

Supporting Information

Heteroatom-doped carbon materials derived from covalent triazine framework@MOF for oxygen reduction reaction

Jing Zhang ^a, Yuping Xu ^a, Maowen Lan ^a, Xiaodong Wang ^b, Ning Fu^c, Zhenglong Yang ^{*, a}

*^aShanghai Key Laboratory of D & A for Metal-Functional Materials, School of Materials Science and Engineering, Tongji University
Shanghai 201804, P. R. China.*

*^bShanghai Key Laboratory of Special Artificial Microstructure Materials and Technology & School of Physics Science and Engineering, Tongji University,
Shanghai 200092, P. R. China.*

*^c School of Chemical and Environmental Engineering, Anyang Institute of Technology
Anyang 455000, P. R. China.*

** Corresponding author.*

E-mail: yangzhenglong@tongji.edu.cn; Tel: +86-21-69584723

Experimental section

Instruments and measurements

Fourier transform infrared spectrum (FTIR, EQUINOX 55, Germany) was used to study the chemical structure of the samples. X-ray diffraction (XRD) patterns was collected by a D/max 2550VB3+/PC. Thermogravimetric analyzer (TGA, STA 449C) was used to confirm the decomposition temperature under N₂ atmosphere with a temperature increase from 30 °C to 1000 °C. The Scanning electron microscopy (SEM, Quanta 200, USA) and Transmission electron microscopy (TEM, JEOL-2100F) were examined to identify the morphology of the samples. X-ray photoelectron spectroscopy (XPS, AXIS UltraDLD) was used to explore the binding states of materials. Raman spectroscopy (Senterra R200-L) was carried out with a 532 nm excitation laser under a power of around 1 mW.

All electrochemical tests were conducted by a CHI 760E (Shanghai Chenhua) electrochemical workstation setup in alkaline solution (0.1M KOH) with a conventional three-electrode (rotating disk electrode (RDE, 0.196 cm²) or rotating ring disc electrode (RRDE, 0.247 cm²) as the working electrode, mercury/mercury oxide electrode (Hg/HgO) as the reference electrode, and platinum wire as counter electrodes). Electrochemical impedance spectroscopy (EIS) was tested in the frequency range and amplitude of 0.01–10⁵ Hz and 5 mV.

For preparing the working electrode, catalysts (10 mg), ethanol (1.25 mL), and Nafion (30 μL, 5 wt.%), then the mixture was sonicated for 2 h by ultrasonication. The catalyst ink (5 μL) was carefully pipetted onto the RDE or RRDE. The potentials of the ORR were converted to the reversible hydrogen electrode (RHE) by using the following equation: $E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.0592\text{pH} + 0.098$.

RDE measurements were recorded with a scan rate of 10 mV s⁻¹ under various rotating speeds (225~1600 rpm). The ORR kinetics were calculated through the Koutecky–Levich equations (1) and (2):²⁸

$$\frac{1}{j} = \frac{1}{j_L} + \frac{1}{j_K} = \frac{1}{B\omega^{\frac{1}{2}}} + \frac{1}{j_K} \quad (1)$$

$$B = 0.62nFC_0D_0^{2/3}\omega^{-1/6} \quad (2)$$

j (mA cm^{-2}) is the measured current density, j_L and j_K are the diffusion-limited and kinetic-current density, ω -the rate of electrode revolution, C_0 ($1.2 \times 10^{-6} \text{ mol/cm}^3$) and D_0 ($1.9 \times 10^{-5} \text{ cm}^2/\text{s}$) is the concentration and diffusion coefficient of O_2 , respectively. F (96485 C/mol) is the Faraday constant, B is the slope of the K-L plot according to equation (2).

The $\text{H}_2\text{O}_2\%$ produced and corresponding n during the reaction was calculated by equations (3) and (4):

$$\text{H}_2\text{O}_2\% = 200 \times \frac{I_R/N}{I_D + I_R/N} \quad (3)$$

$$n = 4 \times \frac{I_D}{I_D + I_R/N} \quad (4)$$

Here I_D - disk current, I_R - ring current, and N (0.37) -the H_2O_2 collection efficiency.

Synthesis of CTF

Typically, 546 mg TBPT, 249 mg BDA, 93.48 mg $\text{Pd}(\text{PPh}_3)_4$ were added into 40 mL DMF, and then 8 mL of 2 M K_2CO_3 solution were added into the solution which was degassed with N_2 for 20 min. The suspension was stirred under a pure N_2 atmosphere at 120°C for 12 h. Then, we collected the CTF powder and washed it with water and acetone, and then the sample was purified by Soxhlet extraction with DCM and methanol for 12 h, the final products were dried at 60°C under vacuum.¹⁷

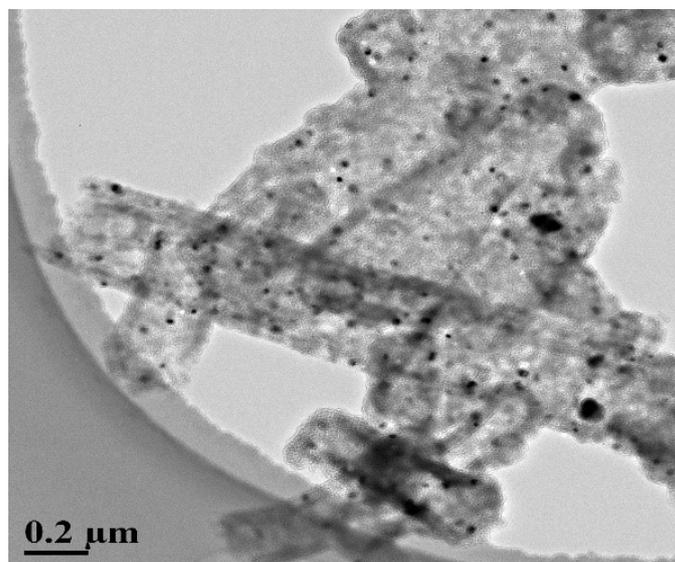


Fig. S1 TEM images of MC-24-700.

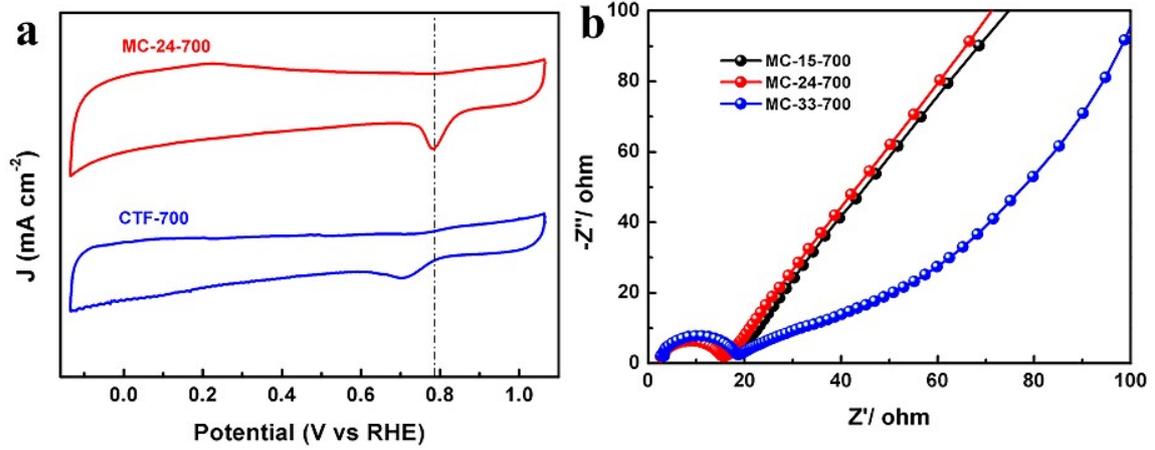


Fig. S2 (a) Comparisons of CV curves of CTF-700 (blue) and MC-24-700 (red).
 (b) Comparisons of the electrochemical impedance spectra for MC-15-700, MC-33-700, and MC-33-700.

Table S1. The surface composition and the relative content of the component elements in different catalysts were evaluated from the XPS analysis.

Samples	C(at%)	N(at%)	O(at%)	pyridinic- N(%)	pyrrolic- N(%)	graphitic- N(%)
CTF-700	92.28	3.19	4.53	13.5	25	61.6
CTF-800	94.58	2.1	3.32	12.1	26.9	61
CTF-900	93.76	3.05	2.79	27	15.1	57.9