

科学研究費助成事業 研究成果報告書

平成 29 年 5 月 26 日現在

機関番号：10101

研究種目：若手研究(B)

研究期間：2015～2016

課題番号：15K20833

研究課題名(和文) Plasmon-enhanced photoelectrochemical energy conversion on Au nanoparticles loaded titanium dioxide thin film

研究課題名(英文) Plasmon-enhanced photoelectrochemical energy conversion on Au nanoparticles loaded titanium dioxide thin film

研究代表者

石 旭 (Shi, Xu)

北海道大学・電子科学研究所・助教

研究者番号：20749113

交付決定額(研究期間全体)：(直接経費) 3,200,000円

研究成果の概要(和文)：本研究では表面増強ラマン散乱計測を利用し、金属ナノ粒子の表面プラズモン増強水酸化反応を観察した。また、金ナノ粒子を担持した酸化チタン電極におけるプラズモン誘起電荷分離に対する界面効果を明らかにした。さらに、表面プラズモン増強水酸化反応とプラズモン誘起電荷分離に対する界面効果の結果に基づいて、広帯域の光捕集のために金属/半導体/金属によって構成される完全光吸収機能を有するプラズモン誘起光エネルギー変換システムの構築にも成功した。

研究成果の概要(英文)：In this study, the plasmon-induced water oxidation process was investigated via a in-situ SERS measurement. The interfacial structure effect on the charge separation was determined at the atomic layer scale. A tight contact between the metal nanoparticles and its support metal oxide is highly demanded for efficient plasmon-induced charge separation. Based on the understanding of the plasmon-induced water oxidation process and the interfacial structure effect on the charge separation, we successfully constructed a novel plasmonic structure, which shows strong light absorption, for broadband plasmon-enhanced solar energy conversion.

研究分野：物理化学

キーワード：plasmon resonance water splitting strong coupling titanium dioxide thin film solar cell

1. 研究開始当初の背景

Metallic nanostructures which exhibit localized surface plasmon resonance (LSPR) are of interest for vary applications due to their large absorption/scattering cross-section and ultrahigh localized electromagnetic field in the vicinity of metal nanostructures under plasmon excitation. Plasmon-enhanced solar energy conversion using metallic nanostructures has been extensively studied for enhancing light trapping in the thin-film solar cells and solar to fuel energy conversion on metal oxide semiconductors.

Despite the experimental successes in the plasmon-enhanced solar energy conversion, the mechanism of plasmon-enhanced solar energy conversion is still unclear, especially for the plasmon-enhanced water splitting. The reaction processes of the plasmon-enhanced water molecule oxidation need to be further clarified to understand the activity of plasmon-excited holes. In addition, the interface of metallic nanostructure/semiconductor, which plays a critical role for the charge separation, also need to be investigated to optimize the plasmon-induced charge separation. The further understanding of the plasmon-enhanced water oxidation and the plasmon-induced charge separation is expected to lay a foundation for developing high efficiency plasmon-enhanced solar energy conversion system.

2. 研究の目的

In this study, three main objectives were explored:

(1) Investigated the plasmon-enhanced water oxidation processes via the in-situ measurement of the intermediate products generated on the metal nanoparticles loaded semiconductor photoanode.

(2) Studied the interfacial effect on the plasmon-induced charge separation using plasmon resonance microscopy.

(3) Constructed a high efficiency plasmon-enhanced solar energy conversion system using a plasmonic nanostructured photoelectrode based on the understanding of the plasmon-enhanced water oxidation and charge separation.

3. 研究の方法

(1) The plasmon-enhanced water oxidation processes were studied on Au nanoislands (Au-NIs) loaded strontium titanate (STO) photoelectrode. The intermediate products generated under plasmon excitation were clarified via in-situ surface-enhanced Raman scattering (SERS) measurement of the bonding vibration between Au and the intermediate

products. Combining the photoelectrochemical (PEC) and the SERS measurements, we can explore the plasmon-enhanced water oxidation processes under a certain electrochemical potential.

(2) The charge separation at the interface of Au-NIs/TiO₂ was monitored by the plasmon resonance spectroscopy. The charge density dependence of the plasmon resonance on metal nanoparticles enables us to detect the charge transfer between metal nanoparticle and semiconductor via monitoring the plasmon resonance band.

The interfacial structures of Au-NIs/TiO₂ which can be controlled by the annealing temperature, were observed by HR-TEM in atomic layer scale. The interfacial structure effect on the charge separation can be succeeded by measuring the behavior of plasmon band shift under the UV light irradiation.

(3) A plasmonic nanostructured photoelectrode, consisting Au-NIs/TiO₂/Au-film sandwich structure, was constructed for plasmon-enhanced solar energy conversion. TiO₂ with thickness around 30 nm deposited on Au-film can support cavity resonance. By optimized design, the cavity resonance in TiO₂ thin film can overlap with the LSPR in Au-NIs, resulting in a strong coupling of these two resonances. The strong coupling in the Au-NIs/TiO₂/Au-film plasmonic structure induced a broadband, high absorption, which dramatically improved the solar energy conversion efficiency. The coupling between the cavity resonance in TiO₂ thin film and the LSPR in Au-NIs can be further enhanced by partially inlaying Au-NIs into TiO₂ thin film. In addition, the partially inlaid Au-NIs also promote the water oxidation reaction.

4. 研究成果

(1) The Au-NIs/STO was fabricated by sputtering a 3-nm Au thin film on STO (110) substrate following by a thermal annealing at 800 °C. To clarify the process of plasmon-enhanced water oxidation on Au-NIs/STO, we studied the intermediate of the plasmon-induced water oxidation by SERS, as Figure 1a shown. Three electrode system was employed with reference electrode of Ag/AgCl and counter electrode of Pt. The 0.1 M NaF aqueous solution was used as electrolyte without any sacrificial material. The SERS spectra were excited with a 785-nm laser.

Figure 1b shows the SERS measurement spectra. The Raman band around 520-580 cm⁻¹

is attributed to the Au-O stretching mode. The observation of the only Raman band around 520-580 cm^{-1} on the Au-NIs surface depicts the only intermediate of plasmon-induced water oxidation on Au-NIs/STO is gold trihydroxide. By measuring the SERS spectra under various applied potential, we observed the onset potential of SERS signal of Au-O vibration on Au-NIs/STO (100) is -0.4 V vs. Ag/AgCl. This observation of the intermediate in neutral electrolyte extends our understanding on the plasmon-enhanced water oxidation reaction.

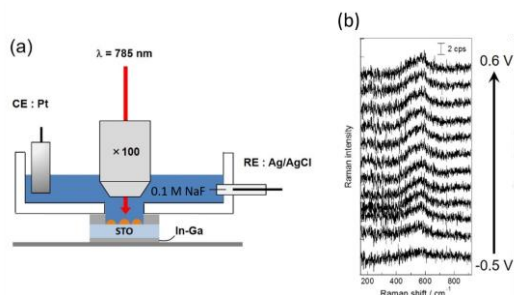


Figure 1. (a) Schematic of SERS measurement. Three electrode system was employed with reference electrode of Ag/AgCl and counter electrode of Pt. The SERS spectra were excited with a 785-nm laser. (b) Potential-dependent SERS spectra of Au-NIs/STO (100) under steady-state conditions.

(2) The plasmon resonance spectroscopy was established by using a microscopy combined with an optical spectrometer and a photoelectrochemical analyzer, as shown in Figure 2a. The plasmon resonance of the metal nanoparticles was in-situ measured during the photochemical reactions on the metal nanoparticles. In my study, the Au-NIs loaded TiO₂ with (110) orientation surface was used. The Au-NIs was fabricated by thermal annealing a 3-nm Au film on TiO₂ surface at 800°C or 150°C. In principle, the plasmon resonance wavelength exhibits a strong dependence on the bulk plasmon frequency which is a function of electron density. Therefore, we can determine the charge change in Au-NIs by monitoring the plasmon resonance wavelength. When applied a negative potential, more negative than the flat-band potential of Au-NIs/TiO₂ electrode, plasmon band blue-shifts was observed due to the electron density increases, as shown in Figure 2b. The onset potential of the plasmon band blue-shift was estimated to be -0.6 V vs. Pt. From the observation of the plasmon band shifts as a function of applied electrochemical potential, we successfully calculated the capacity of the Au-NIs to be about 130 $\mu\text{F}/\text{cm}^2$.

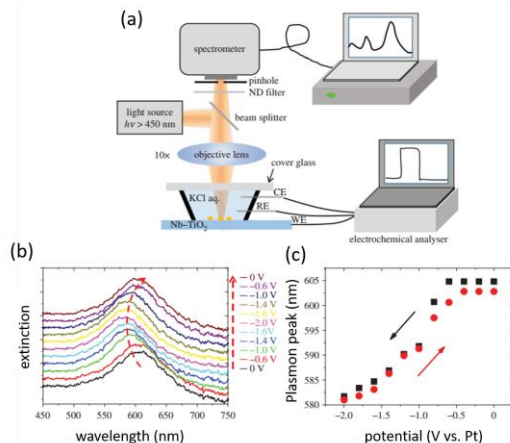


Figure 2. (a) Schematic of the spectroelectrochemical measurement system under photocurrent generations. (b) Extinction spectra of Au-NIs with different applied potentials. (c) Applied potential dependence of the peak wavelength position of the plasmon resonance.

The interfacial structure effect on the charge transfer was studied by the plasmon resonance spectroscopy under a 350-nm light excitation. Two kinds of interfacial structure were fabricated by Au-NIs/TiO₂ annealed at 800°C and 150°C. The interfacial structure of Au-NIs/TiO₂ under 800°C annealing exhibits an intimately contact between the crystal interface, while the interfacial structure of Au-NIs/TiO₂ under 150°C annealing shows an interfacial defects layer, as the inserted TEM images shown in Figure 3. Under 350 nm irradiation, inter-band transition in TiO₂ was excited, and the electron transfer from Au-NIs to TiO₂ occurred on both Au-NIs/TiO₂ under 150°C and 800°C while applied a 0.3 V potential. As a result, the plasmon resonance band of Au-NIs/TiO₂ showed red-shifts. However, while stopping the applied potential, electrons transferred from TiO₂ to Au-NIs occurred only on Au-NIs/TiO₂ under 150°C, depicting by the blue-shift of plasmon resonance band, as Figure 3a and 3b shown.

According to the HR-TEM cross-section observation, EELS measurement and the plasmon resonance spectroscopy, we concluded that the interfacial defect layer under 150°C annealing decreased the Schottky barrier of Au-NIs/TiO₂, which facilitates the electron transfer from the conduction band of TiO₂ to Au-NIs. The intimate contact under 800°C annealing formed a pronounced Schottky barrier at Au-NIs/TiO₂ interface, which prevented electron transfer from the conduction band of TiO₂ to Au-NIs, indicating a better charge separation at the Au-NIs/TiO₂

interface junction. The charge separation at Au-NIs/TiO₂ was further demonstrated by the plasmon-induced photocurrent generation. A higher IPCE value on Au-NIs/TiO₂ annealed at 800°C was observed, which corresponding to the HR-TEM and plasmon spectroscopy measurement. This surface plasmon resonance spectroscopy provides us a feasible in-situ tool to detect the charge separation on the interface junction of metallic nanoparticles loaded semiconductor.

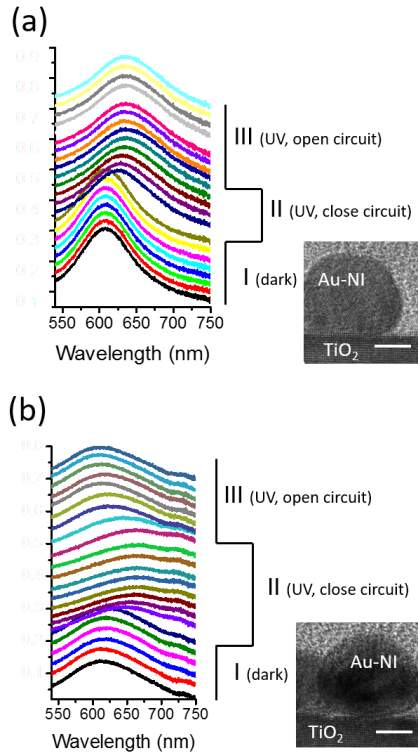


Figure 3 LSPR bands of Au-NIs/TiO₂, fabricated by annealing at (a) 800°C and (b) 150°C, under the conditions of (I) dark, (II) 350 nm light irradiation with applied potential of 0.3 V, and (III) 350 nm light irradiation without applied potential. The inserted images show the interfacial structure of Au-NIs/TiO₂ respectively. The scale bare represents 5 nm.

(3) Based on the understanding of water oxidation mechanism and the interfacial effect on the charge separation, we then proposed a plasmon-enhanced solar energy conversion system using an Au-NIs/TiO₂/Au-film plasmonic structure, as schematic shown in Figure 4a. A strong light absorption was revealed by the black color of the structure. Because of a phase change at the interface of TiO₂/Au-film, the TiO₂ thin film with thickness only 28 nm can support a cavity resonance. The origination of the strong light absorption was demonstrated to be the strong coupling between the cavity resonance in the TiO₂ thin film and the LSPR of Au-NIs, as the energy diagram shown in Figure 4b.

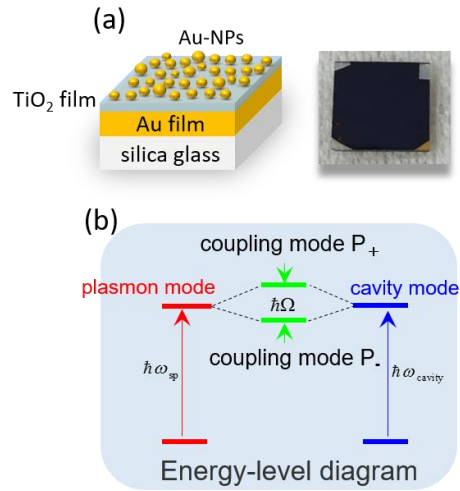


Figure 4. (a) Schematic of the Au-NIs/TiO₂/Au-film plasmonic structure. Right panel shows the photograph of the structure. (b) Energy diagram of the strong coupling between the cavity resonance in TiO₂ thin film and the LSPR resonance of Au-NIs.

On the behave of the strong coupling, a broad dual-band and strong absorption was achieved on Au-NIs/TiO₂/Au-film with partially inlaid Au-NIs, which also was demonstrated by the FDTD simulation. The partially inlaid Au-NIs plays a key feature to enhance the coupling between the cavity mode in TiO₂ thin film and the LSPR resonance in Au-NIs, exhibiting a coupling-induced dual-band absorption, as shown in Figure 5a. In addition, the partially inlaid Au-NIs also promoted the water oxidation reaction via plasmon-excited holes. The IPCE action spectrum was measured in three electrodes

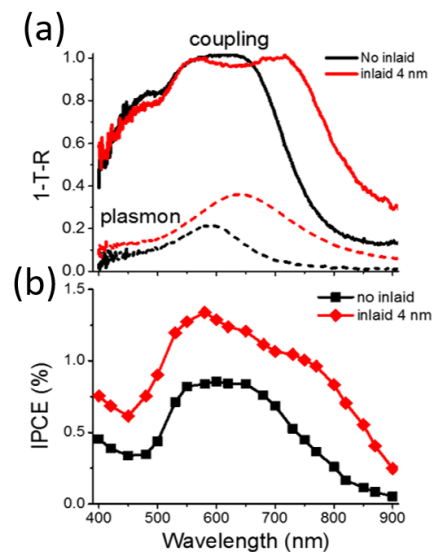


Figure 5 (a) The absorption spectra and (b) IPCE action spectra of Au-NIs/TiO₂/Au-film with Au-NIs inlaid depth of 0 and 4 nm. The dot lines in (a) show the plasmon band of Au-NIs with depth of 0 and 4 nm.

system with saturated calomel electrode (SCE) as reference electrode and Pt wire as counter electrode. The IPCE action spectra of Au-NIs/TiO₂/Au-film with Au-NIs inlaid depth of 0 and 4 nm measured at 0.3 V vs. SCE in 0.1 mol/dm³ of KOH electrolyte are shown in Figure 5b. The closely matching of the absorption spectra and the IPCE action spectra depict that the photocurrent enhancement originates from the strong absorption in the Au-NIs. Water splitting was experimentally demonstrated on this Au-NIs/TiO₂/Au-film structure using a two electrodes system with Pt wire as counter electrode. Under a 0.7 V bias potential, a stoichiometric H₂ and O₂ evolution under visible light irradiation were observed. The H₂ evolution action spectrum further showed highly consist with the IPCE action spectra and the absorption spectra, which illustrating the strong coupling induced energy conversion. Herein, we successfully constructed a plasmonic structure with strong and broad absorption features for solar energy conversion.

5. 主な発表論文等

(研究代表者、研究分担者及び連携研究者には下線)

[雑誌論文] (計 4 件)

- 1) R. Takakura, T. Oshikiri, K. Ueno, X. Shi, T. Kondo, H. Masuda, H. Misawa, "Water Splitting Using a Three-dimensional Plasmonic Photoanode with Titanium Dioxide Nano-tunnels", *Green Chem.*, 19, 2398-2405 (2017). 査読有
DOI:10.1039/C6GC03217F
- 2) K.L. Lee, H. Y. Hsu, M. L. You, C. C. Chang, M. Y. Pan, X. Shi, K. Ueno, H. Misawa, P. K. Wei, "Highly Sensitive Aluminum Based Biosensors Using Tailorable Fano Resonances in Capped Nanostructures", *Sci. Rep.*, 7, 44104 (2017). 査読有
DOI:10.1038/srep44104
- 3) J. Guo, T. Oshikiri, K. Ueno, X. Shi, and H. Misawa, "Plasmon-induced Photoelectrochemical Biosensor for In situ Real-time Measurement of Biotin-streptavidin Binding Kinetics under Visible Light Irradiation", *Anal. Chim. Acta*, 957, 70-75 (2017). 査読有
DOI:10.1016/j.aca.2016.12.025
- 4) A. E. Shalan, T. Oshikiri, S. Narra, M. M. Elshanawany, K. Ueno, H. P. Wu, K. Nakamura, X. Shi, E. W. G. Diau, and H. Misawa, "Cobalt Oxide (CoO_x) as an Efficient Hole-Extracting Layer for High

Performance Inverted Planar Perovskite Solar Cells", *ACS Appl. Mater. Interfaces*, 8, 33592-33600 (2016). 査読有
DOI:10.1021/acsami.6b10803

[学会発表] (計 4 件)

- 1) X. Shi, T. Oshikiri, K. Ueno, K. Sasaki, H. Misawa, "Plasmon-induced photocurrent generation using coupling between localized surface plasmon resonance and cavity mode", The 97th CSJ Annual Meeting, 16th, Mar. 2017, Keio University, Hiyoshi Campus (Kanagawa · Yokohama)
- 2) X. Shi, K. Ueno, T. Oshikiri, K. Sasaki, H. Misawa, "Plasmon-induced photocurrent generation using metal-semiconductor-metal nanostructured perfect absorber", Annual Meeting on Photochemistry 2016, 6th, Sep. 2016, The University of Tokyo, Komaba I Campus (Tokyo · Meguroku)
- 3) X. Shi, K. Ueno, T. Oshikiri, H. Misawa, "Observation of charge separation between gold nanoparticles and titanium dioxide using surface plasmon spectroscopy", The International Chemical Congress of Pacific Basin Societies (PACIFICHEM 2015), 18th, Dec. 2015, Honolulu, Hawaii, USA.
- 4) X. Shi, K. Ueno, T. Oshikiri, H. Misawa, "Improvement of plasmon-enhanced photocurrent generation by interference of titanium dioxide thin-film", 27th International Conference on Photochemistry (ICP 2015), 2nd Jul. 2015, Jeju Island, Korea.

6. 研究組織

(1) 研究代表者

石 旭 (SHI, Xu)

北海道大学・電子科学研究所・助教

研究者番号： 20749113