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## Well-defined $\text{Co}_9\text{S}_8$ cages enable the separation of photoexcited charges to promote visible-light $\text{CO}_2$ reduction†

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Exploring affordable cocatalysts with high performance for boosting charge separation and  $\text{CO}_2$  activation is an effective strategy to reinforce  $\text{CO}_2$  photoreduction efficiency. Herein, well-defined  $\text{Co}_9\text{S}_8$  cages are exploited as a nonprecious promoter for visible-light  $\text{CO}_2$  reduction. The  $\text{Co}_9\text{S}_8$  cages are prepared *via* a multistep strategy with ZIF-67 particles as the precursor and fully characterized by physicochemical techniques. The hollow  $\text{Co}_9\text{S}_8$  cocatalyst with a high surface area and profuse catalytically active centers is

discovered to accelerate separation and transfer of light-induced charges, and strengthen concentration and activation of  $\text{CO}_2$  molecules. In a hybrid photosensitized system, these  $\text{Co}_9\text{S}_8$  cages efficiently promote the deoxygenative reduction of  $\text{CO}_2$  to generate  $\text{CO}$ , with a high yield rate of  $35 \mu\text{mol h}^{-1}$  (*i.e.*,  $35 \text{ mmol h}^{-1} \text{ g}^{-1}$ ). Besides, this cocatalyst is also of high stability for the  $\text{CO}_2$  photoreduction reaction. Density functional theory (DFT) calculations reveal that the  $\text{Ru}(\text{bpy})_3^{2+}$  photosensitizer is strongly absorbed on the  $\text{Co}_9\text{S}_8$  (311) surface through forming four Co–C bonds, which can serve as the “bridges” to ensure quick electron transfer from the excited photosensitiser to the active  $\text{Co}_9\text{S}_8$  cocatalyst, thus promoting the separation of photoexcited charges for enhanced  $\text{CO}_2$  reduction performance.

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Solar-driven  $\text{CO}_2$  reduction, an ideal strategy to afford low-carbon fuels (*i.e.*,  $\text{CO}$  and  $\text{CH}_4$ ) with renewable energy, is long being intensively studied,<sup>1–6</sup> given its promise in addressing the issues of energy and environment. However, as limited by the extreme chemical inertness of linear  $\text{CO}_2$  molecules, the easy recombination feature of photoexcited charges and the intricacy of the multi-electron/proton engaged reaction,<sup>7–10</sup> photocatalytic  $\text{CO}_2$  reduction currently suffers from low efficiency coupled with moderate selectivity that is far behind the criteria of practical utilization.

During the past few decades, a great deal of strategies have been proposed to improve  $\text{CO}_2$  photoreduction efficiency with inspiring progress realized.<sup>11–16</sup> Therein, cocatalyst engineering is verified to be a preferred approach. This is because cocatalysts can enable capture and activation of  $\text{CO}_2$  molecules, accelerate separation and transfer kinetics of charge carriers, and provide catalytically active sites to selectively operate the redox reactions.<sup>17,18</sup> The noble metal nanoparticles are the classic  $\text{CO}_2$  reduction cocatalysts with high catalytic performance,<sup>19–22</sup> and alternatively, the transition metal ions/complexes of cobalt and nickel can serve as efficient promoters for  $\text{CO}_2$  photoreduction in cooperation with specific light-sensitizers.<sup>23–30</sup> Comparatively, considering the requirements of large-scale execution (*i.e.*, low price, high abundance, easy

separation/retrieval), exploring heterogeneous cocatalysts composed of cost-affordable elements for  $\text{CO}_2$  photoreduction is highly desirable.

Besides the chemical composition, designing catalytic materials with favored architectures is also of vital importance for photocatalytic  $\text{CO}_2$  reduction.<sup>31</sup> As a group of multifunctional catalysts for energy storage and conversion,<sup>32,33</sup> hollow structures are actively employed for  $\text{CO}_2$  photoreduction,<sup>34–40</sup> owing to their inherent advantages, such as a shortened perpendicular path for charge transfer to prevent their recombination, plentiful surface-active sites to boost  $\text{CO}_2$  capture and redox catalysis, and strengthened interior reflection/scattering to enhance incident light utilization.<sup>41–43</sup>

With all the aforementioned concerns in mind, in this work, the well-defined  $\text{Co}_9\text{S}_8$  cages are applied as a cocatalyst coupled with  $\text{Ru}(\text{bpy})_3^{2+}$  (abbreviated as Ru, bpy = 2'2'-bipyridine) as a photosensitizer for  $\text{CO}_2$  reduction under visible light. The dodecahedral  $\text{Co}_9\text{S}_8$  cage is created *via* a multi-step method as depicted schematically in Fig. 1. Starting with  $\text{Co}_2^+$  and 2-methylimidazole as the raw materials, the zeolitic imidazolate framework (ZIF-67) dodecahedron is first prepared through a reported precipitation method with some adjustments (step I).<sup>44,45</sup> Next, the ZIF-67 particle is converted to a  $\text{CoS}_x$  cage by a hydrothermal sulfidation reaction (step II). Finally, the  $\text{Co}_9\text{S}_8$  cage is harvested after annealing the  $\text{CoS}_x$  intermediate under a  $\text{N}_2$  atmosphere at 550 °C (step III).

The  $\text{Co}_9\text{S}_8$  cocatalyst is revealed by diverse photo-/electrochemical tests to augment  $\text{CO}_2$  activation and promote separation of light-excited charges. In a tandem photochemical system, the  $\text{Co}_9\text{S}_8$  cocatalyst enables the deoxygenative reduction of  $\text{CO}_2$  by visible light, with a CO formation rate of 35  $\mu\text{mol h}^{-1}$ , under the cooperation of  $\text{Ru}(\text{bpy})_3^{2+}$  as a photosensitizer. Indeed, the reduction ability of the  $\text{Co}_9\text{S}_8$  catalyst in photocatalysis has been demonstrated by hydrogen evolution reactions,<sup>46–50</sup> however, its talent for  $\text{CO}_2$  photoreduction has been seldom exploited so far.

Production of the ZIF-67 precursor was confirmed by powder X-ray diffraction (XRD) and energy-dispersive X-ray (EDX) characterization (Fig. S1, ESI†). The field emission scanning electron microscopy (FESEM) images show that the as-synthesized ZIF-67 particles present a morphology of nearly monodisperse dodecahedra with high uniformity (Fig. 2a and b).

After the sulfidation treatment, the ZIF-67 precursor was entirely transformed into an amorphous cobalt sulfide ( $\text{CoS}_x$ ) product with a Co/S ratio of about 1 : 3.42 (Fig. S2, ESI†). The

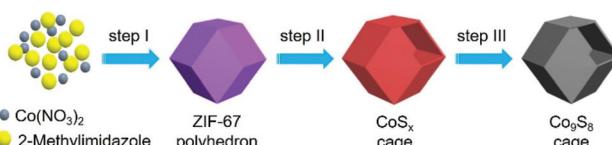


Fig. 1 Schematic illustration of the preparation processes of dodecahedral  $\text{Co}_9\text{S}_8$  cages: (I) self-assembly, (II) sulfidation, and (III) annealing in  $\text{N}_2$ .

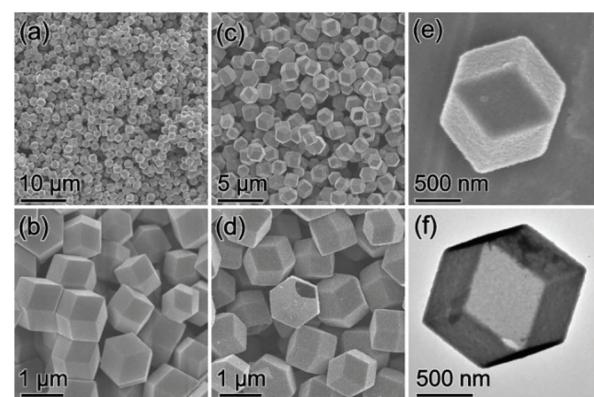


Fig. 2 (a and b) FESEM images of ZIF-67 dodecahedra. (c–e) FESEM images and (f) TEM image of  $\text{CoS}_x$  cages.

FESEM images indicate that the  $\text{CoS}_x$  intermediate can inherit the dodecahedral shape of the parental ZIF-67 particles perfectly (Fig. 2c). From the magnified FESEM images (Fig. 2d and e), it is found that the  $\text{CoS}_x$  particles have a relatively rougher surface than the ZIF-67 precursor, and the observed clear cavity of the broken  $\text{CoS}_x$  dodecahedra implies their hollow structure. The empty interior of the well-defined  $\text{CoS}_x$  cages is then confirmed visually by the TEM image (Fig. 2f). The possible formation process of  $\text{CoS}_x$  cages is clarified as follows. During the hydrothermal sulfidation reaction, the thioacetamide is decomposed to release the sulfide ions to react with the cobalt ions on the ZIF-67 particle surface, yielding an outermost layer of  $\text{CoS}_x$ . Further formation of the  $\text{CoS}_x$  shell continues *via* the reactions between inward diffusing sulfide ions and outward diffusing metal ions, finally producing the polyhedral  $\text{CoS}_x$  cages.<sup>46,51</sup>

The  $\text{CoS}_x$  material was treated by annealing in  $\text{N}_2$  to attain the  $\text{Co}_9\text{S}_8$  product. To monitor the conversion procedure, thermogravimetry (TG) analysis was conducted. As shown in

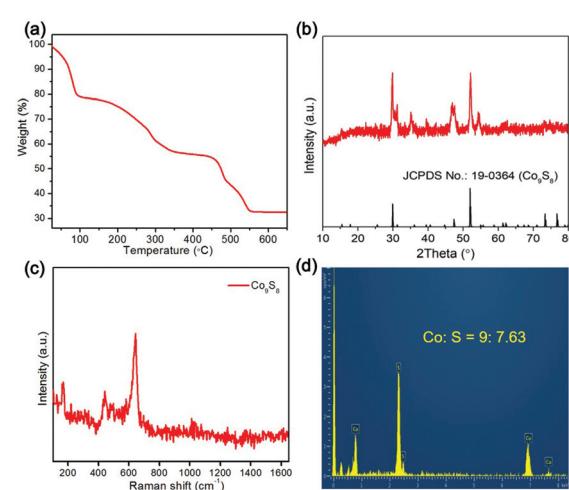


Fig. 3 (a) TG curve of  $\text{CoS}_x$  cages in  $\text{N}_2$ . (b) XRD pattern, (c) Raman spectrum and (d) EDX spectrum of  $\text{Co}_9\text{S}_8$  cages.

Fig. 3a, the result of TG indicates that the  $\text{CoS}_x$  intermediate undergoes gradual weight loss during the thermal treatment due to sulphur volatilization, and finally forms a stable product at 550 °C, which is confirmed to be the  $\text{Co}_9\text{S}_8$  phase (JCPDS card no.: 19-0364) by XRD analysis (Fig. 3b). No impurity XRD peaks are discerned, signifying the high phase purity of the  $\text{Co}_9\text{S}_8$  material. The Raman spectrum of the  $\text{Co}_9\text{S}_8$  sample presents a distinct vibrational peak at around 640  $\text{cm}^{-1}$  together with a set of bands below 750  $\text{cm}^{-1}$  (Fig. 3c), indexing to the characteristic Raman peaks of the  $\text{Co}_9\text{S}_8$  phase.<sup>52,53</sup> The EDX spectrum shows that the  $\text{Co}_9\text{S}_8$  product is only composed of Co and S elements with a molar ratio of about 9:7.63 (Fig. 3d), which is close to the theoretical value.

The morphology and microstructures of the  $\text{Co}_9\text{S}_8$  product were researched by FESEM and TEM. As can be seen from the FESEM images (Fig. 4a and b), the  $\text{Co}_9\text{S}_8$  particles well preserve the pristine polyhedral construction of the  $\text{CoS}_x$  intermediate without perceptible agglomeration or fractures. The careful FESEM analysis discloses that the surface of  $\text{Co}_9\text{S}_8$  particles experiences slight shrinkage after the thermal treatment (Fig. 4c). The structural features of  $\text{Co}_9\text{S}_8$  cages revealed by TEM are consistent with the results of FESEM (Fig. 4d and e). The crystal features of  $\text{Co}_9\text{S}_8$  cages were then checked by high-resolution TEM (HRTEM) analysis. As shown in Fig. 4f, the HRTEM image displays strong lattice fringes with an interlayer *d*-spacing of 0.28 nm determined by the corresponding inverse fast Fourier transformation (IFFT) image and line scans (Fig. 4g and h), which is assigned to the (222) crystal plane of the cubic  $\text{Co}_9\text{S}_8$  phase. The  $\text{Co}_9\text{S}_8$  product is verified to be a polycrystalline material, as revealed by the selected area elec-

tron diffraction (SAED) pattern (Fig. 4i), in which the clear diffraction fringes are attributed to the interplanar spacings of the cubic  $\text{Co}_9\text{S}_8$  phase.

The surface chemical states of elements of the  $\text{Co}_9\text{S}_8$  material were studied by X-ray photoelectron spectroscopy (XPS). As shown in Fig. 5a, the high-resolution Co 2p spectrum is fitted into two sets of spin-orbit doublets and satellite (Sat.) peaks. The first doublet located at 778.3 and 779.4 eV and the second doublet with binding energies of 793.4 and 795.5 eV are attributed to  $\text{Co 2p}_{3/2}$  and  $\text{Co 2p}_{1/2}$ , respectively. The presence of these doublets indicates the coexistence of  $\text{Co}^{3+}$  and  $\text{Co}_2^{+}$ , which is in agreement with the results of previous work.<sup>54–56</sup> In the XPS spectrum of S 2p (Fig. 5b), the fitted peaks with binding energies of about 162.1 and 163.1 eV are assigned to the Co-S species, while the other two peaks centered at 163.7 and 164.9 eV are attributable to the S-O bonds,<sup>46</sup> implying the surface oxidation of the  $\text{Co}_9\text{S}_8$  sample that is generally detected during XPS measurements.

The textural properties of  $\text{Co}_9\text{S}_8$  cages were examined by  $\text{N}_2$  sorption measurements. As displayed in Fig. 5c, classified type-II  $\text{N}_2$  adsorption–desorption isotherms together with a type H3 hysteresis loop are observed, suggesting the formation of mesopores in the material, which can be further confirmed by the corresponding pore size distribution plot (inset, Fig. 5c). Generation of the porous structure of  $\text{Co}_9\text{S}_8$  cages is positive to facilitate mass transportation for heterogeneous photocatalytic applications. The  $\text{Co}_9\text{S}_8$  material is measured to have a high specific Brunauer–Emmett–Teller (BET) surface area of about 137  $\text{m}^2 \text{g}^{-1}$ , which should be mainly contributed by the well-defined hollow configuration. Such a high surface area will enable the capture and concentration of  $\text{CO}_2$  molecules, as reflected by the  $\text{CO}_2$  adsorption isotherm, which gives a maximum  $\text{CO}_2$  uptake of about 13.5  $\text{cm}^3 \text{g}^{-1}$  at 0 °C and 1 atm (Fig. 5d). These textural features of  $\text{Co}_9\text{S}_8$  cages are ben-

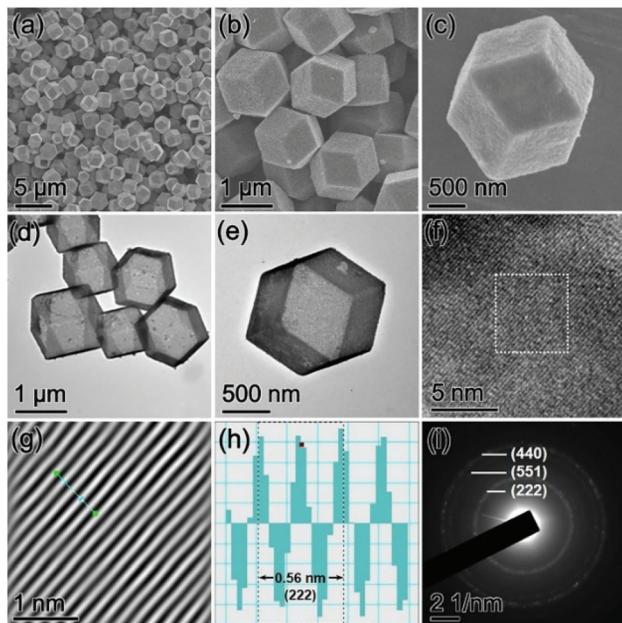


Fig. 4 (a–c) FESEM images, (d and e) TEM images, (f) HRTEM image, (g and h) the corresponding inverse fast Fourier transformation (IFFT) image and line scans of the dotted square region in (f), and (i) SAED pattern of  $\text{Co}_9\text{S}_8$  cages.

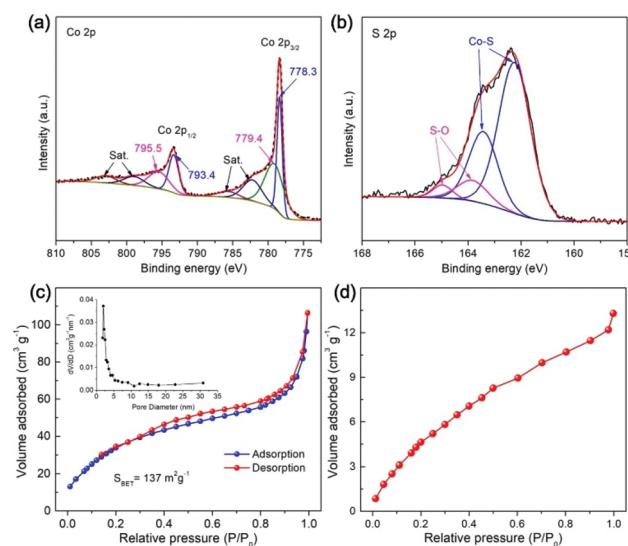


Fig. 5 (a) Co 2p and (b) S 2p XPS spectrum, (c)  $\text{N}_2$  adsorption–desorption isotherms, and (d)  $\text{CO}_2$  adsorption isotherm of  $\text{Co}_9\text{S}_8$  cages.

eficial to afford rich exposed catalytically active sites and boost mass transport for heterogeneous  $\text{CO}_2$  fixation reactions.

We then evaluated the performance of  $\text{Co}_9\text{S}_8$  cages by the visible-light  $\text{CO}_2$  reduction reaction conducted in a classic hybrid system,<sup>2,25,54,57–61</sup> engaging  $\text{Ru}(\text{bpy})_3^{2+}$  as the light-harvester and  $\text{H}_2\text{O}/\text{acetonitrile}/\text{TEOA}$  mixture as the reaction medium. Fig. 6a presents the  $\text{CO}_2$  reduction activity of the  $\text{Co}_9\text{S}_8$  cocatalyst as a function of reaction time. As can be seen, the system manifests a high photocatalytic performance in the initial first 1 h of the reaction, showing a  $\text{CO}_2$ -to-CO conversion rate of  $35 \mu\text{mol h}^{-1}$ , coupled with a  $\text{H}_2$ -releasing rate of  $12 \mu\text{mol h}^{-1}$ . In addition to CO and  $\text{H}_2$ , no detectable formation of hydrocarbon products is observed in the liquid phase. On further continuing the reaction, generation of the products increases progressively, but with a decreased rate, which should result from degradation of the ruthenium photosensitizer.<sup>57,62,63</sup> The total yield of CO reaches  $65 \mu\text{mol}$  after photoreaction for 7 h, corresponding to a catalytic turnover number (TON) of about 54 relative to the cocatalyst.

The working mechanism of the  $\text{CO}_2$  reduction system was inspected by controlling the reaction conditions. As shown in Fig. 6b, compared to that of the normal reaction (column 1),

the evolution of  $\text{CO}/\text{H}_2$  reduces significantly once the  $\text{Co}_9\text{S}_8$  cocatalyst is omitted from the system, highlighting its critical role in promoting the  $\text{CO}_2$  reduction reaction. No product is detected without the introduction of a photosensitizer (column 3) or visible light irradiation (column 4), which indicates that the  $\text{CO}_2$  reduction reaction is a visible-light-sensitized process. It is revealed that TEOA is essential to achieve the  $\text{CO}_2$  reduction photocatalysis, as the reaction would be completely terminated without its participation (column 5), which matches well with the results of reported studies in analogous photochemical systems.<sup>2,25,57,62,64</sup> When employing  $\text{N}_2$  as the gas feedstock to substitute  $\text{CO}_2$  for running the reaction (column 6), the only product generated is  $\text{H}_2$ , suggesting that the CO product should be derived from the  $\text{CO}_2$  gas.

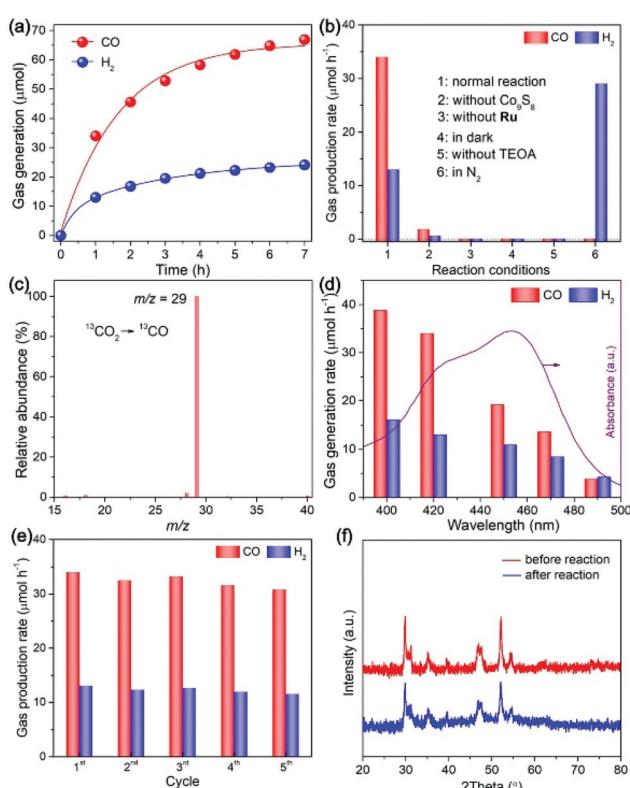
To directly track the origin of CO, we performed a  $^{13}\text{C}$ -labelled reaction with  $^{13}\text{CO}_2$  as the reactant and analyzed the produced CO by mass spectroscopy (MS). As indicated in Fig. 6c, the MS spectrum manifests a predominant peak with a *m/z* value of 29, which is attributed distinctly to  $^{13}\text{CO}$ . This observation firmly validates the source of CO generation, that is, the  $\text{CO}_2$  feedstock.

The  $\text{CO}_2$  photoreduction reactions were also initiated with light irradiation of different wavelengths through applying specific long-pass cut-off filters. As revealed in Fig. 6d, the formation of  $\text{CO}/\text{H}_2$  diminishes gradually under light irradiation of longer wavelengths, because of the decline in the incident photons when extending the wavelength of the light filter. These findings indicate that the  $\text{CO}_2$  reduction is motivated by light excitation of the photosensitizer.

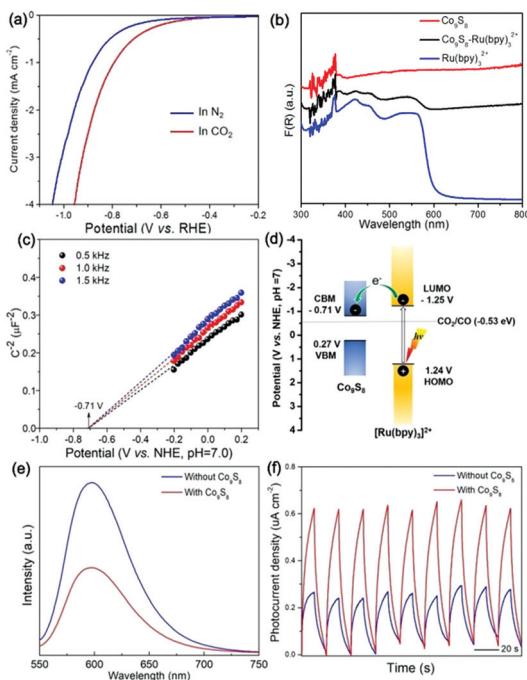
To examine the stability of the  $\text{Co}_9\text{S}_8$  cocatalyst, after  $\text{CO}_2$  photoreduction reactions, it was separated, washed, and re-added into fresh reaction mixtures for repeated operations. No apparent decrease in  $\text{CO}/\text{H}_2$  production is detected during the stability tests (Fig. 6e), pointing to its high activity stability. The results of XRD, FTIR, Raman, and XPS tests for the  $\text{Co}_9\text{S}_8$  cocatalyst before and after photoreaction expose its high stabilities in the crystal, chemical and surface structures in the photocatalytic  $\text{CO}_2$  reduction system (Fig. 6f, and Fig. S3, ESI<sup>†</sup>).

In order to gain an understanding of the high performance of the  $\text{CO}_2$  photoreduction system mediated by  $\text{Co}_9\text{S}_8$  cages, we carried out photo-/electro-chemical measurements. To demonstrate the function of  $\text{Co}_9\text{S}_8$  in the  $\text{CO}_2$  reduction reaction, linear sweep voltammetry (LSV) was conducted. As shown in Fig. 7a, the  $\text{Co}_9\text{S}_8$  catalyst delivers a more positive onset potential and a higher cathodic current in  $\text{CO}_2$ -saturated solution than those under  $\text{N}_2$ -saturated conditions. These outcomes verify that the  $\text{Co}_9\text{S}_8$  cages can activate  $\text{CO}_2$  molecules and drive their reduction reaction.<sup>63,65</sup>

UV-vis diffuse reflectance spectra (DRS) indicate that the  $\text{Co}_9\text{S}_8$  cocatalyst and  $\text{Ru}(\text{bpy})_3^{2+}$  photosensitizer show strong visible light absorption (Fig. 7b), while their hybrid possesses an optical harvesting ability. By using UV-vis DRS and the Tauc curve of  $\text{Co}_9\text{S}_8$  (Fig. S4, ESI<sup>†</sup>), its bandgap energy is measured to be  $0.98 \text{ eV}$ .<sup>37,47</sup> To define the conduction band bottom (CBM) and valence band maximum (VBM) positions, the flat



**Fig. 6** (a)  $\text{CO}_2$  photoreduction activity of the  $\text{Co}_9\text{S}_8$  cocatalyst as a function of reaction time. (b) Performance of the  $\text{CO}_2$  reduction system under various conditions. (c) Mass spectrum of CO yielded from the  $^{13}\text{CO}_2$  isotope reaction. (d) CO and  $\text{H}_2$  generation by visible light with different wavelengths. (e) Stability tests of the  $\text{Co}_9\text{S}_8$  cocatalyst. (f) XRD patterns of the  $\text{Co}_9\text{S}_8$  cocatalyst before and after  $\text{CO}_2$  reduction reactions.



**Fig. 7** (a) LSV curve of the Co<sub>9</sub>S<sub>8</sub> cocatalyst under N<sub>2</sub>- and CO<sub>2</sub>-saturated solutions. (b) DRS spectra of Co<sub>9</sub>S<sub>8</sub>, Ru(bpy)<sub>3</sub><sup>2+</sup> and Ru(bpy)<sub>3</sub><sup>2+</sup>/Co<sub>9</sub>S<sub>8</sub> hybrid. (c) Mott-Schottky plots. (d) Schematic illustration of energy levels and electron transfer from the ruthenium photosensitizer to the Co<sub>9</sub>S<sub>8</sub> cocatalyst. (e) PL spectra and (f) transient photocurrent generation of reaction systems with and without the Co<sub>9</sub>S<sub>8</sub> cocatalyst.

band potential of Co<sub>9</sub>S<sub>8</sub> was estimated by electrochemical Mott-Schottky plots. As shown in Fig. 7c, the derived CBM potential of the Co<sub>9</sub>S<sub>8</sub> cocatalyst is about  $-0.71$  V (vs. NHE, pH = 7.0), which integrated with the bandgap energy determines its VBM position at about 0.27 V (vs. NHE, pH = 7.0). Regarding the band structure of Co<sub>9</sub>S<sub>8</sub>, the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) levels of Ru(bpy)<sub>3</sub><sup>2+</sup>, and the redox potential for reducing CO<sub>2</sub> to CO (Fig. 7d),<sup>26,62,66</sup> the excited electrons of the photosensitizer are encouraged thermo-dynamically to travel to the cocatalyst for driving the CO<sub>2</sub> reduction reaction.

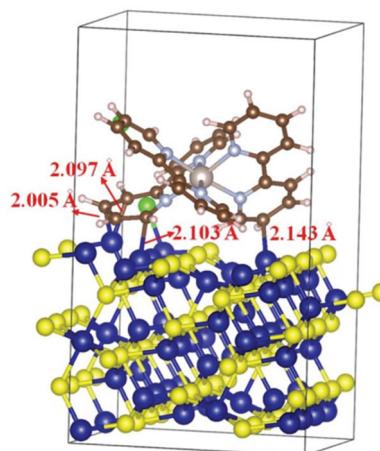
To monitor the separation and transport of light-excited charges in the photochemical system, room temperature photoluminescence (PL) was implemented. As revealed in Fig. 7e, the system involving Co<sub>9</sub>S<sub>8</sub> reveals a quenched PL emission compared to the system free of the cocatalyst, suggesting the prohibited recombination of light-stimulated charges of the former.<sup>31,40</sup> Simultaneously, the time-resolved PL (TRPL) spectra (Fig. S5, ESI†) reveal that the average emission lifetime of the reaction mixture with the cocatalyst (399 ns) is much shorter than that of the mixture without its presence (450 ns), indicating that quick electron transfer exists between the photosensitizer and the cocatalyst. Consistently, the photocurrent generation of the Co<sub>9</sub>S<sub>8</sub>-mediated system is higher than that of the system without its existence (Fig. 7f), which mirrors the boosted transport of charge carriers induced by the metal

sulfide cocatalyst.<sup>26,47,67</sup> All the above results show that the Co<sub>9</sub>S<sub>8</sub> cocatalyst can expedite separation and transfer of light-excited charges and promote activation of CO<sub>2</sub> molecules, thus reinforcing the CO<sub>2</sub> photoreduction efficiency.

Density functional theory (DFT) calculations were carried out to gain some insights into the interaction between the Ru(bpy)<sub>3</sub><sup>2+</sup> photosensitizer and Co<sub>9</sub>S<sub>8</sub> cocatalyst. The results prove that the Ru(bpy)<sub>3</sub><sup>2+</sup> complex can be strongly adsorbed on the Co<sub>9</sub>S<sub>8</sub> (311) surface, in which the carbon atoms of Ru(bpy)<sub>3</sub><sup>2+</sup> and the surface Co atoms of Co<sub>9</sub>S<sub>8</sub> form four Co-C bonds with a length of about 2.1 Å (Fig. 8). The chemical bonds between the photosensitizer and the cocatalyst may serve as the “bridges” to guarantee quick electron migration from the excited photosensitiser to the active Co<sub>9</sub>S<sub>8</sub> cocatalyst to run the CO<sub>2</sub> reduction reaction.

Finally, we have proposed a probable mechanism of the CO<sub>2</sub> photoreduction reaction catalyzed by the caged Co<sub>9</sub>S<sub>8</sub> cocatalyst. Being stimulated by visible light illumination, the ground state photosensitizer Ru(bpy)<sub>3</sub><sup>2+</sup> moves to the excited state of Ru(bpy)<sub>3</sub><sup>2+\*</sup>. Such an excited state will react with the electron donor TEOA through a reductive quenching process, leading to the formation of the photosensitizer in a reduced state of Ru(bpy)<sub>3</sub><sup>+</sup>.<sup>26,64</sup> The excited electrons of the Ru(bpy)<sub>3</sub><sup>+</sup> species will delocalize and move to the porous Co<sub>9</sub>S<sub>8</sub> cocatalyst to run the CO<sub>2</sub>-to-CO conversion reaction,<sup>60,62,65</sup> during which the Co<sub>9</sub>S<sub>8</sub> cages not only strengthen the adsorption and activation of CO<sub>2</sub> molecules but also push the separation and migration of light-generated charges to support the reaction.

In summary, well-defined dodecahedral Co<sub>9</sub>S<sub>8</sub> cages have been fabricated and applied as a new cocatalyst for CO<sub>2</sub> photoreduction with visible light. Owing to the high surface area and plentiful catalytically reactive locations, the hollow Co<sub>9</sub>S<sub>8</sub> cocatalyst effectively boosts CO<sub>2</sub> activation and prevents charge recombination. In a classic light-sensitized system, such a non-noble-metal cocatalyst can powerfully promote the conver-



**Fig. 8** The structure of Ru(bpy)<sub>3</sub>Cl<sub>2</sub> adsorbed on the Co<sub>9</sub>S<sub>8</sub> (311) surface with an adsorption energy of  $-4.5$  eV. The Co, S, Ru, N, C, H, and Cl atoms are denoted by blue, yellow, pink, gray, brown, white, and green, respectively.

sion of  $\text{CO}_2$  to CO with high efficiency and good stability. Inspired by this contribution, future studies about the sulfide semiconductors with narrow bandgaps and the hybrids of  $\text{Co}_9\text{S}_8$ /semiconductor for photocatalytic  $\text{CO}_2$  reduction may be anticipated.

## Author contributions

Xiahui Lin: conceptualization, methodology, feasibility analysis, validation, writing-original draft, and writing-review and editing. Zidong Xie: methodology, feasibility analysis, and validation. Bo Su: methodology, validation, and writing-review and editing. Mei Zheng: theoretical calculation. Wenxin Dai: feasibility analysis. Yidong Hou: writing-review and editing. Zhengxin Ding: writing-review and editing. Wei Lin: theoretical calculation and supervision. Yuanxing Fang: writing-review and editing and supervision. Sibo Wang: validation, writing-review and editing, and supervision.

## Conflicts of interest

There are no conflicts of interest to declare.

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