Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting information

A Graphene-directed Assembly Route to Hierarchically Porous Co-N_x/C Catalysts for High-performance Oxygen Reduction

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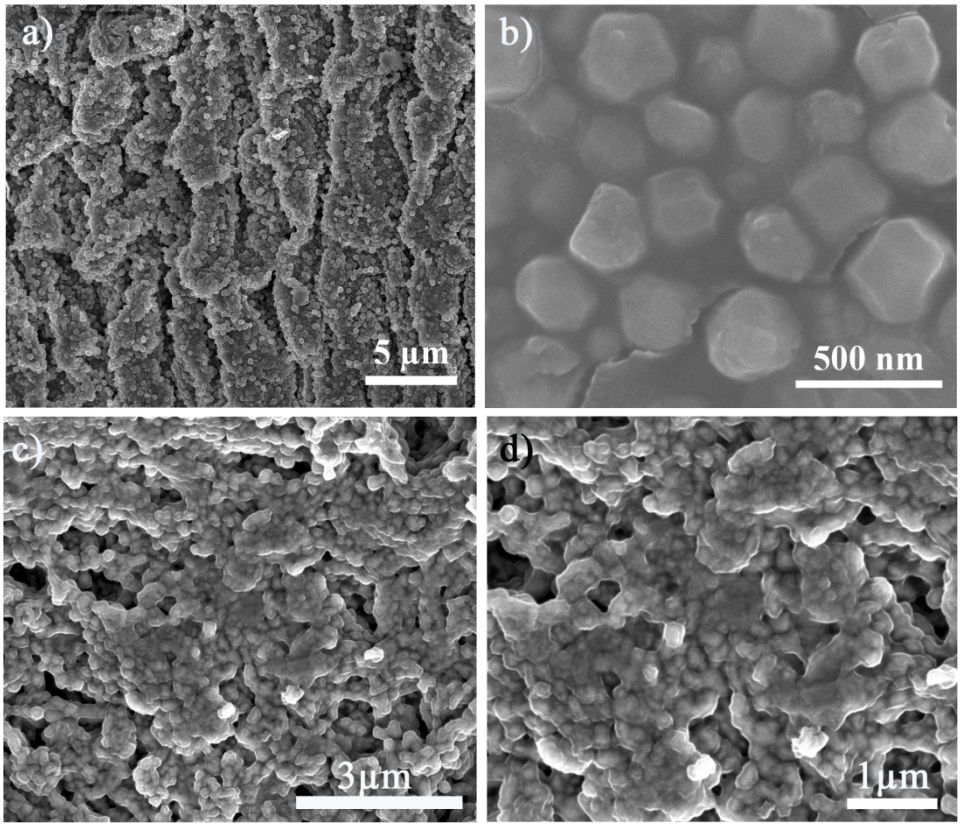

Figure S1 SEM image of a, b) ZIF/GO-90 prepared by growing ZIF-67 nanocrystals on graphene oxide (GO) and drying at 90 ^{o}C in air; c, d) ZIF/rGO-500 prepared by carbonizing ZIF/GO materials at 500 ^{o}C for 3 h in Ar. The SEM images show the macroporous structure is produced as the shrinkage of ZIF and GO during carbonization process.

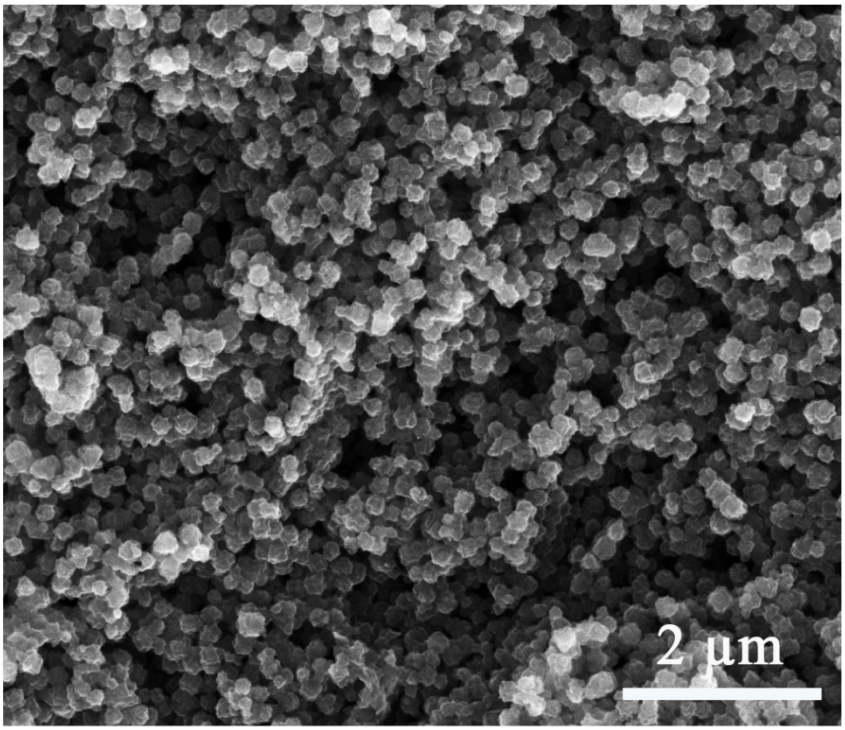

Figure S2 SEM image of ZIF-700-AL prepared via carbonization of ZIF-67 at 700 ^{o}C in Ar followed by acid leaching. The SEM results show loosely packed nanoparticles.

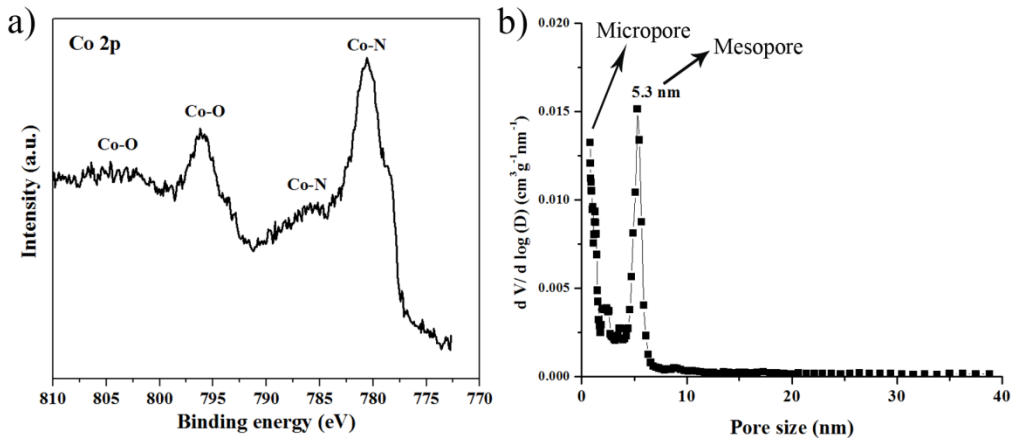

Figure S3 a) High-resolution Co 2p spectra, b) DFT pore size distributions of ZIF/rGO-700-AL. The XPS data shows Co species exist with Co-N and Co-O bands, which is beneficial to ORR performance. DFT pore size distributions reveal the materials possess microporous and mesoporous structure.

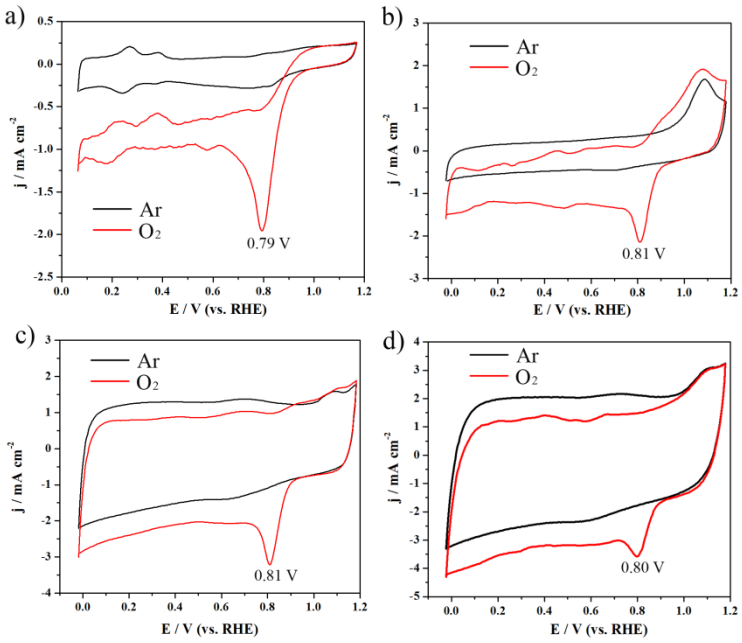

Figure S4 Cyclic voltammogram (CV) curves of a) Pt/C, b) ZIF/rGO-700, c) ZIF/rGO-700-AL, d) ZIF-700-AL in Ar (O_2)-saturated 0.1 M KOH solution with a scan speed of 50 mV/s.

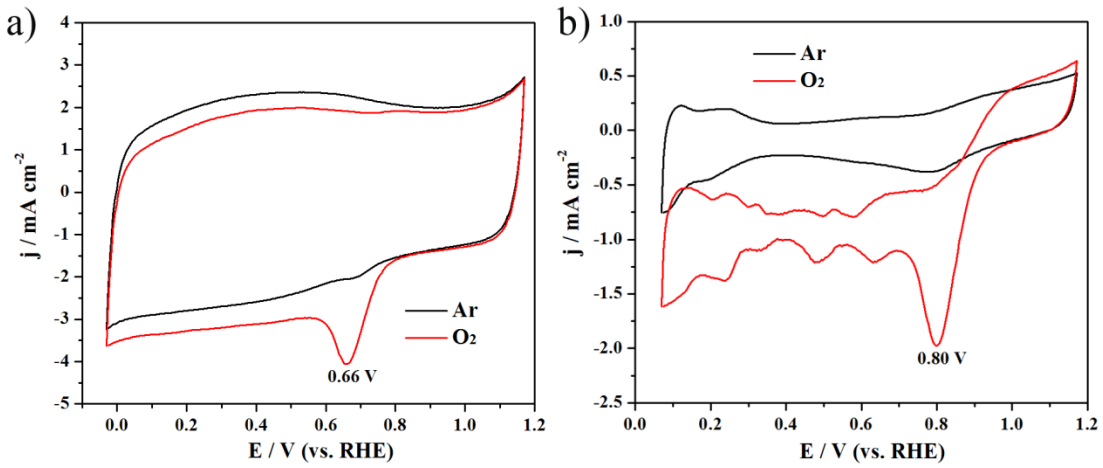

Figure S5 CV curves of a) ZIF/rGO-700-AL and b) Pt/C in Ar (O_2)-saturated 0.1 M $HClO_4$ solution with a scan speed of 50 mV/s.

Table S1. A comparison with the noble metal free ORR catalysts based on Co and N-containing carbons reported recently and our work

Materials	Cathodic peak (V vs RHE)	Onset potential (V vs RHE)	Limiting current (mA/cm^2)	Condition	Reference
ZIF-67-900	~0.8	0.91	~4.8	0.1 M KOH	1
ZIF-67-900-AL	n.a.[1]	0.93	~5.2	0.1 M KOH	1
ZIF-9/ordered mesoporous carbon-700	0.79	0.93	~4.6	0.1 M KOH	2
CoP-CMP800	0.73	0.84	4.62	0.1 M KOH	3
Macrocyclic metal-N_4 complexes	0.70	0.82	n.a.	0.1 M KOH	4
Hierarchical interconnected macro-/mesoporous Co-containing N-doped carbon	0.72	0.87	~5.5	0.1 M KOH	5
Nanosheet-like cobalt–nitrogen–graphene (Co–N–GN) composites	0.78	0.87	~4.4	0.1 M KOH	6
Graphene-based non-noble-metal Co/N/C catalyst	0.77	0.85	~5.3	0.1 M KOH	7
Hierarchical nanoporous Co-N_x/C	0.81	0.93	5.5	0.1 M KOH	This Work
ZIF-67-700-AL	0.80	0.93	4.5	0.1 M KOH	This Work
Pt/C	0.79	0.90	4.6	0.1 M KOH	This Work
ZIF-67-900	~ 0.7	0.85	~3.8	0.5 M H_2SO_4	1
ZIF-67-900-AL	n.a.	0.85	~4.8	0.5 M H_2SO_4	1
ZIF-67-750; with small particles size (300 nm)	~0.66	0.86	~5.5	0.1 M $HClO_4$	8
CoP-CMP800	n.a.	0.74	4.84	0.5 M H_2SO_4	3
Mesoporous cobalt−nitrogen-doped carbon	n.a.	0.87	~4.7	0.5 M H_2SO_4	9
Electrocatalysts derived from polyaniline and cobalt	n.a.	0.80	~ 4	0.5 M H_2SO_4	10
Hierarchical nanoporous Co-N_x/C	0.66	0.83	4.84	0.1 M $HClO_4$	This Work
Pt/C	0.80	0.92	4.98	0.1 M $HClO_4$	This Work

[1] not available

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