Supporting information

Semiconductors-based Z-Scheme Heterojunction Enhanced Photocatalytic Performance for CO_2 Reduction

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Experimental section

Experimental reagents

The distilled water used was prepared by the Qingdao Fulham ultra-pure water machine (with a resistivity of 18.25 Ω). Sodium hydroxide (NaOH), iron (III) nitrate nonahydrate ($Fe(NO_3)_3·9H_2O$), chloroplatinic acid (H_2PtCl_6 $·6H_2O$, 1%), cadmium nitrate tetrahydrate ($Cd(NO_3)_2·4H_2O$), thiourea (CH_4N_2S), ethylenediamine ($C_2H_8N_2$), zinc nitrate hexahydrate ($Zn(NO_3)_2·6H_2O$), anhydrous ethanol (C_2H_5OH), anhydrous methanol (CH_3OH), and N,N'-dimethylformamide (DMF) were obtained from China National Pharmaceutical Group Chemical Reagent Co., Ltd. Anhydrous sodium sulfate (Na_2SO_4), Nafion reagent and triethanolamine (TEOA) were purchased from Adamas Chemical Co. Ltd. Carbon dioxide and nitrogen gas with a purity of 99.99% were purchased from Nanjing Special Gas Co., Ltd. All raw materials and reagents used in the experiment were purchased and used directly without further processing.

Experimental instrumentation

The ultrasonic cell disruptor produced by Ningbo XinZhi Biotechnology Co., Ltd. was used to disperse the solution evenly. Powder X-ray diffraction (PXRD) experiments are recorded on Bruker D8 Advance (operating at 40 kV and 20 mA) with Ni-filtered Cu Ka radiation at 1.5406 (Å) with a speed of 5 o min-1. SEM images are obtained from a FEI NOVA NANO 430 Field Emission Scanning Electron Microscope equipped with an Oxford Energy Dispersive X-ray spectroscopy. TEM and HAADF-STEM images were obtained on a JEOL 2100F microscopy at an accelerating voltage of 200 kV. The infrared spectra of the samples were measured using a Nicolet-6700 spectrometer and the UV-3600 solid UV diffuse reflection model produced by Shimadzu Corporation in Japan. The metal content analysis was performed using an ICP-OES (ICPS-7510 PLUS). The photoluminescence spectrum of the samples was obtained using an FLS980 fluorescence spectrophotometer (Edinburg Instruments, UK). X-ray Photoelectron Spectroscopy (XPS) was carried out on a Thermo ESCALAB 250XI multifunctional imaging electron spectrometer using the binding energy of C as the internal standard. A modified gas chromatograph Shimadzu GC-2010 Plus equipped with a flame ionization detector (FID) and thermal conductivity detector (TCD) was used to detect the gas samples. Raman data was obtained using a Renishaw in Via confocal laser Raman spectrometer with an F300 xenon lamp produced by Beijing Zhongjiao Jinyuan Co., Ltd. The $^{13}CO_2$RR calibration was tested using a GC-MS 2010 PLUS (Shimadzu, Japan) gas chromatograph-mass spectrometer.

Preparation of the Sample

Synthesis of CdS: $Cd(NO_3)_2 \cdot 4H_2O$ (38.3 mg, 0.12 mmol) and CH_4N_2S (28.4 mg, 0.37 mmol) were dissolved in 9 mL of ethylenediamine solution and sonicated for 15 mins to evenly disperse the sample in the solution. The mixture was then heated at 180 °C in an oven for 24 h, cooled to room temperature, centrifuged to obtain bright yellow powder, washed several times with water and ethanol, and vacuum-dried at 80 °C for 12 h.

Synthesis of $ZnFe_2O_4$ nanoparticles: $ZnFe_2O_4 \cdot 6H_2O$ (74.4 mg, 0.25 mmol) and $Fe(NO_3)_3 \cdot 9H_2O$ (202.0 mg, 0.50 mmol) were dissolved in 10 mL of pure water, sonicated for 10 mins to ensure uniform dispersion of the sample. The solution was continuously stirred, and 0.2 M NaOH solution was added dropwise to adjust the pH to 13. The solution was then transferred to an oven, heated at 180 °C for 20 h, cooled to room temperature, centrifuged to obtain brick-red powder, washed several times with water and ethanol, and vacuum-dried at 80 °C for 12 h.

Synthesis of $ZnFe_2O_4$/ZnO: $ZnFe_2O_4 \cdot 6H_2O$ (150 mg, 0.50 mmol) and $Fe(NO_3)_3 \cdot 9H_2O$ (202.0 mg, 0.50 mmol) were dissolved in 10 mL of pure water, sonicated for 10 mins to ensure uniform dispersion of the sample. The solution was continuously stirred, and 0.2 M NaOH solution was added dropwise to adjust the pH to 13. The solution was then transferred to an oven, heated at 180 °C for 20 h, cooled to room temperature, centrifuged to obtain brick-red powder, washed several times with water and ethanol, and vacuum-dried at 80 °C for 12 h. The prepared $ZnFe_2O_4$ nanoparticles were then calcined at 500 °C for 2 hours with a heating rate of 8 °C/min. After calcination, the color of the nanoparticles changed from brick-red to black, resulting in the formation of $ZnFe_2O_4$/ZnO.

Synthesis of ZnO Nanoparticles: $Zn(NO_3)_2 \cdot 6H_2O$ was dissolved in 10 mL of distilled water (74.4 mg, 0.25 mmol), followed by sonication for 10 minutes to achieve uniform dispersion of the sample in the solution. Constant stirring was maintained while adding 0.2 M NaOH dropwise until the pH reached 13. The solution was then heated in an oven at 180 ℃ for 20 hours, followed by cooling to room temperature. Subsequently, the solution was subjected to centrifugation, washed several times with water and ethanol, and ultimately dried under vacuum at 80 ℃ for 12 hours.

Synthesis of $ZnFe_2O_4$/CdS: 30 mg of CdS nanowires were dissolved in a mixture of 30 mL of water and ethanol (v_{H2O}: v_{EtOH} = 2 : 1), sonicated for 1 h using a cell disruptor to create surface defects on the nanowires (dispersion A). 20 mg of $ZnFe_2O_4$ was dissolved in 10 mL of ethanol, sonicated for 30 mins for complete dispersion. The dispersed solution was slowly added to the prepared dispersion A, sonicated for an additional hour to obtain a yellow-green suspension of $ZnFe_2O_4$/ZnO/CdS. After washing several times with water and ethanol, the product was vacuum-dried at 60 °C for 12 h.

Preparation of $ZnFe_2O_4$/ZnO/CdS: 30 mg of CdS nanowires were dissolved in 30 mL of a mixed solvent (v_{H2O}: v_{EtOH} = 2 : 1) and subjected to continuous ultrasound for 1 hour using a cell disruptor to induce surface defects. $ZnFe_2O_4$/ZnO at quantities of 10, 20, and 30 mg were individually dissolved in 10 mL of ethanol, sonicated for 30 minutes for complete dispersion. The dispersed solution was then slowly added to the CdS nanowire solution and sonicated for an additional hour, resulting in yellow-green turbid solutions labelled as $ZnFe_2O_4$/ZnO/CdS-1, $ZnFe_2O_4$/ZnO/CdS-2, and $ZnFe_2O_4$/ZnO/CdS-3. The solutions were thoroughly washed in water and ethanol, followed by vacuum drying at 60 °C for 12 hours.

Preparation of ZnO/CdS: Initially, dissolve 30 mg of CdS nanowires in a mixed solvent of 30 mL (v_{H2O}: v_{EtOH} = 2: 1) and subject the solution to 1-hour sonication using a cell disruptor to induce surface defects on the nanowires. Subsequently, dissolve 20 mg of ZnO in 10 mL of ethanol, followed by 30 minutes of sonication to ensure thorough dispersion. Gradually combine the dispersed ZnO solution with the CdS nanowire solution. Sonicate for an additional hour to obtain the ZnO/CdS composite. Lastly, thoroughly wash the resulting product with water and ethanol, followed by vacuum drying at 60 degrees Celsius for 12 hours.

Deposition of Pt on $ZnFe_2O_4$/ZnO/CdS

The sample $ZnFe_2O_4$/ZnO/CdS is dispersed in a mixed solution of methanol and water with a ratio of 1: 9. A small amount of H_2PtCl_6 is added to the mixed solution, and the reaction is carried out under light irradiation for 2 h. After several washes with water and ethanol, the sample is vacuum dried at 60 °C for 12 h.

Measurement of reduction reactions of photocatalytic CO_2

The CO_2 photocatalytic reduction reaction of the catalyst was measured in a 50mL photoreactor, and the catalyst was subjected to ultrasonic dispersion pretreatment before photocatalysis. Detailly, 5 mg of catalyst was dispersed in 28 mL of pure water and 2 mL of triethanolamine solution, and then sonicated using an ultrasonic cell grinder with a power of 200 W for 15 mins. Subsequently, the uniformly dispersed mixture was transferred to a 50 mL photoreaction device. Use CO_2 gas bubbling to eliminate impurity gases in the reaction system and continue for 40 minutes. A 300 W Xe lamp (wavelength $\geq$ 420 nm) was used to irradiate the reaction mixture. Any possible liquid products are detected using ion chromatography and ^{1}HNMR. Gas products (CO, CH_4, H_2) were analyzed via gas chromatography equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD) every hour. The yields of photocatalytic products were compared by integrating their areas under the respective calibration curves.

Electrochemical measurements

ITO glass sheet loaded with sample (1 cm × 2 cm) is the working electrode, Ag/AgCl electrode and carbon rod was used as the reference electrode and the counter electrode, respectively.

Working electrode preparation: 2 mg sample was dispersed in the mixed solution of 990 μL ethanol and 10 μL 0.1% Nafion, and ultrasonic at 200 W for 30 min to obtain a uniformly dispersed suspension. 200 μL suspension was dropped on each side of the ITO glass sheet. The coating area is 1 cm^2 and can be used after drying at room temperature.

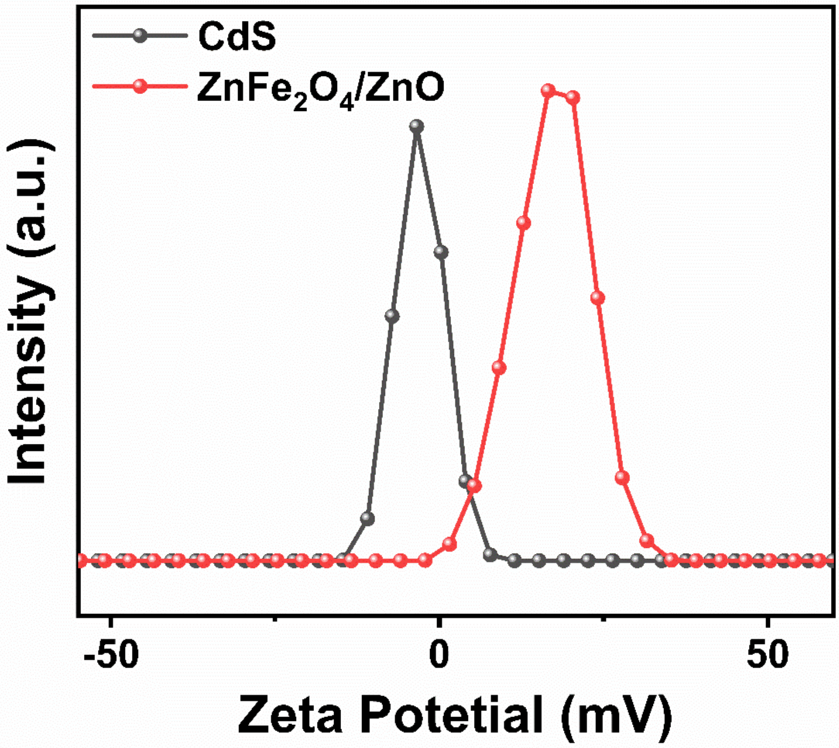

Fig. S1. Zeta potential measurement of CdS and $ZnFe_2O_4$/ZnO.

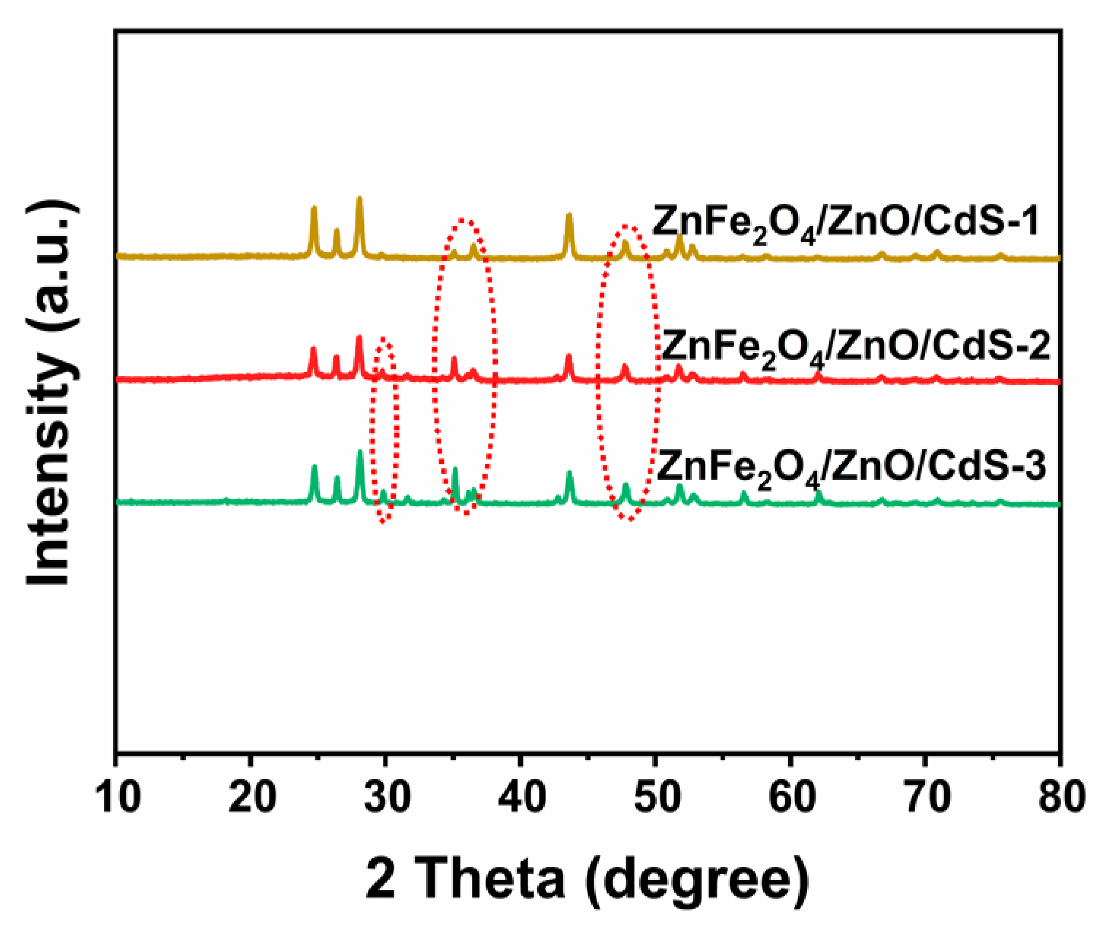

Fig. S2. XRD spectra of $ZnFe_2O_4$/ZnO/CdS with different loadings of $ZnFe_2O_4$/ZnO.

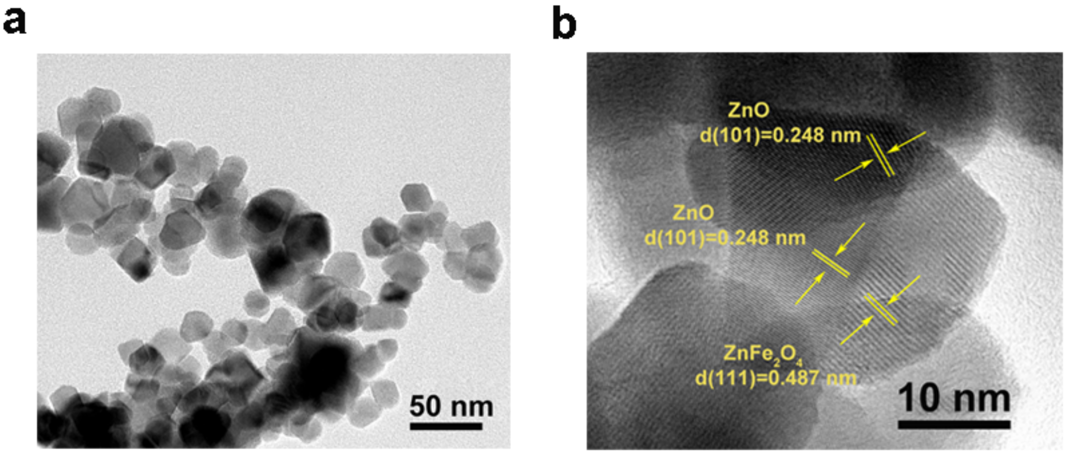

Fig. S3. (a) TEM image of $ZnFe_2O_4$/ZnO. (b) HRTEM image of $ZnFe_2O_4$/ZnO.

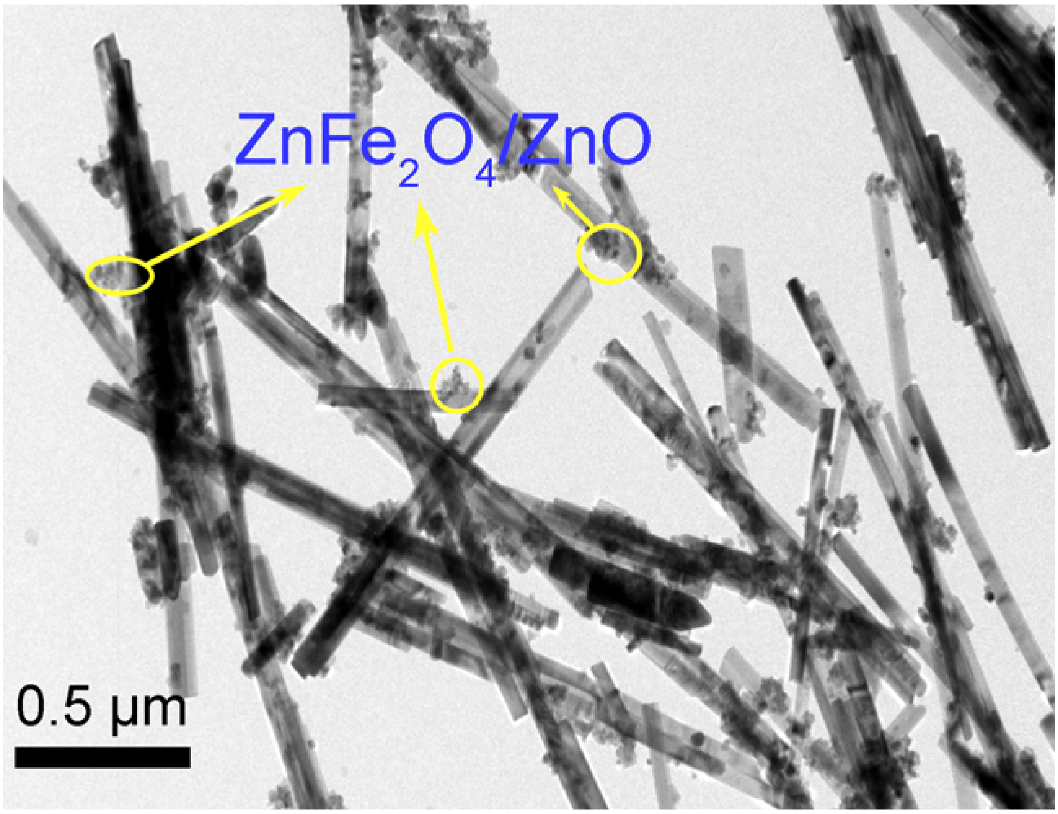

Fig. S4. TEM image of $ZnFe_2O_4$/ZnO/CdS sample.

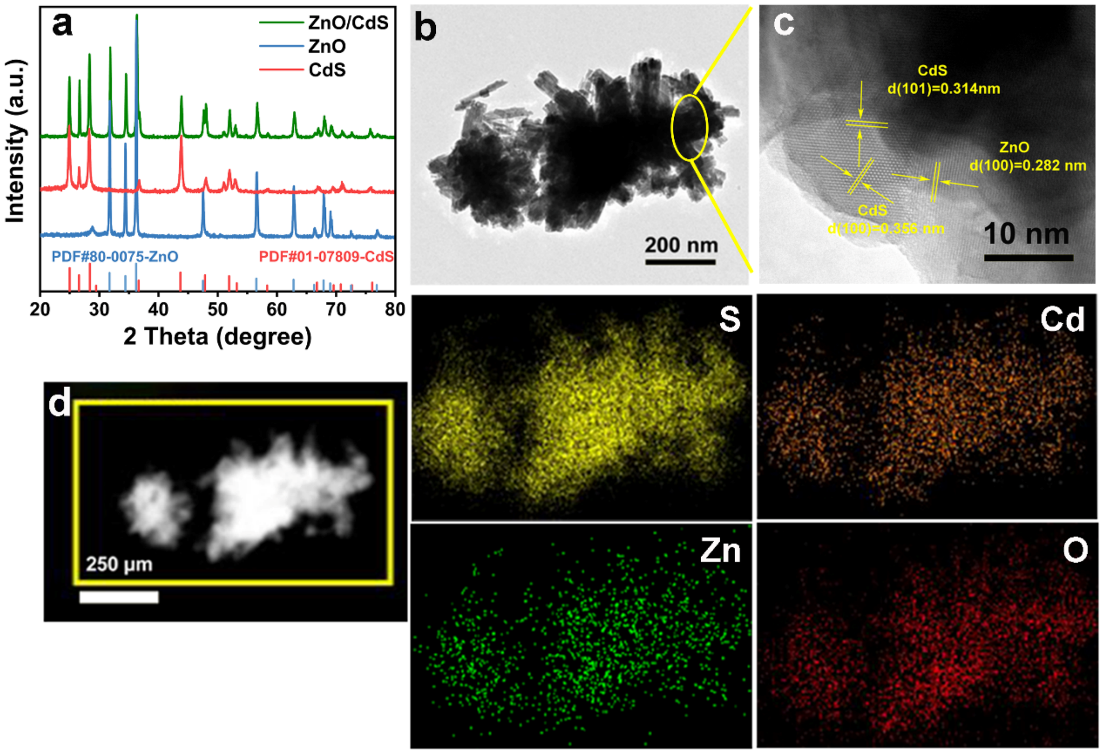

Fig. S5. (a) PXRD spectra of ZnO/CdS. (b) TEM image of ZnO/CdS. (c) HRTEM image of ZnO/CdS. (d) Magnified HRTEM image of ZnO/CdS.

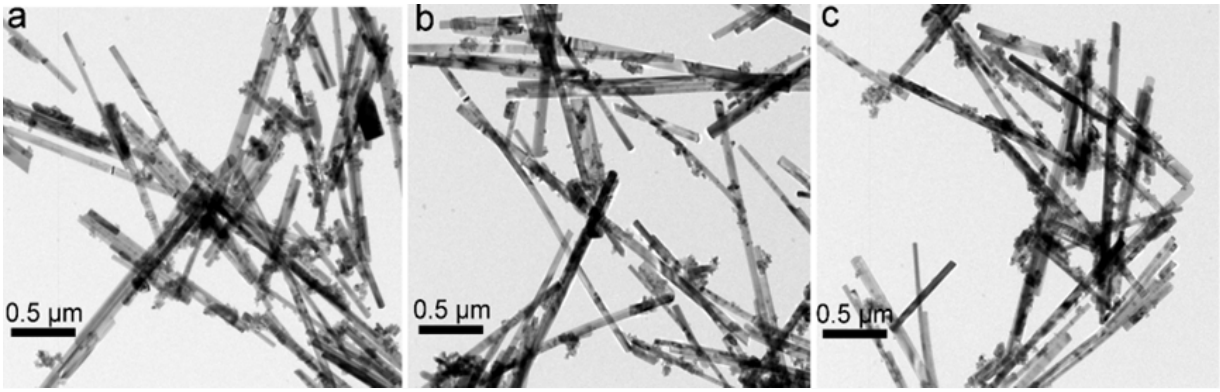

Fig. S6. (a-c) The loading amounts of $ZnFe_2O_4/ZnO$ are 29.37%, 35.25%, and 41.14% in the TEM images.

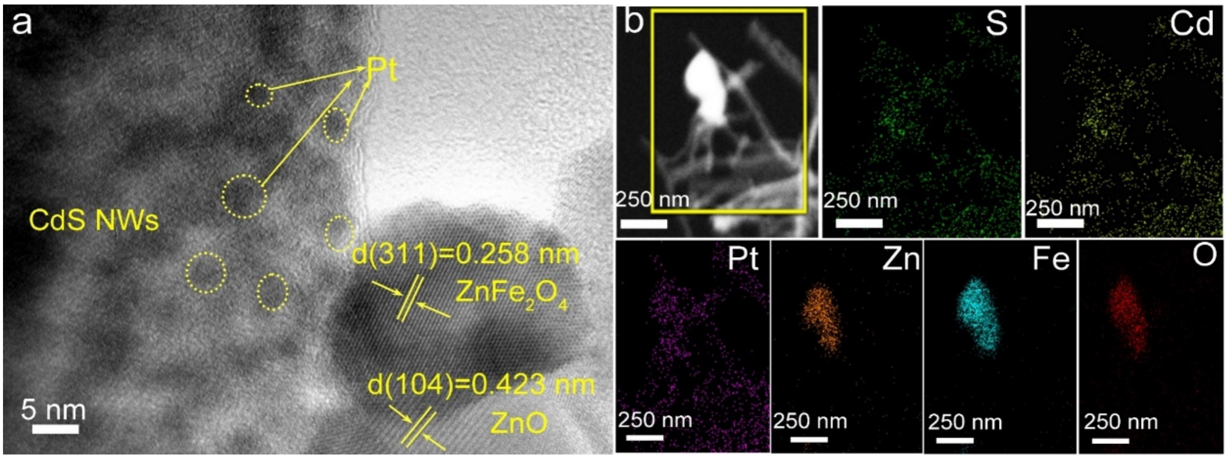

Fig. S7. (a) HRTEM image. (b) STEM image and distribution of Cd, S, Pt, Zn, Fe, and O elements on the sample of $ZnFe_2O_4$/ZnO/CdS with Pt deposition.

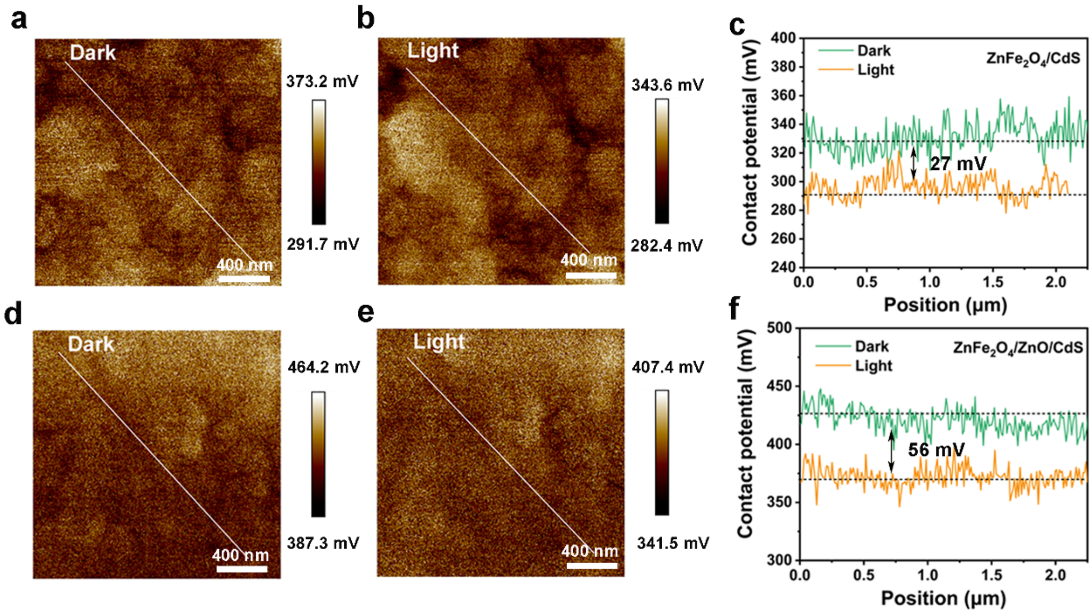

Fig. S8. (a) KPFM images of ZnFe$_2$O$_4$/CdS under dark (a) and light (b) conditions; And the corresponding contact potential (c). KPFM images of ZnFe$_2$O$_4$/ZnO/CdS under dark (d) and light (e) conditions; And the corresponding contact potential (f).

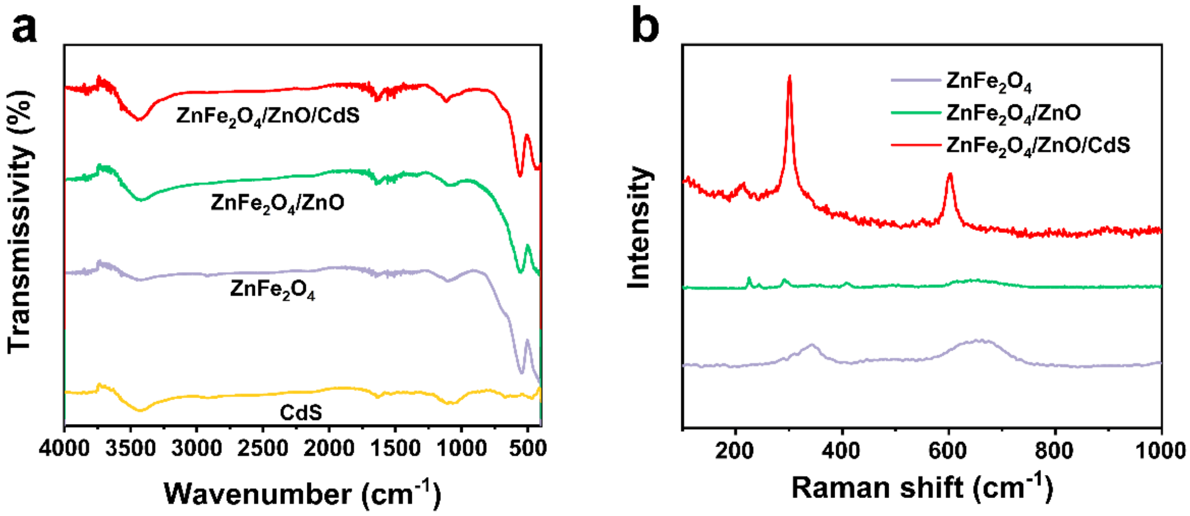

Fig. S9. (a) IR spectra of samples ZnFe$_2$O$_4$, ZnFe$_2$O$_4$/ZnO, and ZnFe$_2$O$_4$/ZnO/CdS, and (b) Raman spectra.

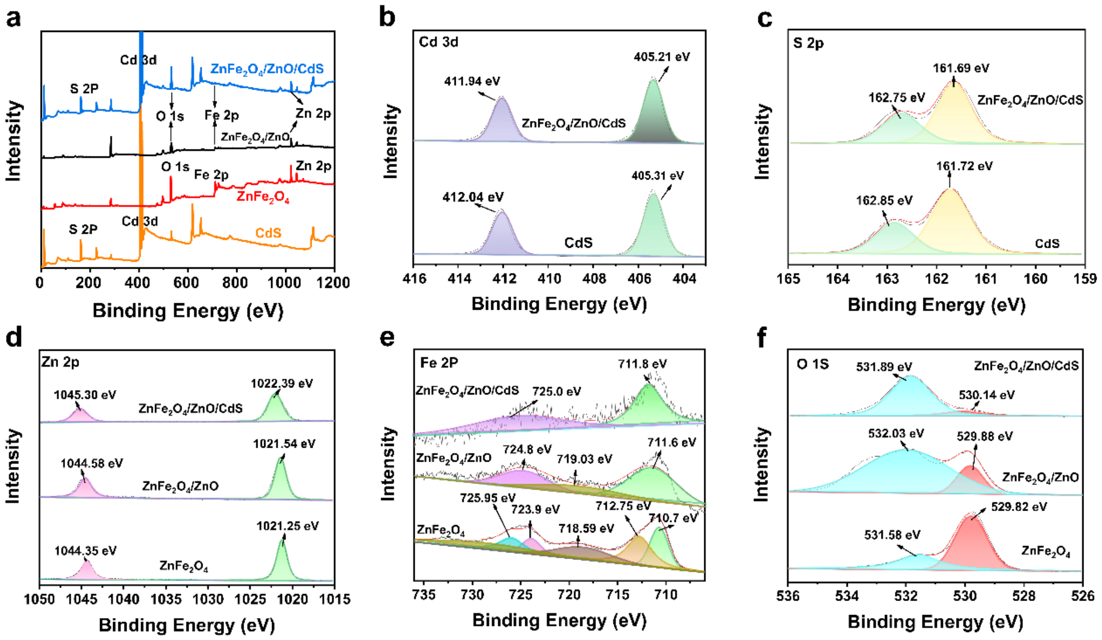

Fig. S10. XPS high-resolution spectra of samples CdS, ZnFe$_2$O$_4$/ZnO/CdS, ZnFe$_2$O$_4$/ZnO: (a) Total spectrum. (b) Cd 3d. (c) S 2p. (d) Zn 2p. (e) Fe 2p. (f) O 1s.

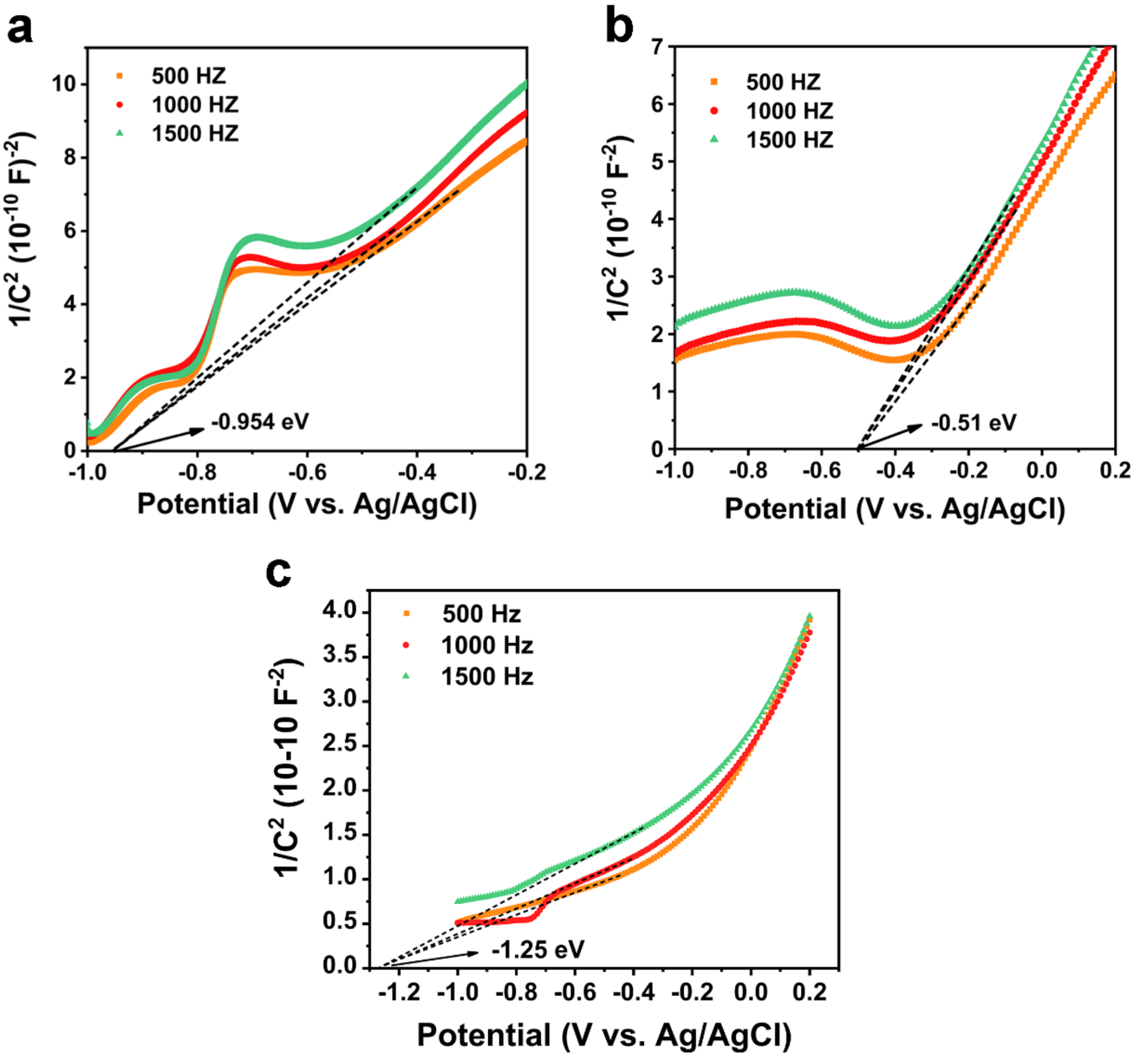

Fig. S11. (a) Mott-Schottky plot of CdS. (b) Mott-Schottky plot of $ZnFe_2O_4$/ZnO. (c) Mott-Schottky plot of $ZnFe_2O_4$/ZnO/CdS.

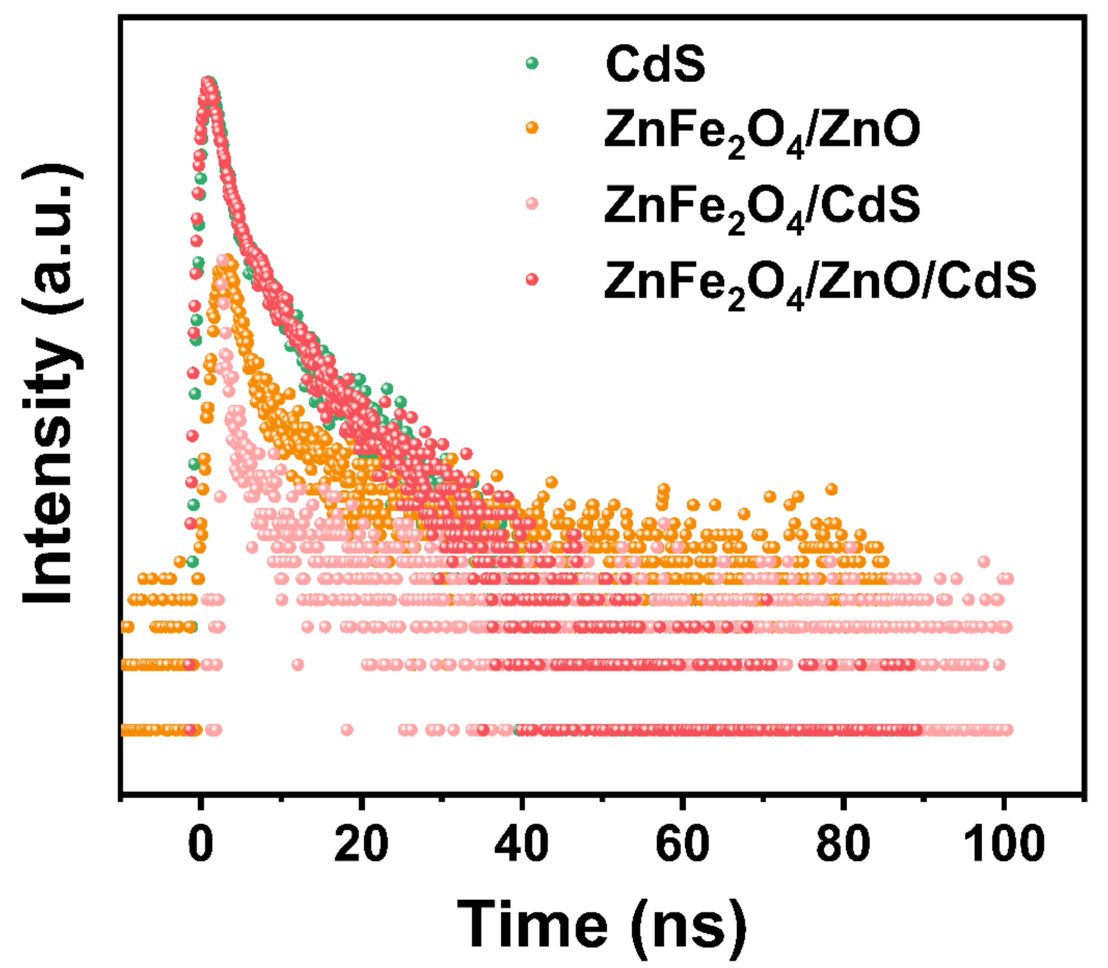

Figure S12. Time-resolved PL decay of $ZnFe_2O_4$/ZnO/CdS and comparisons under excitation at 375 nm.

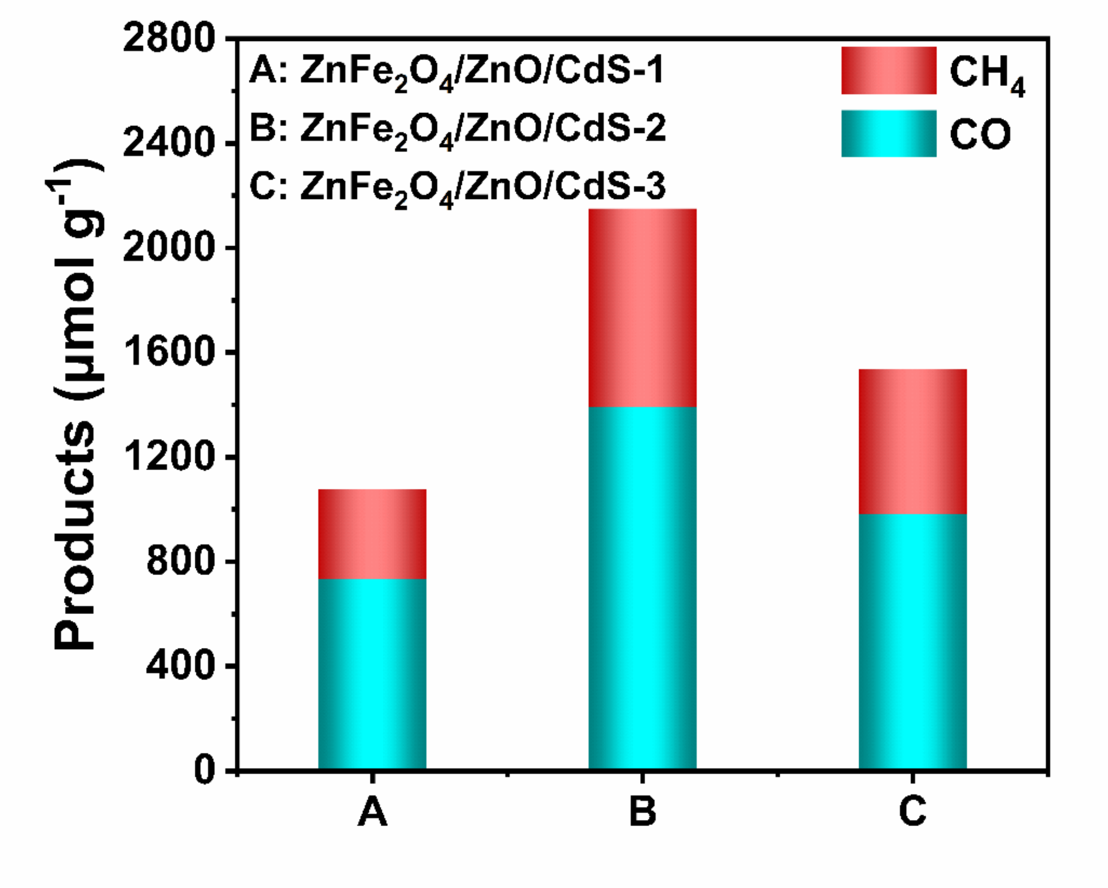

Fig. S13. The production rates of CO and CH_4 with different loading amounts of $ZnFe_2O_4$/ZnO/CdS.

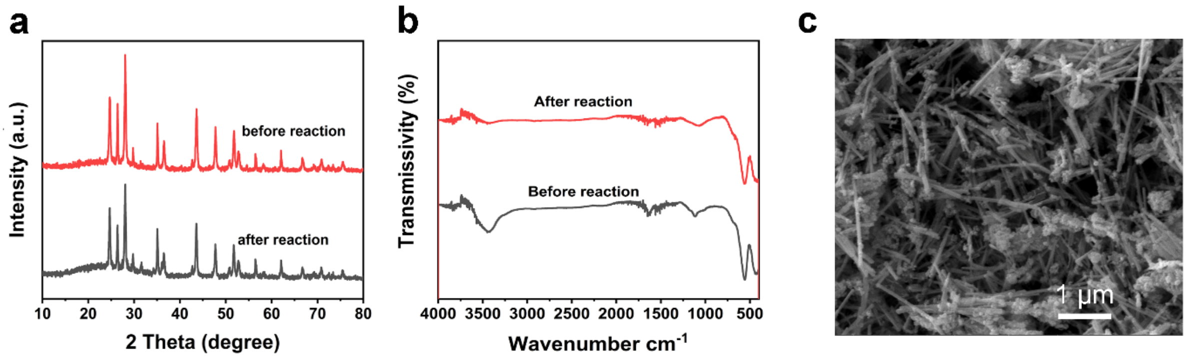

Fig. S14. Comparison before and after photocatalysis of $ZnFe_2O_4$/ZnO/CdS: (a) PXRD spectrum. (b) IR spectrum. (c) SEM image after photocatalytic reaction.

Table S1. The elemental ratios in $ZnFe_2O_4$/ZnO/CdS.

	ICP-OES (wt%)			
Element	Cd	S	Zn	Fe
$ZnFe_2O_4$/ZnO/CdS-1	54.96	15.67	3.19	2.35
$ZnFe_2O_4$/ZnO/CdS-2	50.38	14.37	3.82	2.82
$ZnFe_2O_4$/ZnO/CdS-3	45.8	13.06	4.46	3.29

Table S2. Comparison of photocatalytic CO_2 reduction performance between $ZnFe_2O_4/ZnO/CdS$ and other photocatalysts.

Catalysts	**Conditions**	**Light Sourse**	**Activity (μmol g^{-1} h^{-1})**	**Ref.**
$ZnFe_2O_4/ZnO/CdS$	CO_2, H_2O, TEOA	300 W Xe lamp (λ > 420 nm)	CH_4:105.9 CO: 266.3	This work
Ti_2O_3/TiO_2 (nanosheet)	CO_2, H_2O	300 W Xe lamp	CH_4: 0.65 CO: 2.64	[1]
O/La-CN	Gas-liquid-solid Scrificial agent: TEOA	300 W Xe lamp	CH_4: 5.6 CO: 92	[2]
Co-porphyrin/Carbon nitride(C_3N_4)	TEOA, MeCN	300 W Xe lamp	CH_4: 0.7 CO: 17	[3]
TiO_2-Rh (nanosheet)	CO_2, H_2O, TEOA	300 W Xe lamp	CH_4: 13 CO: 12	[4]
WO_3/CN	TEOA and H_2O	UV ($254 \leq \lambda < 420$nm)	CH_4: 41.47 CO: 58.40	[5]
g-C_3N_4/Ag-TiO_2	CO_2, H_2O	300 W Xe lamp	CH_4: 9.33 CO: 6.33	[6]
Au/C_3N_4	CO_2, H_2O	300 W Xe lamp	CH_4: 1.55 CO: 6.59	[7]
P-g-C_3N_4	CO_2, H_2O, TEOA	vis ($\lambda \geq 420$)	CH_4: 1.81 CO: 2.37	[8]
$Bi_4O_5Br_2$	CO_2, H_2O	300 W Xe lamp	CH_4: 0.5 CO: 3.16	[9]
$ThCN_{12.5}$	CO_2, H_2O, TEOA	300 W Xe lamp ($190>\lambda>1100$ nm)	CH_4: 8.5 CO: 13.4	[10]
$V_{O, N}$-NBCN	H_2O, CH_3CN, TEOA	300 W Xe lamp λ > 420 nm	CH_4: 4.2 CO: 0.2	[11]
Amino-rich g-C_3N_4 (Single Au atom)	EtOH, CO_2	300 W Xe lamp λ > 420 nm	CH_4: 8.0 CO: 1.7	[12]
(Au/A-TiO_2) @g-C_3N_4	CO_2, H_2O	300 W Xe (≥ 420 nm)	CH_4: 37.4 CO: 21.7	[13]
Pd-Au/TiO_2-WO_3	CO_2, H_2O	400 W Hg-lamp	CH_4: 39.1 CO: 271.3	[14]
PbO/TiO_2	CO_2, H_2O	300 W Xe lamp	CH_4: 53.2 CO:6.7	[15]
(Pt/TiO_2) @rGO	CO_2, H_2O	300 W Xe lamp	CH_4: 41.3 CO: 0.4	[16]
rGO/TiO_2	CO_2, H_2O	500 W Hg-lamp	CH_4: 12.8 CO: 11.9	[17]
$Zn_3In_2S_6/TiO_2$	CO_2, H_2O	300 W Xe lamp	CH_4: 6.2 CO: 23.4	[18]

Notes and references

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