Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Edges of graphene and carbon nanotubes with high catalytic performance for oxygen reduction reaction

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1. XPS spectra of graphene, F-graphene, MWCNTs and S-MWCNTs

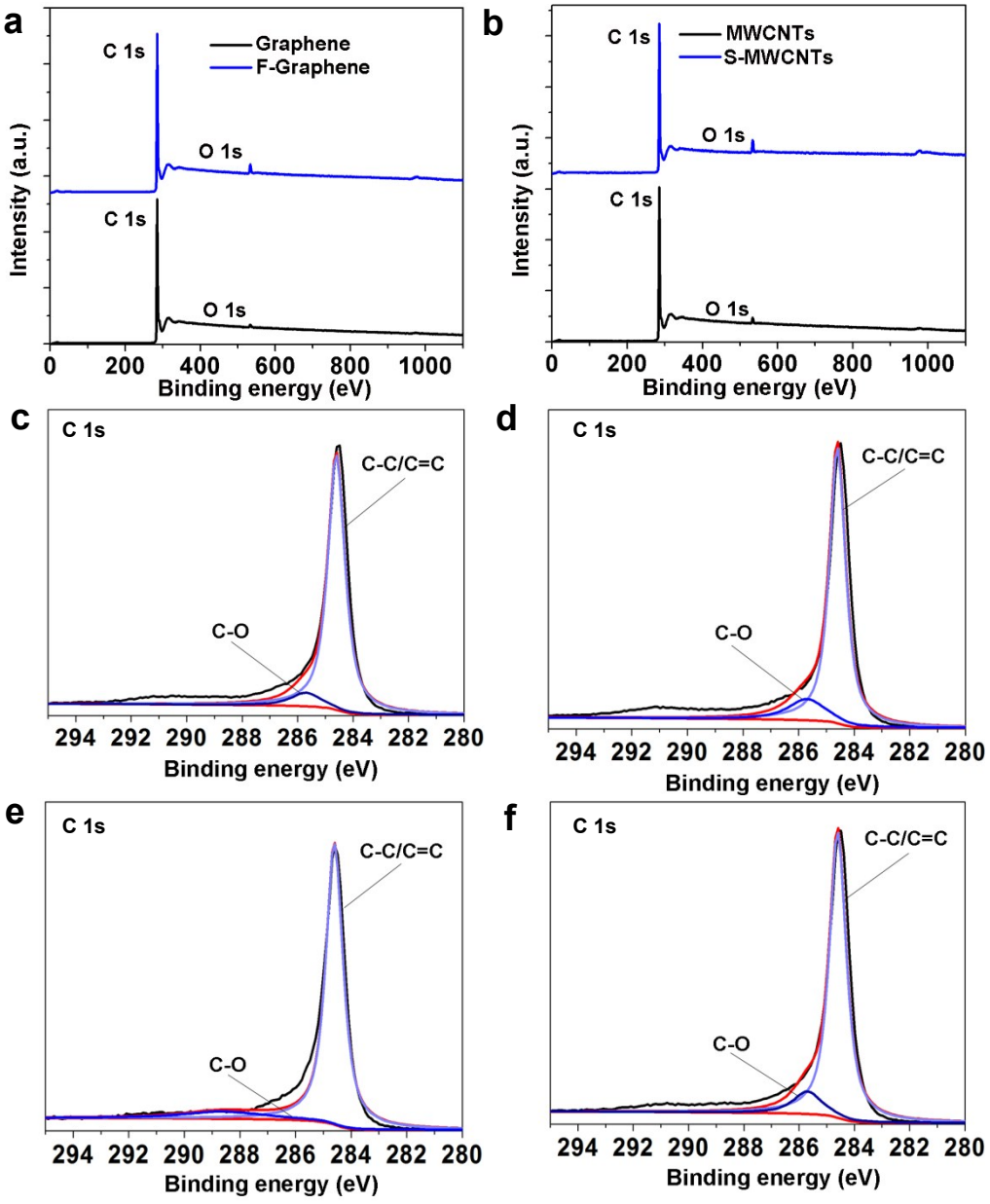

Figure S1. XPS spectra of (a) graphene and F-graphene and (b) MWCNTs and S-MWCNTs, C 1s of (c) graphene, (d)F-graphene, (e) MWCNTs and (f) S-MWCNTs.

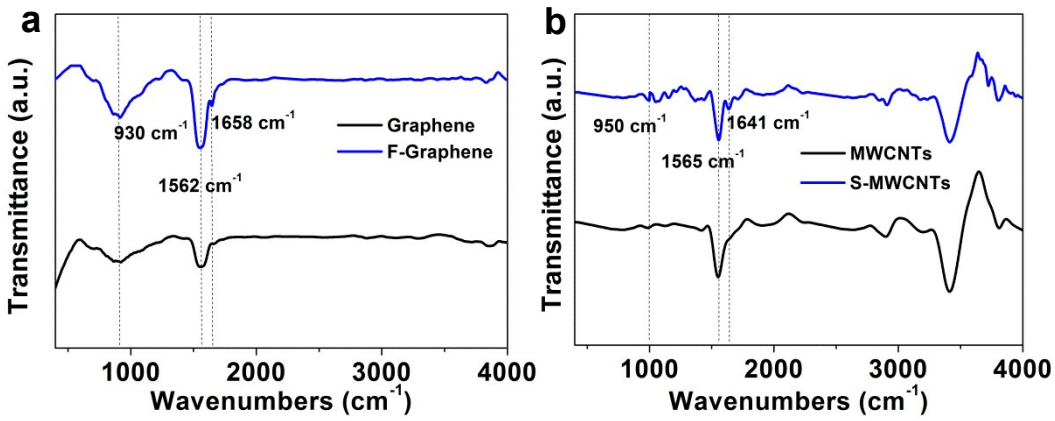

Figure S2. FTIR of (a) graphene and F-graphene and (b) MWCNTs and S-MWCNTs.

XPS spectra shows the graphene and F-graphene contain C and a small quantity of O atoms. The composition of graphene is composed of 99.5 % C atoms and 0.5 % O atoms, while the F-graphene consists of 96.7 % C atoms and 3.3% O atoms, which the O contain is around 5.5 time higher than graphene, possibly attributed to O in the edge plane (Figure S1a). Similar phenomena were also found to MWCNTs and S-MWCNTs. The MWCNTs and S-MWCNTs consist of 99.5%, 95.4 % C and 0.5%, 4.6%O, respectively (Figure S1b).

C1s XPS spectra of the samples show two peaks. The strong peak at around 284.5 eV, can be assigned to typical graphite spectrum (C-C, C=C). The weak peak at 285.7 eV, attributed to C=O. The intensity of C=O of F-graphene, S-MWCNTs is stronger than that of original graphene, MWCNTs, respectively (Figure S1 c, d, e and f). It have been demonstrated that C=O group of carbon nano materials in the edge benefits to improve the ORR performance, making F-graphene, S-MWCNTs exhibiting better ORR catalytic activity.[1]

FTIR spectra of graphene and F-graphene show the bands at 930 cm^{-1}, 1562 cm^{-1} and 1658 cm^{-1}, which indicating the presence of C-C, C=C and C=O, respectively (Figure S2a). The IR band of F-graphene at 1658 cm^{-1} (C=O) is stronger than that of graphene, attributed to its higher content of O atoms. The same phenomena can be found in MWCNTs and S-MWCNTs (Figure S2b), agreeing well with XPS analysis. The tested samples show the bond at around 3460 cm^{-1} indicating the existing of OH due to the adsorption of the H_2O from air.[2]

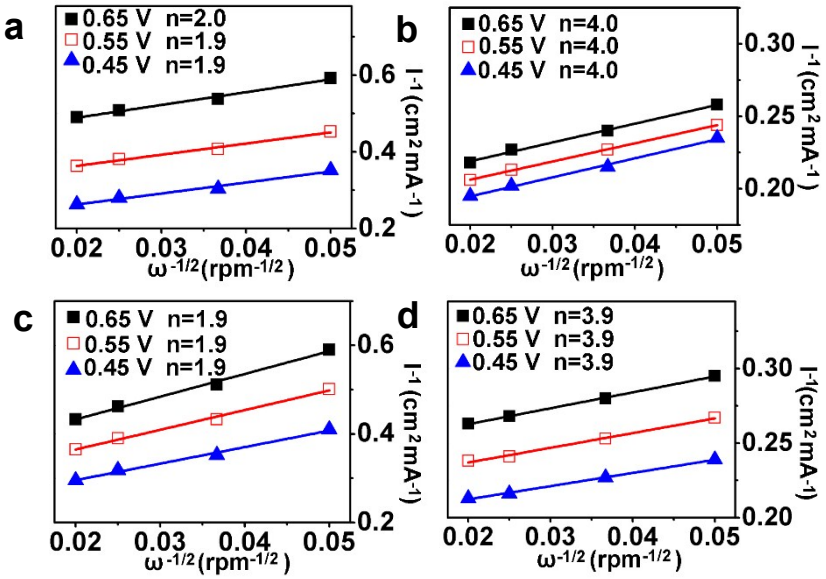

Figure S3. Koutecky–Levich plots of I^{-1} vs. $\omega^{-1/2}$ of (a) graphene, (b) F-graphene, (c) MWCNTs, and (d) S-MWCNT electrodes in a 0.1 M KOH solution saturated with oxygen at different potentials.

2. Metallic impurities of graphene, F-graphene, MWCNTs and S-MWCNTs

Table S1. Content of metallic impurities (ppm) in the graphene, MWCNTs, F-Graphene, S-MWCNTs after purification determined by an atomic absorption spectrometer ICE 3500

Impurity	graphene	MWCNTs	F-Graphene	S-MWCNTs
Mn	4.5	1.2	3.6	0.4
Fe	22.6	7.8	16.1	6.5
Co	0.3	23.7	/	11.1
Ni	11.2	19.2	7.5	18.0
Cu	3.1	1.2	1.7	0.8

3. Optimized adsorption geometries for side-on adsorption of O_2 at the zigzag edge and basal plane of graphene

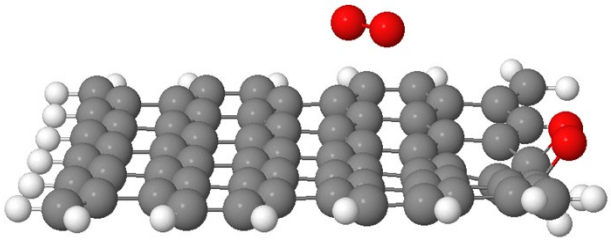

Figure S4. Optimized adsorption geometries for side-on adsorption of O_2 at the zigzag edge and basal plane of graphene.

4. Calculated barrier of each steps of ORR reactions on the H and COC terminated zigzag graphene edge

Table S2. Calculated barrier of each steps of ORR reactions on the H and COC terminated zigzag graphene edge.

	H terminated		COC terminated	
	ΔG	E_a	ΔG	E_a
$O_{2(ads)} + H_2O + e^- \rightarrow OOH_{(ads)} + OH^-$	-0.23	0.63	-0.35	0.63
$OOH_{(ads)} + e^- \rightarrow O_{(ads)} + OH^-$	-0.86	0.64	-1.82	0.31
$O_{(ads)} + H_2O + e^- \rightarrow OH_{(ads)} + OH^-$	-0.16	0.68	0.07	0.80
$OH_{(ads)} + e- \rightarrow OH^-$	-0.13	1.13	-0.88	0.73

Reference

1. D. H. Deng, L. Yu, X. L. Pan, S. Wang, X. Q. Chen, P. Hu, L. X. Sun and X. H. Bao, *Chem. Commun.,* 2011, **47,** 10016.
2. C. Z. Zhu, S. J. Guo, Y. X. Fang and S. J. Dong, *ACS Nano,* 2010, **4,** 2429.