Electronic regulation & improved conductivity of molecular catalysts as electrocatalysts†

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Molecular catalysts with well-designed structures and abundant metal–nitrogen active sites have received a lot of attention for effective electroreduction of carbon dioxide (ERCD) due to the advantages of having clearly defined active sites for mechanism investigations. However, this metal–nitrogen combination with a fixed electronic structure severely restricts the catalytic efficiency and selectivity, resulting in low production efficiency of more valuable compounds. This work presents the synthesis of metal macrocyclic compounds MPc (M = Fe, Co, Ni, and Zn) through in situ anodic oxidation of N-doped Ti3C2T x (N-MXene) nanosheets with anchored MPc nanoparticles (named MPc/o-N-MXene). The resulting catalysts exhibit high activity and more tolerable selectivity for ERCD on CoPc; CoPc/o-N-MXene shows a faradaic efficiency (FE) for methanol as high as 39.0% with a current density of 32.7 mA cm−2 at −1.0 V (vs. RHE). The oxidation process creates a significant contact between the M–N4 active sites and N-MXene, which regulates the selectivity of ERCD. DFT calculations suggest that only the electronic regulation of Co–N4 by N-doped MXene supports the creation of intermediate 1HCO in the generation of methanol in ERCD. Our study presents a new route for the synthesis of efficient catalysts and provides a comprehensive perspective on the mechanism of ERCD on MPc.

Introduction

The electrochemical reduction of CO2 (ERCD) to produce valuable fuels and chemicals is a promising strategy for mitigating greenhouse gas emissions, addressing energy shortages, and combating global famine.1–6 However, the most challenging aspect of this reduction process is the significant amount of energy required to break the C=O bond in CO2 molecules.7–11 Consequently, the first step in ERCD, which is the activation of CO2, has slow kinetics and requires a considerable amount of overpotential to break the C=O bond, thereby significantly reducing ERCD’s production efficiency. The need for highly active electrocatalysts is crucial to accelerate the kinetic process and reduce the ERCD overpotential. Recently, much research in recent years has been focused on metal–nitrogen-doped carbon (M–Nx–C) materials with high activity to investigate the underlying catalysis mechanism due to their clear and conducive structures (M–Nx–C).12–15 Molecular electrocatalysts with well-defined M–Nx active sites, such as FePc, CoPc, and NiPc, are the primary models for electrocatalysts in studying the structure and activity relationship (SAR). It is widely reported that tuning the electronic structure of the metal in the core of molecular electrocatalysts by altering the structure of the ligand can achieve excellent selectivity for ERCD products.16–20

However, in the case of most molecular electrocatalysts, ERCD occurs exclusively through a 2-electron transfer pathway resulting in the formation of CO or formate.19 Efficiently promoting the multi-electron (>2e−) reaction of molecular electrocatalysts and regulating the selectivity in the ERCD process have rarely been studied directly, which are crucial for producing valuable liquid fuels, such as methanol. Poor conductivity and difficulties in the electronic regulation of molecular electrocatalysts are major public problems and the main cause of low efficiency for ERCD. Our research aims to find a solution for this challenging problem of conductivity and electronic regulation. This study investigated the use of Ti3C2 (MXene), which has good conductivity due to its two-dimensional laminar structure. Besides, we propose an atomic doping method for MXene for the electronic regulation of molecular electrocatalysts.
Results and discussion

MPc supported by N-MXene (M = Fe, Co, Ni, and Zn)

To obtain MPc/N-MXene materials with a high density of M–N4 sites, two-dimensional layered compounds of MXene (Ti3C2) doped with N were prepared first of all (Fig. 1a). The existence of C–N bonds is further supported by the fitting of the X-ray photoelectron spectroscopy (XPS) N 1s spectrum (Fig. S1†), which shows a peak at ~400.0 eV, assigned to the N–C interaction,21–23 indicating the successful doping of N in MXene with a concentration of 5.55 wt% (Table S1†). X-ray diffraction was performed, and as shown in Fig. 1b, CoPc/MXene and CoPc/N-MXene were successfully synthesized. The peak intensity was normalized and the peak displacement in the XRD patterns was attributed to N-doping.24,25 Furthermore, all CoPc molecules have uniform dispersion on N-MXene, as confirmed in the HAADF-TEM and EDS images of CoPc/N-MXene (Fig. 1c–g). Similarly, FePc/MXene and FePc/N-MXene, as shown in Fig. S2† NiPc/MXene and NiPc/N-MXene, as shown in Fig. S3† and ZnPc/MXene, as shown in Fig. S4† were successfully synthesized. The peak intensity and displacement in the XRD patterns were attributed to N-doping, too.

Electrochemical performance

The Ti–Tx (–OH, –O, and –F) layer in N-MXene is wrapped outside, preventing the contact between the M in MPc and the N in N-MXene when MPc is directly loaded onto N-MXene; we carried out in situ oxidation on the basis of composite materials to break the shielding of surface atoms, obtaining MPc/o-N-MXene. The oxidation process is shown in the Experimental methods (ESI†). These catalysts were used for ERCD; the current density and faradaic efficiency (FE) of the materials obtained were measured in an H-type cell in CO2-saturated 0.5 M KHCO3 aqueous solution (pH = 7.20). Fig. 2 shows the FE of FePc/MXene (b), FePc/o-N-MXene (c), CoPc/MXene (d), CoPc/o-N-MXene (e), NiPc/MXene (f), NiPc/o-N-MXene (g), ZnPc/MXene (h) and ZnPc/o-N-MXene (i) at different potentials from −0.7 to −1.1 V (vs. RHE) at an interval of 0.1 V for 30 min, and the current density is shown in Fig. 2a. GC (gas chromatography) and NMR were used to analyze the gas and liquid products, respectively. The current density of MPc/o-N-MXene decreased compared with MPc/MXene because of in situ oxidation which partially oxidized MXene, making MXene less conductive, resulting in a lower current density for compound catalysts MPc/MXene. Fig. 2a shows the overlapping lines for MPc/o-N-MXene but not for MPc/MXene, which is due to the difference in the current density of MPc/MXene being larger than that of MPc/o-N-MXene. MXene improves the conductivity of the composite catalysts, which in turn amplifies the current difference of MPc for ERCD; however, the amplification effect of the composite catalysts after in situ oxidation is weakened, so the difference of MPc/o-N-MXene decreases. Notably, methanol is generated in the liquid product of CoPc/o-N-MXene (Fig. S5 and S6†) besides CO in the gas product, and the partial current density versus potential for methanol is shown in Fig. S7†. In contrast, no methanol is generated in the liquid products of the other catalysts, which verifies that methanol can only be produced by ERCD with CoPc/o-N-MXene.
On the one hand, for FePc/o-N-MXene, it produces HCOOH and CO in ERCD, and for NiPc/o-N-MXene and ZnPc/o-N-MXene, they can only produce CO in ERCD; on the other hand, for all four MPc/MXene, they can only produce HCOOH or CO. Therefore, methanol could be produced only that the molecular catalyst is CoPc and the basement is N-doped MXene with \textit{in situ} oxidation occur at the same time. For CoPC/o-N-MXene, as the applied potential increases, the partial current density for methanol increases, while the FE for methanol increases first and then decreases. It was due to that the intense water electrolysis reaction (HER) occurs at high potential; the HER is a competitive reaction to ERCD. The highest current density of 18.14 mA cm$^{-2}$ for methanol is achieved at $-1.1 \text{ V}$, and the best FE for methanol is achieved at 39.5\% at $-1.0 \text{ V}$. Furthermore, we repeated this experiment under the same conditions, but the electrolyte was N$_2$-saturated 0.5 M KHCO$_3$ (not CO$_2$-saturated 0.5 M KHCO$_3$) aqueous solution, and the results reveal that there is no methanol signal in the NMR curve (Fig. S8†), which illustrates that methanol does come from ERCD instead of the electrochemical reduction of the electrode itself or KHCO$_3$. Therefore, N-doping provides the active sites, which are further exposed by \textit{in situ} oxidation, and then CoPc/o-N-MXene can produce high value-added methanol by ERCD.

In addition, the long-term stability of CoPc/o-N-MXene was measured to assess its practical applications. No obvious change is observed in the FE for methanol and CO, and the current density (Fig. S9†) remains steady in the $i$–$t$ curve. These results demonstrate that the obtained CoPc/o-N-MXene possesses excellent stability for ERCD.

**Catalysis mechanism for the ERCD of MPc/o-N-MXene**

**XPS characterization.** Based on the ERCD results that show the indispensability of N-MXene and \textit{in situ} oxidation for producing methanol, we propose that the change of the structure of oxidized N-MXene allows MPc to connect directly with the N in the C layer of N-MXene realizing the electronic regulation for MPc, which is crucial for the selectivity of ERCD. We performed XPS measurements (Fig. 3). The corresponding fine-scan Fe 2p spectrum of FePc/o-N-MXene is shown in Fig. 3a, CoPc/o-N-MXene is shown in Fig. 3b, NiPc/o-N-MXene is shown in Fig. 3c and ZnPc/o-N-MXene is shown in Fig. 3d. The C 1s spectra of MPc/o-N-MXene are shown in Fig. S10–S13.† For Fe 2p (Fig. 3a), it can be deconvoluted into five component peaks. In addition, the signals from Fe–N (707.7 eV, 722.2 eV) and Fe–O (710.6 eV, 725.2 eV) are consistent with those from FePc,-26–28 while there is also a signal from the connection of FePc and N-MXene (Fe–N–M sites in MPc and N-MXene structural moiety in the MPc/o-N-MXene) between the M sites in MPc and N-MXene structural moiety in the MPc/o-N-MXene. Following the characterization above, which proves the existence of M–N–MXene bonds, density functional theory (DFT) was carried out to further explore the SAR of ERCD to methanol.

**Theoretical insights into the electronic regulation of M–N–MXene.** Following the characterization above, which proves the existence of M–N–MXene bonds, density functional theory (DFT) was carried out to further explore the SAR of ERCD to methanol.

The adosorption models of CO$_2$ adsorbed on MPc/o-N-MXene (M = Fe, Co, Ni, and Zn) are shown in Fig. S14.† We propose that N doping can reduce the energy barrier of *CO combining with H* to form *HCO on CoPc/o-N-MXene, which is an indispensable intermediate to produce methanol. Accordingly, *CO and *HCO are fundamental intermediates for ERCD to methanol. Hence, we obtained the PDOS (Fig. 4b–e) and Gibbs free energy for the pathways of ERCD from CO$_2$ to CO and to methanol (Fig. 4f) on FePc/o-N-MXene, CoPc/o-N-MXene, NiPc/o-N-MXene and ZnPc/o-N-MXene by DFT calculations, respectively.

![Fig. 3](image-url)
The Gibbs free energy change of the chemical reaction can be calculated through the following expression:\textsuperscript{42,43}

$$
\Delta G = \Delta E_{\text{ads}} + \Delta ZPE - T \Delta S + \Delta U
$$

(1)

where $\Delta E_{\text{ads}}$ is the adsorption energy change of the chemical reaction and $\Delta ZPE$, $\Delta S$ and $\Delta U$ are the contributions to the free energy from the zero-point vibration energy, entropy, and applied voltage, respectively.

Many literature studies reported that the *CO intermediate can be desorbed to produce CO or combined with $H^+$ to form *HCO, which plays a decisive role in the production of methanol from ERCD.\textsuperscript{44–48} Since the *HCO formation process is the key step for ERCD to methanol, we have focused on it and discussed the selectivity of ERCD. From the PDOS of MPc/o-N-MXene and Co (Fig. 4b–e), we can see that there are no electronic gains and losses before or after CO adsorption on the MPc/o-N-MXene catalyst, the same for HCO; except for CoPc/o-N-MXene, on which there is an electron transfer after HCO adsorption. This suggests that there is a strong interaction between the HCO intermediates and the CoPc/o-N-MXene catalyst, while the other catalysts do not exhibit such an interaction. Thus, *CO can desorb into gaseous CO as a result of losing connection with MPc/o-N-MXene, and form *HCO; due to the strong adsorption effect of HCO on the CoPc/o-N-MXene catalyst, the latter opens up the possibility of methanol formation. And the Bader charge from SUSTech Core Research Facilities.

Conclusions

Effective MPc/o-N-MXene electrocatalysts for ERCD have been successfully synthesized by hybridizing the molecular catalyst MPc on N-MXene with \textit{in situ} oxidation. One of these catalysts, CoPc/o-N-MXene, exhibits high activity and good selectivity to methanol. The electrochemical results reveal that the FE of the optimized CoPc/o-N-MXene for methanol is as high as 39.0\% with a current density of 32.7 mA cm$^{-2}$ at $-1.0$ V (vs. RHE), outperforming state-of-the-art electrocatalysts. By combining the experimental and theoretical results and comparing them with other MPc compounds, we found that CoPc and N doping with \textit{in situ} oxidation play important roles in the methanol selectivity of ERCD. Our work provides a systematic investigation of the selectivity of macrocyclic compounds in ERCD and offers insight into the mechanism behind the conversion of ERCD to methanol.

Data availability

The data supporting this article have been included as part of the ESI\textsuperscript{†}.

Conflicts of interest

There are no conflicts of interest to declare.

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