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Iron porphyrin and carbon black (CB) were utilized to fabricate an iron-nitrogen doped carbon (Fe-N-C) catalyst to create a new heterogeneous catalytic system with CdS to drive CO₂ reduction to CO under UV/vis light (AM 1.5G) irradiation. The system delivers a high CO production yield of 111 mmol g_{cat}^{-1} and a large turnover number (TON) of 1.22×10^3 in 8 h with a selectivity of 85%, all of which are competitive with state-of-the-art systems. The mechanism of the system was investigated by experimental and theoretical methods indicating that the high affinity between the iron active center and the *COOH intermediate facilitates the brilliant catalytic performance. This work provides a new direction for constructing heterogeneous CO₂ photoreduction systems.

Photocatalytic conversion of CO₂ into gaseous fuel precursors or liquid fuels is a promising strategy to reduce CO₂ emission to alleviate the reverse effect of global warming.¹ A photocatalytic system needs to accomplish two tasks: first, the photosensitizer absorbs the sunlight and generates activated electrons; second, the catalyst transfers the activated electrons into the CO₂ molecule.² Although in some systems, these two tasks could be accomplished by one species,^{3,4} the hybrid systems composed of photosensitizers and catalysts are more favorable due to their high efficiency and diversity.²

Many catalysts have been developed for effective CO_2 reduction by photo- and electrocatalysis. Molecular catalysts are mainly metal coordination compounds fabricated with nitrogen-containing ligands, such as polypyridine,⁵ phthalocyanine⁶ and porphyrin.^{7,8} These catalysts are productive and selective for CO_2 reduction. However, the stability issues and the difficulties for separation and reuse prevent their large-scale application.^{6,9} On the other hand, heterogeneous catalysts such as semiconductors,² silver¹⁰ and gold¹¹ are stable and easy for separation and reuse with lower catalytic performance.² Combining the advantages of both molecular and heterogeneous catalysts, a family of metal–nitrogen doped carbon (M–N–C) catalysts such as Fe–N–C^{12–14} and Ni–N–C^{15–17} are promising for CO₂ reduction. They are effective and selective (up to ~99%) for CO₂ reduction even in aqueous solution.^{12,17} Also, as heterogeneous catalysts with high stability, their large-scale application is a certain prospect.¹⁵

Among M-N-C catalysts fabricated by various precursors, zeolitic imidazolate frameworks (ZIFs) derived Fe-N-C catalysts exhibit outstanding electrocatalytic performance due to their pyrrolic N-Fe structure.^{12,18} In this work, iron porphyrin and carbon black (CB) were utilized to fabricate iron-nitrogen doped carbon catalysts based on the following considerations. Metalloporphyrins,^{7,8} a series of macrocyclic complexes with inherent M-N₄-C pyrrolic nitrogen coordinated structures, are desired precursors for the M-N-C catalysts.^{19,20} In addition, commercially available CB was chosen due to its porosity and conductivity that ensure mass transfer and charge mobility during catalysis.^{15,19,21} Incorporating metal meso-tetraphenylthe porphyrin (TPPM, M = FeCl and Ni, Fig. S1, ESI[†]) on the surface of CB and pyrolyzing at 800 °C, M-N-C catalysts with surface supported active centers can be easily achieved, denoting as M-CBs (M = Fe and Ni, see Fig. 1a and ESI[†] for details). We optimized the amount of iron porphyrin utilizing different weight content of TPPFeCl. The results of linear scan voltammetry (LSV) and partial CO current density (j_{CO}) at -0.9 V vs. SHE in the CO₂ saturated 0.5 M KHCO3 aqueous solution show that 20% weight content of the TPPFeCl is the best (Fig. S2, ESI[†]). Thus, we selected 20% as the weight ratio of iron porphyrin in the preparation of Fe-CB, which is the same as Ni-CB.¹⁷

Although promising for photochemical CO_2 reduction, investigations on M–N–C catalysts in photocatalysis are limited.^{2,13,14} The ZIFs-derived Fe–N–C catalysts were integrated with a noble metal-based molecular photosensitizer $[Ru(bpy)_3]^{2+}$ in acetonitrile/water mixed solvent to produce CO under light irradiation.^{13,14} However, a cheap, stable and watercompatible photosensitizer is preferable to be integrated with the M–CB catalysts to avoid the usage of noble-metal-containing

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Fig. 1 (a) Schematic illustration of preparation process for Fe–CB (hydrogen atoms on the porphyrin molecules were omitted for clarity). (b) Typical SEM image of Fe–CB. (c) Fe 2p region XPS spectra of Fe–CB and TPPFeCI. (d) Core level XPS spectra of N 1s region of Fe–CB.

photosensitizer and organic solvents. Also, the heterogeneous photosensitizers are advantageous in the application due to easy separation and reuse. CdS is one of the most widely applied heterogeneous photosensitizers due to its excellent photochemical properties despite its toxicity.^{2,22,23} The conduction band of CdS (E_{CB} , $\sim -0.9 V vs$. SHE, pH = 7.0) is negative enough to promote the reduction of CO₂ to CO (-0.53 V vs. SHE, pH = 7.0).^{2,24,25} Thus, we intended to construct new heterogeneous catalytic systems by using M–CB catalysts with CdS as photosensitizer.

Ni–CB was characterized in our previous report,¹⁷ and here we describe the characterization of Fe-CB. The scanning electron microscope (SEM) image shows that Fe-CB consists of balls crosslinked with each other to form a 3D porous structure (Fig. 1c and Fig. S3, ESI⁺). The surface of Fe-CB is rough and guarantees a high specific surface area of 100.2 $\text{m}^2 \text{g}^{-1}$ (Fig. S4, ESI[†]). The powder X-ray diffraction (PXRD) pattern of Fe-CB only exhibits two pronounced graphite diffraction peaks, while no metallic phase was detected (Fig. S5, ESI⁺). X-ray photoelectron spectroscopy (XPS) was utilized to determine the chemical composition and elemental states of Fe-CB catalyst (Fig. 1c, d and Fig. S6, ESI†). The XPS survey spectrum reveals an iron atomic content of 0.30 at% (1.3 wt%). Compared with the lower weight content of iron measured by inductively coupled plasma mass spectrum (ICP-MS) (0.51 wt%), most of the Fe atoms exist on the surface of the catalyst, ensuring the availability of the active centers during the catalysis.¹⁷ In addition, the binding energy of Fe 2p3/2 in Fe-CB catalysts is ~710.4 eV (Fig. 1c), which is ~0.6 eV lower than that in the TPPFeCl (\sim 711.0 eV), verifying that the iron was partially reduced and exists in a valence state similar with that in the previously reported Fe-N-C catalysts.^{12,18} The high-resolution XPS N 1s spectrum of Fe-CB catalyst was deconvoluted into pyrrolic N-Fe, pyridinic N-Fe, pyrrolic N and graphite N species.¹² Besides, no pyridinic N was detected. The pyrrolic N-Fe (43.8 at%) and pyridinic N-Fe species (14.3 at%) were confirmed in Fe-CB. Compared with the higher content of pyrrolic N-Fe structure (68 at%) and the lower content of pyridinic N-Fe species (2 at%) in the reported ZIF-derived $\mathrm{Fe}^{3+}\mathrm{-N-C}$ catalyst, 12 the pyrrolic N–Fe structure in iron porphyrin precursor was partially transformed to pyridinic N-Fe structure in the pyrolysis process. The high content of pyrrolic N-Fe species



Fig. 2 (a) Mott–Schottky plot of CdS. (b) Total current density, j_{CO} , and FE_{CO} at varied applied potentials around -0.9 V vs. SHE for Fe–CB and Ni–CB. (c) EIS Nyquist plot of the catalysts at -0.9 V vs. SHE. (d) PL spectra of CdS and the mixture of CdS and Fe–CB. (e) Photocurrent measurements of the catalytic systems. (f) Proposed mechanism of the Fe–CB + CdS hybrid system for CO₂ photochemical reduction.

guarantees Fe–CB's efficient catalytic performance. Besides, PXRD and SEM inspection of CdS verified the successful synthesis of CdS following a facile procedure with a ball-like morphology and a particle size of ~200 nm (Fig. S7, ESI⁺).^{22,26}

To validate the viability of our hybrid system, we need to ensure that the photogenerated electrons can drive the reduction of CO₂ on the catalyst while the holes can be quenched effectively by the sacrificial agent.² First, the flat-band potential ($E_{\rm fb}$, corresponding to the E_{CB})²⁷ of CdS is evaluated by the Mott–Shottcky test to be -0.9 V vs. SHE (Fig. 2a), indicating that catalysts need to have an onset potential for CO₂ reduction of less negative than -0.9 V vs. SHE.^{5,27} Thus, we measured the electrocatalytic properties of the M-CBs in a CO₂ saturated 0.5 M KHCO₃ aqueous solution (pH = 7.3). The catalysts' onset potentials for CO_2 to COconversion were determined to be -0.70 and -0.82 V vs. SHE for Fe-CB and Ni-CB, respectively,¹⁷ verified that both the catalysts are qualified to accomplish the hybrid system. Besides, compared with Ni-CB, Fe-CB delivers much higher partial current densities (j_{CO}) and faradaic efficiencies (FE_{CO}) for CO (Fig. 2b), indicating that Fe-CB could be a more efficient catalyst under the excitement of CdS. In addition, the high FE_{CO} of 97% at 0.35 V overpotential on Fe-CB is competitive with the ZIF-derived Fe-N-C catalysts while outperformed other Fe-N-C materials (Table S1, ESI⁺), further illustrated the advantage of the porphyrin precursor used in the synthetic procedure.¹² Also, the electrochemical impedance spectra (EIS) indicated the resistance of charge transfer (R_{ct}) between the Fe-CB and substrates is much smaller than Ni-CB (Fig. 2c). Also, we tested the photoluminescence (PL) spectra of the CdS and Fe-CB + CdS mixture to investigate the electron transfer between the CdS and Fe-CB. In Fig. 2d, the individual CdS exhibits an emission peak at 537 nm wavelength under 420 nm excitation, while the Fe-CB + CdS composite sample displays a sharp decrease of PL emission, implying photogenerated electron transfer between Fe-CB and CdS.^{27,28} In addition, we performed time-resolved PL decay spectra to quantify the average carrier lifetimes (Fig. S8, ESI⁺). The fitting results revealed that the average lifetime of Fe-CB + CdS and CdS are 2.57 and 1.87 ns, respectively. The results indicated that the hybrid system

can effectively prevent the photoexcited charge carriers from recombining, which displays a photogenerated electron transfer between the two components.^{27,28}

Next, we turned to explore the photo-oxidation part of the system. The valence band (E_{VB}) of CdS was estimated using a UV-vis diffusereflectance spectroscopy (UV-vis-DRS). CdS has an absorption in the visible light region (up to \sim 580 nm), suggesting the feasibility for solar-light utilization (Fig. S9a, ESI⁺). The Tauc-plot derived from the UV-vis-DRS indicates that CdS has a band-gap (E_{α}) of 2.45 eV (Fig. S9b, ESI⁺). Combining the Mott-Schottky measurement (Fig. 2a), the $E_{\rm VB}$ was determined to be 1.55 V vs. SHE. Furthermore, photocurrent tests were conducted to measure the photo-oxidation of the hybrid system in the presence of triethanolamine (TEOA), a harmless and efficient sacrificial donor commonly used for photochemical processes.^{4,27} As illustrated in Fig. 2e, pure CdS photosensitizer can photo-oxidize TEOA efficiently under solarlight illumination, delivered a high photocurrent density of \sim 1.4 mA cm⁻². Besides, the mixture of CdS and Fe–CB also shows prominent photocurrent density slightly lower than that of pure CdS, which might be contributing to the low photocurrent response of the CB based materials. This is illustrated in the photocurrent test of pure Fe-CB, which exhibits negligible photocurrent compared with CdS containing samples (Fig. 2e). All the above results ensure that the hybrid system composed of M-CB, CdS and TEOA is capable of CO₂ photochemical reduction, and a proposed mechanism is depicted in Fig. 2f: CdS is excited by light irradiation to generate an electron-hole pair, the generated electrons transfer to the catalyst to reduce CO₂ while TEOA quenches the holes.

Photoreduction of CO_2 catalyzed by Fe–CB was performed using a suspension of 1 mg of Fe–CB and 10 mg CdS dispersed in an aqueous solution of 10 wt% TEOA and 0.5 M KHCO₃. The time-dependent yields of CO and H₂ after 8 h of UV/vis light (AM 1.5G) irradiation are shown in Fig. 3a, CO was the primary product in the gas phase with a yield of 111 mmol g_{cat}^{-1} and a TON of 1.22×10^3 based on the Fe–CB catalyst. The CO production rate was as high as 13.9 mmol g_{cat}^{-1} h⁻¹. H₂ was also observed in the catalytic system with a yield of 19 mmol g_{cat}^{-1} (Fig. S10, ESI†). Besides, the ¹H NMR spectrum confirmed that no formic acid was produced (Fig. S11, ESI†), revealing a high selectivity for CO of 85% of the system during the 8 h catalytic process. This highly efficient CO₂ reduction performance of our hybrid system is exceptionally competitive with the state-of-the-art heterogeneous systems for CO₂ reduction (Table S2, ESI†).



Fig. 3 (a) Photochemical CO and H_2 production as a function of time of the Fe–CB + CdS hybrid system. (b) Comparison of CO and H_2 yield of varied photocatalytic systems.

For comparison, Ni–CB catalyst and commercial CB were also tested as the catalysts in the system, and the photocatalytic performance of bare CdS was also evaluated (Fig. 3b and Fig. S12, ESI†). As depicted in Fig. 3b, only 9.5 mmol g_{cat}^{-1} of CO was produced when 1 mg Ni–CB is utilized as the catalyst during the 8 h process, corresponding to a TON of 97 and a production rate of only 1.2 mmol g_{cat}^{-1} h⁻¹. Nevertheless, the H₂ yield reached 20 mmol g_{cat}^{-1} , which led to a low CO selectivity of 32%. Besides, when utilizing 1 mg of CB in the replacement of Fe–CB, the performance was even worse, delivered only 2.0 mmol g_{cat}^{-1} of CO together with 21 mmol g_{cat}^{-1} of H₂, which is slightly better than the performance of bare CdS due to the better charge mobility in the CB.²²

The origination of photochemical produced CO was confirmed by a labelling experiment with ¹³CO₂ in the absence of KHCO₃ (Fig. S13, ESI[†]).¹⁷ Also, no CO was detected when the reaction is conducted under a N₂ atmosphere. Besides, no CO and H₂ were detected under dark conditions or in the absence of CdS, which emphasized the vital function of the CdS photosensitizer. More importantly, no apparent deactivation was observed after three cycles of photocatalysis (Fig. S14, ESI[†]). The excellent stability is ascribed to the inherent structural stability of the Fe–N–C structure and CdS in the presence of TEOA,²² while the high flat-band potential of CdS is protective for the catalyst from deactivation.^{12,16}

To investigate the origin of Fe–CB's superior catalytic performance over Ni–CB, we performed DFT simulations to draw the catalytic pathways (Table S3 and Fig. S15–S17, ESI†). As exhibited in Fig. 4a, the energy diagrams for CO evolution illustrate that the first electron and proton transfer process generating the *COOH species is the rate-determining step for the evolution of CO. Only 0.63 eV of energy barrier is required to reduce CO₂ to *COOH on the Fe–N–C. In comparison, the formation of *COOH on the Ni–N–C requires a high energy barrier of 1.82 eV, which retards the catalytic process. Thus Fe–CB has better activity over Ni–CB. The energy barriers for



Fig. 4 (a) Free energy diagram for the CO₂ reduction to CO at E = 0 V vs. RHE on Fe–N–C and Ni–N–C. (b) Projected crystal orbital Hamilton populations (pCOHP) for Fe–C and Ni–C bonds in the *COOH intermediate structure and corresponding integrated values (IpCOHP). Calculated electron density differences for Fe–N–C (c) and Ni–N–C (d) coordinated with *COOH intermediate. Electron accumulation and depletion are represented by yellow and cyan, respectively.

 H_2 evolution on the catalysts were also calculated to be 0.72 and 1.65 eV for Fe–CB and Ni–CB, respectively. Although Fe–CB is a better catalyst for H_2 evolution than Ni–CB, its low energy barrier for *COOH generation ensures the excellent selectivity for CO evolution even in the presence of CdS, which is also a good photocatalyst for H_2 evolution (Fig. 3b).²²

To gain more specific insight into the influence of two different metals in the catalysis, we performed the crystal orbital Hamilton population (COHP) analysis to confirm the bonding strength of the two structures (Fig. 4b). The integrated projected COHP (IpCOHP) summed between Fe-C and Ni-C bond below the Fermi level in the *COOH structure are -3.09 and -1.84 eV, respectively, indicating more stable coordination of Fe-C than Ni-C. Besides, the deformation charge density calculated based on the Bader charge analysis and the calculated electron density differences revealed that more electrons transfer from the Fe-N-C to *COOH than Ni-N-C (Fig. 4c and d), demonstrating that Fe-N-C could promote the electron accumulation in *COOH and facilitate the CO₂ reduction.¹³ Thus, we conclude that the stronger coordination of *COOH to the Fe atom is the critical factor that enables the Fe-N-C's outstanding catalytic activity. These theoretical results are consistent with the experiments.

In conclusion, we utilized M–N–C catalysts derived from CB and metalloporphyrins to construct heterogeneous hybrid catalytic systems with CdS, delivering highly efficient CO₂ photoreduction. Significantly, the Fe–N–C and CdS hybrid system efficiently catalyzes the CO₂ reduction to CO under visible light irradiation, delivered a high CO yield of 111 mmol g_{cat}^{-1} and a large TON of 1.22×10^3 based on the Fe–N–C catalyst in 8 h with a selectivity of 85% to outperform most of the current photocatalysis systems. The efficient performance of the Fe–N–C catalysts results from the strong coordination between iron and *COOH intermediate that reduces the energy barrier of the rate-determining step. This effective hybrid catalytic system provides a new perspective for CO₂ photoreduction.

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Conflicts of interest

There are no conflicts to declare.

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