Supplementary Information (SI) for ChemComm.

Electronic Supplementary Information

General aggregation-induced deposition approach for creating asymmetric single-atom catalysts

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Experimental Section

Chemicals and Reagents

Styrene and pyrrole monomers were purified by filtration through neutral alumina prior to use. Histidine (His), potassium persulfate (KPS), ammonium persulfate (APS), and sodium dodecyl sulfate (SDS) were obtained from Aladdin Chemistry Co., Ltd. Commercial Pt/C (20 wt% Pt) was sourced from Alfa Aesar. Deionized (DI) water (>18.2 MΩ·cm) was produced using a Millipore Ultrapure water system. All reagents were employed as received without additional purification.

Catalyst preparation

Synthesis Procedures

Preparation of polystyrene (PS) template:

A solution containing anhydrous Na_2CO_3 (0.1 g, 0.94 mmol) and SDS (0.2 g, 0.69 mmol) in 300 mL DI water was stirred under N_2 purge for 30 min. Styrene monomer (30 mL) was injected into the mixture and vigorously stirred at 60°C for 30 min, followed by dropwise addition of KPS aqueous solution (10 mL, 1 mmol). The reaction proceeded at 70°C for 20 h. The resulting PS nanoparticles were centrifuged (12,000 rpm, 30 min), washed repeatedly with DI water, and redispersed in 100 mL DI water to form the PS mother solution.

Fabrication of Co precursors:

PS mother solution (2 mL), $Co(NO_3)_2·6H_2O$ solution (0.5 M, 5 mL), histidine solution (0.5 M, 20 mL), and pyrrole monomer (30 μL) were sequentially added to 50 mL DI water under vigorous stirring. After 10 min, APS solution (0.5 M, 30 mL) was introduced, and the mixture was magnetically stirred for 3 h to deposit polypyrrole (PPy) onto PS surfaces. The product (denoted as PS@Co-His-PPy) was collected via filtration, washed with DI water/ethanol, and dried at 80°C under vacuum for 12 h.

Control samples:

PS@Co-PPy: Synthesized identically but without histidine.

PS@PPy: Prepared by omitting both $Co(NO_3)_2$ and histidine.

Thermal Conversion to Single-Atom Catalysts:

The precursors (PS@Co-His-PPy and PS@PPy) were pyrolyzed in a tube furnace at 700°C ($5°C·min^{-1}$, Ar flow) for 2 h. After cooling to room temperature, the resulting materials (Co-SAs/NHC and NHC, respectively) were directly collected for use.

Generalization to other metals: Analogous M-SAs/NHC catalysts (M = V, Cr, Mn, Fe, Ni, Cu, Zn, Bi, Ca, Mg) were synthesized by substituting $Co(NO_3)_2 \cdot 6H_2O$ with equimolar $VOSO_4$, $Cr(NO_3)_3 \cdot 9H_2O$, $MnCl_2$, $FeSO_4 \cdot 7H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, $Bi_2(SO_4)_3$, $CaCl_2$, or $MgCl_2$.

Characterization

The sizes and morphologies were characterized by a field emission scanning electron microscope (FESEM, Gemini SEM 300) and a transmission electron microscope (TEM, JEOL JEM-F200) with energy dispersive spectroscopy (EDS, JED-2300T). The high resolution and elemental mappings were obtained on a JEOL JEM-2100F at 200 kV Atomic dispersion and imaging were measured by using a TEM (FEI Spectra 300) at 200 keV, equipped with a probe spherical aberration corrector. The crystalline structure and phase purity were recorded on a Powder X-ray diffraction (XRD) (Philips X'pert PRO with nickel-fleered Cu Kα radiation (λ = 1.5406 Å)). X-ray photoelectron spectroscopic was used to assess the chemical composition and environment (XPS, Thermo Scientific K-Alpha) using Al Kα source (hν = 1486.6 eV). The X-ray absorption spectra (XAS) including X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) of the sample at Co K-edge was collected at the Beamline of TLS07A1 in National Synchrotron Radiation Research Center (NSRRC), Taiwan. Co foil, CoO, and Co_3O_4served as references and were conducted.

XAFS measurements and data analysis details

Data reduction, data analysis, and EXAFS fitting were performed and analyzed with the Athena and Artemis programs of the Demeter data analysis packages that utilizes the FEFF6 program to fit the EXAFS data. The energy calibration of the sample was conducted through a standard Fe foil which as a reference was simultaneously measured. A linear function was subtracted from the pre-edge region, then the edge jump was normalized using Athena software. The $\chi(k)$ data were isolated by subtracting a smooth, three-stage polynomial approximating the absorption background of an isolated atom The K^2-weighted $\chi(k)$ data were Fourier transformed after applying a Kaiser-Bessel window function ($\triangle k$ =1.0). For EXAFS modeling, the global amplitude EXAFS (CN, R σ^2 and $\triangle E_0$) were obtained by nonlinear fitting, with least-squares refinement, of the EXAFS equation to the Fourier-transformed data in R-space, using Artemis software, EXAFS of the Fe foil is fitted and the obtained amplitude reduction factor S_0^2 value (0.701 was set in the

EXAFS analysis to determine the coordination numbers (CNs) in the Co–O/N scattering path in sample.

Wavelet Transform analysis

For Wavelet Transform analysis, the $\chi(k)$ exported from Athena was imported into the Hama Fortran code. The parameters were listed as follow: R range, 0 - 6.0 Å, k range, 0 - 12.0 $Å^{-1}$ for Co-SAs/NHC (0-12.0 $Å^{-1}$ for foil, CoO, Co_3O_4); k weight, 2; and Morlet function with κ=10, σ=1 was used as the mother wavelet to provide the overall distribution.

Zinc–air batteries test

The practical performance of the Co-SAs/NHC catalyst was evaluated using a custom-built electrochemical workstation (OMS-T4, Changsha Spring New Energy Technology Co., China). Galvanostatic charge-discharge cycling experiments were performed using a LAND CT2001A battery analyzer (Wuhan Land Electronic Co., China). For cathode preparation, hydrophobic carbon paper (2 cm × 2 cm) served as the substrate. Uniform deposition of either Co-SAs/NHC ink or commercial Pt/C ink (containing equivalent RuO_2 content) was achieved via spray-coating, maintaining a catalyst deposition density of 1.5 ± 0.1 mg cm^{-2}. A pristine Zn foil anode was paired with an alkaline electrolyte system containing 6 M KOH and 0.2 M zinc acetate, while a Whatman GF/C glass fiber separator completed the cell configuration.

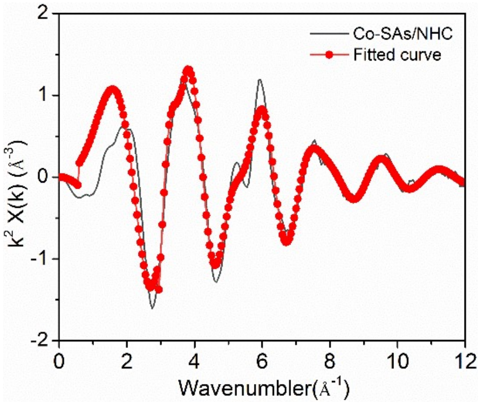

Figure S1. The k-space fitted curves of Co-SAs/NHC.

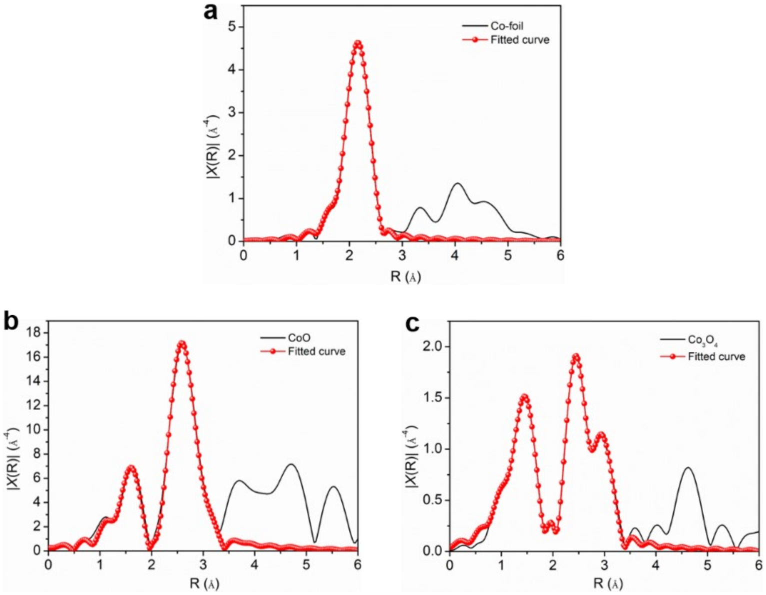

Figure S2. (a-c) The extended X-ray absorption fine structure (EXAFS) R space fitting curves of Co foil, CoO, and Co_3O_4, respectively.

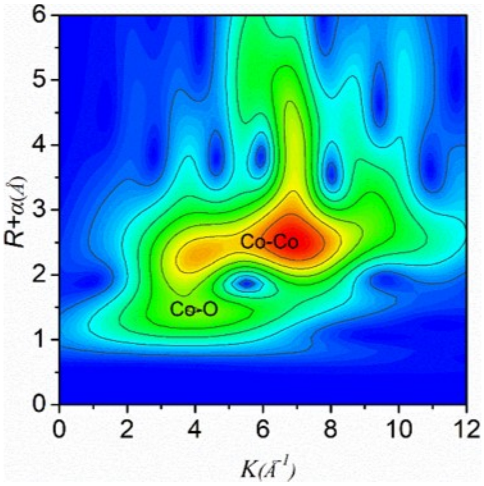

Figure S3. Wavelet transform (WT) of CoO.

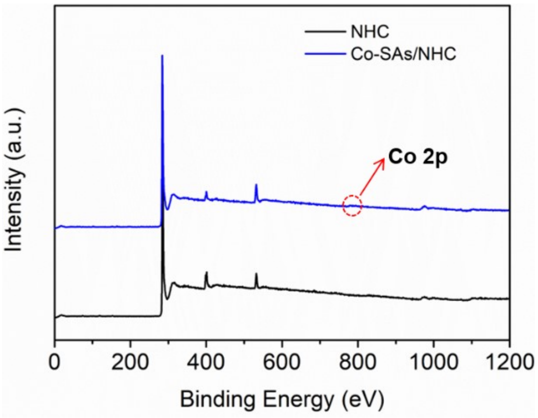

Figure S4. XPS survey spectra of NHC and Co-SAs/NHC.

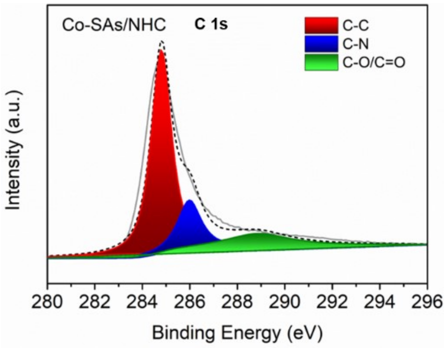

Figure S5. High-resolution C 1s XPS spectra of Co-SAs/NHC.

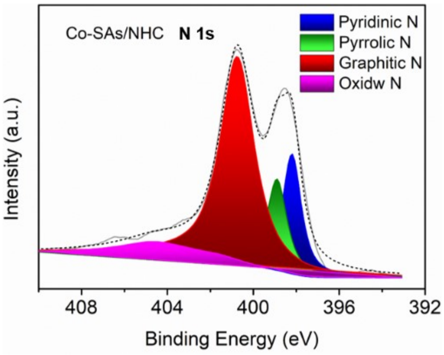

Figure S6. High-resolution N 1s XPS spectra of Co-SAs/NHC.

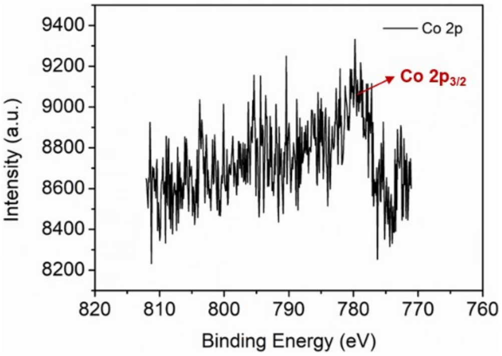

Figure S7. High-resolution Co 2p XPS spectrum of Co-SAs/NHC.

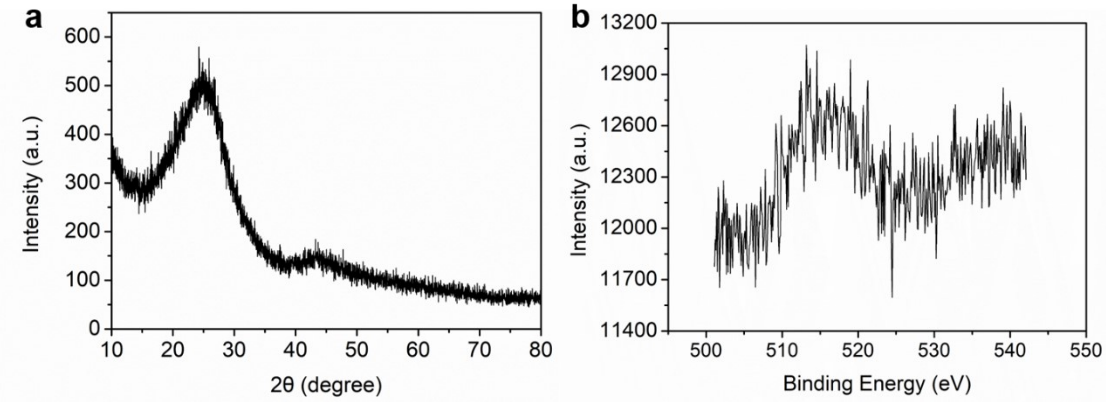

Figure S8. a XRD pattern and b High-resolution V 2p XPS spectrum of V-SAs/NHC.

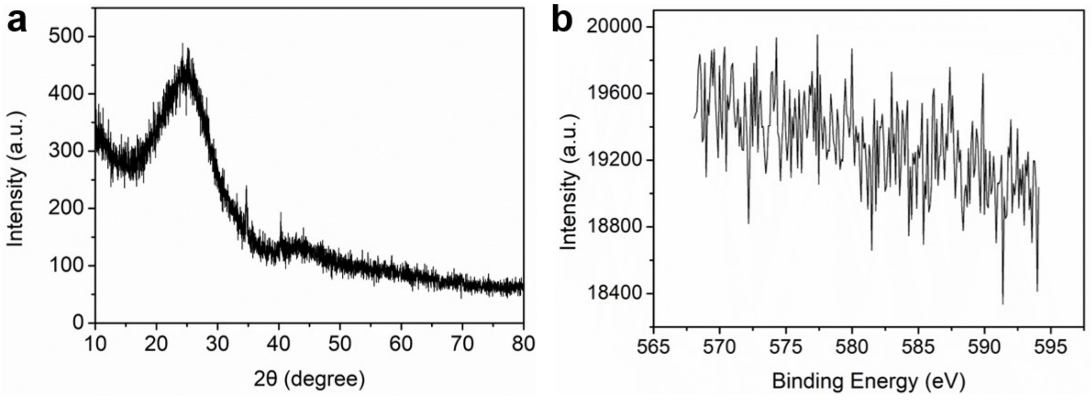

Figure S9. a XRD pattern and b High-resolution Cr 2p XPS spectrum of Cr-SAs/NHC.

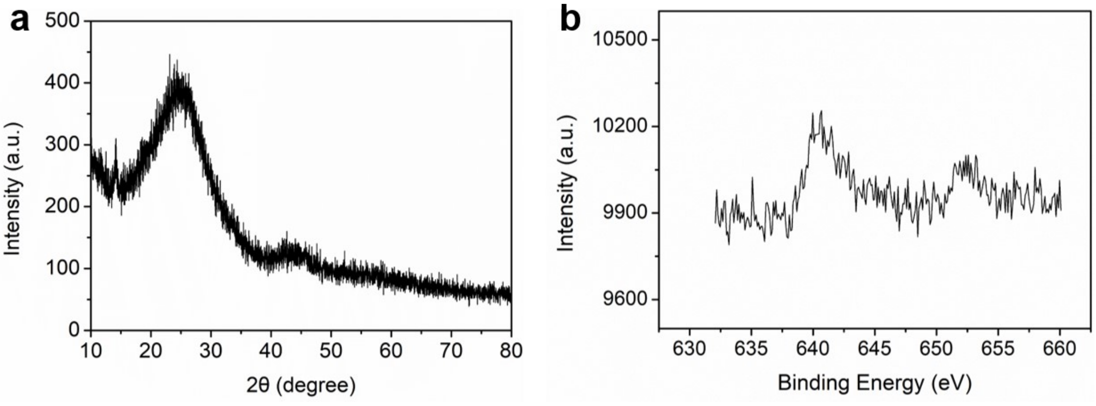

Figure S10. a XRD pattern and b High-resolution Mn 2p XPS spectrum of Mn-SAs/NHC.

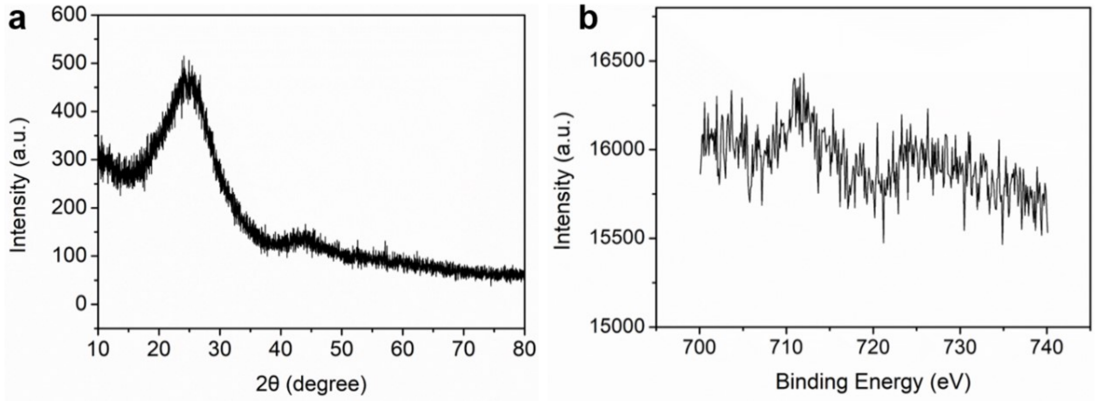

Figure S11. a XRD pattern and b High-resolution Fe 2p XPS spectrum of Fe-SAs/NHC.

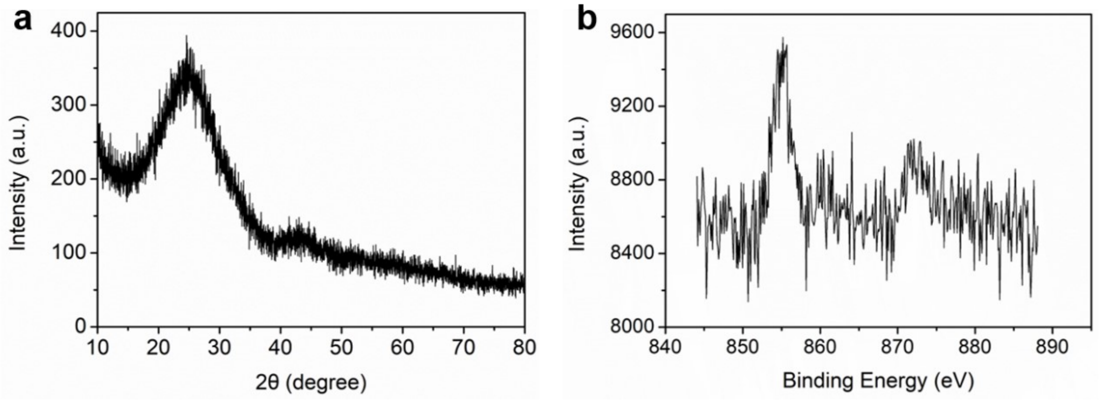

Figure S12. a XRD pattern and b High-resolution Ni 2p XPS spectrum of Ni-SAs/NHC.

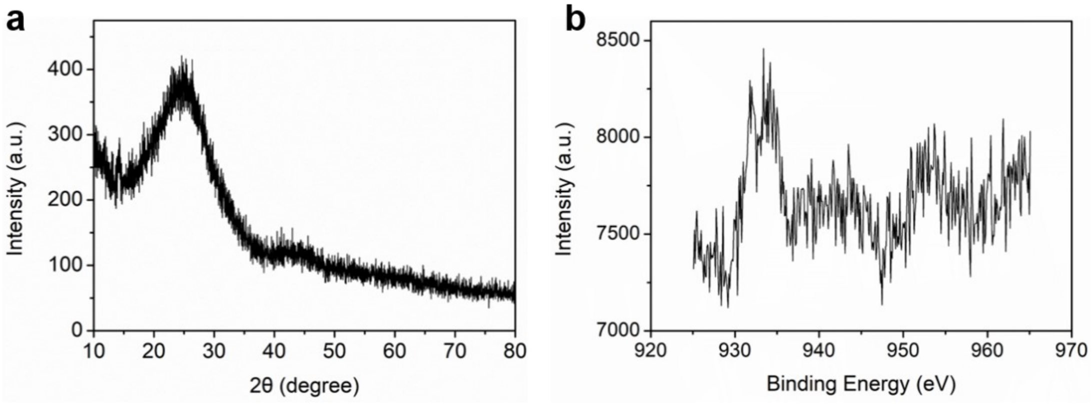

Figure S13. a XRD pattern and b High-resolution Cu 2p XPS spectrum of Cu-SAs/NHC.

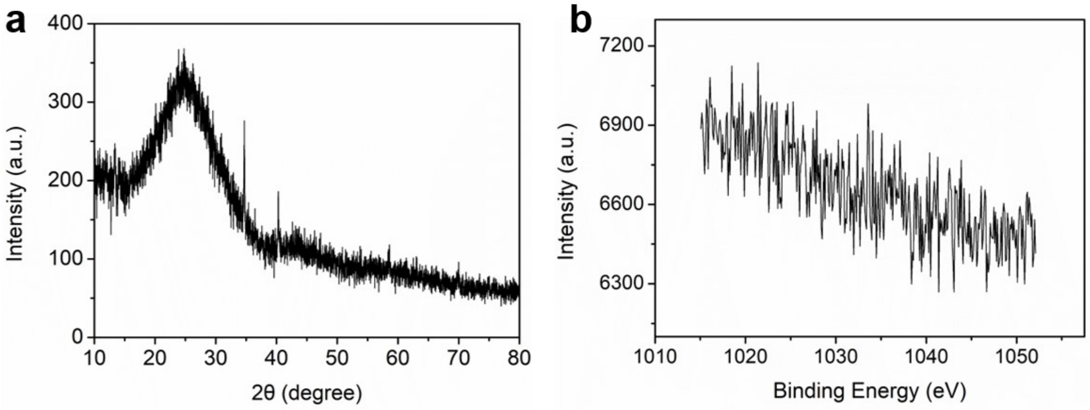

Figure S14. a XRD pattern and b High-resolution Zn 2p XPS spectrum of Zn-SAs/NHC.

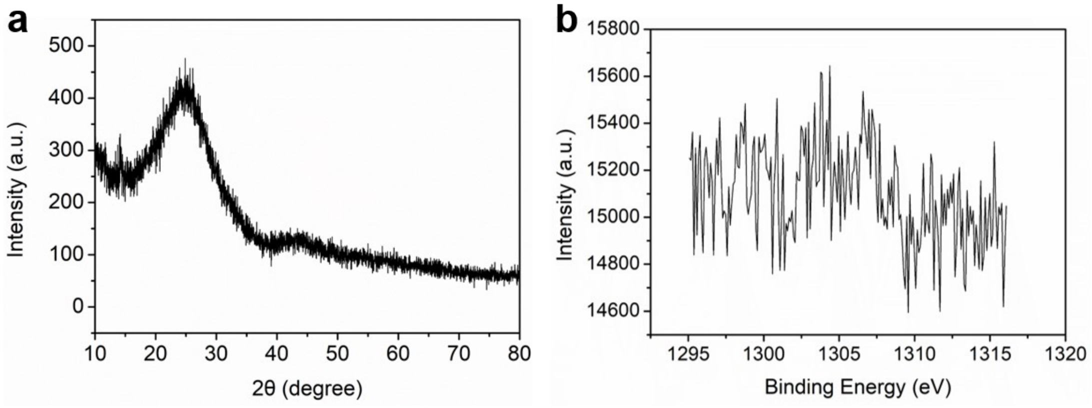

Figure S15. a XRD pattern and b High-resolution Mg 2p XPS spectrum of Mg-SAs/NHC.

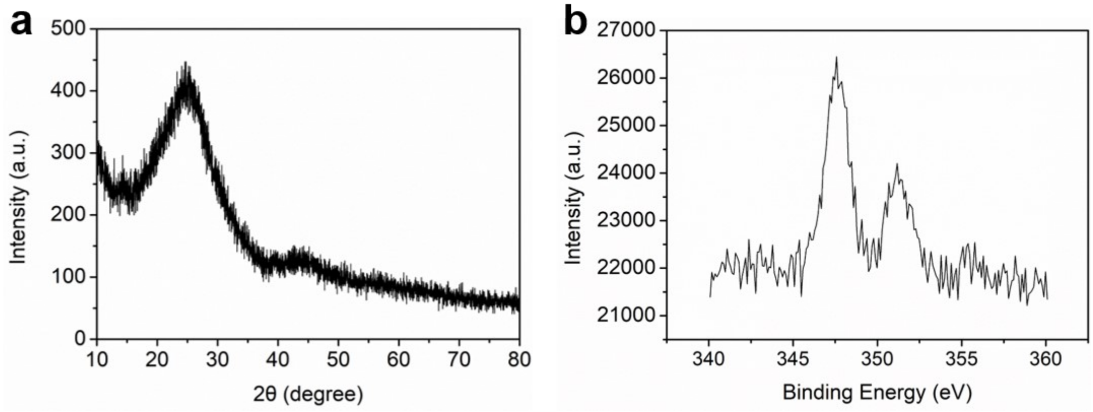

Figure S16. a XRD pattern and b High-resolution Ca 2p XPS spectrum of Ca-SAs/NHC.

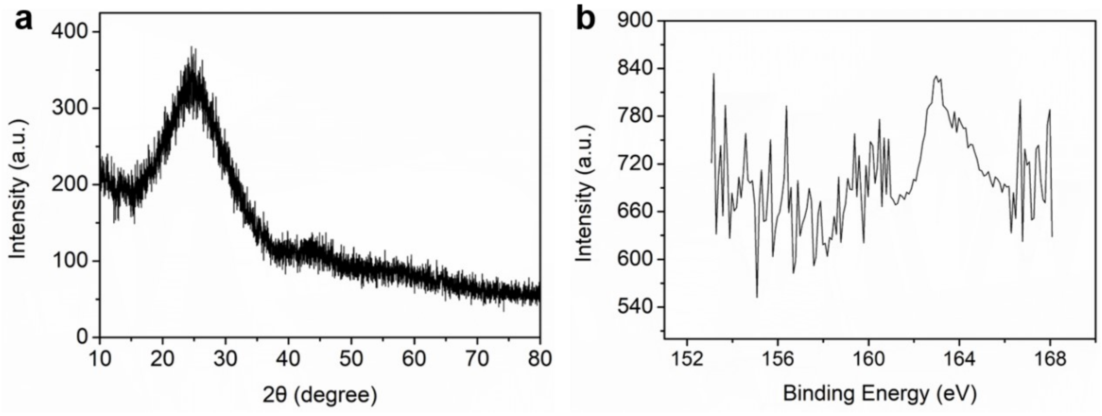

Figure S17. a XRD pattern and b High-resolution Bi 4f XPS spectrum of Bi-SAs/NHC.

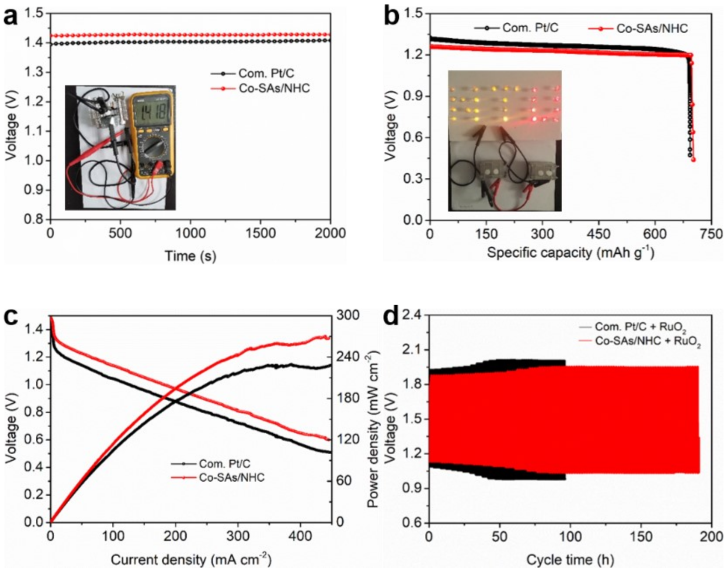

Figure S18. (a) Open-circuit voltage of Co-SAs/NHC- and Com. Pt/C-based Zn-air batteries (ZABs). Inset: Photograph of Co-SAs/NHC-based ZAB. (b) Discharging polarization plots of Co-SAs/NHC- and Com. Pt/C-based ZABs with a current density of 10 mA cm^{-2}. Inset: Photograph of 25 parallel-connected LEDs powered by 2 serially connected Co-SAs/NHC-based ZABs. (c) The corresponding power density profiles of the above mentioned two ZIBs. (d) Discharge-charge cycling curves of the Co-SAs/NHC assembled and Com. Pt/C assembled ZABs, and the charging and discharging time is set to 5 minutes.

Table S1. EXAFS fitting parameters at the Co K-edge for various samples (S_0^2=0.80).

Sample	Shell	CN^a	R(Å)^b	σ^2(Å^2)^c	ΔE_0(eV)^d	R factor
Co K-edge						
Co foil	Co-Co	12*	2.49±0.01	0.0028	8.2	0.002
CoO	Co-O	6.0±0.1	2.11±0.01	0.0083	6.2	0.006
	Co-Co	12.0±0.1	3.00±0.01	0.0083	5.9	
Co_3O_4	Co-O	6.0±0.1	1.92±0.01	0.0026	4.6	0.005
	Co-Co	6.0±0.1	3.08±0.01	0.0069	8.5	
	Co-N	3.1±0.1	1.96±0.01	0.0079	7.9	
Co-SAs/NHC	Co-O	1.1±0.1	2.08±0.01	0.0031	4.1	0.006
	Co-N	3.2±0.1	2.10±0.01	0.0037	5.0	

Note: $^a CN$, coordination number; $^b R$, distance between absorber and backscatter atoms; $^c \sigma^2$, Debye-Waller factor to account for both thermal and structural disorders; $^d \Delta E_0$, inner potential correction; R factor indicates the goodness of the fit. S_0^2 was fixed to 0.80, according to the experimental EXAFS fit of Co foil by fixing CN as the known crystallographic value. Fitting range: $3.0 \leq k$ (/Å) ≤ 12.0 and $1.0 \leq R$ (Å) ≤ 3.0 (Co foil); $3.0 \leq k$ (Å^{-1}) ≤ 12.0 and $1.0 \leq R$ (Å) $\leq$ ~3.0 (Co-SAs/NHC, Co, CoO, Co_3O_4). A reasonable range of EXAFS fitting parameters: $0.700 < S_0^2 < 1.000$; $CN > 0$; $\sigma^2 > 0$ Å^2; $\Delta E_0 < 10$ eV; R factor < 0.02.

* This value was fixed during EXAFS fitting, based on the known structure.

Table S2. The metals content of various SACs measured by ICP-AES analysis.

Catalyst	Metal content (wt%)
V-SAs/NHC	5.6
Cr-SAs/NHC	4.7
Mn-SAs/NHC	5.9
Fe-SAs/NHC	9.3
Ni-SAs/NHC	8.2
Cu-SAs/NHC	7.6
Zn-SAs/NHC	6.6
Mg-SAs/NHC	4.8
Ca-SAs/NHC	4.5
Bi-SAs/NHC	4.6