Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information

Boosting the ORR performance of modified carbon black by C-O bonds

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Chemicals: Carbon black (Vulcan XC72) was purchased from Cabot Corporation. $Zn(NO_3)_2·6H_2O$, $Co(NO_3)_2·6H_2O$, 2-methylimidazole, ethanol, KOH, HCl were A.R. and purchased from Sinopharm Chemical Reagent Co. Ltd. All reagents were used as received without further purification. The commercial Pt/C (20wt%) catalysts was purchased from Sigma-Aldrich (product number: 738549-1G).

Preparation of modified carbon black-3(MCB-3): MCB-3 was prepared by the pyrolysis of carbon black(Vulcan XC72) with the Zn, Co precursors and 2-methylimidazole mixture at 800°C for 4h in N_2 atmosphere. Briefly, 120mg of Vulcan XC72 in 10ml ethanol with 45mg of 2-methylimidazole(2-MI) in 1ml ethanol and the reaction mixture was kept for ultrasonic dispersion for 2min to accomplish the effective blending. Further, 82mg of zinc nitrate in 1ml ethanol and 29mg of cobalt nitrate in 1ml ethanol were added to the Carbon black-MI mixture and the final mixture was retained for mechanical stirring for 12h. After that, the MCB was collected by centrifuge (10000rpm, 5min) and washed another time with ethanol again. At last, the MCB was pyrolysed at 800^{o}C in a furnace under N_2 flow for 4h (temperature ramp: 5 ^{o}C/min).

Preparation of modified carbon black-1(MCB-1)

MCB-1 was prepared in a similar way as MCB-3 except that amount of 2-MI was 90mg in the step of precursors.

Preparation of modified carbon black-2(MCB-2)

MCB-2 was prepared in a similar way as MCB-3 except that amount of cobalt nitrate was 60mg in the step of precursors.

Preparation of modified carbon black-H(MCB-H)

MCB-H was prepared by soaking MCB-3 in 0.1M HCl solution for 8h. After that, the MCB-H was collected by centrifuge (10000rpm, 5min) and washed another time with ethanol again.

Preparation of modified carbon black-4(MCB-4)

120mg of Vulcan XC72 in 30ml ethanol with 500mg of polyvinyl pyrrolidone (PVP) and the mixture was kept for ultrasonic dispersion for 30min to accomplish the effective blending. After that, the carbon black was collected by centrifuge (10000rpm, 5min) and washed another time with ethanol again.

Then we put the carbon black into 400ml methyl alcohol with 0.823g zinc nitrate, 0.456g 2-MI and 0.297g cobalt nitrate, stirring for 24h. After that, the carbon black was collected by centrifuge (10000rpm, 5min) and washed another time with ethanol again. At last, the carbon black was pyrolysed at 800°C in a furnace under N_2 flow for 4h (temperature ramp: 5 °C/min).

Electrochemical tests: The electrochemical tests were performed in 0.1M /0.4M/0.7M/1.0MKOH solutions and conducted with a CHI650D electrochemical workstation using a three electrode configuration. Pt foil served as the counter electrode and Ag/AgCl electrode were used as the reference electrode. RHE potential was calculated as E(RHE) = E(vs Ag/AgCl) + 0.198 + 0.0592*pH. Before electrochemical test, the electrolyte solutions were purged with O_2 (or N_2) for at least 30mins. The cal-CoZIF-VXC72 catalysts (5.0mg) were first dispersed in 1 mL water/ethanol/Nafion

(5%) solutions (volume ratio:0.7:0.25:0.05) and sonicated for at least 30mins to prepare the ink, then 16uL of the ink was dropped on the surface of rotating disk electrode (0.196cm^2) and allowed to dry naturally. The loading amount of Co species was about 2.29 ug/cm^2 and Zn species was 0.56 ug/cm^2 determined by ICP-OES. The electrode of commercial Pt/C catalysts was prepared in a similar way and the loading amount of Pt species was 36.7ug/cm^2. The LSV plots were recorded by applying proper potential ranges at the scan speed of 10mV/s and the Tafel plots were recorded at the scan speed of 1mV/s at proper potential ranges. The electron transfer number (*n*) and kinetic current density (j_K) can be calculated from the Koutecky-Levich equation:

$$\frac{1}{j}=\frac{1}{j_L}+\frac{1}{j_K}=\frac{1}{B\omega^{1/2}}+\frac{1}{j_K}$$

$$B=0.62nFC_0D^{2/3}v^{-1/6}$$

where j is the measured current density, j_K and j_L are the kinetic and limiting current densities, ω is the angular velocity of the disk, n is the electron transfer number, F is the Faraday constant (96485 C/mol), C_0 is the bulk concentration of O_2 (1.2×10^{-6} mol/cm^3), D_0 is the diffusion coefficient of O_2 in 0.1 M KOH (1.9×10^{-5} cm^2/ s), and V is the kinematic viscosity of the electrolyte (0.01cm^2/s).

Characterizations: The X-ray diffraction (XRD) patterns were performed on a Bruker D8 ADVANCE X-ray powder diffractometer operated at 40 kV voltage and 40 mA current with Cu Kα radiation (λ = 1.5406 Å). The X-ray photoelectron spectroscopy (XPS) results were achieved by ESCALAB 250Xi (Thermo Fisher). The calibrations were done with respect to carbon C1s. The morphology and size of the products were determined by a Hitachi H-7700 transmission electron microscope

(TEM) at 100 kV, a JEOL 2100F HRTEM equipped with energy dispersive X-ray spectroscopy (EDS) at 200 kV, was used to perform high-angle annular-dark-field (HAADF)-STEM and EDS mapping. Inductively coupled plasma optical emission spectrometry (ICP-MS) was used to determine the composition of the mass loading for electrochemical test.

EXAFS measurements

The X-ray absorption find structure spectra data (Co K-edge) werecollected at 1W1B station in Beijing Synchrotron Radiation Facility (BSRF, operated at 2.5 GeV with a maximum current of 250 mA) and BL14W1 station in Shanghai Synchrotron Radiation Facility (SSRF, operated at 3.5 GeV with a maximum current of 250 mA), respectively. The data were collected at room temperature (Co K-edge in fluorescence excitation mode using a Lytle detector).

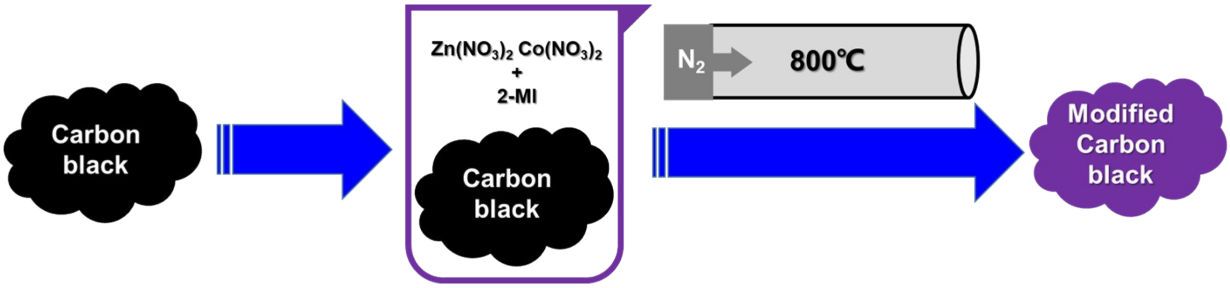

Figure S1 (a) schematic illustration of the synthesis of modified carbon black.

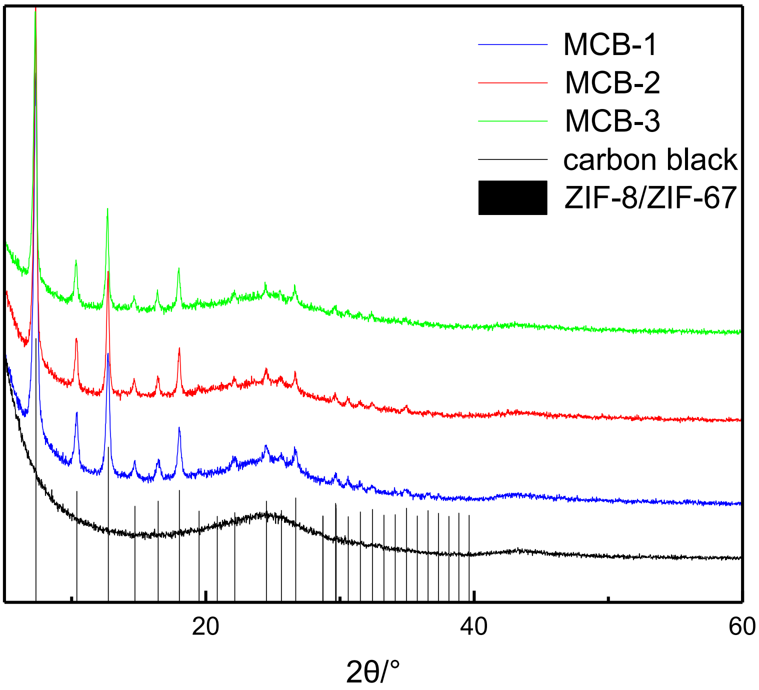

Figure S2 The XRD patterns of the carbon black (VXC72), MCB-1, MCB-2, and MCB-3.

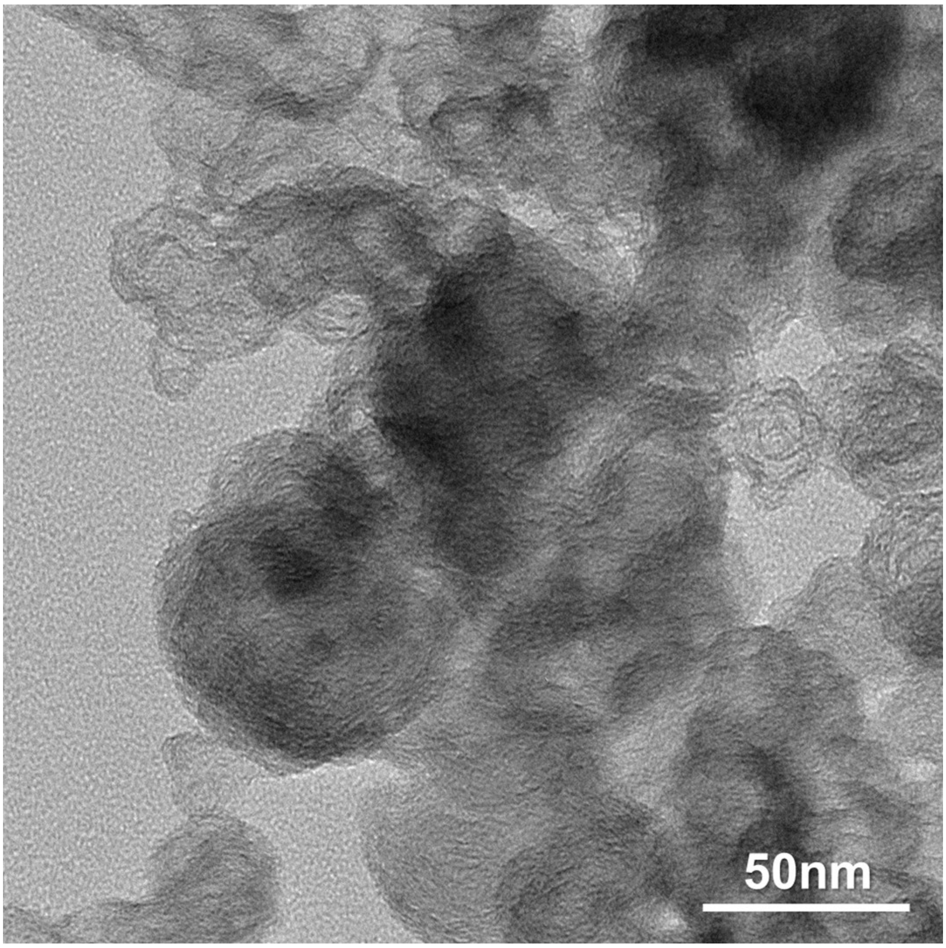

Figure S3 TEM images of the carbon black

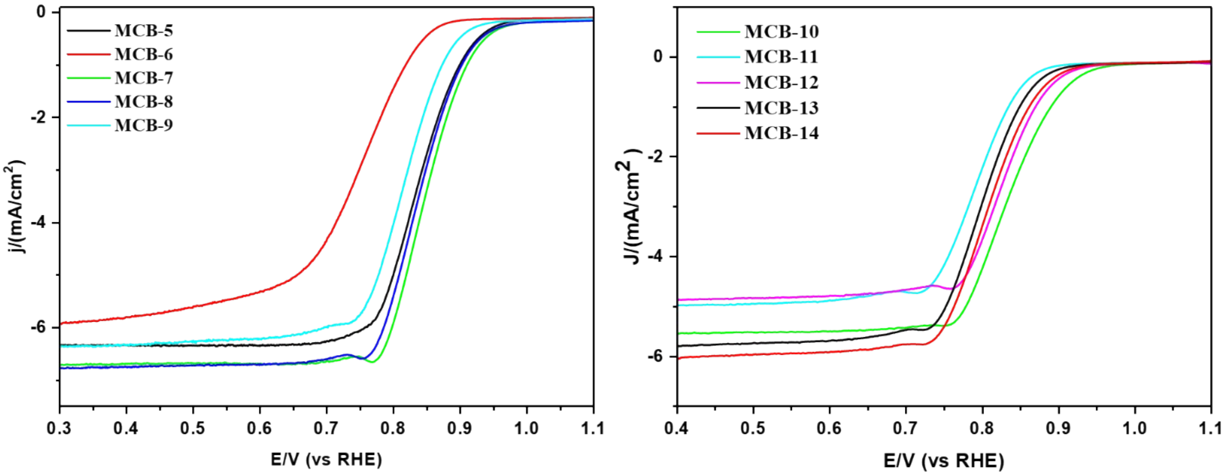

Figure S4 LSV curves of the modified carbon black and other comparative catalysts in 0.1M KOH.

	Step1	Step2	Time/h	concentration1	concentration2	remark
MCB-5	$Zn(NO_3)_2$+ $Co(NO_3)_2$	2-MI	24 Stir	0.028M + 0.01M	0.111M	Add $Zn(NO_3)_2$, $Co(NO_3)_2$ at the same time without ultrasonic
MCB-6	$Zn(NO_3)_2$+ $Co(NO_3)_2$	2-MI	24 Stir	0.028M + 0.01M	0.111M	Add $Zn(NO_3)_2$, ultrasonic for 5min,then add $Co(NO_3)_2$
MCB-7	$Zn(NO_3)_2$+ $Co(NO_3)_2$	2-MI	24 Stir	0.028M + 0.01M	0.111M	Add $Zn(NO_3)_2$, $Co(NO_3)_2$ at the same time ,ultrasonic for 5min
MCB-8	$Zn(NO_3)_2$+ $Co(NO_3)_2$	2-MI	24 Stir	0.028M + 0.01M	0.111M	Add $Zn(NO_3)_2$, stirrring for 5min,then add $Co(NO_3)_2$
MCB-9	$Zn(NO_3)_2$+ $Co(NO_3)_2$	2-MI	24 Stir	0.028M + 0.01M	0.111M	Add $Co(NO_3)_2$, stirrring for 5min,then add $Zn(NO_3)_2$

Table S1 Some syntheses of modified carbon black

	Step1	Step2	Time/h	concentration1	concentration2
MCB-11	$Zn(NO_3)_2$+ $Co(NO_3)_2$	2-MI	12	0.028M + 0.03M	0.111M
MCB-12	$Zn(NO_3)_2$+ $Co(NO_3)_2$	2-MI	12	0.028M + 0.01M	0.222M
MCB-13	$Zn(NO_3)_2$+ $Co(NO_3)_2$	2-MI	12	0.028M + 0.005M	0.111M
MCB-14	$Zn(NO_3)_2$+ $Co(NO_3)_2$	2-MI	12	0.056M + 0.02M	0.222M
MCB-10	$Zn(NO_3)_2$+ $Co(NO_3)_2$	2-MI	12	0.028M + 0.01M	0.111M

Table S2 Some syntheses of modified carbon black

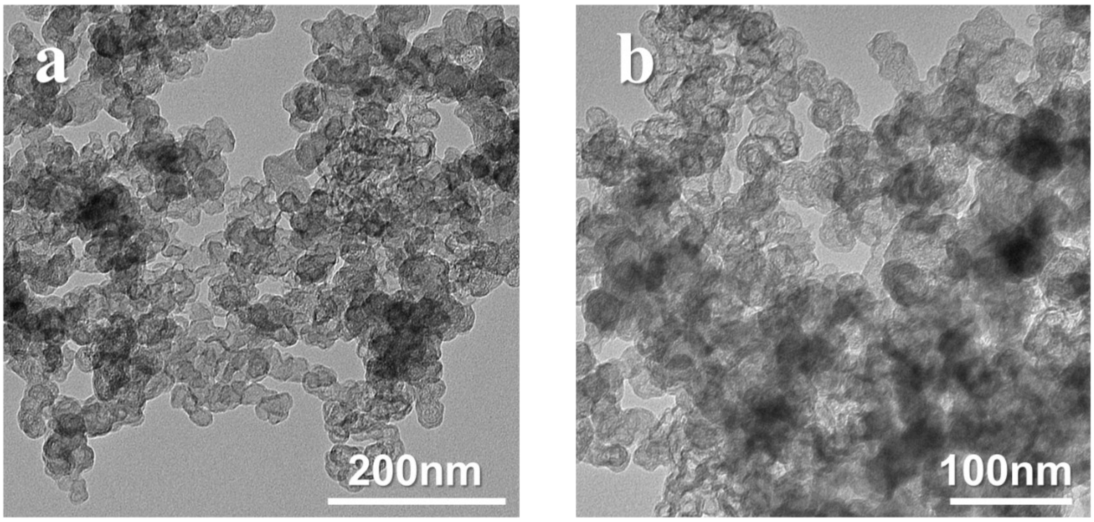

Figure S5 TEM images of the MCB-1(a), MCB-2(b).

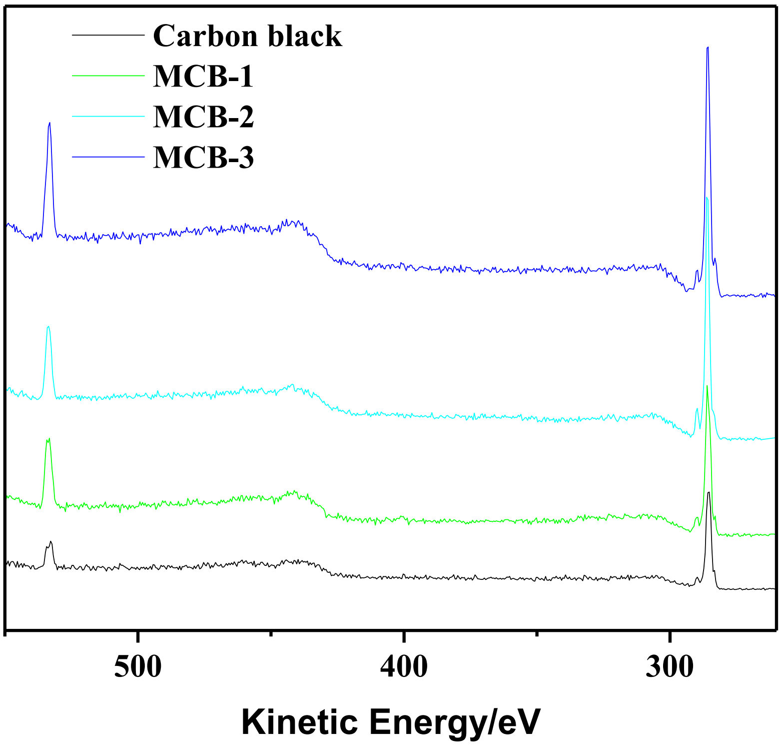

Figure S6 XPS survey spectra of cabon black, MCB-1, MCB-2 and MCB-3

	(O) %	(C) %	(N) %
Carbon black	0.328	98.582	0.377
MCB-1	0.539	98.145	0.542
MCB-2	0.741	98.027	0.514
MCB-3	1.171	97.206	0.528

Table S3 the C, O amounts of carbon black, MCB-1, MCB-2, MCB-3

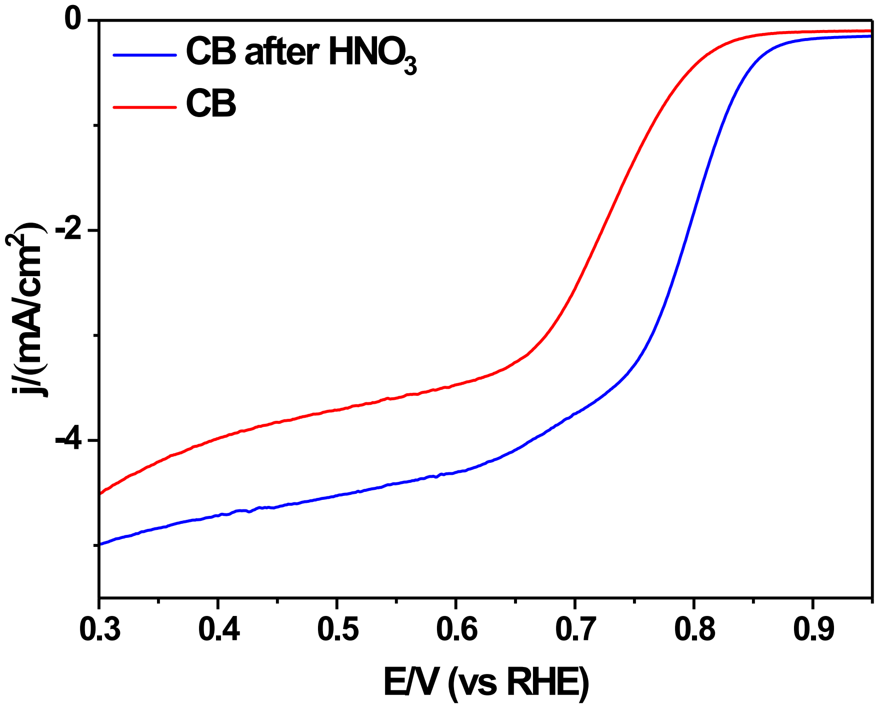

Figure S7 LSV curves of CB and CB after HNO_3.

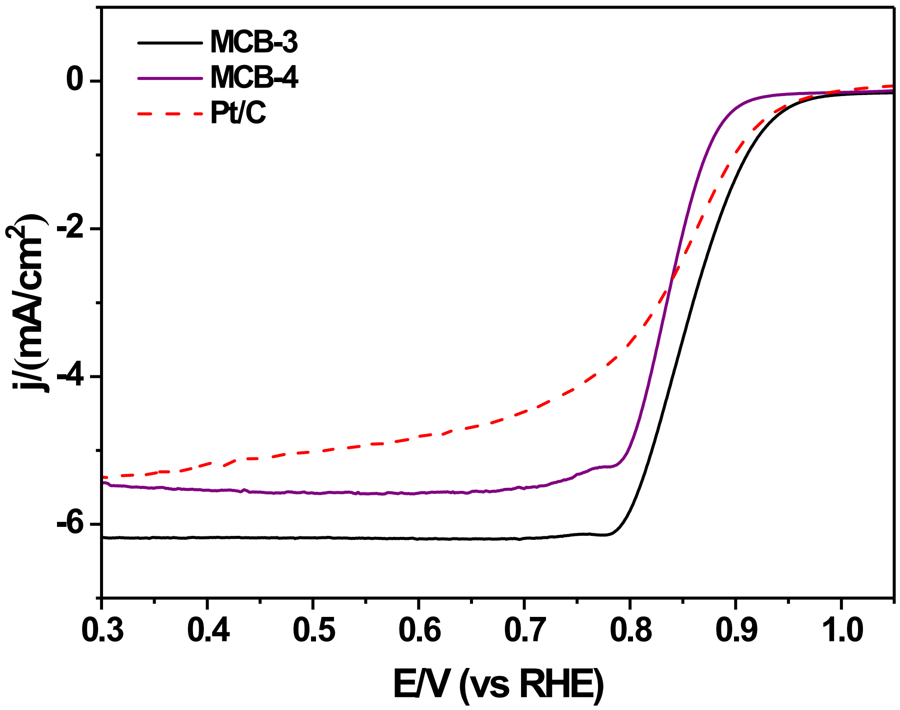

Figure S8 LSV curves of MCB-4 and other comparative catalysts in 0.1M KOH.

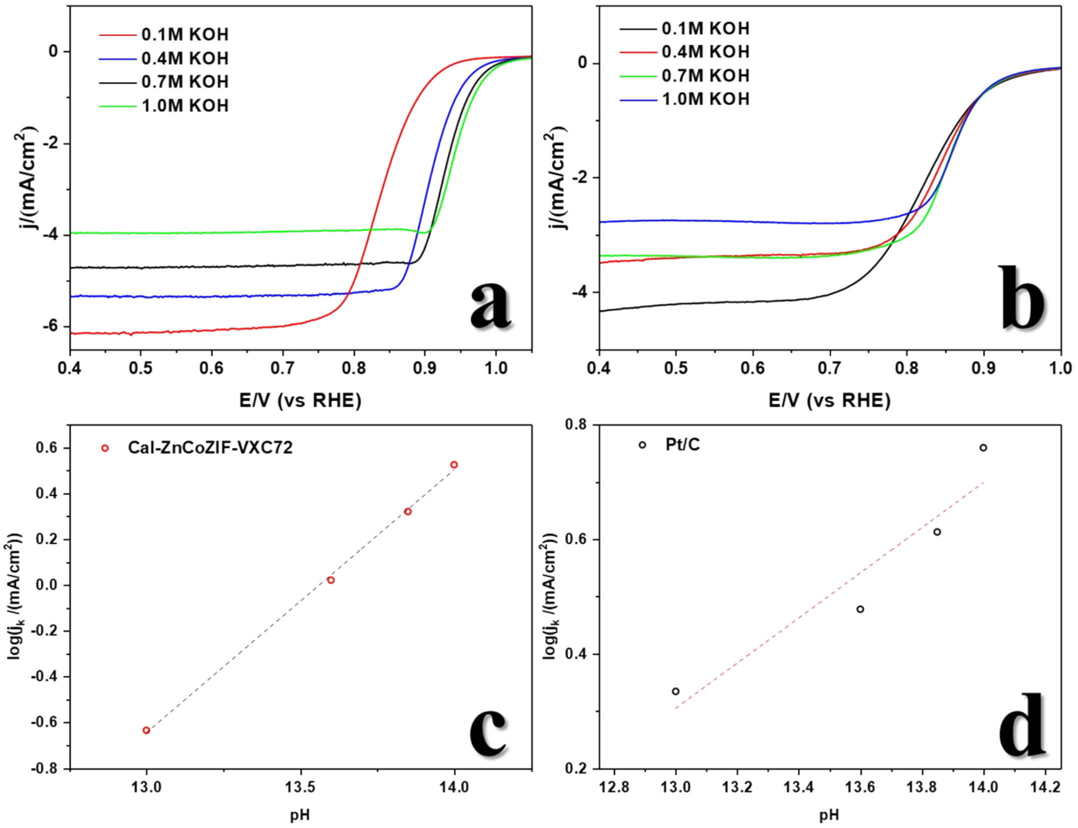

Figure S9 (a) LSV curves of MCB-3 in different concentrations of KOH solution. (b) LSV curves of Pt/C in different concentrations of KOH solution.(c) Jk-pH scatter diagram of MCB-3, It shows a clear linearity (d)) Jk-pH scatter diagram of Pt/C, It doesn’t show a clear linearity

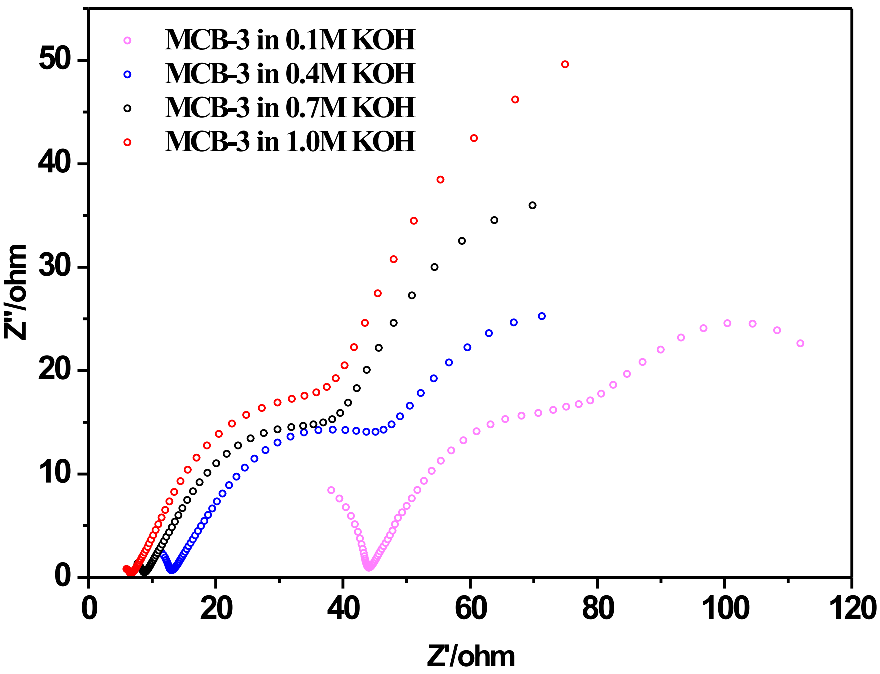

Figure S10 electrochemical impedance spectrum of the MCB-3 in different concentrations of KOH solution.

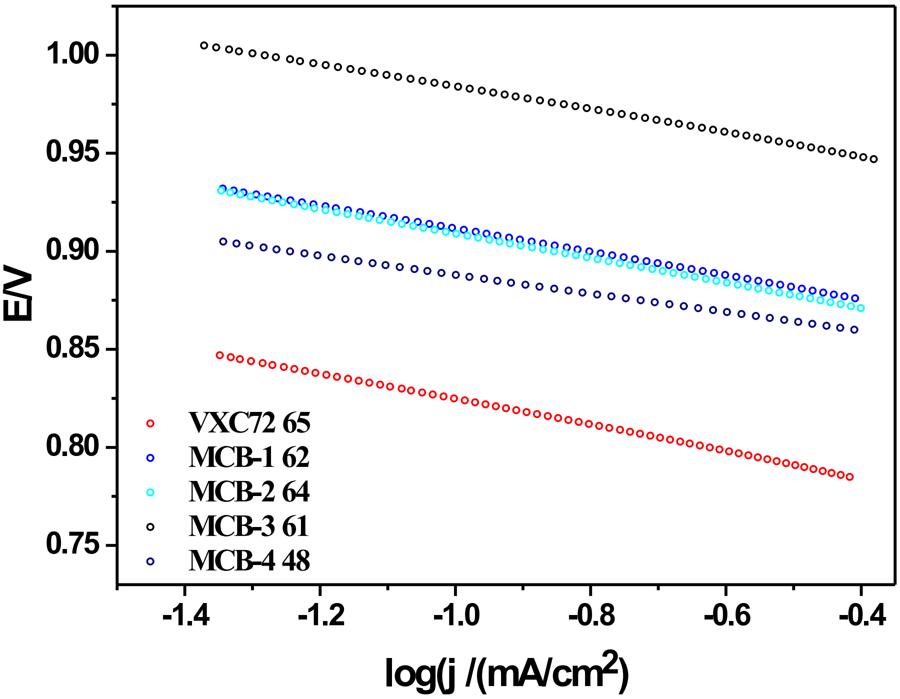

Figure S11 Tafel slopes of MCB-1,2,3,4 and carbon black.

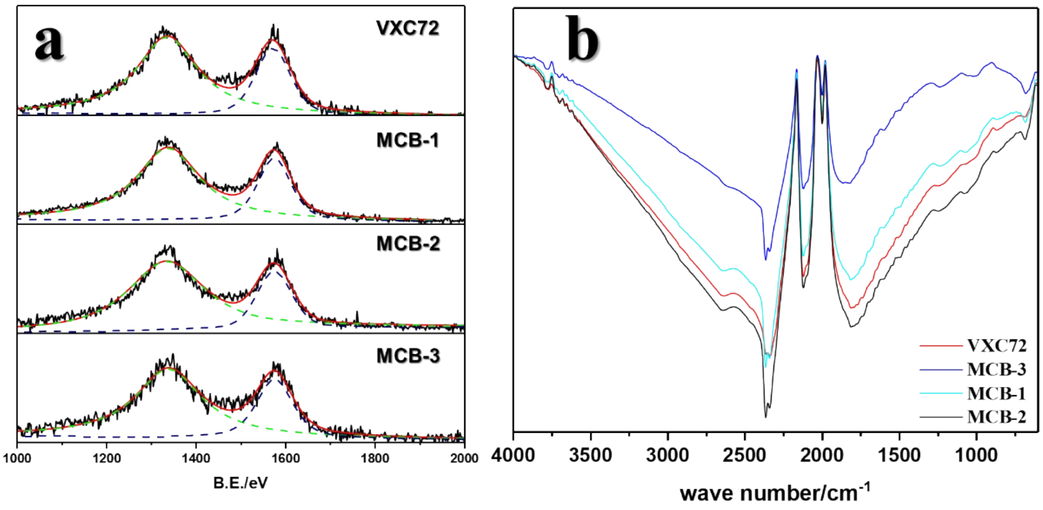

Figure S12(a) FT-IR and (b) Raman spectra of carbon balck and MCB-1,2,3

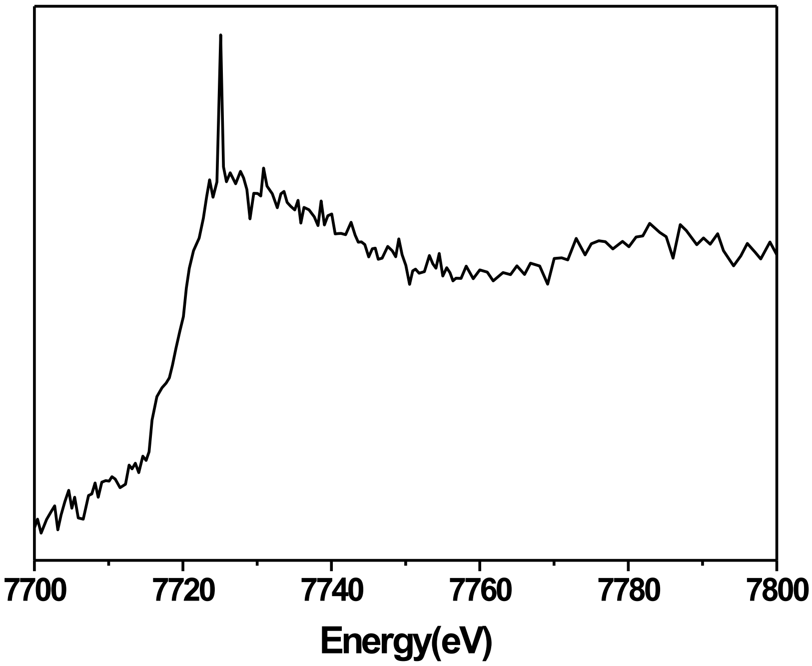

Figure S13 XANES spectra of MCB-H

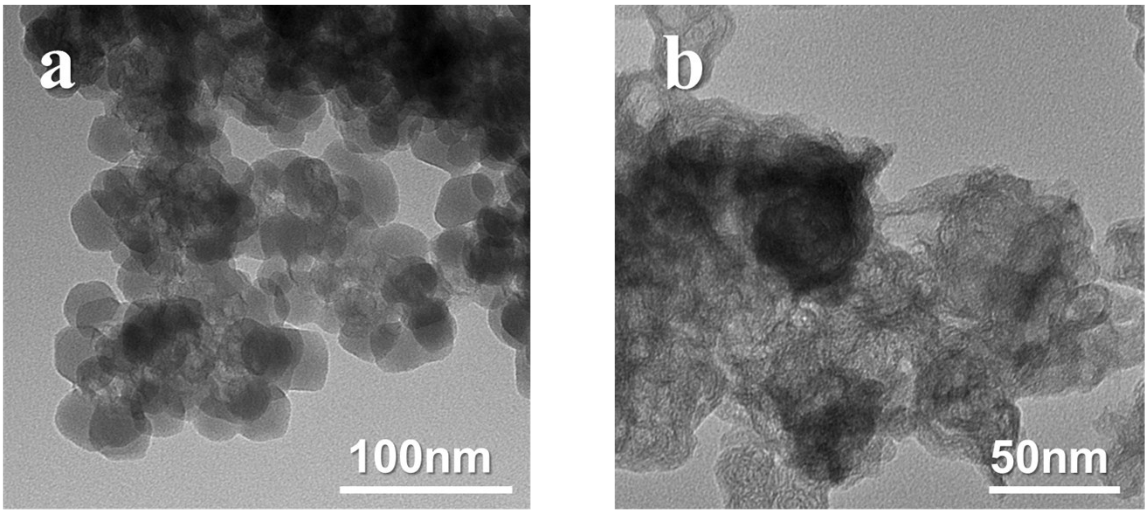

Figure S14 (a) TEM images of the precursor to MCB-4, the ZIF particles can be clearly seen (b) TEM images of MCB-4 , it is different from MCB-3

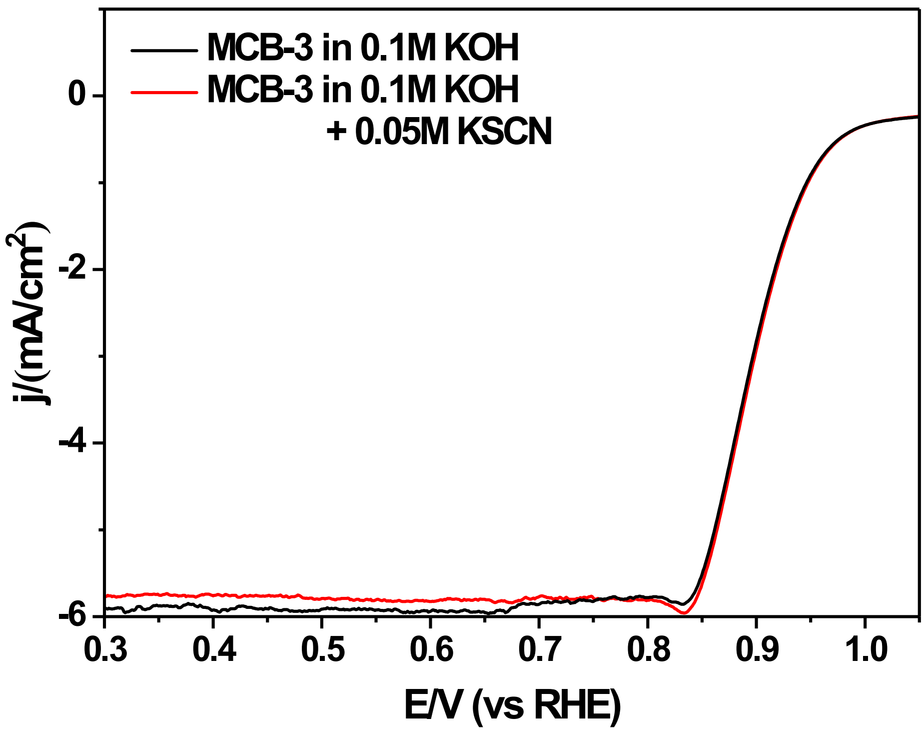

Figure S15 LSV curves of MCB-3 in 0.1M KOH and MCB-3 in 0.1M KOH +0.05M KSCN. The addition of SCN has no significant effect on the catalytic activity of MCB.

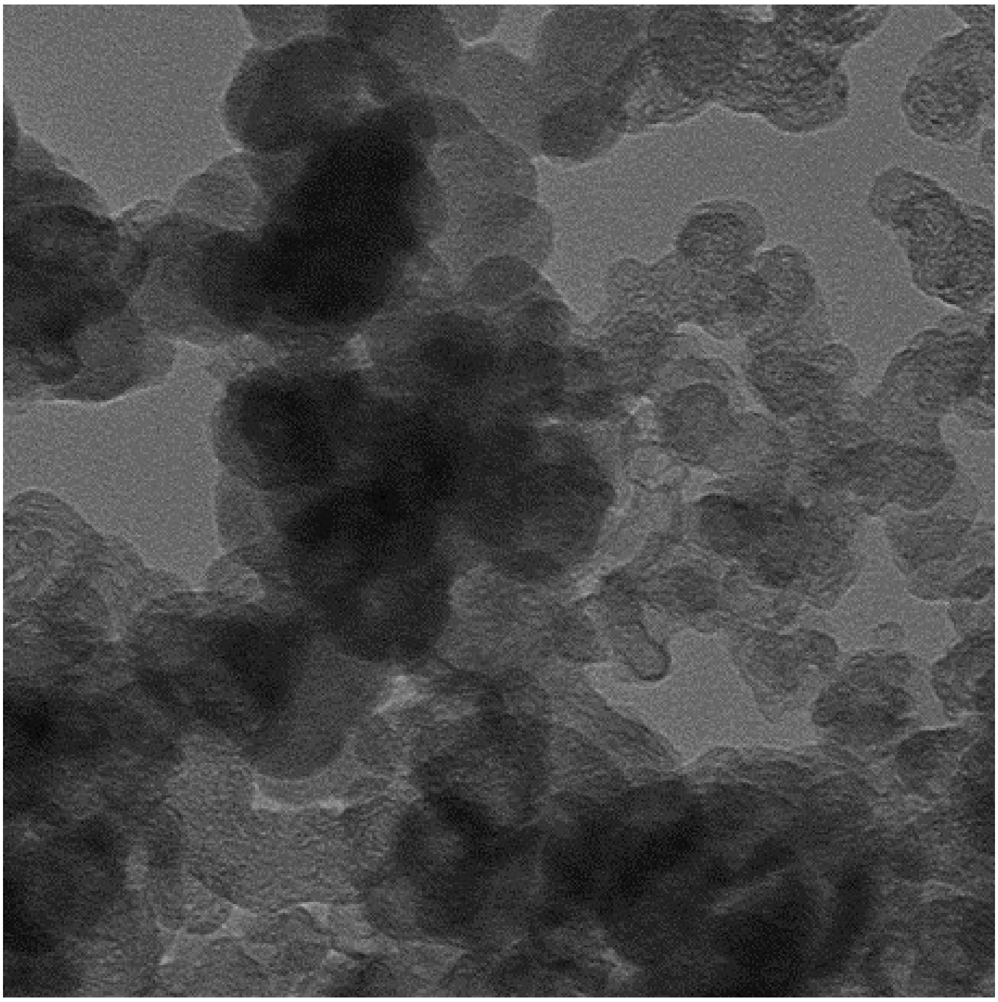

Figure S16 TEM images of the MCB after electrochemical testing.