

Interfacial Arrangements with Atomic/Molecular Resolution for Highly Efficient Photoelectrochemical Energy Conversion

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Development of the efficient solar energy conversion system is one of the most important global issues in the 21st century. In natural photosynthetic systems, highly efficient conversion of solar energy to chemical energy is achieved based on well ordered arrangement of organic and biological molecules with various functions such as photon absorption, electron relay, and catalyst, i.e., enzyme. Many attempts have been made to realize highly efficient artificial solar energy conversion systems by mimicking natural system but there are still many problems to be solved such as low efficiency and low durability before artificial photosynthesis becomes practical.

Here two systems for efficiency enhancement by metal nanoparticles (NPs) and/or metal complexes for photoenergy conversion at metal and semiconductor electrodes modified with molecular layers are described.

1. Plasmonic efficiency enhancement for up-hill photocurrent generation at gold electrode modified with self-assembled monolayer

We have reported highly efficient photoinduced up-hill electron transfer at gold electrode modified with self-assembled monolayer (SAM) of porphyrin-ferrocene coupling thiol molecule as shown in Fig. 1 [1]. Although this system shows very high quantum efficiency, only fraction of solar energy can be utilized because main absorption peak of porphyrin, absorber, is around 420 nm and absorbs not much photons in more high frequency region. Optical antennas, which interface between free-propagating light and localized electromagnetic energy, are indispensable to construct efficient solar-energy conversion system. Since localized electromagnetic fields strongly interact with matter, introduction of optical antennas can increase the population of excited states, leading to high conversion efficiency from photon energy to electric or chemical energy. Surface plasmon polaritons (SPPs), which are collective oscillation modes of free electrons optically excited on a metal surface, are now recognized as a key to manipulate electromagnetic fields on nm scale. When molecules are located near nanostructured metal surface, photon-molecule interactions are greatly enhanced by field localization via excitation of SPPs. One of well-known examples for this concept is surface enhanced Raman scattering (SERS). We have demonstrated that Raman scattering signals from molecular adsorbates are extraordinarily enhanced on nanostructured metal surface [2-7]. Here a metal nano-gap system was introduced as a photon antenna in order to improve the photo-energy conversion efficiency. Theoretical calculation shows that particle plasmon and surface plasmon strongly hybridize in the Au-NP/SAM/Au substrate system. Since such hybridized plasmon is accompanied with extraordinarily enhanced electric field, i.e., photon energy is concentrated in the gap region with the volume of $\sim\text{nm}^3$, one can expect that various optical events would occur more efficiently in the gap. Figure 2 shows photocurrent action spectra of the porphyrin-ferrocene SAM measured in 0.1 M NaClO₄ electrolyte solution containing 50 mM methyl viologen as an electron acceptor without and with 50 nm Au-NPs on top of the SAM. It is clear that photocurrent was significantly increased by the presence of adsorbed Au-NPs, as expected. The wavelength dependence of the enhancement factor is similar to the calculated extinction spectrum, confirming the enhancement of effective photo-energy conversion efficiency by plasmonic resonances in the nano-gap systems [8]. In the present study, the increased photocurrent is 20-fold of the original value around 660 nm. This result opens up a new possibility for design of photofunctionalized molecular devices with plasmonic photon antennas.

2. Construction of photoenergy conversion interfaces by molecularly ordered modification of semiconductor surfaces.

Hydrogen is the most important clean fuels in the future and production of hydrogen from water by solar energy is required. Photoelectrochemical (PEC) and photocatalytic decomposition of water has been studied for long time. Most serious problem of PEC production of hydrogen from water is that while semiconductor electrodes with small energy gap can absorb large fraction of solar energy but unstable, those with large energy gap are stable but can absorb only small fraction of solar energy. This can be solved by using semiconductor of small gap and separating the reaction site from the surface. We have constructed viologen molecular layer on hydrogen terminated Si(111) surface and then Pt nanoparticle was introduced within the molecular layer by ion-exchange reaction followed by electrochemical reduction. Significant decrease of overpotential for hydrogen evolution reaction (HER) at n-Si electrode

was observed by this modification. Further improvement was achieved by constructing multi-viologen-Pt-layers. Viologen acts as molecular wire and Pt acts as HER catalyst. Figure 3 shows photocurrent-voltage relations of hydrogen terminated p-Si(111) electrode and that modified with 1, 3, and 5 viologen-Pt layers. Hydrogen evolution current flowed at more positive potentials than the reversible potential at p-Si(111) electrodes modified with multi-viologen (molecular wire)-Pt (HER catalyst)-layers under illumination [9]. In situ XAFS study carried out under operation shows that Pt particles were not formed even when HER took place and the Pt complexes acted as HER catalysts, i.e., confined molecular catalysts, as schematically shown in Fig.4 [10]. The decrease of white line intensity suggests the formation of a hydride complex as an intermediate of HER, although more detailed experimental and theoretical examinations are required to clarify the mechanism. The formation of Pt particles may have been inhibited since the complexes are separated by molecular layers.

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Figures

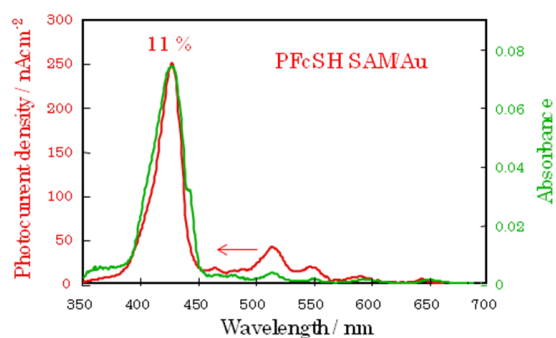


Figure 1. Absorption and photocurrent spectra of gold electrode modified with SAM of porphyrin-ferrocene coupling thiol molecule in a solution containing methyl viologen [1].

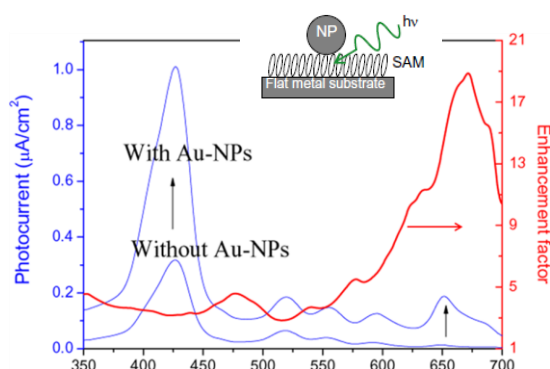


Figure 2. Wavelength dependencies of photocurrent and enhancement factor of the porphyrin-ferrocene SAM without and with adsorbed 50 nm Au-NPs measured in 0.1 M NaClO₄ solution containing 50 mM methyl viologen [8].

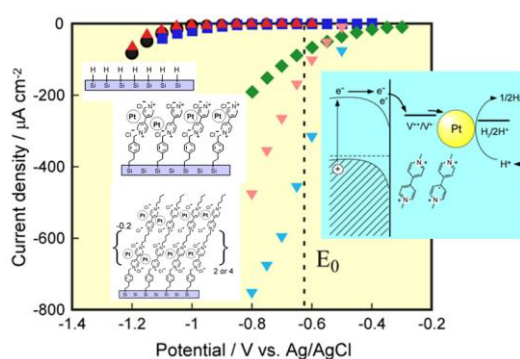


Figure 3. Photocurrent-voltage relations of p-Si(111) electrode modified with various functional layers [9].

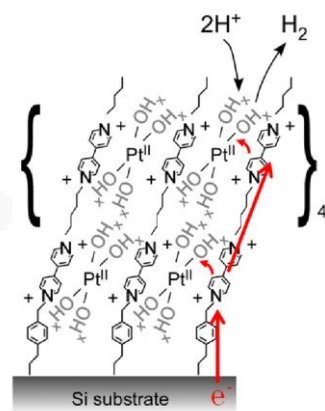


Figure 4. Schematic illustration for electron transfer pathway for HER at Si(111) modified with viologen layer and Pt complex [10].