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Article

Structural engineering of 3D hierarchical $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ for selective photocatalytic CO_2 reduction

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ABSTRACT

The solar-driven catalytic conversion of CO_2 to useful chemical fuels is regarded as an environmentally friendly approach to reduce the consumption of fossil fuels and mitigate the greenhouse effect. However, it is highly intriguing and challenging to promote the selectivity and efficiency of visible-light-responsive photocatalysts that favor the adsorption of CO_2 in photoreduction processes. In this work, three-dimensional hierarchical $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ flowers (C8Z2S-F) with ultrathin petals were successfully synthesized through an *in-situ* self-assembly growth process using sodium citrate as a morphology director. The flower-like $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ solid solution exhibited remarkable photocatalytic performance in the reduction of CO_2 , generating CO up to $41.4 \mu\text{mol g}^{-1}$ under visible-light illumination for 3 h; this was nearly three times greater than that of $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ nanoparticles (C8Z2S-NP) ($14.7 \mu\text{mol g}^{-1}$). Particularly, a comparably high selectivity of 89.9% for the conversion of CO_2 to CO, with a turnover number of 39.6, was obtained from the solar-driven C8Z2S-F system in the absence of any co-catalyst or sacrificial agent. Terahertz time-domain spectroscopy indicated that the introduction of flower structures enhanced the light-harvesting capacity of C8Z2S-F. The *in situ* diffuse reflectance infrared Fourier transform spectroscopy unveiled the existence of surface-adsorbed species and the conversion of photoreduction intermediates during the photocatalytic process. Empirical characterizations and predictions of the photocatalytic mechanism demonstrated that the flower-like $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ solid solution possessed desirable CO_2 adsorption properties and an enhanced charge-transfer capability, thus providing a highly effective photocatalytic reduction of CO_2 .

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1. Introduction

The solar-driven reduction of CO_2 is a promising strategy for obtaining value-added chemicals given the rapid consumption of global energy and expansion of the global warming crisis [1–4]. To date, diverse light-absorbing photocatalysts known for their favorable photochemical and electrical properties have been widely developed as valuable materials to reduce

CO_2 to CO or hydrocarbons [5–7]. However, owing to the inert scaling properties of CO_2 , the reduction is frequently restricted by the strong chemical bonding and inactive carrier excitation, hugely limiting the practical applications of CO_2 reduction [8,9]. In addition, photocatalysts are typically restricted by poor CO_2 adsorption and visible-light responsiveness because their structural control is challenging, and they have a wide bandgap position [10–14]. Thus, the fabrication of photocatalysts with

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sufficient CO_2 adsorption and charge-transfer capabilities is needed [15–18]. So far, a relatively new effort of designing desirable morphologies and architectures benefits solar-harvesting and CO_2 absorption, leading to increased active sites and potential interface functionalities [19,20]. For instance, Liu et al. [21] prepared ultrathin 2D covalent organic framework nanosheets with excellent CO production due to a large surface area and enhanced contact between the substrate and the molecule. Mo et al. [22] reported porous nitrogen-rich $\text{g-C}_3\text{N}_4$ with Lewis basicity for the efficient photocatalytic reduction of CO_2 . Furthermore, Liu et al. [23] synthesized 3D TiO_2 hollow microspheres decorated with abundant surface defects for synergetic tailoring on the visible-light-driven catalytic conversion of CO_2 .

Despite the favorable morphologies and architectures, the activity and selectivity of sacrificial agents limit the development of a CO_2 conversion system. In comparison with metal oxides [24,25], carbides [26], and nitrides [27], a zinc sulfide solid solution is a more advantageous photocatalyst that affords a highly selective catalytic reduction of CO_2 owing to the following: it has (1) a positive response to wide wavelength excitation attributed to a narrow band gap, (2) an appropriate band edge position and tunable bandgap width by adjusting the

atomic ratio of zinc and cadmium, and (3) the nature of an intermetallic compound, which is more negative than CdS , resulting in a well-defined photocatalytic reduction by a non-precious metal under visible-light irradiation [28–32]. In addition, a highly efficient photocatalyst should have a high specific surface area and enriched active adsorption sites to efficiently interact with the surface-adsorbed CO_2 molecules. The present work specifically addresses a 3D hierarchical flower-shaped $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ solid solution with ultrathin petals by using sodium citrate as a structure director; this has rarely been reported. As shown in Fig. 1(a), the formation of hierarchical C8Z2S-F involves self-nucleation, molding, and intergrowth. The morphology of this 3D flower provides a large specific surface area and has enriched CO_2 adsorption sites, thereby improving the capability to anchor CO_2 molecules. C8Z2S-F shows a remarkably high photocatalytic generation of CO and CH_4 , which is far superior to that of C8Z2S-NP, through CO_2 conversion without any co-catalyst or sacrificial agent under visible-light illumination. CO_2 temperature-programmed desorption (CO_2 -TPD) and terahertz time-domain spectroscopy (THz-TDS) were conducted to demonstrate the superior performance in the adsorption of CO_2 and light-harvesting capacity of the flower-decorated $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ solid solution compared to

Fig. 1. Morphology and phase structures of the photocatalyst. (a) Schematic of C8Z2S-F synthesis; (b) HAADF-STEM image; (c) TEM image; (d) XRD pattern; (e) SEM image; (f, g) AFM images of C8Z2S-F. The obtained C8Z2S-F was synthesized through a simple oil-bath treatment of CdCl_2 and ZnCl_2 (the molar ratio of Cd/Zn was 4:1) in thiourea solution with sodium citrate and $\text{NH}_3\cdot\text{H}_2\text{O}$ as structure directors at 60°C for 3 h.

previous photocatalysts. The exploration of the photocatalytic mechanism further illustrated the superiority of the flower-like photocatalyst in the excellent interlayer and interface charge transfer and the anchoring of CO₂ molecules to the adsorption sites. This work provides insights into the engineering of 3D photocatalyst structures and their tailoring for high-yield CO₂ photoreduction.

2. Experimental

2.1. Sample preparation

Cd_{0.8}Zn_{0.2}S flowers (C8Z2S-F) was prepared via a simple oil-bath method [28]. Briefly, sodium citrate (1 mmol) was dissolved into deionized water (50 mL) to a homogeneous solution. A mixture (10 mL) of 0.8-M CdCl₂ and 0.2-M ZnCl₂ was dropped into the as-prepared solution. After stirring for 20 min, concentrated ammonia water (NH₃·H₂O, 28%, 5 mL) and thiourea (0.9 M, 10 mL) were gradually added. Then, the prepared mixture was subjected to a typical oil-bath treatment at 60 °C for 3 h. The yellow powder was collected by centrifuging and drying at 60 °C for 12 h and was marked as C8Z2S-F. Zinc sulfide solid solutions with different flower structures were obtained by changing the atomic ratio of zinc and cadmium. The sample synthesized by adding 0.2-M CdCl₂ and 0.8-M ZnCl₂ was marked as C2Z8S, and the sample synthesized by adding 0.5-M CdCl₂ and 0.5-M ZnCl₂ was marked as C5Z5S.

Synthesis of Cd_{0.8}Zn_{0.2}S nanoparticles (C8Z2S-NP) was similar to that of C8Z2S-F without using the morphology director, viz. sodium citrate. The sample was marked as C2Z8S-NP.

2.2. Characterization

X-ray diffraction (XRD) patterns were obtained using a Bruker D8 Advance X-ray diffractometer with Cu K_α ray source at a scan range of 5°–80°. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and transmission electron microscopy (TEM) were performed with a Tecnai F20 transmission electron microscope (FEI) at an accelerating voltage of 200 kV. Energy-dispersive X-ray spectroscopy (EDS) mapping was performed using the Oxford EDS Inca X-Max equipped with a transmission electron microscope. Atomic force microscopy (AFM) was conducted through a dimension icon atomic force microscope (Bruker, Germany). X-ray photoelectron spectroscopy (XPS) was performed with the Kratos Axis Supra system. The UV-vis diffuse reflectance spectra (UV-vis DRS) were captured via a UV-2600 system (Shimadzu). The Brunauer-Emmett-Teller specific surface area (S_{BET}) and porosity distribution were evaluated using micromeritics ASAP 2020. Scanning electron microscopy (SEM) images were obtained via a FEI Quanta 650 microscope (ESEM). CO₂-TPD was performed with the AutoChem II 2920 analyzer. THz-TDS was conducted with a conventional terahertz time-domain spectrometer (Zomega Fico TDS). The steady-state photoluminescence (PL) emission spectra were recorded on an FLSP920 spectrometer (Edinburgh Instruments).

2.3. Photoelectrochemical measurements

The transient photocurrent response (TPR) technique, Mott-Schottky test and electrochemical impedance spectroscopy (EIS) were conducted on a standard three-electrode system through electrochemical workstation (CHI660E, China). A Na₂SO₄ aqueous solution (0.5 mol L⁻¹) was used as an electrolyte with a Pt wire as the counter electrode and a Ag/AgCl electrode as the reference electrode. A fluorine-doped tin oxide conductive glass was evenly coated with photocatalysts via the scraper method and was utilized as the working electrode (active area, 1 cm²; film thickness, 0.01 mm). The TPR was obtained under 0.5 eV of starting voltage by switching the light on and off every 60 s (PLS-SXE300, Perfectlight, China). Moreover, the EIS was conducted under a 10-mV voltage amplitude with a frequency range from 10⁻² to 10⁵ Hz.

2.4. Photocatalytic CO₂ reduction measurement

The photocatalytic tests were conducted in an automatic photocatalytic reaction system (Labsolar-6A, Perfectlight, China). Photocatalysts (30 mg) were placed at the bottom of a custom-made glass vessel. Then, 500-μL deionized water was added dropwise before sealing the reactor with a quartz glass top. After vacuuming and filling with a CO₂ source (70–80 kPa), a Xenon lamp was positioned 15 cm away from the photocatalyst for irradiation (Fig. S5). The circuit cooling system maintained a system temperature of 5 °C throughout the photocatalytic reduction. The photocatalytic production was captured via online monitoring over gas chromatography including a flame ionization detector (FID) and a thermal conductivity detector (TCD, GC9790II, Fuli instrument), with N₂ as the carrier gas.

2.5. Turnover number calculation

The turnover number (TON) is used to present the number of electrons participating in the photocatalytic process per mole of photocatalyst under illumination for a certain time [33]. In this work, the TONs of the C2Z8S, C5Z5S, C8Z2S-F, and C8Z2S-NP samples for the photocatalytic conversion of CO₂ via visible-light illumination for 3 h were obtained using the following equation. Two and eight correspond to the converted electronic number from CO₂ to CO and CH₄, respectively [34].

$$\text{TON} = \frac{\text{Number of reacted electrons}}{\text{Amount of catalyst}} = \frac{(2C_{\text{CO}} + 8C_{\text{CH}_4}) \times V}{M \times T} \quad (1)$$

where V is the volume of the sealed reaction device, M is the reactant mass, T is the reaction time, and C_{CO} and C_{CH_4} are the concentrations of CO and CH₄, respectively.

2.6. Calculation of the positions of conduction and valence bands

The relative level of the conduction band (CB) was measured via Mott-Schottky plots at different frequencies (from 900 Hz to 1000 Hz) and amplitude of 10 mV without Xenon-lamp

irradiation. The CB energy levels of the as-obtained C8Z2S-F and C8Z2S-NP were -0.83 eV and -0.56 eV (vs. Ag/AgCl at pH = 7) with positive slopes over the Mott-Schottky plots, implying that these samples were of n-type semiconductor. The edge positions of the CB and valence band (VB) under the normal hydrogen electrode (NHE) scale were calculated through the following equations [28,34]:

$$E_{\text{CB}} = E_{\text{Ag/AgCl}} - E_{\text{Ag/AgCl}}^0 + 0.059 \times \text{pH} \quad (2)$$

$$E_{\text{VB}} = E_{\text{CB}} + E_{\text{g}} \quad (\text{NHE, pH} = 7) \quad (3)$$

where $E_{\text{Ag/AgCl}}^0$ (pH = 7) is 0.197 V, and the calculated CB energy levels (vs. NHE, pH = 7) of the as-obtained C8Z2S-F and C8Z2S-NP were -0.61 and -0.34 eV, respectively.

3. Results and discussion

C8Z2S-F was synthesized via a simple oil-bath treatment of CdCl_2 and ZnCl_2 with sodium citrate as a structure director at 60°C for 3 h. The Cd^{2+} and Zn^{2+} ions were seeded to induce the self-nucleation of the zinc sulfide solid solution in an atmosphere containing sulfur. On the basis of similar compatibility, nucleation atoms constantly attracted peripheral atoms, which could recombine and grow under the guidance of sodium citrate (Fig. 1(a)). The detailed flower-structure information, covering blossom, and individual flower of C8Z2S-F were visual-

ized via HAADF-STEM, TEM, and SEM (Figs. 1(b), 1(c), and 1(e)). The diameter of the individual flowers, consisting of ultrathin petals in the range of $0.5\text{--}1\text{ }\mu\text{m}$, was approximately $2\text{ }\mu\text{m}$. Fig. 1(d) shows the phase structure of C8Z2S-F. The diffraction peaks at 24.8° , 26.5° , 43.7° , and 51.9° corresponded to the (100), (002), (110), and (112) planes of zinc sulfide solid solution, respectively (JCPDS No. 49-1302). The thickness of C8Z2S-F was evaluated with AFM. The average feature sizes of the flower cores and petals were approximately 23.8 and 2.8 nm, respectively, which was in agreement with those in the HAADF-STEM and TEM images (Figs. 1(f), 1(g), and S1).

XPS demonstrated the chemical components and elemental status of the as-prepared C8Z2S-F. The typical peaks (Fig. 2(a)) matched the binding energies of Cd, Zn, and S with a Cd/Zn atomic ratio of $\sim 4:1$. The Cd $3d$ spectrum of the as-obtained C8Z2S-F was deconvoluted into two peaks at 405.1 and 411.5 eV, which was consistent with the Cd^{2+} signal. Moreover, the main spectra of Zn $2p_{3/2}$ and Zn $2p_{1/2}$ contained two typical peaks (1021.7 and 1044.8 eV), suggesting the presence of Zn^{2+} (Fig. 2(b)) [32]. The N_2 adsorption-desorption isotherms of C8Z2S-F exhibited type IV with an H3-type hysteresis loop under relative high P/P_0 (Fig. 2(c)), illustrating the existence of narrow slit-shaped pores formed by disordered flaky-packing flowers [15]. Moreover, the pore size distribution was mostly

Fig. 2. Compositional characterizations and photocatalytic CO_2 reduction performance of as-synthesized photocatalysts. (a) XPS spectra; (b) High resolution XPS spectra; (c) N_2 adsorption-desorption isotherms (inset indicates the pore size distribution); (d) UV-vis DRS spectra (inset shows the Kubelka-Munk function vs. photon energy curves); (e) Mott-Schottky plots; (f) Schematic of the electronic band structures of the as-obtained C8Z2S-F sample; (g) Photocatalytic products of CO_2 reduction detected by original chromatograms over C8Z2S-F and C8Z2S-NP samples under visible-light irradiation for 3 h; Photocatalytic activity of CO (h) and CH_4 evolution (i) over C8Z2S-F and C8Z2S-NP samples under visible light irradiation. Reaction conditions: photocatalyst (0.03 g), deionized water ($500\text{ }\mu\text{L}$), Xe lamp (300 W).

1–5 nm, which was consistent with that of mesopores (2–50 nm). The S_{BET} of C8Z2S-F was $52.1 \text{ m}^2 \text{ g}^{-1}$ (Table S1), implying the relatively high surface-to-volume ratio for the flower-like $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ solid solution. The UV-vis DRS of C8Z2S-F showed an absorption edge at approximately 540 nm with a band-gap width of 2.4 eV transformed by the Kubelka-Munk function (Fig. 2(d)) [2,35]. The relative level of the CB (Fig. 2(e)) of C8Z2S-F was estimated at -0.61 eV (vs. NHE at pH = 7) using the Mott-Schottky plots (details in Supporting Information). Accordingly, Fig. 2(f) presents the schematic illustration of the electronic band structures of C8Z2S-F; the measured CB potential was more negative than that of C8Z2S-NP (Figs. S2, S3, and S4), suggesting a strong photoreduction activity for the photocatalytic conversion of CO_2 .

Upon acquiring the desired 3D flower structure and electronic band position, the photocatalytic performances of the as-prepared C8Z2S-F and C8Z2S-NP in the CO_2 conversion under visible-light illumination were evaluated in an automatic photocatalytic reaction system without adding a sacrificial agent (Fig. S5). Figure 2(g) shows the detailed product types during the photocatalytic reduction of CO_2 , which were determined using an original chromatogram equipped with a FID and a TCD. The characteristic peaks of CO and CH_4 suggested that CO was the main product by both C8Z2S-F and C8Z2S-NP, and the evolved O_2 was recorded as the oxidation product of water splitting. The C8Z2S-F photocatalyst achieved photocatalytic yields of $12.9 \mu\text{mol g}^{-1}$ for CO evolution and $0.8 \mu\text{mol g}^{-1}$ for CH_4 generation in 1 h (Figs. 2(h) and 2(i)), which were considerably better than those of C8Z2S-NP (CO: $6.1 \mu\text{mol g}^{-1}$, CH_4 : $0.6 \mu\text{mol g}^{-1}$). The yield of CO continuously increased from 3.3 to $41.4 \mu\text{mol g}^{-1}$ during the initial 3 h, and exceeded that of CH_4 (Figs. S6 and S7), indicating the highly selective and effective photocatalytic CO production by C8Z2S-F. Meanwhile, during control experiments, no typical signals of hydrocarbon or carbon oxide were recorded in the absence of the as-prepared photocatalysts, water, or illumination (Fig. S8). This phenomenon confirmed the necessity of photocatalytic materials, water vapor, and light excitation in the solar-driven catalytic conversion of CO_2 . The photocatalytic stability of CO_2 reduction was evaluated via visible-light illumination for 3 h in each cycle (Fig. S9). C8Z2S-F, which was re-prepared through centrifugation and drying for the next round of the photoreduc-

tion test, retained its high photocatalytic activity for the production of CO after four cycles of testing. Furthermore, the performance of C8Z2S-F was more stable and better than that of C8Z2S-NP through the cyclic photocatalytic CO_2 conversion over four cycles, demonstrating the effective activity and stability of the 3D flower-structured photocatalyst during the photocatalytic reduction of CO_2 .

Considering the highlighted activity enhancement over C8Z2S-F, the key factors involved in the photocatalytic mechanism must be identified. THz-TDS showed that C8Z2S-F and C8Z2S-NP had similar terahertz transmission capabilities (Fig. 3(a)) with a transmittance rate of 80% (Fig. S10). However, the terahertz reflectivity of C8Z2S-F was more responsive than that of C8Z2S-NP (Fig. S11). The appearance of two peaks at 3 and 13 ps in the spectrum of C8Z2S-F indicated the two reflection effects on terahertz penetration (Fig. 3(b)). The stronger response to the THz-TDS reflectivity (Figs. 3(b) and S11) of C8Z2S-F implied the existence of the Fabry-Pérot effect with second or multiple refraction, which further revealed that the special 3D hierarchical flower-like structure with ultrathin petals possessed enriched active faces for light-harvesting (inset diagram of Fig. 2(d)) [36,37]. Before the conversion of CO_2 to CO and CH_4 , the adsorbed CO_2 was activated (CO_2)_{ad} (step 1 in Fig. 4(c)) [22,34]. In the CO_2 -TPD measurements (Fig. 4(a)), two typical adsorption peaks were found at 220 and 370 °C, corresponding to the weak and strong alkaline adsorption centers on the surface of C8Z2S-F, respectively [38,39]. In the second alkaline adsorption center, either the desorption temperature or desorption strength of C8Z2S-F was significantly higher than that of C8Z2S-NP (located at 320 °C). The stronger alkaline adsorption centers on C8Z2S-F indicated the far superior CO_2 adsorption sites and adsorption capacity in comparison with those of C8Z2S-NP, which indirectly contributed to the excellent experimental photocatalytic activity and stability of C8Z2S-F (Figs. 2(h) and 2(i)).

The TPR demonstrated the photocurrent changes in C8Z2S-F and C8Z2S-NP through intermittent illumination. Apparently, the photocurrent density of C8Z2S-F was stronger than that of C8Z2S-NP, indicating the enhancement of the photogenerated carrier separation and transfer of flower-structured photocatalysts (Fig. 4(b)) [40]. The typical EIS (inset of Fig. 4(b)) exhibited photogenerated charge dynamics

Fig. 3. Optical performance of as-synthesized photocatalysts. THz-TDS transmittance (a) and THz-TDS reflectivity (b) of C8Z2S-F and C8Z2S-NP samples.

Fig. 4. Physicochemical properties and mechanism study of as-synthesized photocatalysts. CO₂-TPD profiles (a) and EIS spectra (b) (inset shows the TPR curves) of C8Z2S-F and C8Z2S-NP samples; (c) Schematic of the photocatalytic reduction of CO₂ by using C8Z2S-F sample as photocatalyst.

of C8Z2S-F and C8Z2S-NP [41]. Accordingly, C8Z2S-F exhibited a desirable charge-transfer resistance due to the small impedance of the Nyquist plot, thereby reaffirming the advantage of the 3D flower-shaped Cd_{0.8}Zn_{0.2}S solid solution in the reduction of CO₂. Steady-state PL (Fig. S12) was used to evaluate the dynamic charge behavior of C8Z2S-F and C8Z2S-NP with the excitation at 435 nm; C8Z2S-F showed a weaker emission peak than C8Z2S-NP. The quenching PL intensity of C8Z2S-F indirectly confirmed the suppressed photogenerated carrier recombination and promoted photoelectron separation [42]. The experimental results elucidated the role of C8Z2S-F in enhancing the photocatalytic carrier dynamics, which was consistent with the rapid deoxygenation, and thus resulted in a highly selective photocatalytic reduction of CO₂.

During the light-driven conversion of CO₂, the main reduction products (CO, CH₂O, CH₃OH, or CH₄) depend on a reverse competitive relationship between the hydrogenation and deoxygenation pathways [43–45]. The formation of intermediates and final products is affected not only by the complex substrate-CO₂ molecule contact mechanism but also by the carrier transport capability [46,47]. Upon the visible-light irradiation of photocatalysts, the photogenerated holes induced by photoexcitation were transferred to the VB for water oxidation [H₂O + h⁺ → O₂ + (H⁺)_{ad}] (step 2 in Fig. 4(c)) [40]. The involved (H⁺)_{ad} and activated (CO₂)_{ad} on the surface of photocatalytic materials further interacted through the bridging effect of photogenerated electrons in the CB and assisted the generation of CO [(CO₂)_{ad} + (H⁺)_{ad} + e⁻ → CO + H₂O] (step 2 in Fig. 4(c)). The formation of CH₄ through deoxygenation is shown in step 3 in Fig. 4(c) [48]. The *in situ* DRIFTS (Figs. 5(a) and 5(b)) with the introduction of CO₂/H₂O interactions was performed for the

synthesized C8Z2S-F photocatalyst to further illustrate the surface-adsorbed species and intermediates during the photocatalytic activation and conversion of CO₂. The analysis was conducted in the dark (0–60 min) and under light irradiation (60–120 min, 365-nm Xenon lamp) in a moist CO₂/H₂O continuous-flow system. During the adsorption process by exposing the C8Z2S-F photocatalyst to CO₂/H₂O in the dark, the surface adsorbed bicarbonate (HCO₃⁻) at 1191, 1214, and 1243 cm⁻¹, bidentate carbonate (b-CO₃⁻) at 1650 cm⁻¹, carboxylate (CO₂⁻) at 1284 and 1703 cm⁻¹, as well as monodentate carbonate (m-CO₃⁻) at 1378 cm⁻¹ species, which were formed as shown in Figs. 5(a) and 5(b). The bicarbonate would be formed by the chemical bonding of the adsorbed CO₂ molecules with hydrogen-containing groups, like basic hydroxyl groups, at the surface of C8Z2S-F [23,49]. With the introduction of light illumination, the bands assigned to methoxy groups (–OCH₃, 1040 and 1451 cm⁻¹), formaldehyde (H₂CO, 1158 and 1312 cm⁻¹) and bidentate formate species (HCOO⁻, 1540 and 1743 cm⁻¹) emerged. Furthermore, the band at 1084 cm⁻¹ corresponding to HCO₃⁻ was observed, of which the absorption intensity gradually increased with the illumination time increasing from 90 to 120 min. The results indicated that the formation of photocatalytic intermediates, such as HCOOH, HCHO, and CH₃OH, are involved during the photocatalytic reduction of CO₂ [50–52]. As shown in Fig. 5(c), the reduction pathway included deoxygenation [CO₂ → *CO + H⁺ + e⁻ → CO(g)] and hydrogenation [CO₂ → *CO + H⁺ + e⁻ → *CHO → ... → CH₄(g)]. The final product depends on the steps that determine the formation and decomposition rate of the reaction intermediates [53–55]. The transmission efficiency and lifetime of photogenerated carriers also affect the formation of the final products. The formations

Fig. 5. The *in situ* DRIFTS spectra of CO₂ adsorption over as-synthesized C8Z2S-F photocatalysts. Surface photocatalytic intermediates after introduction of CO₂ + H₂O interaction under dark (0–60 min) and 365 nm light irradiation (60–120 min) in different wavenumber ranges of 1000–1400 cm⁻¹ (a) and 1400–2100 cm⁻¹ (b); (c) schematic of the possible photocatalytic process during the conversion of CO₂ to CO and CH₄ under visible-light irradiation.

of HCOOH, HCHO, CH₃OH, and CH₄ require two, four, six, and eight photoelectrons, respectively, during the photocatalytic CO₂ conversion. The photocatalytic yields of the conversion of CH₄ by C8Z2S-F (0.8 μmol g⁻¹) was significantly higher than those of C8Z2S-NP, C5Z5S, and C2Z8S, further illustrating that the 3D hierarchical Cd_{0.8}Zn_{0.2}S flowers possess desirable electronic separation capability and photocatalytic carrier dynamics; this was consistent with the photoelectrochemical analysis (Figs. 4(b) and 7(d)). Based on the *in situ* DRIFTS analysis and the photocatalytic experiments on the reduction of CO₂ (Figs. 2(g), 2(h), and 2(i)), the photoreduction pathways of the as-synthesized C8Z2S-F photocatalyst could be summarized with the following reactions:

Given that the typical C8Z2S-F involved the distinctive 3D flower structure for a Cd/Zn atomic ratio of only 4:1, the Cd_{0.2}Zn_{0.8}S (C2Z8S) and Cd_{0.5}Zn_{0.5}S (C5Z5S) samples were synthesized by changing the Cd/Zn atomic ratios to 1:4 and 1:1, respectively, to acquire the integral morphological and photoelectrical characteristics. XRD patterns (Fig. S13) showed a variation in the (002) (JCPDS No. 49-1302) plane of the as-obtained C8Z2S-F, C5Z5S, and C2Z8S samples. The C5Z5S exhibited the strongest diffraction peak at 26.5°, revealing a better crystallin-

ity than those of C8Z2S-F and C2Z8S. SEM (Figs. 6(a₁) and S14) and HAADF-STEM (Fig. 6(a₂)) images displayed C2Z8S with a flower-bud structure (Fig. 6(a₃)). As the Cd/Zn atomic ratio gradually increased, the zinc sulfide solid solution experienced self-growth from a flower-bud to a flower-globose (Figs. 6(b), S14, and S15) and finally exhibited a flower structure (Fig.

Fig. 6. Morphological characterizations of the photocatalysts. (a₁–d₁) SEM images; (a₂–d₂) HAADF-STEM images; (a₃–d₃) schematic of the structures of C2Z8S, C5Z5S, C8Z2S-F, and C8Z2S-NP samples.

6(c)). Figs. 6(d) and S16 illustrate the formation of C8Z2S-NP without adding sodium citrate, which reveals the important structure-directing role of sodium citrate in the directional formation of the 3D flower-like structure. Meanwhile, the related CB level (Fig. 7(c)) of C8Z2S-F was estimated at -0.61 eV (vs. NHE at pH = 7) via the Mott-Schottky plots, which was more negative than those of C5Z5S (-0.45 eV) and C2Z8S (-0.39 eV) (Fig. S4). The electrochemical characterizations (Fig. 7(d)) exhibited the photogenerated charge-transfer dynamics of the as-obtained C8Z2S-F, C5Z5S, and C2Z8S. These results showed that C8Z2S-F possessed the strongest photocurrent density and the smallest impedance of the Nyquist plot, confirming the superior photogenerated charge-transfer dynamics of the 3D flower structure compared to the other structures. This finding was further proven by the basic photocatalytic activity of CH_4 and CO evolution over C8Z2S-F, C5Z5S, and C2Z8S under visible-light irradiation (Figs. 7(e) and 7(f)). The photocatalytic yield of the CO evolution reached 4.8 and 7.6 $\mu\text{mol g}^{-1}$ for C2Z8S and C5Z5S, respectively, which were considerably lower than that of C8Z2S-F ($12.9 \mu\text{mol g}^{-1}$), in the first hour. Particularly, a comparably high selectivity of 89.9% for the conversion of CO_2 to CO, as well as a TON of 39.6 were obtained for C8Z2S-F (Table 1), which was considerably better than those of C2Z8S (TON : 21.4) and C5Z5S (TON : 24.4). Furthermore, the yield of CO and CH_4 continuously improved with time, implying the significance of the morphology in the enhancement of the photocatalytic CO_2 reduction (Figs. S17 and S18).

Table 1Evaluation of selective CO_2 photoconversion.^a

Sample	Production rate ^b ($\mu\text{mol g}^{-1} \text{h}^{-1}$)		TON ^c	Selectivity for CH_4 ^d (%)
	CO	CH_4		
C8Z2S-F	17.8	0.5	39.6	89.9
C5Z5S	11.0	0.3	24.4	90.2
C2Z8S	9.5	0.3	21.4	88.8
C8Z2S-NP	4.9	0.4	13	75.4

^a Reaction condition was described in photocatalytic CO_2 reduction measurement.

^b Irradiation time was 3 h.

^c The TON was calculated by calculation equation (1).

^d The selectivity toward CO = $[2 \cdot R(\text{CO})] / [2 \cdot R(\text{CO}) + 8 \cdot R(\text{CH}_4)] \cdot 100\%$.

4. Conclusions

An atomically self-assembled, hierarchical C8Z2S-F ($\sim 2\text{-}\mu\text{m}$ diameter) with ultrathin petals ($\sim 2.8\text{-nm}$ thickness) was successfully engineered by employing sodium citrate as a structure director via a simple oil-bath treatment. This particular 3D petal-to-core structural organization of the $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ solid solution efficiently enhanced its CO_2 adsorption properties and light-harvesting capacity. This phenomenon motivated a significant advantage for anchoring CO_2 molecules to the targeting adsorption sites and reinforced the substrate-molecule contact for CO and CH_4 molecule formation, thereby greatly boosting the selectivity and activity in the photocatalytic reduction of CO_2 . This work offers a novel perspective on the development of photocatalytic materials for the reduction of CO_2 . The de-

Fig. 7. Comparison of electrochemical characterizations and photocatalytic CO_2 reduction performance over a series of photocatalysts. N_2 adsorption-desorption isotherms (a) (inset indicates the pore size distribution); UV-vis DRS spectra (b) (inset shows the Kubelka-Munk function vs. photon energy curves), Mott-Schottky plots (c), and EIS spectra (d) (inset presents the TPR curves) of C8Z2S-F, C5Z5S, and C2Z8S samples; Photocatalytic activity of CO (e) and CH_4 evolution (f) over C8Z2S-F, C5Z5S and C2Z8S samples under visible-light irradiation. Reaction conditions: photocatalyst (0.03 g), deionized water (500 μL), Xe lamp (300 W).

signed 3D structure as proposed in this paper is also applicable to the fabrication of other 3D catalysts for photocatalytic applications.

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Graphical Abstract

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Structural engineering of 3D hierarchical Cd_{0.8}Zn_{0.2}S for selective photocatalytic CO₂ reduction

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The as-prepared self-assembled Cd_{0.8}Zn_{0.2}S flowers with decorating ultrathin petals through an oil-bath method exhibit highly selective photocatalytic CO₂ reduction under visible-light irradiation.

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三维分等级花状 $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ 的结构调控及其光催化 CO_2 还原

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摘要: 近年来, 光催化 CO_2 还原被视为一种既能解决能源短缺又能减少温室气体, 改善人类生存环境的绿色新型技术。然而, 由于 CO_2 气体的相对稳定性, 构建高催化活性和高选择性的催化体系仍然面临着巨大挑战。锌硫镉固溶体作为一种廉价的固溶类材料, 具有吸光范围适宜、化学性质稳定以及能带结构可调控等特点, 在光催化还原 CO_2 的方面表现出巨大的潜力。本文发展了一种简单的原位自组装法合成三维分等级花状结构的 $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$, 主要包括 Cd^{2+} 和 Zn^{2+} 离子在含硫氛围下自组装成核状前体, 然后以柠檬酸钠作为形貌诱导剂进一步组装生长, 同时控制 $\text{Cd}^{2+}/\text{Zn}^{2+}$ 摩尔比和反应时间以实现三维分等级花状 $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ 的合成。结果表明, 三维分等级花状结构的 $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ 在光催化还原 CO_2 的过程中表现出优异的催化活性和稳定性。其中, 在光照3 h后, CO 产量达到 $41.4 \mu\text{mol g}^{-1}$, 大约是相同光照条件下 $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ 纳米颗粒的三倍($14.7 \mu\text{mol g}^{-1}$)。此外, 三维分等级花状结构的 $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ 在光催化过程中展现出对光催化产物 CO 的较高选择性(89.9%), 其中在没有任何牺牲剂或共催化剂作用下的TON为39.6。太赫兹时域光谱(THz-TDS)表明, 这种三维分等级花状结构的 $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ 相较于 $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ 纳米颗粒更有利于对光的吸收, 从而提高对光的有效利用率。原位漫反射傅立叶变化红外光谱表征分析揭示了三维分等级花状结构的 $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ 在光催化过程中表面吸附物质以及光催化还原中间体的存在及转化。通过实验数据和理论机理预测表明, 该种三维分等级花状结构的 $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ 具有较高的电流密度和较好的载流子传输能力。基于这种三维的花状结构, 使得 $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ 具有较大的比表面积和吸附位点, 进一步提升体系的 CO_2 吸附性能和光生电子的转移效率, 从而有效提高光催化 CO_2 还原的活性。

关键词: 花状 $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$; 自组装生长; 光催化 CO_2 还原; 高选择性; 可见光

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