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研究課題名（和文）Investigating the Energetics of Particulate Photocatalysts Co-loaded with Hydrogen- and Oxygen-Evolution Cocatalysts

研究課題名（英文）Investigating the Energetics of Particulate Photocatalysts Co-loaded with Hydrogen- and Oxygen-Evolution Cocatalysts

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研究成果の概要（和文）：光触媒を用いた太陽光による水分解プロセスは盛んに研究が行われているが、そのメカニズムはいまだに明らかにはなっていない。例えば、助触媒を光触媒に堆積させた際にそのエネルギー機構が明らかとなっていない。水素と酸素生成助触媒の共担持によって水分解反応が著しく減少する。本研究では、これらの問題に対しての理解を深めること提案する。Y2Ti2O5S2を助触媒としたIrO2とRhをモデル系として助触媒が表面での反応、界面での再結合やエネルギー機構によって光触媒のプロセスがどのように影響するかの研究を行った。Y2Ti2O5S2モデルシステムを応用することでBiVO4に適応させ、H2O2生成を促進させた。

研究成果の学術的意義や社会的意義

本研究課題では酸化・還元用助触媒の共担持による水分解プロセスに対しての影響を報告する。Rh、IrO2に共担持したY2Ti2O5S2をモデルとして、表面で起こる反応、電荷による再結合及び表面バンド構造の視点から、反応機構を提案し、高効率に太陽光過酸化水素生成反応を駆動する光触媒を作製した。今後、光触媒材料の改良を続けることで、大規模かつ持続可能な人工光合成プロセスの実現ができると期待される。

研究成果の概要（英文）：While solar-driven water splitting with particulate photocatalysts has been studied intensively, their operating mechanisms are still not fully understood. For example, it is unclear how the energetics of the photocatalysts are tuned when loaded with cocatalysts. The H₂- and O₂-evolution cocatalysts facilitate their respective half reaction, but their co-existence on photocatalysts will severely decrease the performance for overall water splitting. This study is proposed to understand this counterintuitive problem. Using IrO₂ and Rh coloaded Y₂Ti₂O₅S₂ as a model system, we studied how co-loading cocatalysts affected photocatalytic processes from the perspectives of surface reactions, interfacial charge recombination, and interfacial the energetics of the system. The principles developed from Y₂Ti₂O₅S₂ model systems were applied to faceted BiVO₄ for enhanced H₂O₂ generation.

研究分野：材料化学

キーワード：光触媒 水分解 人工光合成

1. 研究開始当初の背景

Solar-driven water splitting with particulate photocatalysts has attracted much attention in the past years because of its potential for cost-effective and scalable hydrogen production.[1] To fully take advantage of the solar spectrum, photocatalysts which are visible-light-responsive are highly desirable. However, most of these photocatalysts are only active for either H₂ or O₂ evolution with a sacrificial reagent, but for the full reaction.[2] Among them, the newly developed Y₂Ti₂O₅S₂ is one of the rare cases where overall water splitting can be achieved after loading suitable co-catalysts. Additionally, its light absorption edge reaches 650 nm, corresponding to a maximum solar-to-hydrogen conversion efficiency of 21%. [3] Regardless of these amazing upsides, its recorded efficiency is still far behind the target for practical application. This is partly because the system is not optimized, as the effects of adding cocatalysts to the particle has not been well understood.

Photocatalytic water splitting undergoes the following processes (Fig. 1): 1) light absorption for generating electron-hole pairs; 2) charge separation; 3) charge transfer across interfaces for surface reactions; 4) mass transfer of products. From intuition, co-loading H₂- and O₂-evolution cocatalysts on the photocatalyst should benefit water splitting by facilitating the respective half-reaction kinetics; however, preliminary results on Y₂Ti₂O₅S₂ show that loading IrO₂ for O₂ evolution after loading Rh for H₂ evolution impeded the

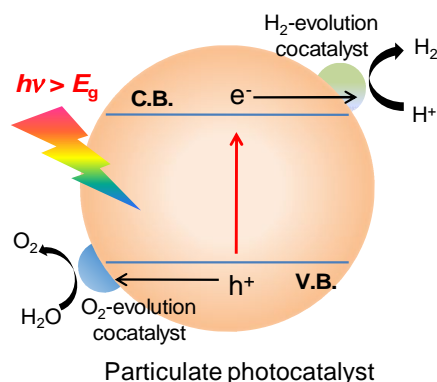


Fig. 1 Schematic of a photocatalyst loaded with H₂ and O₂ evolution cocatalysts for overall water splitting

water splitting reaction. Despite the potential issues of co-loading two kinds of cocatalysts, this approach is indispensable for most visible-light-responsive photocatalysts, like Y₂Ti₂O₅S₂. This is because its shallow valence band can hardly drive O₂ evolution on its bare reaction sites. For the above reasons, it is highly desirable to understand how co-loading H₂- and O₂-evolution cocatalysts affects the photocatalytic water splitting processes and develop a rational approach to taking advantage of their positive effects while avoiding their negative ones.

[1] *Chem. Soc. Rev.*, 2009, 38, 253–278; [2] *J. Photochem. Photobiol. C*, 2010, 11, 179–209; [3] *Nature Materials*, 2019, 18, 827–832.

2. 研究の目的

Using Y₂Ti₂O₅S₂ loaded with Rh and/or IrO₂ as a model system, the study is designed to understand how coloaded cocatalysts affects photocatalytic processes from the perspectives of surface reactions, interfacial charge recombination, and interfacial the energetics of the system. Furthermore, the insight obtained from studying the model system is supposed to be generally applicable to other photocatalysts besides Y₂Ti₂O₅S₂ for improving the cocatalyst coloaded.

3. 研究の方法

$\text{Y}_2\text{Ti}_2\text{O}_5\text{S}_5$ was prepared by a solid-state-reaction method based on a previous study. [1] Rh was loaded on $\text{Y}_2\text{Ti}_2\text{O}_5\text{S}_5$ by photoreduction of its precursor. IrO_2 was loaded on $\text{Y}_2\text{Ti}_2\text{O}_5\text{S}_5$ by adsorption of its nanoparticles. The photocatalytic gas-evolution activities were measured in a closed circulation system. $\text{Y}_2\text{Ti}_2\text{O}_5\text{S}_5$ and cocatalysts were characterized by XRD, DRS, SEM, STEM-EDS, TEM, etc. The cocatalyst-loaded $\text{Y}_2\text{Ti}_2\text{O}_5\text{S}_5$ was loaded on a Ti substrate for (photo)electrochemical analyses in a potentiostat equipped with impedance spectroscopy. The charge-carrier dynamics of cocatalyst-loaded $\text{Y}_2\text{Ti}_2\text{O}_5\text{S}_5$ was studied by transient absorption spectroscopy. The local energetics at the $\text{Y}_2\text{Ti}_2\text{O}_5\text{S}_5$ /cocatalyst interfaces was investigated by a potential-sensing electrochemical atomic force microscopy. The principles developed from $\text{Y}_2\text{Ti}_2\text{O}_5\text{S}_5$ model systems were applied to faceted BiVO_4 for enhanced H_2O_2 generation. Cocatalyst-loaded BiVO_4 were characterized and analyzed by the same methods as cocatalyst-loaded $\text{Y}_2\text{Ti}_2\text{O}_5\text{S}_5$. [1] *Nature Materials*, 2019, 18, 827–832.

4. 研究成果

The possible interplay between co-loaded H_2 - and O_2 -evolution cocatalysts was proposed in Fig. 2. 1) Co-loading H_2 - and O_2 -evolution cocatalysts may perturb their respective catalysis (Fig. 2a). 2) The cocatalysts may be in direct contact and work as efficient charge-recombination centers (Fig. 2b). 2) The energetics at photocatalyst/ H_2 - and O_2 -evolution cocatalyst/water junctions may perturb each other and decrease the charge-separation efficiency (Fig. 2c).

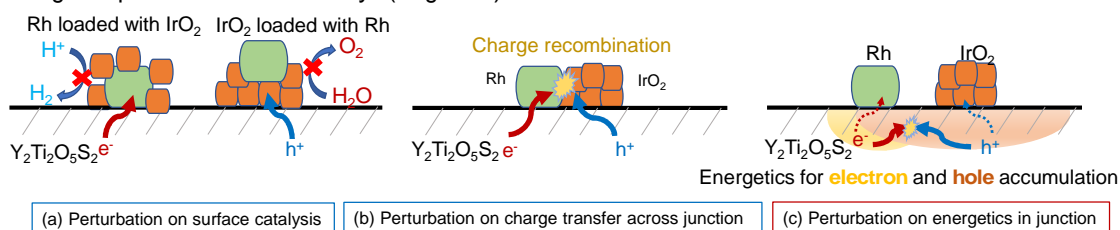


Fig. 2 Plausible mechanisms for the negative effects of co-loading H_2 - and O_2 -evolution cocatalysts

The mechanism proposed in Fig.2a were investigated by comparing the electrochemical activities of cocatalysts. As shown in Fig. 3, Rh, IrO_2 /FTO was more active than Rh/FTO for H_2 evolution and IrO_2 /FTO, respectively. Such results indicate that co-loading Rh and IrO_2 unexpectedly enhanced surface reactions and so the mechanism in Fig.2a is not reliable. To confirm the mechanism proposed in Fig. 2b, the Rh and IrO_2 particles loaded on $\text{Y}_2\text{Ti}_2\text{O}_5\text{S}_5$ were characterized by STEM-EDS. The results confirmed that Rh and IrO_2 particles have a distance in tens of nanometers. Furthermore, even though Rh was coated with Cr_2O_3 to separate it with IrO_2 , the negative effects of co-loading Rh and IrO_2 were still observe. Such results reveal that the mechanism in Fig. 2b is also not convincing.

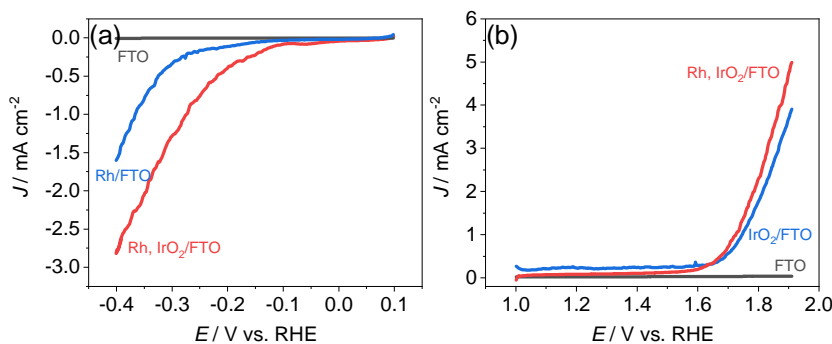


Figure 3. (a) Electrochemical H_2 -evolution activities of Rh/FTO and Rh, IrO_2 /FTO. (b) Electrochemical O_2 -evolution activities of IrO_2 /FTO and Rh, IrO_2 /FTO.

The mechanism shown in Fig. 2c were studied by measuring the local C-V curves of IrO_2 /Rh/ $\text{Y}_2\text{Ti}_2\text{O}_5\text{S}_5$ with a potential-sensing electrochemical atomic force microscopy. By analyzing the local C-V curves with the diode law ($J = J_0 \exp(qV_{\text{app}}/nk_B T - 1)$), the local

built-in potentials which are related with the local energetics can be quantified. However, the $\text{IrO}_2/\text{Rh}/\text{Y}_2\text{Ti}_2\text{O}_7\text{S}_5$ particle surface was too rough and the conductivity of $\text{Y}_2\text{Ti}_2\text{O}_7\text{S}_5$ was too low that reliable local C-V curves were not obtained. Yet, the mechanism in Fig. 2c has been indirectly verified in other studies.[1][2] One way to avoid the side effects of co-loading cocatalysts shown in Fig. 2c is structuring the photocatalyst with reduction and oxidation facets and further loading cocatalysts on the corresponding facets.

The facet engineering and the subsequent selectively cocatalysts loading were applied to Mo-doped BiVO_4 ($\text{Mo}:\text{BiVO}_4$).[3] Pd and CoO_x as a reductive and oxidative cocatalysts were selectively on the $\{010\}$ reduction and $\{110\}$ oxidation facets of $\text{Mo}:\text{BiVO}_4$, respectively, as shown in Fig.4. The obtained $\text{CoO}_x/\text{Mo}:\text{BiVO}_4/\text{Pd}$ was applied to photocatalytic H_2O_2 generation without adding a sacrificial reagent. Its performance was much better than $\text{Mo}:\text{BiVO}_4/\text{CoO}_x\text{-Pd}$ where CoO_x and Pd were randomly loaded (Fig. 5), confirming the importance of manipulating photocatalyst/cocatalyst interfacial energetics. The solar-to- H_2O_2 energy conversion efficiency of $\text{CoO}_x/\text{Mo}:\text{BiVO}_4/\text{Pd}$ reached 0.29%, surpassing other inorganic semiconductor photocatalysts by one order of magnitude

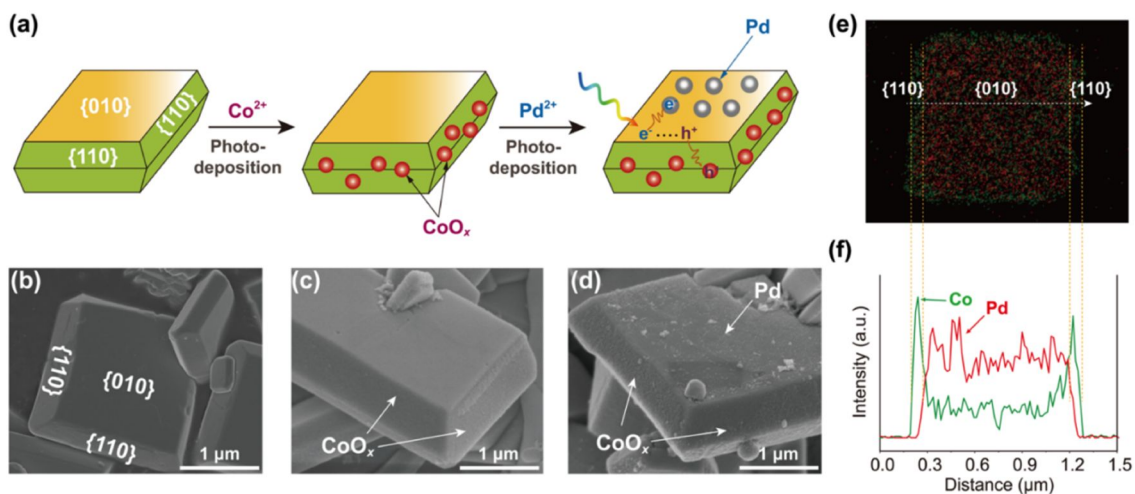


Fig. 4 (a) Schematic deposition processes of CoO_x and Pd on $\text{Mo}:\text{BiVO}_4$ and the corresponding SEM images of (b) $\text{Mo}:\text{BiVO}_4$, (c) $\text{CoO}_x/\text{Mo}:\text{BiVO}_4$, and (d) $\text{CoO}_x/\text{Mo}:\text{BiVO}_4/\text{Pd}$. (e)-(f) Energy-dispersive X-ray spectroscopy (EDS) elemental mapping and line profile along with the white arrow of $\text{CoO}_x/\text{Mo}:\text{BiVO}_4/\text{Pd}$.

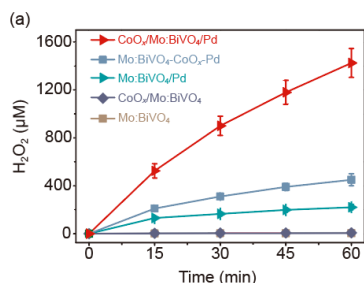


Fig. 5 Time courses of photocatalytic H_2O_2 generation over $\text{CoO}_x/\text{Mo}:\text{BiVO}_4/\text{Pd}$, $\text{Mo}:\text{BiVO}_4\text{-CoO}_x\text{-Pd}$, $\text{CoO}_x/\text{Mo}:\text{BiVO}_4$, $\text{Mo}:\text{BiVO}_4/\text{Pd}$, and $\text{Mo}:\text{BiVO}_4$.

- [1] *J. Phys. Chem. C*, 2014, 118, 23897–23906; [2] *Nature Communications*, 2013, 4, 1432. [3] *Nature Communications*, 2022, 13, 1034.

5. 主な発表論文等

〔雑誌論文〕 計2件（うち査読付論文 2件/うち国際共著 2件/うちオープンアクセス 1件）

1. 著者名 Zhenhua Pan, Rito Yanagi, Tomohiro Higashi, Yuriy Pihosh, Shu Hu and Kenji Katayama	4. 巻 6
2. 論文標題 Hematite photoanodes prepared by particle transfer for photoelectrochemical water splitting	5. 発行年 2022年
3. 雑誌名 Sustainable Energy Fuels	6. 最初と最後の頁 2067
掲載論文のDOI（デジタルオブジェクト識別子） 10.1039/d2se00145d	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 Tian Liu, Zhenhua Pan, Junie Jhon M. Vequizo, Kosaku Kato, Binbin Wu, Akira Yamakata, Kenji Katayama, Baoliang Chen, Chiheng Chu, Kazunari Domen	4. 巻 13
2. 論文標題 Overall photosynthesis of H ₂ O ₂ by an inorganic semiconductor	5. 発行年 2022年
3. 雑誌名 NATURE COMMUNICATIONS	6. 最初と最後の頁 1034
掲載論文のDOI（デジタルオブジェクト識別子） 10.1038/s41467-022-28686-x	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 該当する

〔学会発表〕 計1件（うち招待講演 0件/うち国際学会 0件）

1. 発表者名 Zhenhua Pan, Hiroaki Yoshida, Takashi Hisatomi, Kazunari Domen, Kenji Katayama
2. 発表標題 Effects of co-loading hydrogen- and oxygen-evolution cocatalysts on photocatalytic water splitting processes
3. 学会等名 日本化学会第101春季年会
4. 発表年 2020年～2021年

〔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
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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
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