Cobalt phthalocyanine (CoPc) has drawn increasing attention in CO₂ electroreduction to CO due to its clear coordination structure (Co–N₄–C) and high selectivity. However, its performance is severely restrained by its poor stability and low conductivity. Herein, a promising catalyst for dispersing CoPc on three-dimensional porous carbon (PC) was prepared via a pyrolysis procedure using NaCl as the template. Benefiting from the high intrinsic activity and large exposure of active sites, as well as the unique carbon architecture with facilitated mass transportation, the derived CoPc/PC catalyst shows impressive performance for CO₂ electroreduction. The CO faradaic efficiency achieves a maximum value of 95% accompanied by a CO partial current density of 20.5 mA cm⁻². The study paves a new avenue for the fabrication of high-efficiency molecular catalysts for CO₂ conversion.

1. Introduction

Excessive emissions of CO₂ have caused serious environmental problems, such as glacier melting and global warming. In the context of the double carbon target, searching for effective technologies for CO₂ conversion to high value-added chemicals (e.g., CO, HCOOH, C₂H₄) is desperately needed. Recently, the electrochemical CO₂ reduction reaction (CO₂RR) has received widespread attention due to its mild conditions, controllable process, and utilization of renewable electricity energy. In view of the high chemical stability of CO₂ and the competitive hydrogen evolution reaction (HER), the exploration of active, selective and stable electrocatalysts is the key to promote the CO₂RR. At present, a series of catalytic materials have been reported in the CO₂RR, including metals, metal oxides, metal sulfides, and metal complexes. Among them, transition metal phthalocyanines show great potential in catalyzing the CO₂RR because of its adjustable macrocyclic conjugated structure and clear M–N₄ active sites. In particular, cobalt phthalocyanine (CoPc) has been widely studied for its high selectivity toward CO₂-to-CO conversion. However, the intrinsic low conductivity and easy aggregation of CoPc molecules impose great limitations on electrocatalytic activity, selectivity and stability. Integrating CoPc into highly conductive carbon supports (e.g., carbon nanotubes and N-doped carbon) through π–π interactions is a feasible strategy to improve the catalytic activity. However, most carbon supports mainly contain micropores (<2 nm) and mesopores (2–50 nm). In view of the average free path of CO₂ molecules being 84 nm, the diffusion efficiency and local concentration of CO₂ in the catalytic layer would be reduced, resulting in a decreased catalytic performance. Therefore, to boost the dispersion of CoPc and the mass transportation during the CO₂RR simultaneously, rational structural design of the carbon substrate is highly desirable for more efficient catalysis.

Herein, a three-dimensional (3D) porous carbon (PC) material is constructed via pyrolysis using glucose as the carbon source and NaCl as the template, and then employed as the support for CoPc immobilization. Due to the unique 3D carbon structure with abundant macropores and high CoPc dispersion, the derived CoPc/PC electrocatalyst demonstrated enhanced performance for the CO₂RR. The CO faradaic efficiency (FE_CO) is as large as 95% accompanied by a CO partial current density (j_CO) of 20.5 mA cm⁻² at −0.78 V vs. RHE. These results can provide a feasible research idea for improving the performance of metal complexes.

2. Experimental

All the chemicals used in the experiment were analytically pure. Glucose (AR) was acquired from Shanghai Lianmai Biological Engineering Co., Ltd. Sodium chloride (NaCl, 99.5%) was...
acquired from Shanghai Haohong Biopharmaceutical Technology Co., Ltd. Ethanol (C$_2$H$_5$OH, 99.7%) was bought from Tianjin Damao Chemical Reagent Factory. Cobalt phthalocyanine (CoPc, 90.0%) and N,N-dimethylformamide (DMF, 99.5%) were obtained from Shanghai McLean Biochemical Technology Co., Ltd. Acetic acid (CH$_3$COOH, 99.5%) was obtained from Jinan Ryder Chemical Co., Ltd. Nafion solution (5 wt%) was provided by Sigma-Aldrich Chemical Reagent Co., Ltd. All gases employed in the experiment, such as Ar, N$_2$ and CO$_2$, with a purity of 99.999%, were provided by Henan Yuanzheng Technology Development Co., Ltd.

2.1 Materials preparation

2.1.1 Preparation of the PC support. Typically, 3000 mg NaCl and 300 mg glucose were mixed in 20 mL 2 wt% acetic acid and stirred for 12 h to obtain a uniform mixture. After freeze drying completely, the collected white powder was then placed in a tube furnace and heated at 800 °C for 2 h at a ramping rate of 5 °C min$^{-1}$ in a N$_2$ atmosphere. Finally, the resulting black powder was washed thoroughly to remove the NaCl template and vacuum-dried to achieve the target PC-800. PC-700 and PC-900 heated at 700 °C and 900 °C, respectively, were also acquired using similar preparation procedures to PC-800. For the sake of comparison, the carbon support (C) in the absence of the NaCl template was also prepared.

2.1.2 Preparation of the CoPc/PC catalyst. 6 mg CoPc and 30 mg PC-800 were dispersed in a 15 mL ethanol and 15 mL DMF mixture by ultrasonication for 1 h. After drying and treatment in N$_2$ at 200 °C for 1 h, the target CoPc/PC-800 was obtained. At the same time, CoPc/C, CoPc/PC-700 and CoPc/PC-900 were also prepared by using C, PC-700 and PC-900 as the support, respectively.

2.2 Materials characterization

The structures of the materials were determined by X-ray diffraction (XRD) using a Rigaku D/Max-2500V X-ray diffractometer. Field-emission scanning electron microscopy (FE-SEM, JSM-7001F) and transmission electron microscopy (TEM, JEM-2100) were conducted to analyze the material morphology. Raman spectroscopy (Renishaw, inVia) was used to determine the defect degree of the catalyst. The pore structure and size of the materials were measured by N$_2$ adsorption/desorption analysis (Micromeritics, ASAP2010) using Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods. In order to evaluate the thermal stability of the materials, thermogravimetric analysis (TG) was conducted under air conditions.

![Fig. 1](https://example.com/fig1.png)

(a) The preparation scheme of CoPc/PC-x. The (b) FE-SEM, (c) and (d) TEM and (e)–(g) EDS elemental mapping images of CoPc/Pc-800.
2.3 Electrochemical measurements

The CO$_2$ RR performance of the catalysts was tested using an electrochemical workstation (CHI 760E) and a three-electrode system in an H-type electrolytic cell separated with a cation exchange membrane (Nafion-117). The electrolyte was a 0.5 M KHCO$_3$ solution saturated with CO$_2$ and the pH value was about 7.2. Ag/AgCl (saturated KCl) and a platinum sheet were employed as the reference electrode and counter electrode, respectively. The working electrode was sample-coated carbon fiber paper. To prepare the catalyst ink, 5 mg of catalyst powder was first homogeneously introduced in the mixed solution containing 25 µL 5 wt% Nafion and 475 µL ethanol under ultrasonication. Then, 100 µL catalyst ink was dripped on the surface of the carbon fiber paper to obtain a catalyst loading of 1 mg cm$^{-2}$. The applied potentials were transformed into reversible hydrogen electrode (RHE) potentials according to eqn (1). The performance of the catalyst was tested by controlled-potential electrolysis with CO$_2$ introduction into the electrolyte uninterruptedly at a rate of 20 mL min$^{-1}$. The gas products were detected by online gas chromatography (Panna A91Plus). The Faraday efficiency of the product was calculated using eqn (2):

$$E = E_{\text{vs. Ag/AgCl}} + 0.197 + 0.059 \times \text{pH}$$

$$\text{FE}_{\text{CO}} = \frac{n \times z \times F}{Q} \times 100\%$$

where $n$ represents the transfer number of electrons for a specific product (CO and H$_2$), $z$ is the amount of generated gas, $F$ is the faradaic constant (96 485 C mol$^{-1}$), and $Q$ is the total charge consumed in a given analysis time.

3. Results and discussion

Fig. 1a shows the detailed preparation procedures of the CoPc/PC-x catalyst. Specifically, the PC support was first prepared via the pyrolysis method using NaCl as the template and glucose as...
the carbon source. Then, the target CoPc/PC-x catalyst was achieved by coupling CoPc on the PC surface via π–π interactions. The FE-SEM image (Fig. 1b) of the prepared CoPc/PC-800 showed a uniform interconnected nanosheet-like structure containing massive macropores. No obvious aggregated CoPc can be observed, suggesting its high dispersion across the whole carbon skeleton. The TEM image (Fig. 1c and d) further proved the three-dimensional porous structure of CoPc/PC-800. This porous structure not only facilitated the exposure and utilization of active sites, but also promoted the mass transportation during the electrocatalytic process. The corresponding energy dispersive spectroscopy (EDS) elemental mapping images (Fig. 1e–g) indicated that the Co, C and N elements were homogeneously distributed on the catalyst. The N map overlapped well with the C map, which implied the uniform doping of N elements to the carbon skeleton. These results collectively confirmed the immobilization of highly dispersed CoPc and the formation of abundant macropores on the carbon framework.

The XRD patterns (Fig. 2a and b) of all samples exhibited similar broad peaks at 22°, attributed to the (002) planes of carbon. The absence of diffraction peaks for CoPc confirmed its high dispersion on the PC support, which was consistent with the TEM results. TG analysis under air conditions in Fig. 2c indicated the high thermal stability of CoPc/PC-800, presenting a large oxidation temperature of ~500 °C. The noted weight residual above 500 °C was ascribed to CoO formed by CoPc oxidation. The Raman spectra (Fig. 2d) of CoPc/C-800 and CoPc/PC-x (x = 700 °C, 800 °C and 900 °C) showed two characteristic peaks of D (1336 cm⁻¹) and G (1590 cm⁻¹) bands of carbon with an intensity ratio (I_D/I_G) of around 1. The structural characteristics of CoPc/C-800 and CoPc/PC-x catalysts were analyzed using N₂ adsorption and desorption isotherms. As shown in Fig. 2e, all catalysts presented typical type II isotherms with type-H3 hysteresis loops, reflecting the existence of mesopores in the catalysts. Besides, a steep N₂ uptake at high relative pressures was also observed, indicating that macropores also formed in these catalysts. The

**Fig. 3** The (a) LSV curves, (b) FE and (c) J_{CO} of CoPc/PC-800 and CoPc/C-800 in CO₂-saturated electrolyte. The (d) LSV curves, (e) FE, (f) J_{CO}, (g) Tafel plots, (h) TOF and (i) EIS plots of CoPc/PC-700, CoPc/PC-800 and CoPc/PC-900.
specific surface area of CoPc/PC-800 was 339.7 m² g⁻¹, which were significantly larger than 90.8 m² g⁻¹ for CoPc/PC-700, 74.1 m² g⁻¹ for CoPc/PC-900 and 6.6 m² g⁻¹ for CoPc/C-800. The related pore size distributions (Fig. 2f) showed the more pronounced mesoporous and macroporous structures of CoPc/PC-800 compared with the other catalysts. The large specific surface area and the unique porous structure of CoPc/PC-800 would be advantageous to the utilization of active sites and the mass transportation during the CO₂RR. XPS spectroscopy was also conducted to analyze the chemical status and element compositions of CoPc/C-800 and CoPc/PC-x. Full-scale XPS spectra (Fig. 2g) demonstrated the co-existence of C, N, O and Co elements in these samples. Deconvolution of the Co 2p XPS spectra (Fig. 2h) presented only peaks for Co²⁺ at 781.1 and 796.5 eV, together with two shakeup satellite peaks. Deconvolution of the N 1s XPS spectra (Fig. 2i) depicted two peaks of pyridinic N and Co–N, corresponding to the monomeric CoPc molecule.

The electrocatalytic performance of the prepared catalysts was investigated in an H-type gas-tight cell containing CO₂-saturated 0.5 M KHCO₃ electrolyte. Only CO and H₂ products were detected, with a total faradaic efficiency of nearly 100% at each potential. Fig. 3a shows the LSV curves of CoPc/PC-800 and CoPc/C-800. As observed, CoPc/PC-800 exhibited a significantly higher current density than CoPc/C-800 at each applied potential, which demonstrated the absolute predominance of using PC as the support for the CO₂RR. In addition, an obvious reduction peak corresponding to CoPc reduction was noted from the LSV curve of CoPc/C-800, further indicating the catalytic instability of CoPc in the sample. The FE₇₇₇ and j₇₇₇ calculated from controlled potentiostatic electrolysis are presented in Fig. 3b and c. As expected, CoPc/PC-800 showed good activity and selectivity with an FE₇₇₇ as large as 95% at −0.78 V vs. RHE, accompanied by a much larger j₇₇₇ of 20.5 mA cm⁻², while for CoPc/C-800, the corresponding values of FE₇₇₇ and j₇₇₇ were only 92% and 12 mA cm⁻². We then investigated the influence of the pyrolysis temperature of the PC support on the CO₂RR performance. The LSV curves (Fig. 3d) indicated that CoPc/PC-800 presented a much larger current density (−100 mA cm⁻² at −0.97 V vs. RHE) and a much smaller onset potential (−0.38 V vs. RHE) than CoPc/PC-700 and CoPc/PC-900 catalysts, demonstrating its superior catalytic ability for the CO₂RR to CO. Fig. 3e and f shows the similar high FE₇₇₇ for all CoPc/PC-x catalysts and the significantly larger j₇₇₇.
over CoPc/C-800. Correspondingly, FE_{CO} for all catalysts showed quite the opposite tendency. The differences in the CO_{2}RR performance of CoPc/PC-x indicated that the promising pyrolysis temperature of the PC support was 800 °C. The Tafel slopes (Fig. 3g) for all CoPc/PC-x catalysts were very similar to previous reported values on metal porphyrins and phthalocyanines,\(^\text{32-34}\) presenting values much closer to 110 mV dec\(^{-1}\). The results indicated that the CO_{2}RR process over CoPc/PC-x was limited by initial electron-proton transfer to generate a *COOH intermediate.\(^\text{35}\)

The turnover frequency (TOF) for CO was further calculated to evaluate the intrinsic catalytic activity of the catalysts (Fig. 3h). It is noted that CoPc/PC-800 showed a large TOF value of 1417 h\(^{-1}\) at −0.88 V vs. RHE, well exceeding those of CoPc/PC-700 (1064 h\(^{-1}\)) and CoPc/PC-900 (1216 h\(^{-1}\)), which indicated the higher intrinsic activity of CoPc/PC-800. The result was well consistent with the electrochemical activity test results. In addition, the EIS analyses (Fig. 3i) of the catalysts demonstrated a much decreased charge-transfer resistance with the increase of pyrolysis temperature. Furthermore, the electrochemically active surface area (ECSA) was measured from the double-layer capacitance (\(C_{dl}\)) obtained from CV curves (Fig. 4a–c) to clarify the better activity of CoPc/PC-800. As shown in Fig. 4d, CoPc/PC-800 presented the highest \(C_{dl}\) value of 22 mF cm\(^{-2}\) in comparison with the value of 10 mF cm\(^{-2}\) for CoPc/PC-700 and 12 mF cm\(^{-2}\) for CoPc/PC-900, indicative of its largest ECSA and highest active site exposure for the CO_{2}RR. Fig. 4e shows the long-term stability of CoPc/PC-800 at −0.78 V vs. RHE. As noted, the catalyst demonstrated robust operational stability for more than 18 h, and the gradually increased current density might be due to the demetalation of the Co center in CoPc.\(^\text{36}\) Encouragingly, both FE_{CO} and \(j_{CO}\) remained constant with negligible fluctuations, which demonstrated its robust stability. After electrolysis, CoPc/PC-800 was further characterized by XPS and SEM (Fig. 4f and g). As noted, no distinct changes in phase composition or morphology were observed, indicating its good structural stability. All these results indicated that the high intrinsic activity and the facilitated mass transportation as well as the large ECSA should account for the superior CO_{2}RR performance of CoPc/PC-800. These results also indicated the high-efficiency of the PC-supported CoPc catalyst for CO formation, which is comparable to many previously reported CO_{2}RR electrocatalysts (Fig. 4h).\(^\text{1,17,26,37-40}\)

4. Conclusion

In summary, an outstanding CO_{2}RR catalyst was demonstrated to be composed of a unique 3D carbon support with abundant macropores and highly dispersed CoPc. The designed CoPc/PC catalyst achieved a maximum \(FE_{CO}\) value of 95% accompanied by a large \(j_{CO}\) of 20.5 mA cm\(^{-2}\), which was superior to many reported catalysts. The excellent performance was mainly ascribed to the high intrinsic activity and the large exposure of active sites, as well as the facilitated mass transportation. With these results, we developed a new strategy for the design of CoPc-based electrocatalysts with excellent activity and stability.

Data availability

The authors confirm that the data supporting the findings of this study are available within the article.

Conflicts of interest

There are no conflicts to declare.

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