Electronic Supplementary Information

FeP embedded in N, P dual-doped porous carbon nanosheet: an efficient and durable bifunctional catalyst for oxygen reduction and evolution reactions

Ruizhong Zhang, Chunmei Zhang and Wei Chen

1State Key Laboratory of Electroanalytical Chemistry, Changchun institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, Jilin, China, and

2University of Chinese Academy of Sciences, Beijing 100039, China

E-mail: weichen@ciac.ac.cn

Experimental Details

1. Chemicals and materials.

Ferric chloride (FeCl₃·6H₂O, A.R., ≥99.0%, Tianjin East China Reagent Factory), phytic acid (C₆H₁₈O₂₄P₆, 70%, Xiya Reagent Research Center, Shandong, China), folic acid (C₁₉H₁₉N₇O₆, 98.0%, GEN-VIEW SCIENTIFIC INC.), potassium hydroxide (KOH, A.R., ≥85.0%, Beijing Chemical works), perfluorosulfonic acid-PTFE copolymer (Nafion, 5% w/w Solution, Alfa Aesar), E-TEK Pt/C (nominally 20% by wt. of 2-5 nm Pt nanoparticles on Vulcan XC-72R carbon support, Alfa Aesar). Nanopure water used in all experiments was supplied by a Water Purifier Nanopure water system (resistivity > 18 MΩ cm). All chemicals were commercially available and used without further purification.


2.1 Synthesis of iron phytate (FePA)

Iron phytate was synthesized from phytic acid and ferric chloride by a complexation-precipitation method. Typically, FeCl₃ (16.8 mL, 1.0 mol L⁻¹) and phytic acid (13.87 mL, 100 mg mL⁻¹) were mixed together in a round-bottomed flask. After vigorous stirring for 5 min, the solution color immediately changed to yellowish white. Then the flask was transferred into an oil bath with a pre-setting temperature of 100 °C to continue the complexation reaction for another 1 h. After cooled to room temperature, the resulting colloidal products were collected by centrifugation and washed several times with nanopure water. Finally, the obtained white products were dried in a conventional drying oven at 70 °C for 12 h and finely ground for further use.
2.2 Synthesis of FeP@NPCs hybrid nanomaterials

In a typical synthesis, iron phytate (FePA, 0.3 g) was first dispersed in 20 mL of nanopure water, followed by addition of 0.3 g folic acid for 30 min of stirring treatment. The obtained homogeneous mixture was sonicated for 1 h, further stirred for 8 h at room temperature. After that, the resulting precipitate was collected by centrifugation, and was dried in a conventional oven at 70 °C for 12 h.

The dried mixture was thoroughly ground into a homogeneous fine powder and then transferred into a ceramic boat. Next, the ceramic boat was placed at the center of a tubular furnace and the temperature was raised from 10 to 900 °C at a programming rate of 2.0 °C min\(^{-1}\) and then maintained at 900 °C for 2 h, and finally cooled to room temperature naturally. The whole heating process proceeds under N\(_2\) atmosphere with a gas flow rate of 100 sccm. The carbonized products were leached with 0.5 M H\(_2\)SO\(_4\) at 90 °C for 5 h to remove unstable species, excessive metals and metal oxides. The resulting products were separated by centrifugation, washed with an ethanol-ultrapure water mixture several times, and finally dried in a drying oven. For comparison, the nanocomposites without phytic acid or folic acid or iron salt or FePA were also prepared with the same procedure, which were denoted as Fe@NCs, Fe@PCs, NPCs and NCs, respectively.


The morphologies of the samples were first studied by scanning electron microscope (FE-SEM, XL30 ESEM FEG) operating at 20 kV. The samples were prepared by drop-drying the ethanol suspension of catalysts onto ITO glass substrate. Transmission electron microscopy (TEM), high-resolution TEM (HRTEM) and the corresponding live fast Fourier transform (FFT), high-angle annular dark-field scanning transmission electron microscopy (HAAD-STEM), elements mapping and energy-dispersive X-ray (EDX) characterizations were all performed on a JEM-2010 (HR) microscope operated at 200 kV. The samples were prepared by drop-drying the ethanol suspension of samples onto carbon-coated copper grids. The surface chemical composition was determined by X-ray photoelectron spectroscopy (XPS, VG Thermo ESCALAB 250 spectrometer) operated at 120 W. The binding energies were calibrated against the carbon 1s line. Powder X-ray diffraction (XRD) patterns were collected using a D8 ADVANCE (Germany) Diffractometer using Cu K\(\alpha\) radiation with a Ni filter (\(\lambda = 0.154059\) nm at 30 kV and 15 mA). The surface area and pore structure of the samples were characterized on an automatic gas adsorption/desorption analyzer (Quantachrome Instruments, version 3.01) with N\(_2\) as adsorbate, and the samples were outgassed in vacuum at 200 °C for 24 h before test. The specific surface areas of the samples were calculated by the Brunauer-Emmett-Teller (BET) method using the adsorption
branch in the relative pressure range from 0.05-0.30. Raman spectra were collected on a Micro-Raman spectroscopy system RM 2000 (Renishaw in Via-reflex, 532 nm excitation laser).

4. Electrochemical measurements.

All electrochemical tests were carried out in a standard three-electrode cell at room temperature. A commercial rotating disk electrode (RDE) (AFE2M050GC, geometric area of 0.196 cm², Pine Research Instrumentation) covered by the catalyst with Naﬁon ionomer as a binder, a Pt coil and an Ag/AgCl (saturated KCl) electrode were used as the working electrode, counter electrode and reference electrode, respectively. The rotation rate and potential of the working electrode were controlled by a MSR Electrode Rotator (Pine Research Instrumentation) and a CHI 750 D electrochemical workstation. Before preparing the working electrode, 2 mg of catalyst was dispersed in 0.9 mL of ethanol and 0.1 mL of 5 wt % Naﬁon solution by sonication to form a 2 mg mL⁻¹ homogeneous ink. Then the catalyst layer was prepared by dropping a calculated amount of catalyst ink onto a pre-polished RDE by a micropipettes and drying at room temperature. The loading of the catalysts was adjusted to be 0.2 mg cm⁻². The ORR activities of the catalysts were evaluated by RDE measurements in O₂-saturated 0.1 M KOH solution at a scan rate of 5 mV s⁻¹. Commercial Pt/C and RuO₂ were also measured for comparison, and the loading of Pt and RuO₂ catalysts on RDE was 24 µg cm⁻² and 81 µg cm⁻², respectively.

As for ORR, to obtain the electron transfer number (n), the RDE was scanned cathodically with varying speed from 225 to 2025 rpm in O₂-saturated 0.1 M KOH aqueous solution. The kinetic current density (J_K) can be calculated using the Koutecky-Levich equation which is expressed by

\[
J_K = J_L J / J_L - J
\]

where \( J \) is the experimentally obtained current density, \( J_L \) refers to the measured diffusion-limited current density, and \( J_K \) is the mass-transport free kinetic current density.

The \( J_L \) term can be obtained from the Levich equation:

\[
J_L = 0.2nFD^{2/3}v^{-1/6}\omega^{1/2}C_{O_2}
\]

where \( n \) is the number of electrons transferred; \( F \) is Faraday’s constant (96 485 C mol⁻¹); \( D \) is the diffusion coefficient of O₂ in 0.1 M KOH solution (1.9 × 10⁻⁵ cm² s⁻¹); \( v \) is the kinematic viscosity of the electrolyte (0.01 cm² s⁻¹); \( \omega \) is the RDE rotation rate in rpm, and \( C_{O_2} \) is the concentration of molecular oxygen in 0.1 M KOH solution (1.2×10⁻³ mol L⁻¹).

Rotating ring disk electrode (RRDE) measurements of the samples were tested on a glassy carbon disk (Φ 5.61 mm) with a polycrystalline Pt biased at 1.46 V (vs RHE) in 0.1 M KOH solution. The H₂O₂ yield (HO₂⁻ %) and the electrons transfer numbers (n) per oxygen molecule are calculated using the following equations:
\[ n = \frac{4I_D}{I_D + I_R/N} \]  

(3)

\[ HO_2^-\% = \frac{200I_R/N}{I_D + I_R/N} \]  

(4)

where \( I_R \) and \( I_D \) are ring and disk currents, and \( N \) is collection efficiency (0.37).

The accelerated durability tests (ADTs) of the catalysts were conducted by applying a cyclic potential sweep between 0.6 and 1.0 V (vs RHE) in O\(_2\)-saturated 0.1 M KOH solution at room temperature with a scan rate of 100 mV s\(^{-1}\).

As for OER, linear sweep voltammograms (LSVs) tests were carried out using a catalyst-casted glassy carbon rotating disk electrode (RDE) prepared with the same procedure as ORR measurements and with the mass loading of 0.2 mg cm\(^{-2}\) in 0.1 M KOH with a scan rate of 5 mV s\(^{-1}\). Prior to the measurements, the electrolyte (0.1 M KOH) was purged by O\(_2\) for 15 min to maintain the O\(_2\)/H\(_2\)O equilibrium at 1.23 V (vs RHE) scale, and the working RDE was constantly rotating at 1600 rpm to remove the generated O\(_2\) bubbles during the measurements. All polarization curves are corrected with 95% \( iR \)-compensation. The Tafel slopes are calculated according to the Tafel equation as follows:

\[ \eta = b \log J + a \]  

(5)

where \( \eta \) is the overpotential, \( J \) is the current density, and \( b \) is the Tafel slope. The overpotential is calculated using the following equation:

\[ \eta = E_{RHE} - 1.23 \]  

(6)

The electrochemically active surface areas (ECSA) of the as-prepared samples were roughly estimated from the electrochemical double-layer capacitance (\( C_{dl} \)) by measuring the non-Faradaic capacitive current associated with double-layer charging from the scan rate-dependent cyclic voltammograms in the potential range from 0.96 to 1.16 V (vs RHE). The scan rates of 5, 10, 20, 40, 60, 80 and 100 mV s\(^{-1}\) were used. The curves between \( \Delta J/2 \) at 1.06 V (vs RHE) and different scan rates were plotted. The \( C_{dl} \) was then estimated from the slope of the fitted curve in the linear region.

All the potentials referred to in this work are converted to the pH-dependent reversible hydrogen electrode (RHE): \( E \) (vs RHE) = \( E \) (vs Ag/AgCl) + 0.197 + 0.059 pH, and the current density is normalized to the geometric surface area of RDE or RRDE.
Supplementary Results

**Fig. S1** Energy dispersive X-ray spectra (EDX) of FeP@NPCs. The signals of Sn and In come from the ITO glass substrate.

<table>
<thead>
<tr>
<th>Element</th>
<th>At %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>88.03</td>
</tr>
<tr>
<td>N</td>
<td>10.09</td>
</tr>
<tr>
<td>P</td>
<td>1.24</td>
</tr>
<tr>
<td>Fe</td>
<td>0.64</td>
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</table>
Fig. S2 XRD patterns of (A) FeP@NPCs without leached treatment by 0.5 M H$_2$SO$_4$, (B) Fe@NCs, (C) Fe@PCs and (D) NCs.
Fig. S3 XPS survey spectrum (A) and the corresponding high-resolution XPS spectra of C 1s (B), N 1s (C), P2p (D) and Fe 2p (E) of FeP@NPCs.
**Fig. S4** A low-resolution SEM image of FeP@NPCs.
**Fig. S5** SEM images of Fe@NCs (A, B) and Fe@PCs (C, D). TEM images of NCs (E, F) and NPCs (G, H).
Fig. S6 (A) Nitrogen adsorption/desorption isotherms and (B) the corresponding pore size distribution curves calculated from the desorption branches of FeP@NPCs with (black line) and without (red line) H$_2$SO$_4$ washing treatment. (C) Raman spectra of different samples: (a) FeP@NPCs, (b) FeP@NPCs without H$_2$SO$_4$ washing treatment, (c) Fe@NCs, (d) Fe@PCs and (e) NCs.
Fig. S7 ORR performance of the commercial Pt/C in alkaline medium: (A) Linear sweep voltammograms (LSVs) in O₂-saturated 0.1 M KOH at various rotation speeds with a scan rate of 5 mV s⁻¹, and (B) The corresponding K-L plots at different potentials.
Fig. S8 Linear sweep voltammograms (LSVs) of ORR on (A) Fe@NCs, (C) Fe@PCs and (E) NCs in O$_2$-saturated 0.1 M KOH at various rotation speeds with a scan rate of 5 mV s$^{-1}$. The corresponding K-L plots at different potentials obtained from (B) Fe@NCs, (D) Fe@PCs and (F) NCs.
Fig. S9 RDE polarization curves of ORR on the FeP@NPCs catalyst pyrolyzed at 900 °C with different mass ratios of FePA and folic acid (FA) in O₂-saturated 0.1 M KOH solution with a scan rate of 5 mVs⁻¹ at a rotation speed of 1600 rpm.
Fig. S10 (A) RRDE measurements of oxygen reduction ($J_{\text{Disk}}$) and hydrogen peroxide oxidation ($J_{\text{Ring}}$) on FeP@NPCs and commercial Pt/C in O$_2$-saturated 0.1 M KOH with a scan rate of 5 mV s$^{-1}$ and rotation speed of 1600 rpm. (B) The corresponding H$_2$O$_2$ yield (HO$_2^-$ %) and electron transfer number ($n$) on FeP@NPCs and commercial Pt/C.
Fig. S11 Chronoamperometric measurements for FeP@NPCs and Pt/C catalysts in O₂-saturated 0.1 M KOH with the potential holding at 0.8 V (vs RHE) at a rotation rate of 900 rpm.
Fig. S12 Cyclic voltammograms curves of (A) Fe@NCs, (B) Fe@PCs and (C) NCs in a non-Faradaic region at different scan rates from 5 to 100 mV s\(^{-1}\).
Fig. S13 (A) Comparison of OER catalytic activities of FeP@NPCs prepared at different temperatures. The used mass ratios of FePA/FA precursors are all of 1. (B) Comparison of OER catalytic activities of FeP@NPCs with and without H$_2$SO$_4$ leaching treatment. The annealing temperature is 900 °C and the mass ratio of FePA/FA is 1 for both samples. All of the LSV tests are performed at a rotation rate of 1600 rpm in 0.1 M KOH solution.
Fig. S14 Time-dependent current density of FeP@NPCs at an overpotential of 0.3 V for 12 h.
Table S1. Comparison of the bifunctional catalytic activities of FeP@NPCs with other reported electrocatalysts

<table>
<thead>
<tr>
<th>Electrocatalyst</th>
<th>$E_{\text{onset, ORR}}$ (V)</th>
<th>$E_{\text{onset, OER}}$ (V)</th>
<th>$E_{1/2,\text{ORR}}$ (V) (-3 mA cm$^{-2}$)</th>
<th>$E_{\text{OER}}$ (V) (10 mA cm$^{-2}$)</th>
<th>$\Delta E$ (V) ($E_{\text{OER}}-E_{\text{ORR}}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeNi-LDH@3DG/CNTs</td>
<td>0.83</td>
<td>—</td>
<td>0.71</td>
<td>1.61</td>
<td>0.90</td>
<td>1</td>
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<tr>
<td>N-Co$_9$S$_8$/G</td>
<td>0.94</td>
<td>1.51</td>
<td>—</td>
<td>1.64</td>
<td>—</td>
<td>2</td>
</tr>
<tr>
<td>PCN-CFP</td>
<td>0.94</td>
<td>1.53</td>
<td>0.67</td>
<td>1.63</td>
<td>0.96</td>
<td>3</td>
</tr>
<tr>
<td>CNT@NCNT</td>
<td>0.99</td>
<td>—</td>
<td>0.63</td>
<td>1.76</td>
<td>1.33</td>
<td>4</td>
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<tr>
<td>N$_x$P-GCNS</td>
<td>1.01</td>
<td>1.32</td>
<td>0.86</td>
<td>1.57</td>
<td>0.71</td>
<td>5</td>
</tr>
<tr>
<td>N-graphene/CNT</td>
<td>0.88</td>
<td>—</td>
<td>0.69</td>
<td>1.65</td>
<td>0.96</td>
<td>6</td>
</tr>
<tr>
<td>Co/N-C-800</td>
<td>0.83</td>
<td>—</td>
<td>0.74</td>
<td>1.60</td>
<td>0.86</td>
<td>7</td>
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<tr>
<td>CCH/C-2/C</td>
<td>0.93</td>
<td>—</td>
<td>0.82</td>
<td>1.74</td>
<td>0.92</td>
<td>8</td>
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<tr>
<td>Mn oxide</td>
<td>—</td>
<td>—</td>
<td>0.73</td>
<td>1.77</td>
<td>1.04</td>
<td>9</td>
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<tr>
<td>NiCo$_2$O$_4$-G</td>
<td>0.89</td>
<td>1.56</td>
<td>0.74</td>
<td>1.69</td>
<td>0.95</td>
<td>10</td>
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<tr>
<td>NoCo$_2$S$_4$/N/S-rGO</td>
<td>0.85</td>
<td>1.58</td>
<td>0.72</td>
<td>1.70</td>
<td>0.98</td>
<td>11</td>
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<tr>
<td>Co$_3$O$_4$/N-mGO</td>
<td>0.88</td>
<td>—</td>
<td>0.85</td>
<td>1.54</td>
<td>0.69</td>
<td>12</td>
</tr>
<tr>
<td>FeP@NPCs</td>
<td>0.94</td>
<td>1.47</td>
<td>0.79</td>
<td>1.53</td>
<td>0.74</td>
<td>This work</td>
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</table>

References

nanoparticles embedded in N-doped carbon as an efficient bifunctional electrocatalyst for oxygen reduction and evolution reactions. *Nanoscale* 2014, 6, 15080-15089.


