Supporting Information

Sulfur-Doping Achieves Efficient Oxygen Reduction in Pyrolyzed Zeolitic Imidazolate Frameworks

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Instrumentations and methods

Powder X-ray diffraction (PXRD) were carried out on a Japan Rigaku DMax-γA rotation anode X-ray diffractometer equipped with graphite monochromatized Cu Kα radiation (λ = 1.54 Å). The contents of C, N, and S were quantified by Vario EL III system. The contents of Co were quantified by an inductively coupled plasma mass spectrometry (ICP-MS). The transmission electron microscopy (TEM) and EDX mapping were acquired on JEM-2010, and elemental mapping was measured on Tecnai F30 or JEM 1400 with an electron acceleration energy of 200 kV. Nitrogen sorption measurement was conducted using a Micromeritics ASAP 2020 system at 77 K. Direct current resistance tests were conducted on a Keithley 2400 Source Meter.

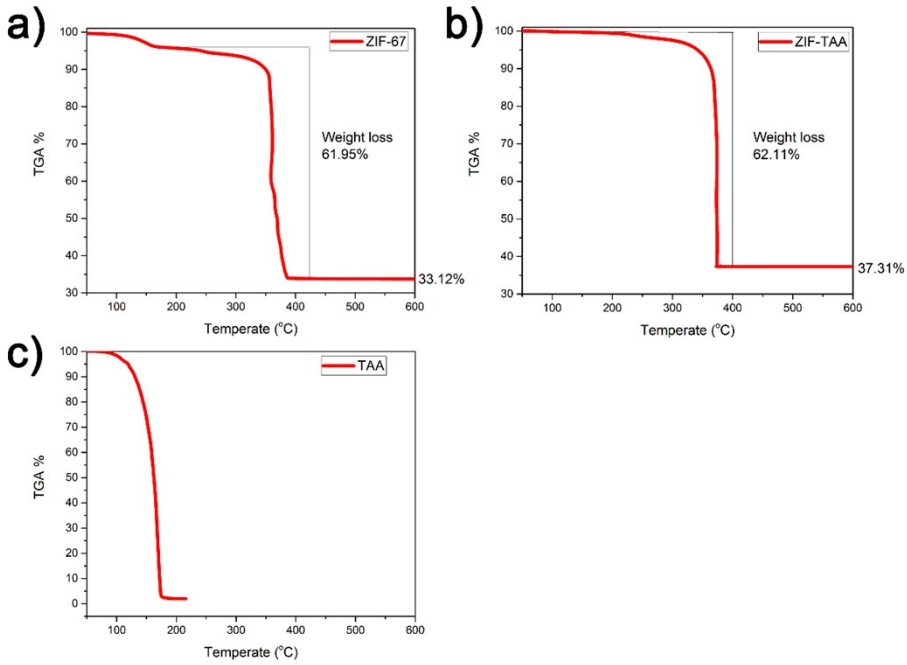

Fig. S1. TGA of a) ZIF-67; b) ZIF-TAA and c) TAA alone in Air atmosphere.

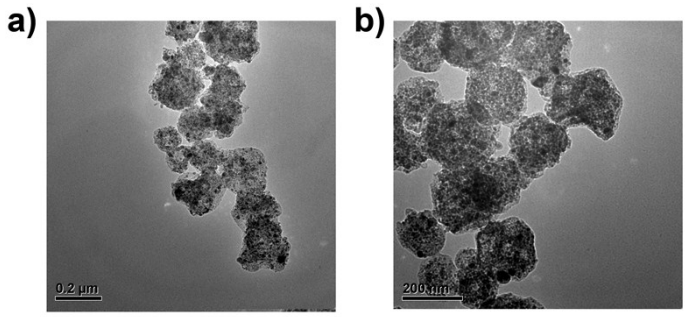

Fig. S2. TEM image of **ZIF-TAA-p**.

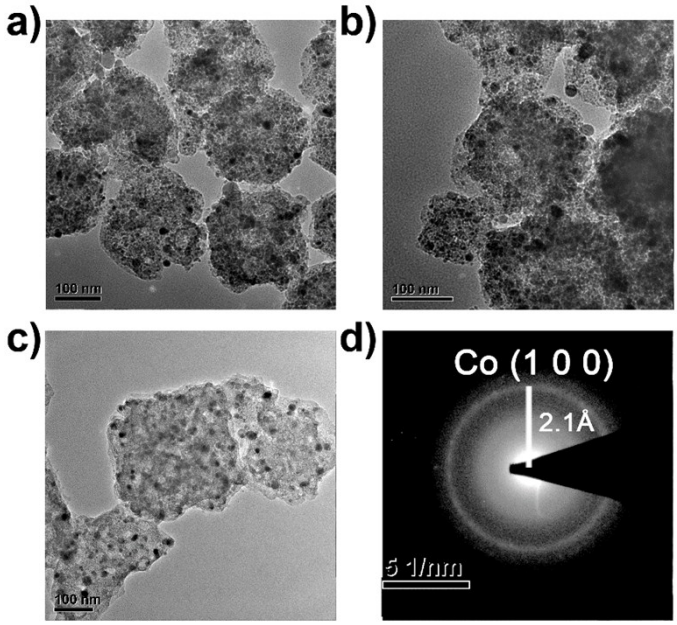

Fig. S3. TEM image and electron diffraction pattern of **ZIF-TAA-p** after treatment with 2 M H_2SO_4 at room temperature for 1 hour.

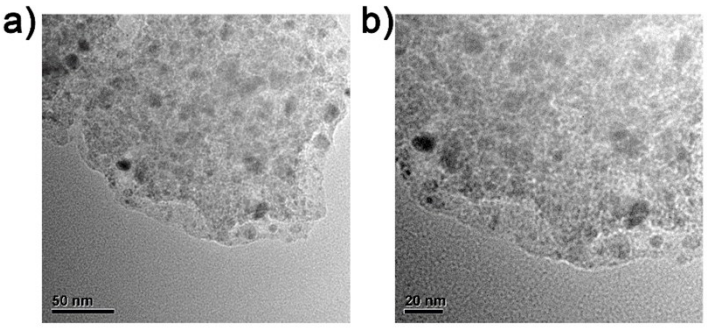

Fig. S4. TEM image of **ZIF-TAA-p** after hydrothermal etching in 10 M HCl at 180 °C for 24 hours.

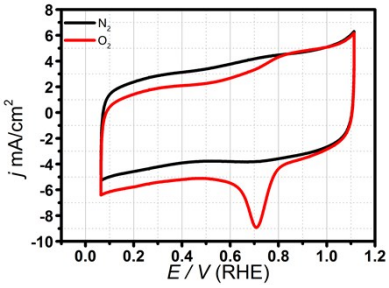

Fig. S5. CV curves of **ZIF-TAA-p** in N_2-saturated and O_2-saturated 0.1 M $HClO_4$. Scan rate: 100 mV / s.

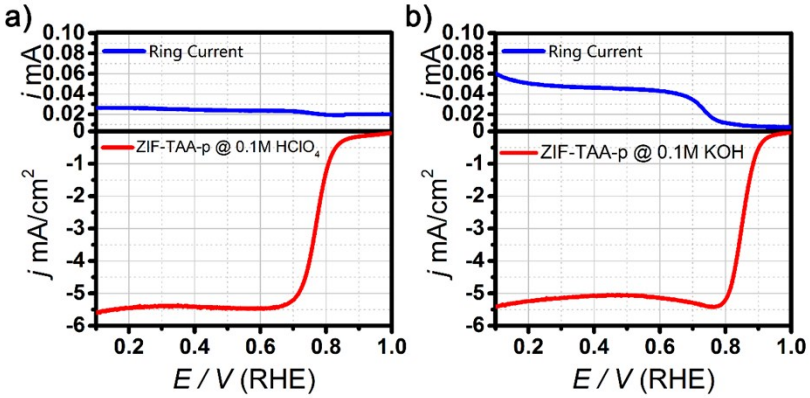

Fig. S6. RRDE Voltammograms of optimized **ZIF-TAA-p** in a) acid and b) alkaline media.

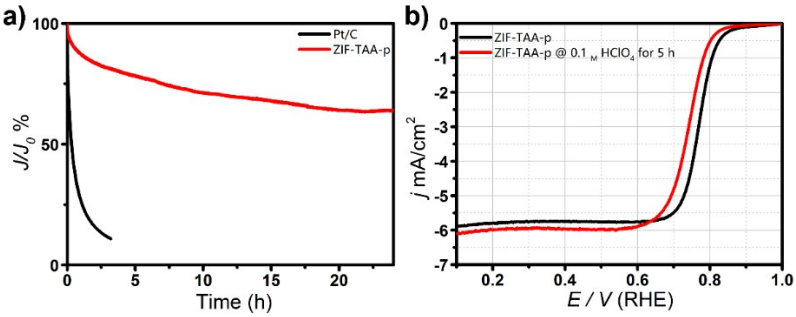

Fig. S7. a) Long-term durability test of **ZIF-TAA-p** and Pt/C by current-time chronoamperometry in O_2-saturated 0.1 M $HClO_4$ (potential: 0.65V vs RHE); b) LSV comparison of **ZIF-TAA-p** and **ZIF-TAA-p** after soaking in 0.1 M $HClO_4$ for 5 hours.

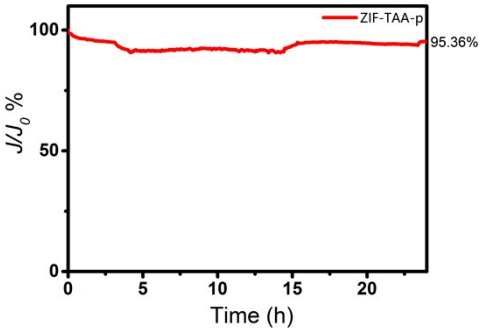

Fig. S8. Long-term durability test of **ZIF-TAA-p** by current-time chronoamperometry in O_2-saturated 0.1 M KOH (potential: 0.65V vs RHE).

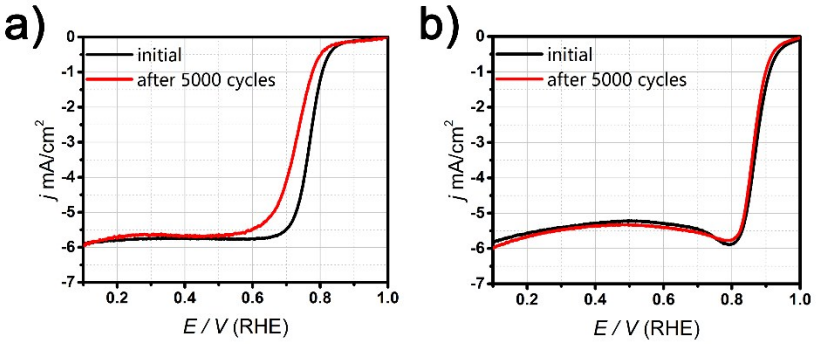

Fig. S9. LSV curves of **ZIF-TAA-p** before and after 5000 cycles in O_2 saturated a) 0.1 M $HClO_4$ and b) 0.1 M KOH.

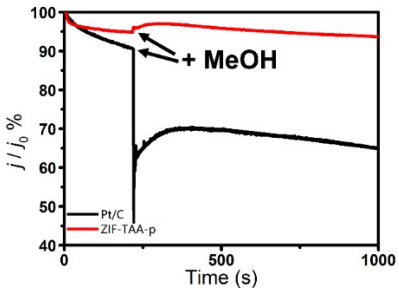

Fig. S10. Methanol tolerance test of **ZIF-TAA-p** and Pt/C conducted by chronoamperometry. All chronoamperometric tests were conducted at 0.65V vs RHE in O_2-saturated 0.1 M $HClO_4$.

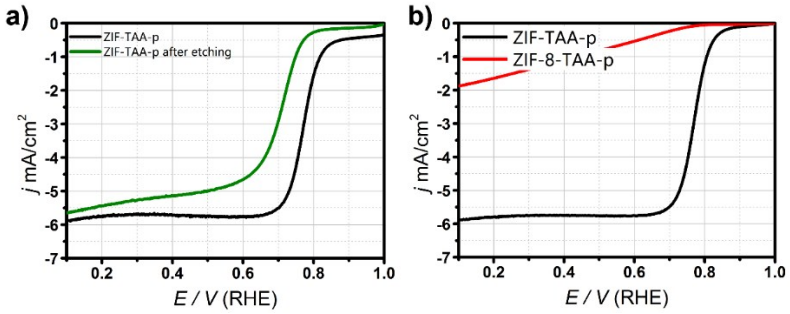

Fig. S11. a) LSV curves of **ZIF-TAA-p** before and after 10 M HCl etching in O_2-saturated 0.1 M $HClO_4$; b) LSV curves of **ZIF-TAA-p** and pyrolyzed/sulfurated ZIF-8 (denoted as **ZIF-8-TAA-p**).

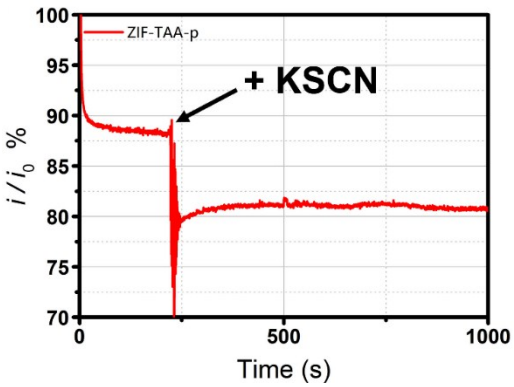

Fig. S12. KSCN Poisoning Experiment. Chronamperometric test of **ZIF-TAA-p** at 0.3 V in O_2-saturated 0.1 M $HClO_4$. The arrow indicates the introduction of KSCN.

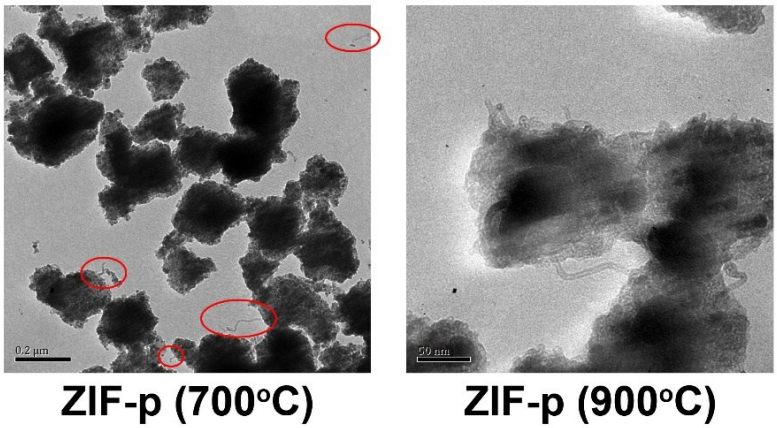

Fig. S13. TEM images of **ZIF-p** at different pyrolysis temperatures. The red circles on the left image point out carbon nanotubes on the external surfaces of **ZIF-p**.

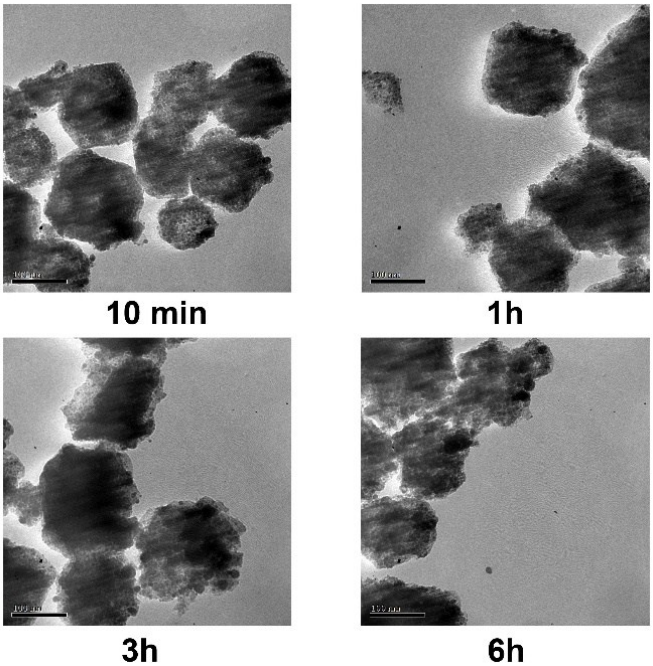

Fig. S14. TEM images of **ZIF-TAA-p** with different pyrolysis durations.

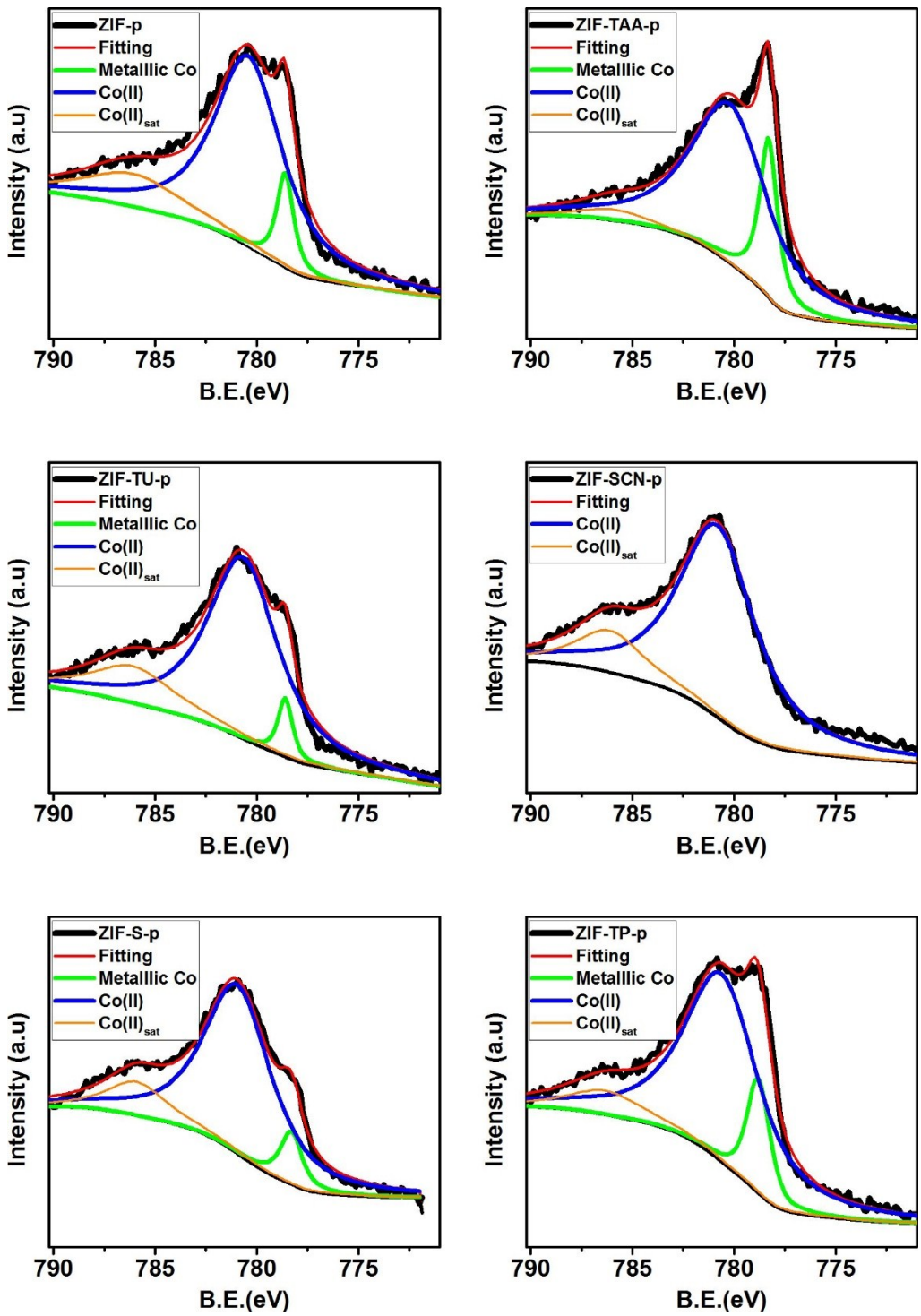

Fig. S15. XPS spectra of Co $2p_{3/2}$ for **ZIF-x-p**.

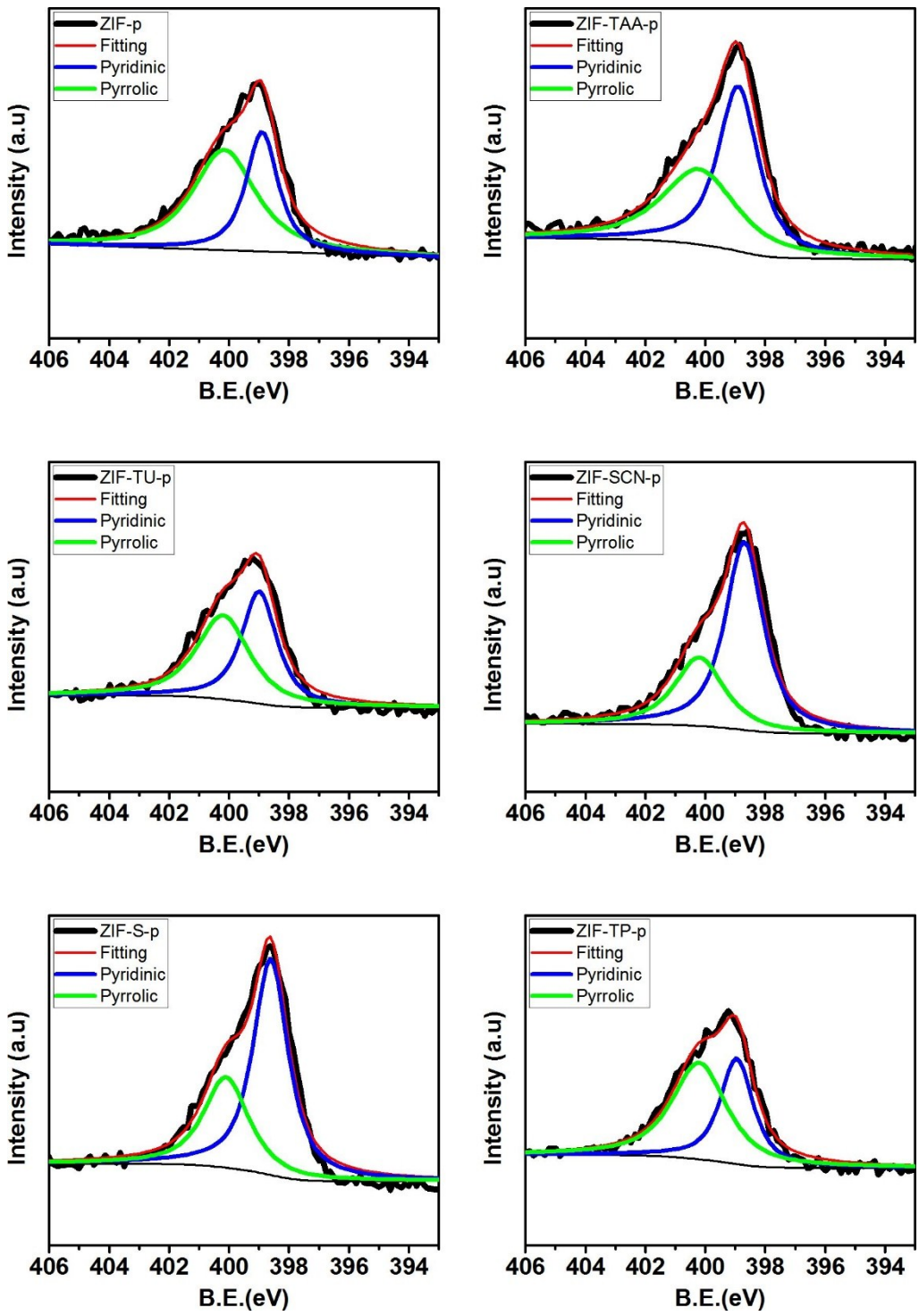

Fig. S16. XPS spectra of N 1s for **ZIF-x-p.**

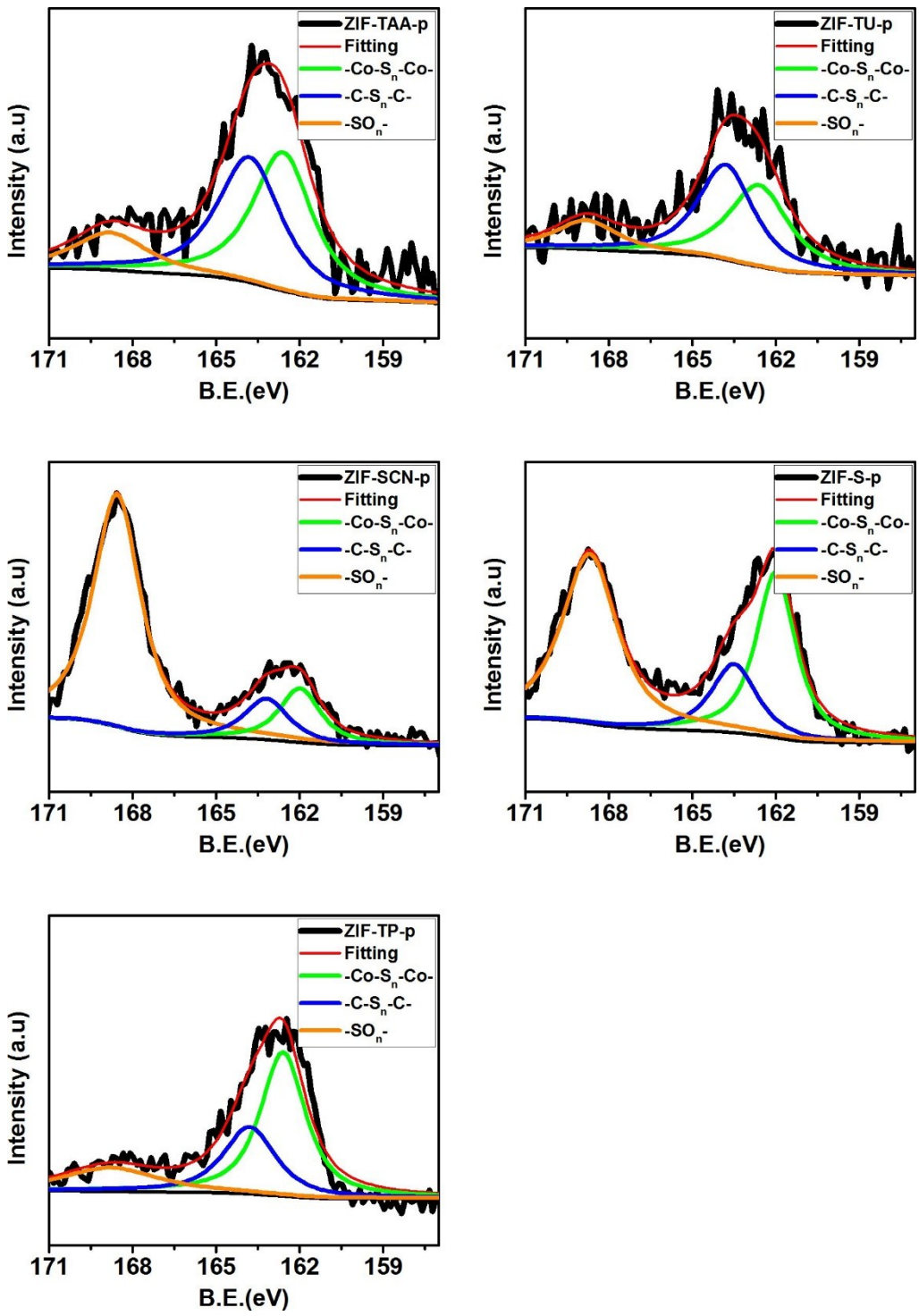

Fig. S17. XPS spectra of S 2p for **ZIF-x-p.**

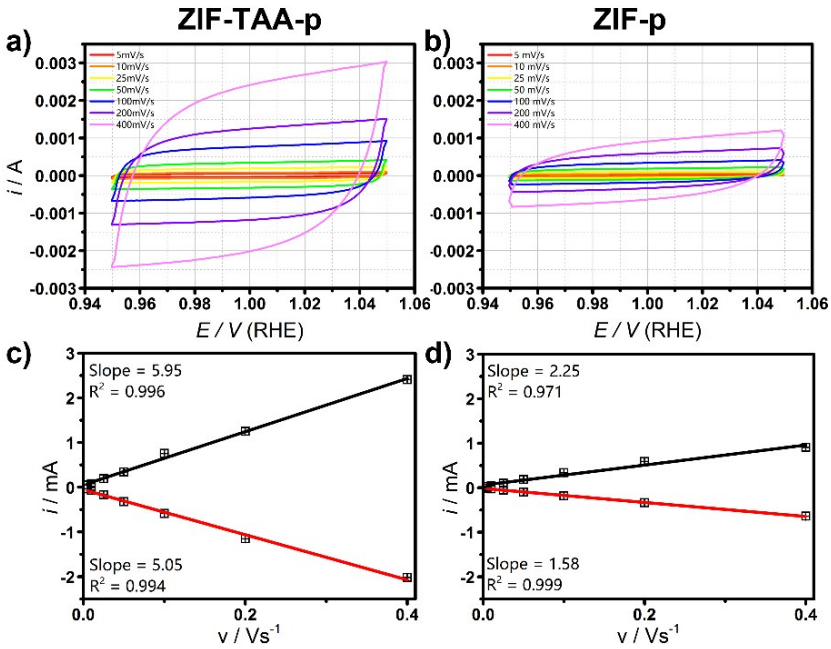

Fig. S18. Charging currents measured for a) **ZIF-TAA-p** and b) **ZIF-p** in the non-Faradaic potential range of 0.95 V - 1.05 V at scan rates of 5, 10, 25, 50, 100, 200, and 400 mV / s, respectively. c) and d) are corresponding cathodic and anodic charging currents measured at 0 V, plotted against the scan rates. The double-layer capacitance is calculated from the average of the absolute value of anodic and cathodic slopes and the catalysts loading (0.1 mg).

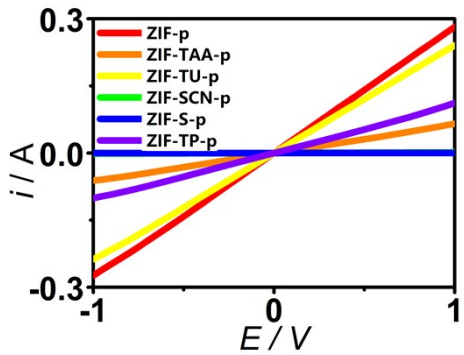

Fig. S19. Direct current I/V plots of **ZIF-*x*-p**.

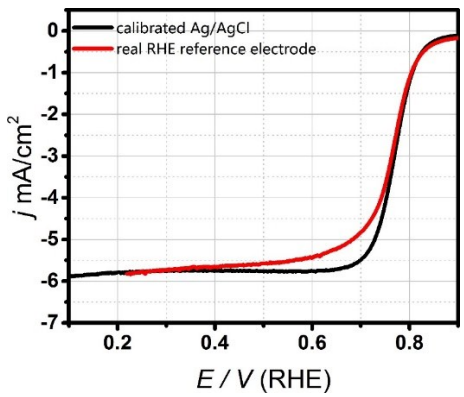

Fig. S20. The comparison of a calibrated Ag/AgCl reference electrode and a RHE reference electrode in 0.1 M $HClO_4$.

Table S1. Comparison of ORR catalytic performances in acid media (electrolyte is 0.1 M $HClO_4$ and rotating speed is 1600 rpm if not marked).

Catalyst	Oneset Potential (V vs RHE)	Half-wave potential (V vs RHE)	diffusion-limited current density at 0.4 V (mA / cm^2, rotating speed 1600 rpm)	Refs
ZIF-TAA-p	0.88	0.78	5.8	This work
CoIM	0.83	0.68	4	[S1]
FeIM/ZIF-8	0.915	0.755	5	[S2]
$Zn(eIm)_2TPIP$	0.914	0.78	5	[S3]
ZIF-67-900-AL	0.85	0.71	4	[S4]
MDC	0.86	0.71	5.2	[S5]
C-N-Co[a]	0.87	0.79	4.8	[S6]
PFeTTPP-1000	0.93	0.76	5	[S7]
Fe/N/C-SCN[b]	0.91	0.836	4.1[c]	[S8]
CPANIFe-NaCl	0.91	0.72	5.1	[S9]
PNGF	0.83	0.67	7.5	[S10]

[a] Electrolyte: 0.5 M H_2SO_4 [b] Electrolyte: 0.1 M H_2SO_4 [c] Rotating speed: 900 rpm

Table S2. Comparison of ORR catalytic performances in alkaline media (electrolyte is 0.1 M KOH and rotating speed is 1600 rpm if not marked).

Catalyst	Oneset Potential (V vs RHE)	Half-wave potential (V vs RHE)	diffusion-limited current density at 0.4 V (mA / cm^2, rotating speed 1600 rpm)	Refs
ZIF-TAA-p	0.98	0.88	5.3	This work
ZIF-67-900-AL	0.92	0.85	5.2	[S4]
P-CNCo-20	0.93	0.85	6	[S11]
Fe-N/C-800	0.98	0.81	4.8	[S12]
N/Co-doped PCP-RGO	0.94	0.87	7.2	[S13]
GNPCSs-800	0.957	0.786	6	[S14]
Co/C-700	0.81	0.86	4	[S15]
PNGF	1.03	0.86	7	[S10]
MIL-800	0.91	0.79	4.8	[S16]

Table S3 C, N and S contents of **ZIF-*x*-p**[a]

Sample	content %		
	C	**N**	**S**
ZIF-TAA	38.22±0.70	27.47±0.62	1.16±0.24
ZIF-TAA-p (10 min)	39.76 ± 0.86	9.91 ± 0.54	1.57 ± 0.14
ZIF-TAA-p (3 hour)	40.59 ± 1.24	7.23 ± 0.31	1.32 ± 0.14
ZIF-TAA-p (6 hour)	32.74 ± 1.21	4.85 ± 0.37	1.20 ± 0.11
ZIF-TU-p	40.33 ± 2.02	6.50 ± 0.30	0.64 ± 0.21
ZIF-SCN-p	28.31 ± 0.54	11.00 ± 0.20	7.17 ± 0.40
ZIF-S-p	30.61 ± 1.85	14.63 ± 0.63	5.12 ± 0.07
ZIF-TP-p	42.68 ± 2.07	6.69 ± 0.39	0.41 ± 0.08
ZIF-p	41.46 ± 0.23	6.7.0 ± 0.11	-

[a] The pyrolysis temperature was 700 ^{o}C under Ar, and the pyrolysis duration was 10 minutes if not marked.

Table S4 Relative Co species contents with respect to total Co of **ZIF-*x*-p** based on XPS

Sample	Co(0)	Co(II)
ZIF-p	11.05%	88.95%
ZIF-TAA-p	19.36%	80.64%
ZIF-TU-P	6.25%	93.75%
ZIF-SCN-P	0.00%	100.00%
ZIF-S-p	9.25%	90.75%
ZIF-TP-p	14.75%	85.25%

Table S5 Relative pyridinic N contents with respect to total N of **ZIF-*x*-p** based on XPS

Sample	pyridinic N
ZIF-p	37.64%
ZIF-TAA-p	53.26%
ZIF-TU-P	47.25%
ZIF-SCN-P	67.97%
ZIF-S-p	34.88%
ZIF-TP-p	39.86%

Table S6 Relative S species contents with respect to total S of **ZIF-*x*-p** based on XPS

Sample	$-SO_n-$	$C-S_n-C$	$Co-S_n-Co$
ZIF-TAA-p	14.48%	41.99%	43.53%
ZIF-TU-P	15.07%	44.01%	40.92%
ZIF-SCN-P	73.15%	12.09%	14.76%
ZIF-S-p	49.25%	16.37%	34.38%
ZIF-TP-p	18.54%	28.48%	52.98%

Table S7 Resistance measurement data of **ZIF-*x*-p**

Sample	**Slope**	**S/L**[a]	**Resistivity**
ZIF-TAA-p	0.0633	9.648	152.41706
ZIF-TU-p	0.24132	26.10692	108.18384
ZIF-SCN-p	0.00145	13.91508	9596.60825
ZIF-S-p	5.52865E-5	3.85932	69805.80816
ZIF-TP-p	0.10613	11.46981	108.07443
ZIF-p	0.28026	13.71198	48.92591

[a] **S**: Areas of conductive adhesive; **L**: Thicknesses of tablets

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