Mechanism of hot electron transfer at Au nanostructure/TiO_2 interface under modal strong coupling conditions

Hiroaki Misawa[1,2]

1. Research Institute for Electronic Science, Hokkaido University, Sapporo, 001-0021 Japan
2. Center for Emergent Functional Matter Science, National Yang Ming Chiao Tung University, Hsinchu, 30010 Taiwan
E-mail: misawa@es.hokudai.ac.jp

Plasmon-induced hot electron transfer at metal/semiconductor interfaces has attracted much attention as a novel mechanism to promote artificial photosynthesis under visible light irradiation [1-4]. Recently, we reported that Au-NPs/TiO_2/Au film (ATA) structures, which exhibit modal strong coupling between the Fabry-Pérot nanocavity mode and localized surface plasmon resonance (LSPR), can be used as photoanodes to enhance water splitting reactions [5]. The light absorption of the ATA structure was promoted across a broad range of wavelengths under the modal strong coupling, followed by a hot electron transfer from Au-NPs to TiO_2. We observed an 11-fold increase in the incident photon-to-current conversion efficiency (IPCE) with respect to a photoanode structure with no Au film. Importantly, the internal quantum efficiency (IQE) of photocurrent generation was enhanced 1.5 times under a strong coupling over that under uncoupled conditions.

We also found that the Au-Ag alloy NPs/TiO_2/Au-film (AATA) structure, in which Au nanoparticles in the ATA structure were replaced by Au-Ag alloy nanoparticles, exhibited a modal ultra-strong coupling with the splitting energy increasing to 520 meV due to the large LSPR oscillator strength of Au-Ag alloy NPs. Under visible light irradiation, the AATA photoanode showed a maximum IPCE of 4.0% and a corresponding IQE of 4.1% at 580 nm [6].

To clarify the mechanism of the IQE enhancement in the ATA structure, we further investigated the ATA structures using well-size-controlled Au nanodisks (Au-NDs) fabricated on nanocavities using electron beam lithography. Absorption spectra were measured by varying the number of Au-NDs per unit area. The integrated intensity of the absorption spectra was almost constant, independent of the number density of Au-NDs. The near-field spectra obtained from the FDTD simulations also showed the same behavior. On the other hand, the integrated intensity of the absorption spectrum of the Au-NDs/TiO_2 (AT) structures increased linearly with increasing Au-ND number density. These results suggest that the LSPR of Au-NDs on the nanocavity has a quantum coherent interaction through the nanocavity. Furthermore, measurements of the near-field spatial distribution of Au-NDs on the nanocavity using photoemission electron microscopy strongly suggest the existence of quantum coherent interactions in the ATA structure. In addition, transient absorption measurements of electrons injected from Au-ND into TiO_2 showed that the apparent quantum efficiency of electron injection increased with increasing Au-ND number density. On the other hand, for AT, the apparent quantum efficiency of injected electrons was independent of the Au-ND number density. From these results, it is inferred that the quantum coherent interaction between Au-NDs through the nanocavity is an important factor that enhances the IQE of photocurrent generation in the ATA structures.

References

[1] Nishijima, Y.; Ueno, K.; Kotake, Y.; Murakoshi, K.; Inoue, H.; Misawa, H., 2012. *J. Phys. Chem. Lett.*, 3, 1248-1252.
[2] Zhong, Y.; Ueno, K.; Mori, Y.; Shi, X.; Oshikiri, T.; Murakoshi, K.; Inoue, H.; Misawa, H., 2014. *Angew. Chem. Int. Ed.*, 53, 10350-10354.
[3] Oshikiri, T.; Ueno, K.; Misawa, H., 2016. *Angew. Chem. Int. Ed.,* 55, 3942-3946.
[4] Okazaki, M.; Suganami, Y.; Hirayama, N.; Nakata, H.; Oshikiri, T.; Yokoi, T.; Misawa, H.; Maeda, K., 2020. *ACS Appl. Energy Mater.*, 3, 5142-5146.
[5] Shi, X.; Ueno, K.; Oshikiri, T.; Sun, Q.; Sasaki, K.; Misawa, H., 2018. *Nat. Nanotechnol.*, 13, 953-958.
[6] Suganami, Y.; Oshikiri, T.; Shi, X.; Misawa, H., 2021. *Angew. Chem. Int. Ed.*, 60, 18438-18442.