Supporting Information

for Adv. Mater. Interfaces, DOI: 10.1002/admi.202200276

Polyhedral Carbon Anchored on Carbon Nanosheet with Abundant Atomic Fe-Nₓ Moieties for Oxygen Reduction

Dong Liu, Chenxi Huyan, Yuanyuan Zhao, Terence Xiaoteng Liu, Ding Wang, Jining Sun, Sheng Dai, Fei Chen, and Ben Bin Xu*
Supporting Information

Polyhedral Carbon Anchored on Carbon Nanosheet with Abundant Atomic Fe-N, Moieties for Oxygen Reduction

Dong Liu, Chenxi Huyan, Yuanyuan Zhao, Terence Xiaoteng Liu, Ding Wang, Jining Sun*, Sheng Dai, Fei Chen and Ben Bin Xu*

Section 1: Experimental Details

Structure, Morphology, and Composition Characterization

The materials were characterized using scanning electron microscopy (SEM, FEI Sirion 200, operated at 30 kV), transmission electron microscopy (TEM, Tecnai G2 T20, 200 kV; JEOM Grand ARM300F, 300 kV). The materials were characterized using X-ray photoelectron spectroscopy (XPS, Escalab 250, Al Kα), X-ray diffraction (XRD, Rigaku Miniflex 600, 40 kV). The specific surface area and pore structure of the samples were investigated with an automatic volumetric sorption analyzer (ASAP 2020 M), in which N₂ acts as the adsorbate at −196 °C. The X-ray absorption spectroscopy measurement at Fe K-edge was performed at the Advanced Photon Source (APS) on the bending-magnet beamline 12-BM and 20-BM with electron energy of 7 GeV and average current of 100 mA. The radiation was monochromatized by a Si (111) double-crystal monochromator. Harmomic rejection was accomplished with Harmonic rejection mirror. All spectra were collected in fluorescence mode by vortex four-element silicon drift detector. For wavelet transform analysis, the χ(k) exported from Athena was input to the Hama Fortran code. The parameters were set as follows: k weight, 0; R range, 1-5 Å; k range, 0-10 Å⁻¹.

Preparation of the Working Electrode

The glassy carbon electrode (GCE, geometric area: 0.2475 cm²) was firstly polished and rinsed to get a mirror-like surface. 2.5 mg of catalysts were ultrasonically dispersed in a mixture solution which containing 990 µL ethanol and 10 µL 0.05 wt% Nafion to form a
concentration of 2.5 mg mL$^{-1}$ homogeneous catalyst ink. Followed by dropping the catalyst ink onto the surface of the GCE disk and dried at room temperature, the electrode loadings were 0.2 mg cm$^{-2}$. Pt/C (20 wt%, Alfa Aesar) with a loading of 0.1 mg cm$^{-2}$ prepared with the same procedure described above were used as the reference sample.

Electrochemical measurements

The electrochemical measurements were performed using a standard three-electrode cell. A graphite rod and an Ag/AgCl electrode served as the counter electrode and reference electrode, respectively. All the potentials vs. Ag/AgCl electrode were referred to a reversible hydrogen electrode (RHE) scale according to the Nernst equation:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.0591pH + 0.197$$  \hspace{1cm} (1)

The O$_2$/N$_2$ was bubbled through the electrolyte in the cell for 30 min before tests to make sure that the electrolyte was saturated with O$_2$/N$_2$. 0.1 M HClO$_4$ was used as the acidic electrolytes. The cyclic voltammetry (CV) experiments were performed in N$_2$ and O$_2$ saturated with a scan rate of 50 mV s$^{-1}$. All Linear sweep voltammetry (LSV) polarization curves for the ORR were obtained at rotating speed of 1600 rpm at the scan rate of 10 mV/s. The current density ($J_k$) of the PCCNS catalysts were calculated based on the Koutecky–Levich equations:

$$J_k = (j * j_L)/(j_L - j)$$  \hspace{1cm} (2)

where $j$ and $j_L$ are the measured current density and diffusion-limiting current density, respectively.

The number of electron transfer ($n$) and the peroxide yield (H$_2$O$_2$ %) can also be precisely evaluated by RRDE, as the following equation:

$$n = (4I_{\text{disk}})/(I_{\text{disk}} + I_{\text{ring}}/N)$$  \hspace{1cm} (3)

$$H_2O_2\% = 100 \times (2I_{\text{ring}}/N)/(I_{\text{disk}} + I_{\text{ring}}/N)$$  \hspace{1cm} (4)

where $I_{\text{disk}}$ is the Faradaic current at the disk, $I_{\text{ring}}$ means the Faradaic current at the ring, and $N$ is the H$_2$O$_2$ collection coefficient at the ring (0.37).
Section 2. Supplementary Figures.

**Figure S1.** TEM image of the Fe-ZIF8@PPy@GO.

**Figure S2.** TEM image of PCCNS catalyst.
**Figure S3.** EDS elemental mapping photo of C, N, O and Zn atoms in PCCNS-20.

**Figure S4.** Raman spectra of PCCNS catalysts
Figure S5. N2 adsorption-desorption isotherm of PCCNS-20 (inset shows the pore size distribution of PCCNS-20).

Figure S6. XPS survey spectra of PCCNS catalysts.
Figure S7. C1s high-resolution spectrum of PCCNS-20.

Figure S8. CV curves of PCCNS catalysts in O2 saturated 0.1 M HClO4 solution
Figure S9. The $E_0$ and $E_{1/2}$ of PCCNS and Pt/C catalysts.

Figure S10. TEM image of PCCNS-30.
Figure S11. XRD curve of PCCNS-30.

Figure S12. Nyquist plots of PCCNS-20 and Fe-ZIF8 derived carbon cluster synthesized by the same procedure of PCCNS catalyst but without adding GO and PANI.
Figure S13. Chronoamperometric response of PCCNS-20 and Pt/C in 0.1 M HClO₄.