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　５ 年　 ５ 月 １５ 日現在

機関番号：１３１０１
研究種目：基盤研究(C)（一般）
研究期間：2020～2022
課題番号：２０Ｋ０５６８４

研究課題名（和文）Understanding and development of highly efficient water splitting catalysts with core-shell structures for solar-hydrogen production

研究課題名（英文）Understanding and development of highly efficient water splitting catalysts with core-shell structures for solar-hydrogen production

研究代表者

ＺＡＨＲＡＮ　ＺＡＫＩ・ＮＡＢＥＩＨ・ＡＨＭＥＤ（Zahran, Zaki Nabeih Ahmed）

新潟大学・自然科学系・特任准教授

研究者番号：６０８２４６４６

交付決定額（研究期間全体）：（直接経費）　　3,300,000円

研究成果の概要（和文）：ニッケルフォーム（NF）上のFeNiWOx フィルムを開発し、η10 = 167 mV という現在報告されている中でも最低の過電圧を達成しました。また、NiSx/C3N4触媒を開発し、72mVという最低の過電圧で電極触媒水分解を実証しました。白金膜を開発し、より効率的で安定したHER性能を実証しました。 最後に、二重接合GaAs/GaAsの光起電力（PV）デバイスをカスタマイズして、FeNiWOx/NFアノードとPt/NFカソードを備えた効率的な電解槽の電流密度-電圧特性と一致させ、13.9%の高い太陽水素効率（STH）を備えた効率的で安定した太陽光水分解が実証されました。

研究成果の学術的意義や社会的意義
Highly efficient and stable water oxidation catalysts with world wide water oxidation performances were developed that leaded to developing highly efficient carbon-free hydrogen production system using renewable energy, aiming at realizing a low-carbon society that does not depend on fossil fuels.

研究成果の概要（英文）：We developed a ternary FeNiWOx film on a nickel foam (NF), attaining the lowest overpotentials of η10 = 167 mV and at least 100 h stability in water oxidation, which compare advantageously with only a few state-of-the-art OER anodes with excellent η10 < 200 mV.We also developed a NiSx/C3N4 catalyst, demonstrating electrocatalytic water splitting at the lowest overall overpotential of 72 mV using the NiSx/C3N4 anode. We developed a platinum (Pt(w-MeIm)) film, demonstrated a more efficient and stable HER performance.Also, A NiOx film prepared from the NiSO4 precursor showed efficient water oxidation properties. Finally, a photovoltaic device of double-junction GaAs/GaAs was customized to match up with the electrolyzer with a FeNiWOx/nickel foam (NF) anode and a Pt/NF cathode. Efficient and stable (one-month) solar water splitting with a high solar-to-hydrogen efficiency (STH) of 13.9% was demonstrated under 1 sun irradiation.

研究分野：Green hydrogen production

キーワード：Green hydrogen　water oxidation　electrocatalysts

１．研究開始当初の背景

Hydrogen is currently considered as the future carbon-free fuel to replace the current fossil one (*Nature 414*, 332–337 , **2001**). However, its sustainable production at a reasonable cost is one of the most crucial challenges in science, technology, and industry. The solar driven water splitting (**Fig. 1**) *via* hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) at a cathode and an anode, respectively is a promising system for sustainable hydrogen production (*Adv. Energy Mater.* 1900954, **2019**). The key task for realizing such a system is developing highly efficient earth abundant catalysts for both HER and OER (*Science 345*, 1593–1596 , **2014**). We developed an efficient $FeNiWO_n$ OER anode that showed a high OER activity and durability, generating a 10 mA/cm^2 current density at only 167 mV overpotential (η^{10}_{OER} = 167 mV), overcoming the performance of the state of the art $NiFeCuO_n$ anode (η^{10}_{OER} = 180 mV, *Nat. Commun.*, *9*, 381, **2018**). However, the mechanism and important factors for the high OER activity has remained open, and we require further improved OER activity of the anode for highly efficient solar-driven hydrogen production system. Moreover, Pt-based electrodes are the state-of-the-art HER cathodes, but the scarcity of Pt hinders its commercial applications. One of the most important issues in the related field is to develop HER cathodes based on earth abundant elements.

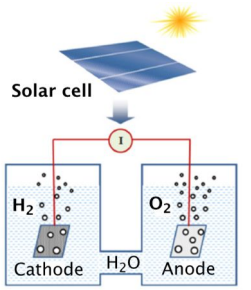


Fig. 1 Solar cell–driven Electrolyzer for H_2 production.

２．研究の目的

In this study, we will work on the following goals, aiming to establish future carbon-free hydrogen production technology at low cost.

1) Understanding the role of W in enhancing the OER performance of $FeNiWO_n$. So far, we reached η^{10}_{OER} = 167 mV using $FeNiWO_n$. We presume that W^{6+} sites in $FeNiWO_n$ adsorb more OH^- /H_2O groups due to its d^0 low spin-state with more outmost vacant orbitals, providing the optimal adsorption energies for OER intermediates to facilitate the O-O bond formation. We will verify this presumption and investigate the active species (Fe, Ni, W, or combination of them) responsible for the catalysis to develop more efficient catalysts.

2) Improving OER anodes of $FeNiWO_n$ and discovering more efficient anodes. In this plan we also aim to further improving η^{10}_{OER} to reach 130 mV or less. One promising approach for further enhancing the OER of $FeNiWO_n$ is fabrication it as a core-shell structure (**Fig. 2**). The core comprises $FeNiWX_n$ (X = N, P, S, Se, and Te) and the shell comprises $FeNiWO_n$ that is formed by partial oxidation of X (X = N, P, S, Se, and Te) into O. The core provides a high conductivity medium for the electron flow from the shell to nickel foam (NF) as a current corrector, enhancing its OER performance.

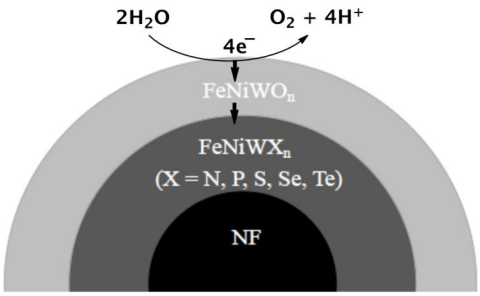


Fig. 2. Proposed core–shell structure of OER $FeNiWX_n$ catalysts.

3) Developing earth abundant HER cathodes of $FeNiWX_n$. Most of the developed earth abundant HER catalysts showed η^{10}_{HER} > 100 mV so far. In this plan, we aim to reach η^{10}_{HER} < 50 mV. The proposed $FeNiWX_n$ (X = N, P, S, Se, and Te) will also partially reduced to the corresponding metallic structures during the HER, forming a core-shell structure for the electron flow from the NF to the surface, enhancing their HER performance.

4) Developing highly efficient electrochemical systems for overall water splitting. So far, the most developed electrochemical systems showed η^{10}_{cell} > 300. In this plan, we aim η^{10}_{cell} < 200 mV based on the proposed bifunctional $FeNiWX_n$ (X = N, P, S, Se, and Te) catalysts for HER and OER.

5) Developing highly efficient solar-powered water splitting systems. So far, the state-of-the-art cell for solar-powered water splitting achieves ~ 24% of conversion efficiency. However, the precious (IrO_n) anode and Pt cathode are used under concentrated light illumination. In this plan, we aim to develop the high-efficiency solar-powered water splitting system that achieves conversion efficiency > 30% using $FeNiWX_n$ (X = N, P, S, Se, and Te) catalysts.

３．研究の方法

1) **Investigation of the role of W in catalysis.** This work will focus on understanding the active site, its oxidation state, cooperativity among the three FeNiW centers *via* investigation of the catalysis process in non-aqueous media using electrochemical methods coupled with spectroscopic methods. We previously

succeeded in studying the mechanism of water oxidation by Mn and MnCa oxides water oxidation catalysts *ACS Catalysis, 6,* 4470-4476, **2016;** *J. Mater. Chem. A, 5,* 15167-15174, **2017**).

2) Preparation, characterization, and investigation of the OER performance of $FeNiWX_n$ (X = N, P, S, Se, and Te). We have developed a facile and general method for the preparation of mixed metal oxides supported on different electrode materials including nickel foam (NF), fluorine doped tin oxide (FTO) and glassy carbon (*Japanese patent application number: 2019-95465, May 21,* **2019**). We will use this method for the preparation of $FeNiWO_n$@NF as the precursor electrode. We also developed a new method for the preparation of mixed metal sulfides (*Japanese patent application number: 2019-90888, May, 13,* **2019**). The method will be extended to the preparation of $FeNiWX_n$ (X = N, P, S, Se, and Te) from $FeNiWO_n$. The catalysts will be characterized using Raman, SEM, TEM, XRD techniques. Their OER performances will be investigated by the electrochemical techniques coupled with product (O_2) analysis methods such as gas chromatography.

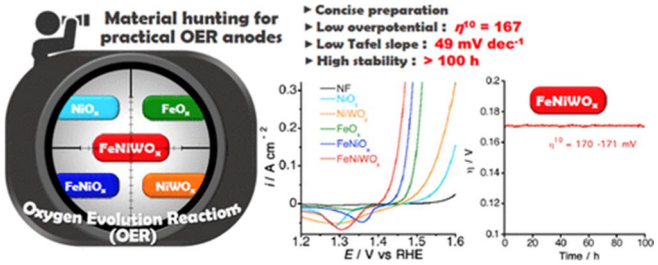
3) Investigation of the HER performances of $FeNiWX_n$ (X = N, P, S, Se, and Te) catalysts. On the basis of the preliminary promising results (**Fig. 3**), the HER performance of the proposed $FeNiWX_n$ will be investigated using the electrochemical methods coupled with products (H_2) analysis on gas chromatography. We will further improve the HER activity of the $FeNiWX_n$ catalysts by controlling the proposed core-shell structures.

4) Construction of electrocatalytic systems for overall water splitting based on the bifunctional $FeNiWX_n$ catalysts for HER and OER. Electrocatalytic systems constructed from the bifunctional $FeNiWX_n$ catalysts for HER and OER will be constructed aiming to develop highly efficient systems for overall water splitting working at $\eta^{10}_{cell} < 200$ mV, which is significantly lower than $\eta^{10}_{cell} > 300$ achieved for the most developed systems under the same conditions so far.

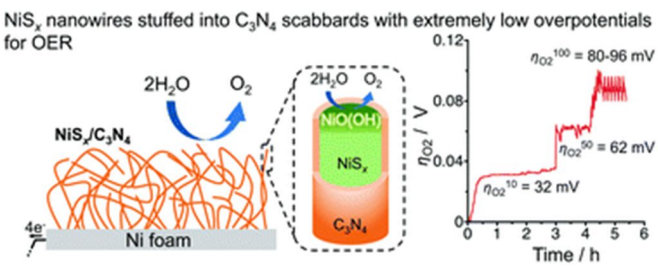
5) Developing high-efficiency solar-powered water splitting systems using solar cells and $FeNiWX_n$ catalysts. The best developed catalysts among the proposed ones will be fabricated in a solar cell / electrolyzer device for solar-powered water splitting (as **Fig. 1**) aiming to reach conversion efficiency of 30 %, which is higher than ~ 24% for the state-of-the-art cell using precious (IrO_n) anode and Pt cathode under concentrated light illumination (*Appl. Phys. Express, 8, 107101,* **2015**).

4．研究成果

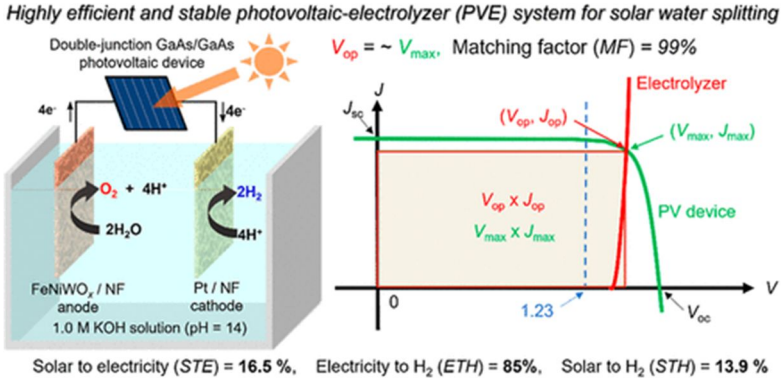
1) We reported a facile and versatile method for the preparation of loading-controllable metal oxide films adhered rigidly on electrode substrates, enabling effectual material hunting for superior OER anodes. This allows us to discover a ternary $FeNiWO_x$ film on a nickel foam (NF), attaining the lowest overpotentials of $\eta^{10} = 167$ (the superscripts represent the attained current densities of 10 mA cm^{-2}) with a Tafel slope of 49 mV dec^{-1} and at least 100 h stability in OER, which compare advantageously with only a few state-of-the-art OER anodes with excellent $\eta^{10} < 200$ mV. The electrochemical data indicate synergistic coupling among ternary metal centers of Ni, Fe, and W to decrease the η value. The OER current is pH dependent for the $FeNiWO_x$ film, showing a non-proton-concerted process in the rate-determining step for OER. This could be explained by coupling of two neighboring lattice $O^{\bullet-}$ radicals to form an O–O bond. The 3d bands of Fe or Ni could be stabilized by the high positive charge on W^{6+} to become close to or penetrate the 2p band of lattice O^{2-}. This not only decreases the highest oxidation energy level for OER but also allows fast electron transfer from the 2p band of O^{2-} to the 3d band in the Fe^{IV} or Ni^{IV} state to form the $O^{\bullet-}$ radicals. These results were published in *ACS Appl. Energy Mater.* 2021, 4, 2, 1410–1420, https://doi.org/10.1021/acsaem.0c02628).



2) We reported the unprecedentedly low overpotential of 32 mV for oxygen evolution attained by the formation of a unique motif of nickel sulfide nanowires stuffed into carbon nitride scabbards (NiS_x/C_3N_4), demonstrating electrocatalytic water splitting at the lowest overall overpotential of 72 mV using the NiS_x/C_3N_4 anode. This motif provides a key to guided thought for the development of efficient catalysts for oxygen evolution.

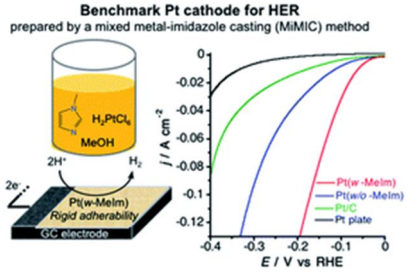


These results were published in ***Energy Environ. Sci.***, 2021,**14**, 5358-5365,

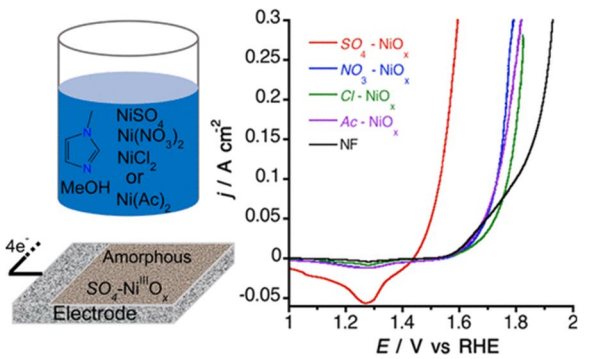


https://doi.org/10.1039/D1EE00509J.

3) We developed a platinum (Pt(*w*-MeIm)) film adhering rigidly on a glassy carbon (GC) substrate prepared by a facile and scalable technique of a mixed metal-imidazole casting (MiMIC) method from a precursor solution containing H_2PtCl_6 in a mixed solvent of methanol/1-methyimidazole (MeIm) (3 : 1). The Pt(*w*-MeIm) film demonstrated a more efficient and stable HER performance compared with a platinum (Pt(*w*/*o*-MeIm)) film deposited from the precursor solution without MeIm due to closely-compacted and well-interconnected Pt nanoparticles for the Pt(*w*-MeIm) film. The Pt(*w*-MeIm) electrode provided an overpotential (η^{10}) = 60 mV at a current density of 10 mA cm^{-2}, Tafel slope = 62 mV dec^{-1} and a mass activity of 0.33 A cm^{-2} mg_{Pt}^{-1} at 100 mV in 1.0 M KOH solution, which are remarkably superior to those of the common Pt-based electrodes of commercially available Pt-loaded carbon (Pt/C) and the Pt plate. The Pt(*w*-MeIm) electrode is of keen interest as a new benchmark cathode for the HER. These results were published in ***Sustainable Energy Fuels***, 2022,**6**, 4265-4274, https://doi.org/10.1039/D2SE00803C.



4) Different NiO_x films adhered rigidly on nickel foam (NF) and fluorine-doped tin oxide substrates were prepared via a mixed metal-imidazole casting method from precursor solutions containing Ni salts with four different counter anions of SO_4^{2-}, NO_3^-, Cl^-, and CH_3COO^- (Ac) in methanol/1-methyimidazole mixed solvents (3:1) followed by calcination at 450 °C. The counter ions of Ni salts are significantly influential on the structure and characteristics of the formed NiO_x films. In the case of the film (SO_4-NiO_x) prepared from the $NiSO_4$ precursor, an amorphous $Ni^{III}O_x$ nanosheet film was formed in contrast to face-centered cubic $Ni^{II}O$ crystalline nanoparticle films formed using the other precursors, under the same conditions. The special characteristics of the SO_4-NiO_x film are caused by the inhibition effect of the SO_4^{2-} ions on the thermochemical formation of $Ni^{II}O$ from the precursor complex, leading to the formation of a $Ni^{III}O_x$ intermediate. The SO_4-NiO_x/NF electrode demonstrated superior OER performance with an overpotential, η^{10} = 228 mV at a current density of 10 mA cm^{-2} in alkaline KOH solutions, which is lower by 145~165 mV than those (η^{10} = 373~393 mV) of the other NiO_x/NF electrodes. The OER performance of the SO_4-NiO_x/NF electrode compares advantageously with that of state-of-the-art Ni-based anodes reported to date. These results were published in *ACS Appl. Energy Mater.* 2022, 5, 2, 1894–1904, https://doi.org/10.1021/acsaem.1c03379.



5) A photovoltaic (PV) device of double-junction GaAs/GaAs was customized to match up with the current density–voltage property of an efficient electrolyzer with a $FeNiWO_x$/nickel foam (NF) anode and a Pt/NF cathode. The customization of the PV device resulted in a perfect matching factor (MF = 99%) in performances between the PV device and the electrolyzer for solar water splitting in a PV-electrolyzer (PVE) system. Efficient and stable (one-month) solar water splitting with a high solar-to-hydrogen efficiency (STH) of 13.9% was demonstrated under 1 sun irradiation conditions. The STH value is comparable with the top values (14.2–16%) in the state-of-art PVE systems. The high STH is based on an obvious progeny of the highest electricity-to-hydrogen efficiency (ETH = 85%) for the electrolyzers among the PVE systems with the non-precious metal-based anode in the electrolyzer and the perfect MF value (99%). This demonstrates that the perfect matching between the PV devices and the electrolyzers, as well

as the development of the efficient electrolyzer successfully contribute to substantial improvement of STH and stability. These results were published in *ACS Appl. Energy Mater.* 2022, 5, 7, 8241–8253, https://doi.org/10.1021/acsaem.2c00768.

５．主な発表論文等

〔雑誌論文〕　計9件（うち査読付論文　9件／うち国際共著　9件／うちオープンアクセス　0件）

１．著者名 Tsubonouchi Yuta、Hayasaka Taichi、Wakai Yuki、Mohamed Eman. A.、Zahran Zaki N.、Yagi Masayuki	４．巻 14
２．論文標題 Highly Efficient and Durable Electrocatalysis by a Molecular Catalyst with Long Alkoxyl Chains Immobilized on a Carbon Electrode for Water Oxidation	５．発行年 2022年
３．雑誌名 ACS Applied Materials & Interfaces	６．最初と最後の頁 15154～15164
掲載論文のDOI（デジタルオブジェクト識別子） 10.1021/acsami.1c24263	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 Berber Mohamed R.、Alenad Asma M.、Althubiti Numa A.、Alrowaili Ziyad A.、Zahran Zaki N.、Yagi Masayuki	４．巻 312
２．論文標題 Bipyridine-based polybenzimidazole as a nitrogen-rich ionomer and a platinum nanoparticle support for enhanced fuel cell performance	５．発行年 2022年
３．雑誌名 Fuel	６．最初と最後の頁 122954～122954
掲載論文のDOI（デジタルオブジェクト識別子） 10.1016/j.fuel.2021.122954	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 Zahran Zaki N.、Mohamed Eman A.、Katsuki Tomohiro、Tsubonouchi Yuta、Yagi Masayuki	４．巻 5
２．論文標題 Nickel Sulfate as an Influential Precursor of Amorphous High-Valent Ni(III) Oxides for Efficient Water Oxidation in Preparation via a Mixed Metal-Imidazole Casting Method	５．発行年 2022年
３．雑誌名 ACS Applied Energy Materials	６．最初と最後の頁 1894～1904
掲載論文のDOI（デジタルオブジェクト識別子） 10.1021/acsaem.1c03379	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 Tsubonouchi Yuta、Kajita Masashi、Hayasaka Taichi、Mandour Hamada S.、Berber Mohamed R.、Zahran Zaki N.、Yagi Masayuki	４．巻 6
２．論文標題 Characterization of electrocatalytic proton reduction and surface adsorption of platinum nanoparticles supported by a polymeric stabilizer on an ITO electrode	５．発行年 2022年
３．雑誌名 Sustainable Energy & Fuels	６．最初と最後の頁 815～821
掲載論文のDOI（デジタルオブジェクト識別子） 10.1039/D1SE01760H	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 Tanahashi Yuki、Takahashi Kosuke、Tsubonouchi Yuta、Nozawa Shunsuke、Adachi Shin-ichi、Hirahara Masanari、Mohamed Eman A.、Zahran Zaki N.、Saito Kenji、Yui Tatsuto、Yagi Masayuki	4．巻 118
2．論文標題 Mechanism of H ⁺ dissociation?induced O-O bond formation via intramolecular coupling of vicinal hydroxo ligands on low-valent Ru(III) centers	5．発行年 2021年
3．雑誌名 Proceedings of the National Academy of Sciences	6．最初と最後の頁 e2113910118
掲載論文のDOI（デジタルオブジェクト識別子） 10.1073/pnas.2113910118	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 Mohamed Eman A.、Zahran Zaki N.、Naruta Yoshinori	4．巻 9
2．論文標題 A flexible cofacial Fe porphyrin dimer as an extremely efficient and selective electrocatalyst for the CO₂ to CO conversion in non-aqueous and aqueous media	5．発行年 2021年
3．雑誌名 Journal of Materials Chemistry A	6．最初と最後の頁 18213～18221
掲載論文のDOI（デジタルオブジェクト識別子） 10.1039/D1TA04176B	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 Zahran Zaki N.、Mohamed Eman A.、Tsubonouchi Yuta、Ishizaki Manabu、Togashi Takanari、Kurihara Masato、Saito Kenji、Yui Tatsuto、Yagi Masayuki	4．巻 14
2．論文標題 Electrocatalytic water splitting with unprecedentedly low overpotentials by nickel sulfide nanowires stuffed into carbon nitride scabbards	5．発行年 2021年
3．雑誌名 Energy & Environmental Science	6．最初と最後の頁 5358～5365
掲載論文のDOI（デジタルオブジェクト識別子） 10.1039/D1EE00509J	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 Zahran Zaki N.、Mohamed Eman A.、Tsubonouchi Yuta、Ishizaki Manabu、Togashi Takanari、Kurihara Masato、Saito Kenji、Yui Tatsuto、Yagi Masayuki	4．巻 4
2．論文標題 Concisely Synthesized FeNiWOx Film as a Highly Efficient and Robust Catalyst for Electrochemical Water Oxidation	5．発行年 2021年
3．雑誌名 ACS Applied Energy Materials	6．最初と最後の頁 1410～1420
掲載論文のDOI（デジタルオブジェクト識別子） 10.1021/acsaem.0c02628	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 Eo Tatsuya、Katsuki Tomohiro、Berber Mohamed R.、Zahran Zaki N.、Mohamed Eman A.、Tsubonouchi Yuta、Alenad Asma M.、Althubiti Numa A.、Yagi Masayuki	4．巻 4
2．論文標題 Handy Protocol of Nitrogen-Doped BiVO4 Photoanode for Visible Light-Driven Water Oxidation	5．発行年 2021年
3．雑誌名 ACS Applied Energy Materials	6．最初と最後の頁 2983～2989
掲載論文のDOI（デジタルオブジェクト識別子） 10.1021/acsaem.1c00261	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0件

〔図書〕　計0件

〔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