【Grant-in-Aid for Scientific Research (S)】

Construction of an innovative photoreaction fields that possess quantum coherent strong coupling and study of its fundamental principle

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Purpose and Background of the Research

●Outline of the Research

Our research group has so far achieved the decomposition of water by visible light using a titanium dioxide (TiO_2) semiconductor electrode loaded with gold nanoparticles (Au-NPs) that exhibit plasmon resonance. Furthermore, when Au-NPs were loaded a TiO_2 thin film electrode with the function of an optical nanocavity, new hybrid modes were formed by modal strong coupling, and the quantum efficiency of the photoelectric conversion using water as the electron source was improved. In this study, we will elucidate the details of the "quantum coherent interaction" between plasmons of gold nanoparticles via nanocavities, which is considered to be the key to this quantum efficiency enhancement, and develop the electrodes with strong coupling that enable further quantum efficiency enhancement.

●Purpose and Background of the Research

Artificial photosynthesis is a scientific technology that is strongly desired for social implementation toward the realization of carbon neutrality. Recently, artificial photosynthesis utilizing visible light using plasmon resonance exhibited by Au-NPs and other materials has been attracting attention. For example, as shown in Fig. 1 when Au-NPs are supported on a TiO_2 electrode and plasmons of the Au-NPs are excited by visible light, hot carriers are generated at the Au/TiO_2 interface and water is oxidized while hydrogen is generated at the counter electrode. To further improve the quantum efficiency of water splitting using plasmon, we fabricated a "strong coupling electrode" consisting of Au-NPs/TiO_2/Au films (ATA structure) using the concept of "modal strong coupling" (Fig. 2a, b). As shown in Fig. 2c, when the plasmon resonance mode coincides with the resonance mode of the Au-NPs, modal strong coupling occurs and two new hybrid modes are formed. This significantly improves the light absorption properties in visible region (Fig. 2d), in addition, we have successfully realized the improvement of the quantum efficiency of photocurrent generation using water as an electron source.

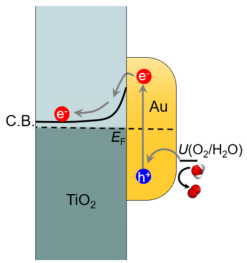

Fig.1 Mechanism of hot carrier generation and water oxidation by plasmons

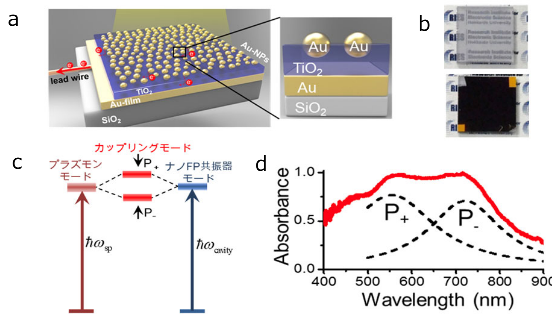

Fig.2 (a) Schematic diagram of ATA strong-coupling electrode, (b) AT: top and ATA: bottom photographs, (c) Energy diagram showing hybrid mode, (d) Absorption spectrum of ATA strong-coupling electrode.

To elucidate the mechanism of this enhancement, we fabricated the ATA structure shown in Fig. 3 and measured the apparent quantum efficiency (AQE) of electron injection from the Au-NDs to TiO_2 by time-resolved absorption measurements with varying Au-ND particle number density (PND). The AQE of ATA increased significantly with increasing PND, while the AQE was nearly constant for structures without nanocavity (Fig. 4). On the other hand, the photoemission electron microscopy (PEEM) measurements of the near-field spatial distribution of the ATA structure have revealed the existence of "quantum coherent interactions" between the plasmons of each Au-ND via nanocavity. Moreover, the following mechanism is shown by model calculation. The plasmon resonance energy can coherently travel in the coherence area. If a particular Au-ND with fast damping is present in the coherence area of ATA, then the excitations relax to electron–hole pairs at that particular Au-ND faster than those at the other excited Au-NDs. Thus, in the case of ATA, it is inferred that with increasing PND, the number of Au-ND with fast damping increases in the system, leading to enhancement of the quantum efficiency (Fig. 5).

In this study, we will elucidate what features of Au-ND in the quantum coherence area can efficiently generate hot carriers as hot spots, and also to verify whether "quantum fluctuations" exist such that the hot spots migrate with time. From these results, we aim to establish design guidelines for electrodes of strong couplings that can achieve higher quantum efficiency.

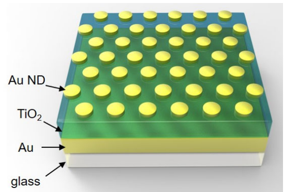

Fig. 3 Schematic diagram of ATA structure with highly ordered gold nanodisks

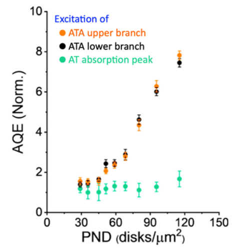

Fig. 4 PND dependence of the AQE of electron injection

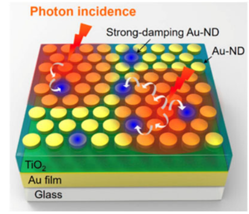

Fig. 5 Conceptual diagram of the mechanism of quantum efficiency enhancement by quantum coherent interaction

Expected Research Achievements

(1) Elucidation of the effect of hot spots on quantum coherent interactions

One hot spot with high hot-carrier generation efficiency will be introduced into a space larger than the predicted quantum coherence area using EB lithography, and the near-field spatial distribution and dephasing time will be measured by PEEM. Since the photoelectron emission intensity from the quantum coherence area containing one hot spot is expected to decrease, this allows the actual size of the quantum coherence area to be determined.

(2) Elucidation of the effect of the number of hot spots on the AQE of electron injection

We will introduce multiple hot spots in the quantum coherence area and investigate how they affect the size of the quantum coherence area, the dephasing time, and the AQE. From these results, we will elucidate the mechanism of energy transfer from quantum coherently interacting Au-NDs to hot spots and the generation of hot carriers.

If the mechanism by which quantum coherent interactions between plasmonic particles accelerate reactions is clarified through this research, it will be possible to create a photochemical reaction field that achieves high quantum efficiency through a new concept.

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