ORR performance Test.

The ORR electrocatalytic activity of the samples was examined by using in a threeelectrode system on an electrochemical workstation (CHI 660D) in 0.1 M KOH electrolyte. Then 8 μ L of the homogeneous ink containing 5 mg of catalyst₃ 30 μ L Nafion solution and 1 ml of 3:1 v/v water/isopropanol mixed solvent was loaded onto a polished glass carbon (GC) disk electrode (5 mm in diameter, 0.196 cm²). The final loading for all catalysts on working electrode is 0.2 mg/cm². While the counter electrode and reference electrode were a Pt wire and an Ag/AgCl (filled with 3 M KCl solution) electrode, respectively. The cyclic voltammetry (CV) measurements for all catalysts in both N₂- and O₂-saturated KOH solutions were performed in the potential range of 0 to 1.2 V with a scan rate of 5 mV s⁻¹. For comparison of the effect of methanol crossover, the CV curves in O₂-saturated mixture solution containing KOH and methanol (KOH, 0.1 M; methanol, 3.0 M) were conducted. The polarization curves for ORR were scanned cathodically at a rate of 5 mVs⁻¹ with varying rotating speed from 400 rpm to 2500 rpm.

On the basis of the RDE data, the number of electron transfer (n) was calculated by the slopes of their Koutecky–Levich (K-L) plots' (J⁻¹ vs. $\omega^{-1/2}$) linear fit lines from the K-L equation¹:

$$1/J = 1/J_{K} + 1/J_{L} = 1/J_{K} + 1/B\omega^{1/2}$$
$$B = 0.62nFC_{o}(D_{o})^{2/3}v^{-1/6} \qquad J_{K} = nFKC_{o}$$

where J is the measured current density, J_K and J_L are the kinetic- and diffusionlimiting current densities, ω is the angular velocity, n is transferred electron number, F is the Faraday constant (96485 C mol⁻¹), D_o is the diffusion coefficient of O_2 (1.9×10⁻⁵ cm² s⁻¹), C_o is the bulk concentration of O_2 (1.2×10⁻⁶ mol cm⁻³), v is the kinematic viscosity of the electrolyte (0.01 cm² s⁻¹), and k is the electron-transfer rate constant.



Figure S1 (a, b, c) SEM images of S-600, S-700 and S-800, (d, e, f) TEM images of S-600, S-700 and S-800.



Figure S2 (a) TEM image of a single sphere of S-650. (b-f) the images of the corresponding elemental mapping of Zn, Co, N and C and EDS line profiles along the yellow line recorded on the single particle in image S2a.



Figure S3 (a and b) enlarged image of Fig 2c.



Figure S4 (a) XPS spectra of S-600, S-700 and S-800, (b) The XPS result of the C1s spectrum enlarged in image

3b, (c) Zn2p performed on S-600 and S-650, (d) Zn2p performed on S-600 S-650 and S-800.



Figure S5 The Koutecky–Levich plots of S-650 at different potentials (0 V - 0.7 V).



Figure S6 (a) LSV curves of Pt/C at different rotation rates, (b) the corresponding Koutecky–Levich plots at different potentials.



Figure S7 (a) Chronoamperometric responses of S-650 and Pt/C upon addition of 20mL methanol into 140mL O2saturated 0.1 M KOH at 0.45V. (b) Chronoamperometric responses of S-650 at 0.45 V.



Figure S8 (d) Durability test of S-650 after 1st and 5000th cycles.

Overall reaction	Reaction pathway				
$4 \text{ OH}^{-} \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^{-}$	$* + OH^{-} \rightarrow *OH + e^{-} (1)$				
(OER)	$*OH + OH^{-} \rightarrow H_2O + *O + e^{-}$ (2)				
	$*O + OH^- \rightarrow *OOH + e^-$ (3)				
	$*OOH + OH^- \rightarrow *O_2 + e^-$ (4)				
	$*O_2 \rightarrow * + O_2$ (5)				
$O_2 + 2H_2O + 4e^- \rightarrow 4 OH^-$	$O_2 + * \to O_2 * (1)$				
(ORR)	$O_2^* + H_2O + e^- \rightarrow OOH^* + OH^-$ (2)				
	$OOH^* + e^- \rightarrow O^* + OH^-$				
	(the four-electron pathway) or				
	$OOH^* + e^- \rightarrow OOH^- + *$				
	(the two-electron pathway)				
	(3)				
	$O^* + H_2O + e^- \rightarrow OH^* + OH^- (4)$				
	$OH^* + e^- \rightarrow OH^- + * \qquad (5)$				
	OOH* + e - OOH + *				

Table s1 Overall reaction equations of OER and ORR in alkaline solutions.²

Table s2 Comparison of the electrocatalytic activity of our materials with some newly reported metalic carbide electrocatalysts for ORR in alkalic media. Some of the information was not specified in the literature and was estimated according to data graphs.

Catalyst	Loading	Onset	Cathodic	Scan	Electrolyt	Current	Reference
	amount	Potential	peak	rate/	e	density	
	(mg cm ⁻	/V	potential/V	mV s⁻		(1600rpm)	
	2)			1		/ mA cm ⁻²	
S-650	0.2	0.912	0.814	5	0.1M KOH	3.72 (0V)	This work
Fe/Fe ₃ C@N-	0.71	0.969	0.724	50	0.1M KOH	About 4.9	3
graphitic layer						(0.164 V)	
Fe/Fe ₃ C@NGL	0.1	About	About 0.82	100	0.1M KOH	About 3.3	4
-NCNT		0.97				(0.164 V)	
Fe ₃ C@NG800-0.2	0.2	0.98	0.811	10	0.1M KOH	About 5.5	5
						(0 V)	
GC-WC nano	0.5	0.75	0.58	50	0.1M KOH	3.65 (0.15	6
powder						V)	
WC/N-C	N/A	About	0.674	20	0.1M KOH	About 3.25	7
		0.88				(0.64V)	
Fe ₃ C@NCNTs	0.6	1.074	N/A	10	0.1M KOH	3.1	8
						(-0.36 V)	

Catalyst	Loading amount	electrolyte	Overpotential at 10 mA cm ⁻²	Tafel	Ref.
	(mg cm ⁻²)		(mV)	plots	
Pt/C	0.344	1 M KOH	566	151.2	This work
Pt/C	0.71	0.1 M KOH	Above 630	N/A	3
Pt/C	0.1	0.1 M KOH	Above 830	N/A	4
Pt/C	~0.2	1 M KOH	About 620 (with IR	168	5
			corrected)		
Pt/C	0.2	1 M KOH	550	118	9
Pt/C	~0.2	0.1 M KOH	556 (with IR corrected)	127	10
Pt/C	0.2	0.1 M KOH	630	149	11

 Table S3 Commercial Pt/C electrocatalysts reported recently for OER in alkalic media. Some of the information was not specified in the

 literature and was estimated according to data graphs.

Table s4 Comparison of the electrocatalytic activity of our Commercial Pt/C electrocatalysts with some newly reported Pt/C electrocatalysts for ORR in alkalic media. Some of the information was not specified in the literature and was estimated according to data graphs.

Catalyst	Loading	Onset	Cathodic	Scan	Electrolyt	Current	Tafel	Referen
	amount	Potential	peak	rate/	e	density	plots	ce
	(mg cm ⁻²)	/ V	potential/V	mV		(1600rpm		
				s-1) / mA cm ⁻		
						2		
Pt/C	0.2	1.036	0.925	5	0.1M	4.93 (0V)	81	This
					КОН			work
Pt/C	0.2	N/A	N/A	N/A	0.1M	About	77	9
					КОН	4.55 (0.2		
						V)		
Pt/C	0.2	N/A	N/A	N/A	0.1M	About 5.1	65	5
					КОН	(0.1 V)		
Pt/C	0.24	About	About 0.92	5	0.1M	About 5.6	N/A	1
		1.03			КОН	(0.2 V)		
Pt/C	0.2	About	About 0.79	10	0.1M	About 5	69	11
		0.95			КОН	(0V)		

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