Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.
This journal is © the Owner Societies 2022

Supplementary Information

High–efficiency photoreduction of CO_2 in low vacuum

Yuxin Liu,[a,e] Shuai Kang,*[a,b] Tinghua Li,[c] Zhuofeng Hu,*[d] Yiwei Ren,[a,b] Ziwei Pan,[b] Xie Fu,[a,b] Liang Wang,[a,b] Shuanglong Feng,[a,b] Jinling Luo,[b] Lei Feng[a,b] and Wenqiang Lu*[a,b]

[a] Chongqing Institute of Green and Intelligent Technology, Chinese Academy of Sciences, Chongqing 400714, China

[b] Chongqing School, University of Chinese Academy of Sciences, Chongqing 400714, China

[c] Technical Center of China Tobacco Yunnan Industrial Co., Ltd, Kunming 650231, China

[d] School of Environmental Science and Engineering, Guangdong Provincial Key Laboratory of Environmental Pollution Control and Remediation Technology, Sun Yat-sen University, Guangzhou 510275, China

[e] University of Chinese Academy of Sciences, Beijing 100049, China

*Corresponding author: Shuai Kang (kangshuai@cigit.ac.cn); Zhuofeng Hu (huzhf8@mail.sysu.edu.cn); Wenqiang Lu (wqlu@cigit.ac.cn)

Table of Contents

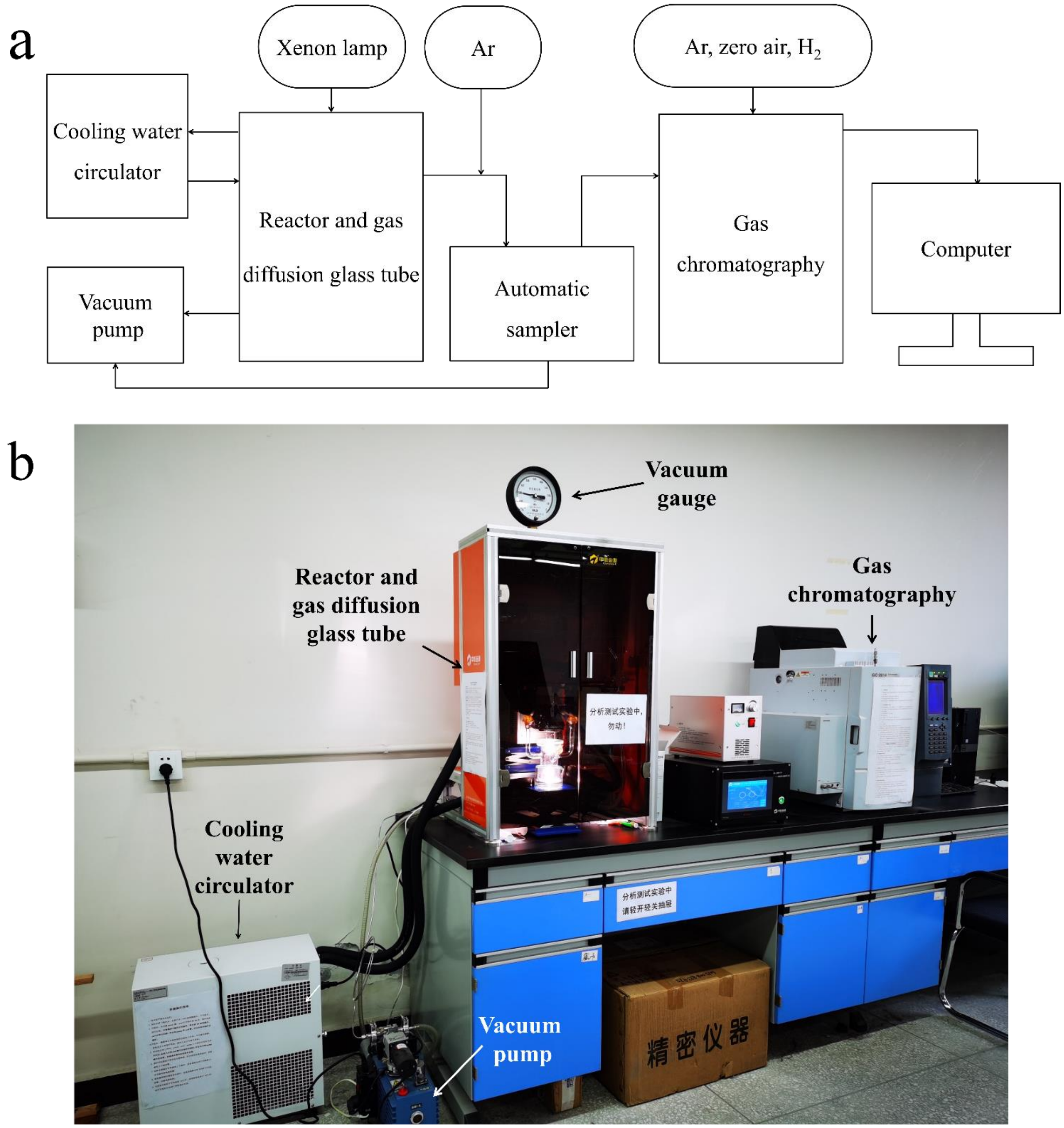

Figure S1. Photocatalytic CO_2 reduction system with online gas analysis. (a) Schematic and (b) photograph.

The total gas pressure:

$$P_{total} = P_{CO_2} + P_{H_2O}$$

According to the Ideal Gas Law:

$$P = \frac{nRT}{V}$$

Where P is the absolute pressure, V is the volume, T is the absolute temperature (T). n is the number of moles, R is the universal gas constant, 8.3145 J/mol K.

In this system, R, T and V is constant.

If we set,

$$a = \frac{RT}{V}$$

Then,

$$P = a \times n$$

Thus,

$$P_{total} = P_{CO_2} + P_{H_2O} = a \times n_{CO_2} + a \times n_{H_2O}$$

$$n_{CO_2} = \frac{1}{a} \times P_{total} - n_{H_2O}$$

From the linear correlation between the absolute gas pressure and CO_2 content in Figure S2, the H_2O content in the system is constant and approximately 0.16 mmol.

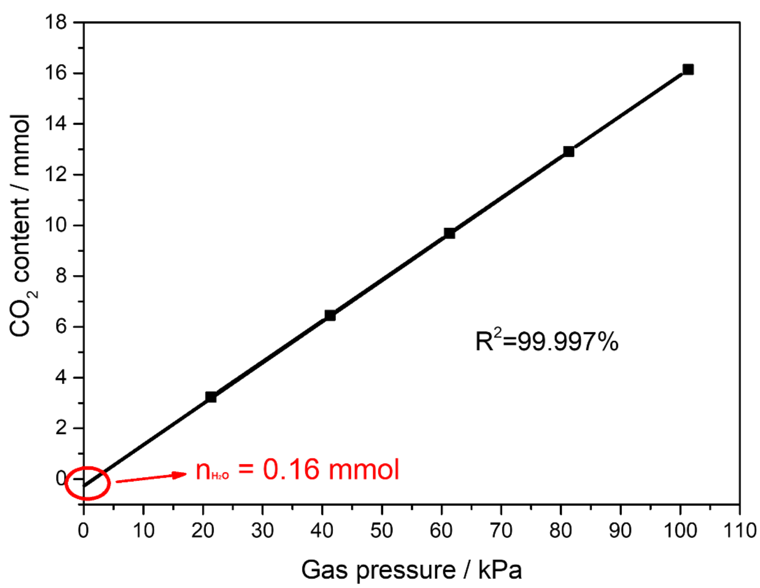

Figure S2. Absolute gas pressure vs. CO_2 content and the approximate H_2O content.

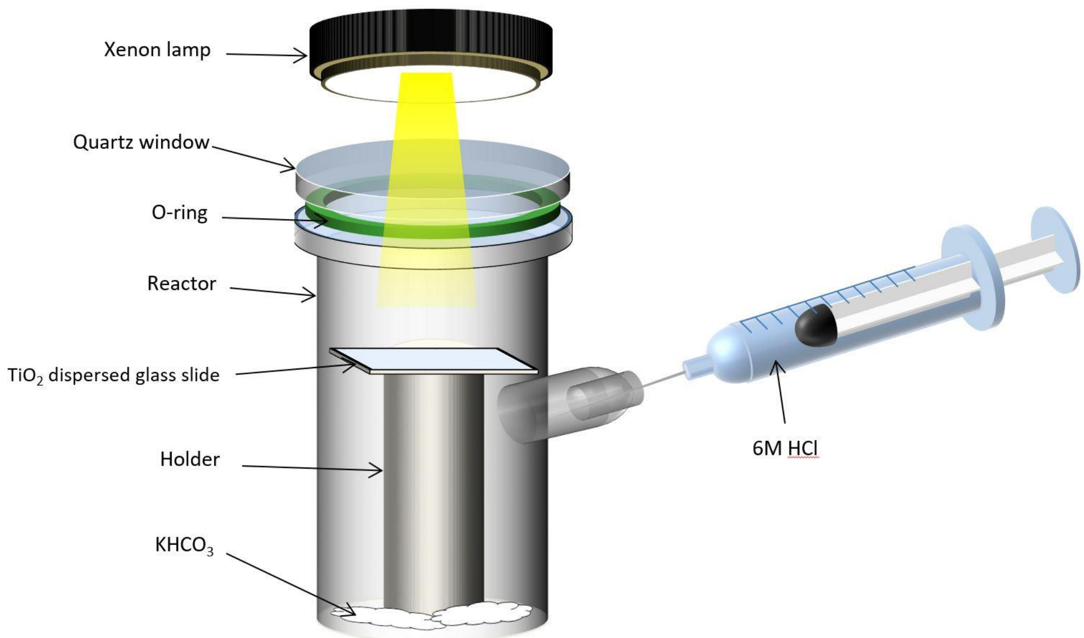

Figure S3. Schematic of the reactor.

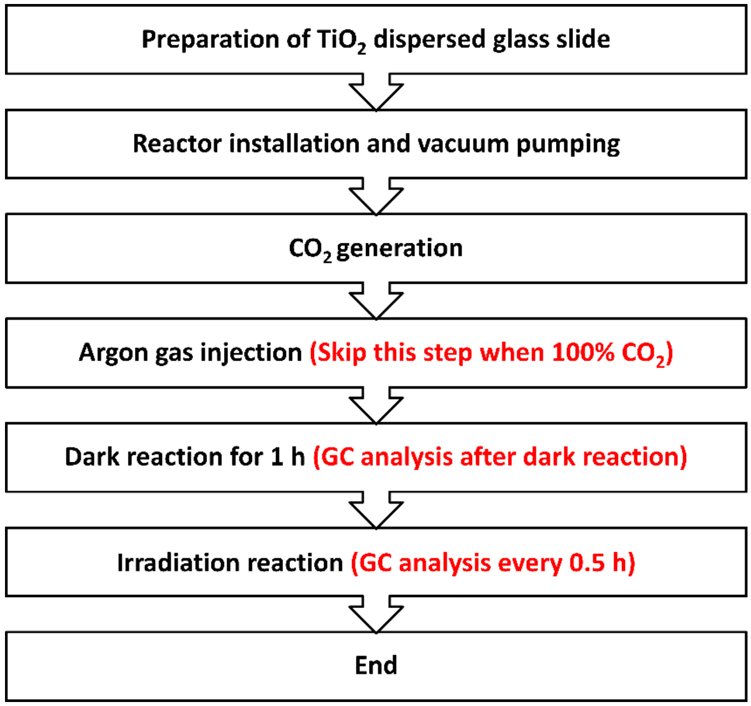

Figure S4. Experimental procedure in this work.

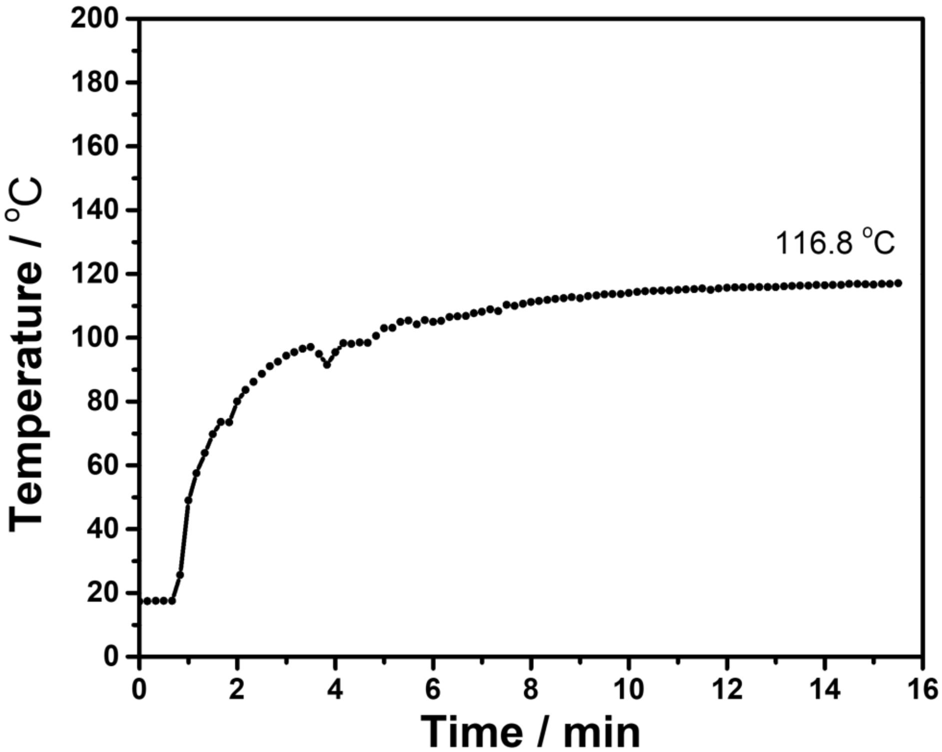

Figure S5. Temperature of the titanium oxide covered glass slide during irradiation.

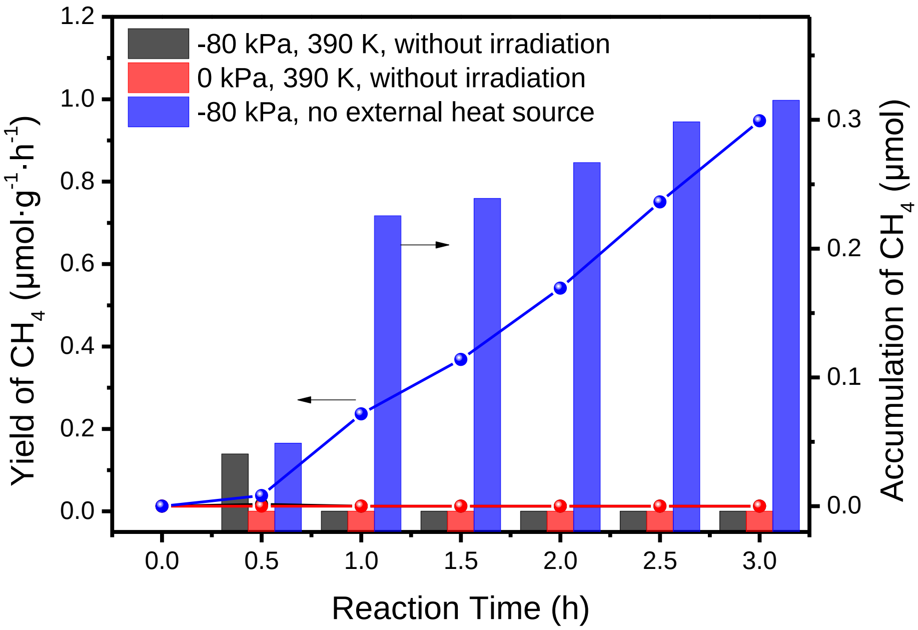

Figure S6. CH_4 yield at 390 K with and without irradiation.

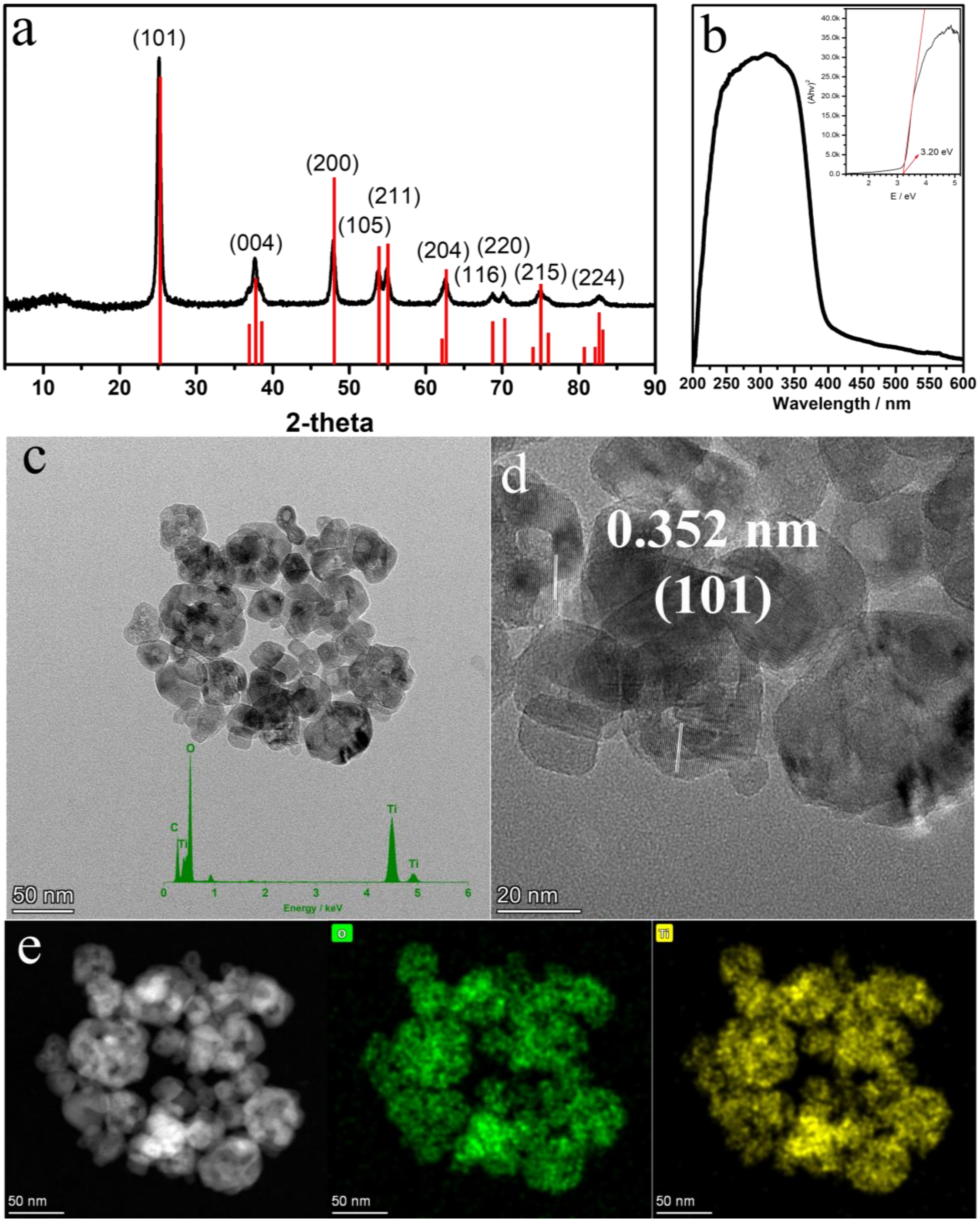

Figure S7. Physical characterizations of the commercial α-TiO_2. (a) XRD pattern of the commercial α-TiO_2. (101) is the most stable lattice plane. (b) Absorption spectrum of the commercial α-TiO_2 covered glass slide. Inset is the Mott-Schottky curve. (c-d) TEM images. Inset is the EDS spectrum. (e) HAADF image and the corresponding elemental mappings of O and Ti.

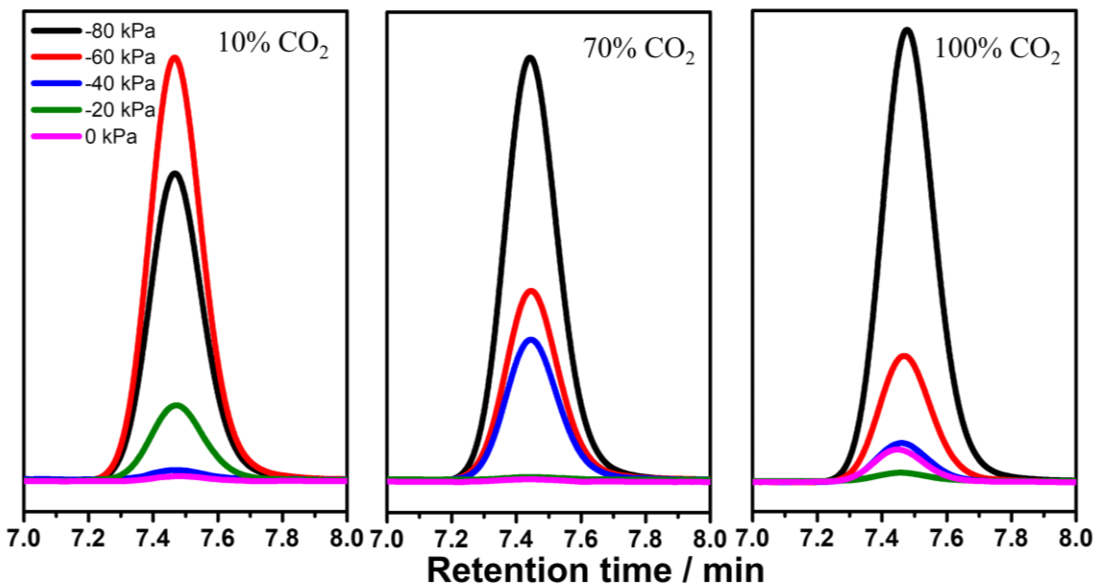

Figure S8. Gas chromatography curves of CH_4 in different CO_2 ratios.

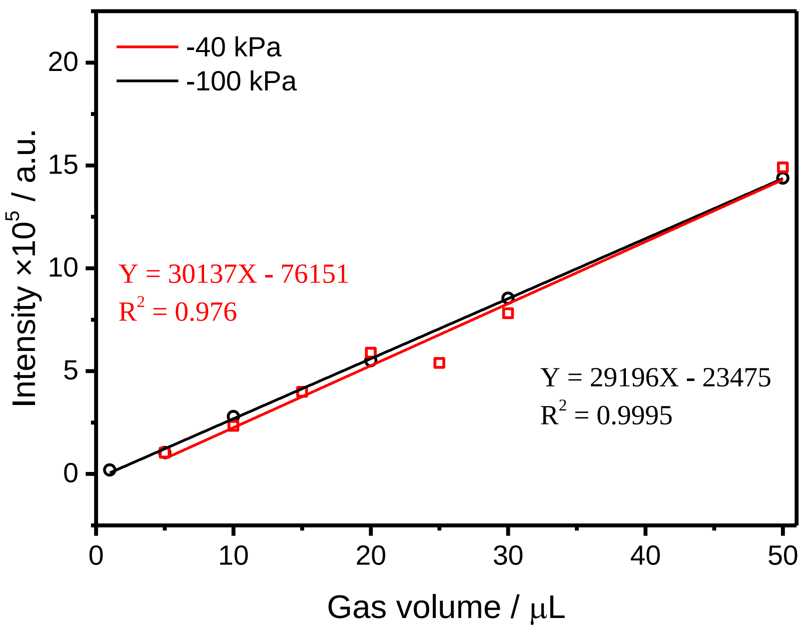

Figure S9. Calibration curves of the gas chromatography of CH_4 at different pressures.

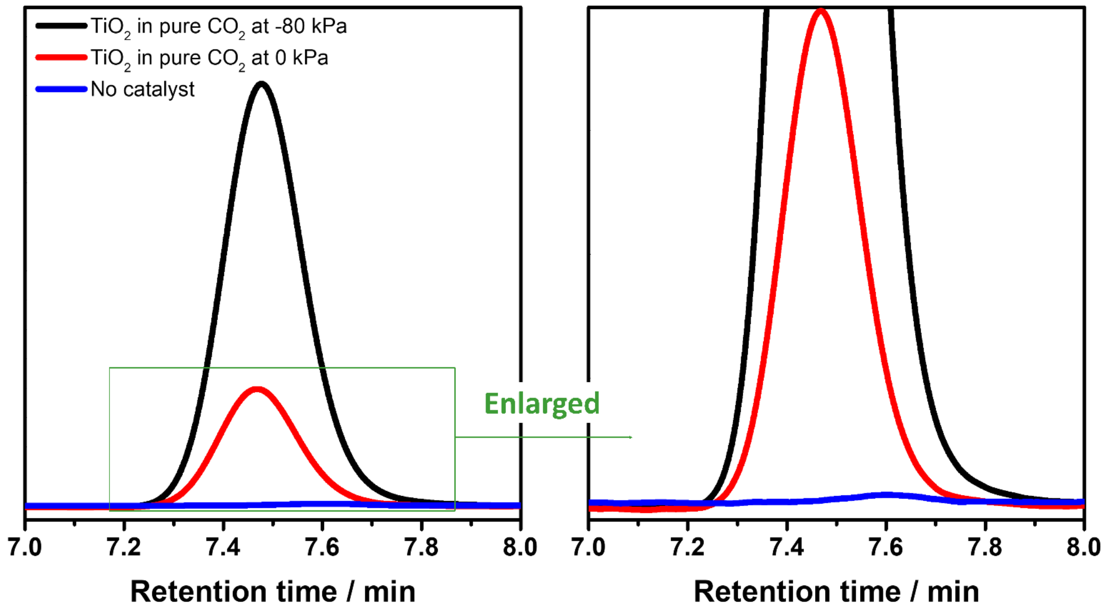

Figure S10. Gas chromatography curves of CH_4 with and without catalysts.

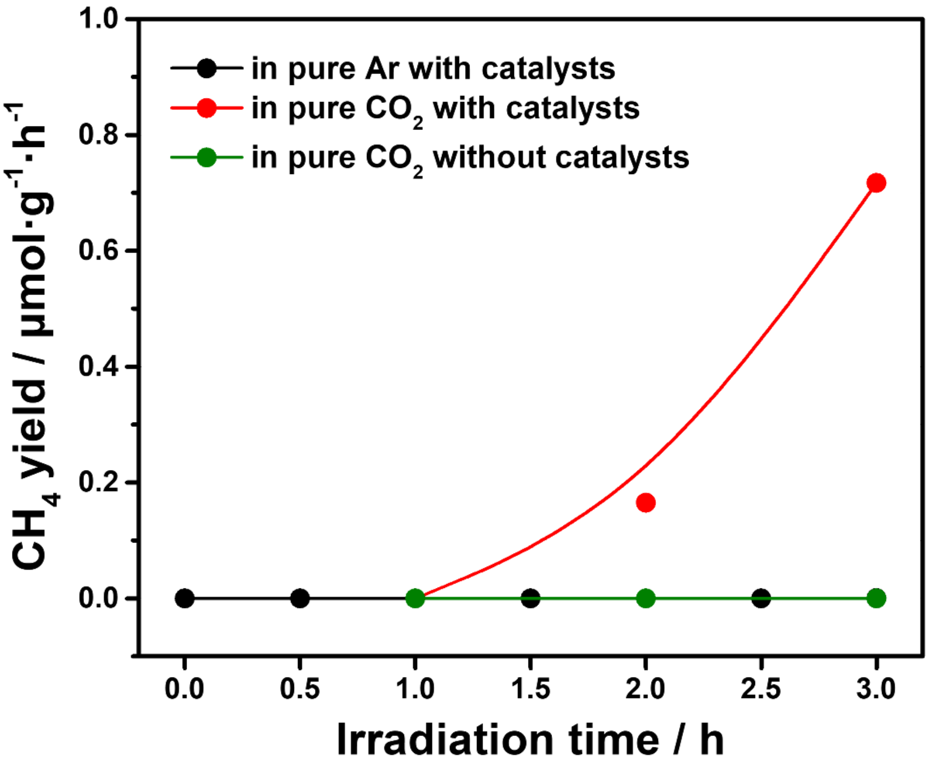

Figure S11. CH_4 yield in different vacuum degrees.

Table S1. CH_4 selectivity at various vacuum degrees.

Unit (%)	**10% CO_2**	**70% CO_2**	**100% CO_2**
-80 kPa	68.52	85	85.89
-60 kPa	64.89	73.5	89.368
-40 kPa	23.894	60.14	95.734
-20 kPa	37.93	95.19	53.987
-0 kPa	46.85	--	95.903

The selectivity of CH_4 in the following discussion is calculated according to the following equation.

$$\text{Selectivity}_{CH_4} = \frac{\text{n}_{CH_4}}{\text{n}_{CH_4} + \text{n}_{CO}}$$

where n is the mole number.

Table S2. CO production rate at different gas pressure and CO_2 content.

Unit (nmol g^{-1} h^{-1})	**10% CO_2**	**70% CO_2**	**100% CO_2**
-80 kPa	180.5	90.63	103.35
-60 kPa	244.97	139.33	33.74
-40 kPa	51.12	254.33	15.03
-20 kPa	335.83	6.23	29.84
0	5.23	6.01	9.34

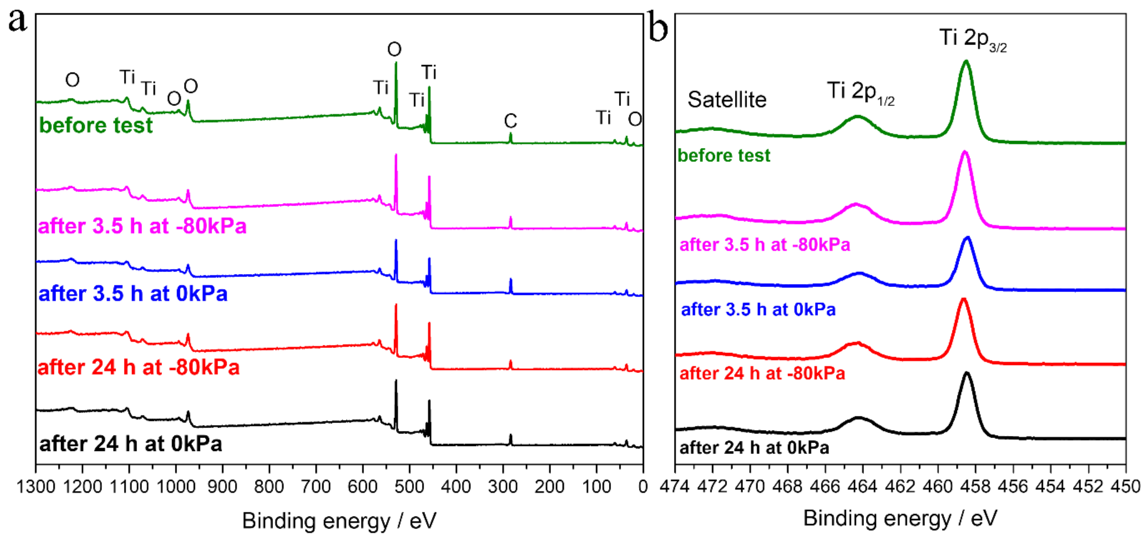

Figure S12. Binding energy evolution of the TiO_2 photocatalyst upon long-term stability test. (a) XPS survey spectra and (b) high-resolution XPS spectra of Ti 2p.

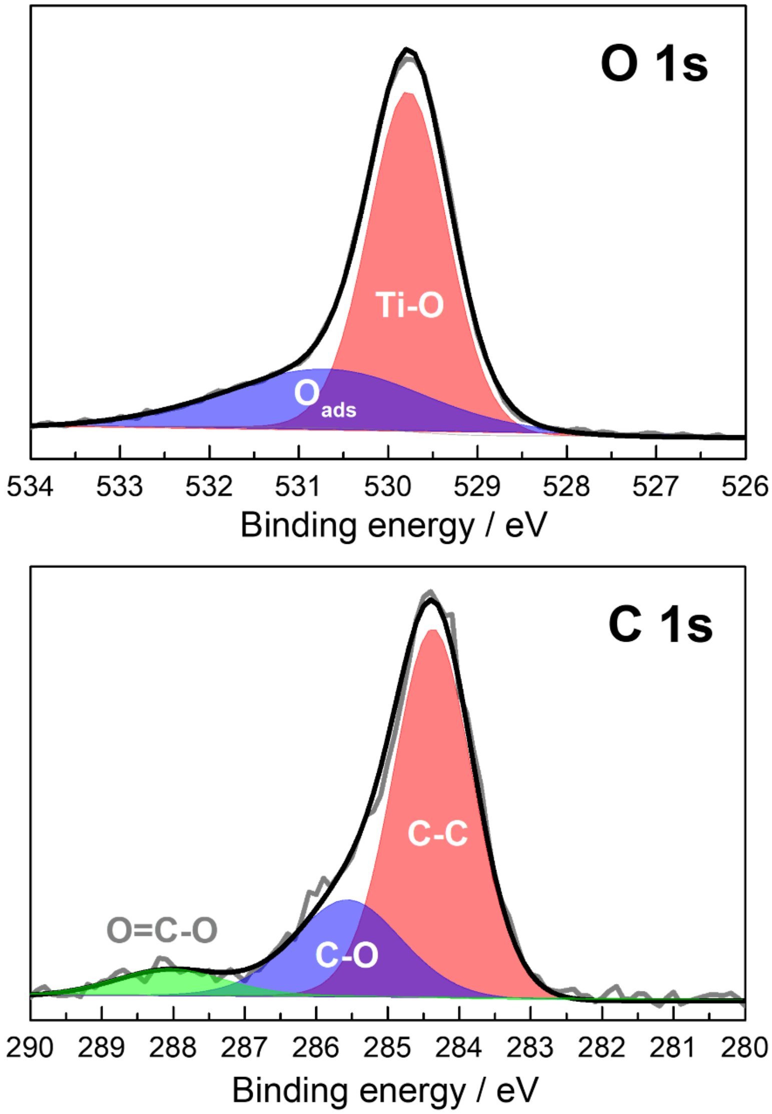

Figure S13. High resolution XPS spectra of O 1s and C 1s on commercial TiO_2 before stability test.

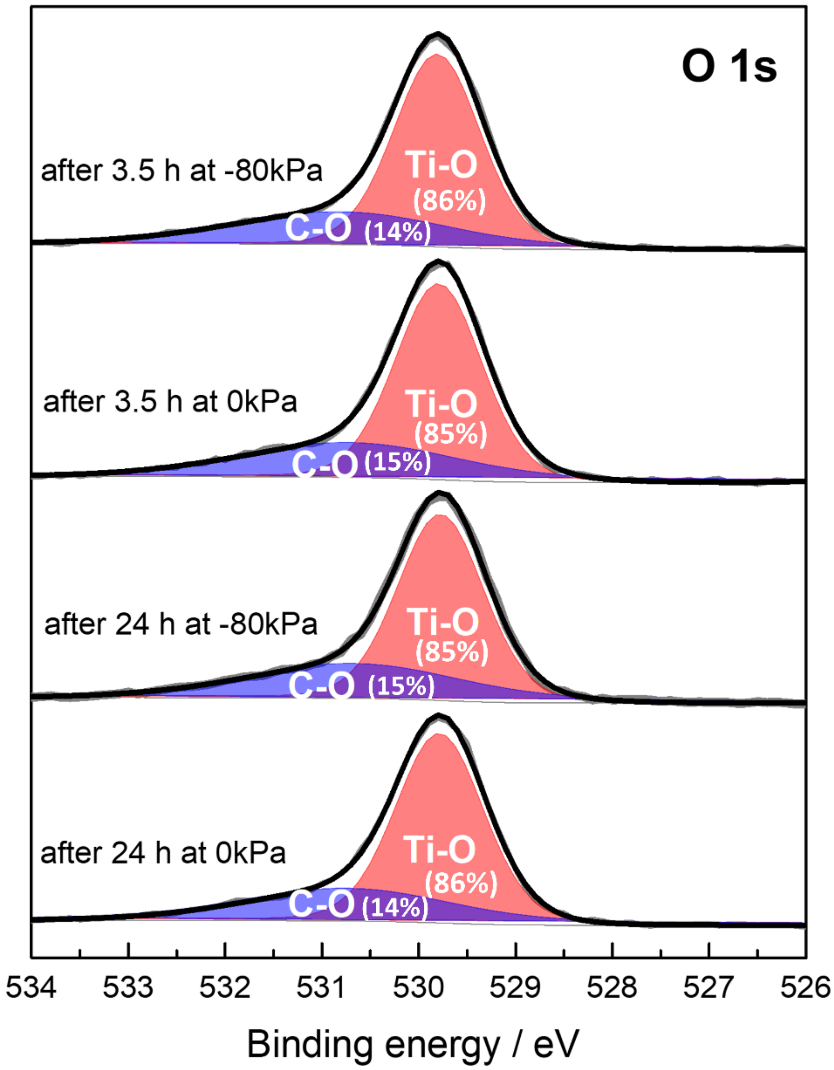

Figure S14. High-resolution XPS spectra of O 1s after running 3.5h and 24 h.

Table S3. Peak fitting parameters of C 1s.

	Name	Peak BE	FWHM eV	Area (P) CPS.eV	Atomic %
Before test	C-C	284.4	1.33	10197.72	74.94
	C-O	285	1.32	2732.26	20.08
	O=C-O	288.1	1.81	678.06	4.98
3.5h at -80kPa	C-C	284.4	1.18	18375.97	80.83
	C-O	285	1.53	3968.54	17.46
	O=C-O	288.1	3.37	389.35	1.71
3.5 h at 0kPa	C-C	284.4	1.14	15922.5	85.19
	C-O	285	1.84	1372.62	7.34
	O=C-O	288.1	1.17	339.88	1.82
24 h at -80kPa	C-C	284.4	1.32	8876.62	79.25
	C-O	285	1.45	1730.15	15.45
	O=C-O	288.1	1.31	507.98	4.54
24 h at 0kPa	C-C	284.4	1.2	10383.1	78.41
	C-O	285	1.35	1970.19	14.88
	O=C-O	288.1	3.37	946.72	7.15

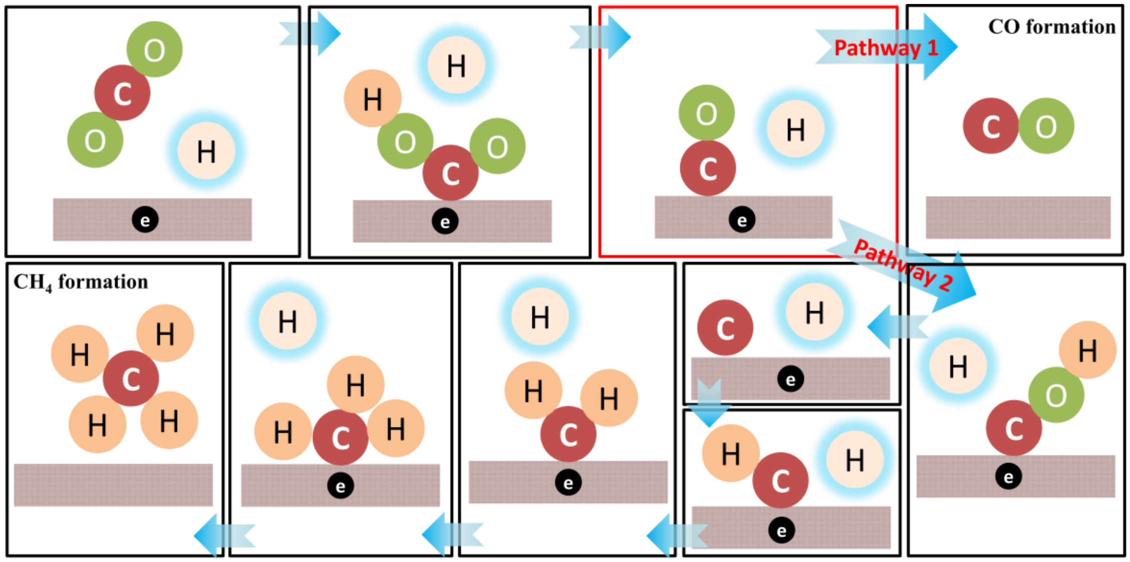

Figure S15. Mechanism of CO_2 photoreduction and the fundamental steps of CO_2 photoreduction in two pathways.

Generally, there are two pathways of CO_2 photoreduction. One is the formation of CO (following the equations S3–S5), the other is the formation of CH_4 (following the equations S3–S4, S6–S12). [1, 2]

$CO_2 + 2H\cdot \rightarrow HCOOH*$ (S3)

$HCOOH* + H\cdot \rightarrow CO* + H_2O$ (S4)

Pathway 1: CO formation

$CO* \rightarrow CO$ (S5)

Pathway 2: CH_4 formation

$CO*+ H\cdot \rightarrow COH*$ (S6)

$COH* + H\cdot \rightarrow C* + H_2O$ (S7)

$C* + H\cdot \rightarrow CH*$ (S8)

$CH*+ H\cdot \rightarrow CH_2*$ (S9)

$CH_2* + H\cdot \rightarrow CH_3*$ (S10)

$CH_3* + H\cdot \rightarrow CH_4*$ (S11)

$CH_4* \rightarrow CH_4$ (S12)

When CO* on the surface of TiO_2 continued to obtain electrons and protons forming COH*, CH_4 generated; otherwise, CO generated.he faster those electrons and H^+ were transferred, the higher CH_4 yield.

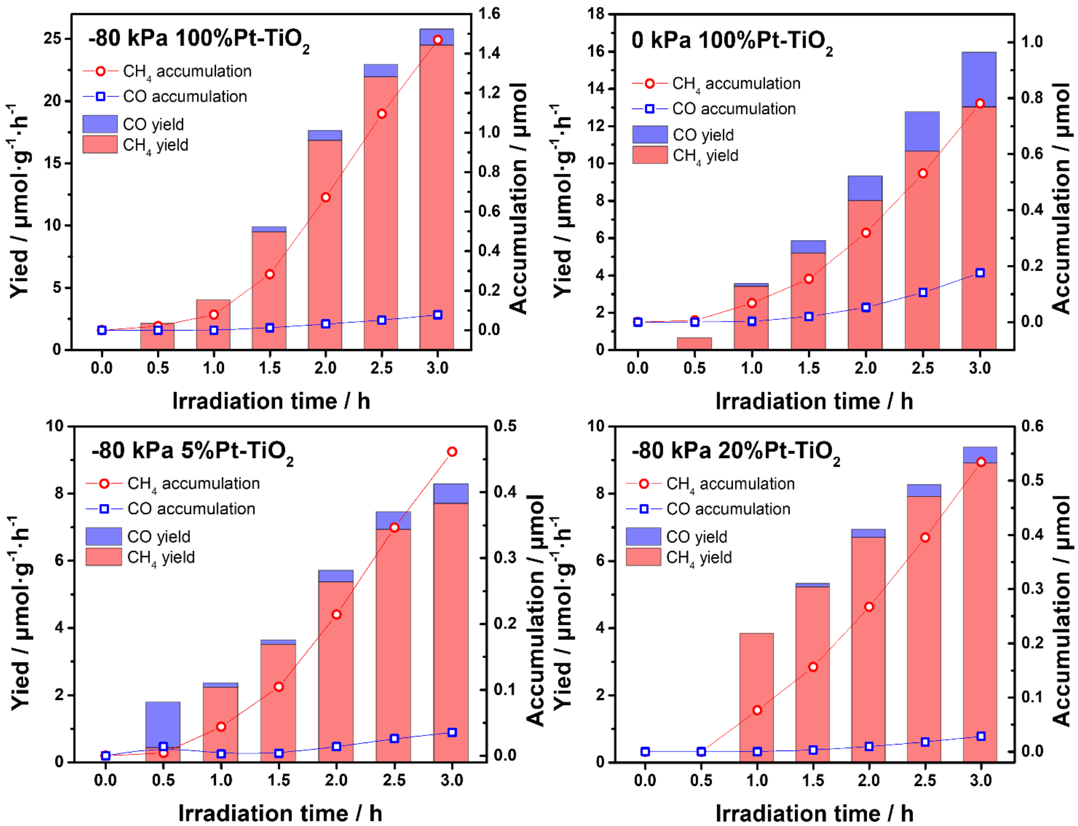

Figure S16. CH_4/CO accumulation and yield of the Pt-TiO_2 catalyst at –80 kPa and 0 kPa.

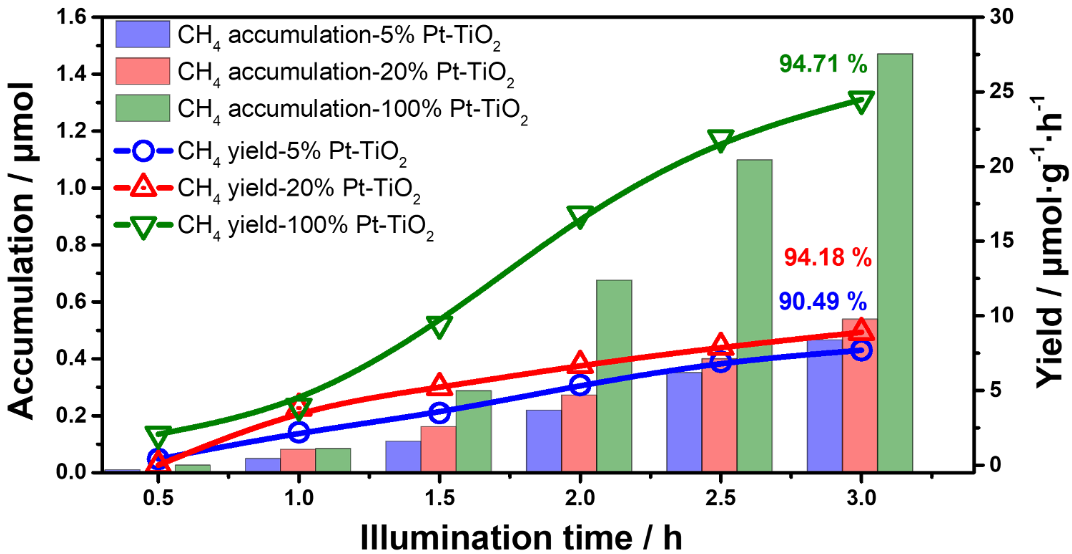

Figure S17. CH_4 accumulation and yield from photocatalytic CO_2 reduction on Pt–TiO_2 catalysts at –80 kPa in pure CO_2. CH_4 selectivity were 94.71%, 94.18%, 90.49% with 100%, 20% and 5% Pt-TiO_2, respectively. For all catalysts, the loading was 20 mg.

References

1. Z. Geng, Y. Cao, W. Chen, X. Kong, Y. Liu, T. Yao and Y. Lin, *Appl. Catal., B*, 2019, **240**, 234-240.
2. J. Fu, K. Jiang, X. Qiu, J. Yu and M. Liu, *Mater. Today*, 2020, **32**, 222-243.