様　式　Ｃ－１９、Ｆ－１９－１、Ｚ－１９　（共通）

科学研究費助成事業　　研究成果報告書

令和　４ 年　 ６ 月 １０ 日現在

機関番号：１０１０１
研究種目：若手研究
研究期間：2020～2021
課題番号：２０Ｋ１５１１３

研究課題名（和文）Study on Dynamics of Plasmon-Induced Charge Carriers under the Modal Strong Coupling Conditions

研究課題名（英文）Study on Dynamics of Plasmon-Induced Charge Carriers under the Modal Strong Coupling Conditions

研究代表者
石　旭（Shi, Xu）

北海道大学・創成研究機構・准教授

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、これまでに構築した革新的なモード強結合プラズモン積層構造電極における、光エネルギー変換の量子収率の増大のメカニズムを理解するため、強結合したプラズモン誘起電子移動反応ダイナミクスを解明しました。金ナノ微粒子のプラズモンを励起すると、金ナノ微粒子から酸化チタンの伝導帯に移動した電子が赤外波長の吸収を示すことから、中赤外波長の時間分解過渡吸収測定によって界面でのプラズモン誘起電子移動ダイナミクスを解析できました。ホワイトライトフェムト秒時間分解分光測定による時間分解過渡吸収スペクトルを測定し、モード強結合状態がプラズモン誘起電子ダイナミクスに与える影響を明らかにしました。

研究成果の学術的意義や社会的意義
Understanding of the enhanced photochemical reactions in the modal strong coupling system by exploring the dynamics of the plasmon-induced electron transfer and the electron-electron, electron-phonon coupling will be beneficial for the future development of plasmonic solar energy conversion system.

研究成果の概要（英文）：In this study, I focused on the dynamics of plasmon-induced electron under the strong coupling conditions. By constructing a Au-NPs/TiO2/Au-film structure with Au-NPs fully inlaid inside the TiO2, the strong coupling between the plasmon resonance of Au-NPs and the cavity resonance is verified to be strongly determined by the electric field in the cavity. Using this coupling strength tunable nanostructures, we studied the electron transfer from Au-NPs to TiO2 as well as the electron-electron, electron-phonon coupling of Au-NPs using transient spectroscopy with a reflection configuration. We found that under the strong coupling conditions, a higher photo-induced electron transfer was observed. In addition, based on the study of electron-electron coupling and electron-phonon coupling of Au-NPs, we found that the electron-electron coupling and/or electron-phonon coupling of Au-NPs were modified under the strong coupling conditions.

研究分野：photochemistry

キーワード：transient spectroscopy　strong coupling　electron dynamics　plasmon　cavity

１．研究開始当初の背景

Solar-to-chemical energy conversion, especially the water splitting, is one of the most viable solutions for sustainable energy resources. Recently, chemically stable, and low-cost TiO_2 based solar-to-chemical energy conversion system shows remarkable visible light response based on the plasmon-induced photochemical reaction, and it has attracted increasing research interests. Very recently, we have successfully developed a novel plasmonic thin-film photoelectrode, which consists of Au-NPs/TiO_2/Au-film sandwich structure, for visible to near-infrared broadband light harvesting and efficient water splitting reaction. This photoelectrode shows a modal strong coupling between the localized surface plasmon resonance (LSPR) of Au-NPs and the cavity mode of TiO_2/Au-film. More interestingly, the quantum efficiency of water oxidation on this photoelectrode is enhanced under the modal strong coupling conditions as compared to the conventional plasmonic photoelectrode. This observation provides an alternative way to improve the quantum efficiency of chemical reactions. However, the mechanism underlying the enhanced quantum efficiency of water splitting under the modal strong coupling is still uncertain. To further understand the mechanism, one of the most important keys is of understanding the dynamics of plasmon-induced charge carriers under the modal strong coupling conditions.

２．研究の目的

In this study, a femtosecond pump-probe ultrafast spectroscopy was employed to study the dynamics of the plasmon-induced energetic charge carriers under the modal strong coupling conditions. Ultrafast spectroscopy is an effective tool to explore the dynamics of plasmon-induced charge separation at the interface of the metal nanoparticle/semiconductor. At Au-NPs/TiO_2 interface, under the excitation by a visible pump, the electrons in Au-NPs transfer to the conduction band of TiO_2, and the electrons in conduction band of TiO_2 absorb the light of an IR probe via intra-band excitation. On the basis of the ultrafast measurement, the dynamics of plasmon-induced electrons under the modal strong coupling could be measured and a better understanding of the dynamics can feed back to the development of plasmon-induced chemical reactions.

３．研究の方法

To explore the dynamics of plasmon-induced energetic electrons, the number of injection and the lifetime of plasmon-induced electrons and the ultrafast electron dynamics in Au-NPs will be measured using femtosecond transient spectroscopy in a reflection configuration. A wavelength-tunable pump pulse is used to excite electron injection from Au-NPs to TiO_2 at the wavelength near the resonance peak; an IR pulse or white light pulse with a certain delay is used to probe the electrons in the condition band of TiO_2 or electron dynamics in Au-NPs. Dynamics of plasmon-induced charge carriers in the structure with and without modal strong coupling were analyzed to figure out the dynamics of charge carriers modified under modal strong coupling conditions.

４．研究成果

I. Efficient charge separation at coherent plasmon–exciton states

Efficient absorption of light is an important operational aspect for any strategy aiming to effectively use the solar energy. Here we showed that near-perfect energy absorption by coherent light–matter states can be realized in a scalable system comprising a monolayer of Au-NPs in direct contact with molecular excitons, both interacting with incident light and an optical resonance supported by a Fabry–Pérot (FP) cavity. The

cavity modifies the radiative rate of the metal nanoparticles, leading to a condition of (near) critical coupling, which is manifest by an absorption of >90% of the incident light at the resonant frequencies. In this system, we demonstrated that simultaneously exhibits coherent plasmon–exciton interactions and high absorption light.

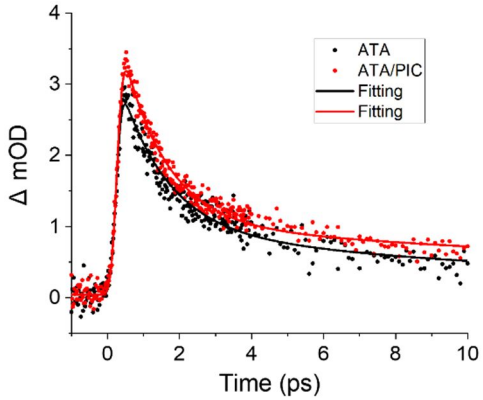

Figure 1. Transient time profile of ATA-PIC (red), ATA (black).

Under the study of electron injection from Au-NPs into TiO_2, we excited the samples using ultrashort laser pulses and measured changes in the magnitude of reflectance ΔR of 3500 nm pulses with a controlled time delay with respect to the pump pulses. The pump pulses were loosely focused on the sample surface at normal incidence. A low incident pump power was used to ensure that the photoinduced electron injection processes were linear with the excitation power. Injected transient electron populations in the conduction band of TiO_2 were characterized by measuring changes in the reflectance of the infrared light pulses. By studying the effect of the photo-excitation of coherent plasmon–exciton states on photoinduced charge carrier generation, we found that the coherent interaction increases the efficiency of charge separation by a factor of about 1.22, as shown in the Figure 1. Further improvements in photoinduced charge transfer could be achieved by creating the molecular J-aggregates directly on the surface of the metal nanoparticles. This could be achieved through self-assembly approaches, that will place the J-aggregates in areas of intense plasmonic near-field, increasing the plasmon–exciton interaction strength.

II. Water Oxidation under Modal Ultrastrong Coupling Conditions

In this study, to understand hot-electron injection phenomena under strong coupling conditions with extremely high splitting energies, we developed a photoelectrode under an ultrastrong coupling condition using Au-Ag alloy nanoparticles/TiO_2/Au-film (AATA) structure. The splitting energies of the AATA and ATA structures were calculated as 520 meV and 350 meV, respectively. The large splitting energy of AATA indicates that this AATA structure fulfils the ultrastrong coupling condition ($\hbar\Omega > 0.2\ \hbar\omega_0$). Under the photoelectrochemical characterizations, the incident photocurrent conversion efficiency (IPCE) of AATA was remarkably higher than that of ATA in the visible light wavelength range. The highest IPCE of AATA was about 2.4 times larger than that of ATA, and the average IPCE in visible region increased by about 1.7 times. Moreover, the internal quantum efficiency (IQE) was calculated by dividing the IPCE by absorption to determine the charge separation efficiency. We found that the IQE of AATA was higher than that of ATA at wavelengths from 420 nm to 900 nm. The IQE enhancements of AATA at the peaks of the upper and lower branches (at 580 nm and 700 nm) were 2.4 and 1.6 times, respectively, as compared to that of ATA.

To explore the mechanism of the IQE enhancement on AATA, we performed transient absorption

measurements of AATA and ATA, as shown in Figure 2a. The maximum ΔOD (ΔOD_{Max}) for each measurement was estimated by extracting the maximum value of the fitted convoluted function of a second-order reaction model that occurred near time zero and was plotted as a function of wavelength in Figure 2b. Obviously, the electron injection in AATA is much larger than the ATA. One of the reasons for the higher electron injection efficiencies of AATA, especially at the upper branch, is the energy distribution of hot electrons because of the blueshift of the absorption peak of the upper branch in AATA structure. Additionally, Au-Ag NPs present interband energy threshold shift to a more negative potential regarding to Au NPs from ultraviolet photoelectron spectroscopy measurement. Both the blueshift absorption and the interband energy threshold negatively shift contribute to a part of the higher hot-electron injection efficiency in AATA. In addition, the near-field intensity of AATA was calculated by FDTD simulation, which is three times higher than that for ATA. This significant near-field enhancement under ultrastrong modal coupling based on the larger oscillation strength of Au-Ag alloy NPs also contributes to efficient electron injection from the metal NPs to TiO_2.

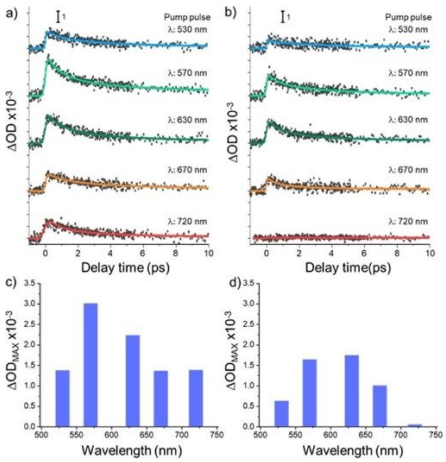

Figure 2. (a), (b) Transient profile of AATA and ATA, respectively. (c), (d) The maximum ΔOD as a function of pump wavelength of AATA and ATA, respectively.

III. Electron-electron, electron-phonon dynamics of Au-NPs under strong coupling

The ultrafast dynamics of photo-excited electrons, such as the electron-electron scattering, electron-phonon scattering, and the interfacial charge transfer at Au-NPs/TiO_2 interface should be essential factors for the efficient energy conversion in this strong coupling system. Here, we explored the dynamics of photo-excited electrons in Au NPs and the charge transfer at the interface of Au-NPs/TiO_2 under strong coupling conditions using femtosecond transient spectroscopy. Substrates consist of TiO_2 thin film (~ 170 nm) on Au film to form a FP cavity and an Au-NPs layer was inlaid inside the TiO_2 thin film. The inlaid position of the Au-NPs was designed to tune the coupling conditions between the LSPR of Au-NPs and the cavity resonance of TiO_2/Au-film. Generally, besides the resonant frequencies overlap between the LSPR and the cavity resonance, the local electric field intensity also determines the strong coupling strength. Because the electric field distribution in the cavity varies as a function of its location, the strong coupling between LSPR and cavity resonance could be controlled by varying the position of Au-NPs layers inside the TiO_2 thin film.

Femtosecond transient reflection measurements were performed to study the dynamics of the electron transfer from Au-NPs to the conduction band of TiO_2 using a visible pump and IR probe at 2000 nm. The pump fluence was set at a range of 2-4 mJ/cm^2; the probe fluence was set at a range of several μJ/cm^2.

Based on this measurement, we observed the electron transfer efficiency as a function of the strong coupling conditions, as shown in Fig. 3 a-c. Experiment results show that the transient signal intensity strongly relates to its inlaid position, trending to be smaller when approaching the Au-film, Fig. 3d. A minimum valley appears at the Z position around 90-120 nm can be attributed to the weak interaction between LSPR and the cavity because electric field amplitude of the cavity resonance is minimized at Z position around 90-120 nm. However, further experiment is needed to clarify the reason why the transient signal decreases as the Z position decreases. We are now planning to combine the electrical measurement to identify the number of injection electrons to deepen our understanding on the transient measurements.

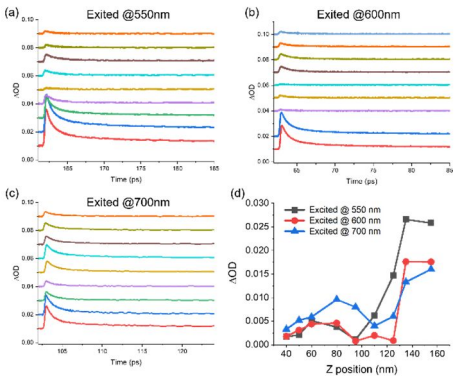

Figure 3. Transient profile of ATA under different excitation wavelengths of (a)550, (b) 600 and (c) 700 nm. (d) Maximum ΔOD near time-zero as a function of Z position.

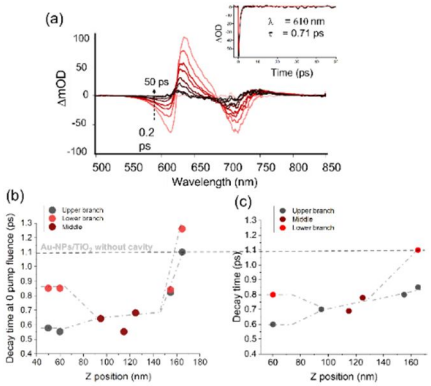

Figure 4. (a) Transient spectrum of ATA with Z position of 60 nm. (b), (c) Decay time at 0 pump fluence of ATA as a function of Z position that excited at 610 and 710 nm, respectively. The dash lines are guide to the eyes.

Besides, transient measurements using a visible pump and white light probe were also carried out to study the dynamics of the electron-electron, electron-phonon coupling of the photo-excited Au-NPs. Fig. 4a shows a typical transient absorption spectrum at various time delay. Based on the transient absorption spectrum, we might extract the lifetime of the photo-excited electron in Au-NPs. Furthermore, we controlled the pump light intensity and measured the lifetime as a function of the pump pulse intensity to derive the lifetime at 0 pump pulse fluence, as shown in Fig. 4b and 4c. The lifetime of lower branch shows a longer lifetime than the upper branch; the lifetime at larger Z positions trends to be longer than the smaller Z positions. A physical model based on the time-dependent electron distribution and two-temperature model is now developing to explain our observations.

It is hopeful to further understand the enhanced photochemical reactions in the modal strong coupling system by exploring the dynamics of the plasmon-induced electron transfer and the electron-electron, electron-phonon coupling after fully analyzing our experiment results, and the understand of the dynamics of plasmon-induced charge carriers from the physical insight will be beneficial for the future development of plasmonic solar energy conversion system.

５．主な発表論文等

〔雑誌論文〕　計8件（うち査読付論文　8件／うち国際共著　3件／うちオープンアクセス　3件）

１．著者名 Cao Yanfeng、Shi Xu、Oshikiri Tomoya、Zu Shuai、Sunaba Yuji、Sasaki Keiji、Misawa Hiroaki	４．巻 57
２．論文標題 Near-field engineering for boosting the photoelectrochemical activity to a modal strong coupling structure	５．発行年 2021年
３．雑誌名 Chemical Communications	６．最初と最後の頁 524～527
掲載論文のDOI（デジタルオブジェクト識別子） 10.1039/D0CC07335K	査読の有無 有
オープンアクセス オープンアクセスとしている（また、その予定である）	国際共著 －

１．著者名 Wang Yaguang、Shi Xu、Oshikiri Tomoya、Zu Shuai、Ueno Kosei、Misawa Hiroaki	４．巻 12
２．論文標題 Plasmon-induced electron injection into the large negative potential conduction band of Ga2O3 for coupling with water oxidation	５．発行年 2020年
３．雑誌名 Nanoscale	６．最初と最後の頁 22674～22679
掲載論文のDOI（デジタルオブジェクト識別子） 10.1039/D0NR06319C	査読の有無 有
オープンアクセス オープンアクセスとしている（また、その予定である）	国際共著 －

１．著者名 Shi Xu、Li Xiaowei、Toda Takahiro、Oshikiri Tomoya、Ueno Kosei、Suzuki Kentaro、Murakoshi Kei、Misawa Hiroaki	４．巻 3
２．論文標題 Interfacial Structure-Modulated Plasmon-Induced Water Oxidation on Strontium Titanate	５．発行年 2020年
３．雑誌名 ACS Applied Energy Materials	６．最初と最後の頁 5675～5683
掲載論文のDOI（デジタルオブジェクト識別子） 10.1021/acsaem.0c00648	査読の有無 有
オープンアクセス オープンアクセスとしている（また、その予定である）	国際共著 －

１．著者名 Gomez Daniel E.、Shi Xu、Oshikiri Tomoya、Roberts Ann、Misawa Hiroaki	４．巻 21
２．論文標題 Near-Perfect Absorption of Light by Coherent Plasmon-Exciton States	５．発行年 2021年
３．雑誌名 Nano Letters	６．最初と最後の頁 3864～3870
掲載論文のDOI（デジタルオブジェクト識別子） 10.1021/acs.nanolett.1c00389	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

1．著者名 Luo Yuan、Chu Cheng Hung、Vyas Sunil、Kuo Hsin Yu、Chia Yu Hsin、Chen Mu Ku、Shi Xu、Tanaka Takuo、Misawa Hiroaki、Huang Yi-You、Tsai Din Ping	4．巻 21
2．論文標題 Varifocal Metalens for Optical Sectioning Fluorescence Microscopy	5．発行年 2021年
3．雑誌名 Nano Letters	6．最初と最後の頁 5133～5142
掲載論文のDOI（デジタルオブジェクト識別子） 10.1021/acs.nanolett.1c01114	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

1．著者名 Suganami Yoshiki、Oshikiri Tomoya、Shi Xu、Misawa Hiroaki	4．巻 60
2．論文標題 Water Oxidation under Modal Ultrastrong Coupling Conditions Using Gold/Silver Alloy Nanoparticles and Fabry?P?rot Nanocavities	5．発行年 2021年
3．雑誌名 Angewandte Chemie International Edition	6．最初と最後の頁 18438～18442
掲載論文のDOI（デジタルオブジェクト識別子） 10.1002/anie.202103445	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 －

1．著者名 Zang Xiaoqian、Shi Xu、Oshikiri Tomoya、Ueno Kosei、Sunaba Yuji、Sasaki Keiji、Misawa Hiroaki	4．巻 125
2．論文標題 Highly Sensitive and Spatially Homogeneous Surface-Enhanced Raman Scattering Substrate under Plasmon?Nanocavity Coupling	5．発行年 2021年
3．雑誌名 The Journal of Physical Chemistry C	6．最初と最後の頁 19880～19886
掲載論文のDOI（デジタルオブジェクト識別子） 10.1021/acs.jpcc.1c05788	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 －

1．著者名 Yan Qiuchen、Cao En、Sun Quan、Ao Yutian、Hu Xiaoyong、Shi Xu、Gong Qihuang、Misawa Hiroaki	4．巻 21
2．論文標題 Near-Field Imaging and Time-Domain Dynamics of Photonic Topological Edge States in Plasmonic Nanochains	5．発行年 2021年
3．雑誌名 Nano Letters	6．最初と最後の頁 9270～9278
掲載論文のDOI（デジタルオブジェクト識別子） 10.1021/acs.nanolett.1c03324	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

〔学会発表〕　計2件（うち招待講演　0件／うち国際学会　1件）

1．発表者名 Xu Shi, Tomoya Oshikiri, Hiroaki Misawa
2．発表標題 Ultrafast Electron Dynamics of Plasmonic Nanoparticles under Modal Strong Coupling Conditions
3．学会等名 The 102nd CSJ annual meeting
4．発表年 2021年～2022年

1．発表者名 Xu Shi, Guiyin He, Tomoya Oshikiri, Hiroaki Misawa
2．発表標題 Dynamics of electron transfer between Au nanoparticle and titanium dioxide under modal strong coupling conditions
3．学会等名 Pacifichem 2021（国際学会）
4．発表年 2021年～2022年

〔図書〕　計1件

1．著者名 Xu Shi, Hiroaki Misawa	4．発行年 2021年
2．出版社 Springer	5．総ページ数 169
3．書名 Progress in Nanophotonics 6	

〔産業財産権〕

〔その他〕

―

6．研究組織

	氏名 （ローマ字氏名） （研究者番号）	所属研究機関・部局・職 （機関番号）	備考

7．科研費を使用して開催した国際研究集会

〔国際研究集会〕　計0件

８．本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関