Supporting Information

Metal-Free 3D Porous Electrode for Full Water Splitting at All pH Values

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Experimental Section

Chemicals and materials.

Ammonium persulfate (APS) was purchased from Beijing Chemical Corp. Aniline and phytic acid were purchased from Sinopharm Chemical Reagent Co.Ltd. (Shanghai, China). Nafion (10%) and commercial Pt/C were purchased from Sigma-Aldrich. All chemicals were analytical-reagent grade and used without further purification. CC is provided by Tsukuba Materials Information Laboratory (TMIL) Ltd.

Apparatus.

Scanning electron microscopy (SEM) images were recorded in a FEI XL30 ESEM FEG Scanning Electron Microscope operated at 25 kV. TEM images were all obtained using a FEI Tecnai G2 F20 microscope operated at 200 kV. Energy dispersive spectrometer (EDS) spectrums were collected in a Hitachi S-4800 Scanning Electron Microscope operated at 20.9 KV. X-ray diffraction (XRD) patterns were recorded on a Bruker D8 ADVANCE X-ray diffractometer (Cu Kα radiation) in the 30 to 80° 2theta range. The Fourier-transform infrared spectroscopy (FT-IR) spectra were recorded from KBr disks using a Perkin-Elmer GX instrument in the wavenumber range of 4000-400 cm⁻¹. Tapping-mode AFM imaging was performed on a Digital Instruments multimode AFM controlled by a Nanoscope IIIa apparatus (Digital Instruments, Santa Barbara, CA) equipped with an E scanner. XPS measurements were performed on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source. Nitrogen sorption isotherms were measured with an ASAP 2020 Physisorption Analyzer (Micrometrics Instrument Corporation).
**Preoxidation of CC.**

CC was washed repeatedly with aqueous solutions of HCl (19 wt.%) and HNO₃ (10 wt.%), followed by washing with water. After drying, the purified CC was functionalized by oxidation treatment with concentrated HNO₃ (65 wt.%) at room temperature for 40 min to generate oxygen-containing functional groups (e.g. carboxylic groups) on its surface. Then the resulting CC was subjected to repeated water washing and drying at 120 °C.

**Preparation of ONPPGC/OCC.**

The preoxidized CC (2 cm × 2 cm) was immersed into the 2 ml water solution containing 0.458 ml aniline monomer (5 mmol) under stirring, and then 0.921 mL phytic acid solution (1 mmol) was added into the mixture under stirring. 0.286 g of ammonium persulfate (APS) (1.25 mmol) was dissolved into the 1 mL water under stirring. After cooling down to about 4 °C, both solutions were mixed together and stirred for 2h. The mixture was transferred into a Teflon-lined autoclave, which was sealed and aged statically at 100 °C for 5 h under autogenous pressure. The resultant precipitation was washed with a large amount of water and dried at 60 °C, followed by annealing at 1000 °C for 2h under N₂. The obtained sample was named ONPPGC/OCC. The weight increment of OCC was directly weighted after the growth of ONPPGC. For ONPPGC/OCC electrode, the loading mass of ONPPGC is 0.1 mgcm⁻².
Electrochemical measurements.

The test solutions were performed with a CHI 660C electrochemistry workstation (Shanghai CHI Instruments Company, China) in a standard three-electrode system using ONPPGC/OCC as the working electrode, a Pt wire as the counter electrode and an Ag/AgCl electrode as the reference electrode. To prepare the Pt/C loaded electrode, the Pt/C catalysts were resuspended in a mixture containing water, isopropanol, and Nafion (10%) (v:v:v 4:1:0.05) to form a 0.5 mg/mL catalyst ink. 2 µL catalyst inks was deposited on glassy carbon electrodes (0.07 cm$^{-2}$) that were polished prior to catalyst deposition by 0.3 µm and 0.05 µm alumina powder and rinsed by sonication in ethanol and in deionized water. The Pt/C catalysts modified electrode was dried at ambient condition. For Pt/C loaded electrode, the loading mass of Pt/C is 0.14 mg cm$^{-2}$. All potentials measured were calibrated to RHE using the following Equation: $E_{\text{RHE}}=E_{\text{Ag/AgCl}}+0.197 \ V+0.059\times\text{pH}$. Polarization curves were obtained using LSV with a scan rate of 2 mVs$^{-1}$ and no activation was used before recording the polarization curves. The long-term durability test was performed using chronoamperometry and chronopotentiometric measurements. All currents presented are corrected against ohmic potential drop. The electrochemical impedance spectroscopy (EIS) measurement was carried out in a frequency range from 100 kHz to 5 Hz with an AC voltage amplitude of 10 mV at a open circuit potential in 0.5 M H$_2$SO$_4$ solution.
Table S1. Comparison of the electrocatalytic activity of ONPPGC/OCC via some representative solid-state water electrolysis catalysts recently reported for basic solutions.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Catalyst amount (mg cm⁻²)</th>
<th>Current Density j 10mAc m⁻²</th>
<th>Potential (vs. RHE) at the corresponding j</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiFe LDH/NF</td>
<td>N</td>
<td>1.7</td>
<td>21</td>
<td></td>
</tr>
<tr>
<td>NiSe/NF</td>
<td>2.8</td>
<td>1.63</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>Ni₂P</td>
<td>5</td>
<td>1.63</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>NiFeOₓ</td>
<td>3</td>
<td>1.51</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Pt/C</td>
<td>0.14</td>
<td>1.69</td>
<td>This work</td>
<td></td>
</tr>
<tr>
<td>ONPPGC/OCC</td>
<td>0.1</td>
<td>1.66</td>
<td>This work</td>
<td></td>
</tr>
</tbody>
</table>

Table S2. Element compositions of ONPPGC/OCC samples.

<table>
<thead>
<tr>
<th>Molar ratio</th>
<th>C at.%</th>
<th>O at.%</th>
<th>N at.%</th>
<th>P at.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>3:1</td>
<td>82.7</td>
<td>16.5</td>
<td>0.39</td>
<td>0.38</td>
</tr>
<tr>
<td>5:1</td>
<td>82.8</td>
<td>16.4</td>
<td>0.46</td>
<td>0.32</td>
</tr>
<tr>
<td>7:1</td>
<td>83.0</td>
<td>16.2</td>
<td>0.57</td>
<td>0.18</td>
</tr>
</tbody>
</table>
**Figure S1.** Fabrication of O, N and P tri-doped mesoporous graphite nanocarbon foams directly grown on oxidized carbon cloth.

**Figure S2.** SEM image of OCC.
Figure S3. SEM image of polyaniline hydrogel on OCC surfaces.

Figure S4. SEM images of the ONPPGC/OCC and corresponding EDX elemental mapping images.
**Figure S5.** AFM images of ONPPGC.

**Figure S6.** XRD pattern of ONPPGC/OCC.
Figure S7. (A) N$_2$ adsorption–desorption isotherms (B) and corresponding DFT pore size distribution curves for OCC and ONPPGC/OCC.

Figure S8. XPS survey spectrum of ONPPGC/OCC.
Figure S9. FTIR of ONPPGC/OCC.

Figure S10. A current density-time ($j$-$t$) curve obtained for OER with ONPPGC/OCC at 1.65 V (vs. RHE) in an alkaline solution (1 M KOH, pH = 14).
**Figure S11.** A current density-time ($j$-t) curve obtained for HER with ONPPGC/OCC at -0.4 V (vs. RHE) in an alkaline solution (1 M KOH, pH = 14).

**Figure S12.** Photograph of the system showing the hydrogen (left) and oxygen (right) generation during water electrolysis.
**Figure S13.** LSV curves for ONPPGC/OCC before and after 1000 CV cycles in 1.0 M KOH.

**Figure S14.** The amount of gas theoretically calculated and experimentally measured versus time for overall water splitting of ONPPGC/OCC.
Figure S15. LSV curves of water electrolysis for ONPPGC/OCC (ONPPGC prepared with various molar ratios of aniline to phytic acid) in a two-electrode configuration with a scan rate of 2 mVs$^{-1}$ in 1.0 M KOH.
**Figure S16.** (A) LSV curves for ONPPGC/OCC with a scan rate of 2 mVs$^{-1}$ for OER. (B) A current density-time ($j$-$t$) curve obtained for OER with ONPPGC/OCC at 1.65 V (vs. RHE). (C) The corresponding Tafel plots. All experiments were carried out in 0.2 M PBS.

**Figure S17.** (A) LSV curves for ONPPGC/OCC with a scan rate of 2 mVs$^{-1}$ for HER. (B) A current density-time ($j$-$t$) curve obtained for HER with ONPPGC/OCC at -0.35 V (vs. RHE). (C) The corresponding Tafel plots. All experiments were carried out in 0.2 M PBS.
Figure S18. (A) LSV curves for ONPPGC/OCC with a scan rate of 2 mVs$^{-1}$ for OER. (B) A current density-time ($j$-t) curve obtained for OER with ONPPGC/OCC at 1.70 V (vs. RHE). (C) The corresponding Tafel plots. All experiments were carried out in 0.5 M H$_2$SO$_4$. 
Figure S19. (A) LSV curves for ONPPGC/OCC with a scan rate of 2 mVs\(^{-1}\) for HER. (B) A current density-time (j-t) curve obtained for HER with ONPPGC/OCC at -0.39 V (vs. RHE). (C) The corresponding Tafel plots. All experiments were carried out in 0.5 M H\(_2\)SO\(_4\).

Figure S20. EIS of the ONPPGC/OCC electrodes.
**Movie S1.** Movie of the system showing the oxygen (left) and hydrogen (right) generation during water electrolysis in 1.0 M KOH.