

Electronic Supplementary Information

Engineering of Carbon Nanotube-Grafted Carbon Nanosheets Encapsulating Cobalt Nanoparticles for Efficient Electrocatalytic Oxygen Evolution

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Experimental Section

Synthesis of CoAl-LDH template: The sample of CoAl-LDH was synthesized in a three-neck flask. Typically, 5 mM $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, 10 mM $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and 35 mM urea were first added in 400 mL of deionized water, and then the above solution was continuously stirred and heated at 97 °C for 48 hours. Finally, the sample was collected by centrifugation and dried for later use.¹

Synthesis of precursors: LDH@ZnCo-ZIFs-2 was prepared in methanol at room temperature. Firstly, a 30 mL 2-methylimidazole (MeIM) methanol solution (0.8 M) was poured into a 50 mL methanol solution in which 0.1 g of CoAl-LDH was dispersed, and then the pre-dissolved 40 mL of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (2mmol) and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (4mmol) methanol solution was added into the former solution under stirring for 15 min. After placed for 24 hours, the powders were collected by centrifugation and washed with methanol, and then dried overnight. Using the above method, LDHs@ZnCo-ZIFs with different Co/Zn molar ratios (denoted as LDH@ZnCo-ZIFs-X (X = 0.5, 1, 2, 3)) were prepared by changing the relative contents of metal salts. The synthesis method of the reference sample LDH@ZIF-67 was the same as above, except that zinc salt was not added to LDH@ZIF-67. Preparation of ZnCo-ZIFs (Co/Zn=2) referred to the synthetic method reported in the literature.²

Synthesis of samples: The as-prepared LDH@ZnCo-ZIFs precursors were annealed in an Ar/H₂ (volume ratio: 95%/5%) atmosphere at 800 °C for 2 hours. Then, the black powder was collected after cooling naturally, and recorded as

LDH-R@Co(v-Zn)-NCNTs-X (X = 0.5, 1, 2, 3). The reference sample precursors LDH@ZIF-67, ZnCo-ZIFs and CoAl-LDH were carbonized under the same conditions to obtain samples, which are denoted as LDH-R@Co-NCNTs, Co(v-Zn)-NCNTs and CoAl-LDH-R, respectively. The LDH@ZnCo-ZIFs-2 precursor was also carbonized in the inert atmosphere to obtain a carbon nanotube-free catalyst, named LDH-I@Co(v-Zn)-C.

Characterization: Scanning electron microscopy (SEM, FEI Quanta FEG 250) and transmission electron microscopy (TEM, JEOL 2100F) were used to observe the morphology and microstructures of as-synthesized samples. The element distributions was observed by the energy-dispersive X-ray spectroscopy analyzer, which was combined with the SEM. The crystal structure and phase composition of the prepared materials were collected using X-ray diffraction (XRD, Cu K α radiation). X-ray photoelectron spectroscopy (XPS) was conducted on Kratos Axis Supra. An Aglient 725-ES inductively coupled plasma (ICP) was employed. The specific surface area and porous structure were investigated by the Brunauer-Emmett-Teller (BET) method using a Quantachrome ASIQM0VH002-5 instrument. Raman characterization was recorded using a Renishaw RM 2000 system with a 633 nm laser source.

Electrochemical Measurements: Catalytic activity evaluations were demonstrated in a solution of 1 M KOH with a typical three-electrode system where an Ag/AgCl (saturated KCl solution) electrode worked as reference electrode and a Pt mesh worked as counter electrode. The glassy carbon electrode (GC, 3 mm in diameter) covered with active materials was utilized as the working electrode. Typically, a

homogeneous ink containing catalyst (2 mg), deionized water (780 μL), ethanol (200 μL) and Nafion (20 μL , 5 wt%) was prepared. Then, the working electrode was prepared by depositing 7 μL of catalyst solution on the GC electrode to achieve catalyst loadings of approximately 0.2 mg cm^{-2} . The linear scan voltammetry (LSV) polarization curves were performed at 5 mV s^{-1} without the ohmic potential drop (iR) correction. All the applied potentials were referenced to a reversible hydrogen electrode (RHE) scale. The C_{dl} was obtained by conducting Cyclic voltammograms (CV) measurements at the scan rates of 5, 10, 20, 40, 60, 80 and 100 mV s^{-1} from 0.20 to 0.30 V versus saturated Ag/AgCl. Faradaic efficiency was calculated by comparing the amount of experimentally quantified gas with that of theoretically calculated gas.^{3,4} The conductivity was estimated by the standard four-probe direct current method using a Keithley 2400 source meter. The long-term stability test was carried out using chronoamperometry measurements. The durability test was conducted by CV for 1000 circles, and the LSV curves before and after CV were tested for comparison.

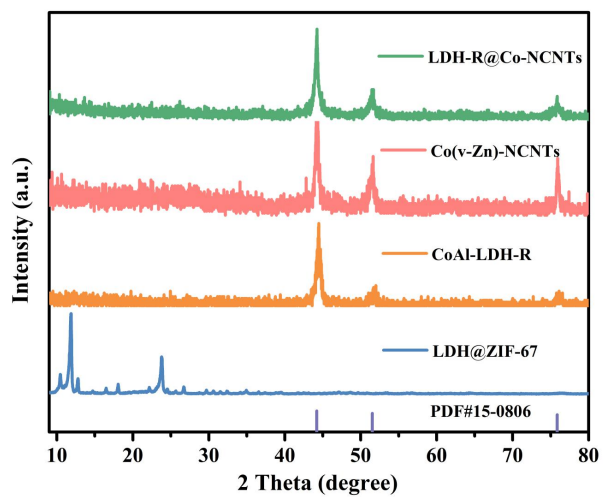


Fig. S1 XRD patterns of LDH@ZIF-67, CoAl-LDH-R, Co(v-Zn)-NCNTs and LDH-R@Co-NCNTs.

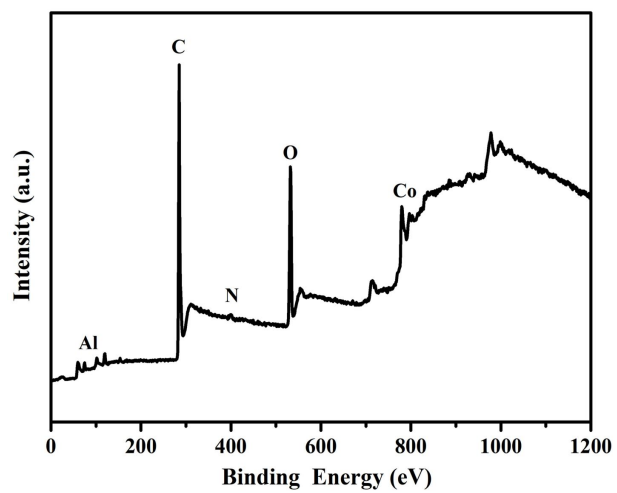


Fig. S2 Full scan XPS spectrum of LDH-R@Co(v-Zn)-NCNTs-2.

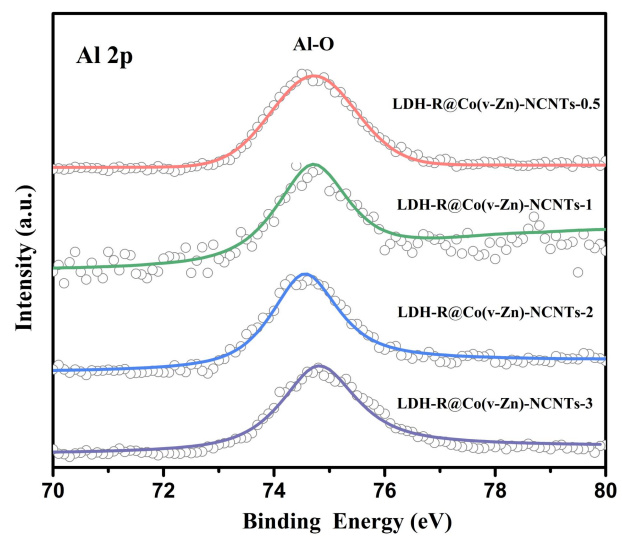


Fig. S3 Al 2p XPS spectra of LDH-R@Co(v-Zn)-NCNTs.

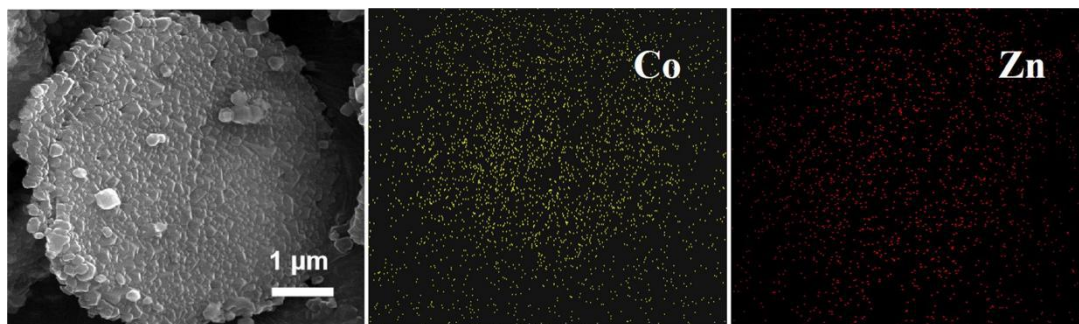


Fig. S4 EDX element mapping of LDH@ZnCo-ZIFs-2.

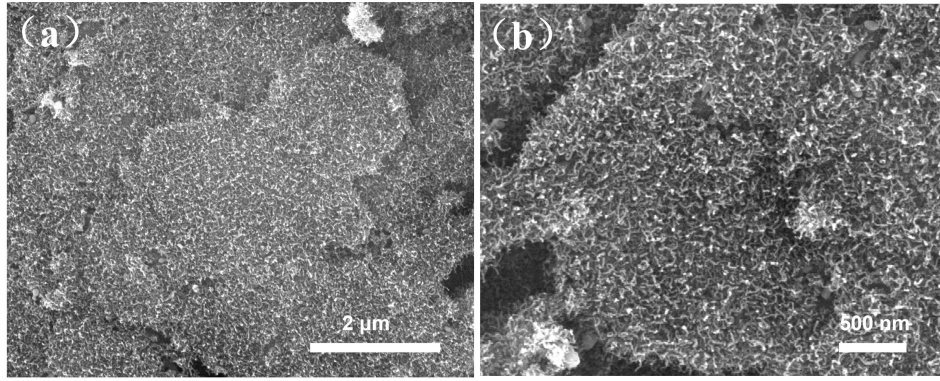


Fig. S5 SEM images of LDH-R@Co(v-Zn)-NCNTs-2 at low and high magnifications.

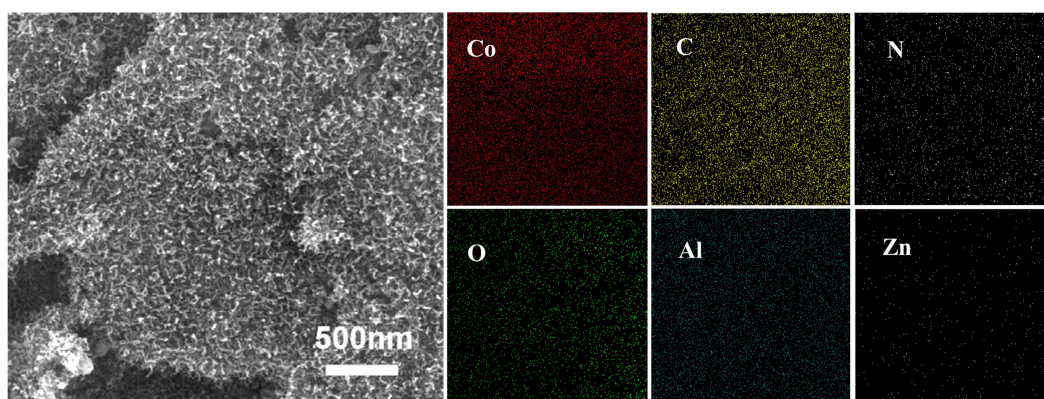


Fig. S6 EDX element mapping of LDH-R@Co(v-Zn)-NCNTs-2.

Table S1 ICP data of LDH-R@Co(v-Zn)-NCNTs-2.

Elements	Mass percentage (wt%)
Co	39.39
Al	1.61
Zn	0.076

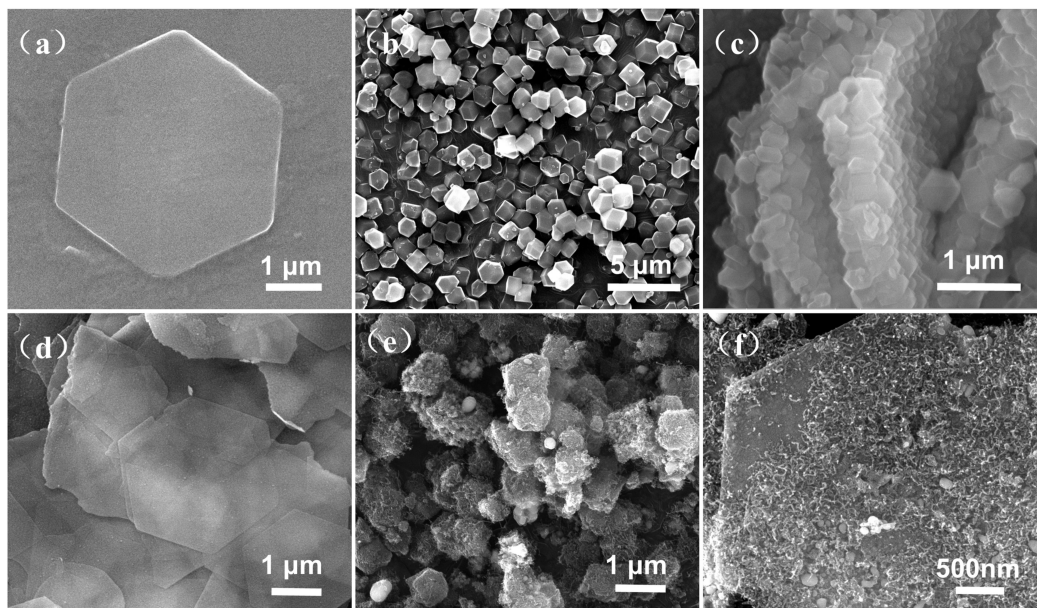


Fig. S7 SEM images of (a) CoAl-LDH, (b) ZnCo-ZIFs, (c) LDH@ZIF-67, (d) CoAl-LDH-R, (e) Co(v-Zn)-NCNTs and (f) LDH-R@Co-NCNTs.

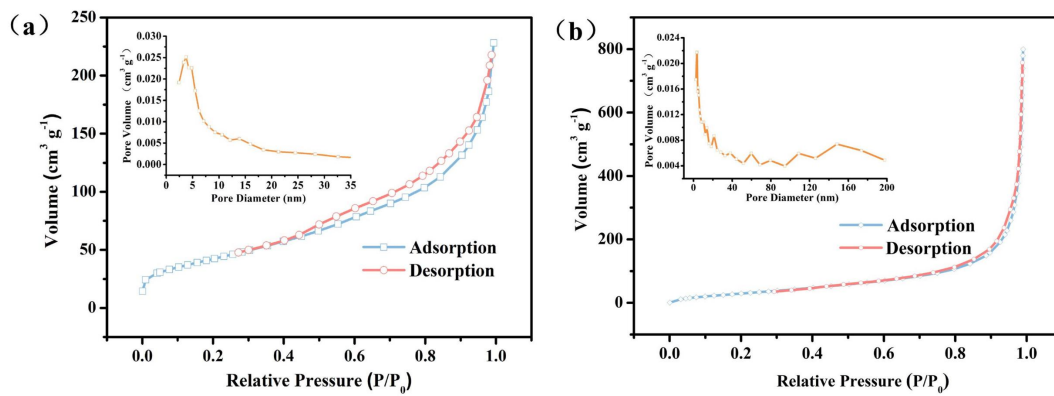


Fig. S8 Nitrogen adsorption-desorption isotherm and pore diameter distribution of (a) LDH-R@Co(v-Zn)-NCNTs-2 and (b) LDH-R@Co-NCNTs.

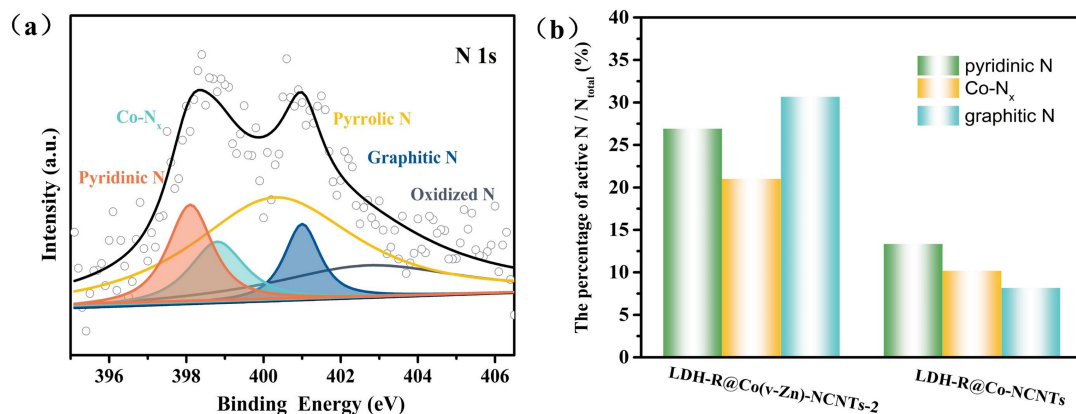


Fig. S9 (a) High-resolution XPS spectra of N 1s for the LDH-R@Co-NCNTs. (b) The percentage of active N/N_{total} (Co-N_x, pyridinic N and graphitic N) of the LDH-R@Co(v-Zn)-NCNTs-2 and LDH-R@Co-NCNTs.

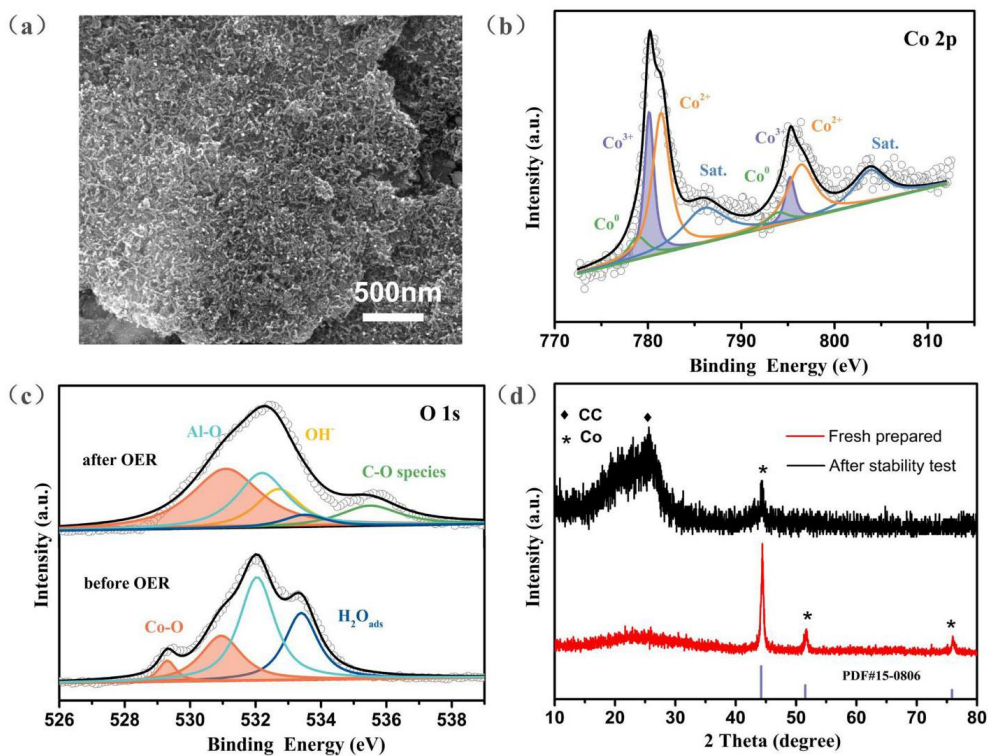


Fig. S10 (a) SEM image, (b and c) XPS and (d) XRD patterns of the LDH-R@Co(v-Zn)-NCNTs-2 catalyst after 10 hours of stable catalysis. (In order to facilitate component confirmation, the catalyst was loaded on carbon cloth (CC) for stability testing.)

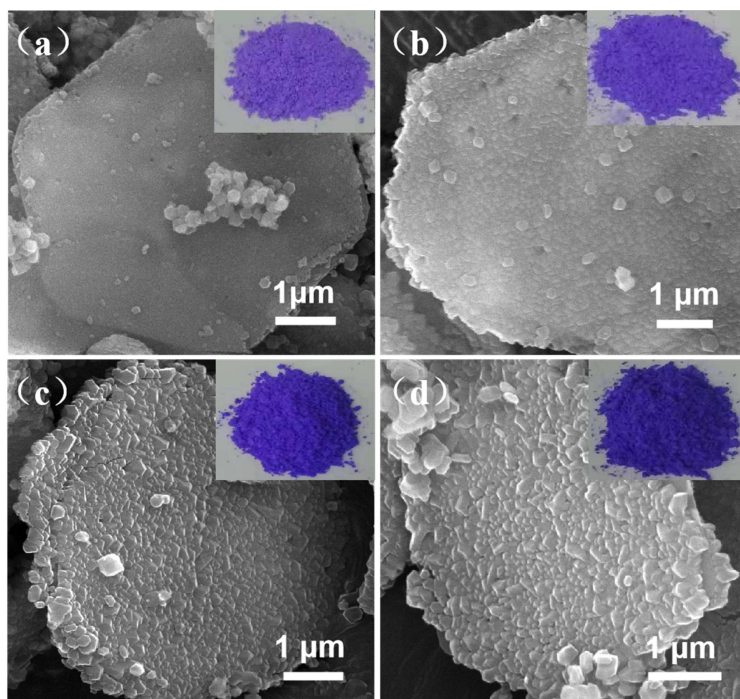


Fig. S11 SEM images and the corresponding photographs (inset) of LDH@ZnCo-ZIFs- X with different Co/Zn molar ratios: (a) $X=0.5$, (b) $X=1$, (c) $X=2$ and (d) $X=3$.

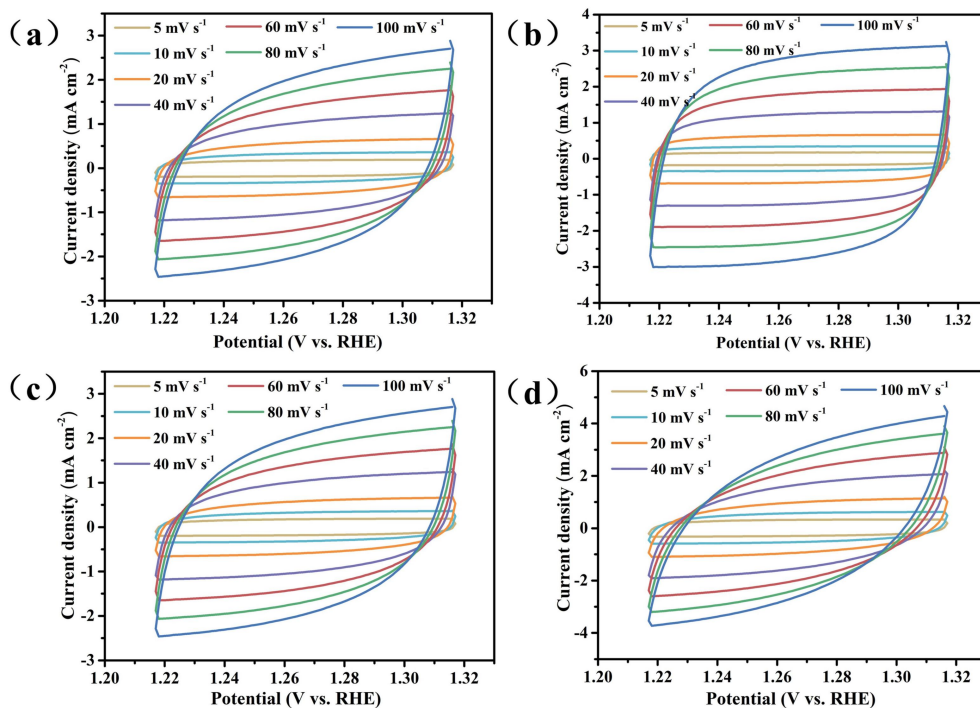


Fig. S12 Cyclic voltammograms in the double-layer region of the electrodes loaded with LDH-R@Co(v-Zn)-NCNTs- X with different Co/Zn molar ratios: (a) $X=0.5$, (b) $X=1$, (c) $X=2$ and (d) $X=3$.

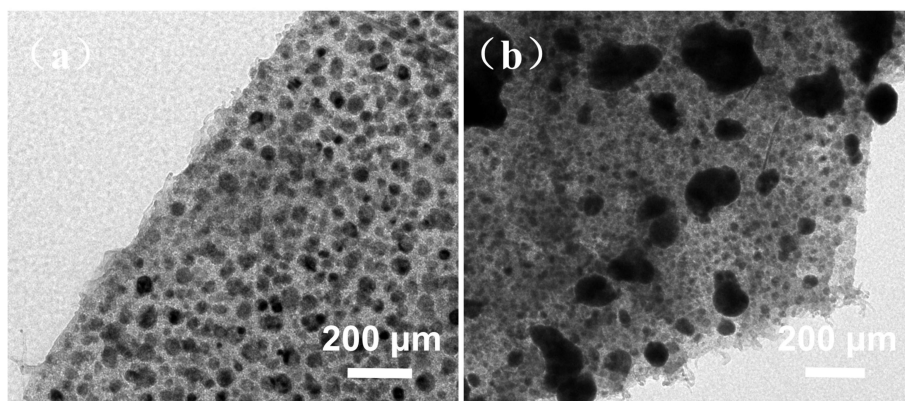


Fig. S13 TEM images of LDH-R@Co(v-Zn)-NCNTs- X with different Co/Zn molar ratios: (a) $X=0.5$ and (b) $X=3$.

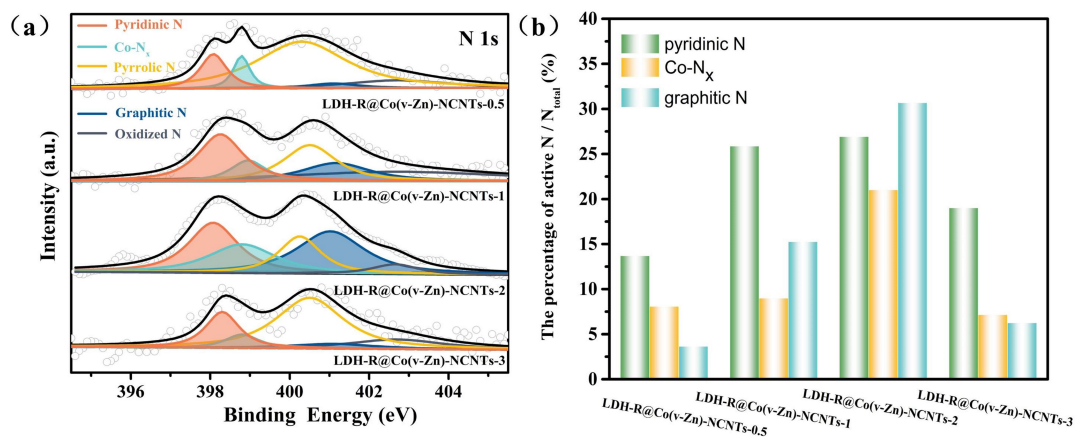


Fig. S14 (a) N 1s XPS spectra (b) the percentage of active N/N_{total} (Co-N_x, pyridinic N and graphitic N) of the LDH-R@Co(v-Zn)-NCNTs-X (X = 0.5, 1, 2, 3).

Table S2 Comparison of catalytic performance of LDH-R@Co(v-Zn)-NCNTs-2 and various reported OER catalysts in alkaline.

Electrocatalysts	Overpotential (mV vs. RHE) at 10 mA·cm⁻²	Tafel slope (mV dec⁻¹)	Electrolyte	Ref
LDH-R@Co(v-Zn)-NCNTs-2	344	75	1 M KOH	This work
Co SA@NCF/CNF	400	56	1 M KOH	5
Co ₂ Mo ₃ O ₈ @NC	331	87.5	1 M KOH	6
Co/Fe-MOFs	410	101	1 M KOH	7
CoP-PBSCF	340	81.5	1 M KOH	8
Co _{3.2} Fe _{0.8} N/MNC-100	350	--	1 M KOH	9
Co-MOFs-1-4	398	59	1M KOH	10
Co-MOF _{72h}	387	90	1 M KOH	11

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