Supporting Information

Unravelling the Role of Iron Carbide in ORR Catalysts for Rechargeable Zinc-Air Battery: A Comprehensive Kinetics & Mechanistic Study

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Estimation of Number of Electron Transferred

The fraction of H_2O_2 produced can be calculated from the equation given below:

$$\%H_2O_2 = \frac{2I_R/N}{I_D + I_R/N}$$

$$n = \frac{4I_D}{I_D + I_R/N}$$

Where, I_D and I_R are the disk and ring currents and N is the collection efficiency of the ring.

Rate constant Calculation

The equations developed by Hsueh et al. to estimate the ORR rate constants from the disk and ring currents of RRDE voltammograms are:

$$k_1 = m_2 Z_1 \frac{b_1 N - 1}{b_1 N + 1} \qquad k_2 = \frac{2m_2 Z_1}{b_1 N + 1} \qquad k_3 = \frac{m_1 Z_2 N}{b_1 N + 1}$$

Where k_2 and k_3 are the kinetic rate constants for the reduction of oxygen to hydrogen peroxide and to water, respectively, and k_1 is the kinetic rate constant for direct four-electron reduction to water. Here, I_D and I_R are the disk and ring currents, I_{DL} is the limiting disk current, and ω is the rotational speed of the RRDE.

b_1 and m_1 represent the intercept and slope of I_D/I_R vs $\omega^{-1/2}$ plot, and m_2 represent the slope of the $I_{DL}/(I_{DL}-I_D)$ vs $\omega^{-1/2}$ plot. The constants Z_1 and Z_2 are calculated from the diffusion coefficient (D) and kinematic viscosity (v).

$$Z_1 = D_{O_2}^{2/3} v^{-1/6}$$

$$Z_2 = D_{H_2O_2}^{2/3} v^{-1/6}$$

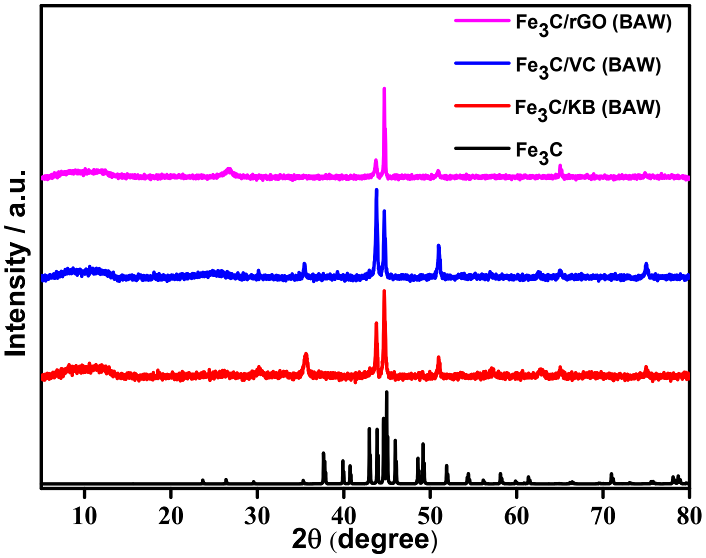

Figure S1. Powder X-ray diffraction patterns of Fe_3C and Fe_3C/C before acid wash (BAW)

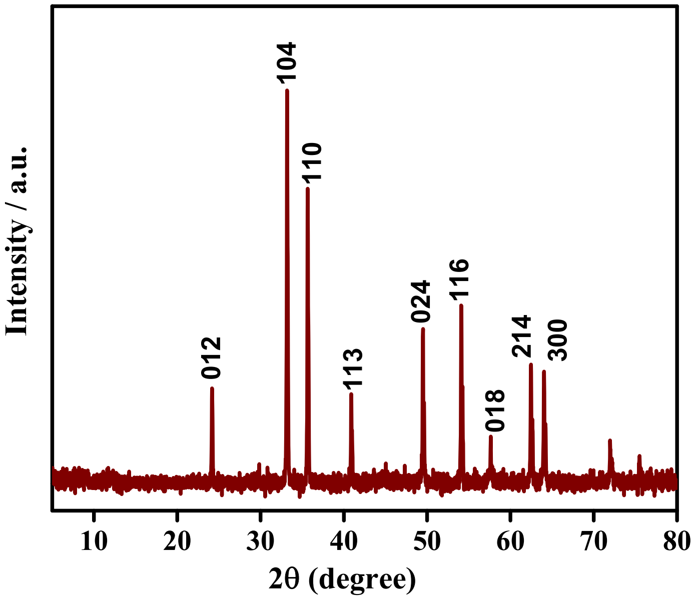

Figure S2. Powder X-ray diffraction pattern of Fe_3C/KB composite after the thermo-gravimetric analysis under air flow. The PXRD pattern clearly matches with α-Fe_2O_3 pattern (JSPDS 33-0664).

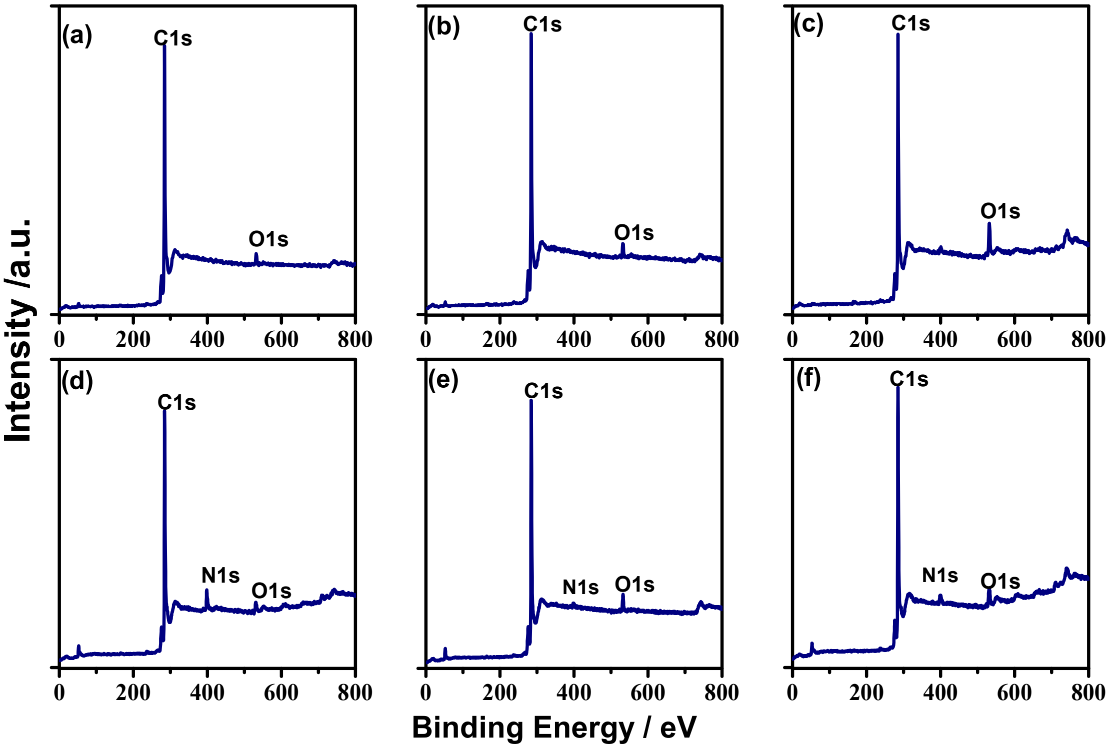

Figure S3. The X-ray photoelectron spectra of (a) Fe_3C/KB (b) Fe_3C/VC (c) Fe_3C/rGO and (d) Fe_3C/NKB (e) Fe_3C/NVC (f) Fe_3C/NrGO composites.

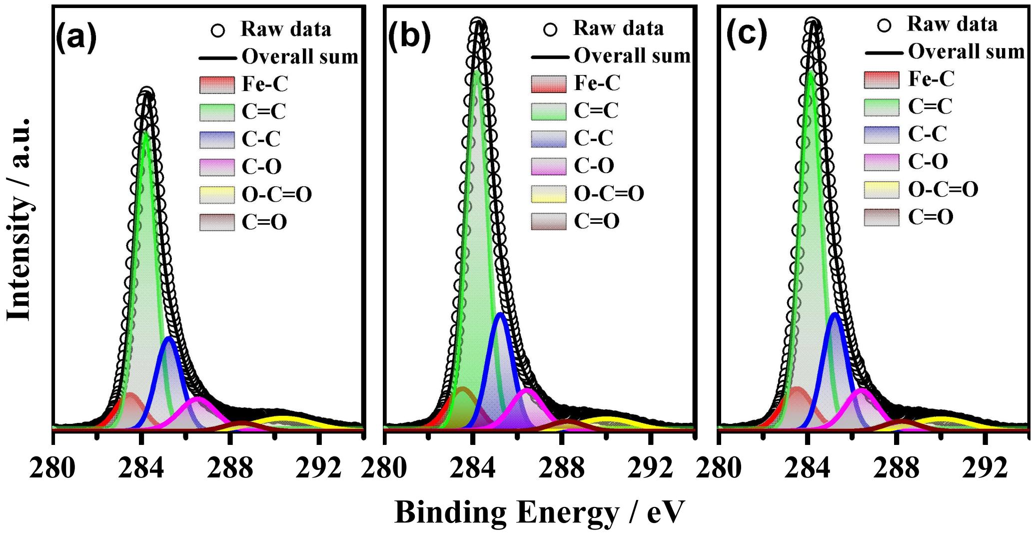

Figure S4. The C1s X-ray photoelectron spectra of (a) Fe_3C/KB (b) Fe_3C/ VC (c) Fe_3C/rGO composites.

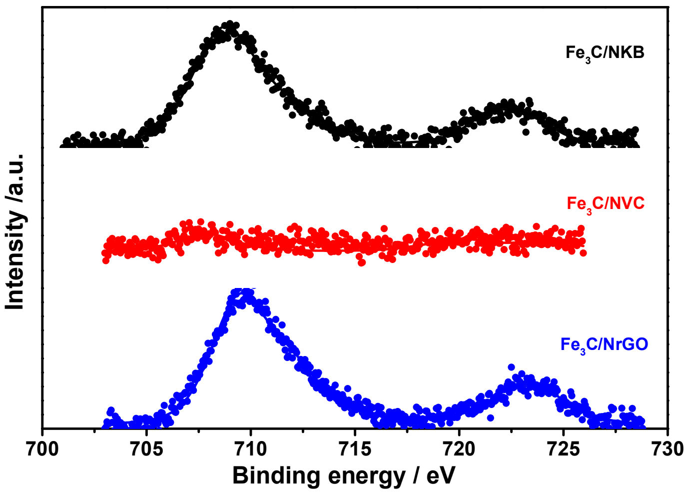

Figure S5. Fe-2p X-ray photoelectron spectra of Fe$_3$C/NC compounds.

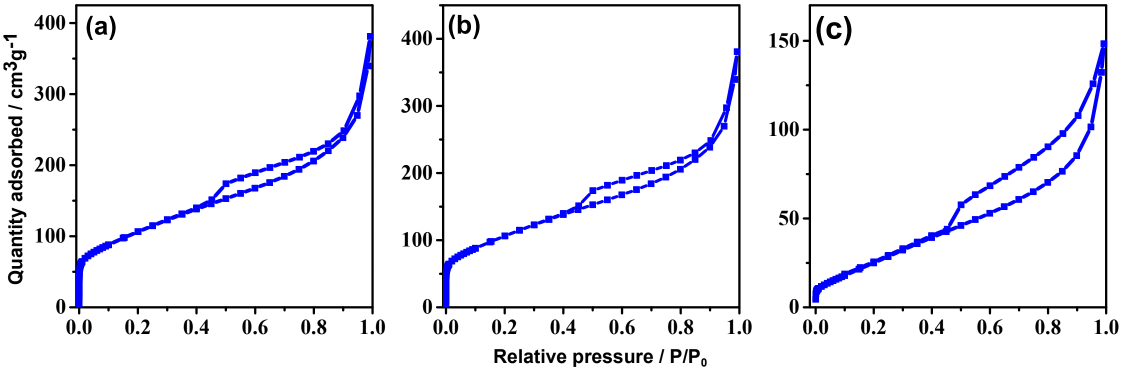

Figure S6. BET isotherms of (a) Fe_3C/KB(BAW) (b) Fe_3C/VC(BAW) (c) Fe_3C/rGO(BAW).

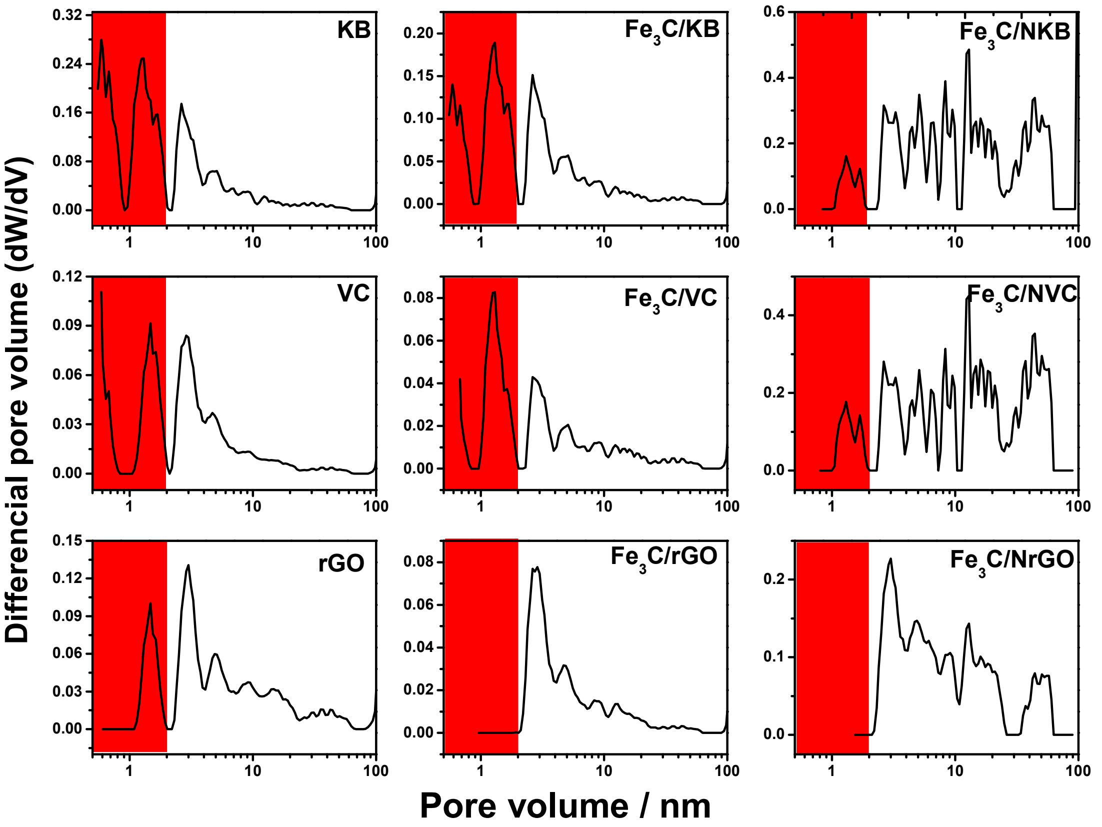

Figure S7. The pore size distribution curve comparison curve for bare carbon substrate and its composites. The highlighted (red) portion refers to the microporous region.

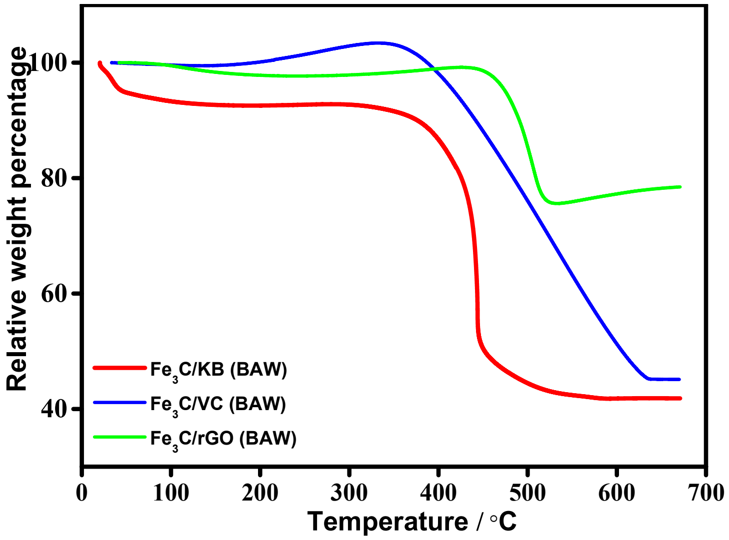

Figure S8. Thermogravimetric plots of Fe_3C/C composites before acid wash in air atmosphere.

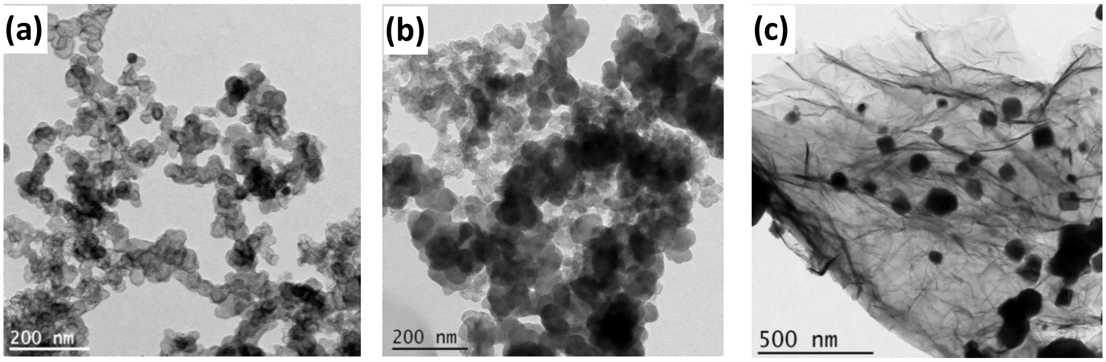

Figure S9. TEM images of the (a) Fe_3C/KB(BAW), (b) Fe_3C/VC(BAW) and (c) Fe_3C/rGO(BAW) (BAW refers to before acid wash)

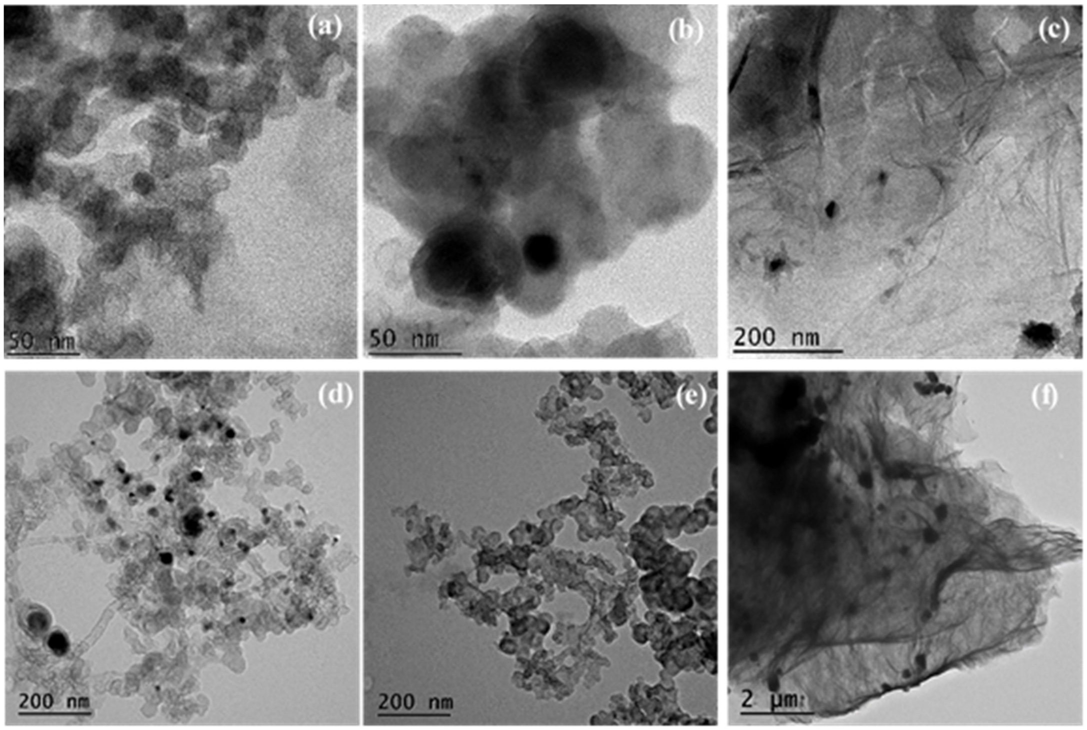

Figure S10. High resolution TEM images of (a) Fe_3C/KB, (b) Fe_3C/VC, (c) Fe_3C/rGO, (d) Fe_3C/NKB, (e) Fe_3C/NVC and (f) Fe_3C/NrGO

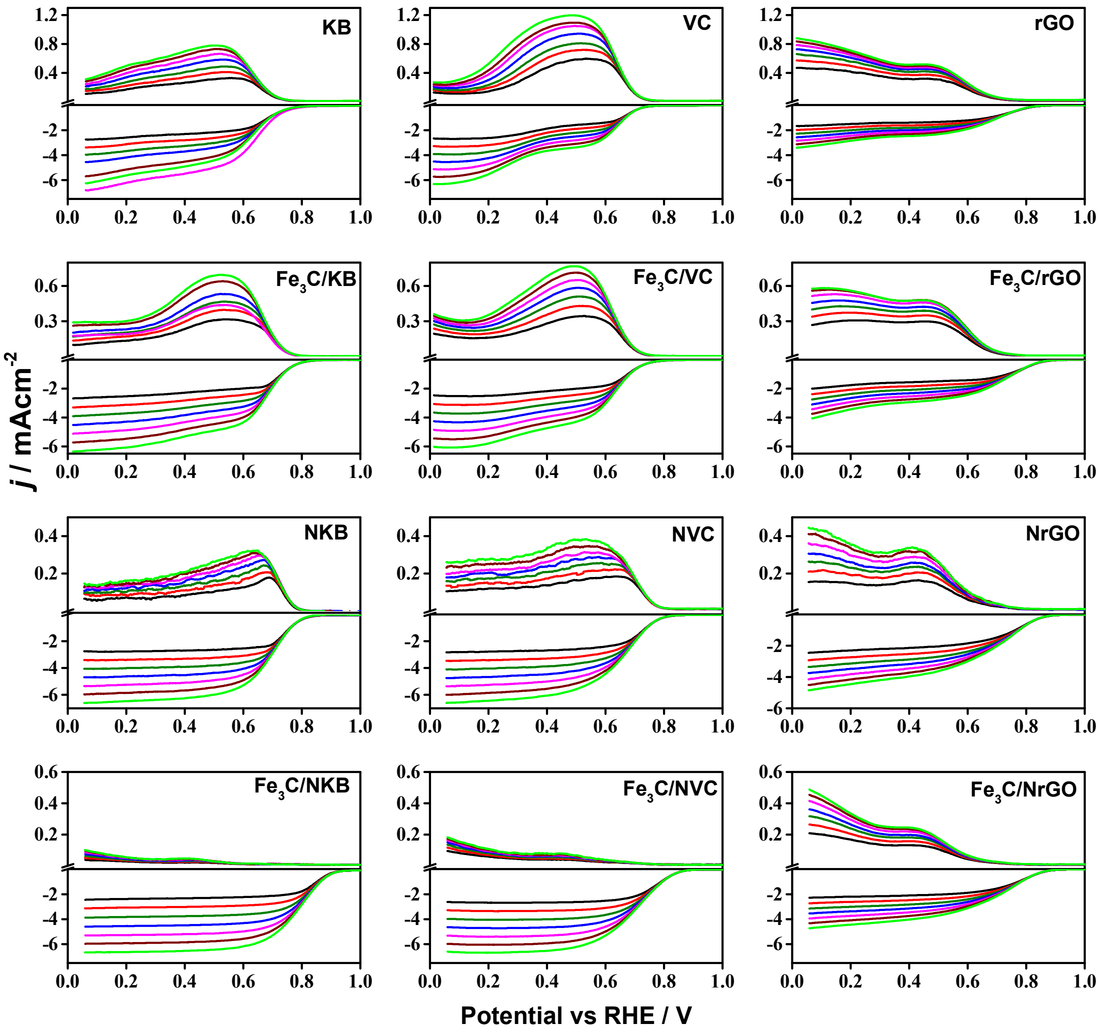

Figure S11. The linear sweep voltammograms of various materials used in this studies on GC disk electrode at O_2-saturated 0.1 M KOH electrolyte solution at different rotational speed. The upper and lower panel in each graph represent the ring and disk currents of RRDE voltammograms, respectively. The colours represents the different rotational speeds; 400 (black), 625 (red), 900 (dark green), 1225 (blue), 1600 (pink), 2025 (brown) and 2500 rpm (light green). Scan rate: 10 mVs^{-1}

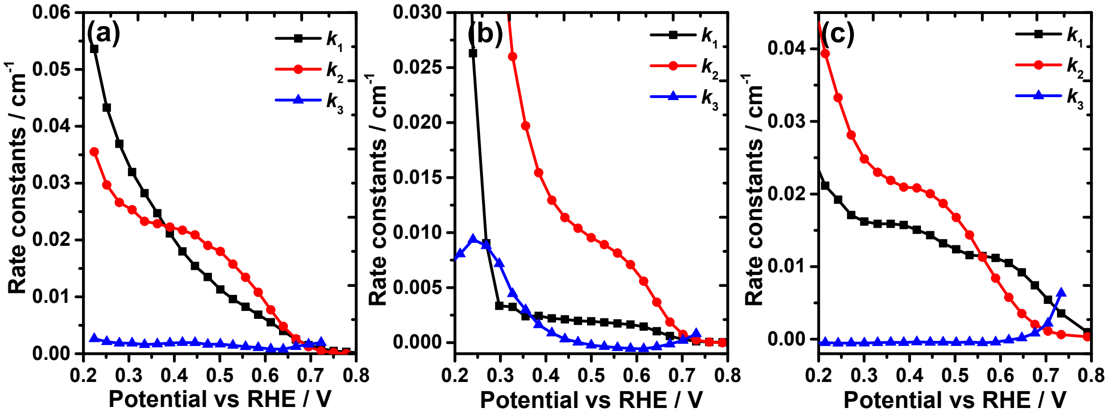

Figure S12. Potential dependent rate constants of the ORR on bare carbon supports (a) KB, (b) VC and (c) rGO

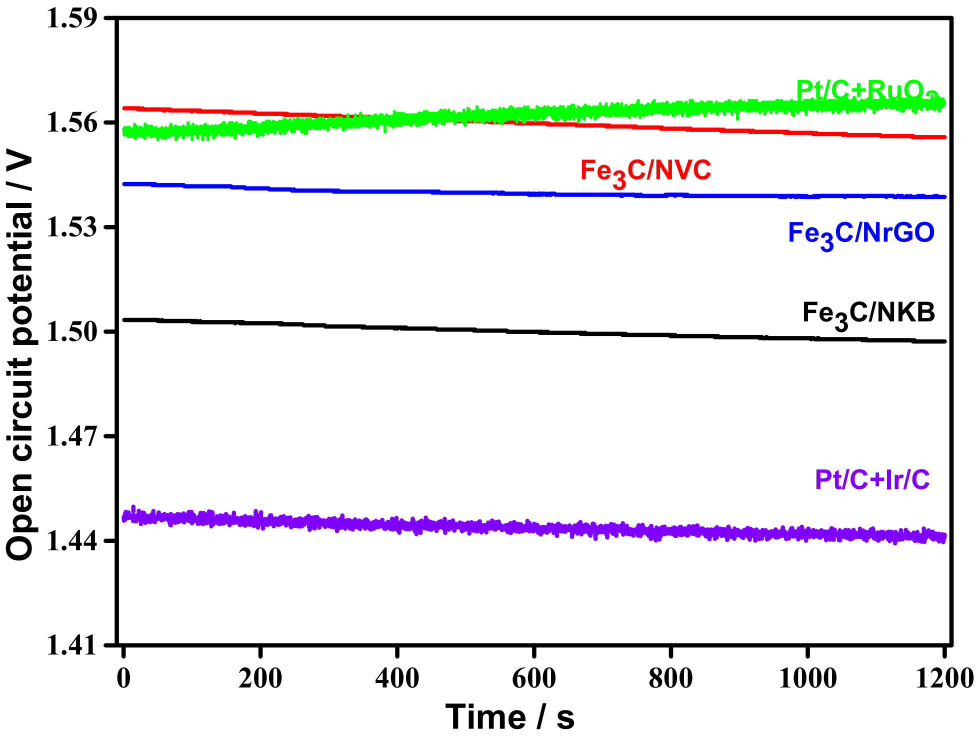

Figure S13. Measurement of open circuit potential of the Fe_3C/NC catalysts and the benchmark Pt/C+RuO_2 and Pt/C+Ir/C catalysts

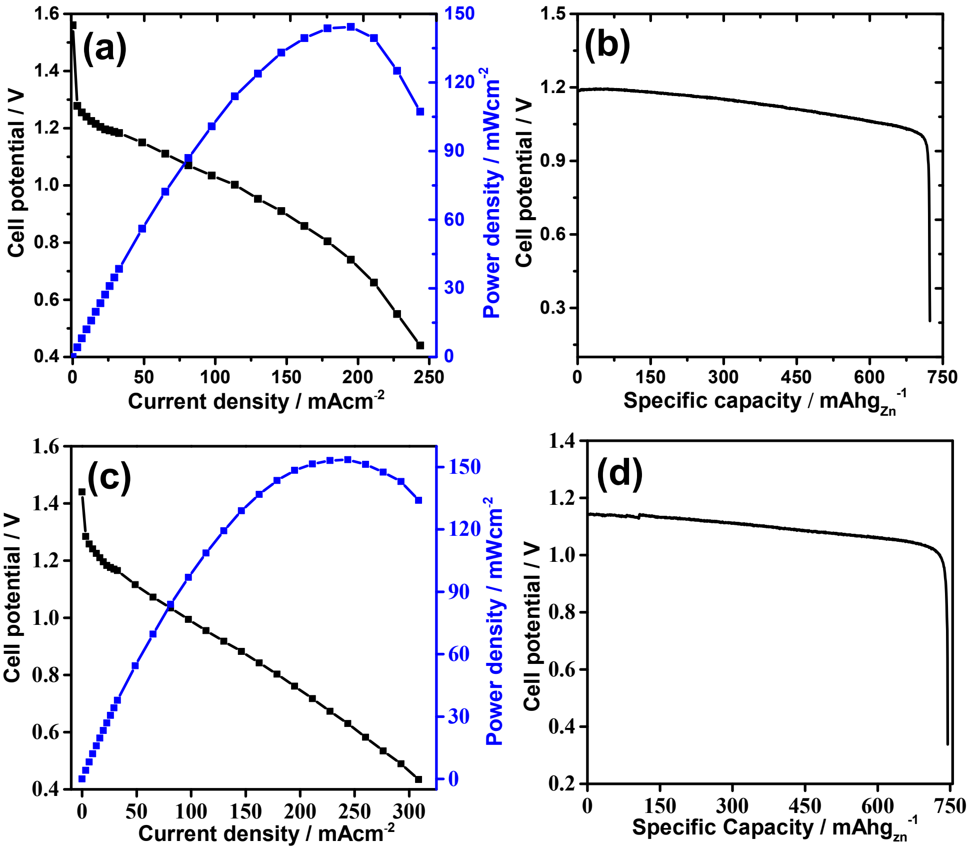

Figure S14. Discharge polarisation curve of the benchmark (a) Pt/C+RuO_2 and (c) Pt/C+Ir/C catalysts. The right y-axis and the blue line refers to the power density values. Discharge chronopotentiometery curves at constant current of 20 mAcm^{-2} of (b) Pt/C+RuO_2 and (d) Pt/C+Ir/C.

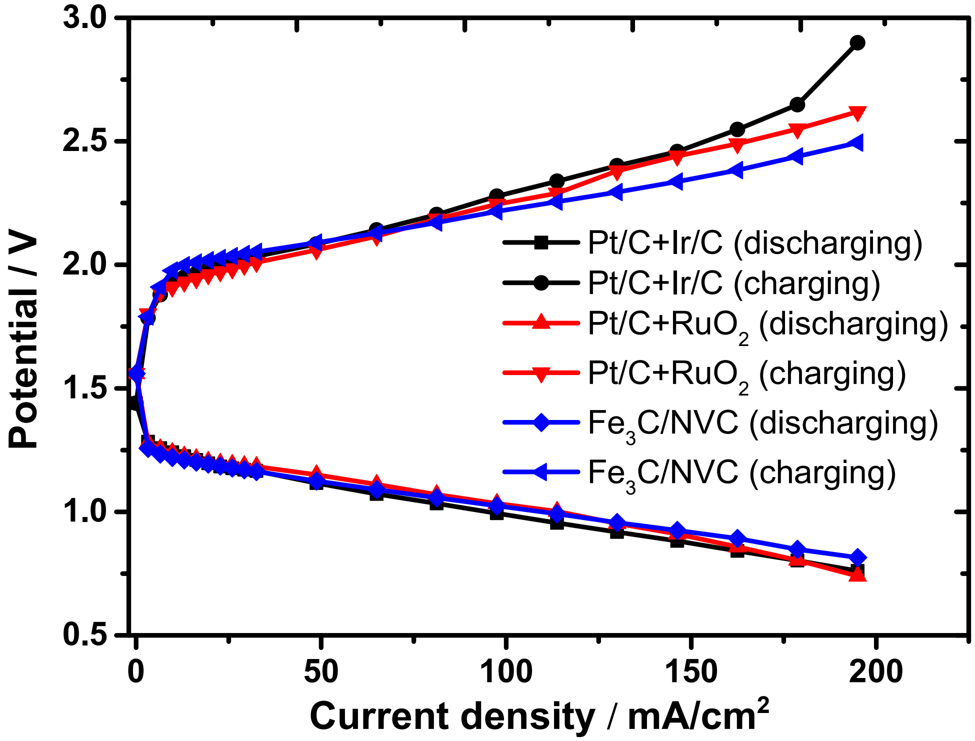

Figure S15. Polarisation curves (both Charge and discharge) of the benchmark Pt/C+RuO$_2$ (1:1) catalysts with the active and stable Fe$_3$C/NVC catalysts.

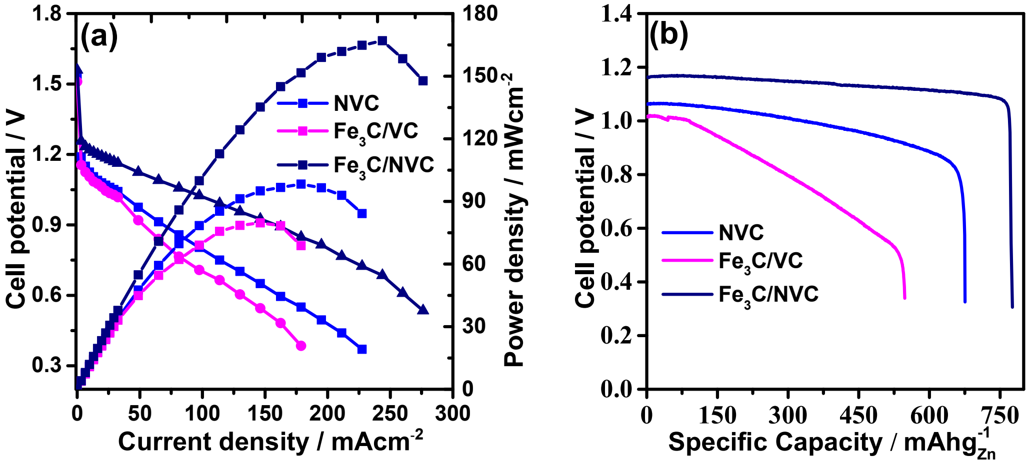

Figure S16. (a) Discharge polarisation curve of Fe_3C/NVC, Fe_3C/VC and NVC catalysts. (b) Specific capacity profile at the discharge current density of 20 $mAcm^{-2}$ of the Fe_3C/NVC, Fe_3C/VC and NVC catalysts.

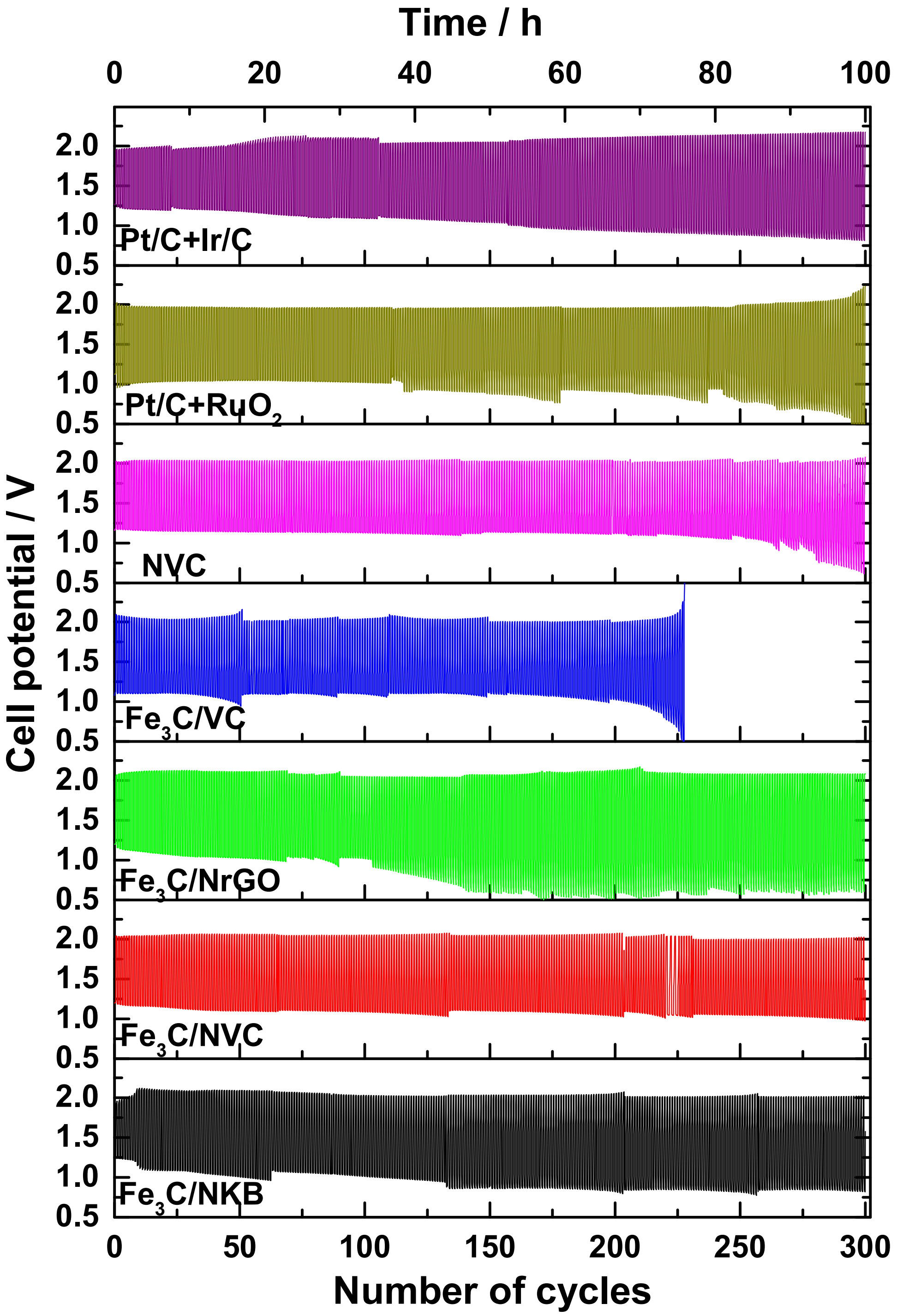

Figure S17. Galvanostatic charge-discharge cycles at 5 mAcm^{-2} current density with the charging and discharging time of 10 minutes each. The potential values above or below the dotted line indicating the degradation of the catalytic materials.

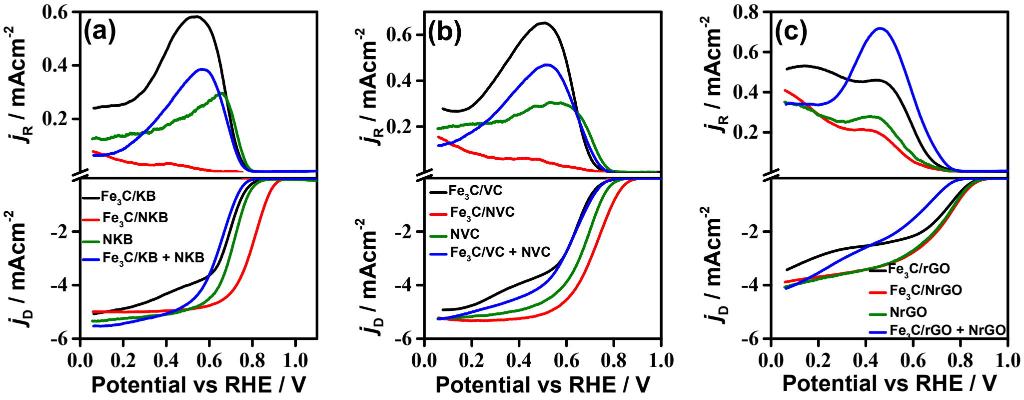

Figure S18. Linear sweep voltammograms of the ORR on the physical mixture of Fe_3C and NC (Fe_3C+NC, N refers to KB or VC or rGO) catalysts at the rotational speed of 1600 rpm and the scan rate of 10 mVs^{-1}. The other compounds like Fe_3C/C, Fe_3/NC and NC are shown to compare the ORR activity.

Table S1. Percentage of Fe-content and N-content from TG and CHN analysis.

Compound	%Fe (from TGA)	% N (CHN analysis)
Fe_3C/KB	2.7	
Fe_3C/VC	2.3	
Fe_3C/rGO	12	
Fe_3C/NKB	12	4.94
Fe_3C/NVC	2.6	1.20
Fe_3C/NrGO	34	2.95

Table S2.BET surface area obtained from N_2 sorption studies (BAW)

Compound	S_{total} (m^2 g^{-1})	$^{a}S_{\text{micro}}$ (m^2 g^{-1})	$^{b}S_{\text{meso}}$ (m^2 g^{-1})	$^{c}V_{\text{total}}$ (cm^3 g^{-1})	$^{d}V_{\text{micro}}$ (cm^3 g^{-1})	$^{e}V_{\text{meso}}$ (cm^3 g^{-1})
Fe_3C/KB(BAW)	378	3.42	165.86	0.590	0.017	0.118
Fe_3C/VC(BAW)	226	24.99	66.00	0.323	0.005	0.05
Fe_3C/rGO(BAW)	92	2.02	94.64	0.229	0.001	0.073

[a] microporous surface area

[b] mesoporous surface area

[c] Total pore volume

[d] microporous Volume obtained from T-plot

[e] mesoporous Volume from Barett-Joyner-Halenda (BJH)

Table S3. Elemental analysis data of N-doped carbon substrate.

Compound	%N	%C	%H
KB/NC	2.08	85.58	0.45
VC/NC	1.09	87.15	0.35
GO/NC	10.42	77.80	0.30

Table S4. Electrochemical Parameters of synthesised compounds.

S. No.	Composite	E_{onset} (V)[a]	$E_{½}$ (V)	j_{DL} (mA cm^{-2})[b]	n
1	Fe_3C	0.81	0.59	2.3	3
2	Fe_3C/KB	0.89	0.69	4.6	3.5
3	Fe_3C/VC	0.85	0.64	4.3	3.3
4	Fe_3C/rGO	0.92	0.73	2.6	2.9
5	Fe_3C/NKB	0.96	0.80	4.9	3.9
6	Fe_3C/NVC	0.90	0.72	5.3	3.9
7	Fe_3C/NrGO	0.95	0.73	3.5	3.5
8	N/KB	0.93	0.70	5.1	3.7
9	N/VC	0.88	0.67	5.0	3.6
10	N/rGO	0.94	0.71	3.6	3.9
11	KB900	0.86	0.68	4.6	2.5
12	VC900	0.79	0.62	3.7	2.8
13	rGO	0.89	0.68	2.2	2.7
14	Pt/C (20 μg$_{Pt}$cm^{-2})	0.99	0.86	5.4	3.95

[a] E_{onset} measured at which current density reaches 10 μAcm^{-2}

[b] j_{DL} values measured at 0.3V in case of all compounds for uniform comparison