Binary Ni$_2$FeO$_x$ anchored on modified graphite towards efficient and durable oxygen evolution electrocatalysis

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Experimental

Materials and reagents

All chemicals were analytical grade and used as purchased without further purification. Solutions were prepared using high purity water (Millipore Milli-Q purification system, resistivity > 18 MΩ•cm).

Synthesis of G-Ph

Typically, the dark gray graphite powder (0.5 g, 41.6 mmol of carbon) was dispersed in benzene (400 mL) in a 500 mL three necked round-bottom flask equipped with a magnetic stir bar. The contents were then stirred vigorously after benzoyl peroxide (10.1 g, 41.6 mmol) was added. The mixture was then heated at 80 °C for 12 h with continuous vigorous stirring. After cooling down, the contents of the flask were centrifuged and washed with ethanol for four times. The black solid was dried at 60 °C overnight, which was nominated as G-Ph.

Synthesis of G-Ph-SO$_3$H
The typical experimental processes include as follows: the phenylated graphite (G-Ph) (200 mg) was dispersed in oleum (70 mL, H$_2$SO$_4$, 25% as free SO$_3$), and heated at 80 °C for 5 h to yield phenyl sulfonated graphite. After cooling down, 300 g of ice block was then carefully added into the suspension. The mixture was then centrifuged and washed with water several times until the pH value of the filtrate reached ~7. The obtained solid was dried at 60 °C overnight, which was nominated as G-Ph-SO$_3$H.

**Synthesis of Ni$_n$FeO$_x$@G-Ph-SN**

Typically, stoichiometric Ni(NO$_3$)$_2$•6H$_2$O, 0.03 g Fe(NO$_3$)$_3$•9H$_2$O, 0.1 g G-Ph-SO$_3$H, and 50 µL of deionized water were added in 20.0 mL of ethanol solution. Under stirring, 75 µL of 28% ammonia was added to the mixture. Afterwards, it was transferred into 30 mL Teflon autoclave and heated at 150 °C for 2 h. After cooling down, the solid was obtained by filtering, washing with water for several times, and drying at 70 °C overnight, which was denoted as Ni$_n$FeO$_x$@G-Ph-SN (where n presents the atomic ratio of Ni/Fe). The loading content of Fe is ca. 4.0 wt.% measured by ICP-AES. The Ni content in NiFeO$_x$@G-Ph-SN, Ni$_2$FeO$_x$@G-Ph-SN, and Ni$_3$FeO$_x$@G-Ph-SN, is 3.9 wt.%, 7.7 wt.%, and 11.5 wt.% determined by ICP-AES.

**Characterizations of samples**
The as-prepared samples were characterized by X-ray powder diffraction (XRD) on a Rigaku D/Max-2500/PC powder diffractometer. The sample powder was scanned using Cu-Kα radiation with an operating voltage of 40 kV and current of 200 mA. The scan rate of 5°/min was applied to record the patterns in the range of 10-80°. Transmission electron microscope (TEM) images were observed by a Hitachi HT7700. High resolution TEM (HRTEM) images were recorded on a JEM-2100 transmission electron microscope (Tokyo, Japan) at 200 kV. The loading amount of manganese oxide in the catalyst was determined using inductively coupled plasma atomic emission spectrometer (ICP-AES) on a Shimadzu ICPS-8100. Prior to ICP-AES measurement, supported manganese oxide was dissolved in aqua regia. The valence state of cobalt oxide cluster was determined using XPS recorded on a Thermo ESCALAB 250Xi. The X-ray source selected was monochromatized Al Kα source (15 kV, 10.8 mA). Region scans were collected using a 20 eV pass energy. Peak positions were calibrated relative to C 1s peak position at 284.6 eV.

**Electrochemical characterization**

The electrochemical water oxidation performances of all the manganese-based electrodes were tested in a conventional three-electrode electrochemical cell with a platinum plate as the auxiliary electrode and a saturated calomel electrode (SCE, saturated KCl) as the reference electrode. 1 M KOH aqueous solution was used as
electrolyte with pH measured at ca. 13.6. The scanning rate was 5 mV/s. All potentials measured were calibrated to RHE using the following equation: \( E_{\text{RHE}} = E_{\text{SCE}} + 0.241V + 0.0591pH \). The steady-state activity and long-term activity were evaluated by chronopotentiometry measurements. The ECSA was determined by measuring the capacitive current associated with doublelayer charging from the scan rate CV-dependence. Here, the CV potential window was 0.15 to 0.25 vs SCE. The scan rates were 20, 40, 60, 80, and 100 mV s\(^{-1}\). The double-layer capacitance (\( C_{\text{dl}} \)) was estimated \( \Delta j = (j_{\text{charge}} - j_{\text{off charge}}) \) at 0.2 V vs SCE against the scan rate. The liner slop is twice of the double-layer capacitance \( C_{\text{dl}} \). Electrochemical impedance spectroscopy (EIS) measurements were performed at open-circuit potential in the frequency range from 100 kHz to 0.1 Hz with an a.c. perturbation of 10 mV.
Figure S1. SEM image of G-Ph-SO$_3$H.
Figure S2. TEM image of G-Ph-SO₃H.
Figure S3. The histogram of size distribution of typical samples: FeO$_x$@G-Ph-SN (a), and NiO$_x$@G-Ph-SN.
Figure S4. XRD patterns of graphite, FeO\textsubscript{x}@G-Ph-SN, NiO\textsubscript{x}@G-Ph-SN, and Ni\textsubscript{2}FeO\textsubscript{x}@G-Ph-SN.
Figure S5. Raman spectra of NiO, G-Ph-SO$_3$H, NiO$_x$@G-Ph-SN, and Ni$_2$FeO$_x$@G-Ph-SN
Figure S6. N\textsubscript{2} adsorption and desorption isotherms of the Ni\textsubscript{2}FeO\textsubscript{x}@G-Ph-SN sample.
Figure S7. TEM image of IrO$_2$ nanoparticles.
Figure S8. Polarization curves of FeO$_x$@G-Ph-SN with different Fe loadings.
Figure S9. Capacitive $j$ vs scan rate for FeO$_x$@G-Ph-SN, NiO$_x$@G-Ph-SN, NiFeO$_x$@G-Ph-SN, and Ni$_3$FeO$_x$@G-Ph-SN. The linear slope is equivalent to twice of the double-layer capacitance $C_{dl}$.
Figure S10. EIS of FeO$_x$@G-Ph-SN, NiO$_x$@G-Ph-SN, and Ni$_2$FeO$_x$@G-Ph-SN. The inset is an equivalent circuit model.
Figure S11. LSV polarization curves of fresh Ni$_2$FeO$_x$@G-Ph-SN, Ni$_2$FeO$_x$@G-Ph-SN after CV for 200 cycles, and Ni$_2$FeO$_x$@G-Ph-SN after CV for 2000 cycles.
Table 1. Comparison of the OER performance of different transition-metal electrocatalysts in 1 M KOH

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$\eta$@ 10 mA•cm$^{-2}$ (mV)</th>
<th>Tafel slope (mV•dec$^{-1}$)</th>
<th>References</th>
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<tr>
<td>Ni$_2$FeO$_x$@G-Ph-SN</td>
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<td>60.2</td>
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<td>$\alpha$-FeCoO$_x$</td>
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<td>NiFe LDH</td>
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<td>Ni$<em>{0.75}$Fe$</em>{0.25}$OOH</td>
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References