**Session:** Photochemistry and Plasmonics

## Plasmon-induced photocurrent generation using strong coupling between localized surface plasmon and cavity modes

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Plasmon-induced photocurrent generation as well as water splitting has recently been proposed as a novel strategy for the solar energy conversion. However, the insufficient absorption and the plasmon resonance band with a restricted wavelength range in the monolayer of metallic nanoparticles limited the solar energy conversion efficiency. In this study, we constructed a novel plasmonic absorber, which is constituted from a sandwich structure of Au nanoislands (Au-NIs)/TiO<sub>2</sub>/Au-film, for plasmon-induced photocurrent generation.

Au film was sputtered on a silica glass, then a  $TiO_2$  thin film with a thickness of ~tens of nanometers was deposited on the Au film by an atomic layer deposition system, and finally a monolayer of Au-NIs with an average size around 12 nm was fabricated by annealing the 3-nm-thick Au thin film on it. Photocurrent measurements were performed by using a three electrodes system with a saturated calomel electrode (SCE) as reference electrode, a Pt wire as counter electrode and 0.1 mol/dm<sup>3</sup> KOH solution as an electrolyte solution.

By the experimental study and the numerical FDTD simulation, we clarified that the strong light absorption originates from the coupling between localized surface plasmon mode of Au-NIs and cavity mode in TiO<sub>2</sub> thin film on Au film. The absorption, which was calculated by 1-T-R, showed a more than 90% light absorption at the wavelength region of 550~650 nm. We found that IPCE action spectrum almost corresponds to the absorption spectrum of Au-NIs. Importantly, the IPCE value reached about 0.8% which is larger than that reported before (~0.4%) because of the strong light absorption. [1,2] Note that the absorption spectrum was broadened and divided into two peaks with inlaying Au-NIs partially in TiO<sub>2</sub> layer due to the strong coupling between plasmon and cavity modes, and the similar spectrum modulation can be also seen in the IPCE action spectrum. The dual-band absorption spectrum and the corresponding IPCE action spectrum observations indicate that hybrid states are formed due to the strong coupling between plasmon and cavity modes.

We have demonstrated that the plasmonic absorber constituted from a sandwich structure of Au nanoislands (Au-NIs)/TiO<sub>2</sub>/Au-film enhanced the efficiency of plasmon-induced photocurrent generation. The strong coupling between localized surface plasmon mode and cavity modes realized a broadband photocurrent generation. This concept can be applied to the broadband solar energy harvesting as well as the photoenergy conversion devices.

## **References:**

- [1] X. Shi, K. Ueno, N. Takabayashi, H. Misawa, J. Phys. Chem. C, 2013, 117, 2494
- [2] X. Shi, K. Ueno, T. Oshikiri, H. Misawa, J. Phys. Chem. C, 2013, 117, 24733