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研究課題名（和文）Bio-abiotic hybrid system for light-driven carbon dioxide conversion to produce ethanol

研究課題名（英文）Bio-abiotic hybrid system for light-driven carbon dioxide conversion to produce ethanol

研究代表者

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研究成果の概要（和文）：本研究では、半導体の優れた光吸収と酸化能力、そしてバクテリア細胞の高い還元能力を組み合わせたハイブリッド型光触媒系を構築し、水と二酸化炭素から酢酸とエタノールを合成することを提案しました。具体的には、Sporomusa ovataまたはClostridium ljungdahlii細菌を水分解ができる光触媒シートに導入し、ハイブリッド光触媒系の開発に成功しました。これにより、光触媒と細菌の特徴を活かして、水と二酸化炭素から酢酸とエタノールが合成できることが示されました。

研究成果の学術的意義や社会的意義
This project developed novel photocatalytic systems composed of microorganisms and semiconductors to produce multicarbon products from CO2 and water. This would advance the field, where most photocatalytic CO2 reduction systems required hole scavengers and obtained mono-carbon compounds only.

研究成果の概要（英文）：This project proposes a strategy for artificial photosynthesis to construct bio-abiotic hybrid systems composed of nonphotosynthetic, CO2-fixing bacteria as the catalyst for CO2 reduction and semiconductors as light absorbers because CO2-fixing bacteria are favored to facilitate the multistep process of CO2 fixation selectively and efficiently. Such systems can harness both the efficient light-harvesting capabilities of semiconductors and the strong catalytic power of living biocatalysts. The proof-of-concept bio-abiotic hybrid systems that interface non-photosynthetic bacteria, such as Sporomusa ovata and Clostridium ljungdahlii, with the photocatalyst sheet consisting of La- and Rh-codoped SrTiO3 and BiVO4 semiconductor powders fixed into a three-dimensional inverse opal-indium tin oxide layer successfully produced acetate and ethanol from CO2 and water.

研究分野：材料工学

キーワード：Photocatalysis

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１．研究開始当初の背景

The primary objective of artificial photosynthesis is to effectively utilize intermittent solar energy for the conversion of water (H_2O) and carbon dioxide (CO_2) into chemically storable fuels and chemicals, thereby closing the carbon cycle and reducing our dependence on fossil fuels.[1,2] However, the main challenge lies in achieving efficient conversion of CO_2 into highly stable, multi-carbon ($C_{2/2+}$) liquid fuels with a high energy density, using only sunlight, CO_2 and H_2O, without the need for sacrificial electron donors or external electricity input.

Although particulate photocatalysts and bias-free photoelectrochemical cells have demonstrated the conversion of CO_2 into fuels using only light, H_2O and CO_2, they have predominantly yielded mono-carbon compounds such as carbon monoxide, methane, and formate.[3-6] However, for long-term stability and direct use as feedstocks for the synthesis of high-energy hydrocarbon fuels and oxygenates, multi-carbon liquid products like ethanol and acetic acid are crucial. While previous reports have shown the feasibility of electrochemical CO_2-to-$C_{2/2+}$ conversion using inorganic materials with electricity input,[7-10] the establishment of solar-driven processes for such conversions has been rare. Moreover, (photo)electrochemical systems have limitations in terms of selectivity, scalability, complexity, and versatility.

An emerging alternative to (photo)electrochemical configurations is the utilization of colloidal systems with particulate semiconductor photocatalysts, offering a simpler design and potentially lower cost. However, semiconductors often exhibit poor selectivity and efficiency in CO_2 reduction reactions due to the lack of active sites. Conversely, nonphotosynthetic, CO_2-fixing bacteria possess metabolic pathways that can selectively convert CO_2 into $C_{2/2+}$ products while maintaining relative stability under environmental perturbations.[11,12] Therefore, a promising solution lies in combining the light-harvesting capabilities of semiconductors with the catalytic power of biological systems. However, among the few reported hybrid systems, the limited oxidising power of the photosensitiser unit necessitates the use of sacrificial reductants, such as cysteine, to ensure sufficient oxidation of water.[13-15]

２．研究の目的

The ultimate objective of this research is the scalable photocatalytic conversion of CO_2 into $C_{2/2+}$ fuels with high selectivity and solar conversion efficiency. The proposed strategy aims to overcome the hurdles of (photo)electrochemical systems limited by the scalability issues and current bio-abiotic systems requiring sacrificial reagents in photocatalytic CO_2RR constructs, and thus provide the possibility for scalable, efficient and selective $C_{2/2+}$ product formation using only sunlight, CO_2 and H_2O.

３．研究の方法

This project constructed nature-inspired colloidal Z-scheme systems composed of a bio-abiotic hybrid photocatalyst for CO_2RR (photocatalyst I) and an oxygen evolution photocatalyst (photocatalyst II), as shown in **Figure 1a**. The Z-scheme pathway based on two-step photoexcitation is exceptionally useful because the bandgap of the photocatalytic material does not have to straddle both the reduction and oxidation potentials, ensuring high light-harvesting capability and also large driving force for the photoexcited carriers to reach catalysts.[16] Hence, such systems can offer both the selectivity and efficiency of biology and strong oxidation power of inorganic semiconductors.

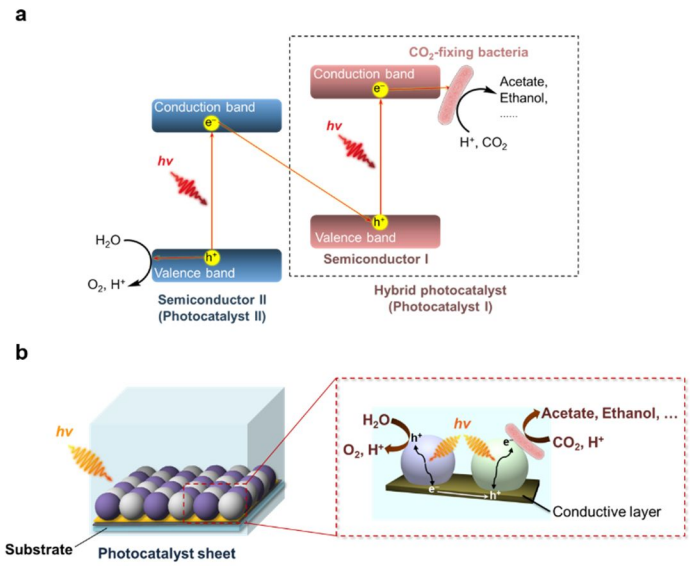

Figure 1. Schematic diagrams of (**a**) artificial photosynthetic solar-to-fuels conversion based on a hybrid Z-scheme system, and (**b**) photocatalyst sheet for Z-scheme CO_2RR coupled with water oxidation.

The immobilisation of semiconductor nanoparticles with narrow bandgaps onto a conductive layer, such as gold and carbon, is achieved in the monolithic photocatalyst sheets (**Figure 1b**).[5,17] These photocatalyst sheets have demonstrated the ability to achieve

scalable and efficient light-driven water splitting without external assistance, thanks to the presence of solid conductive mediators that facilitate interparticle electron transfer. Additionally, the unique structure of the photocatalyst sheet allows for the proximity of reduction and oxidation reactions, resulting in the significant suppression of local pH changes during the redox reactions. This design of the photocatalyst sheet is expected to overcome common challenges observed in (photo)electrochemical and colloidal photocatalytic systems, and it is particularly suitable for the assembly of hybrid bio-abiotic systems. Furthermore, the high solar-to-fuel conversion efficiency of the photocatalyst sheet at neutral pH makes it well-suited for such applications.

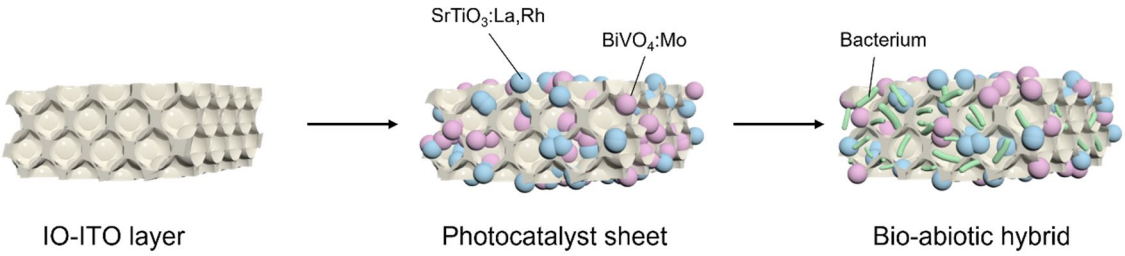

Figure 2. Preparation of the bio-abiotic hybrid.

The bio-abiotic hybrid system was performed by interfacing the non-photosynthetic bacterium *Sporomusa ovata* (*S. ovata*) with a photocatalyst sheet consisting of La- and Rh-codoped $SrTiO_3$ and $BiVO_4$:Mo semiconductor powders fixed into a three-dimensional inverse opal-indium tin oxide (IO-ITO) layer ($SrTiO_3$:La,Rh|IO-ITO|$BiVO_4$:Mo) (**Figure 2**). *S. ovata* was selected as a model microbe because it can efficiently catalyse the CO_2RR to acetate by using H_2 or electrons directly from an electrode in microbial electrosynthesis.[18-20] $SrTiO_3$:La,Rh and $BiVO_4$:Mo were chosen as the semiconductor I and II, respectively, because they are responsive to visible light, easy to prepare, and exhibited the highest activity for photocatalytic water splitting in the photocatalyst sheet configuration.

Incorporation of bacteria into the photocatalyst sheet was realised in an organic-free medium under simulated sunlight irradiation. The sheet acted as the sole electron donor for the bacteria metabolism. Through this way, the bacteria was loaded onto the sheet spontaneously by feeding them with electrons excited in $SrTiO_3$:La,Rh and CO_2 was reduced simultaneously, while the holes in $BiVO_4$:Mo oxidised water to generate oxygen to compete the full reaction.

4．研究成果

In this study, a photocatalyst sheet composed of $SrTiO_3$:La,Rh|IO-ITO|$BiVO_4$:Mo was prepared using a simple drop-casting method. The preparation process involved suspending a mixture of $SrTiO_3$:La,Rh, $BiVO_4$:Mo powders in isopropanol using ultrasonication for a duration of 30 minutes. Subsequently, the suspension was drop-cast onto the IO-ITO layer. The $SrTiO_3$:La,Rh and $BiVO_4$:Mo particle layers on the sheet were modified with Cr_2O_3/Ru and RuO_2 nanoparticles, respectively, through photodeposition. This modification led to the formation of two distinct photocatalysts: the H_2 evolution photocatalyst (Cr_2O_3/Ru-$SrTiO_3$:La,Rh) and the O_2 evolution photocatalyst (RuO_2-$BiVO_4$:Mo).

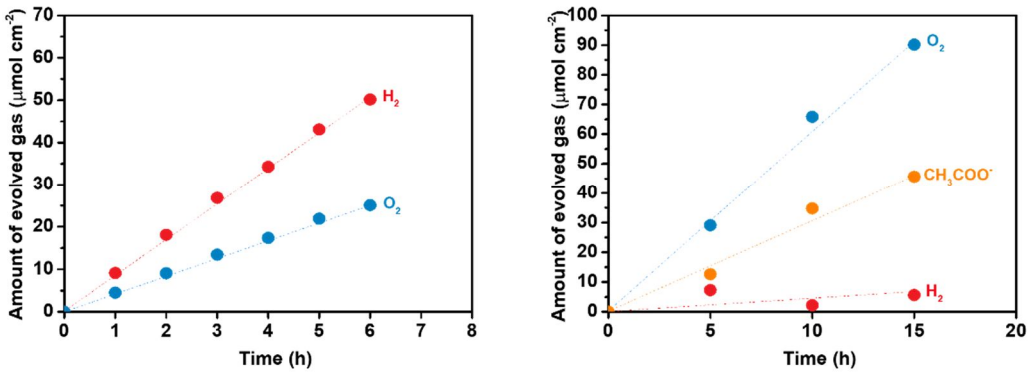

Figure 3. Time courses of (**a**) the water splitting reaction using a Cr_2O_3/Ru-$SrTiO_3$:La,Rh|IO-ITO|RuO_2-$BiVO_4$:Mo sheet and (**b**) the CO_2 reduction coupled with water oxidation using a *S. ovata*|sheet under simulated sunlight (AM 1.5G).

When immersed in a modified *S. ovata* aqueous medium with a pH of 7.0 and purged with a gas mixture of 80% N_2 and 20% CO_2, the obtained photocatalyst sheet demonstrated water splitting with the stoichiometric evolution of H_2 and O_2, as shown in **Figure 3a**. The prepared sheet was then immersed in the same medium containing *S. ovata* cells. The purpose of this step was to investigate the CO_2RR in the

presence of the biohybrid system. Under the same experimental conditions, the biohybrid system simultaneously generated CH_3COO^- and O_2 in a 1:2 ratio, as expected (**Figure 3b**). Proton nuclear magnetic resonance spectroscopy and gas chromatography analyses confirmed that CH_3COO^- was the only detectable product of the CO_2RR, and a small amount of H_2 was also observed. The selectivity for CH_3COO^- formation in the reduction reactions was found to be approximately 90%. Furthermore, scanning electron microscopy images demonstrated the presence of *S. ovata* cells on the photocatalyst sheet after the reaction.

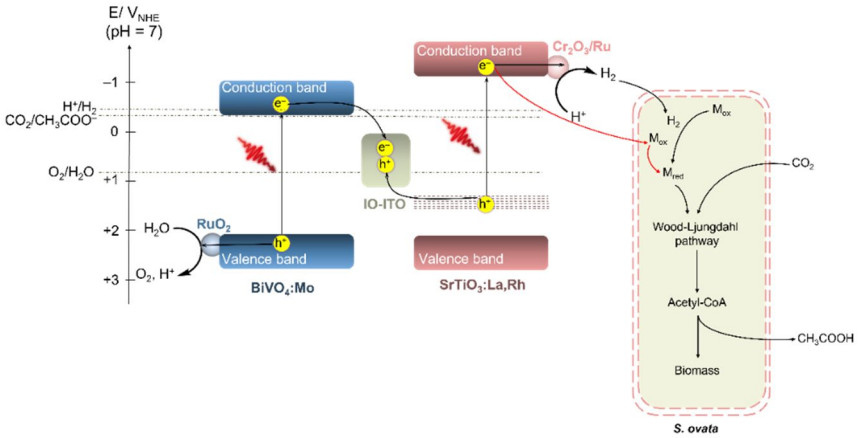

Figure 4. Pathway diagram depicting the acetate and O_2 production from CO_2 and water using the bio-abiotic hybrid.

When the photocatalyst sheet was exposed to simulated sunlight, photoexcitation occurred, generating electrons and holes in both $SrTiO_3$:La,Rh and $BiVO_4$:Mo (**Figure 4**). The electrons transferred from the conduction band of $BiVO_4$:Mo to the donor levels of $SrTiO_3$:La,Rh through the IO-ITO layer. Simultaneously, the electrons in $SrTiO_3$:La,Rh, aided by Cr_2O_3/Ru, catalyse the conversion of H^+ into H_2. On the other hand, the holes in $BiVO_4$:Mo, supported by RuO_2, participate in the oxidation of water, resulting in the production of O_2. These reactions collectively achieved the overall water splitting process. The generated H_2 was utilised by *S. ovata* for the CO_2 reduction process, where it was involved in the production of CH_3COO^- through the acetyl-CoA Wood-Ljungdahl pathway. Additionally, *S. ovata* harnessed photogenerated electrons from illuminated $SrTiO_3$:La,Rh nanoparticles to carry out photosynthesis.

In our study, we extended the application of the same system to another bacterium, *Clostridium ljungdahlii* (*C. ljungdahlii*), with the aim of achieving ethanol production through CO_2 reduction using water as the electron donor. We observed ethanol production using the *C. ljungdahlii*|sheet system under visible light irradiation, yet the main products were H_2 and acetate with a selectivity for ethanol production of only approximately 2% (**Figure 5**). Moreover, the observed reduction and oxidation products did not follow the expected stoichiometric ratio. These findings indicate the need for more careful control of the O_2 concentration in the reaction system and the implementation of protective measures for *C. ljungdahlii* in future investigations. Addressing these aspects will be crucial for further optimising the system and enhancing the selectivity and efficiency of ethanol production.

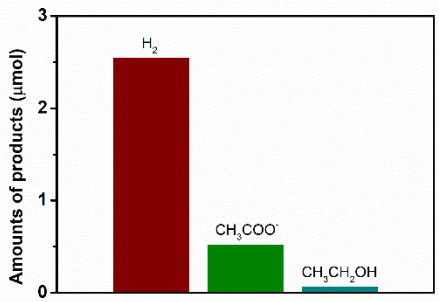

Figure 5. Amounts of products of *C. ljungdahlii*|sheet system for CO_2 reduction with the visible light irradiation ($\lambda \geq 420$ nm) for 24 hours.

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５．主な発表論文等

〔雑誌論文〕　計5件（うち査読付論文　5件／うち国際共著　3件／うちオープンアクセス　1件）

１．著者名 Wang Qian、Pan Zhenhua	４．巻 15
２．論文標題 Advances and challenges in developing cocatalysts for photocatalytic conversion of carbon dioxide to fuels	５．発行年 2022年
３．雑誌名 Nano Research	６．最初と最後の頁 10090～10109
掲載論文のDOI（デジタルオブジェクト識別子） 10.1007/s12274-022-4705-8	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 Tian Bin、Ho Derek、Qin Jiaqian、Hu Jinguang、Chen Zhangxing、Voiry Damien、Wang Qian、Zeng Zhiyuan	４．巻 133
２．論文標題 Framework structure engineering of polymeric carbon nitrides and its recent applications	５．発行年 2023年
３．雑誌名 Progress in Materials Science	６．最初と最後の頁 101056～101056
掲載論文のDOI（デジタルオブジェクト識別子） 10.1016/j.pmatsci.2022.101056	査読の有無 有
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１．著者名 Wu Yaqiang、Sakurai Takuya、Adachi Takumi、Wang Qian	４．巻 15
２．論文標題 Alternatives to water oxidation in the photocatalytic water splitting reaction for solar hydrogen production	５．発行年 2023年
３．雑誌名 Nanoscale	６．最初と最後の頁 6521～6535
掲載論文のDOI（デジタルオブジェクト識別子） 10.1039/D3NR00260H	査読の有無 有
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１．著者名 Yang Ruijie、Fan Yingying、Zhang Yuefeng、Mei Liang、Zhu Rongshu、Qin Jiaqian、Hu Jinguang、Chen Zhangxing、Hau Ng Yun、Voiry Damien、Li Shuang、Lu Qingye、Wang Qian、Yu Jimmy C.、Zeng Zhiyuan	４．巻 62
２．論文標題 2D Transition Metal Dichalcogenides for Photocatalysis	５．発行年 2023年
３．雑誌名 Angewandte Chemie International Edition	６．最初と最後の頁 e202218016
掲載論文のDOI（デジタルオブジェクト識別子） 10.1002/anie.202218016	査読の有無 有
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１．著者名 Wang Qian、Kalathil Shafeer、Pornrungroj Chanon、Sahm Constantin D.、Reisner Erwin	４．巻 5
２．論文標題 Bacteria-photocatalyst sheet for sustainable carbon dioxide utilization	５．発行年 2022年
３．雑誌名 Nature Catalysis	６．最初と最後の頁 633～641
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〔学会発表〕　計5件（うち招待講演　4件／うち国際学会　4件）

１．発表者名 Qian Wang
２．発表標題 Scalable photocatalyst sheet for solar fuel production via artificial photosynthesis
３．学会等名 The Japan Photovoltaic Society Women in Photovoltaics分科会（招待講演）
４．発表年 2021年

１．発表者名 Qian Wang
２．発表標題 Scalable solar fuel production via artificial photosynthesis
３．学会等名 愛知県・名古屋大学・シンガポール国立大学 自動車関連先端技術分野における 産学行政連携オンラインセミナー（招待講演）（国際学会）
４．発表年 2021年

１．発表者名 Qian Wang
２．発表標題 Scalable photocatalyst sheets for solar fuel production from CO2 and water
３．学会等名 International Young Scientists Salon on Photo & Electro Catalytic CO2 Reduction（招待講演）（国際学会）
４．発表年 2022年

１．発表者名 Qian Wang
２．発表標題 Scalable photocatalyst sheets for efficient solar-to-fuel conversion
３．学会等名 The 33rd International Photovoltaic Science and Engineering Conference（国際学会）
４．発表年 2022年

１．発表者名 Qian Wang
２．発表標題 Photocatalyst sheets for scalable solar fuels production via artificial photosynthesis
３．学会等名 Photocatalysis International Forum 2023（招待講演）（国際学会）
４．発表年 2023年

〔図書〕　計0件

〔産業財産権〕

〔その他〕

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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

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