Short communication

Boosting CO_2 photoreduction activity by large Fresnel lens concentrated solar light

Xiaoxiang Fang, Zhihong Gao, Hanfeng Lu, Zekai Zhang*

Institute of Chemical Reaction Engineering, College of Chemical Engineering, Zhejiang University of Technology, Chaowang Road 18, Hangzhou 310014, China

ABSTRACT

CO_2 photoreduction to hydrocarbons is an important process for solar energy. Herein, the reaction rate is massively pushed up by large Fresnel lens (diameter = 1 m) concentrating solar light technology. The maximum CH_4 yield rate reached 3157.2 $\mu mol \cdot g^{-1} \cdot h^{-1}$, C_2H_4 rate to 511.6 $\mu mol \cdot g^{-1} \cdot h^{-1}$, C_2H_6 to 1346.0 $\mu mol \cdot g^{-1} \cdot h^{-1}$, and the CO_2 conversion reached 3.94%. The total solar to chemical energy conversion efficiency got 0.15%. The results are considered from the intensification of reaction conditions such as light intensity, reaction temperature, and pressure of H_2O and CO_2. The findings will be beneficial for the further discussion of CO_2 photoreduction basing upon the existed catalysts system, and decrease the research threshold in CO_2 photoreduction.

1. Introduction

Artificial photosynthesis or CO_2 photoreduction is a chemical conversion process that human being learns from green plants, which can use solar light to generate chemical fuels from CO_2 [1]. Due to the continual increase of CO_2 emission and exhaustion of fossil energy, CO_2 photoreduction has been a hot topic for decades to reduce CO_2 content in atmosphere as well as developing renewable energy. CO_2 photoreduction started from the discovery of Honda and Fujishima in 1970s [2]. From then on, numerous studies have been reported and significant achievements have been made for the process based on heterogeneous catalysis. Some reported reaction rates have reached thousands $\mu mol \cdot g^{-1} \cdot h^{-1}$ [3–5]. Meanwhile, most of the reported reaction rates are several to tens of $\mu mol \cdot g^{-1} \cdot h^{-1}$, especially for the TiO_2 [6,7]. Considering of the used catalyst amount (often lower than 1 g), the CH_4 yield is really quite small. Such results are reasonably questioned by many people, who suspect that the products are probably from the organic residues in the catalysts or reactors while not from CO_2.[8–9] One of three requirements for CO_2 photoreduction research proposed by Teramura and Tanaka in 2017 is still to confirm that the hydrocarbons are really from CO_2RPs (CO_2 reduction products) using isotopically labeled $^{13}CO_2$ (The other two are "determining the relative amounts of H_2 and CO_2 RPs produced, and checking whether a stoichiometric amount of O_2 is produced") [10]. The status raises the research requirement and it needs an efficient way to decrease the threshold.

Besides catalyst system, reactor and reaction conditions also have

important effects on the CO_2 photoreduction. According to the reaction rate law equation [11,12].

$$- r'_{CO_2} = kI^\alpha \frac{P_{CO_2} P_{H_2O}}{(1 + K_{CO_2} P_{CO_2} + K_{H_2O} P_{H_2O})^2} \tag{1}$$

all the increment of light intensity, pressure of CO_2 and H_2O will be beneficial to the reaction rate. More importantly, all the pressure of CO_2, H_2O and k(T) could be realized by increasing the light intensity solely, if the solar light is properly collected and concentrated. It is known that the nature solar light contains less than 7% UV light, 43% visible light and about 50% IR lights. Due to the wide band gap of the catalyst, deep negative potential of CO_2 and complex photoreduction process, only the short wavelength photons with high energy (UV light) are useable, and most of solar lights are converted into useless heat during photocatalysis. While with concentrating solar lights, the catalyst and the reactants can be effectively heated to higher temperature, which will increase CO_2 pressure and take more H_2O into gaseous phase. Such reaction conditions will be superior to the present ambient reaction conditions, as if the reaction is carried out in liquid phase, CO_2 concentration would be much lower than H_2O due to the solubility, and if it is carried out in gas phase, H_2O pressure would be much lower than CO_2.

Wu's group [13,14] and some others [15,16] have developed the optical-fiber photoreactor, monolith photoreactor, and internally illuminated monolith photoreactor to improve the reaction environment for the CO_2 photoreduction. Guan et al. [17,18] also have done some pioneer works with concentrating light reactor in the liquid phase and

---

* Corresponding author.
  E-mail address: zzk@zjut.edu.cn (Z. Zhang).

obtained rather good results, but their catalyst system are Fe-based catalyst and $K_2Ti_6O_{13}$, which is lack of comparability to some extent. Our group also did some work on concentrating light reactor using Xe lamp as the light source and obtained some interesting results. [19,20] However, due to the power limits, it cannot raise the reaction temperature efficiently.

In this manuscript, a concentrating solar light reactor system was set up with a large Fresnel lens (diameter = 1 m). It can effectively raise light intensity, reaction temperature as well as the pressure of CO_2 and H_2O of the reactor system. The CO_2 photoreduction behavior was then investigated in the reactor system. To make comparable results, the most common catalyst P25 was used. The results show that CO_2 photoreduction performance are greatly improved and reaction rates of hydrocarbons are boosted up to very high values.

2. Experimental

2.1. Catalyst preparation and characterization

P25 TiO_2 was purchased from Degussa. The powder were calcined in a muffle furnace at a rate of $2\,°C\cdot min^{-1}$ up to $400\,°C$ and held at this temperature for 2 h to remove the organic impurities.

In order to investigate the structure and crystallinity, powder X-ray diffraction (XRD, X'Pert PRO) was performed. The scanning rate was $0.02°\,min^{-1}$ from $20°$ to $80°$. Ultraviolet–visible absorption spectra of the samples were collected with an UV–Vis-NIR spectrophotometer (UV–vis, UV-2600). Field emission scanning electron microscope (FE-SEM, Hitachi S-4700) measurements were used to disclose the morphologies. Specific surface area was measured by a 3flex physical adsorption apparatus.

2.2. Illustration of reactor system and catalytic tests

The CO_2 photoreduction with H_2O reaction was performed in a self-made concentrating light reactor system, as shown in Fig. 1. The system contains a reactor, a Fresnel lens and an auto tracing system. The lens (diameter = 1 m, PMMA material) was purchased from Mylens Co., Shenzhen. Detailed description of the reactor can be seen in Ref. [19]. The auto tracing system contains a motor, a controller and a sensor, which is used to keep the solar lights perpendicular to the lens and the catalyst. The catalyst amount is about 0.05 g. Before reaction, the
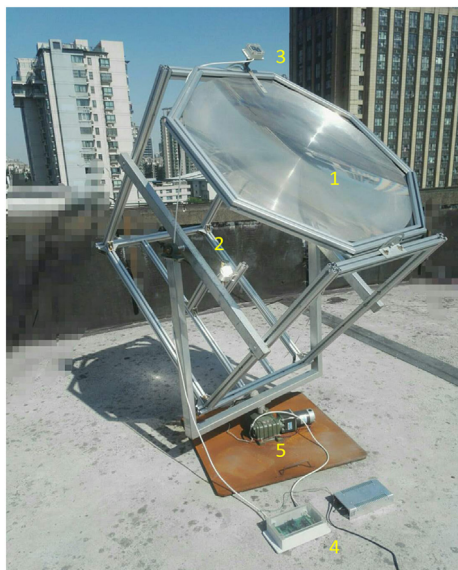

Fig. 1. The concentrating reactor system. 1. Concentrating mirror; 2. Reactor; 3. Sensor for tracing sun; 4. Controller. 5. Motor.

catalyst was prepared to be disc shape and put into the reactor. A k-type thermocouple is passed through a hole on the reactor wall and touched the upper surface of the catalyst to measure the temperature. Then the reactor was sealed and cleaned with nitrogen (99.999%) for half an hour to remove the impurity gas. Next, it was continuously replaced and saturated with CO_2 gas (99.999%) for at least 30 min, and the pressure of the reactor was regulated to 0.1 MPa. 2.0 mL of H_2O was then charged into the reactor. The reaction was operated in batch mode. The gas products were analyzed by a gas chromatograph (GC2014, Shimadzu) equipped with an HT-PLOT Q capillary column (30m × 0.32mm × 20μm), FID detector. The hydrocarbons are determined by external standard method. A standard curve of CH_4 was first obtained. The reaction rate of CO_2 RPs and CO_2 conversion are calculated according to the equations:

$$r_{C_I}(\mu mol\cdot g^{-1}\cdot h^{-1}) = \frac{n_{C_i}}{(w_t \times time)} \tag{2}$$

$$X_{CO_2}(\%) = \frac{n_{CH_4} + 2n_{C_2H_2} + 2n_{C_2H_4} + 2n_{C_2H_6}}{n_{CO_2}} \times 100\% \tag{3}$$

where n_{C_i} is the mole of hydrocarbons (CH_4, C_2H_2, C_2H_4 and C_2H_6) yielded in the system, and w_t is the catalyst weight.

3. Results and discussions

The catalyst characterization results can be seen in Fig.S1-S3 and Table S1, which confirms the catalyst is a typical P25 TiO_2. Blank experiments have been performed to exclude the probable misleading of impurities. [20]

The tests on the large concentrating solar light reactor system show the effect of reaction condition intensification on the CO_2 photoreduction. Fig. 2 first displays a typical products distribution of CO_2 photoreduction under concentration ratio (CR) 800. Compared to most of the reports, it can be seen that besides CH_4, more type of products are detected. [6,7] C_2H_2, C_2H_4, C_2H_6 and C_3H_6 can be observed clearly, which were further confirmed by MS (Seen in Fig.S4 and S5). Then calculated by external standard method, the maximum CH_4 reaction rate reaches $3157.2\,\mu mol\cdot g^{-1}\cdot h^{-1}$ at concentration ratio of 800 after half an hour reaction, as shown in Table 1; at the same time, the C_2H_4 reaction rate reaches $511.6\,\mu mol\cdot g^{-1}\cdot h^{-1}$, and the C_2H_6 reaction rate reaches $1346.0\,\mu mol\cdot g^{-1}\cdot h^{-1}$. Considering all the products are form CO_2 reduction, the total CO_2 reduction rate achieves about $5715\,\mu mol\cdot g^{-1}\cdot h^{-1}$, which is larger than all the values recently reported. [21] At other concentration ratios, the reaction rates of
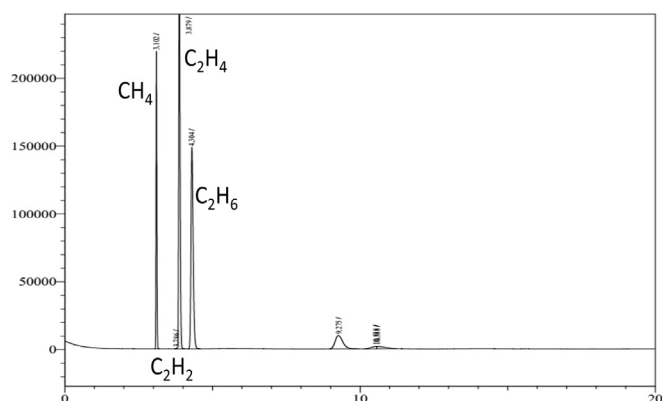

Fig. 2. A typical gas chromatogram map of CO_2 reduction products distribution.

100 mL batch reactor, initial reactants contains 0.1 MPa CO_2 and 2 mL H_2O, concentration ratio 800, temperature 531.5 °C, pressure 1.0 MPa. Concentration ratio is defined as the ratio of Fresnel lens area to catalyst disc area.(The same below).
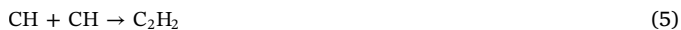
Table 1

CO_2 related products reaction rate under concentrating solar light ($\mu mol \cdot g^{-1} \cdot h^{-1}$).

Concentration ratio (CR)	T[a]/°C	P/MPa	CH_4	C_2H_2	C_2H_4	C_2H_6	Others	Total	X_{CO_2}/%
1000	659.6	1.1	591.5	35.1	579.1	245.1	33.7	1484.4	1.81
800	531.5	1.0	3157.2	13.8	511.5	1346.0	686.5	5715.1	3.94
600	479.6	0.9	1059.3	4.0	562.7	237.1	14.0	1877.1	3.21
400	379.5	0.5	410.8	3.5	596.4	461.9	121.3	1593.9	2.63

[a] The temperatures are obtained from the catalyst surface. Due to the light intensity always changes and there is temperature distribution in the reactor, the temperature of the reactants may be some lower than the measured temperatures here.

hydrocarbons also reach hundreds to thousands $\mu mol \cdot g^{-1} \cdot h^{-1}$, indicating that it is not an accidental or wrong phenomenon. The results also make it possible to calculate the CO_2 conversion. The maximum conversion is about 3.94%, which may be helpful to further confirm the transformation of CO_2. As all we need to do is adding a concentrator on the reaction system, the method is easy to be spread and the results are convenient to be testified.

The type enrichment of CO_2 reduction products (CO_2 RPs) also provides the chance to discuss the reaction route of CO_2 photoreduction. CO_2 photoreduction is a very complicated process, which contains the transfer of multiple electrons and protons, breaking of C−O bonds, and formation of C−H bonds. Reaction mechanism of CO_2 activation, such as glyoxal pathway, formaldehyde pathway, carbene pathway and hydrogen carbonate (bicarbonate) pathway, is still in debate [22]. Here, according to the products distribution in Fig. 2, the existence of C_2H_2, C_2H_4 and C_2H_6 may indicate the generation of CH, CH_2 and CH_3 intermediates during the process. Interestingly, there are no oxygen-contained products yielded, such as HCOOH, HCHO etc. (Benzene was also used as solvent to wash and adsorb the products after the reaction, and no more products are detected). It may be appropriate to explain the results with the carbene pathway.

$$CO_2 \rightarrow CO \rightarrow C \rightarrow CH \rightarrow CH_2 \rightarrow CH_3 \rightarrow CH_4 \tag{4}$$

$$CH + CH \rightarrow C_2H_2 \tag{5}$$

$$CH_2 + CH_2 \rightarrow C_2H_4 \tag{6}$$

$$CH_3 + CH_3 \rightarrow C_2H_6 \tag{7}$$

Another important issue is the solar to chemical energy conversion efficiency of the process. Apparent quantum efficiency is a common criteria, meanwhile, it seems more directly to use solar to chemical energy conversion (STC) efficiency, as the CO_2 RPs are the energy carriers [23].

$$STC = \frac{\text{Output energy as a chemical}}{\text{Energy of incident solar light}} = \frac{r \times \Delta G_r}{P_{sun} \times S} \tag{8}$$

where r, ΔG_r, P_{sun} and S are the production rate of the chemical of interest, the Gibbs energy of the related products, the solar intensity, and the incident light area. The STC efficiency is then calculated based on the intensity measured at experimental time (Hangzhou) and AM 1.5 standard, as listed in Table 2. The maximum STC efficiency is about 0.15% (Hangzhou) and 0.10% (AM1.5) respectively. If we only consider the UV part of the incident light, the maximum STC could reach

Fig. 3. CH_4, C_2H_2, C_2H_4 and C_2H_6 contents evolution with time under concentrating ratio 800.

about 2.12% (Hangzhou) and 1.44% (AM1.5) respectively.

Fig. 3 and Fig.S6 displays the evolution of the main products, CH_4, C_2H_4, C_2H_6 and C_2H_2 with reaction time. It can be seen that the products are not increased linearly with reaction time. In some cases, the product yields fluctuate. Many reasons maybe account for the fluctuation, such as the inconstant solar light in all day in Hangzhou, and the continues reaction in the system. The high temperature changes the catalyst property. The main crystal phase of TiO_2 is converted from Anatase phase to Rutile phase, as shown in Fig. 4, which will decrease the catalyst activity. While a possible reason is that the products are further reacted under high temperature. Fig. S7 shows that coke is clearly formed on the reactor wall after reaction under concentrating ratio 800.

4. Conclusions

In general, CO_2 photoreduction with H_2O was performed under concentrating solar light. The general reaction rate was greatly enhanced to thousands of $\mu mol \cdot g^{-1} \cdot h^{-1}$ with the large Fresnel lens. The effects are believed to be not only derived from the light intensity increment, but also profited from reaction temperature as well as the

Table 2

solar to chemical energy (STC) efficiencies of TiO_2 under concentrating solar light.

CR	Products yield/($\mu mol \cdot g^{-1}$)					Total	H_{RX}	STC[a]/%		STC[b]/%	
	CH_4	C_2H_2	C_2H_4	C_2H_6	Other	carbon	/J	UV	Total	UV	total
1000	295.74	17.53	289.55	122.54	16.85	742.21	830.36	0.62	0.04	0.42	0.03
800	1578.60	6.89	255.76	673.02	343.25	2857.53	2848.50	2.12	0.15	1.44	0.10
600	529.66	2.01	281.33	118.56	7.00	938.56	974.03	0.72	0.05	0.49	0.03
400	205.38	1.75	298.22	230.94	60.66	796.94	939.35	0.70	0.05	0.47	0.03

[a] Calculated based on Hangzhou light intensity at experimental days, $60\,mW/cm^2$.
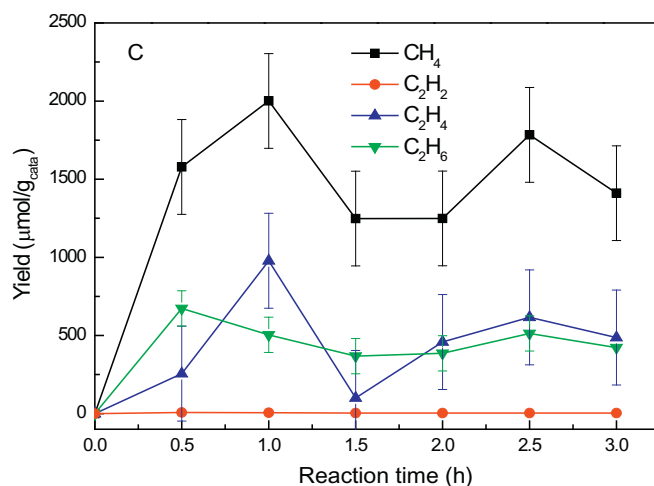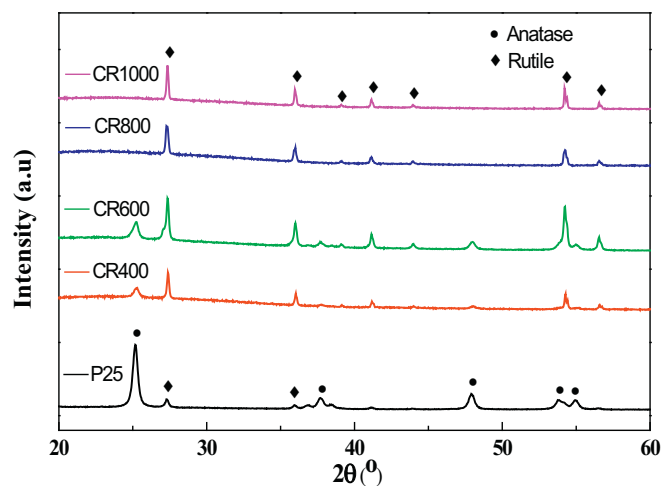[b] Calculated based on AM1.5 spectra and intensity, $100\,mW/cm^2$.

Fig. 4. XRD patterns of TiO$_2$ before and after reaction under different concentration ratios.

pressure of CO_2 and H_2O. The concentrating reactor system will be convenient for the discussion of CO_2 photoreduction using the existed catalyst system, and accelerate the related research works.

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.catcom.2019.03.022.

References

[1] D. Gust, T.A. Moore, A.L. Moore, Solar fuels via artificial photosynthesis, Acc. Chem. Res. 42 (2009) 1890–1898.

[2] T. Inoue, A. Fujishima, S. Konishi, K. Honda, Photoelectrocatalytic reduction of carbon dioxide in aqueous suspensions of semiconductor powders, Nature 277 (1979) 637–638.

[3] S.B. Wang, B.Y. Guan, X.W.D. Lou, Construction of ZnIn$_2$S$_4$-In$_2$O$_3$ hierarchical tubular Heterostructures for efficient CO_2 Photoreduction, J. Am. Chem. Soc. 140 (2018) 5037–5040.

[4] Ş. Neaţu, J.A. Maciá-Agulló, P. Concepción, H. Garcia, Gold-copper Nanoalloys supported on TiO2 as Photocatalysts for CO_2 reduction by water, J. Am. Chem. Soc. 136 (2014) 15969–15976.

[5] W.N. Wang, W.-J. An, B. Ramalingam, S. Mukherjee, D.M. Niedzwiedzki, S. Gangopadhyay, P. Biswas, Size and structure matter: enhanced CO_2 photo-reduction efficiency by size-resolved ultrafine Pt nanoparticles on TiO$_2$ single crystals, J. Am. Chem. Soc. 134 (2012) 11276–11281.

[6] E.V. Kondratenko, G. Mul, J. Baltrusaitis, G.O. Larrazbál, J. Pérez-Ramírez, Status and perspectives of CO_2 conversion into fuels and chemicals by catalytic, photo-catalytic and electrocatalytic processes, Energy Environ. Sci. 6 (2013) 3112–3137.

[7] A. Izumi, Recent Advances (2012–2015) in the Photocatalytic Conversion of Carbon Dioxide to Fuels Using Solar Energy: Feasibilty for a New Energy, Advances in CO_2 Capture, Sequestration, and Conversion, ACS Symposium Series, American Chemical Society, Washington, DC, 2015.

[8] C.C. Yang, Y.H. Yu, B. van der Linden, J.C.S. Wu, G. Mul, Artificial photosynthesis over crystalline TiO$_2$-based catalysts: fact or fiction? J. Am. Chem. Soc. 132 (2010) 8398–8406.

[9] J.D. Hong, W. Zhang, J. Ren, R. Xu, Photocatalytic reduction of CO_2: a brief review on product analysis and systematic methods, Anal. Meth. 5 (2013) 1086–1097.

[10] K. Teramura, T. Tanaka, Necessary and sufficient conditions for the successful three-phase photocatalytic reduction of CO_2 by H_2O over heterogeneous photo-catalysts, Phys.Chem.Chem.Phys. 20 (2018) 8423–8431.

[11] M. Tahir, N.A.S. Amin, Indium-doped TiO$_2$ nanoparticles for photocatalytic CO_2 reduction with H_2O vapors to CH$_4$, Appl. Catal. B 162 (2015) 98–109.

[12] C.S. Turchi, D.F. Ollis, Photocatalytic degradation of organic water contaminants: mechanisms involving hydroxyl radical attack, J. Catal. 122 (1990) 178–192.

[13] V.H. Nguyen, J.C.S. Wu, Recent developments in the design of photoreactors for solar energy conversion from water splitting and CO_2, reduction, Appl. Catal. A 550 (2018) 122–141.

[14] P.Y. Liou, S.C. Chen, J.C.S. Wu, D. Liu, S. Mackintosh, M. Maroto-Valerb, R. Linforth, Photocatalytic CO_2 reduction using an internally illuminated monolith photoreactor, Energy Environ. Sci. 4 (2011) 1487–1494.

[15] H.Y. Chen, F.M. Chu, L.J. Yang, O. Ola, X.Z. Du, Y.P. Yang, Enhanced photocatalytic reduction of carbon dioxide in optical fiber monolith reactor with transparent glass balls, Appl. Energy 230 (2018) 1403–1413.

[16] M. Tahir, Photocatalytic carbon dioxide reduction to fuels in continuous flow monolith photoreactor using montmorillonite dispersed Fe/TiO$_2$ nanocatalyst, J. Clean. Prod. 170 (2018) 242–250.

[17] G.Q. Guan, T. Kida, A. Yoshida, Reduction of carbon dioxide with water under concentrated sunlight using photocatalyst combined with Fe-based catalyst, Appl. Catal. B 41 (2003) 387–396.

[18] G.Q. Guan, T. Kida, T. Harada, M. Isayama, A. Yoshida, Photoreduction of carbon dioxide with water over K$_2$Ti$_6$O$_{13}$ photocatalyst combined with cu/ZnO catalyst under concentrated sunlight, Appl. Catal. A 249 (2003) 11–18.

[19] S.S. Han, Y.F. Chen, S. Abanades, Z.K. Zhang, Improving photoreduction of CO_2 with water to CH$_4$ in a novel concentrated solar reactor, J. Energy Chem. 26 (2017) 743–749.

[20] D. Li, Y.F. Chen, S. Abanades, Z.K. Zhang, Enhanced activity of TiO$_2$ by con-centrating light for photoreduction of CO_2 with H_2O to CH4, Catal. Commun. 113 (2018) 6–9.

[21] C.L. Wang, Z.X. Sun, Y. Zheng, Y.H. Hu, Recent progress in visible light photo-catalytic conversion of carbon dioxideJ, Mater. Chem. A 7 (2019) 865–887.

[22] S.N. Habisreutinger, L. Schmidt-Mende, J.K. Stolarczyk, Photocatalytic reduction of CO_2 on TiO$_2$ and other semiconductors, Angew. Chem. Int. Ed. 52 (2013) 7372–7408.

[23] T. Hisatomi, K. Domen, Introductory lecture: sunlight-driven water splitting and carbon dioxide reduction by heterogeneous semiconductor systems as key processes in artificial photosynthesis, Faraday Discuss. 198 (2017) 11–35.