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钴原子团簇用于高效氧还原反应

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Atomic Co Clusters for Efficient Oxygen Reduction Reaction

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1 Experimental

1.1 Chemicals

Zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, AR), 2-Methylimidazole ($C_4H_6N_2$, AR), Methanol (CH_4O, AR), and Cobalt chloride ($CoCl_2 \cdot 6H_2O$, AR) were obtained from Shanghai Macklin Biochemical Co., Ltd. Hydrochloric acid (HCl, 37%) was bought from XILONG SCIENTIFIC CO., LTD. The all chemicals were used without further purification.

1.2 Material characterizations

HAOYUAN powder diffractometer (DX-2700BH) was used to test X-ray diffraction (XRD) pattern. Thermo Scientific Talos F200X G2 microscope was applied to collect the TEM and HRTEM images. Aberration-corrected high-angle annular dark field scanning transmission electron microscopy (AC HAADF-STEM) images were carried out on an aberration-corrected FEI Titan G2 60-300 field emission TEM (FEI, USA). Thermo Scientific K-Alpha X-ray photoelectron (XPS) spectrometer was employed to collect the XPS data. Specific surface area and pore distribution of the prepared catalysts were measured by the N_2 adsorption/desorption isotherm curves analyzed by Micromeritics APSP 2460.

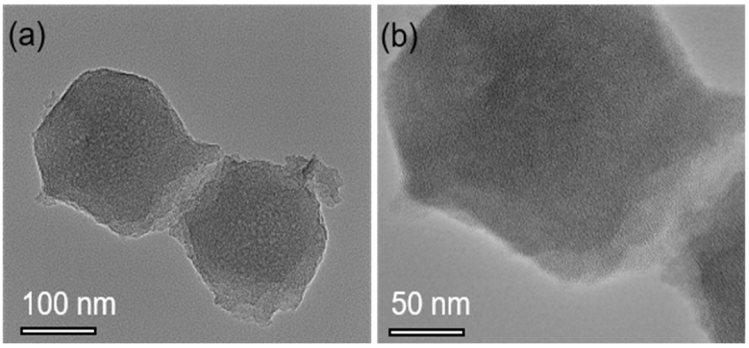

Fig. S1 (a, b) The TEM images of the prepared Co_{AC}/NC catalyst.

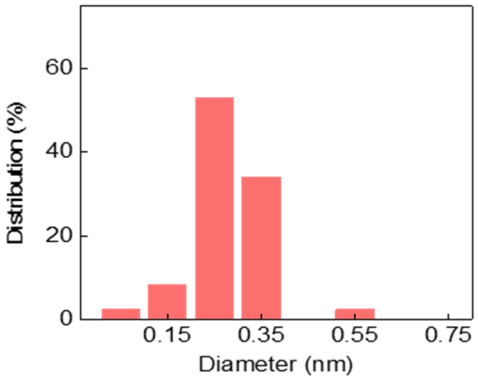

Fig. S2 The atomic spacing data of the Co_{AC}/NC.

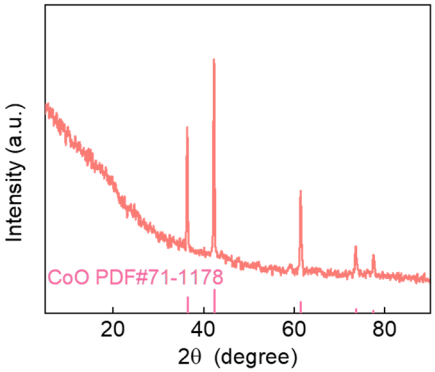

Fig. S3 XRD pattern of the Co_{AC}/NC catalyst before acid washing treatment.

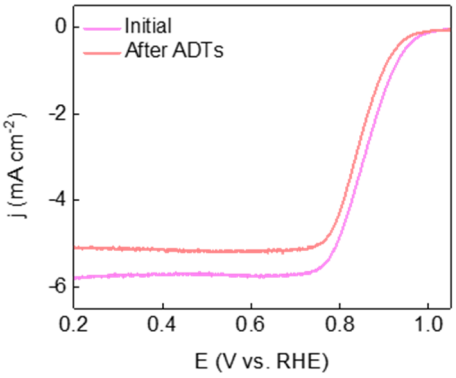

Fig. S4 LSV curves of the Pt/C before and after ADT test.

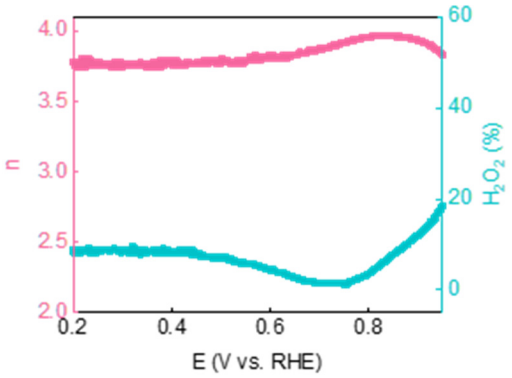

Fig. S5 RRDE data of the prepared Co_{AC}/NC.

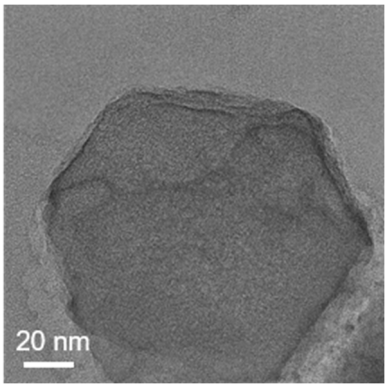

Fig. S6 TEM image of the prepared Co_{AC}/NC-S.

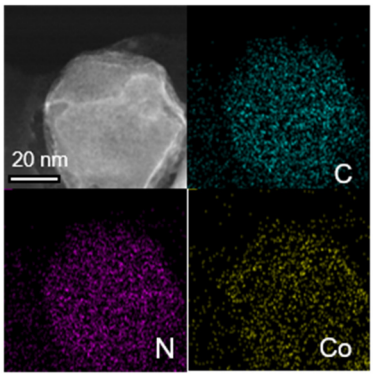

Fig. S7 HAADF-STEM and EDX-Mapping images of the prepared Co_{AC}/NC-S.

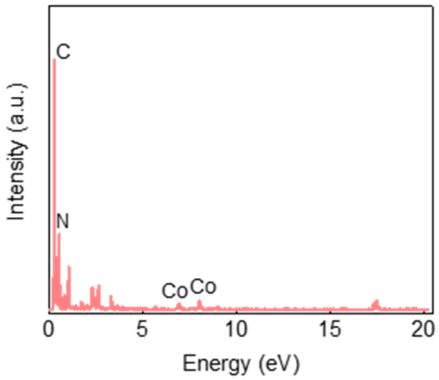

Fig. S8 EDX-profile image of the prepared Co_{AC}/NC-S.

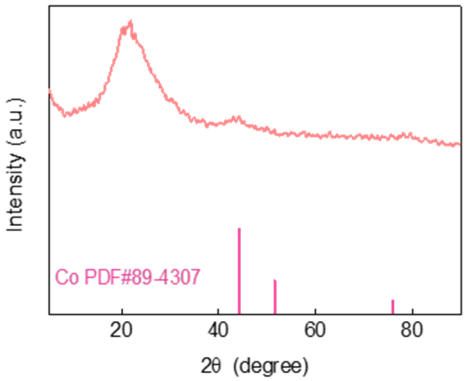

Fig. S9 XRD pattern of the prepared Co_{AC}/NC-S.

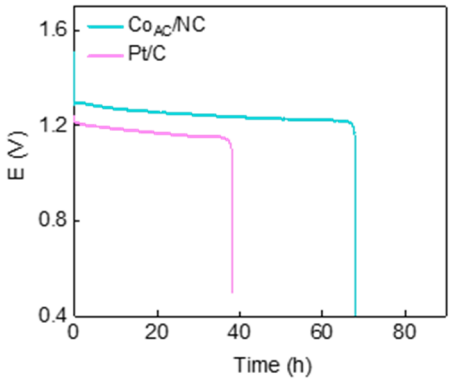

Fig. S10 The long-term stability of the assembled Co_{AC}/NC-based ZAB.

Table S1 The distribution of the atom spacing of the Co atomic cluster clusters.

Diameter (nm)	0–0.1	0.1–0.2	0.2–0.3	0.3–0.4	0.4–0.5	0.5–0.6
Distribution (%)	2.35	8.24	52.94	34.12	0	2.35

Table S2 The Co metal loading of the prepared Co_{AC}/NC catalyst.

	Metal loading (*w*/%)
Co_{AC}/NC	2.67

Table S3 Comparation of the ORR performance of catalysts at RDE-level in recent published works.

	E_{ONSET}/V *vs*. RHE	$E_{1/2}$/V *vs*. RHE	References
Co_{AC}/NC	**1.019**	**0.887**	**This work**
Pt/C	**0.970**	**0.857**	**This work**
Co/Zn-NC	0.98	0.83	*Angew. Chem. Int. Ed.* **2021,** *60*, 14005.
FeN_4-PN	1.0 *	0.91	*ACS Catal*. **2021,** *11*, 6304.
CoSAs-NGST	0.99	0.89	*Adv. Funct. Mater.* **2021,** *31*, 2010472.
SA-CuNC	0.99 *	0.78	*Adv. Energy Mater.* **2021,** *11*, 2100303.
Fe SA-NSC-900	0.94	0.86	*ACS Energy Lett.* **2021,** *6*, 379.
Pt-SCFP/C-12	0.90	0.81	*Adv. Energy Mater.* **2020,** *10*, 1903271.
Cu@Cu-N-C	0.97	0.85	*Small* **2019,** *15*, 1902410.
Fe-NCNWs	0.99	0.90	*ACS Catal.* **2019,** *9*, 5929.
Fe-SAs/NSC	1.00	0.87	*J. Am. Chem. Soc.* **2019,** *141*, 20118.
Cu-N_4-C	0.915	0.84	*ACS Nano* **2019,** *13*, 3177.
Fe-ISA/SNC	0.98	0.89	*Adv. Mater.* **2018,** *30*, e1800588.

* The data is not given, but excavated from the LSV curves.

Table S4 Comparison of the ZAB performance of the prepared catalysts and recently reported catalysts.

Catalysts	Power density ($mW \cdot cm^{-2}$)	Specific capacity ($mAh \cdot g^{-1}$)	Stability (h)	Ref.
Co_{AC}/NC	**181.5**	**789.5**	**67**	**This work**
SA-Co-N_4-GCs	149.3	764.8	–	*Nano Res*. **2022,** *15*, 7209.
CoFe-N-C	142.1	917.4	–	*Nano Lett*. **2022,** *22*, 3392.
HESAC-based	195	810	81	*Nat. Commun*. **2022,** *13*, 5071.
SAC-Fe/NC	263	803	–	*Cell Rep. Phys. Sci*. **2022,** *3*, 100880.
C-MOF-C_2-900	105	768	–	*Adv. Mater*. **2018,** *30*, 1705431.
Co_4N/CNW/CC	174	–	–	*J. Am. Chem. Soc*. **2016,** *138*, 10226.
Ni@N-HCGHF	117.1	706	–	*Adv. Mater*. **2020,** *32*, 2003313.
NGM-Co	152	749.4	–	*Adv. Mater*. **2017,** *29*, 1703185.
$NiCo_2S_4$/N-CNT	147	431.1	–	*Nano Energy* **2017,** *31*, 541.
Co_4N@NC-2	74.3	769.4	–	*Appl. Catal. B: Environ*. **2020,** *275*, 119104.