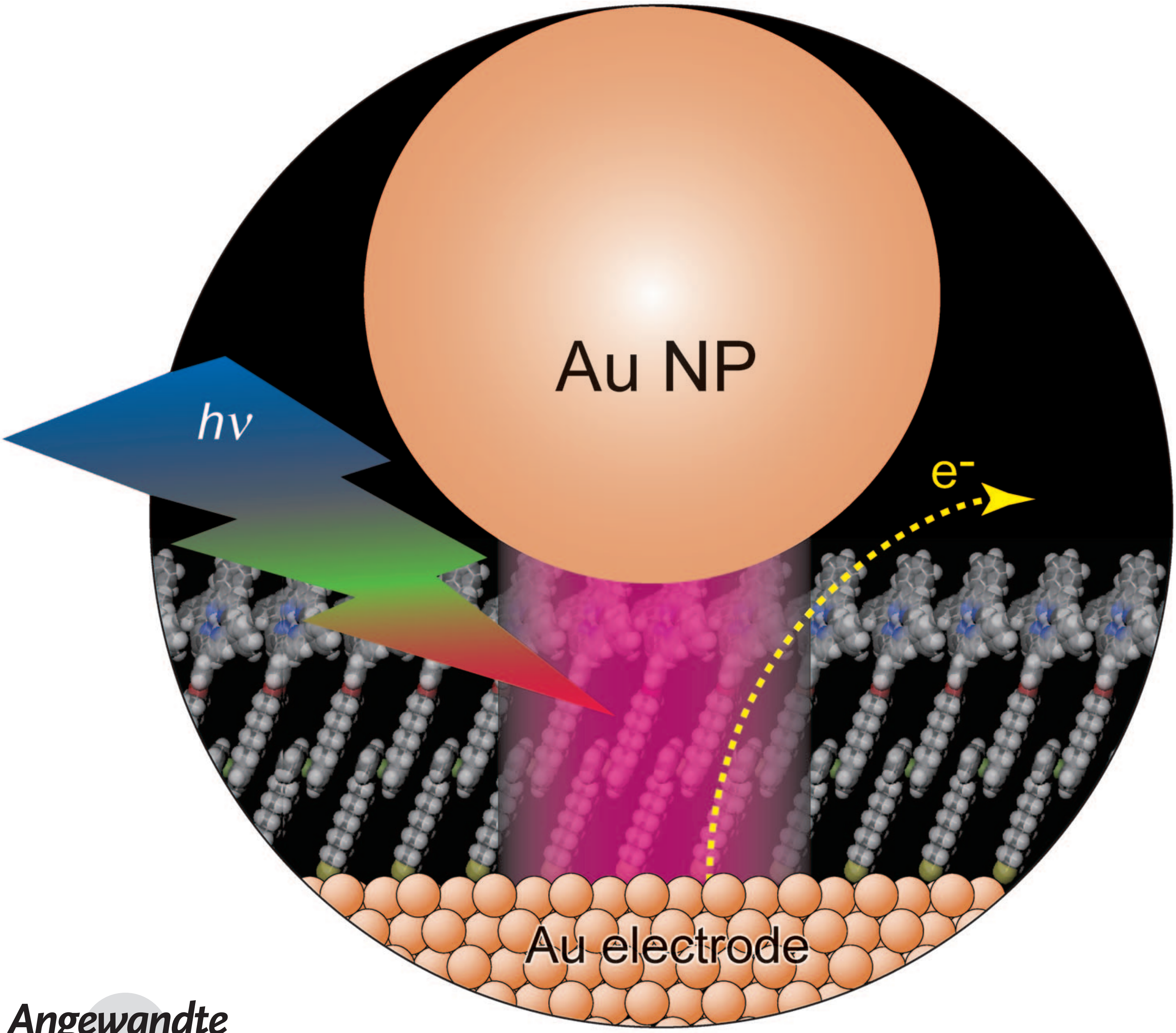

Photosynthesis is one of the most elegant examples in solar energy conversion systems, and a number of artificial photosynthetic molecular systems have been constructed by taking into account of the mechanism of photosynthesis.[1–5] To achieve efficient photoenergy conversion, various functional groups such as photon absorbers and electron donors and acceptors have to be arranged so that they are optimally connected. One potential advantage in a molecular-based system is a variety and flexibility of molecular design that enables the arrangements of the functional groups to be optimized. 2D alignment of molecules on an electrode surface can be also controlled by the use of molecular self-assembly. For example, we have synthesized a porphyrin–ferrocene–thiol molecule to realize photoinduced uphill electron transfer, where the porphyrin, ferrocene, and thiol units correspond to photon absorber, electron relay, and surface binding group, respectively.[3] The quantum efficiency of the photoinduced reaction exceeds 10 % when a well-organized molecular layer is formed on an atomically smooth surface. Despite these significant advantages for achieving a high quantum efficiency, the incident photon-to-current efficiency (IPCE) in such a monolayer system is rather low because of the limited photon absorption. Therefore, incorporation of photon-absorbing antennae should enhance the efficiency of the photoenergy conversion. When photon-absorbing antennae are introduced to the system, it is essential to maintain well-organized metal interfaces because the performance of monolayer systems is highly sensitive to the surface morphology.[6] Herein we show that plasmonic photon-absorbing antennae, which are optimized to "squeeze" photonic energy into a molecular monolayer system formed on a smooth electrode surface, substantially improve the photoenergy conversion efficiency.

Surface plasmon polaritons, which are collective oscillation modes of free electrons at a metal surface, are currently attracting a great deal of attention because they account for highly efficient coupling between photons and molecules through electric-field enhancement adjacent to the metal surface.[7,8] Since plasmonic resonances are generally found to appear in the visible and near-IR regions, a substantial improvement of photoenergy conversion efficiency is, in principle, expected in this wavelength region. However, the excitation of plasmons is allowed by matching the wave vector of the incident photons and the plasmon modes, thus the metal substrate must have nanostructured surface features. Hence, it is generally difficult to apply the plasmonic enhancement method to well-organized molecular systems. Although several attempts have been made in various photochemical systems,[9–11] it is hard to confirm purely plasmonic effects[12] because the reported enhancement was often caused by the increase of the surface area of the electrode, that is, the increase of total number of molecules.

The plasmonic resonance properties of a metal structure reflect the shape and size of the surface features in optical (10–100 nm) dimensions. Conversely, the performance of a molecular-based system is affected by the atomic arrangements of the substrate surface in subnanometer dimensions.[6] To achieve highly efficient photoenergy conversion, it is therefore necessary to control the surface morphology of plasmonic photon-absorbing antennae. Unfortunately, it is still difficult to satisfy this requirement by using currently available techniques in nanotechnology. The top-down approach, such as lithography, is not suitable for the control of surface morphology, while this approach is effective for the control of plasmonic features.[13–15] The bottom-up approach, such as metal colloid aggregates, usually fails to obtain reproducible plasmonic effects, although significant developments have been made in the synthesis of faceted metal nanoparticles.[16,17]

The localization of optical fields is the most important factor in the enhancement of photon–molecule interactions. Generally, a nanosphere dimer is widely recognized as an effective unit for field localization as the electromagnetic fields are localized in the gap between two spheres as a result of hybridization of the particle plasmons.[18,19] If such localized plasmons, that is, the so-called gap-mode plasmons, are realized at a well-defined metal surface, a large IPCE enhancement would be expected in an organic monolayer system. Under these circumstances, we propose that a sphere–plane-type plasmonic structure[20–22] is a most promising photon-absorbing antenna for molecular devices (Figure 1 a). In this structure, highly localized fields can be excited in the gap between the substrate and the nanosphere. Importantly, this structure is easily constructed by adsorption of Au nanoparticles (AuNPs) onto the organic layer formed on the electrode. Since the gap distance is determined by the monolayer thickness, the plasmonic resonances are precisely controlled in this system by using monodispersed AuNPs; the degree of the plasmon hybridization is related to the gap distance and the sphere diameter.[18,19] Such precise control of plasmon resonances is almost impossible in other conventional plasmonic structures. We have already shown that this plasmonic antenna is useful for the enhancement of the Raman scattering intensity at atomically smooth single-crystalline metal electrodes.[21,22]

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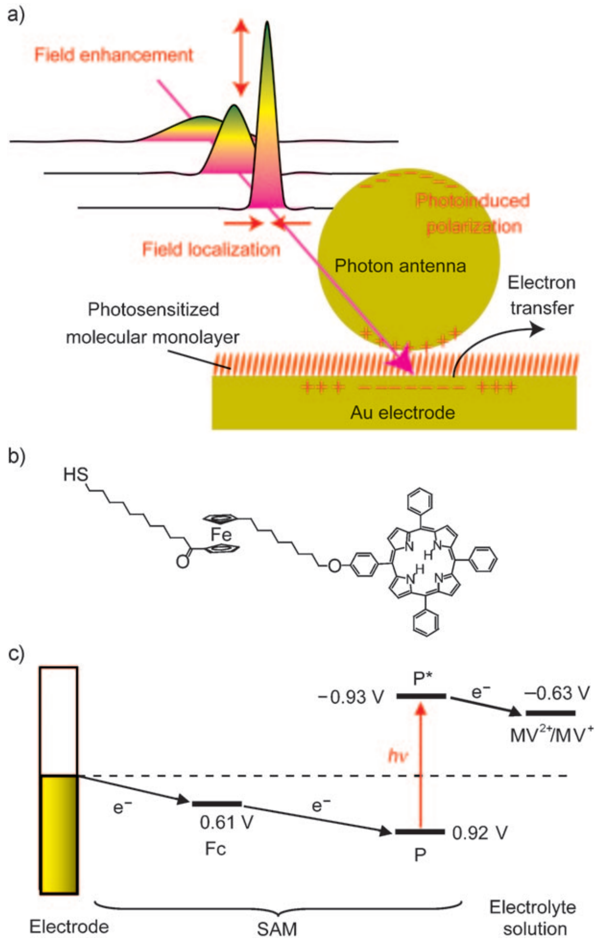

Figure 1. a) Plasmonic photon-absorbing antenna for photoenergy conversion enhancement in a molecular-based system. The sphere–plane type plasmonic cavity enables incoming light to be squeezed into the gap. b) Structure of $PC_8FcC_{10}SH$. c) Energy diagram for photoinduced upconversion in a $PC_8FcC_{10}SH$ SAM on an Au electrode. P = porphyrin, Fc = ferrocene, and MV = methyl viologen.

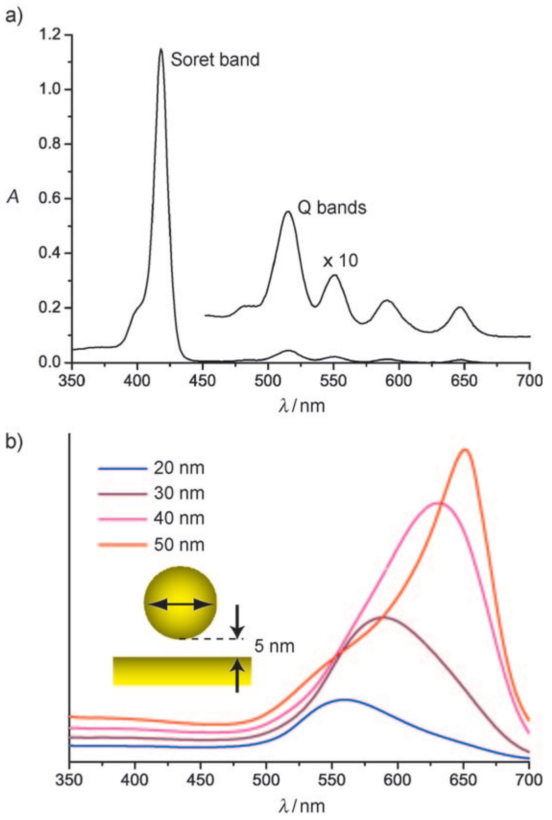

Figure 2. a) Absorption spectrum of $PC_8FcC_{10}SH$ in dichloromethane. b) Calculated extinction spectra of an AuNP with various diameters above an Au electrode. The gap distance is set to 5 nm.

The experimental confirmation of this plasmonic cavity effect in the photoenergy conversion is presented in the monolayer system of the $PC_8FcC_{10}SH$ molecules (Figure 1 b). Details of this molecule have been reported elsewhere.[3] Briefly, each functional group is linked by alkyl chains so that the obtained SAMs can be well-ordered by intermolecular interactions. The well-organized molecular assembly suppresses undesirable reverse electron-transfer and energy-transfer processes from the porphyrin to the electrode. Hence, highly efficient uphill electron transport from the gold electrode to the electron acceptors such as methyl viologen cations has been observed under photoexcitation of the porphyrin. The energy diagram of this photoinduced process is shown in Figure 1 c.

We focus on the elucidation of photoabsorption properties of the molecular system and the plasmonic cavity. Figure 2 a shows an absorption spectrum of a solution of $PC_8FcC_{10}SH$ in dichloromethane. The visible region contains only weak absorption bands (Q bands), although an intense absorption band (Soret band) appears in the near-UV region.[3,23] On the other hand, the plasmonic resonance energy in the sphere–plane-type cavity depends on the gap distance and the sphere diameter. Although the gap distance is fixed by the thickness of the $PC_8FcC_{10}SH$ layer, the plasmon resonance energy can be tuned by changing the diameter of the AuNPs. If the plasmon resonance energy overlaps with the Q band, the photon–molecule interactions are expected to be enhanced in the visible region. Figure 2 b shows the calculated extinction spectra of an Au sphere with various diameters above an Au plane (gap distance: 5 nm) in an electrolyte solution (refractive index: 1.6) under p-polarized illumination with an incident angle of 45°. In the calculation, multipole interactions were considered under a static field approximation, according to Wind's method.[24,25] The peak position is shifted to lower energy as the sphere diameter is increased. This shift is due to the increase of plasmon hybridization, which corresponds to the stronger localization of electromagnetic fields.

In order to obtain direct evidence of plasmonic enhancement in photoenergy conversion, photoinduced current responses of the Au electrode modified with a $PC_8FcC_{10}SH$ SAM were compared without and with the photon-absorbing antennae. The AuNPs were adsorbed on the SAM by immersion of the SAM-covered substrate into a colloidal solution of AuNPs for 30 minutes. The AuNPs used in this experiment have uniform octahedral shapes of 50 nm diameter. Undesirable reverse electron transfer from acceptors to the system is thought to be avoidable as each AuNP is covered with polydiallydimethylammonium chloride (PDDA).[26] Photoirradiation was carried out using an Xe lamp with a monochromator (light intensity of 3 mW cm^{-2}) and the photocurrent was recorded under an applied potential of -200 mV (vs. Ag/AgCl).

Action spectra of the monolayer before and after the adsorption of the octahedral AuNPs are shown in Figure 3 a. The five distinct peaks that are observed are consistent with the absorption bands of the $PC_8FcC_{10}SH$ molecule, thus indicating that the photocurrent generation is caused by the excitation of porphyrin.[3] After formation of the photon-absorbing antennae, the photocurrent generation was substantially enhanced in the entire visible region. Since the molecular density on the electrode does not change during the procedure of antennae formation, the enhancement factor of the photocurrent generation is equal to the ratio of the photocurrent with and without the photon-absorbing antennae. As shown in Figure 3 b, the wavelength dependence of the enhancement factor is quite similar to the calculated extinction spectrum for the 50 nm AuNP above the Au substrate (see Figure 2 b). The maximum enhancement effect is obtained around the characteristic resonance position of the gap-mode plasmons, which is lower than that of particle plasmons, thus strongly suggesting the contribution of the gap-mode plasmon resonances.

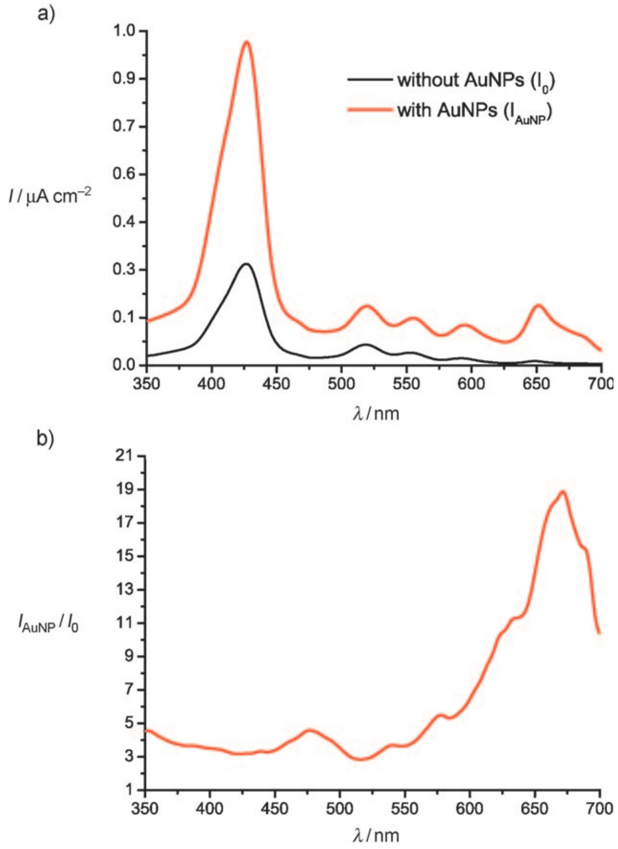

Figure 3. a) Action spectra of $PC_8FcC_{10}SH$ SAM on an Au electrode without AuNPs (I_0) and with AuNPs (I_{AuNP}), measured in 0.1 M $NaClO_4$ electrolyte solution under an applied potential of -200 mV (vs. Ag/AgCl). b) Excitation wavelength dependence of the efficiency enhancement.

The enhancement factor at 670 nm as a function of the immersion time in the colloidal solution is shown in Figure 4 a. The enhancement factor was gradually increased as the immersion time was increased. The final photocurrent was 20 times larger than the initial value, thus the efficiency enhancement must have a correlation with the density of the photon-absorbing antennae in this system. The enhancement factor as a function of the surface coverage of AuNPs on the electrode, as estimated from SEM photographs is shown in Figure 4 b. As expected, the enhancement factor has a linear relationship with the surface coverage. This result clearly proves that the increased photocurrent was indeed caused by the gap-mode plasmons excited in each sphere–plane cavity. In the meantime, the observed enhancement is thought to be averaged for the entire surface area of the electrode since our photon-absorbing antenna effect is spatially inhomogeneous. According to the surface coverage with AuNPs, the intrinsic enhancement in each "hot spot" can be estimated to be more than 50.

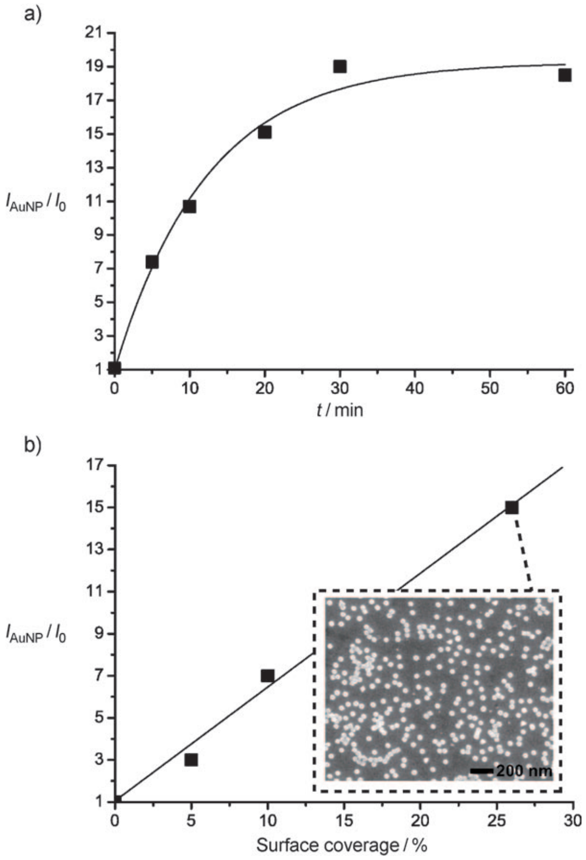

Figure 4. a) Enhancement factor at 670 nm as a function of the immersion time of the $PC_8FcC_{10}SH$ SAM/Au electrode into the Au colloidal solution. b) Enhancement factor at 670 nm as a function of the surface coverage of the AuNPs. Inset: a SEM image of the adsorbed AuNPs on the $PC_8FcC_{10}SH$ SAM/Au electrode.

In summary, the plasmonic enhancement was successfully introduced by the use of the sphere–plane type nanogap structures in a molecular-based photoelectrochemical system.

Highly localized electromagnetic fields were excited at the well-defined interfaces between the organic monolayer and the smooth Au electrode and result in enhancement of the photocurrent by a factor of 50 at each photon-absorbing antenna. Such a large enhancement is surprising in rather complicated photoelectrochemical systems because of some potential difficulties. For example, energy transfer from excited dye molecules to metals can be a serious problem in decreasing the quantum efficiency of the systems.[27] The adsorption of AuNPs on the molecular layers should prohibit partial mass transport of electron-acceptor molecules from the solution to the monolayer surface. Therefore, our result suggests that these disadvantages can be compensated for if the field enhancement is sufficiently large. In this sense, the use of highly localized gap-mode plasmons is essential for practical enhancement in photoelectrochemical systems. The molecular design used in this experiment is not optimized for the use in the plasmonic cavity but rather for conventional electrochemical systems. Therefore, much larger enhancement is expected by optimization of molecular structures. For example, the position of the porphyrin in the linked molecule might affect the enhancement and efficiency of the system.[28] The molecular length, which determines the sphere–plane distance, is also an important factor in achieving high efficiencies. In principle, a shorter molecular length is better for increasing the plasmonic effect, although the plasmon resonance energy has to be matched with the molecular absorption bands.

The sphere–plane-type photon-absorbing antennae are suitable for use in ultrathin organic monolayers. This remarkable feature could lead to the use of this technique in molecular electronic devices. One of possible application would be a nanoscale photoelectric converter incorporated in molecular integrated devices. This strategy should open new possibilities in the design of molecular devices.

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