An all-solid-state Z-scheme system array consisting of an Fe$_2$V$_4$O$_{13}$ nanoribbon (NR)/reduced graphene oxide (RGO)/CdS nanoparticle grown on the stainless-steel mesh was rationally designed for photoconversion of gaseous CO$_2$ into renewable hydrocarbon fuels (methane: CH$_4$).

Z-scheme photocatalysis systems with two different photocatalysts and a shuttle redox mediator, which resembles natural photosynthesis, involve a two-photon excitation process for water splitting. One photocatalyst as a H$_2$ evolution system offers the reduction sites by conduction band (CB) electrons, and the other photocatalyst as a O$_2$ evolution system provides the oxidation sites by valence band (VBO) holes. A shuttle redox mediator as an electron conductor transfers the electrons from the CB of the Fe$_3$/Fe$_2$ and IO$_3$ /I$^-$ as an electron transfer mediator has various negative effects, such as back reactions during water splitting. These redox mediators also strongly absorb visible light, reducing the light absorption of semiconductor photocatalysts. Moreover, because of the limitation of the Fe$_3$/Fe$_2$ and IO$_3$ /I$^-$ pairs, these types of Z-scheme systems can only run in the solution environment.

The all-solid-state Z-scheme systems have been greatly developed in recent years. The noble-metal particles (such as Au and Ag) and some low-cost metal oxides and nonmetal materials with good conductivity were explored to function as excellent electron mediators. In addition, graphene or reduced graphene oxide (RGO) was also found to be a good gap linker of Z-schemes for coupling with various photocatalysts for increasing photocatalytic activity.

Almost all of the Z-scheme photocatalysts developed to date are powder systems. For practical application, an integrated nanosystem of two individual components closely connected by charge transport unite is actually desirable. While historical Z-scheme photocatalysis systems were mostly used for water splitting, the exploration of Z-scheme systems for photoconversion of gaseous CO$_2$ conversion into renewable hydrocarbon fuel in the presence water vapor has been seldom reported.

In this paper, we rationally design an all-solid-state Z-scheme system array built on the stainless-steel mesh (SSM) for the photoconversion of gaseous CO$_2$ into methane (CH$_4$). The so-interesting Z-scheme consists of the Fe$_2$V$_4$O$_{13}$ nanoribbon (NR) and CdS nanoparticle (NP) as the visible-light active photocatalysts and RGO as a solid electron mediator. Combining with an active CdS photocatalyst, the selection of Fe$_2$V$_4$O$_{13}$ material is ascribed to its visible-light active, low-cost, non-toxic, earth-abundant, and easily reduplicated characteristics with good ability to bring about the conversion of CO$_2$ into CH$_4$. RGO as an interlayer between Fe$_2$V$_4$O$_{13}$ NR and CdS NP offers a high speed charge transfer channel, leading to enhanced charge separation efficiency, and also protects CdS against photocorrosion. The broadening solid–solid contact interface between quasi-two-dimensional Fe$_2$V$_4$O$_{13}$ NR and the RGO nanosheet provides extensive channels for the Z-scheme carrier transfer. The advantage over precedent powder Z-scheme systems was the present "artificial lawn" may provide a suggestive model for designing an integrated system for the practical application of photocatalytic conversion of CO$_2$ into renewable solar fuel in the future.
First, the array of the Fe$_2$V$_4$O$_{13}$ NR was directly grown on SSM through a simple and facile hydrothermal approach, as described in our previous report.\textsuperscript{13} The SSM serves as both the Fe source and the substrate for the deposition of vanadium and oxide elements. Then, a GO aqueous solution was uniformly dripped onto the Fe$_2$V$_4$O$_{13}$-growing SSM, followed by water evaporation, which allows hydrophilic GO to be well distributed on and closely contact with the surface-polar Fe$_2$V$_4$O$_{13}$ NR. Subsequent annealing in inert atmosphere transfers the GO into RGO. Third, CdS NPs were uniformly grown on the Fe$_2$V$_4$O$_{13}$/RGO through a chemical vapor deposition technique.

The color of the SSM obviously changes from silver white (Fig. 1a) to yellow brown after the hydrothermal growth of Fe$_2$V$_4$O$_{13}$ NRs (Fig. 1b). The FE-SEM image shows that the as-prepared Fe$_2$V$_4$O$_{13}$ NRs with a length of 10–20 µm, a width in the range of 300–400 nm, and a thickness of 20–30 nm were perpendicularly grown on the entire surface of the SSM (Fig. 2a and b), resembling the blades of grass. With the GO coating and subsequent annealing treatment, the resulting SSM color changes into gray brown (Fig. 1c). The RGO-coated surface of the Fe$_2$V$_4$O$_{13}$ NR appears obvious a crumpled-layer structure, which is assigned to sheet-like RGO (Fig. 2c and d). After CVD of CdS NPs, the color of SSM/Fe$_2$V$_4$O$_{13}$/RGO/CdS becomes dark brown (Fig. 1d) due to the further deoxidation of RGO. Large numbers of the tiny CdS particles were observed on the surface of the SSM/Fe$_2$V$_4$O$_{13}$/RGO/CdS (Fig. 2e and f). The corresponding line-scanning analysis of energy-dispersive X-ray spectroscopy (EDX) clearly proves the well-defined spatial distribution of the elements O, S, Cd, Fe, and V. The approximate atomic ratio of S and Cd is 1:1, indicating the existence of CdS (Fig. S1, see ESI†).

The transmission electron microscopy (TEM) images of the Fe$_2$V$_4$O$_{13}$/RGO/CdS shows close contacting interfaces among Fe$_2$V$_4$O$_{13}$, RGO, and CdS (Fig. 3). The two-dimensional RGO sheet was clearly observed on the surface of Fe$_2$V$_4$O$_{13}$ NR as denoted by an arrowhead symbol. With distinctly interlayed RGO sheets, the CdS NP with a diameter of about 10 nm was dispersedly decorated on the RGO panel. The high-resolution TEM (HRTEM) image demonstrates the interplanar $d$-spacing of the lattice fringes of 0.4065 nm and 0.3096 nm, corresponding to (200) lattice planes of Fe$_2$V$_4$O$_{13}$ and (101) lattice planes of CdS, respectively. The RGO obviously protects CdS from aggregation through the suppression of nanoparticle growth.

The XRD patterns demonstrate the successful growth of the Fe$_2$V$_4$O$_{13}$ NR and CdS NP on the SSM. All the X-ray diffraction peaks for the Fe$_2$V$_4$O$_{13}$ NR can be attributed to the monoclinic phase (Fig. S2, ESI†). After the deposition of CdS, additional peaks (Fig. 2e and f). The corresponding line-scanning analysis of energy-dispersive X-ray spectroscopy (EDX) clearly proves the well-defined spatial distribution of the elements O, S, Cd, Fe, and V. The approximate atomic ratio of S and Cd is 1:1, indicating the existence of CdS (Fig. S1, see ESI†).
appearance at 24.8°, 26.5°, 28.2°, and 51.8°, which can be indexed to the hexagonal CdS. No observation of the typical diffraction pattern of RGO may be attributed to low loading content. Raman spectroscopy demonstrates the existence of the RGO layers between the Fe₂V₄O₁₃ NR and CdS NP (Fig. S3, ESI†). Two typical peaks at 1346 and 1586 cm⁻¹ correspond to the D and G bands of RGO, respectively. The increase in the D band-to-G band intensity ratio of Fe₂V₄O₁₃/RGO/CdS (1.58), Fe₂V₄O₁₃/RGO (1.57), and as-used GO (1.53) indicates the decrease of oxygenic groups with continuous annealing treatments, which is propitious to photocarrier transfer, owing to its better conductivity.¹⁴ X-ray photoelectron spectroscopy (XPS) also confirms the presence of Cd, S, C, V, and Fe elements (Fig. S4, ESI†). The high-resolution C 1s spectrum of RGO displays two fitted peaks at 284.3 and 288.2 eV, which are assigned to the C–C/C≡C and O–C=O configurations, respectively. The peak assigned to C–O/O=O (286.5 eV) bond almost vanishes relative to GO, demonstrating the complete removal of most graphitic oxygen-bound carbon groups.¹⁵

The ultraviolet-visible (UV-vis) diffuse reflectance spectra show that the absorption edge of the Fe₂V₄O₁₃ NR with the estimated band gap of 1.83 eV extends to the visible-light region, which indicates the possibility of high photocatalytic activity of these materials under visible-light illumination (Fig. S5, ESI†). A high absorption background for the Fe₂V₄O₁₃/RGO in the entire wavelength range studied is attributed to the absorption of RGO itself in the visible-light and UV-light regions, as well as the possible synergistic effect between Fe₂V₄O₁₃ and RGO.¹⁶ After coupling with CdS NPs, the absorption of both Fe₂V₄O₁₃ and Fe₂V₄O₁₃/RGO in the visible-light region increases. This uniform CdS NP will be quite beneficial in improving charge separation and enhancing the visible-light absorption of the Fe₂V₄O₁₃ NR-based Z-scheme system, which allows a more efficient utilization of the solar energy.

Photocatalytic conversion of CO₂ into renewable hydrocarbons using solar energy is perhaps one of the potential solutions to both global warming and energy shortage concerns. Generally, in the presence of water vapor, CO₂ could be photo-reduced into CH₄ using the appropriate bandgap semiconductor as a photocatalyst through water oxidation of 2H₂O + 4H⁺ → O₂ + 4H⁺ (E°ox = 0.82 V vs. NHE) and CO₂ reduction of CO₂ + 8e⁻ + 8H⁺ → CH₄ + 2H₂O (E°red = −0.24 V vs. NHE). The edge of the VB (EVB) of Fe₂V₄O₁₃ was determined to be 1.28 eV (vs. normal hydrogen electrode, NHE),¹⁹ which is more positive than that of E°ox. The edge of the CB (ECB) of Fe₂V₄O₁₃ was determined to be −0.55 eV (vs NHE), more negative than that of E°red, which indicates that the photogenerated electrons and holes on the irradiated NRs can react with absorbed CO₂ and H₂O to produce CH₄. As a classic visible-light active photocatalyst, the bandgap of CdS is estimated to be about 2.40 eV, and the corresponding EVB and ECB are generally located at 1.88 eV and −0.52 eV,¹⁸ respectively, which meets the prerequisite for CO₂ photoreduction potential. The CO₂ photocatalytic activity was performed with visible light (λ > 420 nm) under CO₂ in the presence of water vapor. The CH₄ rate of generation of the bare Fe₂V₄O₁₃ NR is measured to be 0.55 μmol h⁻¹ g⁻¹ (Fig. 4a). Coupling Fe₂V₄O₁₃ NR with RGO shows the rate of generation of CH₄ to be 0.57 μmol h⁻¹ g⁻¹, no significant change relative to bare Fe₂V₄O₁₃ NR (Fig. 4b). This indicates no obvious improvement in separation of electrons and holes originating from the electron transfer from the excited Fe₂V₄O₁₃ NR to the RGO matrices. Because the CB energy level of Fe₂V₄O₁₃ NR is thermodynamically beneficial for transporting photogenerated electrons from Fe₂V₄O₁₃ NR to RGO, the observed electron transfer restraint is possibly due to kinetic limitation. The combination of CdS NP with Fe₂V₄O₁₃ to form a Fe₂V₄O₁₃/CdS type-II heterostructure enhances the evolution of CH₄ three times (1.57 μmol h⁻¹ g⁻¹) (Fig. 4b), relative to the bare Fe₂V₄O₁₃ NR. The enhanced photocatalytic activity is attributed to the fact that the photogenerated electrons on the CB of the Fe₂V₄O₁₃ were transitioned to the CB of CdS, and the photogenerated holes on the VB of CdS shift to the VB of Fe₂V₄O₁₃, extending the lifetime of the photogenerated carrier. The photocatalytic activity of the Fe₂V₄O₁₃/RGO/CdS further increases to about 30%, compared with Fe₂V₄O₁₃/CdS by interlaying RGO between Fe₂V₄O₁₃ and CdS (Fig. 4b). This improvement may be attributed to the mechanism of the Z-scheme system, as graphically illustrated in Scheme 2.

**Scheme 2** Schematic illustration of photocatalytic conversion of CO₂ into CH₄ over Fe₂V₄O₁₃/RGO/CdS Z-scheme system. (Fe₂V₄O₁₃, ECB: −0.55 eV, EVB: 1.28 eV; CdS, ECB: −0.52 eV, EVB: 1.88 eV vs. NHE).
The photoexcited electrons from CB of CdS may transfer to RGO and release to the VB of Fe$_2$V$_4$O$_{13}$ to recombine with the existing holes of Fe$_2$V$_4$O$_{13}$. The holes stored by the CdS oxidize H$_2$O to O$_2$, whereas the electrons stored by the Fe$_2$V$_4$O$_{13}$ reduce CO$_2$ to CH$_4$. The presence of RGO may enhance the stability of existing holes of Fe$_2$V$_4$O$_{13}$. The holes stored by the CdS oxidize the Fe$_2$V$_4$O$_{13}$/RGO/CdS than that of the Fe$_2$V$_4$O$_{13}$/CdS may be responsible for the quenching. In the case of Fe$_2$V$_4$O$_{13}$/RGO/CdS, the average decay time was measured to be 0.53 ns. Similar to the case of Fe$_2$V$_4$O$_{13}$/CdS, the emission of the CdS NP in the Fe$_2$V$_4$O$_{13}$/CdS can be considered almost quenched, confirming another possible decay channel of the hole transfer from VBs of CdS to Fe$_2$V$_4$O$_{13}$ which may be mainly responsible for the quenching. In the case of Fe$_2$V$_4$O$_{13}$/RGO/CdS, the average decay time was measured to be 0.53 ns. Similar to the case of Fe$_2$V$_4$O$_{13}$/CdS, the emission of the CdS NP in the Fe$_2$V$_4$O$_{13}$/RGO/CdS was also believed to be almost quenched. The most permissible method to quenching is considered to be the electron transfer from CB of CdS to VB of Fe$_2$V$_4$O$_{13}$ along highly conductive RGO. The depletion of the hole of Fe$_2$V$_4$O$_{13}$ by the CdS electron decreases the recombination opportunity of the Fe$_2$V$_4$O$_{13}$ electron, allowing the longer survival time of the Fe$_2$V$_4$O$_{13}$ electron. The stronger ability of electron transfer from CdS CB to Fe$_2$V$_4$O$_{13}$ VB for the Fe$_2$V$_4$O$_{13}$/RGO/CdS than that of the Fe$_2$V$_4$O$_{13}$/CdS may be due to smaller electrical resistances of the contact interfaces of RGO/CdS and Fe$_2$V$_4$O$_{13}$/RGO than that of Fe$_2$V$_4$O$_{13}$/CdS. The two-dimensional compact contact between RGO and Fe$_2$V$_4$O$_{13}$ NR also extends the transfer channels of the carrier.

The production of O$_2$ has also been detected in the present system, but the molar ratio of O$_2$ to CH$_4$ is less than 2:1 to some extent (CO$_2$ + 2H$_2$O → CH$_4$ + 2O$_2$). The stoichiometric imbalance for O$_2$ to CH$_4$ may be attributed to the photoabsorption of oxygen molecules on the surface of the photocatalyst. No appearance of CH$_4$ production was detected when a CO$_2$ reduction experiment was performed under darkness or in the absence of the photocatalysts, proving that the CO$_2$ reduction reaction is driven by visible light with the photocatalysts. Isotopic experiments using $^{13}$CO$_2$ as the carbon source leads to the formation of $^{13}$CH$_4$, demonstrating that the carbon moity of photoreduction products comes from applied CO$_2$ (Fig. S6, ESI†).

A Fe$_2$V$_4$O$_{13}$/RGO/CdS Z-scheme system perpendicularly growing on the SSM was rationally prepared for the photocatalytic reduction of CO$_2$ into methane. The introduction of the RGO interlayer provides a high-speed charge channel in the Fe$_2$V$_4$O$_{13}$/RGO/CdS heterostructure due to its high electronic mobility, leading to more efficient spatial separation of the electrons and holes and subsequent high photocconversion efficiency of CO$_2$.

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Notes and references