アカデミックプログラム［Ｂ講演］ | 08. 触媒：口頭Ｂ講演

2024年3月20日(水) 13:00 ~ 15:30 A1458(14号館 [5階] 1458)

[A1458-3pm] 08. 触媒

座長：影島 洋介、小寺 正徳

英語
13:00 ~ 13:20
[A1458-3pm-01]
窒素含有炭素材料の光触媒作用を利用した抗菌特性評価

○川口 雅之[1]、三宅 一樹[1]、村上 飛龍[1]、齊藤 安貴子[1]、森田 成昭[1] (1. 大阪電気通信大学)

英語
13:20 ~ 13:40
[A1458-3pm-02]
大面積化に向けた反応器による過酸化水素の人工光合成

○潘 振華[1]、片山 建二[1]、Shu Hu[2]、Chiheng Chu[3] (1. 中央大学、2. イェール大学、3. 浙江大学)

日本語
13:40 ~ 14:00
[A1458-3pm-03]
メタン存在下における光触媒水分解反応の特異的な促進

○斎藤 晃[1]、佐藤 宏祐[1]、東 泰佑[1]、杉本 敏樹[1,2] (1. 分子科学研究所、2. 総合研究大学院大学)

英語
14:00 ~ 14:20
[A1458-3pm-04]
アルカン酸化と水素生成を同時駆動する光レドックスカスケード触媒系の構築

○小林 厚志[1] (1. 北海道大学)

14:20 ~ 14:30
休憩

英語
14:30 ~ 14:50
[A1458-3pm-05]
非混和性二相溶液間を自発的に移動する電子伝達体により水の酸化と統合された新規光触媒反応系の開発

○板垣 廉[1,2]、中田 明伸[1,3]、鈴木 肇[1]、冨田 修[1]、張 浩徹[4]、阿部 竜[1] (1. 京大院工、2. 学振DC1、3. JSTさきがけ、4. 中大理工)

英語
14:50 ~ 15:10
[A1458-3pm-06]
Scalable and efficient water-splitting photocatalyst sheets based on carbon-based conductors

○Chen Gu[1], Yi-Wen Ma[1], Tsuyoshi Takata[1], Takashi Hisatomi[1], Yuta Nishina[3], Nobuyuki Zettsu[1], Kazunari Domen[1,2] (1. Shinshu University, 2. The University of Tokyo, 3. Okayama University)

英語
15:10 ~ 15:30
[A1458-3pm-07]

Development of charge carrier-selective heterodyne transient grating spectroscopic technique and its application in the distinction of surface trap states in hematite

〇Woon Yong Sohn[1] (1. Chungbuk National University)

Antimicrobial property evaluation using photocatalytic action of carbonaceous materials containing nitrogen

([1]*Faculty of Engineering, Osaka Electro-Communication University*) ○ Masayuki Kawaguchi,[1] Kazuki Miyake,[1] Hiryu Murakami,[1] Akiko Saito,[1] Shigeaki Morita[1]

Keywords: Carbonaceous Materials Containing Nitrogen; Photocatalytic Properties; Antimicrobial Properties; Visible Light Irradiation; Reaction Mechanism

Photocatalysts such as titanium dioxide (TiO_2) and graphitic carbon nitride (g-C_3N_4) have been studied to purify polluted water and air and to electrolyze water at low voltage.[1] Among the photocatalysts, materials with antimicrobial properties under visible light irradiation have attracted attention in recent years in order to protect people's living environment from various viruses. We previously prepared carbonaceous materials containing nitrogen (called "C/N materials" in this presentation) and investigated their application to capacitors[2,3] and photocatalysts.[4] In this presentation, we report antimicrobial property evaluation using photocatalytic action of the C/N materials with the irradiation of visible light.

C/N materials having compositions C_2N,[2] C_3N[3] and $C_6N_9H_3$[5] were prepared by thermal decomposition of organic compounds. Yeast was applied onto the C/N material and the antimicrobial properties were evaluated by the colony forming unit (CFU) counting after irradiation with visible light. Comparisons were also made with cases where titanium oxide, which has photocatalytic properties, was used and cases where no light irradiation was used. Figure 1 shows an example of the CFU results of C_2N compared with the case of TiO_2. Almost no colonies were observed on the agar medium treated with the C/N materials (Fig. 1-a), indicating antimicrobial activity due to photocatalytic action caused by visible light irradiation.

We have measured UV-visible spectra of the C/N materials to investigate the mechanism of photocatalytic action of the materials and will discuss it at the presentation.

(a) (b) (c)

Figure 1. The CFU results of (a) C_2N with irradiation of visible light, (b) C_2N without irradiation of light, (c) TiO_2 with irradiation of visible light.

The authors would like to thank Nippon Soda Co., Ltd for providing the precursors of C/N materials and supporting this research.

1) W. Iqbal, *et. al*, *Catal. Sci. Technol.* **2018**, *8*, 4576. 2) M. Kawaguchi, T. Yamanaka, Y. Hayashi, H. Oda, *J. Electrochem. Soc.* **2010**, *157*, A35. 3) M. Kawaguchi, A. Itoh, S. Yagi, H. Oda, *J. Power Sources* **2007**, *172*, 481. 4) M. Kawaguchi, Y. Ishida, *CARBON2013*, Rio de Janeiro, Brazil, **2013** Abstract No. 113. 5) M. Kawaguchi, K. Nozaki, *Chem. Mater.* **1995**, *7*, 257.

Photosynthesis of hydrogen peroxide by a scaled-up reactor

([1]*Department of Applied Chemistry, Chuo University*, [2]*Department of Chemical and Environmental Engineering, Yale University*, [3]*Faculty of Agriculture, Life, and Environmental Sciences, Zhejiang University*) ○Zhenhua Pan,[1] Kenji Katayama,[1] Shu Hu,[2] Chiheng Chu[3]

Keywords: *Photocatalyst, Hydrogen peroxide, Panel reactor*

Particulate photocatalysis (PC) has been widely investigated for environmentally friendly production of hydrogen peroxide (H_2O_2).[1] Yet, most existing PC systems for H_2O_2 generation are based on powder suspensions, which are not applicable to large-scale H_2O_2 synthesis.[2, 3] Consequently, the development of a scalable PC system has remained a formidable obstacle, impeding the practical implementation of H_2O_2 photosynthesis.

In this study, we report a flexible photocatalyst sheet based on visible-light-responsive $BiVO_4$ ($\lambda < 520$ nm) for the scalable production of H_2O_2 from water and oxygen. We successfully upscaled the production by deploying $BiVO_4$ photocatalyst sheets in a 1-m^2-flow-by reactor in a 4×4-panels array (Figure 1). The H_2O_2 synthesis on this panel reactor exhibited durability, with no loss of activity over one -month field test.

To illustrate the practical utility of the photosynthesized H_2O_2, we applied it to disinfection, achieving over 99.9% inactivation of a coronavirus surrogate within 60 minutes. Furthermore, a techno-economic analysis demonstrates the economic viability of H_2O_2 photosynthesis using the panel reactor. Our findings underscore the scalability and economic feasibility of photocatalytic H_2O_2 generation, enhancing its readiness for practical applications.

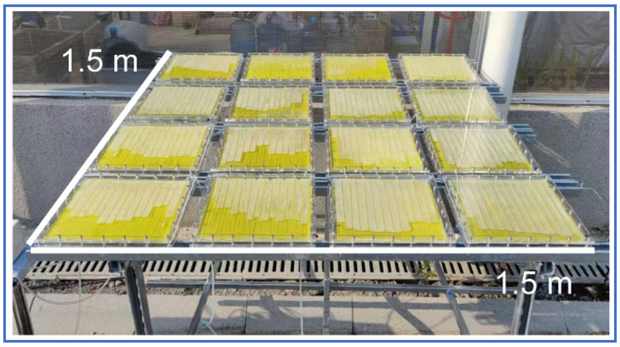


Figure 1 Digital photo of the 1-m^2 arrayed panel flow reactor.

1. Y. Xue, Y. Wang, Z. Pan and K. Sayama, *Angew. Chem. Int. Ed.* , **2020**, 60, 1433-7851.
2. T. Liu, Z. Pan, K. Kato, J. J. M. Vequizo, R. Yanagi, X. Zheng, W. Yu, A. Yamakata, B. Chen, S. Hu, K. Katayama and C. Chu, *Nat. Commun.*, **2022**, 13, 7783.
3. T. Liu, Z. Pan, J. J. M. Vequizo, K. Kato, B. Wu, A. Yamakata, K. Katayama, B. Chen, C. Chu and K. Domen, *Nat. Commun.*, **2022**, 13, 1034.

メタン存在下における光触媒水分解反応の特異的な促進

(分子研[1]・総研大[2]) ○斎藤 晃[1]・佐藤 宏祐[1]・東 泰佑[1]・杉本 敏樹[1, 2]

Accelerating Photocatalytic Water Splitting by Methane Molecules

([1]*Department of Materials Molecular Science*, *Institute for Molecular Science*, [2]*Graduate Institute for Advanced Studies, SOKENDAI*) ○Hikaru Saito,[1] Hiromasa Sato,[1] Taisuke Higashi,[1] Toshiki Sugimoto[1, 2]

Interfacial water systems on solid surfaces are a crucial energy conversion platform in the field of catalysis[1)]. However, it remains a challenge to control reactivity of interfacial water species for enhancing catalytic performance. Here, we report that incorporation of methane in the interfacial water systems on the Pt/Ga_2O_3 surfaces[2)] dramatically accelerate the photocatalytic water splitting ($2H_2O \rightarrow 2H_2+O_2$). By infrared absorption spectroscopy, we revealed that the structure of the hydrogen bond network of the interfacial water was reconstructed by methane. Because hydrogen bonding has significant impact on the hole transfer process at catalyst–water interfaces[3)], this reconstruction of the hydrogen bond network indicates the increase in the reactive interfacial water species that easily accept photogenerated holes. Thus, our study demonstrates the critical impacts of the interfacial hydrogen bond network on the water splitting activity. Notably, the enhancement mechanism induced by methane is stark contrast to the conventional promoter molecules such as methanol as a hole scavenger[4)]. Therefore, our study also provides a novel method for enhancing photocatalytic performance.

Keywords : Water Splitting; Methane; Photocatalysis; Interfacial Hydrogen Bond; Infrared Absorption Spectroscopy

固体と水分子の界面は光触媒や電極触媒をはじめとした重要な反応場である[1)]。そのため、触媒性能の向上のためには界面水分子の反応性制御が鍵となる。本研究では、水とメタンが共存する Pt/Ga_2O_3 光触媒系[2)]において水分解反応($2H_2O \rightarrow 2H_2+O_2$)の活性が劇的に向上することを見出した。赤外吸収分光法によってメタンによる光触媒表面の吸着水への影響を調べた結果、メタンが存在すると吸着水の O–H 伸縮振動ピークが特異的に波数シフトしており、水素結合環境が変調されていることが明らかとなった。吸着水の水素結合状態は光触媒表面からの電荷移動と密接に関わっている[3)]ことから、メタン導入によって光誘起正孔を受け取りやすい吸着水の増加が活性向上に寄与していると考えられる。このように、本研究では吸着水の水素結合環境がマクロな触媒性能と密接に関わっていることを実証した。また、吸着水の水素結合環境を変調によって水分子を活性化させるというメタンの役割はメタノールに代表される正孔犠牲剤による水素生成の促進[4)]とは全く異なり、新たな活性向上のコンセプトを提供するものである。

本研究は JST さきがけ[JPMJPR16S7]、JST-CREST[JPMCR22L2]、JSPS 科研費[JP22J1039; JP22H00296]、自然科学研究機構分野融合型共同研究事業[01112104]、環境省「地域資源循環を通じた脱炭素化に向けた革新的触媒技術の開発・実証事業」の支援の下で実施された。

1) M. Yamauchi, H. Saito, T. Sugimoto, S. Mori, S. Saito, *Coord. Chem. Rev.* **2022**, *472*, 214773.
2) H. Sato, A. Ishikawa, H. Saito, T. Higashi, K. Takeyasu, T. Sugimoto, *Commun. Chem.* **2023**, *6*, 8; H. Saito, H. Sato, T. Higashi, T. Sugimoto, *Angew. Chem. Int. Ed.* **2023**, *62*, e202306058; F. Amano, A. Ishikawa, H. Sato, C. Akamoto, S. P. Singh, S. Yamazoe, T. Sugimoto, *Catal. Today* **2024**, *426*, 114375.
3) K. Shirai, G. Fazio, T. Sugimoto, D. Selli, L. Ferraro, K. Watanabe, M. Haruta, B. Ohtani, H. Kurata, C. D. Valentin, Y. Matsumoto, *J. Am. Chem. Soc.* **2018**, *140*, 1415–1422.
4) V. Kumaravel, S. Mathew, J. Bartlett, S. C. Pillai, *Appl. Catal. B* **2019**, *244*, 1021–1064.

Development of photoredox cascade catalyst for alkane-oxidation and solar hydrogen production

(*Faculty of Science, Hokkaido University*) ○Atsushi Kobayashi

Keywords: Photocatalyst; Hydrogen production; Alkane oxidation; Photosensitization; Electron mediation

Solar water splitting reaction has been attracted considerable attention as a means of building a sustainable *hydrogen* society. However, water splitting producing hydrogen and oxygen cannot provide valuable organic chemicals. To overcome this issue, we have constructed a photo-redox cascade catalyst (PRCC) consisting of Ru(II) dual-dye sensitized Pt-TiO_2 photocatalyst that generates hydrogen photocatalytically not only from redox-reversible electron donors[1] but also hydroxyl group-containing biomass.[2] In this work, to extend this strategy to oxidative transformation of various organic substrates, a new PRCC system was designed by using *N*-hydroxyphthalimide (NHPI) as an hydrogen-atom transfer (HAT) catalyst which generates carbon radicals while extracting hydrogen atoms from less reactive alkanes (Figure 1). H_2 successfully evolved in the 5 mM NHPI solution and the estimated turn over number per Ru(II) dye (PS TON) over 97 indicates the photocatalytic H_2 production as a result of NHPI oxidation. The activity was remarkably enhanced by increasing the NHPI concentration to 30 mM and addition of 0.1 M ethylbenzene (EB) or toluene (Tol), suggesting the HAT reaction from EB/Tol by phthalimido-*N*-oxyl (PINO) radical generated by the proton-coupled one-electron oxidation of NHPI. Further, a large isotope effect was observed by replacing from Tol to the deuterated one (Tol-d_8), suggesting that the HAT reaction by PINO is the rate-limiting step in this PRCC system. Details will be discussed.

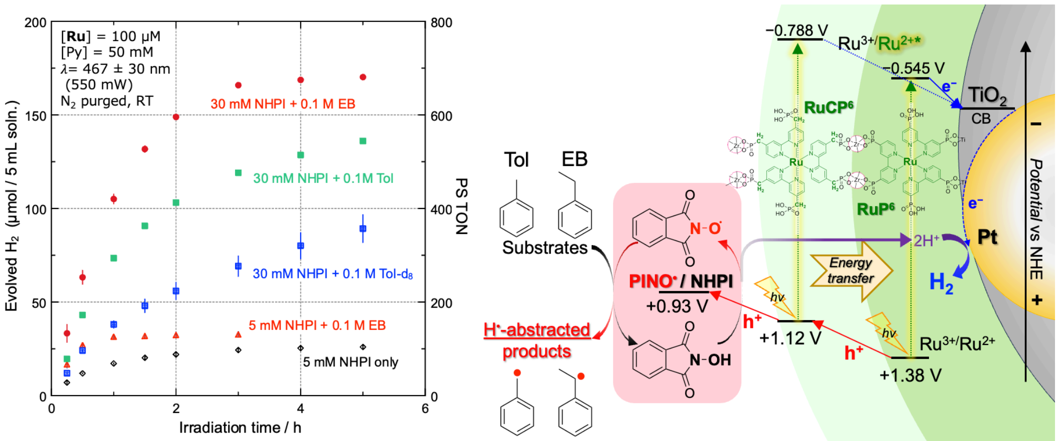


Figure 1. (left) Photocatalytic H_2 production and (right) schematic energy diagram of PRCC coupled with HAT reaction from EB/Tol.

1) N. Yoshimura, M. Yoshida, A. Kobayashi, *J. Am. Chem. Soc.* **2023**, *145*, 6035.
2) A. Kobayashi, *Angew. Chem. Int. Ed.* **2023**, *62*, e202313014.

Photocatalytic System Integrated with Water Oxidation by a Liquid-Liquid Phase-Migrating Electron Mediator

([1]*Grad. Sch. of Eng., Kyoto Univ.*, [2]*JSPS Research Fellow DC1*, [3]*PRESTO/JST*, [4]*Fac. of Sci. Eng., Chuo Univ.*) ○Ren Itagaki,[1,2] Akinobu Nakada,[1,3] Hajime Suzuki,[1] Osamu Tomita,[1] Ho-Chol Chang,[4] Ryu Abe[1]

Keywords: Photocatalyst; Separation of Reaction Fields; Electron Mediator; Photoinduced Electron Transfer; Phase Migration

Photocatalytic molecular conversions giving value added product are of great interest. Ideally, it is desirable to utilize water as an electron source for these molecular conversion reactions. Artificial Z-scheme reaction system composed of two-different photocatalysts is a potential strategy to connect various reductive molecular conversions with water oxidation, as demonstrated in overall water splitting.[1] However, it is basically difficult to perform organic molecular conversions integrated with water oxidation due to low solubility of organic reactants in water. In this study, we develop a stepwise Z-scheme photocatalytic system utilizing a water/1,2-dichloroethane (DCE) biphasic solution with a ferrocenium/ferrocene (Fc^+/Fc) phase-migrating electron mediator to connect reductive coupling of benzyl bromide in DCE phase and water oxidation (Figure 1a).

In an aqueous solution, (Fe,Ru)O_x-modified Bi_4TaO_8Cl photocatalyzed water oxidation with a Fc^+ electron acceptor, generating O_2 and Fc (Figure 1b). On the other side, Fc can be utilized as an electron donor for photocatalytic reduction of benzyl bromide (Bn-Br) with an $[Ir(C6)_2(dmb)](PF_6)$ photoredox catalyst in a DCE phase (Figure 1c). Importantly, the latter reaction regenerated Fc^+ which is spontaneously going back to aqueous phase.[2] Eventually, the Fc^+/Fc redox couple transports an electron by the photoredox induced liquid-liquid phase migration to achieve photoreduction of Bn-Br coupled with water oxidation.

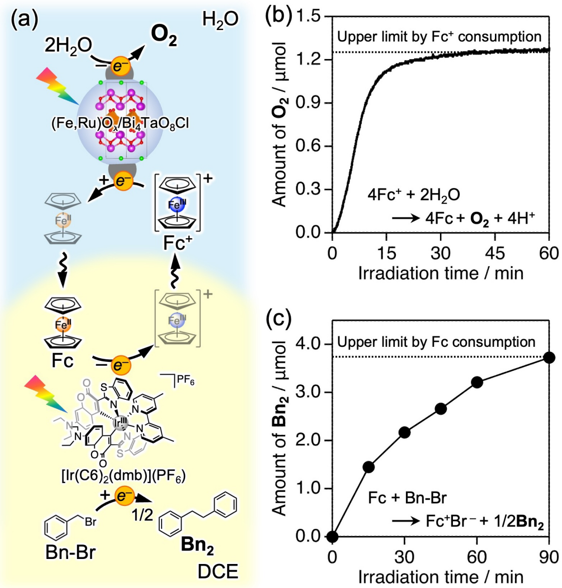


Figure 1. (a) Conceptual scheme of a biphasic photocatalysis. Time course of half reactions of (b) O_2 evolution using (Fe,Ru)O_x/Bi_4TaO_8Cl and Fc^+ electron acceptor and (c) dibenzyl (Bn_2) formation using $[Ir(C6)_2(dmb)](PF_6)$ and Fc electron donor.

1) Abe, R.; Tang, J. *et al. Chem. Rev.* **2018**, *118*, 5201.
2) Itagaki, R.; Takizawa, S.; Chang, H.-C.; Nakada, A. *Dalton Trans.* **2022**, *51*, 9467.

Scalable and efficient water-splitting photocatalyst sheets based on carbon conductors

([1]*Research Initiative for Supra-Materials, Shinshu University,* [2]*National Institute of Advanced Industrial Science and Technology,* [3]*Institute for Engineering Innovation, The University of Tokyo,* [4]*Department of Materials Chemistry, Shinshu University,* [5]*Graduate School of Natural Science and Technology, Okayama University,* [6]*Office of University Professors, The University of Tokyo)* ○Chen Gu[1], Tsuyoshi Takata[1], Yi-Wen Ma[1], Miseki Yugo[2], Li-Hua Lin[1], Hiroshi Nishiyama[3], Mamiko Nakabayashi[3], Nobuyuki Zettsu[4], Yuta Nishina[5], Takashi Hisatomi[1] and Kazunari Domen[1,6]

Keywords: *Oxysulfide, electron transfer, Photocatalyst sheet, Visible light*

Particulate photocatalyst sheet is a structure that can potentially realize scalable and economical solar-to-hydrogen energy conversion via overall water splitting (OWS). In our previous study, a 100 m^2-scale photocatalyst sheet/panel system based on Al-doped $SrTiO_3$ (STO:Al) was developed.[1] However, the STH is still below the level (5% or higher) targeted for practical and scaled industrial applications. This gap is difficult to overcome with STO:Al because it cannot utilize visible light which accounts for the majority of solar energy.[2]

A two-step excitation system, also known as a Z-scheme system, is an approach to utilize long-wavelength visible light efficiently in OWS.[3] However, the size of most efficient Z-scheme photocatalyst sheets is typically 10 cm^2 or less, which is far below practical and industrial requirements. The size is limited by the need for an elaborate and complicated particle transfer process that involves the evaporation of conductive materials and the peeling and transfer of the composite using an adhesive film during sheet formation.

In this work, we demonstrate efficient Z-scheme OWS using scalable particulate photocatalyst sheets composed of cocatalyst-loaded $Sm_2Ti_2O_5S_2$ and $BiVO_4$ combined with carbon material, where the use of vacuum processes or organic media during the sheet fabrication and Z-scheme OWS was ruled out. The carbon material-based photocatalyst sheets exhibited higher activity in OWS than the conventional sheet using Au as the electron conductor, and the problems of back reaction, stability, and pressure dependence were largely solved by refining the surface modification procedure.

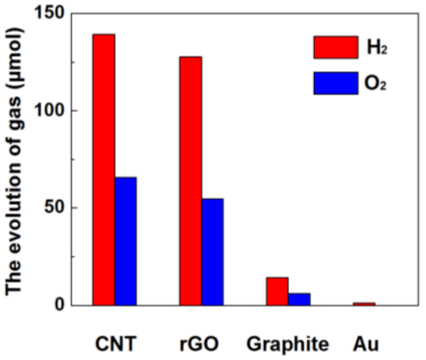


Figure 1. The ZOWS activity of sheets with different electron mediators

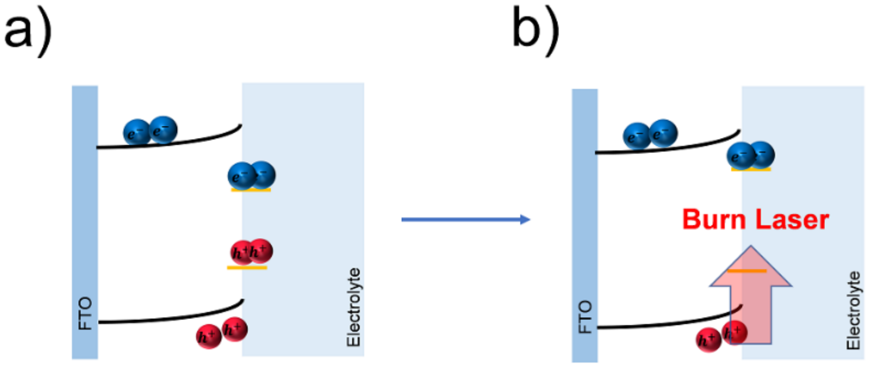
1) Nishiyama *et al.*, *Nature* **2021**, *598*, 304. 2) Takata *et al.*, *Nature* **2020**, *581*, 411. 3) Nandy *et al., Joule* **2023**, 7, 1641–1651.

Development of Charge Carrier-Selective Heterodyne Transient Grating Spectroscopic Technique and Its Application in the Distinction of Surface Trap States in Hematite

(*Department of Chemistry, Chungbuk National University*) Young Hyun Kim Yu Gyeong Bae and ○Woon Yong Sohn

Keywords: Hematite; Photo-electrochemical water splitting; Trap state; Time-resolved spectroscopy

We newly developed a spectroscopic technique which is named charge carrier-selective heterodyne transient grating (CS-HD-TG) method for the distinction of the surface trap states existing in the photocatalysts and photovoltaic materials. For the measurment of the CS-HD-TG response, a burn laser was employed which could induce the depletion of the photo-excited charge carriers trapped in the surface states. In this study, the population of the photo-excited holes in hematite could be depleted by the excitation of the electrons originating from the valence band when the wavelength of the burn laser was resonant as shown in the Scheme. In addition, as a case study, we measured the CS-HD-TG responses of hematite under bias condition with and without the burn laser and revealed that two distinct trap states co-exist at the surface in the hematite film and only one of them could act as the reaction intermediate for oxygen evolution reaction (OER), which is consistent with former studies.[1-3]



Schematic illustrations of photo-generated charge carriers in a photoanode a) without burn laser and b) with burn laser.

1) Zandi, O.; Hamann, T. W., *J. Phys. Chem. Lett.* **2014**, 5, 1522. 2) Palmolahti, L.; Ali-Löytty, H.; Khan, R.; Saari, J.; Tkachenko, N. V.; Valden, M., *J. Phys. Chem. C* **2020**, 124, 13094. 3) Pan, Z.; Chen, S.; Katayama, K., *J. Phys. Chem. C* **2023**, 127, 3904.