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Boosting Electrochemical CO₂ Reduction on Metal-Organic Frameworks via Ligand Doping

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Abstract: Electrochemical CO₂ reduction relies on the availability of highly efficient and selective catalysts. In this work, we report a general strategy to boost the activity of metal-organic frameworks (MOFs) towards CO₂ reduction via ligand doping. A strong electron-donating molecule of 1,10-phenanthroline was doped into Zn-based MOFs of zeolitic imidazolate framework-8 (ZIF-8) as CO₂ reduction electrocatalyst. Experimental and theoretical evidences reveal that the electron-donating nature of phenanthroline enables the charge transfer effect, which induces the adjacent active sites of sp² C atoms in imidazole ligand possessing more electrons, and facilitates the generation of *COOH, hence leading to improved activity and faradic efficiency towards CO production.

Carbon dioxide conversion using electrochemical approach to obtain high value-added products has been regarded as a promising strategy to recycle and utilize this abundant and inexpensive carbon resource.^[1] However, due to the thermodynamically stable and kinetically inert nature of CO₂, as well as the competing reaction of hydrogen evolution reaction (HER) in aqueous electrolyte, highly efficient and selective electrocatalysts are crucial in this endeavor.^[2] As a typical product of CO₂ reduction, CO is important for synthesizing more complex carbon-based fuels and feedstocks, which holds great significance for the chemical industry.^[3] Low-cost and earth-abundant transition-metal based nanomaterials, such as Co^[4], Ni^[5], Cu^[6], and Zn^[7] etc., have been widely investigated to electrochemically catalyze CO₂ reduction reaction (CO₂RR) to produce CO during the recent years.

Metal-organic based complexes and frameworks, with accurate molecular structures, and well-dispersed metal center, have exhibited promising activity in electrocatalysis.^[8] Among these kinds of metal-organic based catalysts, the metal centers usually act as catalytic active sites. However, it is very interesting that the main electrocatalytic active sites in Zn-based complex or MOFs are usually not the metal center for CO₂RR process, due to the fully occupied 3d orbital of Zn (II), but the ligands coordinating with Zn center.^[9] This bestows new opportunities to optimize the electrocatalytic activity by tuning the ligand itself. From another aspect, it has been proven that an

electron-rich active center could facilitate the CO₂ molecule activation by enhancing electron move from the active sites to the antibonding orbitals of CO₂ and couples with proton followed by generating *COOH (the key intermediate for CO production).^[7c, 10] Thus, increasing the charge density on the catalytic sites would be a promising strategy to enhance CO₂RR activity. To this end, we propose a new strategy to induce more electron density on the ligand sites of ZIFs by a post-treatment process. By virtue of ligand doping process, a new ligand with strong electron-donating ability could act on the MOFs to induce more charge density on the adjacent original ligand sites, subsequently enhancing their electrocatalytic activity towards CO₂RR. Although MOFs-based materials with ligand doping or functionalization have shown feasibility to enhance the performance in photocatalytic CO₂ reduction,^[11] to the best of our knowledge, studies on configuring the charge density of active sites by ligand modification for electrocatalysis are still at an early stage.

Herein, 1,10-phenanthroline molecule with strong electron-donating ability was doped into ZIF-8 to form the CO₂RR electrocatalyst. The electron-donating nature of phenanthroline induces the adjacent active sites in ZIF-8 (sp² C atoms in imidazole ligand) possessing more electrons to facilitate *COOH formation. By the ligand doping, the as-modified ZIF-8 exhibited an obviously improved activity and faradic efficiency for CO (FE_{CO}) compared to the pristine ZIF-8, and high selectivity of 90.57% of FE_{CO} was obtained by mixing the doped ZIFs with a conductive filler. The Gibbs free energy of *COOH formation obtained by density functional theory (DFT) calculation reveals that the sp² C atoms in imidazolate ligand adjacent to the introduced phenanthroline molecules exhibit lower energy barrier to generate *COOH compared to other sites as well as the sp² C atoms in pristine ZIF-8. This result indicates that the sp² C atoms in the doped ZIFs are still the main active sites for CO₂RR, and the weaker barrier for CO₂ activation obtained on ligand doped ZIFs, resulted from the charge transfer effect, are induced by the doped phenanthroline molecules. Overall, the strategy developed here demonstrated a novel route to realize enhanced electrocatalytic activity of MOFs for CO₂RR by charge transfer effect through ligand doping.

The preparation of ligand doped ZIF-8 was illustrated in Figure 1a. To realize the ligand doping, synthesized ZIF-8 was first activated to generate open Zn sites (denoted as ZIF-A)^[12], which facilitated the coordination of Zn with N atoms in phenanthroline to form the ligand doped product (denoted as ZIF-A-LD)^[13]. It should be noted that since Zn²⁺ could facilitate coordinate with N atom in phenanthroline molecule^[13], the new ligand may also be grafted on ZIF-8 directly by a ligand exchange effect without the activation^[14], however, the high energy barrier makes it rather difficult to happen which would be discussed later. To investigate the possible structural change after ligand doping, XRD characterization was first employed on the pristine ZIF-8 and ZIF-A-LD. Figure 1b shows that the patterns of the two samples, as well as that of ZIF-A in Figure S1, reveal the same

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peaks as the simulated ZIF-8. Furthermore, negligible morphological change between the ZIF-A-LD and the pristine ZIF-8 could be observed through the Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images. These results indicate that despite being treated at 250 °C followed by mechanical stirring in methanol at 60 °C, the main structure of ZIFs was well retained. From another aspect, the enhancement of FT-IR peak at 1584 cm^{-1} for ZIF-A-LD in Figure 1c, which can be assigned to the C=N stretch mode^[15], confirms the successful doping of phenanthroline molecule in ZIF-A-LD. UV-vis spectroscopy was also used to demonstrate the presence of phenanthroline in ZIFs. We could see from Figure 1d that the phenanthroline molecule exhibits characteristic adsorption peak at 264 nm. After ligand doping, absorption peak appeared at ~273 nm on the ZIF-A-LD. The presence of such red-shifted adsorption peak, confirms the successful coordination of phenanthroline with Zn, as well as the presence of charge transfer effect ($\pi \rightarrow \pi^*$ charge transfer).^[16]

Figure 1. a) Illustration the preparation of phenanthroline-doped ZIF-8; b) XRD patterns of pristine ZIF-8, ZIF-A-LD, and simulation; c) FT-IR spectra of pristine ZIF-8 and ZIF-A-LD; and d) normalized UV-vis absorption spectra of pristine ZIF-8, ZIF-A-LD, and phenanthroline molecule.

Due to the strong electron-donating ability, charge would transfer to the linked Zn center as well as the adjacent imidazole molecule after ligand doping. To investigate the charge transfer effect, Raman spectroscopy was employed on the pristine ZIF-8 and ZIF-A-LD (Figure 2a). The Raman peaks at around 686 cm^{-1} and 1147 cm^{-1} corresponded to the imidazole ring puckering and the bond stretching between sp^2 C and N atoms in imidazole, respectively.^[17] After doping of phenanthroline, the red-shift of characterized Raman peaks clearly indicates the charge transfer from the introduced electron-donor ligand to the original imidazole.^[18] The electron-donating nature of phenanthroline could also induce the change of charge density on the metal center, which could be deduced from X-ray photoelectron spectroscopic (XPS) measurement in Figure S5. Figure 2b shows the high-resolution N1s peaks in ZIFs before and after ligand doping, both the signals could be deconvoluted into three peaks (Zn-N, N_A , and N_B). The N_A and N_B located at 398.1 and

400.1 eV are related to the unprotonated and protonated N atoms ($=\text{N}-$ and $-\text{NH}-$), respectively, in ligand molecule.^[19] In the imidazolate, N atoms equally split to $=\text{N}-$ and $-\text{NH}-$ types, therefore these two types of N atoms hold the similar area in the N1s spectra of pristine ZIF-8 and ZIF-A (Figure S6). Nevertheless, after ligand doping, the percentage of N_A obviously increased by the addition of the only $=\text{NH}-$ type N atoms in phenanthroline. This result further verifies the successful introduction of foreign ligand in the ZIFs. Element analysis (EA) was used to evaluate the doping level of phenanthroline in ZIF-A-LD. Table S1 shows the mass percentage of carbon and nitrogen atoms in pristine ZIF-8, ZIF-A, and ZIF-A-LD. After ligand doping, the percentage of carbon obviously increased as the newly added molecule owns more carbon atoms than nitrogen atoms. The amount of doped phenanthroline was estimated to be 2.19 wt%.

Electron paramagnetic resonance (EPR) spectroscopy is a powerful tool to characterize the electron structure of metal center in materials.^[20] As shown in Figure 2c, the pristine ZIF-8 is EPR silent because Zn sites are coordinately saturated with ligand and solvent molecule. In contrast, the EPR spectrum of ZIF-A-LD exhibits higher peak of unpaired Zn center at g value of 1.998,^[21] which confirms the present phenanthroline induces charge transferring to the Zn sites. However, ligand doped Zn sites with high coordination number are difficult to act as catalytic sites because of the stereo-hindrance effect for hindering adsorption of reactant and intermediate on the tetrahedral Zn center. It is interesting that without the activation process, the reaction between the pristine ZIF-8 and phenanthroline could also occur to generate ligand-exchanged ZIF-8 (ZIF-LE). But as can be seen in Figure 2c, the weak signal in the EPR spectrum of ZIF-LE implies that the unpaired electron generated on the Zn sites is limited, which means that direct introduction of phenanthroline to the pristine ZIF-8 is quite difficult without the activation. X-ray absorption near-edge spectroscopy (XANES) was also used to further determine the charge transfer effect. As seen in Figure 2d, the Zn K-edges of the pristine ZIF-8 and ZIF-A-LD exhibit similar

Figure 2. a) Raman spectra of pristine ZIF-8 and ZIF-A-LD; b) High-resolution N1s XPS spectra of pristine ZIF-8 and ZIF-A-LD; c) EPR spectra of pristine ZIF-8, ZIF-A-LD, and ZIF-LE; d) XANES spectra at Zn K-edge of pristine ZIF-8 and ZIF-A-LD, with the Zn foil and ZnO for comparison.

profile. After careful comparison of the two samples, we could see in the inserted figure that due to the charge transfer induced by the phenanthroline, the absorption edge of ZIF-A-LD shifted to lower energy, implying lower oxidation state of Zn due to receive charges from the ligand in the doped sample. From the Figure S7, we could see that the Fourier transfer spectra of pristine ZIF-8 and ZIF-A-LD at Zn K-edge show a similar peak at around 1.5 Å which are attributed to the Zn-N₄ structure. The feeble change of peak intensity also confirms the retained coordination number of 4 on Zn center after ligand doping.^[7d, 22] All these results clearly confirm that due to the electron-donating nature of phenanthroline molecule, the charge transfer happened on the ZIF-8.

The electrochemical CO₂RR performance on the modified ZIF-8 electrocatalysts was measured at various potentials by using an H-type two-compartment cell with anion exchange membrane in 0.1 M KHCO₃ solution. Online gas chromatography shows that CO and H₂ were obtained as the main products for all the catalysts, and no liquid product was detected by liquid chromatography. To evaluate the electrocatalytic CO₂RR activity of the as-prepared ZIF-A-LD, linear sweep voltammetry (LSV) curves of ZIF-A-LD electrode in N₂- and CO₂-saturated KHCO₃ electrolyte were first measured. The current density started to increase from ~-0.8 V vs. RHE in the N₂-saturated electrolyte, which is due to the HER (Figure 3a). In contrast, higher current density could be seen in the CO₂-saturated electrolyte by the additional CO₂RR on ZIF-A-LD electrode. It should be noted that one of the drawbacks of MOFs materials is their poor conductivity. Further improvement in current density can be observed when 20 wt% of carbon-black was added to the catalyst ink of ZIF-A-LD (denoted as ZIF-A-LD/CB). To elaborate the role of phenanthroline doping during the CO₂RR, FE_{CO} on ZIF-A-LD was measured to compare with that of the pristine ZIF-8. As seen in Figure 3b, poor CO selectivity of lower than 50% of FE_{CO} was obtained at most of the applied potentials on pristine ZIF-8. By contrast, after ligand doping, a higher FE_{CO} of ~75% was obtained from -1.0 V onwards. After addition of conductive filler, the FE_{CO} of ZIF-8 and ZIF-A-LD were both enhanced, which resulted from the faster electron transfer

pristine ZIF-8, ZIF-A-LD, pristine ZIF-8/CB, and ZIF-A-LD/CB; c) current density for CO production on pristine ZIF-8/CB and ZIF-A-LD/CB; d) stability test of ZIF-A-LD at -1.0V vs. RHE (inset: XRD pattern of ZIF-A-LD after testing).

the electrocatalysis. We could see that the pristine ZIF-8/CB shows similar FE_{CO} to and benchmarks well with the literature report.^[9a] In contrast, the FE_{CO} of ZIF-A-LD electrode reaches to a higher value of 90.57% at -1.1 V. We then studied the electrocatalytic activity of the ZIF-LE. The CO₂RR activity in Figure S8 clear shows that without activation, improvement of FE_{CO} is limited comparing to the ZIF-A-LD. We also investigated the influence of ZIF-A/phenanthroline ratio and obviously decreased CO selectivity was obtained when too much phenanthroline was added (Figure S9). This is probably due to that too much phenanthroline could block the channel and cover up the active sites in ZIF-8 and thus hinder the accessibility between the reactant and the active sites. The partial current density for CO (*j*_{CO}) production on different electrodes was measured as shown in Figure 3c. At all applied potentials, the *j*_{CO} of ZIF-A-LD/CB is higher than the pristine one. Tafel slope of ZIF-A-LD and pristine ZIF-8 are found to be 198, and 276 mV dec⁻¹, respectively, which implies improved kinetics for CO₂RR after ligand doping (Figure S10). Excellent long-term stability is an important specification for an electrocatalyst.^[23] Thus, we performed continuous electrolysis of CO₂ at -1.0 V for 10h on the ZIF-A-LD electrode. As shown in Figure 3d, negligible change of current density and FE_{CO} could be observed here, and the structure of ZIF-A-LD after the stability test investigated by XRD (Figure 3d inset) and SEM image in Figure S11 also indicate that the main structure of ZIFs is retained. We also carried out the same test at higher potential of -1.2 V, stable current density could be obtained during the potentiostatic tests (Figure S12). ¹³C₂ isotopic experiment clearly verifies the obtained CO comes from the reduction of CO₂, instead of ligand decomposition (Figure S13).

To theoretically elaborate the occurrence of charge transfer effect by ligand doping, DFT calculation was used to evaluate the charge density on the unite of ZIF-8 and ZIF-A-LD. It can be seen from Figure S14 that comparing to the pristine ZIF-8 (upper), after phenanthroline doping (below), the charge density on this unit of ZIFs changed. As the main catalytic active sites of ZIF-8^[9a], the charge density on the sp² C atom in imidazole increased from 3.702 to 4.884 e⁻, validating the charge transfer effect by phenanthroline. To further investigate the reaction mechanism, Gibbs free energy for each step of CO₂RR at 0 V vs. RHE on the pristine ZIF-8 and ZIF-A-LD was calculated. For the pristine ZIF-8, the Gibbs free energy requirements on different sites of ZIF-8 were illustrated in Figure S15 and S16. It is found that the sp² C atoms (marked with rectangles in Figure 4) in imidazolate ligand would act as the optimal catalytic active sites due to the lowest barrier for *COOH formation. After ligand doping, the most stable structure is that the Zn sites would coordinately bond with two N atoms from one phenanthroline molecule and two N atoms from two imidazole molecule. Thus, we also carried out DFT calculation on the different sites of ZIF-A-LD to determine the optimal catalytic active sites for CO₂RR. The model of ZIF-A-LD is exhibited in Figure S17, and the

Figure 3. a) LSV curves of ZIF-A-LD in N₂- and CO₂-saturated 0.1 M KHCO₃ solution, with the comparison of ZIF-A-LD/CB; b) FE_{CO} at various potentials on

calculated Gibbs free energies in Figure S18 reveal that the optimal active site on the ZIF-A-LD is the sp^2 C atoms in imidazolate ligand adjacent to the introduced phenanthroline which shows the lowest energy barrier to form the *COOH . Comparing the calculated results before and after ligand doping, the Gibbs free energy of *COOH formation decreases from 1.206 eV (pristine ZIF-8) to 0.686 eV. Due to the charge transfer effect induced by the phenanthroline doping, it exhibited a decreased barrier for the *COOH formation, which would further result in a higher CO production.

Figure 4. Free energy diagrams for electrochemical reduction of CO_2 to CO on the sp^2 C atom sites in imidazole ligand of pristine ZIF-8 (upper) and ZIF-A-LD (below), respectively.

To further confirm the feasibility of our strategy to enhance the CO selectivity for CO_2RR by ligand doping, another Zn-based ZIFs (ZIF-7) was also employed here to be doped with phenanthroline molecule using the same strategy. Successful ligand doping is realized from the enhancement of C=N stretch mode in FT-IR (Figure S21). The SEM images and XRD patterns of pristine ZIF-7 and phenanthroline doped ZIF-7 (denoted as ZIF-7-A-LD) reveals the well-kept structure after activation and ligand doping (Figure S22 and 23). As can be seen in Figure S24, enhanced CO_2RR activity could also be obtained on ZIF-7-A-LD, although the overall activity of ZIF-7 is poorer than that of ZIF-8.

In summary, a ligand doping strategy was realized to enhance the CO_2RR activity of MOFs in this work. Combining the experimental and DFT results, it could be concluded that the sp^2 C atoms in imidazolate ligand are still the main catalytic sites after the ligand doping. Due to the electron-donating nature of ligand dopant, charge would transfer from the introduced phenanthroline molecule to the adjacent sp^2 C atom sites in imidazolate which enables stronger electron to move from the active sites to the antibonding orbitals of CO_2 to facilitate *COOH formation and boost its CO_2RR activity.

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COMMUNICATION

An electron-donating molecule of 1,10-phenanthroline was doped into ZIF-8 to form a CO₂ reduction electrocatalyst. The introduced molecule enables the occurrence of charge transfer, which induces the adjacent active sites of sp² C atoms in imidazole ligand possessing more electrons, and thus facilitates the generation of *COOH, hence leading to improved activity and faradic efficiency towards CO production.

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