Electronic Supplementary Information for

**Deflagration synthesis of nitrogen/fluorine co-doped hollow carbon nanoparticles with excellent oxygen reduction performance**

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Figure S1. (a) Mass spectra and (b) emission spectra of NaN$_3$/TiO$_2$ deflagration generated by a 532-nm laser at 90 Jcm$^{-2}$.

Na nanoclusters and N radicals generated from NaN$_3$ deflagration have been detected in our previous work (Nano Research, just accepted, http://www.thenanoresearch.com/work_just.asp) as shown in Fig. S1.

Figure S2. Emission spectra of Si/PTFE deflagration.$^2$

The deflagration reaction of Na nanoclusters capturing partial F from C$_3$F$_5$N is difficult to be investigated because of its occurring in an air-tight reactor. So, we cannot obtain some reliable experimental proofs of N/F contained C radicals. However, from the emission spectra of Si/PTFE(polytetrafluoroethylene) deflagration as shown in Fig. S2, some F contained C radicals (CF$_2^*$) have been detected in the Si capturing F from PTFE deflagration process. Thus, it can be inferred that N/F contained C radicals will be generated in the Na capturing partial F from C$_3$F$_5$N deflagration process.
Figure S3. TEM (a-b) and STEM (c) images of the N/F-HC-2 sample without being washed with deionized water.

Figure S4. (a) TEM image and (b-f) C, N, F and Na mapping of unwashed N/F-HC-2 sample.

Figure S5. (a) TEM image and (b-f) C, N, F and Na mapping of N/F-HC-2 sample after washed.
Figure S6. XRD pattern (a), TEM images (b-c) and Carbon, Nitrogen, Fluorine, Sodium elemental mapping (d) of raw N/F-HC-0.5 sample without being washed with deionized water.

Figure S7. XPS spectra of the N/F-HC-X samples
Figure S8. XPS spectra of the obtained carbon product from NaN₃ deflagration with polytetrafluoroethylene. Inset is the C, N, F and O elemental percentage in the sample.

Figure S9. N₂ adsorption/desorption isotherms of N/F-HC-X samples.

Figure S10. CV curves of N/F-HC-X samples in O₂ saturated 0.1 M KOH aqueous solution with a scan rate of 50 mV s⁻¹.
**Figure S11.** LSV curves of Pt/C before and after cycling for 5000 cycles with a rotation rate of 1600 rpm.

**Figure S12.** (a) Raman spectra and (b) LSV of N/F-HC-0, N/F-HC-0.5 and N/F-HC-1 samples after calcination at 900 °C for 2 h.

**Figure S13.** (a) Raman spectra and (b) LSV of N-GR and N-RGO samples.
**Table S1.** The element compositions and contents in N-RGO and N-GR samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>C (at%)</th>
<th>N (at%)</th>
<th>O (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-RGO-1</td>
<td>76.476</td>
<td>1.808</td>
<td>21.725</td>
</tr>
<tr>
<td>N-RGO-2</td>
<td>84.292</td>
<td>2.181</td>
<td>13.526</td>
</tr>
<tr>
<td>N-RGO-3</td>
<td>85.163</td>
<td>2.994</td>
<td>11.843</td>
</tr>
<tr>
<td>N-GR</td>
<td>97.754</td>
<td>0.248</td>
<td>1.998</td>
</tr>
</tbody>
</table>

Considering that the pressure will be further increased to cause some danger if we fabricated N/F-HC-X (X>2), a contrast experiment has been conducted to obtain N doped carbon materials with similar graphitization degree and incremental N doping lever to clarify the reason why we aimed at high doping level. We fabricated a series N doped reduced graphene oxides (labeled as N-RGO-X, where X represents the amount of NaN₃ addition (g) when 0.3 g GO was added) via NaN₃/GO deflagration. And N-GR referred to the graphene treated by NaN₃ deflagration. It can be observed from the almost same I_D/I_G intensity ratios in Fig. S13a that N-RGO samples showed similar graphitization degrees, which of course are worse than that of N-GR. As shown in Table S1, N-GR contained only 0.248 at% N dopant, which is far more less than those of N-RGO series samples (1.808 at%, 2.181 at% and 2.994 at% for N-RGO-1, N-RGO-2 and N-RGO-3, respectively). From Fig. S13b, it can be observed that N-RGO series samples show better ORR activity than N-GR due to their higher N doping levels although they exhibit lower graphitization degrees. Additionally, it also can be observed that the ORR activities of N-RGO increase with their N doping levels. All the results above indicate that the ORR activities of N doped carbon materials increase with their N doping levels when they possess similar graphitization degrees. Therefore, we designed the NaN₃/C₅F₅N deflagration method to prepare N/F co-doped carbon hollow nanospheres with both high doping level and graphitization degree to exhibit excellent ORR activities.

**References:**