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Supplementary Materials

Photothermally Assisted Photocatalytic CO₂-H₂O Conversion over a WN-

WO₃ Z-Scheme Heterostructure

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1. Experimental Details

1.1 Chemicals

Tungsten trioxide (WO₃) and ethanediamine (EDA) were purchased from Aladdin Ltd. (Shanghai, China). The potassium tetrachloropalladate (K_2PdCl_4) was bought from Shanghai Titan Scientific Co., Ltd. The ammonia (NH₃), air, oxygen (O₂) and carbon dioxide (CO₂) gas were bought from Air Liquide (Tianjin) Co., Ltd. Deionized was used in all the experimental processes. All chemicals were analytical grade and used without further purification.

1.2 Synthesis of materials

Synthesis of WN nanorods. commercial WO₃ (0.4 g) was dispersed in 12 mL EDA under vigorous stirring for 30 min in a 15 mL Teflon-lined stainless-steel autoclave. Then the system was treated at 180 °C for 8 h and cooled down naturally. The white product formed at the end of the reaction were washed by deionized water (DIW) and dried in a vacuum oven. Then the white product was put into a quartz tube with diameter of 6 mm and heated to 700 °C with a rate of 1 °C /min for 5 h in oxygen. The obtained product was put into a quartz tube. Then the sample was heated to 700 °C with a rate of 2 °C /min for 3 h in ammonia. The whole procedure was conducted under constant NH₃ gas flow (100 mL/min).

*Synthesis of WN-WO*₃ *heterostructure*. To obtain the WN-WO₃ heterostructure, the as-prepared WN was heated to 300 °C with a rate of 2 °C/min for 1 h in air (40 mL/min). Then it was cooled down naturally.

Synthesis of Pd-loaded WN-WO₃ heterostructure. 300 mg of corresponding WN-WO₃ heterostructure was dispersed in a 150 mL aqueous solution containing 10 mL methanol and 7 mg K_2 PdCl₄. Then, the suspension was irradiated under stimulated sunlight with a constant stirring in Ar atmosphere. After reaction for 1 hour, the resulting precipitate was obtained by centrifugation, followed by washing with deionized water and ethanol for three times, respectively, and dried at 40 °C for 12 hours in a vacuum oven.

2. Materials Characterization

Powder XRD was performed on a Bruker D8 Focus Diffraction System using a Cu K α source (λ =0.154178 nm). SEM was taken with a Hitachi S-4800 scanning electron microscope. Transmission electron microscopy (TEM) and higher-magnification transmission electron microscopy (HRTEM) were obtained with JEOL-2100F system. X-ray photoelectron spectroscopy (XPS) measurements were conducted with a PHI-1600 X-ray photoelectron spectrometer equipped with Al K α radiation. Different from the routine XPS instrument, the *in situ* irradiated XPS was carried out under photo-irradiation imported by an optical fiber,

and a 300 W Xe arc lamp was equipped for providing UV-vis light. UV-vis diffuse reflectance spectra (UVvis DRS) were recorded on a Lambda 750 UV-vis-NIR spectrometer (Perkin-Elmer) equipped with an integrating sphere. The UV-vis DRS of solid samples were collected in 200-1800 nm against BaSO₄ reflectance standard. Ultraviolet photoelectron spectroscopy (UPS) measurements were performed with an unfiltered He I (21.2 eV) gas discharge lamp and a total instrumental energy resolution of 100 meV. Electrochemical transient photocurrent response measurements were performed in a three-electrode electrochemical cell with a Pt counter electrode (1×2 cm) and saturated calomel electrode (SCE) reference electrode in 0.5 M Na₂SO₄ electrolyte. The working electrode was fabricated by spreading 100 µL of the catalyst ink, which was obtained through dispersing 2 mg of catalyst powder in 1 mL of 4:1 v/v water/ethanol and 20 µL Nafion solutions for 30 min, onto a FTO conducting glass electrode and drying the coated substrate at room temperature. The electron spin resonance (ESR) analysis was conducted with an electron paramagnetic resonance A300 spectrometer (Bruker AXS Company, Germany). The ESR analysis was performed to detect the spin reactive \cdot OH and \cdot O₂⁻ species adsorbed on the photocatalysts or dissolved in water/methanol under UV-vis light irradiation by using 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as a spin trap. The *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) analysis was carried out in two sequential steps in a continuous-flow mode. First, CO₂ adsorption on the sample surface was studied by introducing a CO₂/H₂O mixture to the IR cell at 150 °C for 60 min in the dark when the intensities of adsorption peaks reached saturation. Next, the LED light (365 nm) was turned on for 30 min to investigate the photocatalytic conversion of reaction intermediates. A certain amount of silica was added to WN and WN-WO₃ heterostructure to enhance the signal of DRIFTS. It should be noted that, prior to the CO₂ adsorption, we collected the IR spectrum of the photocatalyst first as the background. When introducing the CO₂ onto the photocatalyst, we obtained the IR spectra of the adsorbed species by subtracting the background. Photoluminescence (PL) spectra were obtained using afluorescence spectrometer (Shimadzu; UV-3600) with 366 nm excitation wavelength. The actual content of Pd in photocatalyst was detected by the Agilent 7700X Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). Temperature-programmed desorption of carbon dioxide (CO2-TPD) measurement was performed on a conventional flow apparatus. Prior to measurements, 100 mg of the sample was pretreated in He gas (60 cm³ min⁻¹) at 300 °C for 1 h and then cooled down to room temperature. Next, the sample was exposed to CO₂ flow of 30 cm³ min⁻¹ for 0.5 h to ensure the sufficient adsorption of CO_2 . Before desorption, the sample was flushed in He gas for 1 h. Subsequently, CO₂ desorption was performed in the range of 30-600 °C at a

heating rate of 5 °C min⁻¹ under an He flow of 30 cm³ min⁻¹. The water vapor adsorption-desorption experiment was investigated by 3H-2000PW Multi-station weight method vacuum vapor sorption analyser.

3. Photocatalytic CO₂-H₂O Conversion Measurements

The CO₂-H₂O conversion was conducted in a home-made sealed reaction chamber with a quartz window at the top for light irradiation. The volume of the chamber was 75 mL. The sample (50 mg) was spread in the reaction chamber. Prior to the photoreaction, the chamber was evacuated by a mechanical pump. Then, CO₂ (Air Liquide (Tianjin) Co., Ltd 99.999%) bubbled through water was added to the chamber to achieve a pressure of 0.12 MPa. The products formed under irradiation (300 W Xe lamp with AM 1.5G light-filter, Beijing Perfectlight Co. Ltd, PLS-SXE-300UV) were determined at regular intervals from the chamber. The intensity of simulated sunlight is about 0.4 W/cm⁻². The products were analyzed by BID-GC using a Shimadzu GC-2010 chromatograph, equipped with an active-carbon-packed column (carrier gas: He).

4. Additional Characterizations and Measurements

4.1 The SEM and HRTEM images of WN

The scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images (Fig. S1) reveal that WN nanorods composed of particles are successfully prepared. The lattice fringe of 0.24 nm in Fig. S1b is indexed to the WN (111) plane.



Fig. S1 (a) SEM and (b) HRTEM (inset: TEM) images of WN.

4.2 CO₂-TPD profiles of WN and WN-WO₃ heterostructure

The CO₂ chemical adsorption capacities of WN and WN-WO3 heterostructure were investigated by CO₂ temperature-programmed desorption (CO₂-TPD). In Fig. S2a, there were two types of desorption peaks which represent CO₂ weak adsorption (be noted as I peak, 60~100 °C) and strong adsorption (be noted as II peak, 300~500 °C), respectively. Compared with WN, the II peaks of WN-WO₃ shift to higher temperature, suggesting a stronger CO₂ adsorption. Meanwhile, as shown in Table S1, the amount of CO₂ strong adsorption was largely enhanced in WN-WO₃ heterostructure. The amount of CO₂ weak adsorption (I peak) so small that could be ignored. Therefore, it could be proposed that the WN-WO₃ heterostructure exhibited a better CO₂ chemical adsorption capacity. Fig. S2b showed the water vapor adsorption/desorption isotherms of WN and WN-WO₃ heterostructure. Compared with WN, the adsorption capacity of WN-WO₃ to water vapor was decreased. It resulted from the formation of WO₃, whose adsorption capacity to water vapor was poor.



Fig. S2 (a) CO₂-TPD profiles and (b) water vapor adsorption/desorption isotherms of WN and WN-WO₃ heterostructure.

4.3 XPS analysis of WN-WO₃ heterostructure

The XPS survey spectra (Fig. S3) show the presence of W, N, and O elements in WN and WN-WO₃. The weak peak of O 1s is presented in WN due to inevitable exposure in the air before XPS measurement. While fresh WN is used for photocatalytic test. The intensity of O 1s peak increases after oxidation treatment due to increased oxide content. As a result, the intensity of N 1s peak is reduced.



Fig. S3 The XPS survey spectra of WN and WN-WO₃.

4.4 The XPS spectra of Pd 3d for Pd-loaded WN-WO₃ heterostructure

To study the chemical state of Pd, the XPS analysis was carried out on Pd-loaded WN-WO₃ heterostructure. In Pd 3d spectra (Fig. S4), two characteristic peaks at 335.5 and 340.8 eV were attributed to metallic Pd(0). Besides, the weak peak at 338.1 eV was ascribed to Pd-Cl bond, which may result from the residue of potassium tetrachloropalladate on the catalyst surface^[1]. Thus, the Pd element is present in the form of metallic palladium on the catalyst surface.



Fig. S4 The XPS spectra of Pd 3d for Pd-loaded WN-WO₃ heterostructure.

4.5 The CO₂ conversion performance of WN-WO₃ and Pd-loaded WN-WO₃ heterostructures

To further demonstrate the effect of Pd on performance, we carried out the CO₂ conversion experiments on as-prepared WN-WO₃ as well as Pd-loaded WN-WO₃ heterostructures (Fig. S5). For both samples, the major products observed were H₂, CO, and CH₄. Fig. S5 showed that the yield of H₂, CO, and CH₄ increased from 500.9, 64.3, and 112.7 μ mol g⁻¹ on WN-WO₃ heterostructure to 2113.1, 78.4, and 213.5 μ mol g⁻¹ on Pd-loaded WN-WO₃ heterostructure. Thus, Pd nanoparticles as a co-catalyst not only enhances photocatalytic efficiency of CO₂ conversion but also increases the selectivity of CH₄.



Fig. S5 The CO₂ conversion performance of WN-WO₃ and Pd-loaded WN-WO₃ heterostructures under simulative sunlight irradiation for 5 h.

4.6 The oxygen evolution rates of photocatalysts during CO₂ conversion

To demonstrate the overall photocatalytic mechanism, the evolution rate of oxygen as the oxidation product was measured. Fig. S6 showed the O_2 evolution rate of WO_3 , WN, and WN- WO_3 heterostructure. The O_2 evolution rates over WN and WN- WO_3 heterostructure were 1.63 and 5.08 µmol h⁻¹, equivalent to 6.52 and 20.32 µmol h⁻¹ of electrons, respectively. However, the O_2 evolution rate of WO_3 was too low to be detected. In the reduction reaction, the WN and WN- WO_3 heterostructure consumed about 5.38 and 18.27 µmol h⁻¹ of electrons, respectively, to produce H_2 , CO and CH_4 . The electrons from the water oxidation were almost comparable to the consumed electrons for the reduction reaction both on the WN and WN- WO_3 . This result clearly demonstrated that H_2O as an electron donor in the whole photocatalytic process.



Fig. S6 The O_2 evolution rates of WO_3 , WN, and $WN-WO_3$ with Pd loading during photocatalytic CO_2 conversion under simulated sunlight irradiation.

4.7 The SEM image and XRD pattern of WN-WO₃ heterostructure after CO₂-H₂O conversion

Fig. ST shows the SEM image and XRD pattern of WN-WO₃ heterostructure after long-term CO_2 reduction test. These results demonstrate that the WN-WO₃ heterostructured catalyst preserves their morphology and components after long-term CO_2 reduction test.



Fig. S7 (a) The SEM image and (b) XRD pattern of WN-WO₃ heterostructured catalyst after long-term CO₂-H₂O conversion test.

4.8 The XPS analysis of the WN-WO3 heterostructure after CO2-H2O conversion



Fig. S8 XPS spectra for (a) W 4f and (b) N 1s of WN-WO₃ heterostructure after after CO₂-H₂O conversion.

4.9 The in situ DRIFTS analysis for WN, WN-WO₃, and Pd-loaded WN-WO₃ heterostructure

To identify the surface intermediates and explore the role of heterostructure for CO₂ activation and conversion, the in situ DRIFTS is conducted on WN, WN-WO₃, and Pd-loaded WN-WO₃ at short time intervals with the presence of CO₂ and H₂O (Fig. S9). The DRIFTS analysis was carried out in two sequential steps in a continuous-flow mode. First, CO₂ adsorption on the sample surface was studied by introducing a CO₂/H₂O mixture to the IR cell at 150 °C for in the dark until the intensities of adsorption peaks remain unchanged. Next, the LED light (365 nm) was turned on for 30 min to investigate the photocatalytic conversion of reaction intermediates. As shown in Fig. S9, those prepared samples exhibited similar DRIFTS spectra. The peaks at 1683, 1669, 1622, 1573, 1521, 1507, 1434, and 1318 cm⁻¹ were attributed to carbonate species, those at 1868, 1844, 1826, 1794, 1699, 1649, 1556, 1539, 1488, 1456, 1397, 1375, and 1339 cm⁻¹ were ascribed to adsorbed formate (HCOO), and those at 1773, 1748, 1717, 1420, and 1243 cm⁻¹ were assigned to adsorbed formaldehyde (HCHO). The peaks at 1732, and 1472 resulted from vibration of CH₃O groups.^[2] The results of DRIFTS analysis demonstrated that these adsorbed CO₂ and H₂O were converted into carbonate, HCOO, HCHO, and CH₃O before their transformation into the CO and CH₄ under UV light irradiation. In addition, the peak intensity of HCOO, HCHO, and CH₃O gradually increased over Pd/WN-WO₃ heterostructure under irradiation. However, those of species almost remained unchanged over WN and WN-WO₃. It revealed a higher photocatalytic efficiency of Pd/WN-WO₃ heterostructure.



Fig. S9 *In situ* DRIFTS spectra for CO_2/H_2O vapor adsorption on (a) WN, (b) WN-WO₃ and (c) Pd/WN-WO₃ heterostructure in the dark and under UV light irradiation.

4.10 The CO₂-H₂O conversion performance of Pd-loaded WN-WO₃ under simulated sunlight irradiation with different intensities



Fig. S10 The CO₂-H₂O conversion performance of Pd-loaded WN-WO₃ under simulated sunlight irradiation with different intensities for 5 h.

4.11 The infrared thermal images of Pd-loaded WN-WO₃ heterostructure



Fig. S11 The infrared thermal images of Pd-loaded WN-WO₃ heterostructure in the dark and under simulated solar light irradiation

4.12 Temperature-dependent kinetic analysis

The temperature-dependent kinetic experiment on the photocatalytic CO_2 conversion is taken out to further investigate the role of heat. The rate constant for the overall reaction can be estimated using a pseudo-zero order model due to the dominant electron consumption selectivity and linear increase of CH_4 production. Fig. S12 presented the Arrhenius plot based on the kinetics experiments by varying the reaction temperature (50, 75, 100 and 150 °C) on the photocatalyst surface. The photocatalyst was surrounded by the circulating water in a jacketed reactor to adjust the temperature. The actual temperature on the surface of the photocatalyst was measured using an infrared camera. The apparent activation energy value of the overall reaction over Pd/WN-WO₃ heterostructure is calculated to be 46.9 kJ/mol. The result clearly explains that the elevation of surface temperature has positive effect on the CO_2 conversion. It can be inferred that the local photothermal effect will enhance the movement of gas molecules and charge carriers, both of which may contribute to the improved CO_2 conversion efficiency.



Fig. S12 Temperature-dependent kinetic analysis of CH₄ production rate over Pd/WN-WO₃ heterostructure.

4.13 The UV-vis diffuse reflectance spectroscopy and ultraviolet photoelectron spectroscopy (UPS) of WN and WO₃

Fig. S13a shows the UV-visible diffuse-reflectance spectra (UV-vis DRS) of WO₃, WN, and WN-WO₃ heterostructure. It demonstrates that the WO₃ has the highest diffuse reflectance in the ultraviolet-visible range, suggesting the worst ability to harvest photons among these photocatalysts. The WN and WN-WO₃ heterostructure both exhibit strong ability to harvest photons whose diffuse reflectance less than 10%. However, the diffuse reflectance of WN-WO₃ is slightly higher than that of WN (inset in Fig. S13a). Thus, the ability of WN to harvest photons is slightly decreased after partially in situ oxidation. It maybe resulted from the existence of WO₃ in the WN-WO₃ heterostructure. To measure the optical bandgap energy (E_{o}) of WN and WO₃, UV-vis diffuse reflectance spectroscopy (UV-vis DRS) was carried out. Fig. S13a,b show that the (E_g) of WN and WO₃ are obtained to be 1.9 and 2.4 eV by fitting the UV-Vis diffuse reflectance spectrum with a modified Kubelka-Munk function. In addition, the UPS is used to confirm the ionization potential (equivalent to the valence band energy E_v) of WN (Fig. S13c). The cutoff (E_{cutoff}) and onset (E_i) energy are 15.48 and 0.19 eV, respectively. The E_v is calculated to be 5.93 eV by subtracting the width of the UPS spectra from the excitation energy (21.22 eV). The conduction band energy E_c is thus estimated at 4.03 eV from $E_v - E_g$. Thus, the conduction band (CB) and valence band (VB) positions of WN are approximately -0.82 and 1.08 V versus normal hydrogen electrode (NHE). Similarly, the CB and VB positions of WO₃ are deduced at 0.63 and 3.03 V in the same way (Fig. S13d).



Fig. S13 (a) UV-vis DRS of WO₃, WN, and WN-WO₃ heterostructure. (b) The modified Kubelka-Munk function of WN and WO₃. (c) UPS spectra in the onset and the cutoff energy regions of WN and (d) WO₃.

4.14 The transient photocurrent response measurements for WN and WN-WO₃ heterostructure

The transient photocurrent response measurement (Fig. S14) directly indicates that the WN-WO₃ heterostructure shows higher separation efficiency of photogenerated charge carriers compared with WN.



Fig. S14 Transient photocurrent response of WN and WN-WO₃.

4.15 The photoluminescence and lifetime analysis based on the fluorescence decay for WN and WN-

WO₃ heterostructure

The photoluminescence (PL) was used to explore the carrier separation of WN and WN-WO₃ heterostructure because PL emission arises from the recombination of free carriers. The PL spectra of WN and WN-WO₃ heterostructure in the wavelength range 390-600 nm were shown in Fig. R15a. Obviously, the WN emitted strong PL signals with peaks at 408, 432, and 459 nm. Compared with WN, the PL signals intensity of WN-WO₃ heterostructure significantly decreased, indicating a much lower recombination rate of photogenerated electrons and holes. The PL results revealed that the WN-WO₃ heterostructure showed higher photogenerated electron-hole separation efficiency. The separation behaviours of photogenerated carries were further confirmed by the lifetime analysis based on the fluorescence decay shown in Fig. R15b. The average lifetime of WN-WO₃ is longer than WN, suggesting a more effective separation and migration of the photogenerated carries in WN-WO₃ heterostructure.



Fig. S15 (a) PL spectra under 366 nm excitation; (b) Fluorescence lifetime of WN and WN-WO₃ heterostructure.

Photosotalyst	Temperature at I	Quantity of I peak	Temperature at II	Quantity of II peak	
Thotocatalyst	peak (°C)	(mmol/g)	peak (°C)	(mmol/g)	
WN	98.4	0.056	369.1	0.229	
WN-WO ₃	71.6	0.033	397.9	0.579	

Table S1 CO₂-TPD data of WN and WN-WO₃ heterostructure.

Table S2 The photocatalytic CO_2 -H₂O reduction performance of WN-WO₃ heterostructure and other photocatalysts without sacrificial reagent.

			H_2	СО	CH ₄	CH ₃ OH	TCEN
Photocatalyst	Condition	Light source	(µmol	(µmol	(µmol	(µmol g⁻	(µmol
			g-1 h-1)	g ⁻¹ h ⁻¹)	g ⁻¹ h ⁻¹)	¹ h ⁻¹)	g ⁻¹ h ⁻¹)
WN-WO ₃	CO ₂ +H ₂ O	Simulated	368.5	15.2	40.6		355.2
		sunlight					
Rb _{0.33} WO ₃ ^[3]	$Air + H_2O$	Full light		0.07	0.02	3.73	22.7
BVO/C/Cu ₂ O ^[4]	CO ₂ +H ₂ O	Visible light		3.0	~0.5		10.0
Al-O bridged g-	$CO_2 + H_2O$	Full light		24	~5		88
C_3N_4/α -Fe ₂ O ₃ ^[5]							
Bi ₂₄ O ₃₁ Cl ₁₀ -OV ^[6]	$CO_2 + H_2O$	Full light		0.9			1.8
$Ag_2CrO_4/g\text{-}C_3N_4/GO^{[7]}$	$CO_2 + H_2O$	Simulated			~0.1	~0.8	5.6
		sunlight					
layered zinc silicate ^[8]	8kPa	Full light		126.7			253.4
	$CO_2 + H_2O$						
Pd/CsPbBr ₃ ^[9]	1bar	Visible light	1.1	1.9	3.5		31.8
	$CO_2 + H_2O$						
CdS-WO ₃ ^[10]	$CO_2 + H_2O$	Visible light			1.0		8.0
$Ag/TiO_{2}^{[11]}$	$CO_2 + H_2O$	Visible light			1.7		13.6
TiO ₂ /Bi/Bi ₂ O ₃ ^[12]	$CO_2 + H_2O$	Full light		~0.7			1.4
Pt/GaN ^[13]	80kPa	Full light		~50	~14.8		218.4
	$CO_2 + H_2O$						
$g-C_3N_4/Bi_2WO_6^{[14]}$	$CO_2 + H_2O$	Visible light		5.2			10.4
N-doped WO _{3-x} ^[15]	$CO_2 + H_2O$	Simulated	12.6		12.6		100.8
		sunlight					
$TiO_2\{001\}$ and $\{101\}^{[16]}$	$CO_2 + H_2O$	Full light			1.35		10.8
ZnIn ₂ S ₄ ^[17]	CO ₂ +H ₂ O	Simulated		33.2			66.4
		sunlight					
$TiO_2/g-C_3N_4^{[18]}$	$CO_2 + H_2O$	Visible light		0.8	5.2		43.2
m-CeO ₂ / g-C ₃ N ₄ ^[19]	$CO_2 + H_2O$	Full light		0.5	0.7		6.6
Carbon@TiO ₂ ^[2]	$CO_2 + H_2O$	Simulated			4.2	9.1	88.2

		sunlight					
g-C ₃ N ₄ /ZIF-8 ^[20]	$CO_2 + H_2O$	Full light				0.8	4.8
O-doped g-C ₃ N ₄ ^[21]	$CO_2 + H_2O$	Visible light				0.9	5.4
Co-ZIF-9/TiO ₂ ^[22]	$CO_2 + H_2O$	UV-Vis	2.6	17.6	2.0		51.2
COP-27-Mg/TiO ₂ ^[23]	$CO_2 + H_2O$	365 nm		4.1	2.4		27.4
Amine-functionalized	40°C	Visible light		0.2	2.8		22.8
graphene/CdS ^[24]	$CO_2 + H_2O$						
HCP-TiO ₂ -FG ^[25]	$CO_2 + H_2O$	Full light		39.5	51.2		488.6
TiO ₂ -graphene ^[26]	$CO_2 + H_2O$	Full light		5.2	26.7		224
Ti ₃ C ₂ /Bi ₂ WO ₆ ^[27]	$CO_2 + H_2O$	Simulated			1.8	0.4	16.8
		sunlight					
Pd ₇ Cu ₁ -loaded TiO ₂ ^[28]	$CO_2 + H_2O$	Ultraviolet light	1.5	1.9	19.6		160.6

Table S3 The catalytic activity of CO_2 conversion on Pd-loaded WN-WO₃ heterostructure under different conditions.

Food gos	illuminatio	Intensity	Temperature	Formation rate (µmol h ⁻¹ g ⁻¹)			
r eeu gas	n	$(\mathrm{mW/cm}^{2})$	(°C)	H ₂	СО	CH ₄	
CO ₂ +H ₂ O	dark	0	70	n.d. ^[a]	n.d.	n.d.	
CO ₂ +H ₂ O	dark	0	150	n.d.	n.d.	n.d.	
Ar+H ₂ O	sun light	400	150	129.3	n.d.	n.d.	
	[a]:	n.d.= not detec	table			1	

References

- H. Bahruji, M. Bowker, G. Hutchings, N. Dimitratos, P. Wells, E. Gibson, W. Jones, C. Brookes, D. Morgan and G. Lalev, *J. Catal.*, 2016, 343, 133-146.
- [2] W. Wang, D. Xu, B. Cheng, J. Yu and C. Jiang, J. Mater. Chem. A, 2017, 5, 5020-5029.
- [3] X. Wu, Y. Li, G. Zhang, H. Chen, J. Li, K. Wang, Y. Pan, Y. Zhao, Y. Sun and Y. Xie, J. Am. Chem. Soc., 2019, 141, 5267-5274.
- [4] C. Kim, K. M. Cho, A. Al-Saggaf, I. Gereige and H. T. Jung, ACS Catal., 2018, 8, 4170-4177.
- [5] J. Wang, C. Qin, H. Wang, M. Chu, A. Zada, X. Zhang, J. Li, F. Raziq, Y. Qu and L. Jing, *Appl. Catal. B: Environ.*, 2018, **221**, 459-466.
- [6] X. Jin, C. Lv, X. Zhou, L. Ye, H. Xie, Y. Liu, H. Su, B. Zhang and G. Chen, *ChemSusChem*, 2019, 12, DOI: 10.1002/cssc.201900621.
- [7] D. Xu, B. Cheng, W. Wang, C. Jiang and J. Yu, Appl. Catal. B: Environ., 2018, 231, 368-380.
- [8] L. Wang, D. W. Bahnemann, L. Bian, G. Dong, J. Zhao and C. Wang, Angew. Chem. Int. Ed., 2019, 58, 8103-8108.
- [9] Y. F. Xu, M. Z. Yang, H. Y. Chen, J. F. Liao, X. D. Wang and D. B. Kuang, ACS Appl. Energy Mater., 2018, 1, 5083-5089.
- [10] J. Jin, J. Yu, D. Guo, C. Cui and W. Ho, Small, 2015, 11, 5262-5271.
- [11]S. Feng, M. Wang, Y. Zhou, P. Li, W. Tu and Z. Zou, APL Mater., 2015, 3, 104416.
- [12]G. Yang, W. Miao, Z. Yuan, Z. Jiang, B. Huang, P. Wang and J. Chen, *Appl. Catal. B: Environ.*, 2018, 237, 302-308.
- [13] B. AlOtaibi, S. Fan, D. Wang, J. Ye and Z. Mi, ACS Catal., 2015, 5, 5342-5348.
- [14] M. Li, L. Zhang, X. Fan, Y. Zhou, M. Wu and J. Shi, J. Mater. Chem. A, 2015, 3, 5189-5196.
- [15]D. Liu, C. Wang, Y. Yu, B. H. Zhao, W. Wang, Y. Du and B. Zhang, Chem, 2019, 5, 376-389.
- [16] J. Yu, J. Low, W. Xiao, P. Zhou and M. Jaroniec, J. Am. Chem. Soc., 2014, 136, 8839-8842.
- [17]X. Jiao, Z. Chen, X. Li, Y. Sun, S. Gao, W. Yan, C. Wang, Q. Zhang, Y. Lin, Y. Luo and Y. Xie, J. Am. Chem. Soc., 2017, 139, 7586-7594.
- [18]K. Li, B. Peng, J. Jin, L. Zan and T. Peng, Appl. Catal. B: Environ., 2017, 203, 910-916.
- [19] M. Li, L. Zhang, M. Wu, Y. Du, X. Fan, M. Wang, L. Zhang, Q. Kong and J. Shi, *Nano Energy*, 2016, 19, 145-155.
- [20] S. Liu, F. Chen, S. Li, X. Peng and Y. Xiong, Appl. Catal. B: Environ., 2017, 211, 1-10.

- [21] J. Fu, B. Zhu, C. Jiang, B. Cheng, W. You and J. Yu, Small, 2017, 13, 1603938.
- [22] S. Yan, S. Ouyang, H. Xu, M. Zhao, X. Zhang and J. Ye, J. Mater. Chem. A, 2016, 4, 15126-15133.
- [23] M. Wang, D. Wang and Z. Li, Appl. Catal. B: Environ., 2016, 183, 47-52.
- [24]K. Cho, K. Kim, K. Park, C. Kim, S. Kim, A. Al-Saggaf, I. Gereige and H. T. Jung, ACS Catal., 2017, 7, 7064-7069.
- [25]S. Wang, M. Xu, T. Peng, C. Zhang, T. Li, I. Hussain, J. Wang and B. Tan, Nat. Commun., 2019, 10, 676.
- [26] M. Xu, X. Hu, S. Wang, J. Yu, D. Zhu and J. Wang, J. Catal., 2019, 377, 652-661.
- [27] S. Cao, B. Shen, T. Tong, J. Fu and J. Yu, Adv. Funct. Mater., 2018, 28, 1800136.
- [28] R. Long, Y. Li, Y. Liu, S. Chen, X. Zheng, C. Gao, C. He, N. Chen, Z. Qi, L. Song, J. Jiang, J. Zhu and Y. Xiong, J. Am. Chem. Soc., 2017, 139, 4486-4492.