Supplementary Information

Boosting Bifunctional Oxygen Electrocatalysis of Graphitic C$_3$N$_4$ using Non-covalently Functionalized Non-oxidized Graphene Aerogels as Catalyst Supports

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Experimental Section

Fabrication of g-C$_3$N$_4$ Nanosheets: Melamine (100 mg) was heated at 550 °C for 4 hours in air with elevating temperature of 5 °C min$^{-1}$. The resulting bulk g-C$_3$N$_4$ was immersed in De-ionized (DI) water (100 ml) and exfoliated using a probe sonicator for 2 hours. The g-C$_3$N$_4$ solution was centrifuged at 1500 rpm for 30 min and the supernatant was collected.

Fabrication of NOGFs: Bulk potassium metal and naphthalene were dissolved in anhydrous tetrahydrofuran (THF) in 1 M concentration to prepare potassium-naphthalenide solution. Graphite powder (Sigma Aldrich) was immersed in the potassium-naphthalenide solution for at least 24 hr to obtain graphite intercalation compound (GIC). The GIC was thoroughly washed with anhydrous THF to remove remaining potassium and naphthalene. The GIC ultrasonicated using a probe sonicator in Dimethyl for 30 minutes. For obtaining surface modified NOGFs, the GIC was immersed in PVP-Dimethyl Sulfoxide (2 mg ml$^{-1}$) or PBA-Dimethyl Sulfoxide (2 mg ml$^{-1}$) solution. The exfoliated NOGF solution was then centrifuged at 1500 rpm for 30 min and the supernatant was collected.

Fabrication of Aerogel: NOGFs and g-C$_3$N$_4$ nanosheets were first redispersed in DI water in 1:1 ratio and redispersed in DI water in 4 mg ml$^{-1}$ concentration under probe sonication for 3 min. Nafion binder was sequentially added to the solution at 1:4 weight ratio of NOGFs and g-C$_3$N$_4$ nanosheets. The precursor solution was then poured into a polylactic acid (PLA) mold with one end having 20° wedge. The mold was placed on a metal stage cooled by liquid nitrogen for bi-directional freeze casting. The aerogel was obtained after freeze dried in a freeze dryer (TFD8501, iSBio) for 48 hr.

Characterization: SEM (S-4800, Hitachi) with a field-emission source at 10 keV and built-in EDS was used to examine the structure and composition of CN-NOGAs. TEM analysis was performed with F2 F20 (Tecnai) at an acceleration voltage of 200 keV. Raman spectroscopy was carried out on a Senterra system (Bruker). XPS was performed on a Sigma Probe system (Thermo VG Scientific) with AlKα radiation source. XRD (D/MAX-2500) with Cu Kα radiation (λ = 1.518 Å) was used to examine phases and composition of Cn-NOGAs. Fourier transform infrared (FT-IR) spectroscopy was carried out by FT-IR-4100 type-A FT-IR
spectrometer (Jasco). Hall measurement was performed with Ecopia. For accurate comparison, the CN-NOGAs were formed into films with the same dimension by compressing to 5 µm thickness and cut into 5 cm x 5 cm. The films were placed above the film holder and measured.

**Electrochemical Characterizations:** The aerogels were cut with a punch hole with diameter of 3 mm, in the direction parallel to the pore alignment direction. The samples were placed on top of glassy carbon electrode. 5 µl of Nafion 117 solution (5%) was drop casted on the sample which was dried in an oven at 65 °C overnight. The electrocatalytic properties were measured on a VersaSTATE 3 (principle applied research) electrochemical workstation equipped with a rotating disk electrode system (AMETEK, principle applied research, 616B). The electrochemical performance was evaluated using a three-electrode system (where the working electrode was the active material/glassy carbon, the reference electrode was Ag/AgCl in 3 M KCl, and the counter electrode was a Pt mesh) in 1 M KOH (pH = 13.6) electrolyte. All of the potentials were calibrated to a RHE, $ERHE = E_{Ag/AgCl} + 0.196 + 0.0591 \text{pH V}$. 
Details for calculating the Koutecky-Levich plots:

The Koutecky-Levich plots and the kinetic parameters of ORR can be analysed on the basis of the Koutecky-Levich equations:

\[
\frac{1}{j} = \frac{1}{j_L} + \frac{1}{j_K} = \frac{1}{B \omega^2} + \frac{1}{j_K}
\]

(1)

\[
B = 0.62nFC_0 \left( \frac{2}{D_0^3} \right)^{\frac{1}{6}}
\]

(2)

\[
j_K = nFkC_0
\]

(3)

Where \( j \) (mA cm\(^{-2}\)) is the measured current density, \( j_K \) and \( j_L \) (mA cm\(^{-2}\)) are the kinetic- and diffusion-limiting current densities, \( \omega \) is the angular velocity of the rotating disk (\( \omega = 2\pi N \), \( N \) is the linear rotating speed in rpm), \( n \) is the overall number of electrons transferred in ORR, \( F \) is the Faraday constant, \( C_0 \) is the bulk concentration of O\(_2\), \( D_0 \) is diffusion coefficient of O\(_2\), \( \nu \) is the kinematic viscosity of the electrolyte, and \( k \) is the electron transfer rate constant, respectively. According to the Equations (1) and (2), the number of electrons transferred \( (n) \) and the kinetic-limiting current \( j_K \) can be obtained from the slope and intercept of the Koutecky-Levich plots \((1/j \text{ versus } \omega^{-1/2})\). For the calculation of electron transfer number \( n \) and \( j_K \) in 0.1M KOH electrolyte, values of different constants are estimated as:

\( F = \) Faraday constant = 96485 C mol\(^{-1}\)

\( A = \) electrode area = 0.071 cm\(^2\)

\( D_0 = \) Diffusion coefficient of O\(_2\) = \( 9 \times 10^{-5} \)

\( \nu = \) kinematic viscosity of the electrolyte solution = 0.01 cm\(^2\) s\(^{-1}\)

\( C_0 = \) concentration of dissolved O\(_2\) = \( 1.2 \times 10^{-6} \)

After putting these values in equation (2) we got the final equation as:

\[
n = \frac{28.15}{\text{slope of } K-L \text{ plot}}
\]

(4)

Furthermore, for the calculation of the production yield of H\(_2\)O\(_2\), we have used the following equation:

\[
H_2O_2 \% = 100 \times \frac{4 - n}{2}
\]

(5)
Values for the samples:

<table>
<thead>
<tr>
<th>Samples</th>
<th>Electron transfer number (ne)</th>
<th>Kinetic current density (j_k)</th>
</tr>
</thead>
<tbody>
<tr>
<td>g-C$_3$N$_4$</td>
<td>0.10</td>
<td>0.15 mA cm$^{-2}$</td>
</tr>
<tr>
<td>CN-NOGA</td>
<td>0.35</td>
<td>0.31 mA cm$^{-2}$</td>
</tr>
<tr>
<td>p-type CN-NOGA</td>
<td>0.65</td>
<td>1.62 mA cm$^{-2}$</td>
</tr>
<tr>
<td>n-type CN-NOGA</td>
<td>3.80</td>
<td>5.20 mA cm$^{-2}$</td>
</tr>
<tr>
<td>Pt/C</td>
<td>3.99</td>
<td>5.90 mA cm$^{-2}$</td>
</tr>
</tbody>
</table>

**Details for calculating the ne based on rotating ring disc electrode (RRDE) measurements:**

$n_e$ of the n-type CN-NOGA was calculated on the basis of the RRDE measurements using the following equation:

$$n_e = \frac{4I_D}{I_D + I_R/N} \quad (6)$$

Where $N (= 0.36)$ is the collection efficiency, $I_D$ is the faradic disk current, and $I_R$ is the faradic ring current.
Fig. S1. Lateral size distribution of 60 g-C$_3$N$_4$ nanosheets.

Fig. S2. Characterization of the exfoliated g-C$_3$N$_4$ nanosheets. (a) X-ray diffraction pattern (XRD) showing characteristic peaks of g-C$_3$N$_4$. X-ray photoelectron spectroscopy (XPS) analysis of g-C$_3$N$_4$ nanosheets in (b) survey and (c) C1s peak showing characteristic 60 % nitrogen and C-N content.
**Fig. S3.** Characterization of the non-oxidized graphene flake (NOGF). (a) Transmission electron microscopy (TEM) image of a single NOGF and (b) enlargement of its edge (inset shows Fast Fourier Transform (FFT) pattern of hexagonal symmetry, indicating of high crystallinity).

**Fig. S4.** Composition analysis of NOGFs with different surface modifications. (a) Raman spectrum showing low $I_D/I_G$ ratios of NOGFs even after surface modification with PVP or PBA. (b) XPS C1s peaks and (c) Fourier Transform Infrared Spectroscopic (FT-IR) analysis showing characteristic components of corresponding surfactant. (d) Thermogravimetric analysis (TGA) estimating the quality of functionalized surfactant.
**Fig. S5.** Magnified SEM image of n-type CN-NOGA pore walls.

**Fig. S6.** Magnified SEM image of p-type CN-NOGA pore walls.
**Fig. S7.** (a) SEM image of the cross section of bare CN-NOGA. (b) TEM image of bare CN-NOGA pore wall and corresponding (c) energy-dispersive X-ray spectroscopy (EDS) elemental maps of C, O and N. Characterization of bare NOGF, g-C$_3$N$_4$ and bare CN-NOGA in (d) X-ray Diffraction (XRD), (e) X-ray photoelectron spectroscopy (XPS) survey and (f) Fourier transform infrared (FT-IR) spectroscopy.

**Fig. S8.** Digital image of (a) film holder for Hall measurement. (b) Film holder with CN-NOGA in 5 cm x 5 cm and 5 µm thickness dimension.
Fig. S9. Ideal oxygen reduction reaction through four electron donation.

\[
O_2 \rightarrow O_2^* \rightarrow OOH^* \rightarrow 2OH^* \rightarrow OH^- + H_2O \rightarrow 2H_2O
\]

Fig. S10. Electron transfer number (n_e) and kinetic current density (j_k) of bare g-C_3N_4, CN-NOGAs in different electric states and commercial Pt/C.

Fig. S11. RRDE polarization curves of n-type CN-NOGA in 1.0 M KOH at a rotation rate of 1600 rpm.
Fig. S12. Cyclic voltammetry of (a) bare CN-NOGA, (b) n-type CN-NOGA and (c) p-type CN-NOGA.

Fig. S13. Composition analysis of n-type CN-NOGA before and after ORR stability test: (a) XRD spectra, XPS in terms of (b) survey, (c) C1s peaks and (d) N1s peaks.
**Fig. S14.** Linear sweep voltammetry curves of as-prepared g-C$_3$N$_4$ and CN-NOGAs normalized by ECSAs.

**Fig. S15.** Composition analysis of p-type CN-NOGA before and after OER stability test: (a) XRD spectra, XPS in terms of (b) survey, (c) C1s peaks and (d) N1s peaks.
Table S1. Hall measurement of NOGFs in different surface modifications.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Carrier Concentration (cm⁻³)</th>
<th>Mobility (cm² V⁻¹ s⁻¹)</th>
<th>Resistivity (Ω cm)</th>
<th>Conduction Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 CN-NOGA (Bare)</td>
<td>0.588 · 10¹⁹</td>
<td>1.451 · 10²</td>
<td>7.31 · 10⁻³</td>
<td>n</td>
</tr>
<tr>
<td>n CN-NOGA (PVP)</td>
<td>4.114 · 10¹⁹</td>
<td>1.238 · 10²</td>
<td>1.23 · 10⁻³</td>
<td>n</td>
</tr>
<tr>
<td>p CN-NOGA (PBA)</td>
<td>1.348 · 10¹⁹</td>
<td>1.202 · 10²</td>
<td>3.85 · 10⁻³</td>
<td>p</td>
</tr>
</tbody>
</table>

Table S2. Comparison of present work with other reported bifunctional oxygen electrocatalysis based on g-C₃N₄ supported on various conductive supports. All shown V₀ values are vs. RHE.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Overpotentials (V₀ vs RHE) for ORR/electron transfer no. (nₑ)</th>
<th>Overpotential of OER (V₀ vs RHE) @10 mA cm⁻²</th>
<th>Tafel slope</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-C₃N₄/C</td>
<td>V₀ = 0.95 V, nₑ = 3.80</td>
<td>V₀ = 1.65 V</td>
<td>Tafel = 53 mV dec⁻¹</td>
<td>Niu et al. ACS Catal. 2018, 8, 1926–1931</td>
</tr>
<tr>
<td>Co-C₃N₄/CNT</td>
<td>V₀ = 0.90 V, nₑ = N/A</td>
<td>V₀ = 1.61 V</td>
<td>Tafel = 68 mV dec⁻¹</td>
<td>Zheng et al. J. Am. Chem. Soc. 2017, 139, 3336–3339</td>
</tr>
<tr>
<td>g-C₃N₄/Ti₃C₂ nanosheets</td>
<td>V₀ = 0.80 V, nₑ = N/A</td>
<td>V₀ = 1.65 V</td>
<td>Tafel = 74 mV dec⁻¹</td>
<td>Ma et al. Angew. Chem. Int. Ed. 2016, 55, 1138–1142</td>
</tr>
<tr>
<td>phosphorus-doped g-C₃N₄/carbon-fiber paper</td>
<td>V₀ = 0.84 V, nₑ = N/A</td>
<td>V₀ = 1.63 V</td>
<td>Tafel = 61 mV dec⁻¹</td>
<td>Ma et al. Angew. Chem. Int. Ed. 2015, 54, 4646–4650</td>
</tr>
<tr>
<td>NiCo₂S₄@g-C₃N₄-CNT</td>
<td>V₀ = 0.85 V, nₑ = N/A</td>
<td>V₀ = 1.58 V</td>
<td>Tafel = 57 mV dec⁻¹</td>
<td>Han et al. Adv. Mater. 2019, 31, 1808281</td>
</tr>
<tr>
<td>Ag@g-C₃N₄/Co₃O₄</td>
<td>V₀ = 0.82 V, nₑ = 4.00</td>
<td>V₀ = 1.65 V</td>
<td>Tafel = N/A</td>
<td>Guo et al. J. Energy Chem. 2020, 41, 185–193</td>
</tr>
<tr>
<td>Co₄N@g-C₃N₄</td>
<td>V₀ = 0.94 V, nₑ = 3.90</td>
<td>V₀ = 1.54 V</td>
<td>Tafel = 69 mV dec⁻¹</td>
<td>Wang et al. Chem. Eng. J. 2021, 413, 127954</td>
</tr>
<tr>
<td>g-C₃N₄/NOGA</td>
<td>V₀ = 0.79 V, nₑ = 3.80</td>
<td>V₀ = 1.49 V</td>
<td>Tafel = 68 mV dec⁻¹</td>
<td>This Work</td>
</tr>
</tbody>
</table>

(n-type CN-NOGA)                  | (p-type CN-NOGA)                                                    |                                             |              |                                   |