【Grant-in-Aid for Specially Promoted Research】

Science and Engineering

Title of Project : Development and elucidation of highly efficient photoreaction systems using a strong coupling between nanocavity and plasmon

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【Purpose and Background of the Research】

To realize a sustainable society, it is essential to develop innovative photochemical reaction systems that can efficiently utilize the abundant visible light contained in sunlight. We have elucidated that a titanium dioxide (TiO_2)/Au-film, which is a constituent element of the Au nanoparticle (Au-NPs)/TiO_2/Au-film electrode, becomes a nano-sized Fabry-Pérot (FP) resonator and that the nano-FP resonator is strongly coupled with the localized surface plasmon resonance (LSPR) of Au-NPs on TiO_2. We have also elucidated that the strongly coupled structure shows a large near-field enhancement in a wide wavelength range and a remarkable enhancement of the quantum yield in photoelectric conversion using water as an electron source compared with that with an uncoupled electrode. In this study, we aim to clarify the theory of plasmon-induced electron transfer and explore a strongly coupled electrode that enables further enhancement of the near-field and quantum yield.

【Research Methods】

To realize a plasmon-induced electron transfer reaction exhibiting a high quantum yield, the key steps are 1) to optimize strongly coupled electrodes and 2) to elucidate the plasmon-induced electron transfer reaction mechanism. Fig. 1a shows a strongly coupled electrode. The characteristic of this electrode is that its color changes from yellow to black due to strong light absorption with a wide wavelength in the visible range when Au-NPs are formed on the TiO_2/Au-fim (Fig. 1b). In this study, we derive the design of the nano-FP resonator and Au-NPs using electromagnetic simulations to achieve a larger near-field enhancement, in collaboration with Prof. Sasaki of Hokkaido University (Co-I). The strongly coupled electrode is fabricated by the obtained optimum structural design, and its spectral and photoelectric conversion properties are provided as feedback to the structural design.

In parallel with these studies, we promote research to elucidate the mechanism of plasmon-induced electron transfer. A laser pulse with a pulse duration of ~20 fs, a center wavelength of 800 nm as a fundamental wavelength (ω) and its third harmonic generation (3ω, 267 nm) are introduced into the existing photoemission electron microscopy (PEEM) via an optical delay system, and the time-resolved two-photon PEEM is constructed (Fig. 2a). LSPR is excited by ω to generate hot electrons, and these are further excited by 3ω to generate photoelectrons. By measuring the energy distribution of the electron, we investigate the energy distribution of the hot electrons and holes involved in the electron transfer reaction (Fig. 2b). The near-field spectrum, phase relaxation time, and electron transfer dynamics are also studied. Furthermore, we explore the intermediates of water oxidation by surface-enhanced Raman scattering spectroscopy and elucidate the mechanism of oxygen evolution, in collaboration with Prof. Murakoshi of Hokkaido University (Co-I).

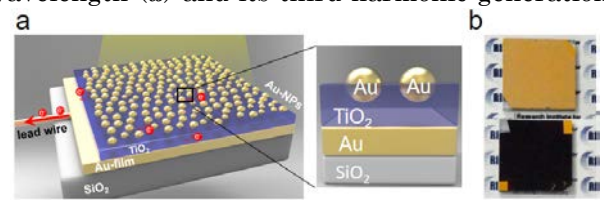

Fig. 1. a, An illustration of strongly-coupled electrode, **b**, Photographs of the TiO_2/Au-film (upper) and the strongly-coupled electrode (lower).

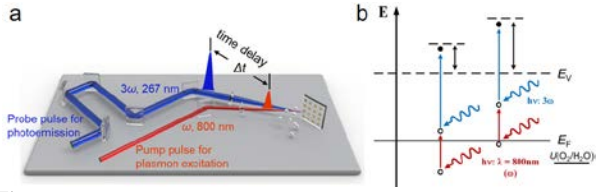

Fig. 2. a, Optical systems of time-resolved two-photon PEEM, **b**, Conceptual diagram of photoemission by 3ω.

【Expected Research Achievements and Scientific Significance】

The electron transfer reaction using a strongly coupled electrode can realize not only the efficient utilization of light but also a near-field enhancement in the entire visible region and an increase in the quantum yield of the reaction. It is expected to make great impacts in plasmon-induced solar energy conversion and photocatalytic studies. Moreover, it is possible to freely tune the wavelength at which the near-field enhancement is induced by selecting the size of the Au-NPs and the resonator length of the nano-FP resonator. Therefore, we believe that this technology induces a paradigm in shift not only plasmonic chemistry but also a wide range of other research fields, such as plasmonics, nanophotonics and spectroscopic research.

【Publications Relevant to the Project】

- H. Yu, Q. Sun, H. Misawa et al., "Exploring coupled plasmonic nanostructures in the near field by photoemission electron microscopy", *ACS Nano* **10**, 110373-10381 (2016).
- K. Ueno, T. Oshikiri, Q. Sun, X. Shi, H. Misawa, "Solid-state plasmonic solar cells", *Chem. Rev.* **118**, 2955-2993 (2018).

【Term of Project】 FY2018-2022

【Budget Allocation】 477,700 Thousand Yen

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