Supporting Information

Artificial Lawn: All Solid-State Z-Scheme System Arrays of Fe₂V₄O₁₃ /RGO/CdS for Visible Light-Driving Photocatalytic CO₂ Reduction into Renewable Hydrocarbon Fuel

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Experiment

Synthesis of Fe₂V₄O₁₃/RGO/CdS Z-scheme system: Fe₂V₄O₁₃ nanoribbons growing on a stainless steel mesh were prepared using a previously reported method¹. GO nanosheets were prepared using a modified Hummer's method from graphite powders². A 1mL GO solution with a concentration of 0.01 mg/mL was dropped on the Fe₂V₄O₁₃ nanoribbons and filtrated. The filtrated Fe₂V₄O₁₃ nanoribbons /GO was annealed at 400 °C in nitrogen atmosphere for 30 min to improve the adhesion between the GO sheets and Fe₂V₄O₁₃ nanoribbons and partial reduction of GO into RGO. The sample was then mixed with 50 mL of distilled water and irradiated with filtered light ($\lambda > 420$ nm) from a 300 W Xenon lamp (Spectra Physics) to further reduce the GO sheets to RGO. The obtained Fe₂V₄O₁₃ nanoribbons /RGO was finally washed with distilled water to remove remanent RGO left in suspension.

The Fe₂V₄O₁₃/RGO/CdS Heterostructure was synthesized by chemical vapour deposition³. In brief, 0.1 g CdS powder (99.9% purity) was placed in a quartz tube acting as a source material. The substrates with pre-grown Fe2V₄O₁₃/RGO were placed in the downstream in the quartz tube ~150 mm away from the source. With 100 sccm of Ar gas, the furnace temperature was raised to 850 °C. During the growth, the pressure in the quartz tube was controlled at ~50 Pa. After 20 min of deposition, the furnace was allowed to cool to room temperature under the argon flow. Thus, the CdS was successfully deposited on the Fe₂V₄O₁₃/RGO.

Characterizations: The purity and crystallinity of the as-prepared samples were characterized by powder X-ray diffraction (XRD) (Rigaku Ultima III, Japan) using Cu-Ka radiation ($\lambda = 0.154178$ nm) with scan rate of 10° min⁻¹ at 40 kV and 40 mA, respectively. The scanning electron microscope (SEM) characterizations were performed on FEI NOVA NanoSEM230. The transmission electron microscope (TEM) analyses were performed by a JEOL-3010 field emission electron microscope. Ultraviolet-visible (UV-vis) diffuse reflectance spectra were measured by using a UV-vis spectrophotometer (UV-2550, Shimadzu) at room temperature. The samples were investigated by X-ray photoelectron spectroscopy (XPS) (K-Alpha, THERMO FISHERSCIENTIFIC). The XPS spectrum was calibrated with respect to the binding energy of the adventitious C1s peak at 284.5 eV. Raman spectra were measured on a JY HR800 laser Raman spectrometer (JOBIN YVON, France) with 532 nm argon laser excitation. Fluorescence decay spectra were recorded with a fluorescence spectrometer (FLS920, Edinburgh Instruments).

Photocatalytic CO₂ conversion test: Photocatalytic activity of as-prepared samples were evaluated with photocatalytic reduction of CO_2 under the light irradiation of a

300 W Xe lamp. They were performed in a gas-tight system. First, high purity CO_2 was injected into the reaction system which was vacuumed several times until ambient pressure was reached. Then 0.4 ml of deionized water was injected into the system, which vaporized in the presence of high purity CO_2 . Before illumination, the gases were stored in the dark until it reached the equilibrium of carbon dioxide and deionized water and the adsorption-desorption equilibrium between the photocatalyst (about 0.025 g sample) and gases. The volume of reaction system was about 230 ml. A gas pump was used to accelerate gas diffusion. The electric current of Xe lamp was 20 A. During irradiation, about 0.5 mL of gas was continually taken from the reaction cell at given time intervals for subsequent CH_4 concentration analysis by using a gas chromatography (GC-14B, Shimadzu Corp, Japan). Every three hours, the gas amount of O_2 from CO_2 reduction was determined using gas chromatography (GC-8A, MS-5A column, TCD, Ar carrier).

- 1. Y. Z, P. Li, W. G. Tu, Q. Liu, S. C. Yan and Z. G. Zou, *ChemPlusChem*, 2013, **78**, 274-278.
- 2. L. J. Cote, R. Cruz-Silva and J. X. Huang, J. Am. Chem. Soc, 2009, **131**, 11027-11032.
- H. Li, Y. Zhou, L. Chen, W. Luo, Q. Xu, X. Wang, M. Xiao and Z. Zou, Nanoscale, 2013, 5, 11933-11939.

Figure S1. EDX spectrum of Fe₂V₄O₁₃/RGO/CdS.

Figure S2. XRD patterns of various $Fe_2V_4O_{13}$ -based photocatalysts, SSM.

Figure S3. Raman spectra of various $Fe_2V_4O_{13}$ -based photocatalysts and GO

Figure S4. XPS pattern of $Fe_2V_4O_{13}/RGO/CdS$ (a), C 1s spectra of $Fe_2V_4O_{13}/RGO/CdS$ and GO (b).

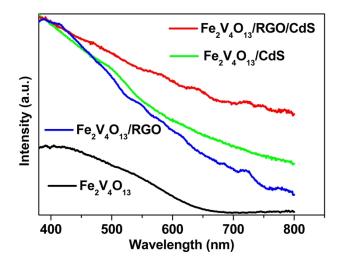


Figure S5. UV-Vis absorbance spectra of various $Fe_2V_4O_{13}$ -based photocatalysts.

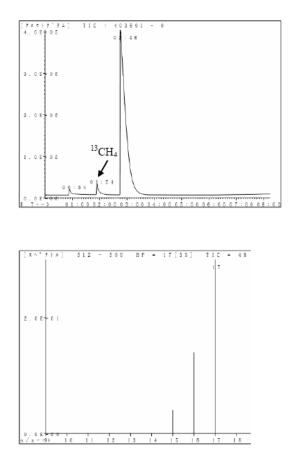


Figure S6 Gas chromatogram (top) and mass spectrum of ${}^{13}CH_4$ (down). Carbon dioxide ${}^{13}CO_2$ was used.