Bimetallic phthalocyanine heterostructure used for highly selective electrocatalytic CO₂ reduction

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ABSTRACT Heterogeneous molecular catalysts, such as metal phthalocyanines, are efficient electrocatalysts for CO₂ reduction reaction (CO₂RR). However, the rational design and synthesis of a molecular catalyst-based heterostructure for CO₂RR remains challenging. Herein, we developed a crystal-line bimetallic phthalocyanine heterostructure electrocatalyst (CoPc/FePc HS), which achieved an excellent CO₂-to-CO conversion efficiency (99%) and outstanding long-term stability after 10 h of electrocatalysis. Density functional theory calculations revealed that the enhancement of CO₂RR performance could be attributed to the distinct electron transfer pattern between FePc and CoPc. The heterostructural engineering in molecular catalysts would inspire a unique approach for improving CO₂RR performance.

Keywords: molecular catalyst, phthalocyanine heterostructure, CO₂ reduction, electronic effect

INTRODUCTION

Due to the consumption of fossil fuels after the industrial revolution, the concentration of ambient CO₂ has significantly increased, leading to several concerns such as global warming and abnormal global climate [1–3]. The increasing concern regarding CO₂ content in the atmosphere pushed governments to increase their investment to address the CO₂ issue and encouraged numerous researchers to explore this field using different technologies that enabled the effective, safe, and sustainable utilization of CO₂ [4–6]. Unlike the thermal catalysis operated at high temperatures, the electrochemical reduction is an ideal and attractive approach for creating a carbon-neutral energy cycle, which can transform into the sustainable production and regeneration of carbon-based value-added chemicals and fuels by harvesting intermittent electricity from renewable energy sources [7–10]. However, activating CO₂ is difficult because of the multiple electrons and proton transfer involved in electrocatalysis; therefore, new high-performance electrocatalysts that can enhance sluggish reaction kinetics must be exploited to overcome the massive energy barrier resulting from

the excessive chemical inertness of molecules and the related multielectron transfer methods [11–13].

Although noble-metal catalysts (Au, Ag, etc.) exhibit competitive activity, their depletable resource and high price considerably hinder their general and widespread applications in the energy field [14–16]. Considering their large specific surface area and good electrical conductivity, atomically dispersed transition metals embedded in nitrogen-doped carbon supports are attractive for CO₂ reduction reaction (CO₂RR), but precisely regulating the topography of the catalytic sites is difficult [17–19]. Molecular catalysts, which combine transition-metal elements such as Co, Ru, Fe, Ni, and Cu with organic ligands such as phthalocyanine, polypyridine, porphyrin, and other macrocyclic structures, contain well-defined active sites and uniform and tunable structures, contributing to investigating catalytic mechanisms for the electrochemical reduction of CO₂ [20–24]. Metal phthalocyanines (MPcs) used as dyes have been recently studied to convert CO₂ to CO because of their low cost and stable structure, and they exhibit high catalytic activity [25,26]. The natural M-N₄ molecular structure (one metal center, four coordinated nitrogen atoms) can effectively adjust the binding ability of the metal center to key intermediates and facilitate the rapid transfer of electrons [27–35].

Some studies have reported that the electron-withdrawing or electron-donating group is externally attached to the macrocyclic structure of M-N₄ to change the electron cloud density around the metal center, thereby changing the binding energy of the key intermediate CO and improving the selectivity of the reaction. For example, CoPc with pyridine moieties (CoPc-Pyr) supported on a carbon electrode has been recently synthesized, and the Faradaic efficiency (FE) of CO (FE_{CO}) reached 90% with a partial CO current density of 2.5 mA cm⁻² [36]. Wang *et al.* [37] synthesized CoPc with cyano groups (CoPc-CN) for CO₂-to-CO conversion and achieved an FE of 95%. Because of the difference in electron cloud density around different metal centers, the possible synergistic effect of MPcs with different metal centers is beneficial to changing the electron cloud density around the metal center, which consequently changes the binding energy of CO and improves the selectivity of reaction

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products. However, the synergistic effect between MPcs with different metal centers for CO₂RR remains unclear. In this work, the crystalline cobalt/iron bimetallic phthalocyanine heterostructure (CoPc/FePc HS) was synthesized *via* the solvothermal treatment, in which FePc was distributed in the two ends, and CoPc was concentrated in the middle of the HS.

The obtained CoPc/FePc HS could efficiently enhance the electrocatalytic performance of CO₂RR because of the strong coupling effect between CoPc and FePc. It can also rationally regulate CO₂ reduction selectivity toward CO by adjusting the ratio of CoPc/FePc in the HS. The CoPc/FePc HSs exhibit prominent performance with a high FE of 99.2% and an outstanding CO partial current density of 15.9 mA cm⁻² at the potential of -0.87 V *versus* reversible hydrogen electrode (RHE) in a near-neutral aqueous solution, which can considerably suppress the competitive hydrogen evolution reaction (HER). Density functional theory (DFT) calculations reveal that the formation of intermediate *COOH is the rate-determining step for CO₂-to-CO conversion, and CoPc is regarded as the dominating active center. The enhancement of CO₂RR performance could be attributed to the moderate adsorption of reaction intermediates at the HS between FePc and CoPc induced by the distinct electron transfer.

EXPERIMENTAL SECTION

Materials

CoPc (95%) and FePc (97%) were purchased from TCI. Potassium bicarbonate (KHCO₃), *N,N*-dimethylformamide (DMF, 99.7%), ethanol (C₂H₅OH, 99.5%), and isopropyl alcohol (C₃H₈O, 99.5%) were purchased from Aladdin. Ketjen black carbon and 5 wt% Nafion solution were purchased from the Fuel Cell Store. All chemicals were used without further purification.

Characterization

Scanning electron microscopy (SEM) measurements were performed using an SU8010 microscope. High-resolution transmission electron microscopy (HRTEM), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), and energy dispersive spectroscopy (EDS) elemental mapping were performed using an FEI Talos F200X G2 microscope operated at 200 kV. Powder X-ray diffraction (PXRD) patterns were analyzed using a Rigaku SmartLab 9 KW with Cu K α radiation ($\lambda = 1.542 \text{ \AA}$) operating at 45 kV and 200 mA. X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB-250Xi spectrometer (Thermo Fisher Scientific) using Al K α radiation. Fourier transform infrared (FTIR) spectra were collected using a Bruker Vertex 70 FTIR spectrometer. Thermogravimetric analysis (TGA) was conducted using a Mettler Toledo TGA 2 thermal analysis system. Raman measurements were conducted using DXR2xi (Thermo Fisher Scientific, CN) with 532 nm as the excitation wavelength. The solid-state absorption spectra were collected using a Shimadzu UV-3600 spectrophotometer.

CoPc/FePc HS synthesis

CoPc/FePc HS with different Co/Fe molar ratios (3:1, 1:1, 1:3), CoPc, FePc, were elaborately prepared [38]. First, a 200-mg mixture of CoPc and FePc was dispersed into 70 mL of DMF and sonicated for 60 min to obtain a homogeneous solution. Then, the solution was transferred into a 100-mL Teflon-lined

solvothermal autoclave and heated in an oven at 180°C for 24 h. After cooling down to room temperature, the purple microrod-shaped precipitates in the solution were collected, washed with ethanol thrice, centrifuged, and dried at 60°C for 4 h. Finally, the prepared precipitates were calcined in the furnace at 450°C for 3 h to obtain CoPc/FePc HS. The high-purity Ar (99.999%) was used as the carrier gas with a flow rate of 220 sccm.

Working electrode preparation

CoPc/FePc HS (1 mg) and Ketjen black carbon (1 mg) were dispersed into a mixture of 320 μL isopropyl alcohol, 60 μL deionized water, and 20 μL commercial 5wt% Nafion solution and sonicated for 40 min to yield a homogeneous ink. Subsequently, 100 μL of the ink was uniformly coated on a Sigracet 29 BC GDL (1 cm $\times$ 1 cm) to prepare a composite with a loading density of 0.25 mg cm⁻². The coated carbon paper was dried overnight at ambient temperature and pressure.

Electrochemical measurement

All electrochemical measurements were performed in a three-electrode system with a sealed two-compartment H-type cell separated by a Nafion-117 proton exchange membrane. Each compartment was filled with 40 mL KHCO₃ solution with a concentration of 0.5 mol L⁻¹. A saturated Ag/AgCl and a platinum plate (1.5 $\times$ 1.5 cm²) were used as the reference and counter electrodes, respectively. The testing potential can be converted to the RHE using the formula $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + E_{\text{Ag/AgCl}}^0 + 0.0592 \times \text{pH}$. Electrochemical measurements were performed using a CHI760E workstation. Prior to the measurements, the electrolyte was thoroughly degassed by purging with CO₂ (99.999%) for 30 min with a flow rate of 20 sccm. The catholyte was stirred at a speed of 500 rpm, and its pH was measured to be 7.4. Cyclic voltammetry (CV) was performed 20 times in the potential range of 0.03 to -1.37 V (vs. RHE) at a scan rate of 100 mV s⁻¹ to activate the working electrode and remove adsorbed gases. Linear sweep voltammetry (LSV) was performed in the same potential range with CV at a scan rate of 5 mV s⁻¹. The chronoamperometry (CA) was measured at different fixed potentials to evaluate the CO₂RR performance. Gas products were analyzed using a gas chromatograph (GC7900, Tianmei) equipped with a thermal conductivity detector for H₂/CO analysis and with a flame ionization detector for hydrocarbon analysis. The FE of gas products was calculated using the equation $\text{FE} (\%) = nFV/Q \times 100$, where n is the number of transferred electrons of CO₂RR or HER, F is the Faraday constant (96,485 C mol⁻¹), c is the volume ratio of gas products, V is the total molar flow rate of gas, and Q is the total consumed charge in electrolysis.

Computational details

The geometric optimizations and projected density of states (PDOS) calculations were performed using Vienna *ab-initio* Simulation Package [39]. Projector-augmented wave [40] pseudopotentials with Perdew–Burke–Ernzerhof [41] exchange-correlation functional were used. Standard Monkhorst–Pack grid [42] samplings were employed at 3 $\times$ 3 $\times$ 3 and 7 $\times$ 7 $\times$ 7 for the geometric optimizations and PDOS analyses, respectively. The energy cutoff was set to 500 eV, and the convergence thresholds for the electronic structure and forces were set to 10⁻⁵ eV and 0.02 eV $\text{\AA}^{-1}$, respectively. The Hubbard $U_{\text{eff}} = 3.0$, which was used in previous phthalocyanine metal complex calculations [43], was used to correct the strong Coulombic interactions of d

electrons for Fe and Co. The van der Waals (vdW) corrections were estimated in the DFT-D3BJ form [44].

The free energy diagrams of CO₂RR were estimated using the Nørskov equation,

$$\Delta G = \Delta E + \Delta ZPE - T\Delta S + \Delta G_U + \Delta G_{pH} + \Delta G_{field},$$

where ΔE , ΔZPE , and ΔS are the total energy, zero-point energy, and entropy difference of the products and reactants, respectively; T is the temperature (considered as 298.15 K); ($\Delta E + \Delta ZPE - T\Delta S$) is the Gibbs free energy difference, which can be directly obtained using DFT calculations; ΔG_U is defined as eU where U and e are the electrode potential with respect to standard hydrogen electrode and the charge transferred, respectively; $\Delta G_{pH} = 2.303 k_B T \times \text{pH}$, where k_B is the Boltzmann constant and the pH is 7.4 in the present work; ΔG_{field} is the free energy correction resulting from the electrochemical double layer and is neglected in the present study considering the previous studies [45]. The free energy of CO was not calculated *via* DFT simulation, but was obtained from the known free energy change of the reaction $\text{CO}_2(\text{g}) + \text{H}_2(\text{g}) = \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{l})$ under the standard condition, i.e., 0.22 eV. The CO₂RR involves two electron transfers, with a free energy correction of 0.43 eV in each electronic transfer step. After the correction of ΔG_{pH} , the final $\Delta G = 0.22 + 0.43 \times 2 = 1.08$ eV.

RESULTS AND DISCUSSION

SEM characterization was performed to study the morphology and growth regulation of the prepared CoPc/FePc HS (Fig. 1b and Fig. S1). As the FePc content increased, the tips of the prepared microrods became sharper, and the length of the microrods increased accordingly. This result indicates that the mass ratio of CoPc/FePc considerably affects the HS morphology. The PXRD patterns were applied to analyze the crystallinity of the prepared microrods (Fig. S2). The commercial CoPc and FePc exhibit poor crystallinity, but the prepared CoPc and FePc microrods become highly crystalline. After comparison with the

standard card (JCPDS: 14-0948, JCPDS: 14-0926), CoPc and FePc can be assigned to β -phase CoPc and β -phase FePc, respectively. The as-obtained FePc/CoPc HS also exhibits high crystallinity with strong diffraction peaks at 7.06°, 9.25°, 18.24° and 18.66°, which correspond to the β phase CoPc. TGA measurement indicates that the weight of CoPc/FePc HS changes slightly in the range of 0–600 °C, indicating that the HSs exhibit excellent stability in the subsequent annealing process (Fig. S3). UV-vis absorption spectra (Fig. S4) indicate that the characteristic peaks of CoPc/FePc HS overlap with those of CoPc and FePc, confirming the existence of macrocycle structure in the HS. The characteristic peaks of CoPc/FePc HS at approximately 330 and 674 nm belong to B and Q bands, respectively [46]. When the CoPc/FePc HS is formed, the Q-band exhibits a slight red shift relative to CoPc. FTIR and Raman spectra further confirm that the CoPc/FePc HS shows the characteristic peaks of FePc and CoPc, indicating that the molecular structures of FePc and CoPc remain in the HS (Fig. S5). The Raman spectrum shows the stretching vibration of the macrocycle. A_{1g} symmetry of 592 and 834 cm⁻¹ bands can be ascribed to benzene ring deformation, and B_{1g} at 684 and 1542 cm⁻¹ and B_{2g} at 1498 cm⁻¹ (macrocycle breathing) connect with pyrrole stretch. These regions correspond to heavy atom–nitrogen (M–nitrogen) in-plane stretching and bending vibrations as well as displacements on the C–N–C bridge bond of the phthalocyanine molecule. The peak at 1338 cm⁻¹ belongs to C–N stretching vibration and that at 1537 cm⁻¹ belongs to C=C stretching vibration [47]. The characteristic peaks in the FTIR spectra at 731, 756, 780, and 1088 cm⁻¹ in CoPc/FePc HS indicate the presence of β -phase, which is consistent with the conclusion obtained *via* XRD. The characteristic peak at 911 cm⁻¹ in CoPc/FePc HS belongs to the metal–ligand vibration band, indicating the existence of the M–N₄ macrocycle structure [48–50]. The stable M–N₄ macrocycle structure in CoPc/FePc HS is expected to facilitate rapid electron transfer during catalysis [51–53]. TEM was performed to further

Figure 1 (a) Schematic of CoPc/FePc HS. (b) SEM image of CoPc/FePc HS; the inset displays the TEM image of CoPc/FePc HS. (c–h) HAADF-STEM image and the corresponding overlaid EDS mappings of CoPc/FePc HS.

confirm the morphology and element distribution of CoPc/FePc HS (inset in Fig. 1b). HAADF-STEM image and the corresponding EDS maps indicate that the Co element is mainly enriched at the middle of the microrod, whereas the Fe element is distributed in the ends (Fig. 1c–h). Furthermore, the EDS spectrum shows that the Co/Fe atomic fraction ratio in the microrod is consistent with the CoPc/FePc feedstock ratio (3:1), as shown in Fig. S6. Considering the above characterizations, we speculate that the special structure of heterojunction is related to the nucleation and growth rate of CoPc and FePc during the solvothermal reaction. CoPc preferentially nucleates and crystallizes to form the body of the HS microrod. Then, because of the similar crystal structure of FePc and CoPc, FePc crystallizes along CoPc to form the tips on both sides.

XPS tests were performed to study the surface elemental compositions and electronic structures of CoPc/FePc HS, FePc, and CoPc (Fig. S7) [54]. The N 1s spectrum of CoPc/FePc HS shows only one peak at 399.1 eV, which corresponds to the pyridinic N in the M-N₄ structure of phthalocyanine. The Co 2p spectrum of CoPc/FePc HS exhibits two peaks at 796.3 and 780.6 eV, corresponding to Co 2p_{1/2} and Co 2p_{3/2}. Each peak is divided into two doubles, which can be ascribed to Co²⁺ and Co³⁺, respectively [55–57]. Co²⁺ is derived from the Co site in the CoPc part, and Co³⁺ is possibly derived from the oxidation of Co²⁺ [58,59]. Compared with CoPc, the slight shift of Co 2p in

CoPc/FePc HS to high binding energy confirms the change in the coordination environment of Co sites in CoPc/FePc HS, which reduces the charge in the surface of CoPc. The Fe 2p spectrum of CoPc/FePc HS also shows the valence states of Fe²⁺ and Fe³⁺. The Fe 2p in CoPc/FePc HS shifts to low binding energy, indicating an increased local electron density of the Fe site in CoPc/FePc HS [60–62]. Notably, the inhomogeneous Co/Fe elemental distribution causes an electronic effect between Co and Fe species, which might bring the unexpected electrical property of CoPc/FePc HS.

The catalytic activity of CoPc/FePc HS for electrochemical CO₂ reduction was investigated in a saturated 0.5 mol L⁻¹ KHCO₃ solution using a sealed three-electrode H-type cell. The as-prepared CoPc/FePc HS and Vulcan XC-72R carbon black were ultrasonically mixed with 5 wt% Nafion solution in isopropyl alcohol and deionized water, and the resulting homogeneous paste was coated onto Sigracet 29 BC GDL to prepare the working electrode. The electrodes containing CoPc and FePc were prepared similarly (Fig. S8). In the LSV test, the CoPc/FePc HS (Co/Fe ratio of 3:1) exhibits a steep increase in current density at the potential of -0.32 V vs. RHE, indicating that CO₂ is successfully reduced on CoPc/FePc HS (Fig. 2a). The geometric current density of CoPc/FePc HS reaches up to 37.86 mA cm⁻² at -1.17 V vs. RHE, whereas CoPc and FePc exhibit low current densities of 27.69 and 18.69 mA cm⁻²,

Figure 2 Electrochemical CO₂RR performance of CoPc/FePc HS. (a) LSV curves at 5 mV s⁻¹ of FePc, CoPc, and CoPc/FePc HS. (b) CA measurements of CoPc/FePc HS at different fixed potentials. (c) FE_{CO} and (d) CO partial current of FePc, CoPc, and CoPc/FePc HS at different potentials in 0.5 mol L⁻¹ KHCO₃ solution. (e) FEs of CO and H₂ for CoPc/FePc HS in 0.5 mol L⁻¹ KHCO₃ solution. (f) Tafel plots for CoPc/FePc HS. (g) Stability measurement of CoPc/FePc HS at -0.87 V vs. RHE.

respectively. The CA test was performed to evaluate the time-dependent geometric current density of CoPc/FePc HS at different potentials ranging from -0.47 to -1.17 V vs. RHE (Fig. 2b). Notably, the CoPc/FePc HS shows excellent stability in CO₂RR under the whole potential range. CO and H₂ were the only reduction products determined using GC, and the presence of liquid products in the electrolyte was not detected by NMR. CoPc/FePc HS shows higher FE_{CO} and the CO current density from -0.67 to -1.17 V vs. RHE compared with pure CoPc and FePc (Fig. 2c, d). By contrast, pure FePc and CoPc can only reduce CO₂ into CO with low FEs of 32.63% and 89.19% at -0.87 V vs. RHE, respectively. The CoPc/FePc HS produces CO with a maximum FE of 99.2% at -0.87 V vs. RHE, with the CO current density of 15.9 mA cm^{-2} (Fig. 2e), which is superior to those given in the references listed in Table S1. In addition, we performed electrochemical tests on CoPc/FePc HS with different Co/Fe content ratios of 3:1, 1:1, and 1:3 (Fig. S9). The FEs and current densities of CoPc/FePc HS (Co/Fe of 3:1) are demonstrably superior to those of the samples with Co/Fe ratios of 1:1 and 1:3 in the whole potential range of -0.67 to -1.17 V vs. RHE. We suspect that Co is the active site of CoPc/FePc HS in CO₂RR, and the reduction of Co sites results in a substantial decrease in the catalytic performance of the HS.

We obtained the Tafel slope of CoPc/FePc HS (Fig. 2f) to study the catalytic mechanism. According to the overpotentials of 0.22 – 0.37 V, the CoPc/FePc HS presents a Tafel slope at approximately 107 mV dec^{-1} , indicating that the CO₂RR is kinetically limited and the formation of CO₂ intermediate *via* one-electron transfer from CoPc/FePc HS to CO₂ is the rate-determining step. To better understand the intrinsic catalytic

activity, the electrochemical active surface area of CoPc/FePc HS was estimated *via* the electrochemical double-layer capacitance (C_{dl}), which can be obtained through CV in a non-Faradaic region. The C_{dl} of CoPc/FePc HS was calculated to be 4.03 mF cm^{-2} (Fig. S10). We investigated the long-term stability of CoPc/FePc HS. The FEs and current density show no significant loss at -0.87 V vs. RHE over 10 h (Fig. 2g). The average FE_{CO} reaches up to 99%, and the average current density is 16 mA cm^{-2} . The morphology and structure of CoPc/FePc HS were characterized *via* XRD and SEM to ensure the integrity of HS after the CO₂RR test. The obtained XRD pattern is in accordance with that of a new one (Fig. S11). The SEM image (Fig. S12) shows that the morphology of the CoPc/FePc HS exhibits almost no change, indicating the excellent structural stability of HS.

DFT calculations were performed to reveal the origin of the CO₂RR reactivity of CoPc/FePc HS. The crystal and cluster models for CoPc, FePc, and CoPc/FePc HS are presented in Fig. 3a. Pure FePc and CoPc are semiconductors with band gaps of 0.28 and 0.61 eV, respectively, according to the PDOS analyses in Fig. 3b. The geometric optimizations for the crystal models of FePc and CoPc indicate their antiferromagnetic ground states and that the Fe atoms in FePc are in high spin states (Fig. 3c). Three double-layer cluster models were simulated as the reaction surfaces. The following catalytic pathway (Fig. 4a) was investigated, and the free energy diagrams (Fig. 4b) of CO₂RR were estimated using the Nørskov equation [63,64].

The adsorption of CO₂ is an endothermic process with entropy reductions. The first electron transfer step from CO₂* to COOH* is the rate-determining step, which is consistent with

Figure 3 (a) Crystal and cluster models for FePc, CoPc, and CoPc/FePc HS. (b) Calculated PDOS for FePc and CoPc. (c) Valence 3d electron occupations on Fe and Co in the ground states of FePc and CoPc.

Figure 4 (a) Proposed mechanism for the electroreduction of CO₂ to CO over CoPc/FePc HS. (b) Calculated free energy profiles of FePc, CoPc, and CoPc/FePc HS. (c) Proposed electron transfer pattern for the high CO₂RR activity of CoPc/FePc HS.

the Tafel plot. The required free energy changes (ΔG) for FePc and CoPc are 1.40 and 1.15 eV, respectively, indicating a higher CO₂RR activity of CoPc [65]. The CoPc/FePc HS has Fe and Co atoms as two reaction centers, and the ΔG values are 1.38 and 1.12 eV, which are approximately equal to those of the pure FePc and CoPc. This result indicates that the mutual influence between Co and Fe atoms is very limited in terms of local reactions. Moreover, the adsorption energies of CO₂(CO) on FePc and CoPc are 0.45(0.53) eV and 0.51(0.76) eV, suggesting that CO₂ and CO tend to desorb on CoPc. The enhancement of CO₂RR activity can be explained by the electronic structures of FePc and CoPc and an electron transfer pattern at the HS (Fig. 4c). Electron transfer from CoPc to FePc occurs because CoPc exhibits a higher valence band maximum (VBM) of -0.04 eV, whereas FePc exhibits a lower conduction band minimum (CBM) of 0.17 eV. Thus, a Co³⁺ defect center is generated, and it delivers electrons from electrode to CO₂* and COOH* step by step, forming the Co³⁺/Co²⁺ redox couple. The calculated band structure for CoPc/FePc HS in Fig. S13 indicates that the HS is a semiconductor with a direct band gap of 0.62 eV, which is larger than those of FePc (0.28 eV) and CoPc (0.61 eV). This phenomenon can be explained by charge density population analysis, suggesting that the VBM of the HS is mainly contributed by the d_{z^2} (e_g) orbital of Co in CoPc, and the CBM is mainly contributed by the d_{xz}/d_{yz} (t_{2g}) orbital of Fe in FePc. The electron transfer from t_{2g} of Fe to the e_g orbital of Co can decrease the energy of the e_g band and increase the energy of the t_{2g} band, leading to its larger band gap. The above results indicate that an electron transfer occurs between the CoPc and FePc phases inside the CoPc/FePc HS.

CONCLUSION

The molecular catalyst of CoPc/FePc HS exhibiting active

interface, high crystallinity, and regulated composition was successfully prepared. The obtained CoPc/FePc HS with a Co/Fe molar ratio of 3:1 exhibited 99% CO₂-to-CO conversion efficiency and outstanding stability. DFT calculations revealed that the enhancement of CO₂RR activity could be attributed to the promoted rate-determining step of CO₂* to COOH* induced by the electron transfer at the interface between CoPc and FePc. The HS engineering in molecular catalysts can inspire a unique approach for improving CO₂RR performance.

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Supplementary information Supporting data are available in the online version of the paper.

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双金属酞菁异质结构高选择性电催化CO₂还原

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摘要 自工业革命以来, 化石燃料的大量消耗导致大气中CO₂浓度显著增加, 引发了全球气候变暖等问题。电化学CO₂还原能够利用可再生能源产生的间歇性电力可持续地将CO₂转化为高附加值化学品或燃料, 是实现碳中和的有效途径。目前, 非均相分子催化剂如金属酞菁能够有效催化CO₂还原反应(CO₂RR), 但是分子催化剂异质结构的合理设计与合成仍极具挑战。基于此, 我们发展了一种具有高结晶度的双金属酞菁异质结构(CoPc/FePc HS), 其电催化CO₂还原为CO的法拉第效率高达99%, 并在运行10小时后性能基本保持不变。密度泛函理论计算表明, FePc和CoPc之间不同的电子转移模式能够有效提高CO₂RR性能。构筑分子催化剂异质结构有望成为CO₂RR性能提升的有效策略。