Supporting information

S1. Synthesis of NH$_2$- and SO$_3$H- functionalized carbon black (NH$_2$-CB, SO$_3$H-CB)

For the synthesis of p-phenyl-NH$_2$-CB, p-phenylenediamine, concentrated nitric acid, and sodium nitrite (NaNO$_2$) were added in a molar ratio of 1:1:1, and the mixture was then kept at 60 °C for 4 hours. The obtained product was washed with DI water and ethanol, yielding NH$_2$-CB. The preparation of p-phenyl SO$_3$H-CB follows similar procedures, except that sulfanilic acid and concentrated sulfuric acid were used instead of p-phenylenediamine and concentrated nitric acid, respectively. The loading of p-phenyl NH$_2$-and p-phenyl SO$_3$H- functional groups on carbon black surface was determine to be ca. 15.5 wt.% and ca. 21.5 wt.%, respectively, under Ar flow by TGA.

S2. Synthesis of graphitic carbon nitride nano-sheets (g-C$_3$N$_4$ NSs)

The graphitic carbon nitride nano-sheets (g-C$_3$N$_4$ NSs) catalysts were synthesized through thermal polycondensation and exfoliation processes. 5.0 g dicyandiamide was grounded using mortar and pestle to get uniformly white powder, followed by annealing in ambient pressure N$_2$ gas with a 200ml min$^{-1}$ flow rate. The temperature was kept at 550 °C for 4 hours, after a heating rate of 10 °C min$^{-1}$. The yellow bulk carbon nitride (b-g-C$_3$N$_4$) was collected after cooling down. To further obtain graphitic carbon nitride nano-sheets, 500 mg b-g-C$_3$N$_4$ was dispersed into iso-propanol solvent, followed by ultra-sonication-exfoliation for 5 h. The mixture was centrifuged at 2500 rpm to remove unexfoliated aggregates, while the obtained light yellow suspension was further centrifuged at 8000rpm, washed thoroughly with deionized water and freeze-drying to gain g-C$_3$N$_4$ NSs.
Figure S1. Photographs of the dispersions of bulk g-C₃N₄ in various solvents after ultrasonication for 2 hours and storage for 1 hour under ambient conditions. It clearly demonstrates that IPA and NMP are promising solvents to exfoliate bulk g-C₃N₄ without apparent precipitation.
Figure S2. Zeta potential of the g-C₃N₄, P-g-C₃N₄ nanosheets, and NH₂- as well as SO₃H- functionalized carbon materials.
Figure S3. a) SEM image of bulk P-g-C₃N₄; b) SEM image of 3-D P-g-C₃N₄@NH₂-CB with 3:1 weight ratio of NH₂-CB to P-g-C₃N₄ NSs; c) TEM image of P-g-C₃N₄@NH₂-CB with 1:3 weight ratio of NH₂-CB to P-g-C₃N₄ NSs; d) SEM, e) TEM images of P-g-C₃N₄@SO₃H-CB
Figure S4. Nitrogen adsorption–desorption isotherms and pore size distribution of bulk P-g-C₃N₄, P-g-C₃N₄@NH₂-CB, and NH₂-CB.
Figure S5. XRD patterns of bulk g-C\textsubscript{3}N\textsubscript{4} and g-C\textsubscript{3}N\textsubscript{4} nano-sheets.
Figure S6. a) XPS high-resolution spectra of N\textsubscript{1s}, b) C\textsubscript{1s}, and survey spectrum of g-C\textsubscript{3}N\textsubscript{4} NSs.
Figure S7. Potential calibration of the Hg/HgO reference electrode in 0.1 M H₂-saturated KOH solution with the Pt wire as the working and counter electrodes. In this case, the potentials showed were calculated by the following equation: $E_{(RHE)} = E_{(Hg/HgO)} + 0.888\, V$. 
Figure S8. Cyclic voltammograms (CV) of P-g-C$_3$N$_4$ NSs, P-g-C$_3$N$_4$@SO$_3$H-CB, and P-g-C$_3$N$_4$@NH$_2$-CB in 0.1 M KOH solution saturated with N$_2$ at a scan rate of 50 mV s$^{-1}$. 
Figure S9. Tafel plots of ORR currents for P-g-C$_3$N$_4$ based catalysts and 20 wt% Pt/C.
Figure S10. Comparative ORR polarization curves for different catalysts with the same loading measured at 1600 rpm in O₂-saturated 0.1 M KOH solution.
Figure S11. Ring current density of RRDE for different catalysts with the same loading measured at 1600 rpm in O_2-saturated 0.1 M KOH solution.
Figure 12. ORR polarization curves of commercial 20wt% Pt/C before and after 3000 potential cycles in O$_2$-saturated 0.1 M KOH solution.
Figure S13. Time-drifting stability of the P-g-C$_3$N$_4$@NH$_2$-CB and commercial 20wt% Pt/C at 0.4 V vs. RHE for 36000 s with a rotating rate of 1600 rpm.
Table S1. some recently reported g-C3N4/carbon composite and heteroatom doped carbon as ORR catalysts

<table>
<thead>
<tr>
<th>Material</th>
<th>Onset potential (V vs. RHE)</th>
<th>Current density at 0.4V vs. RHE (mA cm(^{-2}))</th>
<th>Potential at -3 mA cm(^{-2}) (V vs. RHE)</th>
<th>Rotating Rate (rpm)</th>
<th>Ref.</th>
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<tr>
<td>g-C3N4/C</td>
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<td>4.20</td>
<td>0.63</td>
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<td>g-C3N4/rGo</td>
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<td>3.30</td>
<td>0.48</td>
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<tr>
<td>hp-GSGCN_2x</td>
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<td>3.90</td>
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<tr>
<td>G-CN800</td>
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<td>3.90</td>
<td>0.67</td>
<td>1600</td>
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<tr>
<td>g-CN/C-2</td>
<td>0.90</td>
<td>4.30</td>
<td>0.73</td>
<td>1600</td>
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<tr>
<td>P-g-C3N4@NH(_2)-CB</td>
<td>0.90</td>
<td>4.87</td>
<td>0.73</td>
<td>1600</td>
<td>This work</td>
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<td>N-doped CMK(_3)</td>
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<td>0.72</td>
<td>1600</td>
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<td>B(<em>{12})C(</em>{77})N(_11)</td>
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<tr>
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<td>4.75</td>
<td>0.71</td>
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References:


