



Surface Modifications of Heterogeneous Photocatalysts for Photocatalytic Conversion of CO₂ by H₂O as the Electron Donor

Takechi Nakamoto,^[a] Shoji Iguchi,^{*[a]} Shimpei Naniwa,^[a] Tsunehiro Tanaka,^[a, b, c] and Kentaro Teramura^{*[a, b, c]}



ChemCatChem 2024, 16, e202400594 (1 of 17)



The photocatalytic conversion of CO_2 using H_2O over heterogeneous photocatalysts has attracted worldwide attention because it enables direct solar-to-chemical energy conversion. However, further development of this technology requires solutions to overcome the low formation rates of CO_2 reduction products and their insufficient selectivity, mainly caused by the rapid charge recombination of photogenerated electron/hole pairs, competition for thermodynamically preferential H_2 evolution from H_2O , and the relatively low concentration of CO_2 on the surface of the photocatalysts. Surface modification of

1. Introduction

The photocatalytic conversion of CO₂ using H₂O as an electron donor over heterogeneous photocatalysts, known as artificial photosynthesis, has attracted considerable attention as a promising method for reducing CO₂ emissions and solving energy and environmental problems.^[1] Considering photocatalysts for CO₂ reduction have been widely investigated, we recently proposed three evaluation criteria to verify that the photocatalyst achieves the photocatalytic reduction of CO₂ by H₂O.^[2] (I) The origin of carbon in CO₂ reduction products (CO₂RPs), such as CO, HCOOH, HCOH, CH₃OH, and CH₄, should be confirmed using isotopically labelled CO₂. (II) The number of photogenerated electrons consumed for CO₂RPs evolution is greater than that for H₂ evolution; in other words, the selectivity of photogenerated electrons toward CO₂RPs evolution (S_{CO2RPs} , %), defined by Equation (1), should exceed 50%.

$$\begin{split} S_{CO_2RPs} &= & \left(2R_{HCOOH} + 2R_{CO} + 4R_{HCHO} + 6R_{CH_3OH} + 8R_{CH_4} \right) / \\ & \left(2R_{HCOOH} + 2R_{CO} + 4R_{HCHO} + 6R_{CH_2OH} + 8R_{CH_4} + 2R_{H_2} \right) \times 100 \end{split}$$
(1)

where R_X represents the formation rate of product X. Gas-phase CO_2RPs , such as CO and CH_4 , were detected by gas chromatography (GC). A thermal conductivity detector (TCD) was used to quantify CO, CH_4 , and H_2 . In terms of sensitivity and product identification, a flame-ionisation detector with a methaniser is recommended to quantify CO and CH_4 . Liquid-phase CO_2RPs , such as HCOOH, HCOH, and CH_3OH , can be detected by liquid

 [a] T. Nakamoto, S. Iguchi, S. Naniwa, T. Tanaka, K. Teramura Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Kyoto-daigaku Katsura, Nishikyo-ku, Kyoto 615-8510, Japan E-mail: iquchi.shoji.4k@kyoto-u.ac.jp

teramura.kentaro.7r@kyoto-u.ac.jp

[b] T. Tanaka, K. Teramura Elements Strategy Initiative for Catalysts & Batteries (ESICB), Kyoto University, 1-30 Goryo-Ohara, Nishikyo-ku, Kyoto 615-8245, Japan

- [c] T. Tanaka, K. Teramura Fukui Institute for Fundamental Chemistry, Kyoto University, Takano Nishibiraki-cho 34–4, Sakyo-ku, Kyoto 606-8103, Japan
- © 2024 The Authors. ChemCatChem published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution Non-Commercial NoDerivs License, which permits use and distribution in any medium, provided the original work is properly cited, the use is noncommercial and no modifications or adaptations are made.

heterogeneous photocatalysts is crucial for improving their formation rates and selectivity. This review article introduces four strategies for designing photocatalyst surfaces for the photocatalytic conversion of CO₂ by H₂O: (I) loading of an Ag cocatalyst, (II) utilisation of cocatalysts for H₂O oxidation, (III) suppression of undesired H₂ evolution, and (IV) loading of basic materials for CO₂ adsorption. The strategies introduced in this review successfully enhanced the formation rates of the products and/or their selectivity in the heterogeneous photocatalytic conversion of CO₂ by H₂O.

chromatography. Note that the formation rate multiplied by the number of consumed electrons should be added to the numerator and denominator if other CO₂RPs are formed. (III) Stoichiometric O₂ evolution as a product of H₂O oxidation should be observed compared to the total formation rates of CO₂RPs and H₂. In other words, the balance of consumed electrons and holes (e^-/h^+) defined by Equation (2) should be 1.

$$\begin{split} & e^{-/h} + = (2R_{HCOOH} + 2R_{CO} + 4R_{HCHO} + 6R_{CH_3OH} \\ & + 8R_{CH_4} + 2R_{H_3}) \; / \; 4R_{O_2} \end{split}$$

The generated O_2 can be detected by TCD-GC. TCD-GC with Ar carrier gas can simultaneously detect several hundred nmol h⁻¹ O_2 and H₂. Moreover, TCD-GC with a He carrier gas can be used to analyse concentrations of O_2 lower than that of Ar. The stoichiometric evolution of O_2 strongly indicates that H₂O acts as an electron donor for the photocatalytic conversion of CO_2 , whereas several studies have ignored the quantitative analysis of O_2 . Despite the recent enthusiasm for artificial photosynthesis and the increase in the number of related studies, few reports have satisfied these criteria.

Criterion (II) is the most important factor in the discussion of photocatalysts for CO₂ conversion. However, satisfying criterion (II) is difficult because CO₂ reduction is thermodynamically and/ or kinetically more difficult than competitive H⁺ reduction. Equations (3)–(8) show the chemical equations for H⁺ reduction to H₂, possible CO₂ reduction, and their standard redox potentials (vs. NHE at pH=0).^[3] Producing CO, HCOOH, and HCOH from CO₂ is thermodynamically more difficult than H₂O reduction because the standard redox potentials of CO₂/HCOH, and CO₂/HCOH are more negative than those of H⁺ (Equations (3)–(5)). HCOH, CH₃OH, and CH₄ productions from CO₂ are kinetically more unfavourable than H⁺ reduction because 4–8 electrons are required to generate them (Equations (6)–(8)).

 $2H^+ + 2e \longrightarrow H_2 \qquad \qquad E^\circ = 0 \ V \tag{3}$

 $CO_2 + 2H^+ + 2e \longrightarrow HCOOH \qquad E^\circ = -0.25 \text{ V} \tag{4}$

- $CO_2 + 2H^+ + 2e \rightarrow CO + H_2O = -0.11 V$ (5)
- $CO_2 + 4H^+ + 4e \rightarrow HCHO + H_2O E^\circ = -0.07 V$ (6)

$$CO_2 + 6H^+ + 6e^{-} \rightarrow CH_3OH + H_2O E^\circ = 0.016 V$$
 (7)

$$CO_2 + 8H^+ + 8e \rightarrow CH_4 + 2H_2O E^\circ = 0.17 V$$
 (8)

Therefore, CO₂RPs are not generated, or S_{CO2RPs} are extremely low if the photocatalysts reported for H₂O splitting are employed for the photocatalytic conversion of CO₂ by H₂O without any modifications. Additionally, modifying photocatalysts to improve bulk properties, such as charge separation, light harvesting, and band alignment, does not necessarily enhance S_{CO2RPs} because these modifications simultaneously increase R_{H2} . Accordingly, appropriate surface modifications of heterogeneous photocatalysts are indispensable for the selective conversion of CO₂ using H₂O. Surface modification of heterogeneous photocatalysts can transform them into suitable photocatalysts for CO₂ reduction by H₂O if they satisfy the thermodynamic requirements; in other words, the conduction band minimum of the photocatalyst is more negative than the standard redox potential of CO₂.



Takechi Nakamoto was born in Nagasaki, Japan, in 1999 and raised in Fukuoka until high school. After graduating from Undergraduate School of Industrial Chemistry, Kyoto University for his undergraduate degree, he has studied at Department of Molecular Engineering, Graduate School of Engineering, Kyoto University for his graduate degree, under the supervision of Prof. Kentaro Teramura. He was accepted as Research Fellowship for Young Scientists DC1 by Japan Society for the Promotion of Science (JSPS). His current research interest is photocatalytic conversion of CO_2 over heterogeneous photocatalysts.



Shoji Iguchi received his Ph.D. in Engineering from Kyoto University in 2016. He joined the National Institute of Advanced Industrial Science and Technology (AIST) as a post-doc researcher in 2016. In 2018, he moved to the Tokyo Institute of Technology as an assistant professor. Currently, he is a program-specific associate professor at Graduate School of Engineering, Kyoto University. His research interests include photocatalysis and electrolysis for CO_2 conversion.



Shimpei Naniwa was born in Shimane, Japan, in 1993. He received his Ph.D. in 2022 from the Graduate school of Human and Environmental Studies, Kyoto University, under the supervision of Prof. Hisao Yoshida. After receiving his Ph.D., he joined to the group of Prof. Tsunehiro Tanaka and Prof. Kentaro Teramura as an assistant professor at Graduate School of Engineering, Kyoto University. His current research interest is in heterogenous catalysis and photocatalysis for conversion of various molecules including CO_2 .

The reaction systems used for the photocatalytic conversion of CO₂ by H₂O are mainly divided into two groups: gas-solid and gas-liquid-solid reaction systems. In the gas-liquid-solid reaction system, buffers, such as NaHCO₃, Na₂CO₃, and KHCO₃, are added to the reaction solution to maintain a suitable solution pH and increase the solubility of CO₂ in H₂O. In this system, dissolved CO₂ molecules can be reduced into CO₂RPs, such as HCO₃⁻ and CO₃²⁻, which are difficult to be converted directly.^[4] In the gas-solid system, the photocatalyst is in contact with gaseous CO_2 , therefore the CO_2 solubility does not regulate the activity. On the other hand, two types of reactors are primarily used for the reaction: closed and flow systems. In a closed system, CO₂RPs can be detected because they accumulate in the reactor even with a low photocatalytic activity. Moreover, a backward reaction, namely the reaction of CO₂RPs back to CO₂, occurred. In the flow system, CO₂ gas was continuously supplied, and the backward reaction could be suppressed. However, trace amounts of CO₂RPs are sometimes overlooked because they are constantly released from the reactors. The reaction system was selected based on the expected activities of the photocatalyst.



Prof. Tsunehiro Tanaka received his Ph.D. in 1987 at Kyoto University for the study of photocatalysis and XAFS spectroscopy under the supervision of Prof. Emeritus Satohiro Yoshida. Thereafter he joined the group of Prof. Kozo Tanabe at Department of Chemistry, Hokkaido University as an assistant professor. He moved to Department of Hydrocarbon Chemistry, Kyoto University as a member of Prof. S. Yoshida's group in 1990. He was promoted to associate professor in 1997 and to full professor in 2004 at Department of Molecular Engineering, Kyoto University. He has been conducting research on photocatalysis, environmental catalysis, and in situ characterization of catalysts.



acterization of catalysts. Kentaro Teramura received his Ph.D. in Engineering from Kyoto University in 2004. He joined the University of Tokyo as a postdoctoral fellow of Japan Science & Technology Agency in 2004, and became an assistant professor in 2005. In 2006, he moved to Kyoto University as an assistant professor at Research Unit for Next Generation, was promoted to a lecturer at the Department of Molecular Engineering, Graduate School of Engineering in 2011, an associate professor in 2013, and a professor in 2021. His interest is in heterogeneous catalysts and catalysis that contribute to carbon neutrality.

Chemistry Europe

European Chemical Societies Publishing



Wang et al. altered the reactivity of Pt-loaded TiO₂ photocatalysts via surface modification.^[5] TiO₂ is generally considered an active oxide for photocatalytic H₂O splitting since Honda and Fujishima elucidated that photoirradiation of TiO₂ electrodes can shift the anode potential for H₂O oxidation in electrochemical H₂O splitting to a more negative value.^[6] Wang et al. prepared core-shell structured Pt (core) and Cu (shell) binary cocatalyst-loaded TiO₂ photocatalysts (Cu/Pt/TiO₂) using a stepwise photodeposition process, with the results indicating that Cu/Pt/TiO₂ showed 85% of S_{CO2RPs} , whereas H₂ was preferentially generated over Pt/TiO₂ (S_{CO2RPs}=41%). Notably, Cu/TiO₂ exhibits good S_{CO2RPs} (80%), indicating that the Cu cocatalyst was responsible for high S_{CO2RPs}. Furthermore, introducing a Pt core, which can effectively extract photogenerated electrons, considerably enhanced the total consumption rate of photogenerated electrons compared to Cu/TiO₂. Hence, both R_{CO2RPs} and S_{CO2RPs} were enhanced by modifying TiO₂ with Cu and Pt as effective cocatalysts for CO₂ reduction and extracting photogenerated electrons, respectively.

Domen et al. discovered that TaON can photocatalytically reduce H^+ to H_2 in the presence of methanol as a sacrificial electron donor under visible-light irradiation.^[7] They reported the conduction band minimum of TaON based on empty Ta 5 d orbitals was estimated to be -0.3 V vs. NHE at pH = 0, meaning that photogenerated electrons in TaON have sufficient potential to reduce CO₂ and H⁺. Ishitani *et al.* successfully constructed a hybrid photocatalyst comprising Ag-modified TaON and a Ru(II)-binuclear complex.^[8] Many metal complexes are revealed to function as redox photosensitizers and/or catalysts for selective CO₂ conversion after Lehn et al. discovered that $[Re(bpy)(CO)_3CI]$ (bpy = 2,2'-bipyridine) photochemically reduces CO2-CO.^[9] Z-schematic electron transfer with step-by-step photoexcitation of the Ru(II) photosensitizer unit and TaON resulted in efficient CO₂ conversion to HCOOH with notable selectivity ($S_{HCOOH} > 85\%$) in a mixed aqueous solution of EDTA and Na₂CO₃ under visible-light irradiation. Hence, modifying the surface of heterogeneous photocatalysts with metal complexes for selective CO₂ conversion can alter their reactivity toward CO₂RPs evolution.

Thus, appropriate surface modification of heterogeneous photocatalysts is considered an indispensable strategy contributing toward the enhanced and selective photocatalytic conversion of CO₂ by H₂O. As such, four effective methods for surface modification to improve R_{CO2RPs} and/or S_{CO2RPs} are discussed in this review.

2. Discussion

2.1. Ag Cocatalyst

Modifying photocatalysts with an Ag cocatalyst is widely known as an effective method for improving the efficiency of the photocatalytic conversion of CO_2 . Ag was originally found to be efficient for CO_2 reduction in the field of the electrochemical reduction of CO_2 . Hori *et al.* conducted an electrochemical CO_2 reduction using various metal plates as cathodes.^[10] They classified Cd, Sn, Pb, In, Cu, Ag, Au, Ni, and Fe metal plate electrodes into four groups based on the selectivity of the products as follows: Cd, Sn, Pb, and In electrodes predominantly produced HCOO⁻ in addition to H₂; Ag and Au electrodes principally convert CO₂ into CO; Cu electrode exhibited significant CH₄ production from CO₂; H₂ was generated exclusively at the Ni and Fe electrodes, indicating that these metals were insufficient for CO₂ conversion. Many reports of electrochemical CO₂ reduction using metal cathodes are consistent with these pioneering results.^[11] Hara and Sakata investigated the electrochemical reduction of CO₂ using various metals,^[12] whose electrocatalytic activities were evaluated using a gas diffusion electrode (GDE). The supported metals (Pd, Ag, Co, Rh, Ni, and Pt) in GDE act as catalysts for electrochemical CO₂ reduction. For Pd- and Ag-GDEs, CO was the predominant reduction product, whereas H₂ was mainly generated on Co-, Rh-, Ni-, and Pt-GDEs. Especially, selectivity toward CO₂ reduction on the Ag-GDE was remarkably high ($S_{CO} = \sim 96\%$), indicating that Ag metal significantly promoted CO₂ conversion to CO as a catalyst. Thus, Ag was found to be highly effective for the catalytic conversion of CO₂.

According to our research, the first reported photocatalyst which could reduce CO₂ with unity of the ratio of consumed electrons and holes (i.e., H₂O acted as an electron donor) and more than 50% of selectivity toward CO₂RPs was loaded by the Ag cocatalyst. Kudo et al. reported that ALa₄Ti₄O₁₅ (A=Ca, Sr, and Ba) photocatalysts showed CO evolution activity in the presence of an Ag cocatalyst.[13] As shown in Table 1, the amount of evolved CO was negligible ($R_{co} < 0.1 \,\mu mol \,h^{-1}$) in the absence of cocatalysts, highlighting that the Ag cocatalyst dramatically improves the photocatalytic activity and the selectivity toward CO_2RPs in the photocatalytic CO_2 conversion by H₂O. Ag loading was clearly effective for all CaLa₄Ti₄O₁₅, SrLa₄Ti₄O₁₅, and BaLa₄Ti₄O₁₅ photocatalysts, indicating the versatility of this strategy. Among the NiO_x, Ru, Cu, Au, and Ag cocatalysts, the Ag cocatalyst was found to be the best for the photocatalytic reduction of CO₂, although Au and Cu electrodes have also been reported as effective metal cathodes for CO₂ conversion. Furthermore, after optimising the synthesis processes, the BaLa4Ti4O15 photocatalyst loaded by 2.0 wt.% of the Ag cocatalyst via a liquid-phase reduction method was the first to show significant activity for CO_2 conversion ($R_{CO} =$ ~22 $\mu mol\,h^{-1})$ with good selectivity (S_{CO}=~69\%) and stoichiometric O₂ evolution ($e^{-}/h^{+}=1$). As shown in Figure 1, stoichiometric and selective CO evolution was observed continuously for 7 h, attributed to photocatalyst modification with the Ag cocatalvst.

Although many studies on the photocatalytic conversion of CO_2 agree that Ag cocatalysts are essential for the selective conversion of CO_2 to $CO_r^{[14]}$ their effectiveness for CO_2 conversion remains to be investigated. Some considerations have been presented. Yoshida *et al.* performed *in situ* FT-IR measurements of Ag-loaded gallium oxide (Ag/Ga₂O₃) to reveal the effect of Ag cocatalysts on the state of chemically adsorbed carbon species.^[15] Figure 2 shows the differences in the FT-IR spectra of Ag/Ga₂O₃ after CO_2 introduction. Monodentate bicarbonate (1635 cm⁻¹ and 1420 cm⁻¹) and bidentate



Table 1. CO ₂ redu Chemical Society.	iction over $Ala_4Ti_4O_{15}$ (A	=Ca, Sr, and Ba) photocata	lysts with various cocatalys	sts ^a . Reprinted	d with permis	sion. ^[13] Copyrig	ght 2011 Americar		
Photocatalyst	Bandgap (eV)	Cocatalyst (wt.%)	Loading method	Activity	Activity (μmol h ⁻¹)				
				H ₂	O ₂	CO	НСООН		
BaLa ₄ Ti ₄ O ₁₅	3.9	None		5.3	2.4	0	0		
BaLa ₄ Ti ₄ O ₁₅	3.9	NiO _x ^b (0.5)	impregnation	58	29	0.02	0		
BaLa ₄ Ti ₄ O ₁₅	3.9	Ru (0.5)	photodeposition	84	41	0	0		
BaLa ₄ Ti ₄ O ₁₅	3.9	Cu (0.5)	photodeposition	96	45	0.6	0		
BaLa ₄ Ti ₄ O ₁₅	3.9	Au (0.5)	photodeposition	110	51	0	0		
BaLa ₄ Ti ₄ O ₁₅	3.9	Ag (1.0)	photodeposition	10 ^c	7.0 ^c	4.3 ^c	0.3 ^c		
CaLa ₄ Ti ₄ O ₁₅	3.9	none		1.3	0.6	0.07	0		
CaLa ₄ Ti ₄ O ₁₅	3.9	Ag (1.0)	photodeposition	5.6	2.1	2.3	1.3		
SrLa ₄ Ti ₄ O ₁₅	3.8	none		0.8	0.5	0.06	0		
SrLa ₄ Ti ₄ O ₁₅	3.8	Ag (1.0)	photodeposition	2.7	1.8	1.8	0.5		
[a] Catalyst 0.3 g,	[a] Catalyst 0.3 g, water 360 mL, a CO ₂ flow system (15 mLmin ⁻¹), a 400 W high-pressure mercury lamp, and an inner irradiation guartz cell. [b] Pre-								

treatment: reduced at 673 K and subsequently oxidised at 473 K after impregnation (543 K for 1 h). [c] Initial activity.



Figure 1. CO₂ reduction over BaLa₂Ti₄O₁₅ photocatalyst with Ag (2 wt.%) cocatalyst loaded by a liquid-phase reduction method. Catalyst 0.3 g, water 360 mL, a CO₂ flow system (15 mLmin⁻¹), a 400 W high-pressure mercury lamp, an inner irradiation quartz cell, and H₂ (\circ), O₂ (\bigcirc), CO (\triangle). Reprinted with permission.⁽¹³⁾ Copyright 2011 American Chemical Society.



Figure 2. Difference FT-IR spectra of the adsorbed species after introducing 45 Torr of CO₂ on bare Ga₂O₃ (a), 0.1 wt.% Ag/Ga₂O₃ (b), 0.2 wt.% Ag/Ga₂O₃ (c), 0.5 wt.% Ag/Ga₂O₃ (d), and 1.0 wt.% Ag/Ga₂O₃ (e). Used with permission of Royal Society of Chemistry.^[15]





Figure 3. Difference FT-IR spectra of the adsorbed species after CO_2 introduction, followed by evacuation and photoirradiation for 1 h on bare Ga_2O_3 (a), 0.1 wt.% Ag/Ga_2O_3 (b), 0.2 wt.% Ag/Ga_2O_3 (c), 0.5 wt.% Ag/Ga_2O_3 (d), and 1.0 wt.% Ag/Ga_2O_3 (e). Used with permission of Royal Society of Chemistry.^[15]

monodentate bicarbonate and/or bidentate carbonate species on the Ga_2O_3 surface and not the monodentate carbonate species on the Ag cocatalyst. As shown in Figure 3, Ag included in Ag/Ga₂O₃ considerably promotes the formation of bidentate formate species, indicating that the Ag cocatalyst on the Ga₂O₃ photocatalyst is one of the photocatalytically active sites that can form CO *via* the bidentate formate species as the intermediate.

As the Ag cocatalyst on heterogeneous photocatalysts is a promising candidate for selective CO_2 conversion, we employed an Ag cocatalyst for the photocatalytic conversion of CO_2 . Photocatalysts for CO_2 conversion have been actively developed over the last decade—most loaded with Ag cocatalysts, as partially displayed in Table 2.^[17]

The listed photocatalysts successfully converted CO₂ into CO with more than 50% selectivity toward CO ($S_{CO} > 50\%$) and approximately stoichiometric O₂ evolution ($e^-/h^+ = \sim 1$). Sr₂KTa₅O₁₅,^[18] K₂LnTa₅O₁₅ (Ln=La, Pr, Nd, Sm, Gd, Tb, Dy, or Tm),^[19] SrNb₂O₆,^[20] Ta₂O₅,^[21] Ga₂O₃,^[22] La₂Ti₂O₇,^[23] and Al-doped SrTiO₃^[24] have also been used as heterogeneous photocatalysts for H₂O splitting or H₂ evolution, with a drastic improvement in selectivity toward CO evolution achieved by modifying the photocatalysts with Ag-containing cocatalysts.

Furthermore, the particle size of the Ag cocatalyst on the heterogeneous photocatalysts significantly affected the photocatalytic activity. Generally, Ag metal particles show increased work function when the particle size is reduced^[25] and promote charge separation because the Schottky barrier height at the metal-semiconductor junction, i.e., the difference between the metal work function and the semiconductor electron affinity, becomes large.^[26] The FT-IR spectra shown in Figure 3 corroborate this result, i.e., the formation of the bidentate formate species was enhanced on the relatively small Ag particles (0.1 wt.% $Ag/Ga_2O_3).$

Relatively small Ag particles are formed using a chemical reduction (CR) method.^[27] Ag cocatalysts tend to form dispersed nanoparticles with relatively small particle diameters via the CR method, while conventional photodeposition (PD) and impregnation (IMP) methods result in relatively large or aggregated Ag particles.^[13] Therefore, the CR method is often employed in addition to the conventional PD and IMP methods, as listed in Table 2. However, Ag cocatalysts loaded via the CR method face difficulties because of their instabilities. In the CR method, Ag⁺ from precursors such as AgNO₃, Ag₂SO₄, C₈H₁₅O₂Ag (silver 2ethylhexonate), and AgClO₄ is reduced to metallic Ag by reducing agents such as NaH₂PO₂, NaBH₄, C₆H₅O₇Na₃, and N₂H₄, followed by deposition of Ag on the surface of the photocatalysts. Therefore, in several cases, the loaded Ag nanoparticles were distributed over the entire surface of the photocatalyst, with some deposited on the oxidation sites where photogenerated holes were transferred. These Ag nanoparticles can easily be oxidised by the photogenerated holes and dissolve in the reaction suspension during photocatalytic reactions, resulting in reprecipitation over the other Ag nanoparticles because the Ag cocatalyst received the photogenerelectrons and reduced Ag⁺ in the reaction ated suspension. $^{\scriptscriptstyle [13,17(o)]}$ This dissolution and reprecipitation can cause undesirable growth of the Ag nanoparticles. Consequently, the photocatalytic activity tends to gradually decrease over time. Strategies and methods for blocking the instability of cocataon heterogeneous photocatalysts lvsts have been investigated. $^{\scriptscriptstyle [28]}$ Figure 4 shows the formation rates of the products and the selectivity toward CO evolution in the photocatalytic conversion of CO_2 by H_2O over previously

Table 2. Summary of photocatalysts tested for the photocatalytic reduction of CO ₂ by H ₂ O.									
Photocatalyst	Loading method	Formation r	Formation rate of product/ μ mol h ⁻¹			e^{-}/h^{+}	Ref.		
		H ₂	0 ₂	СО					
Ag/La ₂ Ti ₂ O ₇ ^a	CR	4.9	5.3	5.2	52	0.95	[17(a)]		
Ag/SrO/Ta ₂ O ₅ ^a	IMP	19	24	36	65	1.1	[17(b)]		
Ag/ZnGa ₂ O ₄ ^a	CR	8.5	74	160	95	1.1	[17(c)]		
Ag/Sr ₂ KTa ₅ O ₁₅ ^a	CR	8.3	34	66	89	1.1	[17(d)]		
Ag/ZnGa ₂ O ₄ /Ga ₂ O ₃ ^a	PD	17	70	120	87	1.0	[17(e)]		
Ag/SrNb ₂ O ₆ ^a	CR	1.1	25	51	98	1.1	[17(f)]		
$Ag/Sr_{1.6}K_{0.37}Na_{1.43}Ta_5O_{15}^{a}$	CR	16	54	95	86	1.0	[17(g)]		
Ag/Yb ₂ O ₃ /Ga ₂ O ₃ ^a	PD	140	170	210	59	1.0	[17(h)]		
Ag/Pr/Ga ₂ O ₃ ^a	PD	65	150	250	79	1.0	[17(i)]		
Ag/Mg–Al LDH/Ga ₂ O ₃ ^a	IMP	130	170	210	62	1.0	[17(j)]		
Ag/K ₂ YTa ₅ O ₁₅ ^a	CR	16	43	92	85	1.3	[17(k)]		
Ag–Cr/Ga ₂ O ₃ ^a	PD	92	330	530	85	0.95	[17(l)]		
Ag–Cr/CaGa ₄ O ₇ /Ga ₂ O ₃ /CaO ^a	PD	49	400	830	95	1.1	[17(m)]		
Ag/Al-SrTiO ₃ ^b	CR	0.20	3.6	7.2	97	1.0	[17(n)]		
Ag–Co/Mg-SrTiO ₃ ^c	CR	0.055	8.9	20	99.7	1.1	[17(°)]		

Light source: [a] 400 W high-pressure Hg lamp. [b] 400 W high-pressure Hg lamp with a Pyrex jacket (λ > 300 nm). [c] Monochromatic LED lamp at 365 nm. CR: chemical reduction; PD: photodeposition; IMP: impregnation.

24, 22, Downloaded from https://chemistry-europe.onlinelibrary.wiley.com/doi/10.1002/cccc.202400594 by Cochrane Japan, Wiley Online Library on [28/11/2024]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

Review doi.org/10.1002/cctc.202400594



Figure 4. Formation rates of CO (red), H_2 (blue), and O_2 (green), and the selectivity toward CO evolution (black diamond) in the photocatalytic conversion of CO₂ by H_2O over Mg-doped SrTiO₃ photocatalyst with Ag and Co cocatalysts loaded by the (a) CR and (b) PD methods.

reported Mg-doped SrTiO₃ photocatalysts with Ag and Co cocatalysts loaded by CR and PD methods.^[17(o)] In contrast to the PD method, the photocatalyst with cocatalysts loaded by the CR method showed gradually reduced photocatalytic activity, while the initial activity was notable. The unstable photocatalytic performance of photocatalysts loaded with the Ag cocatalyst *via* the CR method is a problem that should be addressed.

When the Ag cocatalyst is applied to photocatalytic reactions under visible light irradiation, possible advantages and disadvantages are suggested. In terms of the disadvantages, the light absorption of solid photocatalysts can be weakened by light shielding owing to the presence of Ag nanoparticles. Ag exhibits plasmonic absorption in the visiblelight region in its metal and nanoparticle forms.^[29] Therefore, if the amount of loaded Ag cocatalyst is inappropriately large, photoirradiation of the photocatalyst can be interrupted, resulting in insufficient light absorption. In contrast, some studies have shown that photogenerated electrons can be enhanced by the plasmonic absorption of Ag nanoparticles. Ag nanoparticles can produce photogenerated electrons via surface plasmon resonance (SPR) in addition to the intrinsic band gap excitation of the photocatalyst. Zou et al. fabricated double-shelled Ag-TiO₂ hollow spheres and applied them to the photocatalytic conversion of CO2 into CH4 under visible-light irradiation.^[30] As shown in Figure 5, CH₄ was generated over Ag-



Figure 5. Photocatalytic CH_4 evolution amounts as a function of light irradiation time for (a) Ag-TiO₂ hollow spheres and (b) bare TiO₂ under visible light (>420 nm) illumination. (c) Schematic illustration of the Ag-SPR-enhanced photocatalytic activity of Ag-TiO₂ under visible light.^[30]

TiO₂, although bare TiO₂ showed negligible responsiveness to visible light, suggesting that the electrons generated from the SPR-induced Ag migrated to and were injected into the conduction band (CB) of TiO₂, contributing to the improvement in the photocatalytic performance, as schematically illustrated in Figure 5(c). This strategy is applicable when the Ag cocatalyst is used in photocatalytic reactions under visible-light irradiation.^[31]

Loading of the Ag cocatalyst is a promising method for achieving selective and enhanced conversion of CO_2 using H₂O. Nanoparticles of Ag metal on the surface of heterogeneous photocatalysts can efficiently extract photogenerated electrons and transfer them to adsorbed carbon species to generate CO. Photocatalysts reported for H₂O splitting or H₂ evolution can be used for photocatalytic CO₂ conversion by modification with Ag cocatalysts.

2.2. Cocatalysts for H₂O Oxidation

In the field of photocatalysis, loading cocatalysts supplying active sites for CO₂ reduction (e.g. Ag, Au, and Cu) is considered an indispensable strategy for achieving the photocatalytic conversion of CO₂.^[32] Promoting the oxidation of H₂O often enhances the reduction of CO₂ because both reduction and oxidation occur over a single photocatalyst particle. However, many studies on the photocatalytic conversion of CO₂ using H₂O as the electron donor have focused only on the reduction of CO₂. The oxidation of H₂O is recognised as a thermodynamically and kinetically unfavourable reaction because it requires the transfer of four electrons and a relatively large overpotential.^[33] Therefore, improving photocatalytic H₂O oxidation could help achieve enhanced photocatalytic conversion of CO₂ using H₂O.^[34] Hence, cocatalysts designed for enhanced H₂O oxidation should be actively developed. In addition to precious metal oxides, such as RuO₂ and IrO₂,^[35] transition metal oxides, phosphates, hydroxides, and oxyhydroxides are considered effective cocatalysts for promoting H₂O oxidation.^[36]

Cobalt phosphate, often represented as Co-Pi, is a wellknown catalyst for H₂O oxidation in electrochemical H₂O splitting.^[37] Co-Pi was first reported by Nocera et al. in 2008, who examined the possibility of Co-Pi formation via electrolysis over an indium tin oxide (ITO) electrode in a neutral potassium phosphate electrolyte containing Co²⁺.^[38] The Co-Pi-loaded ITO electrode demonstrated the electrochemical activity for H₂O oxidation at neutral pH with low overpotentials, with almost 100% Faradaic efficiency of O₂ evolution observed. Inspired by this discovery, Gamelin et al. applied the Co-Pi as a cocatalyst on an α -Fe₂O₃ photoanode for photoelectrochemical H₂O oxidation.^[39] The Co–Pi/ α -Fe₂O₃ composite photoanode was prepared by electrodeposition of the Co-Pi on α -Fe₂O₃ and revealed that the Co-Pi/a-Fe2O3 photoanode enabled smaller overpotentials for photoelectrochemical H₂O oxidation under simulated solar irradiation (AM 1.5 G) compared to the bare α -Fe₂O₃ photoanode. Furthermore, incident photon to current efficiency (IPCE) of the Co-Pi/a-Fe₂O₃ photoanode was above 15% at 550 nm at the applied potential of 1 V vs. RHE, while

Chemistry Europe

European Chemical Societies Publishing



Figure 6. Current–potential characteristics of a BiVO₄ photoanode obtained under AM 1.5 G illumination (100 mM cm⁻²) in (a) 0.1 M KH₂PO₄ and (b) 0.1 M KH₂PO₄ with 0.1 M Na₂SO₃, both at pH 7. a' and b' are the corresponding LSV obtained in the dark (scan rate = 10 mV s⁻¹). Reprinted with permission.^[41(a)] Copyright 2012 American Chemical Society.



Figure 7. Current–potential characteristics of BiVO₄/FeOOH photoanodes obtained in 0.1 M KH₂PO₄ (pH 7) under AM 1.5 G illumination (100 mM cm⁻²); solid line: top 10% sample; dotted line: average sample; grey lines: dark currents for both cases (scan rate = 10 mV s⁻¹). Reprinted with permissio-n.^[41(a)] Copyright 2012 American Chemical Society.

the bare α -Fe₂O₃ showed the negligible photocurrent. Co modification of α -Fe₂O₃ from Co(NO₃)₂ resulted in a smaller photocurrent density than that from phosphate, highlighting the effectiveness of the Co–Pi cocatalyst, thus suggesting that the deposition of cocatalysts for H₂O oxidation facilitates the interfacial hole transfer from α -Fe₂O₃ to Co–Pi; moreover, electrodeposition of Co–Pi onto α -Fe₂O₃ passivates surface defects.

Transition-metal oxyhydroxides are also effective catalysts for enhanced H₂O oxidation. In particular, CoOOH, FeOOH, and NiOOH deposited on photoanodes have been frequently reported as essential cocatalysts for photoelectrochemical H₂O oxidation^[40] as they contribute to the improvement in the photocurrent densities and a shift in the onset potential of the photocurrent in the negative direction by several hundred millivolts. Seabold et al. reported an FeOOH cocatalyst deposited on a BiVO₄ photoanode using an electroassisted photodeposition method.^[41] Figure 6 and Figure 7 display the linear sweep voltammetry (LSV) of the bare $BiVO_4$ and γ -FeOOHdeposited BiVO₄ photoanodes, respectively, under the irradiation with simulated sunlight (AM 1.5 G) or in the dark. Comparing Figures 6(a) and 7, the FeOOH deposited on BiVO₄ remarkably improved the anodic photocurrent by efficiently collecting photogenerated holes from the BiVO₄ layer. Furthermore, the onset potential of the photocurrent for FeOOH/BiVO₄ was 500 mV lower than that for bare BiVO₄. Therefore, the FeOOH/BiVO₄ photoanode showed an outstanding photocurrent density, particularly in the low-bias region (below 0.8 V vs. RHE), and the generated photocurrent density was the highest among all known BiVO₄-based photoanodes at that time, highlighting the potential of the FeOOH cocatalyst for enhanced H₂O oxidation.

Recently, an FeOOH cocatalyst was successfully applied for the photocatalytic conversion of CO₂ using H₂O. Table 3 shows the results of the photocatalytic conversion of CO₂ by H₂O over Al-doped SrTiO₃ (Al-SrTiO₃) photocatalysts loaded with different cocatalysts.^[42] Ag/Al-SrTiO₃ produced a slight amount of CO (R_{co} =2.6 µmol h⁻¹). The formation rates of both CO and O₂ were dramatically enhanced (R_{co} =32.3 µmol h⁻¹ and R_{o2} = 17.5 µmol h⁻¹) by loading the Fe cocatalyst along with the Ag cocatalyst. Stoichiometric O₂ evolution (e^-/h^+ =0.93) was also observed in the case of the Ag and Fe cocatalysts. Photogenerated electrons and holes on Al-SrTiO₃ show an isotropic

Table 3. Photocatalytic conversion of CO₂ into CO by H₂O over different dual cocatalyst-modified photocatalysts ^a. Reprinted with permission.^[42] Copyright 2021 American Chemical Society.

Photocatalyst	Formation rates of products (μ mol h ⁻¹)		n ⁻¹)	Consumed e^-/h^+	Selectivity toward CO (%)
	H ₂	O ₂	CO		
Ag/Al-SrTiO ₃	0.3	1.3	2.6	1.03	89.7
Ag – Fe/Al-SrTiO ₃	0.3	17.5	32.3	0.93	99.1
Ag – Co/Al-SrTiO ₃	11.2	18.8	24.6	0.95	68.7
Ag – Ni/Al-SrTiO ₃	10.4	5.30	2.20	1.19	17.4
Ag – Pt/Al-SrTiO ₃	10.2	3.00	0.00	1.68	0.0

[a] Photocatalyst: 0.5 g; cocatalyst loading amount: 1.7 mol.% Ag; amount of cocatalyst (Pt, Fe, Co, and Ni): 0.85 mol.%; reaction solution: 1.0 L, 0.1 M NaHCO₃; CO₂ flow rate: 30 mL min⁻¹; light source: 400 W high-pressure Hg lamp with a Pyrex jacket to cut off light at λ < 300 nm.

distribution, i.e., they are transferred to the {100} and {110} facets of the Al-SrTiO₃ surface, respectively.^[24] We employed the photodeposition method to load dual Ag and Fe cocatalysts on Al-SrTiO₃, and EDX measurements of the Ag and Fe-loaded Al-SrTiO₃ surface revealed that the Ag and Fe cocatalysts were selectively deposited on the {100} and {110} facets, respectively. Furthermore, the loaded Fe was revealed to form α -FeOOH on Al-SrTiO₃ by XAFS analysis. Accordingly, we considered that α -FeOOH on Al-SrTiO₃ serves as the cocatalyst to promote H₂O oxidation and reduces the recombination of the photogenerated electron/hole pair in the single Al-SrTiO₃ particles, while the Ag cocatalyst acts as the reaction sites for CO₂ reduction, as explained above. Moreover, we discovered that the loading of the Co cocatalyst along with the Ag cocatalyst promoted both CO and O₂ evolution. Hence, such transition-metal-based cocatalysts, including Fe cocatalyst (Table 3)-effective for electrochemical or photoelectrochemical H₂O oxidation-can also promote charge separation over heterogeneous photocatalysts by capturing photogenerated holes. Consequently, CO₂ reduction, i.e., the main objective of this study, can be simultaneously accelerated. Thus, this strategy contributes considerably toward improving the photocatalytic performance of CO₂ conversion using H₂O.

Notably, the simultaneous deposition of cocatalysts designed for reduction and oxidation sometimes deteriorates the photocatalytic performance compared to the case of a single cocatalyst. Some studies have suggested that if two kinds of cocatalysts are randomly loaded onto a single photocatalyst using the conventional impregnation method or the chemical reduction method, the probability of collision between photogenerated electrons and holes increases, possibly inducing unfavourable charge recombination.^[43] In addition, some studies have suggested that loaded transition-metal-based cocatalysts promote both photocatalytic H₂O oxidation and CO₂ reduction. For instance, the Co-Pi cocatalyst introduced above was reported to capture photogenerated holes and function as an adsorption site for CO2.[44] Therefore, the Co-Pi cocatalyst can positively affect both the CO₂ reduction and H₂O oxidation reactions, particularly when Co-Pi is loaded randomly on a photocatalyst. Thus, determining the roles of cocatalysts, i.e., whether the cocatalysts promote reduction and/or oxidation reactions, should be carefully considered.

The transfer of photogenerated holes from the surface of the photocatalyst to the cocatalyst was observed using transient absorption measurements.^[45] Yamakata *et al.* performed time-resolved infrared absorption spectroscopy to investigate the behaviour of photogenerated holes in a CoO_x -loaded LaTiO₂N photocatalyst,^[46] which exhibited high photocatalytic activity for O₂ evolution.^[47] In this experiment, the transient absorptions at 17000 cm⁻¹, 6000 cm⁻¹, and 2000 cm⁻¹ were measured to observe the behaviour of photogenerated holes, trapped electrons, and free electrons, respectively. Figure 8 shows the decay processes of the photogenerated species on the CoO_x -loaded LaTiO₂N photocatalyst in the microsecond region. As shown in Figure 8(A), the loading of 0.5 wt.% CoO_x accelerated the decay of photogenerated holes by capturing them. However, as seen in Figure 8(B) and 8(C), the numbers of



Figure 8. Decay of transient absorption of CoO_x -loaded LaTiO₂N photocatalysts in a vacuum. Transient absorption was measured at 17000 cm⁻¹ (A), 6000 cm⁻¹ (B), and 2000 cm⁻¹ (C), as indicated in the plots. The sample was excited by 355 nm UV laser pulses (6 ns duration, 0.5 mJ cm⁻², 1 Hz). The inset shows the decay in the second region (pump pulse repetition rate at 0.01 Hz). Reprinted with permission.^[46] Copyright 2014 American Chemical Society.

trapped and free electrons increased in the presence of CoO_v suggesting that the photogenerated electrons in LaTiO₂N hardly recombined with the holes captured by CoO_x. As a result, the lifetimes of the trapped and free electrons increase, i.e., electrons and holes are spatially separated between LaTiO₂N and CoO_x. Furthermore, the initial process of charge separation on the Pt or CoO_x-loaded LaTiO₂N photocatalysts was investigated using femtosecond time-resolved absorption spectroscopy. As shown in Figure 9(B), the decay curves for free electrons on bare and Pt-loaded LaTiO₂N were almost identical in the picosecond region. The decay curves for the holes were also not affected by the Pt loading (Figure 9(A)), suggesting that electron transfer from LaTiO₂N to Pt did not occur between 0 and 1000 ps. As for CoO_x loading, apparent decay acceleration at 17000 cm⁻¹ was confirmed compared to the bare LaTiO₂N (Figure 9(A)). Additionally, the number of free electrons was increased by CoOx loading in the picosecond region (Figure 9(B)); in other words, the photogenerated holes were captured within a few picoseconds by the CoO_x cocatalyst. Electron transfer to Pt can be observed in the microsecond

^{24, 22,} Downloaded from https://chemistry-europe.onlinelibrary.wiley.com/doi/10.1002/cccc.202400594 by Cochrane Japan, Wiley Online Library on [28/11/2024]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License



Figure 9. Decay of transient absorption at 17000 cm⁻¹ (A) and 2000 cm⁻¹ (B) for bare and CoO_x⁻ and Pt-loaded LaTiO₂N photocatalysts measured in air. The sample was excited by 500 nm laser pulses (90 fs duration, 6 μ J, 500 Hz). Reprinted with permission.^[46] Copyright 2014 American Chemical Society.

region, suggesting that hole transfer to CoO_x was significantly faster than electron transfer to Pt in the case of LaTiO₂N. H₂ evolution over LaTiO₂N was not improved by Pt loading, while O₂ evolution was drastically enhanced by CoO_x loading.^[47] These results indicate that inefficient electron transfer to Pt and effective hole transfer to CoO_x are responsible for the unbalanced improvement of photocatalytic activity over Pt or CoO_x loaded LaTiO₂N.

As stated in the Introduction, NaHCO₃ and KHCO₃ are considered as buffers to increase the solubility of CO₂ in the reaction solution. However, various researchers suggested another role for these buffers, that is, HCO_3^- promotes the oxidation of H₂O, which may act as a hole scavenger. Sayama *et al.* reported the highly promoted photoelectrochemical H₂O oxidation using a BiVO₄/WO₃ photoanode in an aqueous solution of KHCO₃.^[48] They discovered the specific H₂O₂ production in a KHCO₃ electrolyte solution, whereas trace amounts of H₂O₂ were generated in a K₂SO₄, phosphate buffer and H₃BO₃ aqueous solution. HCO₄⁻, which was generated *via* oxidation of HCO₃⁻, oxidised H₂O into H₂O₂. The photocatalytic oxidation of H₂O₄⁻ and H₂O₂. Some reports showed the generation of H₂O₂ by the photocatalytic oxidation of H₂O in

ChemCatChem 2024, 16, e202400594 (10 of 17)

aqueous solutions containing $HCO_3^{-[49]}$ Otherwise, H_2O_2 easily decomposes to O_2 under photoirradiation, resulting in a stoichiometric O_2 evolution. The behaviours of HCO_4^- in the photocatalytic conversion of CO_2 is still under discussion. Intermediate species of oxidation, which are recognized as strong oxidants, may interact with CO_2 reduction products or other intermediates, and inhibit the progress of CO_2 reduction.

Promotion of H_2O oxidation plays an important role in enhancing the photocatalytic conversion of CO_2 by H_2O over heterogeneous photocatalysts. In the fields of electrolysis and photoelectrolysis, transition metal oxides, phosphates, hydroxides, and oxyhydroxides are effective as materials for H_2O oxidation because they can easily extract photogenerated holes from the surface of photocatalysts and reduce charge recombination, thereby contributing to the improvement in photocatalytic activity.

2.3. Suppression of H₂ Evolution

The selectivity toward a desired product is generally considered an important factor as well as formation rates of products and catalyst stability, in evaluating catalyst ability. Accordingly, in the case of photocatalytic CO₂ conversion using H₂O, the suppression of competitive H₂ evolution is indispensable for increasing the S_{co} . However, improving S_{co} is a considerable challenge as H₂ evolution from $H^+(E^{\circ}(H^+/H_2) = -0.41$ V vs. NHE at pH=7) is thermodynamically more favoured than CO production from CO₂ ($E^{\circ}(CO_2/CO) = -0.53$ V vs. NHE at pH = 7). Therefore, undesired H₂ evolution could be accelerated in addition to CO₂ reduction by improving the properties of the photocatalyst, such as band alignment, particle shape, and light absorption. Hence, appropriate surface modification of photocatalysts for the suppression of H⁺ reduction is key to achieving high S_{CO2RPs} rather than improving the photocatalytic activity of the bulk.

Ga₂O₃ is known to be a highly active photocatalyst because of the sufficiently negative potential of its conduction band (dominated by the Ga 4 s orbitals) and the suitable potential of its valence band maximum for $\mathsf{H}_2\mathsf{O}$ oxidation. $^{\scriptscriptstyle[22,50]}$ Therefore, Ga₂O₃ is a promising candidate for the photocatalytic conversion of CO₂ by H₂O. However, in the case of photocatalytic CO_2 conversion, the bare Ga_2O_3 photocatalyst principally reduced H^+ rather than CO_2 , resulting in an insufficient S_{CO} . Furthermore, introducing the aforementioned Ag cocatalysts does not necessarily improve S_{CO} , indicating the difficulty of increasing S_{CO} over the Ga₂O₃ photocatalyst.^[51] We addressed this problem by surface modification of the Ga₂O₃ photocatalyst with Zn species^[52]—introducing Zn²⁺ ions into Ga₂O₃ using the conventional wet impregnation method (denoted as Zn-Ga₂O₃), followed by loading the Ag cocatalyst using the photodeposition method. Table 4 lists the formation rates of H₂, O₂, and CO in the photocatalytic conversion of CO₂ using H₂O over the four Ga₂O₃-based photocatalysts. Pristine Ga₂O₃ exhibited a considerable CO formation rate. However, the formation rate of H₂ was much higher than that of CO, resulting in $S_{CO} < 50$ %, even in the presence of the Ag cocatalyst (entries 2 and 4). As

Chemistry Europe

European Chemical Societies Publishing



Societies Publishing

a [52a]								
Sample	Formation rate ^b (μ mol h ⁻¹)		Consumption r	rate (µmol h^{-1})	Selectivity toward CO (%)			
	H ₂	O ₂	CO	Electrons	Holes			
Zn-Ga ₂ O ₃ (homemade)	16.9	70.1	117	268	280	87.4		
Ga ₂ O ₃ (homemade)	266	126	95.3	723	504	26.4		
Zn-Ga ₂ O ₃ (commercial)	14.4	56.1	82.0	192	224	85.1		
Ga ₂ O ₃ (commercial)	101	72.7	73.7	349	291	42.2		

[a] Amount of catalyst: 1.0 g, volume of water: 1.0 L, flow rate of CO_2 : 30 mLmin⁻, concentration of NaHCO₃: 0.1 molL⁻. [b] Rates of evolution of all products reacted quickly in a steady state (after approximately 2 h of photoirradiation). Steady-state formation rates were obtained by exponential curve fitting.

presented in Entries 1 and 3, above 80% of S_{CO} was achieved by the impregnation of Zn^{2+} in both cases of the homemade Ga_2O_3 and the commercial one. Note that the sum of the reduction products ($R_{H2} + R_{CO}$) over Zn-Ga₂O₃ is smaller than that over the corresponding Ga₂O₃; in other words, Zn introduction affects S_{CO} rather than the intrinsic photocatalytic activity of Ga₂O₃. The considerable formation rate of CO, corresponding to the excellent photocatalytic activity of Ga₂O₃ and sufficient S_{CO} derived from surface modification with Zn and Ag, continued for at least 48 h with good stability, accompanied by almost stoichiometric O₂ evolution.

Further investigation revealed that the ZnGa₂O₄ layer formed on the surface of Ga₂O₃ efficiently eliminated H⁺ reduction.^[53] We fabricated Ag-loaded Ga₂O₃ photocatalysts modified with different amounts of Zn species. XRD patterns, SEM images, UV-Vis spectra, and N₂ adsorption/desorption isotherms of the samples at 77 K revealed that the crystallinity, crystal structure, particle size, morphology, absorption edge, and specific surface area of Ga_2O_3 were not affected by Zn modification. Furthermore, the particle size of the Ag cocatalyst loaded onto Zn-Ga₂O₃ was consistent among the samples; in other words, the Zn species caused insignificant changes in the particle size, dispersion, chemical state, and loading amount of the Ag cocatalyst. In contrast, the state of the Zn species on the surface of Ga₂O₃ depends on the Zn loading amount. XRD patterns and Zn K-edge XANES spectra of Zn-Ga₂O₃ clarified that the high-temperature treatment of Zn(NO₃)₂-impregnated Ga₂O₃ induces a surface reaction between Zn(NO₃)₂ and Ga₂O₃ to form a $ZnGa_2O_4$ layer on the surface of Ga_2O_3 . Using extremely low amounts of Zn (0.1%) results in isolated and dispersed Zn ions on the surface of Ga₂O₃. Higher than 0.5 mol.% Zn content resulted in the formation of a mixture of the ZnGa₂O₄ layer and ZnO; for samples with more than 3.0 mol.% Zn species, the compounds were identical to purephase ZnGa₂O₄. Figure 10 shows the formation rates of the products and S_{CO} in the photocatalytic conversion of CO₂ using H₂O over Ag/Zn-Ga₂O₃ with varying amounts of Zn species. As mentioned previously, H₂ evolution was dominant in the absence of Zn species in Ag/Ga₂O₃. However, the formation rate of H₂ decreased proportionally with an increase in the amount of Zn species and was negligible over Ga₂O₃ modified with higher than 3.0 mol.% of Zn species. Importantly, the formation rate of CO was not influenced by the amount of added Zn



Figure 10. Rates of CO (black), O_2 (white), and H_2 (grey) evolution and selectivity toward CO evolution in the photocatalytic conversion of CO_2 with H_2O over Ag-loaded Zn-modified Ga_2O_3 with various amounts of Zn species. Reproduced from Ref.^[53] with permission from the Royal Society of Chemistry.

species, suggesting that the Zn species on Ga₂O₃ selectively erased the active sites for reducing H⁺ over Ga₂O₃, while the ability of Ga₂O₃ to reduce CO₂ was not altered by introducing Zn. To confirm the function of ZnGa₂O₄, a physical mixture of ZnGa₂O₄ and Ga₂O₃ was tested for the photocatalytic conversion of CO₂ using H₂O, resulting in a similar S_{CO} to that of Ag/ Ga_2O_3 . These results clearly indicate that covering a Ga_2O_3 photocatalyst with a ZnGa₂O₄ layer considerably inhibited H₂ production. Furthermore, UV-vis and X-ray photoelectron spectroscopy revealed a more negative conduction band minimum of ZnGa₂O₄ than that of Ga₂O₃, contributing to the transfer of photogenerated electrons from ZnGa₂O₄-Ga₂O₃ via a type II electron transfer (Figure 13). Consequently, the electron density in the ZnGa₂O₄ structure for H⁺ reduction diminished with the electrons mainly extracted from the Ag cocatalyst, that is, the active sites for CO₂ reduction. According to a previous study, Ga₂O₃ without Ag produces only H₂, which was blocked by the formation of ZnGa2O4. Notably, the valence band potential of Ga₂O₃ was more positive than that of ZnGa₂O₄, indicating that photogenerated holes can be transferred from Ga_2O_3 -Zn Ga_2O_4 and H_2O oxidation was not inhibited. The selective suppression of undesirable H₂ evolution was achieved by modifying the Ga₂O₃ photocatalyst with a ZnGa₂O₄ layer, as depicted in Figure 11, while the reason why ZnGa₂O₄ layer













Figure 11. Proposed mechanism for the photocatalytic conversion of CO₂ in and with H₂O over Ag-loaded Ga₂O₃ (A), Ag-loaded Zn-modified Ga₂O₃ with a low Zn content (B), and Ag-loaded Zn-modified Ga₂O₃ with a high Zn content (C). Reproduced from Ref.^[53] with permission from the Royal Society of Chemistry.

blocks competitive H_2 evolution is still under investigation. Thus, forming an inhibitor layer to erase H_2 evolution sites with suitable band alignment can play an important role in enhancing S_{CO} during the photocatalytic conversion of CO_2 using H_2O .

2.4. Materials for CO₂ Adsorption

Surface modification of heterogeneous photocatalysts with materials exhibiting strong CO₂ adsorption properties can increase the local CO₂ concentration on the surface of the photocatalysts, supplying more CO₂ molecules to form CO₂RPs, which improves R_{CO2RPs} . Furthermore, this strategy did not promote H₂ evolution from H₂O, leading to a simultaneous improvement in S_{CO2RPs} . Generally, CO₂ molecules act as Lewis acids and are preferentially adsorbed on basic sites on the surface of photocatalysts.^[54] CO₂RPs evolution is remarkably diminished by adding acidic anions such as SO₄^{2–} and NO₃⁻



because these anions easily poison the basic sites where CO_2 should be adsorbed.^[4(a)] Therefore, solid basic hydroxides or oxides such as NaOH,^[55] MgO,^[56] ZrO₂,^[32(a),57] and SrO^[17(b)] are suitable for these materials because they can capture CO_2 molecules. MgO, a typical alkaline-earth-metal-based oxide, is a representative material which provides basic sites for CO_2 adsorption. Fukuda and Tanabe demonstrated that two types of bidentate carbonates are formed on MgO at room temperature, as depicted in Figure 12, and discovered that species B is weakly adsorbed on MgO and easily reduced to a surface-active intermediate rather than species A.^[58]

Inspired by these reports, Xie et al. elucidated that modifying a Pt-loaded TiO₂ photocatalyst with MgO significantly enhances both R_{CH4} and S_{CO2RPs} .^[59] Pt/TiO₂ showed low S_{CO2RPs} in the photocatalytic conversion of CO_2 by H_2O vapour in the absence of MgO, whereas Pt loaded on TiO₂ exhibited the best ability to extract photogenerated electrons and accelerate the separation of electron/hole pairs among several noble metals (Pt, Pd, Rh, Au, and Ag) on TiO₂. Various amounts of MgO were impregnated onto the surface of TiO₂, followed by Pt loading via photodeposition. While the mean size of Pt was almost independent of the presence of MgO, the amount of chemisorbed CO₂ on TiO₂ evaluated by CO₂ temperature-programmed desorption (CO2-TPD) analysis clearly increased with increasing MgO content, as expected based on previous reports. As a result, R_{CH4} and S_{CO2RPs} were enhanced with an increase in the MgO content from 0-1 wt.%. The consumption rate of photogenerated electrons-calculated from the formation rates of CO₂RPs and H₂, did not change significantly with MgO addition—suggesting that the intrinsic properties of TiO₂ were not altered by MgO. These results clearly indicate that an increase in chemisorbed CO2 molecules was responsible for the enhanced R_{CH4} and S_{CO2RPs} .^[60]

Rare-earth metal oxides are also known for CO₂ capture and storage.^[61] In particular, Y,^[62] La,^[63] Pr,^[64] Nd,^[65] Sm,^[66] and Yb^[66] oxides have been reported to show interesting features; their surfaces can be easily transformed into the corresponding hydroxide and/or carbonate species, indicating that these rareearth metal oxides exhibit the potential for CO₂ capture and storage. Among these, Pr cations are proven particularly suitable for the evolution of CO from CO₂. Borchert *et al.* reported that CO is hardly adsorbed on Pr cations,^[67] indicating that Pr cations can promote the desorption of the generated CO during the photocatalytic conversion of CO₂. Based on these



Figure 12. Nature of two speculated species. Reprinted with permission.^[58(d)] Copyright 2004 American Chemical Society.

© 2024 The Authors. ChemCatChem published by Wiley-VCH GmbH



unique properties, we synthesised a Pr-modified Ga₂O₃ photocatalyst *via* the impregnation method with various amounts of Pr (denoted as *x* Pr/Ga₂O₃, where *x* represents the content of Pr as a molar percentage), followed by the loading of the Ag cocatalyst by the photodeposition method.^[17(0] XRD, XAFS, FT-IR, and SEM analyses confirmed that a mixture of Pr(OH)₃ and Pr₂O₂CO₃ was formed on Ga₂O₃ with a high dispersion, as mentioned above. Table 5 shows the formation rates of products in the photocatalytic conversion of CO₂ in a 0.1 M aqueous solution of NaHCO₃ over Ag/Ga₂O₃ with or without Pr modification. As introduced in the previous section, bare Ga₂O₃ exhibited a low *S*_{CO} even in the presence of the Ag cocatalyst. However, the modification of Ga₂O₃ with Pr significantly improved both *R*_{CO} and *S*_{CO} in all Pr/Ga₂O₃ samples. We calculated the amount of preserved CO₂ on the photocatalysts using the peak areas in the CO₂-TPD profiles and found that the amount of preserved CO₂ proportionally increased with the Pr content on Ga₂O₃. Furthermore, we elucidated that Pr(OH)₃ and Pr₂O₂CO₃ on Ga₂O₃ can easily be converted into Pr₂(OH)_{2(3-x}(CO₃)_x and Pr₂(CO₃)₃·8H₂O in 0.1 M NaHCO₃. Subsequently, the Pr species can be transformed to only Pr₂(CO₃)₃·8H₂O by flowing CO₂. Therefore, Pr(OH)₃ and Pr₂O₂CO₃—easily generated from Pr oxides by exposure to air—can capture and store CO₂ to form the Pr₂(CO₃)₃·8H₂O in the NaHCO₃ solution and flowing CO₂, contributing to an increase in the CO₂ concentration on the surface of Ga₂O₃—responsible for enhanced *R*_{CO} and *S*_{CO} in the photocatalytic conversion of CO₂ by H₂O.

Table 6 summarises the formation rates or amounts of products and S_{CO2RPs} over several photocatalysts, with or without materials for CO₂ adsorption during the photocatalytic con-

Table 5. Surface area, CO_2 stored, product formation rate, selectivity toward CO evolution, and electron balance for photocatalytic conversion of CO_2 using H_2O as an electron donor. Reproduced from Ref. ⁽¹⁷⁰⁾ with permission from the Royal Society of Chemistry.								
Entry	Photocatalyst	Surface area ^a ($m^2 g^{-1}$)	CO ₂ stored ^b (µmol g ⁻¹)	Formation rate ^c (μ mol h ⁻¹)			Selectivity ^d (%)	e^{-}/h^{+}
				H ₂	O ₂	СО		
1	Bare Ga ₂ O ₃	12	7.90	131	124	136	51.0	1.07
2	1.0 Pr/Ga ₂ O ₃	9.4	119	102	148	215	67.7	1.07
3	3.0 Pr/Ga ₂ O ₃	8.9	382	64.7	150	249	79.4	1.04
4	5.0 Pr/Ga ₂ O ₃	6.9	425	50.1	129	236	82.5	1.11
5	10.0 Pr/Ga ₂ O ₃	8.0	498	39.0	88.9	163	80.7	1.14
1								

[a] BET surface area. [b] Measured by CO₂-TPD. [c] Formation rate after 1 h of irradiation. [d] Selectivity toward CO evolution.

Table 6.	Summary of the	materials for CO ₂ adso	rption to enhance R_{co2}	RPs and S _{CO2RPs.}				
Entry	Photocatalyst	CO ₂ adsorption	Formation rate of pr	S _{CO2RPs} ^a	Ref.			
		material	H ₂	O ₂	CO	CH ₄		
1	Ta ₂ O ₅	SrO	19 (37) μ mol h ⁻¹	24 (20) $\mu mol h^{-1}$	36 (8) μmol h ⁻¹	_	65 (18)	[17(b)]
2	Ga_2O_3	Yb ₂ O ₃	144 (141) $\mu mol h^{-1}$	171 (67.3) μmol h ⁻¹	209 (4.8) μmol h ⁻¹	-	59.2 (3.3)	[17(h)]
3	Ga_2O_3	Nd	84.8 (141) μmol h ⁻¹	117 (67.3) μmol h ⁻¹	167 (4.8) μmol h ⁻¹	-	66.3 (3.3)	[17(h)]
4	Ga_2O_3	Pr(OH) ₃ , Pr ₂ O ₂ CO ₃	64.7 (131) μmol h ⁻¹	150 (124) μmol h ⁻¹	249 (136) μmol h ⁻¹	-	79.4 (51.0)	[17(i)]
5	Ga_2O_3	Mg-Al LDH	107.6 (147.3) μmol h ⁻¹	125.0 (101.6) μmol h ⁻¹	145.3 (62.9) μmol h ⁻¹	-	57.5 (29.9)	[17(j)]
6	Ga_2O_3	Cr(OH) ₃ ·xH ₂ O	93 (320) $\mu mol h^{-1}$	280 (200) μmol h ⁻¹	480 (75) μmol h ⁻¹	-	84 (19)	[17(l)]
7	NaTaO₃	Cr(OH) ₃ ·xH ₂ O	43.7 (248.4) μmol h ⁻¹	118.8 (154.2) μmol h ⁻¹	194.8 (67.7) μmol h ⁻¹	-	81.7 (21.4)	[17(l)]
8	CaGaO ₇ / Ga ₂ O ₃	CaO, Cr(OH) ₃ · x H ₂ O	176.5 (248.3) μmol h ⁻¹	448.2 (172.7) μmol h ⁻¹	794.2 (102.1) μmol h ⁻¹	-	82 (29)	[17(m)
9	TiO ₂	NaOH	20 (n.d.) μ mol g ⁻¹	-	-	20 (trace) μmol g ^{–1}	69 (N/ A)	[55]
10	TiO ₂	MgO	11 (33) μmol h ⁻¹ g ⁻¹	-	0.03 (1.1) $\mu mol h^{-1} g^{-1}$	11 (5.2) μmol h ⁻¹ g ⁻¹	79 (40)	[59(b)]
11	In_2O_3	CeO _x	84 (72) $\mu mol g^{-1}$	-	166 (23) μmolg ⁻¹	52 (20) $\mu mol g^{-1}$	82 (59)	[73]
12	TiO ₂	rGO	5.6 (72.7) μmol h ⁻¹ g ⁻¹	98.4 (67.3) μmol h ⁻¹ g ⁻¹	0.4 (1.3) $\mu mol h^{-1} g^{-1}$	41.3 (13.3) μmol h ⁻¹ g ⁻¹	96.7 (42.8)	[75]
[a] The r	numbers in parent	theses represent forma	tion rates of products of	or S _{CO2RPs} over the corre	sponding photocatal	ysts without CO ₂ adsor	ption materi	als.

 $\ensuremath{^{\odot}}$ 2024 The Authors. ChemCatChem published by Wiley-VCH GmbH

version of CO₂. In all cases, CO₂RPs evolution and S_{CO2RPs} were successfully enhanced by introducing materials for CO₂ adsorption. In addition to alkali- or alkali-earth-metal oxides and rareearth-based materials, modifying the Ga₂O₃ photocatalyst with a Mg-Al layered double hydroxide (LDH) drastically improves both R_{co} and S_{co} in the photocatalytic CO₂ reduction by H₂O.^[16(j)] LDHs act as solid base materials for base-catalysed reactions such as Michael addition, alkenylation of amides, and aldol reactions.^[68] More importantly, they can capture and store CO₂ in H₂O.^[69] Some studies have also demonstrated that LDHs can photocatalytically reduce CO2.^[70] Based on these findings, we demonstrated that LDH loaded on the surface of photocatalysts can function as a material for CO₂ adsorption in the photocatalytic conversion of CO₂ by H_2O , with R_{CO} and S_{CO} considerably enhanced, as shown in Entry 5 in Table 6. Hence, we propose that LDHs are promising candidates for CO₂ adsorption in the selective conversion of CO_2 by H_2O .

We also reported that Cr(OH)₃·xH₂O on photocatalysts preserve CO₂ by forming Cr(OH)_x(CO₃)_y and increasing R_{CO} and S_{CO} , as represented in Entry 6 and Entry 7 in Table 6. Notably, the Cr species on the photocatalysts acted as the material for CO2 storage and suppressed the backward reaction on the cocatalysts. The core-shell structure of the Cr species (shell) and Rh cocatalyst (core) can inhibit the backward reaction in the photocatalytic overall H₂O splitting, i.e., the formation of H₂O from H₂ and O₂, because the Cr species can block the approach of O₂ molecules to the Rh cocatalyst, whereas H₂ molecules can pass through the Cr shell.^[71] In the case of the photocatalytic conversion of CO₂, the Cr shell surrounding the Ag cocatalyst can suppress the backward reaction, i.e., CO₂ formation from the generated CO and O₂.^[17(l)] Accordingly, both the functions of the Cr species as CO₂ storage and suppression of the backward reaction can improve $R_{\rm CO}$ and $S_{\rm CO}$ in the photocatalytic conversion of CO_2 by H_2O .

Similarly, impregnation with CeO_x provides basic sites for CO₂ adsorption.^[72] Kulandaivalu *et al.* reported that a CO₂-TPD profile of a CeOx/In2O3 photocatalyst shows a new peak assigned to the strong CO₂ adsorption in the relatively hightemperature region (723-813 K) compared with the profile of pure In₂O₃, suggesting the formation of additional CO₂ adsorption sites on CeO_x/In₂O₃.^[73] Furthermore, CeO_x plays other roles in enhancing photocatalytic activity. The presence of relatively high content of Ce3+ creates a strong interfacial contact between CeO_x and In₂O₃, resulting in the formation of a type-II band alignment (Figure 13), which allows photogenerated electrons to transfer from the conduction band of In₂O₃ to that of CeO_x. The type-II band alignment promotes charge separation between CeO_x and In₂O₃, contributing to the improvement in photocatalytic activity. Modifying photocatalysts with CeO_x increases the amount of adsorbed CO₂ on the surface and induces enhanced charge separation if the band structure of the photocatalyst is suitable for forming type-II band alignment with CeO_x.^[74]

As shown in Entry 12 in Table 6, organic materials such as reduced graphene oxide (rGO),^[75] amine groups,^[76] and metalorganic frameworks^[77] are also candidates for CO₂ storage. However, the origins of the products should be carefully



Figure 13. Schematic illustration of band structure and charge transfer process in CeO_x/ln_2O_3 for photoreduction CO_2 with CH_4 or H_2O under light irradiation. Reprinted^[73] with permission from Elsevier. Copyright 2022.

checked through isotopic experiments, as explained in the Introduction section, especially when organic-material-modified photocatalysts are used for the photocatalytic conversion of CO_2 .^[78]

Moreover, using buffers is a strategy to increase the supply of CO₂ to the reaction solution. Buffers, such as NaHCO₃, NaOH, Na₂CO₃, KHCO₃, and KOH, can maintain the reaction solution at a suitable pH for CO₂ dissolution and significantly increase the concentration of dissolved CO₂. An increase in the CO₂ concentration of the reaction solution enhances both R_{CO2RPS} and S_{CO2RPS} . Moreover, some studies have demonstrated that CO evolution does not occur in the absence of buffers.^[4(a),17(o)] Under ambient temperature and pressure, adding buffers represents an effective strategy to increase the CO₂ concentration of the reaction solution as well as the loading of the materials for CO₂ adsorption.

The loading of basic materials onto heterogeneous photocatalysts contributed to the adsorption and storage of CO₂ molecules, as confirmed by FT-IR measurements and CO₂-TPD profiles. This strategy is particularly promising because an increased local concentration of CO₂ can lead to the simultaneous enhancement of both R_{CO2RPs} and S_{CO2RPs} .

3. Summary

Herein, we introduced four strategies to accomplish the selective and enhanced photocatalytic conversion of CO_2 using H_2O based on surface modifications of heterogeneous photocatalysts.

- (I) Ag cocatalysts: Ag nanoparticles can supply active sites for CO₂ reduction by extracting photogenerated electrons from the surfaces of heterogeneous photocatalysts.
- (II) Cocatalysts for H₂O oxidation: Transition metal oxides, phosphates, hydroxides, and oxyhydroxides over photocatalyst particles can efficiently transfer photogenerated holes to H₂O molecules, resulting in the suppression of charge recombination and enhancement of R_{CO2RPs} .
- (III) Suppression of H₂ evolution: Zn species introduced on the surface of Ga_2O_3 inhibited undesired H₂ evolution, contributing to enhanced S_{CO2RPs} .



(IV) Materials for CO_2 adsorption: Basic materials loaded onto heterogeneous photocatalysts act as CO_2 adsorption sites, improving both R_{CO2RPs} and S_{CO2RPs} .

Thus, surface modification of heterogeneous photocatalysts is key to realising artificial photosynthesis, i.e., the photocatalytic conversion of CO₂ using H₂O as an electron donor. Furthermore, surface properties as stated in this review and the bulk properties such as charge separation efficiency, light absorption, and band alignment, significantly contribute to the photocatalytic activity for CO₂ conversion. In other words, welldesigned photocatalysts based on the optimisation of those factors should promote the photocatalytic activity to mmol h^{-1} level in the future.

Acknowledgements

The authors gratefully acknowledge the financial support provided by the Program for Elements Strategy Initiative for Catalysts and Batteries (ESICB) commissioned by the Ministry of Education, Culture, Sports, Science, and Technology (MEXT) of Japan. This work was also supported by JSPS KAKENHI Grant Number 21H01716, 22 K14541, and a Research Grant against Global Warming of the Ichimura Foundation for New Technology, and the Mitsubishi Foundation.

Conflict of Interests

The authors declare no conflict of interest.

Keywords: Photocatalysis • Heterogeneous catalysis • Photocatalytic conversion of CO_2 by $H_2O \cdot$ Surface modification • Cocatalyst

- a) S. N. Habisreutinger, L. Schmidt-Mende, J. K. Stolarczyk, Angew. Chem. Int. Ed. 2013, 52, 7372; b) M. Marszewski, S. Cao, J. Yu, M. Jaroniec, Mater. Horiz. 2015, 2, 261; c) S. Wang, X. Han, Y. Zhang, N. Tian, T. Ma, H. Huang, Small Struct. 2021, 2, 2000061; d) S. Yoshino, T. Takayama, Y. Yamaguchi, A. Iwase, A. Kudo, Acc. Chem. Res. 2022, 55, 966; e) Y. Chen, B. Guan, X. Wu, J. Guo, Z. Ma, J. Zhang, X. Jiang, S. Bao, Y. Cao, C. Yin, D. Ai, Y. Chen, H. Lin, Z. Huang, Environ. Sci. Pollut. Res. 2023, 30, 11246.
- [2] K. Teramura, T. Tanaka, Phys. Chem. Chem. Phys. 2018, 20, 8423.
- [3] a) J. Qiao, Y. Liu, F. Hong, J. Zhang, *Chem. Soc. Rev.* 2014, *43*, 631; b) J. L. White, M. F. Baruch, J. E. Pander, Y. Hu, I. C. Fortmeyer, J. E. Park, T. Zhang, K. Liao, J. Gu, Y. Yan, T. W. Shaw, E. Abelev, A. B. Bocarsly, *Chem. Rev.* 2015, *115*, 12888.
- [4] a) K. Teramura, K. Hori, Y. Terao, Z. Huang, S. Iguchi, Z. Wang, H. Asakura, S. Hosokawa, T. Tanaka, J. Phys. Chem. C 2017, 121, 8711; b) M. Morishita, H. Asakura, S. Hosokawa, T. Tanaka, K. Teramura, ACS Catal. 2023, 13, 6966; c) R. Yanagi, T. Zhao, M. Cheng, B. Liu, H. Su, C. He, J. Heinlein, S. Mukhopadhyay, H. Tan, D. Solanki, S. Hu, J. Am. Chem. Soc. 2023, 145, 15381.
- [5] Q. Zhai, S. Xie, W. Fan, Q. Zhang, Y. Wang, W. Deng, Y. Wang, Angew. Chem. Int. Ed. 2013, 52, 5776.
- [6] a) A. Fujishima, K. Honda, *Nature* **1972**, *238*, 37; b) H. Arakawa, K. Sayama, *Res. Chem. Intermed.* **2000**, *26*, 145; c) M. Ni, M. K. H. Leung, D. Y. C. Leung, K. Sumathy, *Renew. Sustain. Energy Rev.* **2007**, *11*, 401.
- [7] a) G. Hitoki, T. Takata, J. N. Kondo, M. Hara, H. Kobayashi, K. Domen, *Chem. Commun.* **2002**, *16*, 1698; b) D. Yamasita, T. Takata, M. Hara, J. N. Kondo, K. Domen, *Solid State Ion.* **2004**, *172*, 591.
- [8] a) S. Sato, T. Morikawa, S. Saeki, T. Kajino, T. Motohiro, Angew. Chem. Int. Ed. 2010, 49, 5101; b) T. M. Suzuki, H. Tanaka, T. Morikawa, M. Iwaki, S.

Sato, S. Saeki, M. Inoue, T. Kajino, T. Motohiro, *Chem. Commun.* **2011**, *47*, 8673; c) A. Nakada, T. Nakashima, K. Sekizawa, K. Maeda, O. Ishitani, *Chem. Sci.* **2016**, *7*, 4364.

- [9] a) J. Hawecker, J. M. Lehn, R. Ziessel, *Helv. Chim. Acta* **1986**, *69*, 1990;
 b) A. J. Morris, G. J. Meyer, E. Fujita, *Acc. Chem. Res.* **2009**, *42*, 1983; c) Y. Yamazaki, H. Takeda, O. Ishitani, *J. Photochem. Photobiol. C: Photochem. Rev.* **2015**, *25*, 106.
- [10] Y. Hori, K. Kikuchi, S. Suzuki, Chem. Lett. 1985, 11, 1695.
- [11] a) Y. Hori, H. Wakebe, T. Tsukamoto, O. Koga, *Electrochim. Acta* 1994, *39*, 1833; b) H. Noda, S. Ikeda, Y. Oda, K. Imai, M. Maeda, K. Ito, *Bull. Chem. Soc. Jpn.* 1990, *63*, 2459; c) M. Azuma, K. Hashimoto, M. Hiramoto, *J. Electrochem. Soc.* 1990, *137*, 1772.
- [12] K. Hara, T. Sakata, Bull. Chem. Soc. Jpn. 1997, 70, 571.
- [13] K. lizuka, T. Wato, Y. Miseki, K. Saito, A. Kudo, J. Am. Chem. Soc. 2011, 133, 20863.
- [14] a) X. Tao, Y. Wang, J. Qu, Y. Zhao, R. Li, C. Li, J. Mater. Chem. A 2021, 9, 19631; b) K. Li, A. D. Handoko, M. Khraisheh, J. Tang, Nanoscale 2014, 6, 9767; c) Y. Wang, Q. Lai, Y. He, M. Fan, Catal. Commun. 2018, 108, 98; d) H. Nakanishi, K. lizuka, T. Takayama, A. Iwase, A. Kudo, ChemSusChem 2017, 10, 112; e) Y. Wang, M. Liu, W. Chen, L. Mao, W. Shangguan, J. Alloys Compd. 2019, 786, 149.
- [15] M. Yamamoto, T. Yoshida, N. Yamamoto, T. Nomoto, Y. Yamamoto, S. Yagi, H. Yoshida, J. Mater. Chem. A 2015, 3, 16810.
- [16] a) N. M. Dimitrijevic, B. K. Vijayan, O. G. Poluektov, T. Rajh, K. A. Gray, H. He, P. Zapol, J. Am. Chem. Soc. 2011, 133, 3964; b) L. Liu, H. Zhao, J. M. Andino, Y. Li, ACS Catal. 2012, 2, 1817.
- [17] a) Z. Wang, K. Teramura, S. Hosokawa, T. Tanaka, Appl. Catal. B: Environ. 2015, 163, 241; b) K. Teramura, H. Tatsumi, Z. Wang, S. Hosokawa, T. Tanaka, Bull. Chem. Soc. Jpn. 2015, 88, 431; c) Z. Wang, K. Teramura, S. Hosokawa, T. Tanaka, Mater. Chem. A 2015, 3, 11313; d) Z. Huang, K. Teramura, S. Hosokawa, T. Tanaka, Appl. Catal. B: Environ. 2016, 199, 272; e) Z. Wang, K. Teramura, Z. Huang, S. Hosokawa, Y. Sakata, T. Tanaka, Catal. Sci. Technol. 2016, 6, 1025; f) R. Pang, K. Teramura, H. Asakura, S. Hosokawa, T. Tanaka, Appl. Catal. B: Environ. 2017, 218, 770; g) Z. Huang, S. Yoshizawa, K. Teramura, H. Asakura, S. Hosokawa, T. Tanaka, ACS Omega 2017, 2, 8187; h) H. Tatsumi, K. Teramura, Z. Huang, Z. Wang, H. Asakura, S. Hosokawa, T. Tanaka, Lanamuir 2017, 33, 13929; i) Z. Huang, K. Teramura, H. Asakura, S. Hosokawa, T. Tanaka, Mater. Chem. A 2017, 5, 19351; j) S. Iguchi, Y. Hasegawa, K. Teramura, S. Kidera, S. Kikkawa, S. Hosokawa, H. Asakura, T. Tanaka, Sustain. Energy Fuels 2017, 1, 1740; k) Z. Huang, K. Teramura, H. Asakura, S. Hosokawa, T. Tanaka, Catal. Today 2018, 300, 173; I) R. Pang, K. Teramura, H. Asakura, S. Hosokawa, T. Tanaka, ACS Sustainable Chem. Eng. 2019, 7, 2083; m) R. Pang, K. Teramura, M. Morishita, H. Asakura, S. Hosokawa, T. Tanaka, Commun. Chem. 2020, 3, 137; n) S. Wang, K. Teramura, T. Hisatomi, K. Domen, H. Asakura, S. Hosokawa, T. Tanaka, ACS Appl. Energy Mater. 2020, 3, 1468; o) T. Nakamoto, S. Iguchi, S. Naniwa, T. Tanaka, K. Teramura, Catal. Sci. Technol. 2023, 13, 4534.
- [18] P. Wang, L. Schwertmann, R. Marschall, M. Wark, J. Mater. Chem. A 2014, 2, 8815.
- [19] A. Kudo, H. Okutomi, H. Kato, Chem. Lett. 2000, 10, 1212.
- [20] I. Cho, S. Lee, J. H. Noh, D. W. Kim, D. K. Lee, H. S. Jung, D. Kim, K. S.
- Hong, J. Mater. Chem. **2010**, *20*, 3979. [21] a) J. Zou, C. Liu, Y. Zhang, *Langmuir* **2006**, *22*, 2334; b) Y. Noda, B. Lee, K. Domen, J. N. Kondo, *Chem. Mater.* **2008**, *20*, 5361.
- [22] a) Y. Sakata, Y. Matsuda, T. Yanagida, K. Hirata, H. Imamura, K. Teramura, *Catal. Lett.* **2008**, *125*, 22; b) X. Wang, Q. Xu, M. Li, S. Shen, X. Wang, Y. Wang, Z. Feng, J. Shi, H. Han, C. Li, *Angew. Chem. Int. Ed.* **2012**, *51*, 13089.
- [23] D. W. Hwang, J. S. Lee, W. Li, S. H. Oh, J. Phys. Chem. B 2003, 107, 4963.
- [24] a) Y. Ham, T. Hisatomi, Y. Goto, Y. Moriya, Y. Sakata, A. Yamakata, J. Kubota, K. Domen, *Mater. Chem. A* **2016**, *4*, 3027; b) T. Takata, J. Jiang, Y. Sakata, M. Nakabayashi, N. Shibata, V. Nandal, K. Seki, T. Hisatomi, K. Domen, *Nature* **2020**, *581*, 411; c) M. Nakabayashi, T. Takata, N. Shibata, K. Domen, *Chem. Lett.* **2022**, *51*, 978.
- [25] D. M. Wood, PRL 1981, 46, 11.
- [26] a) R. T. Tung, *Appl. Phys. Rev.* **2014**, *1*, 011304; b) F. Ruffino, M. G. Grimaldi, F. Giannazzo, F. Roccaforte, V. Raineri, *Appl. Phys. Lett.* **2006**, *89*, 243113; c) J. A. Lee, Y. R. Lim, C. S. Jung, J. H. Choi, H. S. Im, K. Park, J. Park, G. T. Kim, *Nanotechnology* **2016**, *27*, 425711.
- [27] a) K. S. Tan, K. Y. Cheong, J. Nanopart. Res. 2013, 15, 1537; b) V. R. Manikam, K. Y. Cheong, K. A. Razak, Mater. Sci. Eng. B 2011, 176, 187.
- [28] W. Kurashige, R. Kumazawa, D. Ishii, R. Hayashi, Y. Niihori, S. Hossain, L. V. Nair, T. Takayama, A. Iwase, S. Yamazoe, T. Tsukuda, A. Kudo, Y. Negishi, J. Phys. Chem. C 2018, 122, 13669.

ChemCatChem 2024, 16, e202400594 (15 of 17)

^{© 2024} The Authors. ChemCatChem published by Wiley-VCH GmbH



- [30] S. Feng, M. Wang, Y. Zhou, P. Li, W. Tu, Z. Zou, *APL Mater.* 2015, 3, 104416.
 [31] D.M. Tabir, P. Tabir, N. A.S. Amin, Ampl. Cat. 4, 2015. doi:10.1016/j.
- [31] a) M. Tahir, B. Tahir, N. A. S. Amin, *Appl. Catal. B: Environ.* 2017, 204, 548;
 b) H. Yu, G. Cao, F. Chen, X. Wang, J. Yu, M. Lei, *Appl. Catal. B: Environ.* 2014, 160, 658; c) E. Liu, Y. Hu, H. Li, C. Tang, X. Hu, J. Fan, Y. Chen, J. Bian, *Ceram. Int.* 2015, 41, 1049.
- [32] a) K. Sayama, H. Arakawa, J. Phys. Chem. 1993, 97, 531; b) X. Liu, M. Ye,
 S. Zhang, G. Huang, C. Li, J. Yu, P. K. Wong, S. Liu, J. Mater. Chem. A
 2018, 6, 24245; c) S. Neatu, J. A. Macia-Agullo, P. Concepcion, H. Garcia,
 J. Am. Chem. Soc. 2014, 136, 15969.
- [33] a) M. P. Dare-Edwards, J. B. Goodenough, A. Hamnett, P. R. Trevellick, J. Chem. Sos., Faraday Trans. 1 1983, 79, 2027; b) I. C. Man, H. Y. Su, F. Calle-Vallejo, H. A. Hansen, J. I. Martinez, N. G. Inoglu, J. Kitchin, T. F. Jaramillo, J. K. Norskov, J. Rossmeisl, ChemCatChem 2011, 3, 1159; c) C. C. L. McCrory, S. Jung, J. C. Peters, T. F. Jaramillo, J. Am. Chem. Soc. 2013, 135, 16977.
- [34] a) Q. Liu, Y. Zhou, J. Kou, X. Chen, Z. Tian, J. Gao, S. Yan, Z. Zou, J. Am. Chem. Soc. 2010, 132, 14385; b) G. Yang, S. Wang, Y. Wu, H. Zhou, W. Zhao, S. Zhong, L. Liu, S. Bai, ACS Appl. Mater. Interfaces 2023, 15, 14228; c) T. Soltani, X. Zhu, A. Yamakata, S. P. Singh, E. Fudo, A. Tanaka, H. Kominami, H. Yoshida, Appl. Catal. B: Environ. 2021, 286, 119899; d) Y. Bai, L. Ye, L. Wang, X. Shi, P. Wang, W. Bai, Environ. Sci.: Nano 2016, 3, 902.
- [35] a) J. Kiwi, M. Gratzel, Angew. Chem. Int. Ed. Engl. 1979, 18, 624; b) S. D. Tilley, M. Cornuz, K. Sivula, M. Gratzel, Angew. Chem. 2010, 122, 6549;
 c) Y. Lee, J. Suntivich, K. J. May, E. E. Perry, Y. Shao-Horn, J. Phys. Chem. Lett. 2012, 3, 399.
- [36] a) X. Deng, H. Tüysüz, ACS Catal. 2014, 4, 3701; b) H. Zhao, Q. Mao, L. Jian, Y. Dong, Y. Zhu, Chin. J. Catal. 2022, 43, 1774; c) M. E. G. Lyons, M. P. Brandon, J. Electroanal. Chem. 2010, 641, 119; d) M. W. Louie, A. T. Bell, J. Am. Chem. Soc. 2013, 135, 12329; e) B. M. Hunter, H. B. Gray, A. M. Muller, Chem. Rev. 2016, 116, 14120; f) H. Zhao, L. Jian, M. Gong, M. Jing, H. Li, Q. Mao, T. Lu, Y. Guo, R. Ji, W. Chi, Y. Dong, Y. Zhu, Small Struct. 2022, 3, 2100229.
- [37] a) S. K. Pilli, T. E. Furtak, L. D. Brown, T. G. Deutsch, J. A. Turner, A. M. Herring, *Energy Environ. Sci.* 2011, *4*, 5028; b) D. K. Zhoug, M. Cornuz, K. Sivula, M. Gratzel, D. R. Gamelin, *Energy Environ. Sci.* 2011, *4*, 1759; c) B. Klahr, S. Gimenez, F. Fabregat-Santiago, J. Bisquert, T. W. Hamann, *J. Am. Chem. Soc.* 2012, *134*, 16693.
- [38] a) M. W. Kanan, D. G. Nocera, *Science* **2008**, *321*, 1072; b) Y. Surendranath, M. Dinca, D. G. Nocera, *J. Am. Chem. Soc.* **2009**, *131*, 2615; c) D. A. Lutterman, Y. Surendranath, D. G. Nocera, *J. Am. Chem. Soc.* **2009**, *131*, 3838.
- [39] D. K. Zhong, J. Sun, H. Inumaru, D. R. Gamelin, J. Am. Chem. Soc. 2009, 131, 6086.
- [40] a) C. Liu, Y. Xu, H. Luo, W. Wang, Q. Liang, Z. Chen, J. Chem. Eng. 2019, 363, 23; b) I. V. Bagal, M. Arunachalam, A. Waseem, A. Abdullah, S. H. Kang, S. Ryu, Appl. Surf. Sci. 2021, 558, 149873; c) D. Chen, Z. Liu, S. Zhang, Appl. Catal. B: Environ. 2020, 265, 118580.
- [41] a) J. A. Seabold, K. S Choi, J. Am. Chem. Soc. 2012, 134, 2186; b) J. A. Seabold, K. Zhu, N. R. Neale, Phys. Chem. Chem. Phys. 2014, 16, 1121.
- [42] S. Wang, K. Teramura, T. Hisatomi, K. Domen, H. Asakura, S. Hosokawa, T. Tanaka, ACS Sustainable Chem. Eng. 2021, 9, 9327.
- [43] a) S. Zhu, W. Liao, M. Zhang, S. Liang, J. Chem. Eng. 2019, 361, 461; b) R. Li, Y. Zhao, C. Li, Faraday Discuss. 2017, 198, 463.
- [44] X. Zhang, Z. Yuan, J. Chen, G. Yang, D. D. Dionysiou, B. Huang, Z. Jiang, Catal. Today 2020, 340, 204.
- [45] a) Y. Li, S. Yu, J. Xiang, F. Zhang, A. Jiang, Y. Duan, C. Tang, Y. Cao, H. Guo, Y. Zhou, ACS Catal. 2023, 13, 8281; b) Z. Yan, L. Du, D. L. Phillips, RSC Adv. 2017, 7, 55993; c) M. Yabuta, T. Takayama, K. Shirai, K. Watanabe, A. Kudo, T. Sugimoto, Y. Matsumoto, J. Phys. Chem. C 2014, 118, 10972.
- [46] A. Yamakata, M. Kawaguchi, N. Nishimura, T. Minegishi, J. Kubota, K. Domen, J. Phys. Chem. C 2014, 118, 23897.
- [47] a) A. Kasahara, K. Nukumizu, G. Hitoki, T. Takata, J. N. Kondo, M. Hara, H. Kobayashi, K. Domen, J. Phys. Chem. A 2002, 106, 6750; b) A. Kasahara, K. Nukumizu, T. Takata, J. N. Kondo, M. Hara, H. Kobayashi, K. Domen, J. Phys. Chem. B 2003, 107, 791; c) F. Zhang, A. Yamakata, K. Maeda, Y. Moriya, T. Takata, J. Kubota, K. Teshima, S. Oishi, K. Domen, J. Am. Chem. Soc. 2012, 134, 8348.
- [48] a) K. Fuku, K. Sayama, Chem. Commun. 2016, 52, 5406; b) K. Fuku, Y. Miyase, Y. Miseki, T. Gunji, K. Sayama, ChemistrySelect 2016, 1, 5721.

[49] T. Soltani, A. Yamamoto, S. P. Singh, A. Anzai, E. Fudo, A. Tanaka, H. Kominami, H. Yoshida, *ACS Appl. Energy Mater.* **2021**, *4*, 6500.

- [50] a) L. Binet, D. Gourier, J. Solid State Chem. 1994, 113, 420; b) S. J. Pearton, J. Yang, P. H. Cary IV, F. Ren, J. Kim, M. J. Tadjer, M. A. Mastro, Appl. Phys. Rev. 2018, 5, 011301.
- [51] a) Y. Kawaguchi, M. Akatsuka, M. Yamamoto, K. Yoshioka, A. Ozawa, Y. Kato, T. Yoshida, J. Photochem. Photobiol. A: Chem. 2018, 358, 459; b) Q. Li, Y. Zhang, L. Zhang, J. Xia, X. Liu, L. Hu, F. Wang, X. Chu, P. Zhao, J. Yin, D. Yang, Catal. Commun. 2019, 120, 23.
- [52] a) K. Teramura, Z. Wang, S. Hosokawa, Y. Sakata, T. Tanaka, *Chem. Eur. J.* 2014, 20, 9906; b) Y. Sakata, Y. Matsuda, T. Nakagawa, R. Yasunaga, H. Imamura, K. Teramura, *ChemSusChem* 2011, 4, 181; c) S. Wang, K. Teramura, H. Asakura, S. Hosokawa, T. Tanaka, *J. Phys. Chem. C* 2021, 125, 1304.
- [53] Z. Wang, K. Teramura, Z. Huang, S. Hosokawa, Y. Sakata, T. Tanaka, Catal. Sci. Technol. 2016, 6, 1025.
- [54] a) I. Bhugun, D. Lexa, J. Saveant, J. Phys. Chem. **1996**, 100, 19981; b) K. Teramura, S. Okuoka, H. Tsuneoka, T. Shishido, T. Tanaka, Appl. Catal. B: Environ. **2010**, *96*, 565.
- [55] X. Meng, S. Ouyang, T. Kato, P. Li, Q. Yu, T. Wang, J. Ye, Chem. Commun. 2014, 50, 11517.
- [56] a) L. Liu, C. Zhao, H. Zhao, D. Pitts, Y. Li, *Chem. Commun.* 2013, *49*, 3664;
 b) X. Feng, F. Pan, B. Z. Tran, Y. Li, *Catal. Today* 2020, *339*, 328; c) N. Li, M. Huang, J. Zhou, M. Liu, D. Jing, *Chin. J. Catal.* 2021, *42*, 781.
- [57] a) Y. Kohno, T. Tanaka, T. Funabiki, S. Yoshida, *Phys. Chem. Chem. Phys.* 2000, 2, 5302; b) Y. Kohno, T. Tanaka, T. Funabiki, S. Yoshida, *Chem. Commun.* 1997, 9, 841.
- [58] a) Y. Fukuda, K. Tanabe, *Bull. Chem. Soc. Jpn.* **1973**, *46*, 1616; b) H. Tsuji, T. Shishido, A. Okamura, Y. Gao, H. Hattori, H. Kita, *J. CHEM. SOC. FARADAY TRANS.* **1994**, *90*(5), 803; c) Y. Yanagisawa, K. Takaoka, S. Yamabe, *J. Phys. Chem.* **1995**, *99*, 3704; d) K. Teramura, T. Tanaka, H. Ishikawa, Y. Kohno, T. Funabiki, *J. Phys. Chem. B* **2004**, *108*, 346.
- [59] a) S. Xie, Y. Wang, Q. Zhang, W. Fan, W. Deng, Y. Wang, *Chem. Commun.* 2013, 49, 2451; b) S. Xie, Y. Wang, Q. Zhang, W. Deng, Y. Wang, ACS *Catal.* 2014, 4, 3644.
- [60] C. Lo, C. Hung, C. Yuan, J. Wu, Sol. Energy Mater. Sol. Cells 2007, 91, 1765.
- [61] a) S. Bernal, G. Blanco, J. J. Calvino, J. A. P. Omil, J. M. Pintado, J. Alloys Compd. 2006, 408, 496; b) S. Sato, R. Takahashi, M. Kobune, H. Gotoh, Appl. Catal. A Gen. 2009, 356, 57.
- [62] Y. Kuroda, H. Hamano, T. Mori, Y. Yoshikawa, M. Nagao, *Langmuir* **2000**, *16*, 6937.
- [63] P. Fleming, R. A. Farrell, J. D. Holmes, M. A. Morris, J. Am. Ceram. Soc. 2010, 93, 1187.
- [64] a) S. Bernal, F. J. Botana, R. Garcia, J. M. Rodriguez-Izquierdo, *React. Solids* **1987**, *4*, 23; b) S. Bernal, F. J. Botana, G. Cifredo, J. J. Calvino, A. Jobacho, J. M. Rodriguez-Izquierdo, *J. Alloys Compd.* **1992**, *180*, 271.
- [65] S. Bernal, F. J. Botana, R. Garcia, J. M. Rodriguez-Izquierdo, J. Mater. Sci. 1988, 23, 1474.
- [66] R. Alvero, I. Carrizosa, J. A. Odriozola, J. M. Trillo, J. Less Common Met. 1983, 94, 139.
- [67] Y. Borchert, P. Sonstrom, M. Wilhelm, H. Borchert, M. Baumer, J. Phys. Chem. C 2008, 112, 3054.
- [68] B. F. Sels, D. E. De Vos, P. A. Jacobs, Catal. Rev. 2001, 43, 443.
- [69] M. K. R. Reddy, Z. P. Xu, G. Q. Lu, J. C. D. da Costa, Ind. Eng. Chem. Res. 2006, 45, 7504.
- [70] a) K. Teramura, S. Iguchi, Y. Mizuno, T. Shishido, T. Tanaka, Angew. Chem. Int. Ed. 2012, 51, 8008; b) X. Zhao, H. Jiang, Y. Xiao, M. Zhong, Nanoscale Adv. 2024, 6, 1241; c) S. Iguchi, K. Teramura, S. Hosokawa, T. Tanaka, Appl. Catal. A: Gen. 2016, 521, 160; d) S. Iguchi, Y. Hasegawa, K. Teramura, S. Hosokawa, T. Tanaka, J. CO2 Util. 2016, 15, 6; e) X. Xiong, Y. Zhao, R. Shi, W. Yin, Y. Zhao, G. I. N. Waterhouse, T. Zhang, Sci. Bull. 2020, 65, 987; f) L. Tan, S. Xu, Z. Wang, Y. Xu, X. Wang, X. Hao, S. Bai, C. Ning, Y. Wang, W. Zhang, Y. K. Jo, S. Hwang, X. Cao, X. Zheng, H. Yan, Y. Zhao, H. Duan, Y. Song, Angew. Chem. Int. Ed. 2019, 58, 11860.
- [71] a) K. Maeda, K. Teramura, H. Masuda, T. Takata, N. Saito, Y. Inoue, K. Domen, J. Phys. Chem. B 2006, 110, 13107; b) K. Maeda, K. Teramura, D. Lu, N. Saito, Y. Inoue, K. Domen, J. Phys. Chem. C 2007, 111, 7554; c) M. Yoshida, K. Takanabe, K. Maeda, A. Ishikawa, J. Kubota, Y. Sakata, Y. Ikezawa, K. Domen, J. Phys. Chem. C 2009, 113, 10151.
- [72] a) C. Binet, M. Daturi, J. Lavalley, *Catal. Today* **1999**, *50*, 207; b) Z. Xu, Z. Qian, K. Tanabe, H. Hattori, *Bull. Chem. Soc. Jpn.* **1991**, *64*, 1664; c) D. P. H. Tran, M. Pham, X. Bui, Y. Wang, S. You, *Sol. Energy* **2022**, *240*, 443.

ChemCatChem 2024, 16, e202400594 (16 of 17)



European Chemical Societies Publishing

8673899,

- [73] T. Kulandaivalu, A. R. Mohamed, K. A. Ali, S. Kulandaivalu, J. CO2 Util. 2022, 63, 102115.
- [74] a) J. Jiao, Y. Wei, Z. Zhao, J. Liu, J. Li, A. Duan, G. Jiang, Ind. Eng. Chem. Res. 2014, 53, 17345; b) M. Li, L. Zhang, M. Wu, Y. Du, X. Fan, M. Wang, L. Zhang, Q. Kong, J. Shi, Nano Energy 2016, 19, 145; c) Q. Mou, Z. Guo,
- Y. Chai, B. Liu, C. Liu, J. Photochem. Photobiol. B: Biol. 2021, 219, 112205. [75] Y. Zhao, Y. Wei, X. Wu, H. Zheng, Z. Zhao, J. Liu, J. Li, Appl. Catal. B: Environ. 2018, 226, 360.
- [76] a) Y. Liao, Z. Hu, Q. Gu, C. Xue, Chem. Eur. J. 2014, 20, 10220; b) Y. Liao, S. Cao, Y. Yuan, Q. Gu, Z. Zhang, C. Xue, Molecules 2015, 20, 18847.
- [77] a) Q. Li, Z. Low, L. Li, A. Razmjou, K. Wang, J. Yao, H. Wang, J. Mater. Chem. A 2013, 1, 11563; b) C. Chen, T. Wu, H. Wu, H. Liu, Q. Qian, Z. Liu,

G. Yang, B. Han, Chem. Sci. 2018, 9, 8890; c) Y. Ma, Q. Tang, W. Sun, Z. Yao, W. Zhu, T. Li, J. Wang, Appl. Catal. B: Environ. 2020, 270, 118856. [78] a) J. You, M. Xiao, S. Liu, H. Lu, P. Chen, Z. Jiang, W. Shangguan, Z. Wang, L. Wang, Mater. Chem. A 2023, 11, 10149; b) C. Yang, Y. Yu, B.

van der Linden, J. C. S. Wu, G. Mui, J. Am. Chem. Soc. 2010, 132, 8398.

Manuscript received: March 28, 2024 Revised manuscript received: July 31, 2024 Accepted manuscript online: August 1, 2024 Version of record online: September 24, 2024