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Introduction

The non-renewability of fossil fuels and global warming are enormous challenges for the sustainable development of human society. Developing clean energy, such as hydrogen energy, is a promising method to solve energy problems.^{1,2} Compared with other carriers, ammonia has excellent hydrogen storage capacity. The mass content of hydrogen is 17.6% in liquid ammonia and ammonia is the only carbonfree proton carrier that will not release CO₂ when it is finally decomposed.³⁻⁶ As the second most important substance, ammonia (NH₃) is commonly used in the production of fertilizers, pharmaceuticals, and synthetic fibers. In industry, ammonia is mainly produced by the Haber-Bosch process which requires high temperature and high pressure (about 400-450 °C, 10-30 MPa), but this process will lead to energy consumption and greenhouse gas emissions.7-11 Therefore, exploring an efficient, clean and sustainable ammonia synthesis method is required.

The electrocatalytic nitrogen reduction reaction (NRR) achieves pollution-free conversion of N_2 to NH_3 with

Single-atom metal–N₄ site molecular electrocatalysts for ambient nitrogen reduction†

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Electrochemical N₂ reduction to NH₃ is an emerging energy technology, attracting much attention due to its features of mild reaction conditions and being non-polluting. In this work, we demonstrate that a well-defined cobalt tetraphenylporphyrin (CoTPP) molecule as a model catalyst exhibits good electrocatalytic nitrogen reduction activity in 0.1 M HCl electrolyte with an ammonia yield of 15.18 \pm 0.78 µg h⁻¹ mg⁻¹_{cat}. calculated by the indophenol blue method and a Faraday efficiency (FE) of 11.43 \pm 0.74%. The catalyst also has satisfactory electrolytic stability and recycling test reusability. The activity displayed by the porphyrin molecular catalysts is attributed to the full exposure of the metal–N₄ sites. To trace the source of ammonia, an isotope labeling experiment (¹⁵N₂ as the feed gas) is used to calculate the ammonia yield *via* ¹H nuclear magnetic resonance (NMR), which is close to that of the indophenol blue method. In addition, we replace the central metal to prepare CuTPP and MnTPP, and they also show electrocatalytic nitrogen reduction reaction (NRR) ability. This work proves the feasibility and versatility of using metalloporphyrin molecules as model electrocatalysts for NRR and offers a new strategy for the further development of molecular NRR catalysts.

renewable energy under ambient conditions. Due to its mild reaction conditions and safe operation, the electrocatalytic NRR is currently a popular research method for ammonia synthesis.^{12,13} However, due to the low solubility of N₂ in water and the high bond energy of the N \equiv N triple bond, N₂ activation is still a great challenge.14-18 Both the NRR and hydrogen evolution reaction (HER) involve a proton coupled electron transfer process, but the HER has inherently more favorable kinetics which hinders the rapid progress of the NRR. As a result, the electrocatalytic NRR usually suffers from relatively low ammonia yield and Faraday efficiency (FE).¹⁹⁻²¹ Excitingly, various NRR electrocatalysts have been reported to effectively address the above problems, including noble-metal catalysts (Ru, Au, Pt, Ir, etc.),²²⁻²⁴ transitionmetal compound catalysts (V2O3/C, Nb2O5, MO2C/C, N-NiO, $CaCoO_x$, etc.)²⁵⁻²⁹ and metal-free catalysts (boron-doped graphene, nitrogen-doped porous carbon, Cl-doped graphdiyne, etc.).³⁰⁻³³ Although the commonly used noble metal and noble metal oxide electrocatalysts have excellent performance, their scarcity and hign cost have limited their application to a certain extent. Metal-based electrocatalysis also suffers from low selectivity, and the Faraday efficiency is often less than 10%. Moreover, the mechanism and reaction intermediates in the NRR process cannot be accurately studied because of non-defined structure in these catalysts. Therefore, there is an urgent need to find defined structure, high selectivity and cost-effective alternatives.

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Paper

Molecular catalysts have been widely used in electrochemical energy conversion, such as the oxygen reduction reaction, CO2 reduction reaction, and NRR, because of the tunability of their electronic structure to clarify the structure-activity relationship.34-37 Porphyrin molecules with highly delocalized electrons and uniform electron density are widely distributed in nature. The stable coordination environment and the diversity of central metals in metal-porphyrin achieve efficient electron and energy transfer, so they have been used in chemical sensing, catalysis, and photosensitive materials.³⁸⁻⁴³ Metal-porphyrin is an atom-dispersed single-atom molecular electrocatalyst with maximum atom utilization efficiency, which can greatly reduce metal consumption. Most transition metals have incompletely filled orbitals that can provide or accept electrons, which makes them more suitable for N₂ activation. Meanwhile, the fully exposed metal-N₄ sites metalloporphyrins are beneficial to N2 adsorption. However, there are few studies on the application of metal-porphyrin molecules in the electrocatalysis NRR.

Here, CoTPP molecules with well-defined Co-N4 sites exhibit good NRR electrocatalytic activity, the ammonia yield reaches 15.18 \pm 0.78 μg h^{-1} $mg^{-1}{}_{cat.}$ and FE is 11.43 \pm 0.74% at -0.3 V vs. RHE in 0.1 M HCl electrolyte. The comparison with H₂TPP molecules confirms the importance of the metal-N₄ site for the NRR. The long-term electrolytic test and cycle test prove the stability and durability of the catalyst. We also used an isotope labeling experiment $({}^{15}N_2$ as the feeding gas) and ¹H NMR method to detect and calculate the ammonia yield, the result matches the data calculation by the indophenol blue method. In order to further illustrate the feasibility of metalloporphyrins as NRR model molecular electrocatalysts, the central metal of porphyrin was further extended to other transition metals, thereby synthesizing CuTPP and MnTPP. Experimental results show that they also show good electrocatalytic activity.

Results and discussion

Metal-tetraphenylporphyrin (MTPP) was synthesized by a simple method. The successful coordination of the metal with tetraphenylporphyrin was confirmed by FT-IR (Fig. S1†). The peaks at 3321 cm⁻¹ and 962 cm⁻¹ belong to N–H stretching vibration and bending vibration of the porphyrin ligand, respectively. When the metal replaces the H in the ring and coordinates with the ligand, these two peaks weaken or disappear. A new peak at about 1000 cm⁻¹ was detected in the MTPP, which was due to the strengthening of the ring vibration (caused by the metal ion entering the porphyrin ring).^{44,45}

The scanning electron microscopy (SEM) images and the transmission electron microscopy (TEM) images in Fig. 1 show the nanostripe morphology of CoTPP molecules, the width of the nanostripe is about 100 nm. The nanomorphology and uniform size distribution of CoTPP molecules increase the active surface area and facilitate the adsorption of N_2 . X-ray photoelectron spectroscopy (XPS)

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Fig. 1 (a and b) SEM images of CoTPP. (c and d) TEM images of CoTPP. (e and f) TEM images and the corresponding elemental mapping image of CoTPP.

characterization was performed, and the results confirmed the successful synthesis of CoTPP (Fig. S2⁺).

Electrochemical NRR experiments were performed in 0.1 M HCl electrolyte using an H-shape electrochemical cell. Acidic electrolytes can provide more protons and promote the hydrogenation process of nitrogen. A Nafion-115 membrane was used to separate the anode and cathode compartments, each compartment containing 50 mL of electrolyte (Fig. S3⁺). CoTPP was coated on carbon paper (mass load: 1 mg cm^{-2}) as the working electrode, while the Ag/AgCl electrode and graphite rod worked as the reference electrode and the counter electrode, respectively. The N2 gas or Ar gas flowed into 0.1 M KOH solution, 0.1 M KMnO₄ solution and 0.1 M HCl solution in advance for purification to ensure that no N-containing impurities in the gas enter the electrolyte. After 2 h of electrolysis, the produced ammonia was detected and quantified by the indophenol blue method⁴⁶ and isotope labeling experiment method ($^{15}N_2$ as the feeding gas), respectively. Possible by-product N2H4 was detected and quantified by the method of Watt and Chrisp.47 Corresponding calibration curves are presented in Fig. S4-S6.†

During the electrocatalytic NRR process, high-purity feed gas (N₂ gas or Ar gas) was continuously passed into the electrolyte to ensure gas saturation. The linear scanning voltammetry (LSV) curves of CoTPP in Ar and N2 saturated environments are shown in Fig. 2a. Obviously, the current density obtained in the N2-saturation state is higher, which confirms the NRR activity of the CoTPP. After 2 h of electrolysis, the chronoamperometry curves at potentials from -0.1 V to -0.5 V vs. RHE are shown in Fig. 2b. The constant current density over time indicates that the CoTPP catalyst has good durability during the NRR test. Fig. 2c shows UV-vis absorption spectra for the determination of ammonia content using the indophenol blue method after 2 h of potentiostatic electrolysis, and the maximum absorption intensity at a wavelength of 655 nm at -0.3 V vs. RHE, indicating the highest ammonia yield at this potential. The average ammonia yield and Faraday efficiency for three tests were calculated and are plotted in Fig. 2d, the ammonia yield



Fig. 2 (a) Linear-sweep voltammetric curves of the CoTPP in N₂saturated (red line) and Ar-saturated (black line) 0.1 M HCl aqueous electrolyte with a scan rate of 5 mV s⁻¹. (b) Chronoamperometric curves of CoTPP for the NRR at different applied potentials. (c) UV-vis absorption spectra of electrolytes stained with an indophenol indicator under different applied potentials for the NRR. (d) Average ammonia yield (left *y*-axis) and Faraday efficiency (right *y*-axis) for three tests of CoTPP at different potentials.

and Faraday efficiency reach their maximum values, $15.18 \pm 0.78 \ \mu g \ h^{-1} \ mg^{-1}_{cat.}$ and $11.43 \pm 0.74\%$ at $-0.3 \ V \nu s.$ RHE, respectively (the values of the three experiments are shown in Fig. S7†). Under the same conditions, CoTPP exhibits superior electrocatalytic NRR performance to H₂TPP (Fig. 3a), which is attributed to the Co–N₄ sites formed by the introduction of Co atoms, and the sites facilitate the adsorption and activation of N₂. The performance of CoTPP molecular NRR electrocatalysts is also comparable to most molecular and non-noble metal NRR electrocatalysts (Table S1†). Furthermore, compared to ammonia production, the production of hydrazine is negligible (Fig. 3b).

A series of control experiments at -0.3 V vs. RHE were conducted to verify that the source of NH₃ was generated via the electrocatalytic reduction of nitrogen by CoTPP. First, we used the indophenol blue method to detect the 0.1 M HCl electrolyte and found a small amount of NH4⁺, and measured corresponding absorbance by UV-vis absorption the spectroscopy. This explains the inevitable NH₃ background in the electrolyte, which is consistent with previously reported studies.^{48,49} Then we conducted the following experiments: (a) the catalyst was electrolyzed in Ar-saturated electrolyte for 2 h; (b) the catalyst was electrolyzed in N₂-saturated electrolyte at open circuit potential (OCP) for 2 h; (c) bare carbon paper without a catalyst was electrolyzed in N2-saturated electrolyte for 2 h. The UV-vis absorption spectra (Fig. 3c) of the control experiments show only weak signals, which is consistent with the measured data of pure electrolytes. In other words, the NH₃ generated in the system was mainly derived from the NRR reaction on the CoTPP catalyst.

The stability of the catalyst is an important indicator for evaluating the catalytic performance. After 10 h of continuous electrolysis in N₂-saturated electrolyte at -0.3 V νs . RHE potential, the current density of the chronoamperometry



Fig. 3 (a) Average ammonia yield and Faraday efficiency of the catalysts (CoTPP and H₂TPP) at -0.3 V vs. RHE in 0.1 M HCl electrolyte. (b) NH₃ and N₂H₄ yield rates of CoTPP at -0.3 V vs. RHE in 0.1 M HCl electrolyte. (c) UV-vis absorption spectra of electrolytes stained with an indophenol indicator under different control experimental conditions.

curve does not change significantly (Fig. 4a), which confirms that the CoTPP electrocatalyst has long-term stability. During the 10 h continuous electrolysis process, we sampled every 2 h, the ammonia yield and Faraday efficiency did not change significantly, confirming that CoTPP has stable electrocatalytic activity (Fig. S8 and S9⁺). Fig. 4b shows five cycles of testing at -0.3 V vs. RHE. The changes in ammonia yield and Faraday efficiency are negligible. It further illustrates that CoTPP is a stable electrocatalyst for the NRR. XPS reveals that the composition of the catalyst has not changed after long-term stability testing (Fig. S10[†]). Fig. S11[†]



Fig. 4 (a) Time-dependent current density curve of CoTPP for 10 h of electrolysis at -0.3 V vs. RHE. (b) Ammonia yield and Faraday efficiency after cyclic stability test for 5 cycles. (c) ¹H NMR spectra of commercial ^{15/14}NH₄Cl samples and the product obtained by using ^{15/14}N₂ as the feed gas. (d) Ammonia yield calculated by the indophenol blue method using ¹⁴N₂ as feed gas and by ¹H NMR using ¹⁵N₂ as feed gas, respectively.

shows SEM images of CoTPP after 2 h of electrolysis. The nanostripe morphology is not significantly different from that before catalysis, indicating the stability of CoTPP as an NRR molecular electrocatalyst.

To further prove the ability of the CoTPP electrocatalyst in reducing N₂ to NH₃ and ensure the source of ammonia, we conducted an isotope labeling experiment. After electrolysis using ¹⁴N₂ as the feed gas, the ¹H NMR spectra showed ¹⁴NH₄⁺ triplet coupling, which was well coupled to the peak of the standard ¹⁴NH₄Cl sample. Under the same condition, we also used ¹⁵N₂ as the feed gas for electrolysis, and the ¹H NMR spectra showed only ¹⁵NH₄⁺ doublet coupling (Fig. 4c). The results further suggested that the appearance of ¹⁵NH₄⁺ was produced by the electrochemical nitrogen reduction of the CoTPP electrocatalyst. Because the integrated area of the peak in ¹H NMR can directly reflect the ammonia content, we used ¹H NMR and a series of known concentrations of standard ¹⁵NH₄Cl solution to quantitatively determine the ammonia yield in the NRR. As shown in Fig. 4d, the ammonia yield calculated from the integrated area of the peaks in ¹H NMR is close to the value previously calculated by the indophenol blue method. The coincidence of the two detection methods reveals that CoTPP is an efficient and stable nitrogen reduction molecular electrocatalyst.

In order to explore the versatility of molecular porphyrins as NRR electrocatalysts, CuTPP and MnTPP were synthesized with a similar reflux method. Their molecular structure was characterized by FT-IR, as shown in Fig. S1,† indicating that they have the same coordination environment. The average ammonia yield of CuTPP reached a maximum of 10.53 \pm 6.5 µg h⁻¹ mg⁻¹_{cat.} at -0.3 V vs. RHE (the values of the three experiments are shown in Fig. S12[†]) and the maximum Faraday efficiency was 14.97% at -0.1 V vs. RHE (Fig. 5a). The highest ammonia yield of MnTPP at -0.4 V vs. RHE was 7.98 ± 0.8 $\mu g h^{-1} m g^{-1}_{cat.}$ (the values of the three experiments are shown in Fig. S13[†]), while the highest Faraday efficiency was 8.21% at -0.5 V vs. RHE (Fig. 5b). The time-dependent current density curves of CuTPP and MnTPP for 10 h of electrolysis (Fig. S14 and S15[†]) show that the current density does not change significantly. These results indicate the feasibility of metalloporphyrin molecules as model NRR electrocatalysts, which provides a broader idea for the design of NRR electrocatalysts. Electrochemical impedance is related to electrocatalytic kinetics, so we conducted an electrochemical impedance test of H₂TPP and MTPP. Fig. S16⁺ shows that MTPP exhibits lower impedance, thus higher conductivity and faster NRR kinetics than H₂TPP. Importantly, the superior activity of CoTPP is attributed to the proper adsorption of N2 and N* intermediates by the Co-N4 active site, which is consistent with the theoretical calculation results in the known literature.^{50,51} Beyond, the nanostructured CoTPP increases the number of surface active sites, which further enhances the electrocatalytic NRR activity.



Fig. 5 (a) Average ammonia yield (left *y*-axis) and Faraday efficiency (right *y*-axis) for three tests of CuTPP at different potentials. (b) Average ammonia yield (left *y*-axis) and Faraday efficiency (right *y*-axis) for three tests of MnTPP at different potentials. (c) NH₃ yield rate over MTPP (M = Co, Cu, Mn) in 0.1 M HCl electrolyte.

Experimental

Materials and measurements

Tetraphenylporphyrin and all other chemicals were commercially purchased and used without further purification. UV-vis spectra were recorded using a Shimadzu UV-3100PC spectrophotometer. FT-IR was performed using a Nicolet Magna 560 IR spectrometer with a wavelength range of 4000-400 cm⁻¹, with KBr pellets. ¹H NMR spectra were recorded on a Varian 600 MHz spectrometer. A scanning electron microscope (Hitachi, SU-70) was used with an operating voltage of 3 kV and transmission electron microscopy was carried out on a JEM-2100F (JEOL) electron microscope. XPS measurement was carried out on a VG ESCALABMKII, Al-Kα radiation.

Synthesis of metal-tetraphenylporphyrin (MTPP)

The MTPP (Co, Cu and Mn) molecules were synthesized according to the previous literature⁵² with appropriate modification.

1.5 g H₂TPP was dissolved in 100 mL DMF to form solution A, and 0.8 g of the corresponding metal acetate was dissolved in 30 mL CH₃OH to form solution B. Solution B was slowly added to solution A and heated at 160 °C for 3 h. Finally, the mixed solution was poured into 300 mL deionized water, and then the precipitate was collected by filtration, washed with deionized water and dried overnight at 80 °C.

Electrochemical measurements

All electrochemical data were collected using a Princeton Electrochemical Workstation (PMC CHS08A) under ambient conditions. The standard three-electrode system in an H-shape electrochemical cell equipped with a Nafion 115 membrane was used in electrochemical measurements. Catalyst coated carbon paper was used as the working electrode, while the Ag/AgCl electrode and graphite rod worked as the reference and the counter electrode, respectively. Before the NRR measurements, the feed gas flowed into 0.1 M KOH solution, 0.1 M KMnO4 solution and 0.1 M HCl solution for purification to ensure no N-containing impurities in the gas and then high-purity feed gas was purged to 50 mL 0.1 M HCl electrolyte for at least 30 min. The gas was maintained throughout the electrochemical measurements. The potentials for this work were converted to the reversible hydrogen electrode (RHE) to calibrate the saturated Ag/AgCl electrode using the following formula:

 $E(vs. \text{ RHE}) = E(vs. \text{ Ag/AgCl}) + 0.059 \times \text{pH} + 0.197 \text{ V}$

Determination of ammonia

The concentration of produced NH₃ was determined via the indophenol blue method using UV-vis spectrophotometry. In detail, 2 mL electrolyte after reaction was taken from the electrochemical cathodic chamber. This was added into 2 mL 1 M NaOH solution containing 5 wt% salicylic acid and 5 wt% sodium citrate, and then 1 mL 0.05 M NaClO and 0.2 mL 1 wt% sodium nitroferricyanide was added to the electrolyte. After keeping for 2 h at room temperature, the absorption spectra were measured using an UV-visible spectrophotometer. Indophenol blue was formed at a wavelength of 655 nm and absorbance at this wavelength was used to estimate the yield of ammonia according to the standard curve. The concentrationabsorbance standard curve was calibrated using NH4Cl standard solution with a series of concentrations of 0, 0.2, 0.4, 0.8 and 1.0 $\mu g \text{ mL}^{-1}$ in 0.1 M HCl solution. The fitting curve ($y = 0.382x + 10^{-1}$ 0.030, $R^2 = 0.999$) shows a good linear relationship of absorbance value with NH₃ concentration by three times independent calibrations to confirm the accuracy of the system.

Determination of hydrazine

 N_2H_4 production was spectrophotometrically determined using the Watt and Chrisp method. A mixed solution of 5.99 g *para*-(dimethylamino)benzaldehyde (C₉H₁₁NO), 30 mL concentrated HCl, and 300 mL ethanol was used as the color reagent. 5 mL electrolyte after reaction was taken from the electrochemical cathodic chamber and the above 5 mL color reagent was added. The mixture was kept stirring at room temperature for 20 min. The absorbance of the solution was measured at a wavelength of 455 nm, and the yield of N_2H_4 was evaluated according to the standard curve. The concentration–absorbance curve was calibrated by the known of concentrations of hydrated hydrazine solution with a series of concentrations of 0, 0.2, 0.4, 0.8 and 1.0 μ g mL⁻¹ in 0.1 M HCl solution. After three times of independent calibrations, the calibration curve of N₂H₄ is y = 0.637x + 0.008, $R^2 = 0.999$.

Calculations of ammonia yield rate and faradaic efficiency (FE)

The rate of NH₃ yield was calculated using the following equation:

$$NH_3 yield = (c \times V)/(17 \times t \times m_{cat.})$$

where $c (\mu g \text{ mL}^{-1})$ is the measured NH₃ concentration, V (mL) is the volume of the electrolyte, t (h) is the reduction reaction time and $m_{\text{cat.}}$ is the mass of catalyst loading on carbon paper.

The faradaic efficiency for the NRR was defined as the percentage of the amount of electric charge used for synthesizing NH_3 in the total charge passed through the electrodes during electrolysis. Assuming three electrons were needed to produce one NH_3 molecule, the FE in 0.1 M HCl solution could be calculated as:

$$FE = 3F \times c \times V/(17 \times Q)$$

where F (96 500 C mol⁻¹) is the Faraday constant, c (µg mL⁻¹) is the measured NH₃ concentration, V (mL) is the volume of the electrolyte, and Q (C) is the quantity of applied electricity.

¹⁵N₂ isotope labeling experiment

Isotope labeling experiments use labeled ${}^{15}N_2$ as the feed gas to obtain the accurate catalytic performance of CoTPP. The method for preparing the calibration curve is as follows: (i) prepare standard ${}^{15}NH_4^+$ solutions in 0.1 M HCl at 2.5, 5.0, 10, 25 and 50 µg mL⁻¹, respectively. (ii) Take 540 µL ${}^{15}NH_4^+$ solution of each concentration and mix with 60 µL D₂O in the nuclear magnetic tube, and perform ${}^{1}H$ NMR measurement. (iii) Integrate the peak area, and ${}^{15}NH_4^+$ has a positive correlation with the integrated area to obtain a calibration curve. The reaction solution was mixed with D₂O in proportion to test ${}^{1}H$ NMR, and the ${}^{1}H$ NMR peak area was obtained by integration, then the ammonia yield was calculated according to the calibration curve.

Conclusions

In summary, CoTPP with uniform nanostructure is an efficient and stable electrocatalyst for reducing N_2 to NH_3 under ambient conditions. In addition, we further explored CuTPP and MnTPP, both of which exhibited good NRR catalytic activity. This proves the reliability of metalloporphyrin molecules as NRR model electrocatalysts, because molecular catalysts have a well-defined structure and clear mechanism, which is convenient for further optimization of the catalytic process. The activity of the metalloporphyrin electrocatalyst is attributable to the full exposure of the metal– N_4 sites, which fully adsorbs N_2 and

accelerates the N_2 activation. This work provides more choices and new ideas for the design of NRR electrocatalysts.

Conflicts of interest

There are no conflicts to declare.

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