Electronic Supplementary Information for

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

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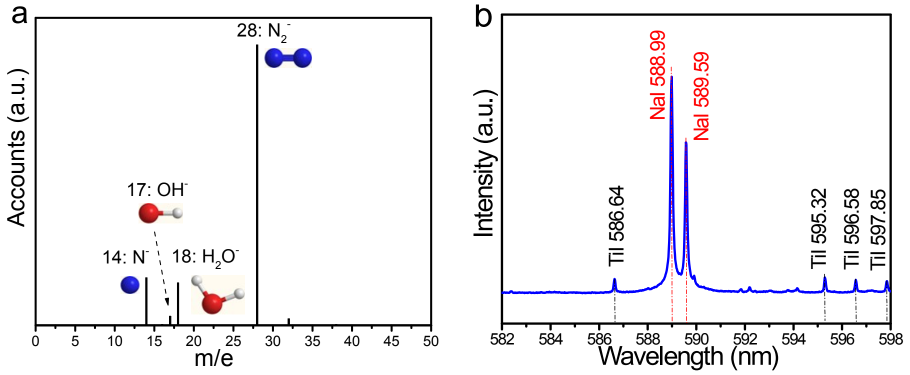

Figure S1. (a) Mass spectra and (b) emission spectra of NaN_3/TiO_2 deflagration generated by a 532-nm laser at 90 Jcm^{-2}.[1]

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.

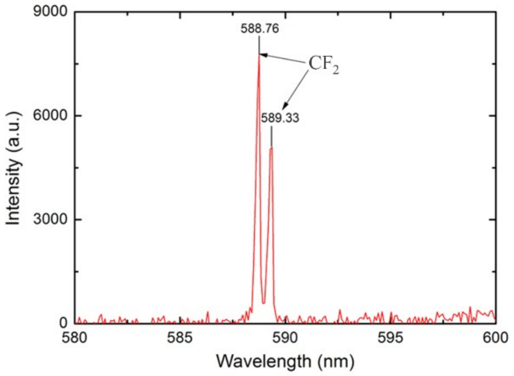

Figure S2. Emission spectra of Si/PTFE deflagration.[2]

The deflagration reaction of Na nanoclusters capturing partial F from C_5F_5N 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_5F_5N deflagration process.

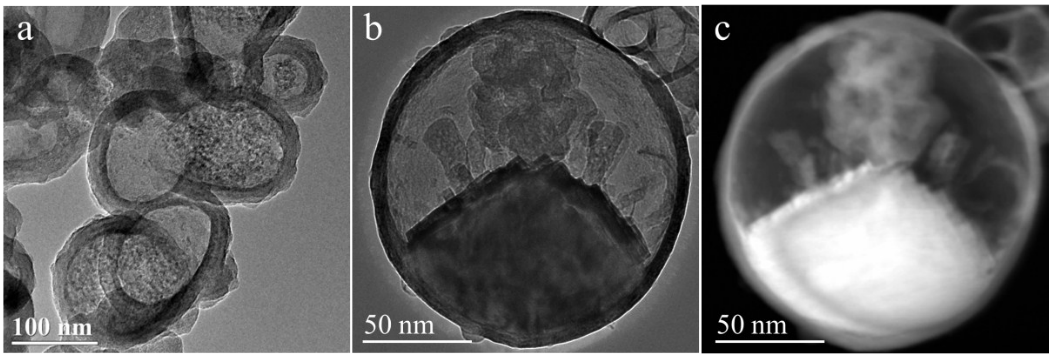

Figure S3. TEM (a-b) and STEM (c) images of the N/F-HC-2 sample without being washed with deionized water.

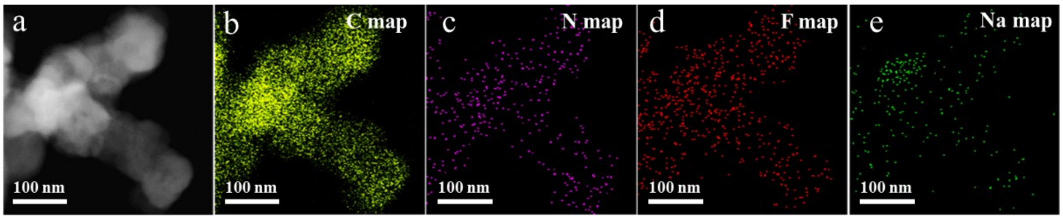

Figure S4. (a) TEM image and (b-f) C, N, F and Na mapping of unwashed N/F-HC-2 sample.

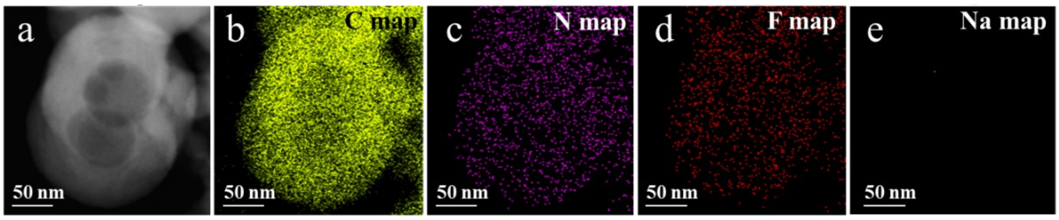

Figure S5. (a) TEM image and (b-f) C, N, F and Na mapping of N/F-HC-2 sample after washed.

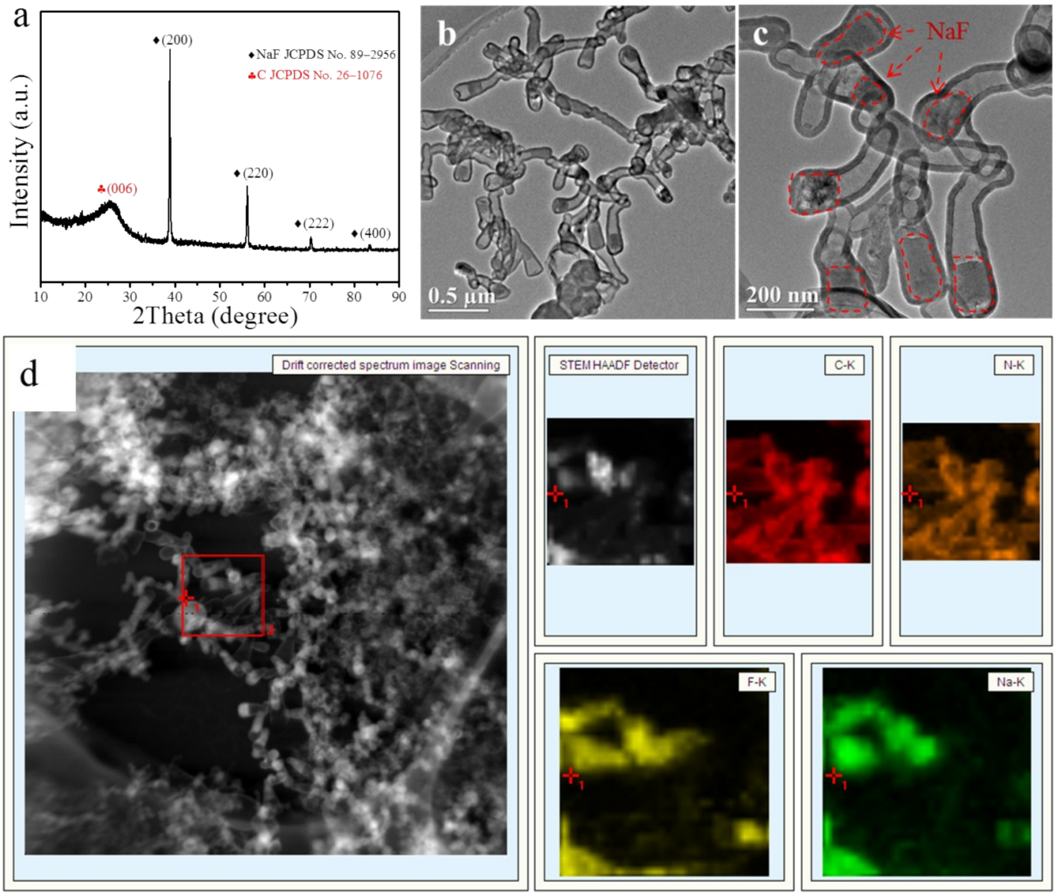

Figure S6. XRD pattern (a), TEM images (b-c) and Carbon, Nitrogen, Fluorine, Sodium elemental mapping (d) of raw N/F-HC-0.5 sample without being washed with deionized water.

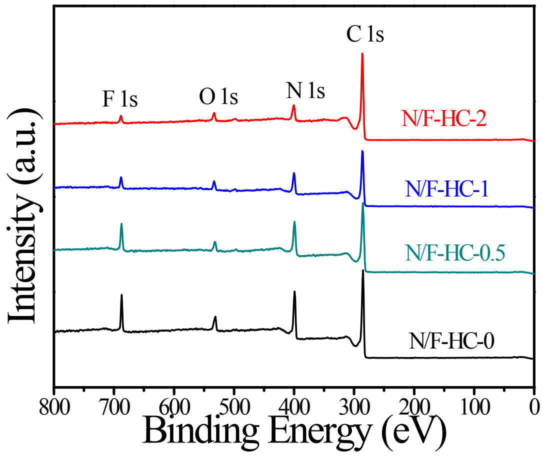

Figure S7. XPS spectra of the N/F-HC-X samples

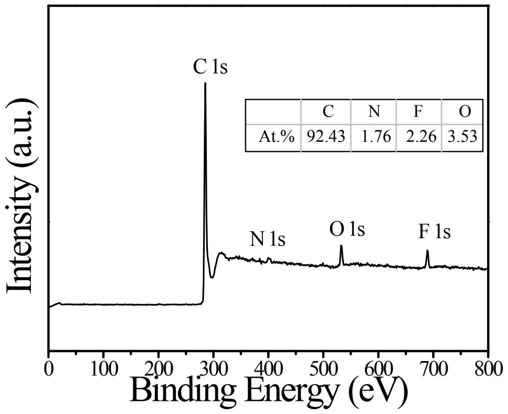

Figure S8. XPS spectra of the obtained carbon product from NaN_3 deflagration with polytetrafluoroethylene. Inset is the C, N, F and O elemental percentage in the sample.

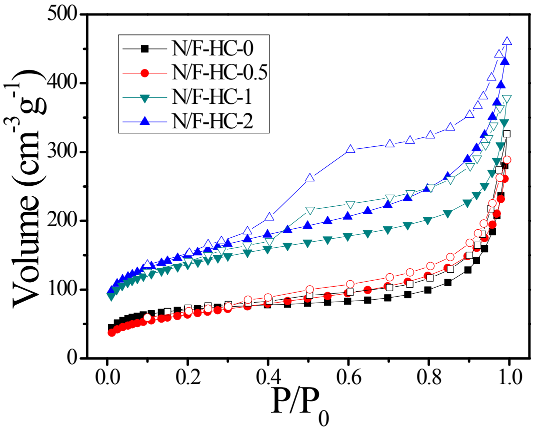

Figure S9. N_2 adsorption/desorption isotherms of N/F-HC-X samples.

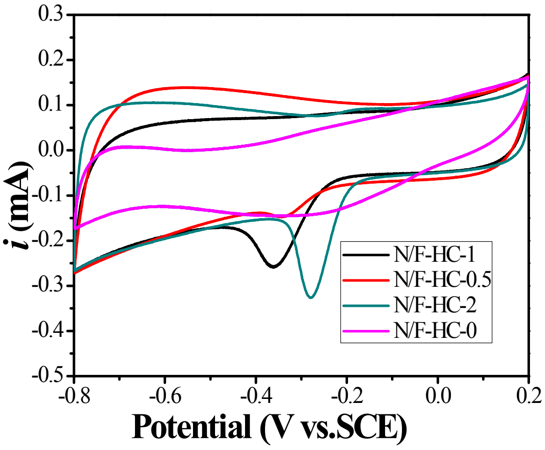

Figure S10. CV curves of N/F-HC-X samples in O_2 saturated 0.1 M KOH aqueous solution with a scan rate of 50 mV s^{-1}.

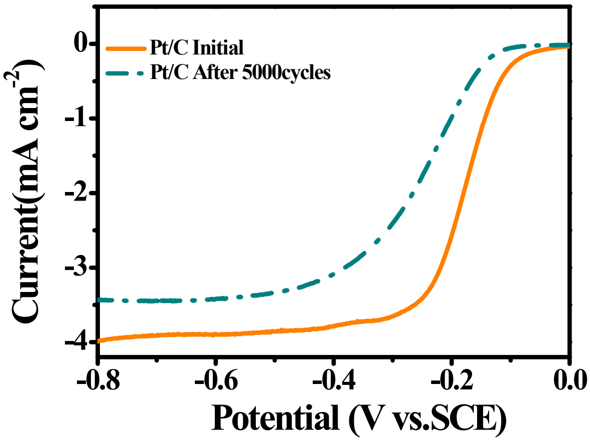

Figure S11. LSV curves of Pt/C before and after cycling for 5000 cycles with a rotation rate of 1600 rpm.

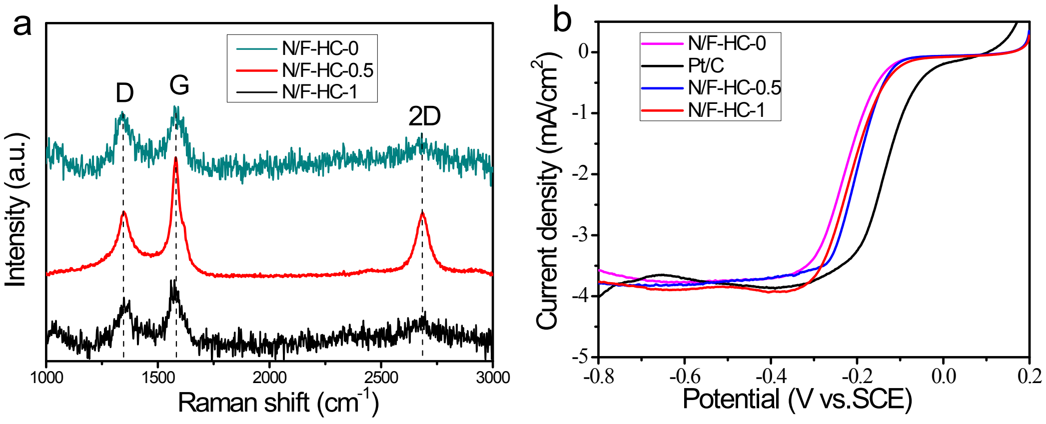

Figure S12. (a) Raman spectra and (b) LSV of N/F-HC-0, N/F-HC-0.5 and N/F-HC-1 samples after calcinated at 900 °C for 2 h

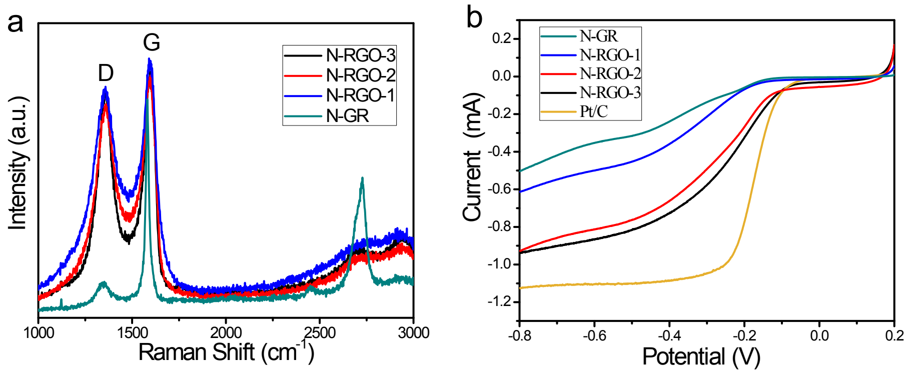

Figure S13. (a) Raman spectra and (b) LSV of N-GR and N-RGO samples

Table S1. The element compositions and contents in N-RGO and N-GR samples

Sample	C (at%)	N (at%)	O (at%)
N-RGO-1	76.476	1.808	21.725
N-RGO-2	84.292	2.181	13.526
N-RGO-3	85.163	2.994	11.843
N-GR	97.754	0.248	1.998

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 NaN_3 addition (g) when 0.3 g GO was added) via NaN_3/GO deflagration. And N-GR referred to the graphene treated by NaN_3 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 NaN_3/C_5F_5N 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:

1 Y. S. Liu, S. X. Ouyang, W. C. Guo, H. H. Zong, X. D. Cui, Z. Jin and G. C. Yang, *Nano Res.*, 2018, DOI: 10.1007/s12274-018-2058-0.

2 Y. S. Liu, B. Gao, Z. Q. Qiao, Y. J. Hu, W. F. Zheng, L. Zhang, Y. Zhou, G. B. Ji, G. C. Yang, *Chem. Mater.*, 2015, **27**, 4319-4327.