

Supporting Information

Theoretical calculations-driven rational screening of d-block single-atom electrocatalysts based on d-p orbital hybridization for durable aqueous zinc-iodine batteries

Jin Yang, Yuanhong Kang, Fanxiang Meng, Weiwei Meng, Guanhong Chen, Minghao Zhang, Zeheng Lv, Zhipeng Wen, Cheng Chao Li, Jinbao Zhao,* and Yang Yang**

Experimental Procedures

Materials:

All commercially available reagents and solvents were purchased from Maclin and Aladdin and used directly without additional purification unless specifically mentioned.

Synthesis of ZIF-8:

After 3.28 g 2-methylimidazole and 2.97 g $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were completely dissolved in 100 mL methanol, respectively, the two solutions were quickly mixed homogeneously while stirring and the white suspension was obtained by vigorous stirring for 10 h at room temperature. After aging for 12 h, the white product ZIF-8 was obtained by centrifugation at 11000 r/min. Then the white product was washed with methanol for at least three times or more, and finally dried under vacuum at 80 °C for 10 h.

Synthesis of precursor NC-650

The white product ZIF-8 obtained above was placed in a magnetic boat, and after being heated up to 650 °C at 5 °C /min under a flowing argon protective atmosphere and kept at a constant temperature for 1 h, the pre-pyrolyzed precursor NC-650 was obtained after cooling down.

Synthesis of Nb-NC and Fe-NC monoatomic catalysts

After 0.1 g NC-650 was added to 100 mL ethanol, 7 μL niobium ethoxide was added, and after vigorous stirring for 10 h, the obtained product was centrifuged at 11,000 r/min (washed by anhydrous ethanol for more than three times), dried, and then heated at a constant temperature of 960 °C in argon environment for 3 h to obtain Nb-NC powder. The niobium source mentioned above was replaced with 16.3 mg ferric acetylacetonate as the iron source, and the Fe-NC powder was obtained using the same experimental procedure.

In addition, in order to evaluate the degree of catalytic activity of different metal single-atom catalysts, the precursor NC-650 was directly used to obtain NC powders following the same experimental method without the addition of metal source.

Synthesis of M-NC/I₂

The M-NC catalyst and I₂ were grinded homogeneously in the ratio of 1:2 by mass and placed in serum vials, which were sealed and heated at 120 °C for 6 h to make the iodine adsorbed on the catalysts, and then left open and heated at 80 °C for 2 h to eliminate the iodine monomers adsorbed on the surface of the catalysts, and the resultant materials were named as Nb-NC/I₂, Fe-NC/I₂, and NC/I₂. The prepared M-NC/I₂ material, acetylene black and PTFE mixture (60 wt%) were mixed in a mass ratio of 7:2:1, and a little isopropyl alcohol was added dropwise for shaping to obtain a uniform slurry in the form of playdough. The slurry was then rolled into a sheet with a thickness of about 100 μm using a roller press, dried at room temperature for more than 10 h, and then punched into a circular electrode sheet with a diameter of 12 mm, and the I₂ loading was controlled to be in the range of 2.0-3.0 mg cm⁻².

Material Characterization:

Field scanning electron microscope (FESEM, Zeiss Merlin Gemini) was used to analyze the surface morphology. Transmission electron microscopy (TEM, Tecnai F30 TWIN, FEI) was used to obtain the morphology and element distribution. The crystal structure was characterized by XRD (Rigaku Corporation, Japan) with Cu-K α radiation. The XPS profile was obtained by Thermo Scientific ESCALAB Xi+ (Al-K α , 1486.68eV). UV-vis absorption spectroscopy measurements were carried out on a UV-2600 spectrometer (Shimadzu). In situ UV spectroscopy was performed in a home-made electrochemical cell: zinc foil and Nb-NC/I₂ electrode were attached to each side of the cuvette, with 2 M ZnSO₄ electrolyte inside. UV spectra were collected at timed intervals during the charging and discharging processes. Raman spectra were obtained by LabRAM HR Evolution (Horiba) with a laser wavelength of 532 nm.

In situ Raman spectroscopy was performed in a home-made electrochemical cell. The cell was structure from top to bottom as follows: the CR2016 positive battery case, Nb-NC/I₂ electrode, GF/D separator, 100 μm zinc foil, and CR2016 negative battery case. There are holes in the center of positive battery case, Nb-NC/I₂ electrode, and GF/D separator, allowing the Raman laser directly detecting signals from the electrolyte near the zinc metal anode region during the charging and discharging processes. Values of specific surface area and pore size distribution of Nb-NC and NC were tested using an ASAP 2020 (micromeritics, Inc., USA) physicochemical adsorption and desorption apparatus. The XAFS data were collected through the Shanghai Synchrotron Radiation Facility (SSRF, BL11B) with Si (311) crystal monochromators for Nb K-edge. The Nb K-edge XAFS spectra were recorded in transmission mode.

Electrochemical Measurements:

The cells were assembled in CR2032-type coin cells using M-NC/I₂, 2 M aqueous ZnSO₄, Zn foil (with a diameter of 16 mm) and glass fiber (Whatman® GF/D Glass microfiber filters) as cathode, electrolyte, anode, and separator, respectively. The galvanostatic charge/discharge (GCD) tests were carried out by using Neware BTS test system. Cyclic voltammetry (CV) tests were recorded by CHI 660E electrochemical workstation and Autolab PGSTAT-302N instrument.

Theoretical calculation:

This work was completed by using the Vienna Ab-initio Simulation Package (VASP) and Density functional theory (DFT).^[1,2] Projector augmented wave (PAW)^[3] and generalized gradient approximation (GGA)^[4] were used to describe the electron exchange-correlation energies using PBE function, and D3 dispersion correction was added.^[5] The cutoff energy was set to 500 eV for the plane wave basis. The M-NC (M = Co, Cu, Fe, Nb, Ni, Zn, Mo, Pt, Rh,

W, Ru and Ti) and ionic species (I^- , I_2 , I_3^- , I_5^-) were optimized using the Conjugate Gradient method. The total energy convergence criterion of electron relaxation was 1.0×10^{-5} eV, and the convergence criterion of ion relaxation is 0.02 eV/Å. The strong correlation correspondence of d or f electrons was corrected by DFT+U. The U-J values of Co, Cu, Fe, Nb, Ni, Mo, Pt, Rh, W, Ru and Ti were set to 2.0 eV, 2.0 eV, 2.0 eV, 2.5 eV, 2.5 eV, 2.0 eV, 2.0 eV, 2.0 eV, 2.0 eV, 2.0 eV and 2.0 eV, respectively. The Gamma k-points mesh was set to be $3 \times 3 \times 1$. The adsorption energy calculation formula was as follows: $E_{\text{ads}} = E_{\text{AB}} - E_{\text{A}} - E_{\text{B}}$, where E_{ads} is adsorption energy, E_{AB} is the total energy of the optimized structures for $I^-/I_2/I_3^-/I_5^-$ adsorbed on M-NC, E_{A} is the energy of isolated $I^-/I_2/I_3^-/I_5^-$, E_{B} is the energy of M-NC. The Gibbs free energy was calculated as ΔG the equation: $\Delta G = E_{\text{total}} + E_{\text{ZPE}} - TS$, where E_{total} and E_{ZPE} refer to DFT calculated total energy and zero point energy, and TS is the entropic contribution.

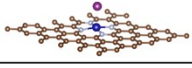
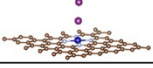
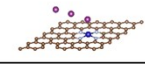
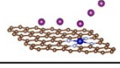
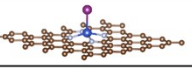
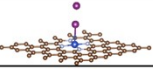
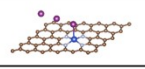
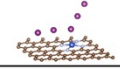
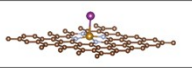
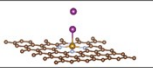
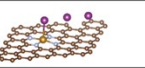
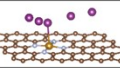
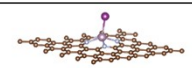
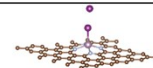
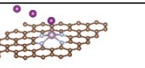
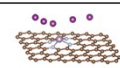
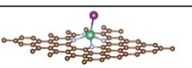
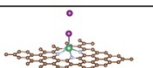
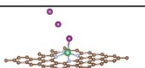
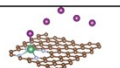
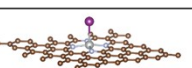
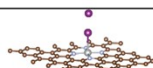
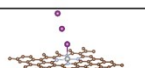
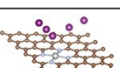
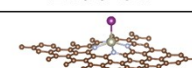
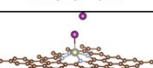
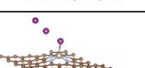
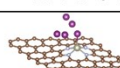
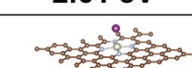
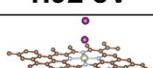
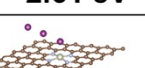
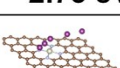
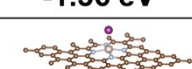
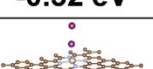
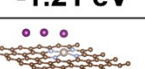
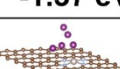
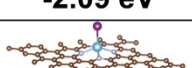
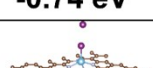
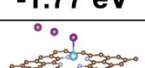
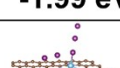
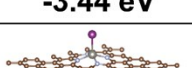
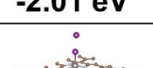
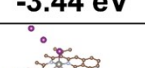
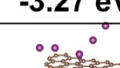
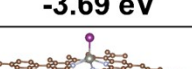
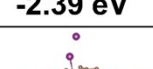

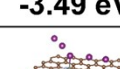
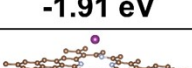
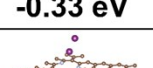

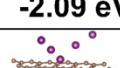
	I^-	I_2	I_3^-	I_5^-
Co-NC				
	-1.91 eV	-0.52 eV	-1.64 eV	-1.79 eV
Cu-NC				
	-1.18 eV	-0.29 eV	-1.38 eV	-1.47 eV
Fe-NC				
	-1.47 eV	-0.37 eV	-1.48 eV	-1.54 eV
Mo-NC				
	-2.42 eV	-1.00 eV	-2.22 eV	-2.16 eV
Nb-NC				
	-4.27 eV	-3.22 eV	-3.63 eV	-3.92 eV
Ni-NC				
	-2.58 eV	-1.90 eV	-2.29 eV	-1.41 eV
Re-NC				
	-2.61 eV	-1.92 eV	-2.61 eV	-2.73 eV
Rh-NC				
	-1.36 eV	-0.32 eV	-1.21 eV	-1.37 eV
Ru-NC				
	-2.09 eV	-0.74 eV	-1.77 eV	-1.99 eV
Ti-NC				
	-3.44 eV	-2.01 eV	-3.44 eV	-3.27 eV
W-NC				
	-3.69 eV	-2.39 eV	-3.15 eV	-3.49 eV
Zn-NC				
	-1.91 eV	-0.33 eV	-1.86 eV	-2.09 eV
NC				
	-0.70 eV	-0.58 eV	-0.50 eV	-1.03 eV

Figure S1. Adsorption models and adsorption energy values of M-NC (M = Co, Cu, Fe, Nb, Ni, Re, Rh, Ru, Ti, W, and Zn) and NC for I^- , I_2 , I_3^- and I_5^- .

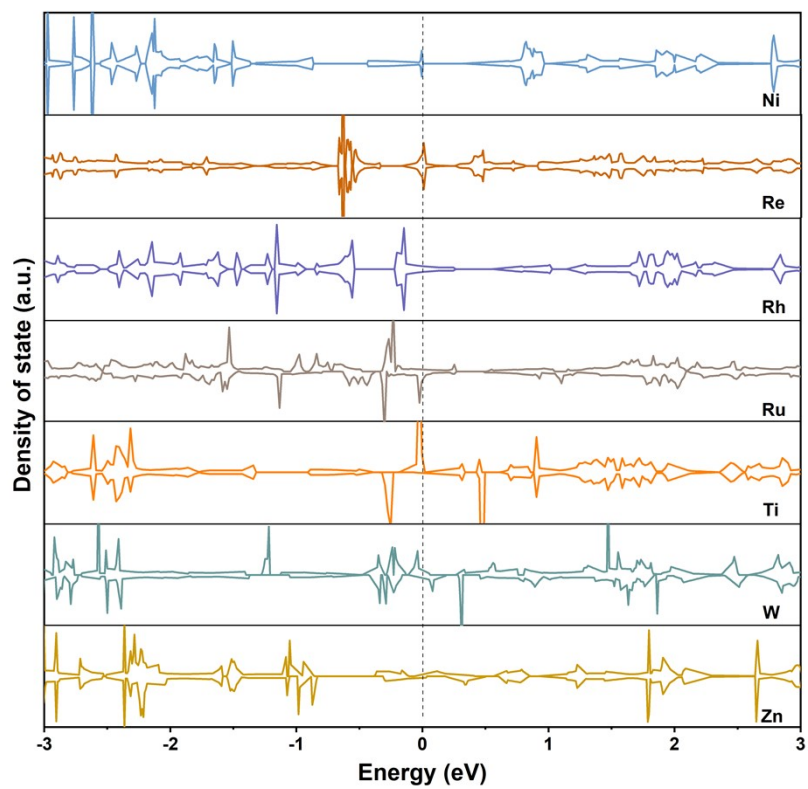


Figure S2. DOS for the different M-NC (M =Ni, Re, Rh, Ru, Ti, W, Zn).

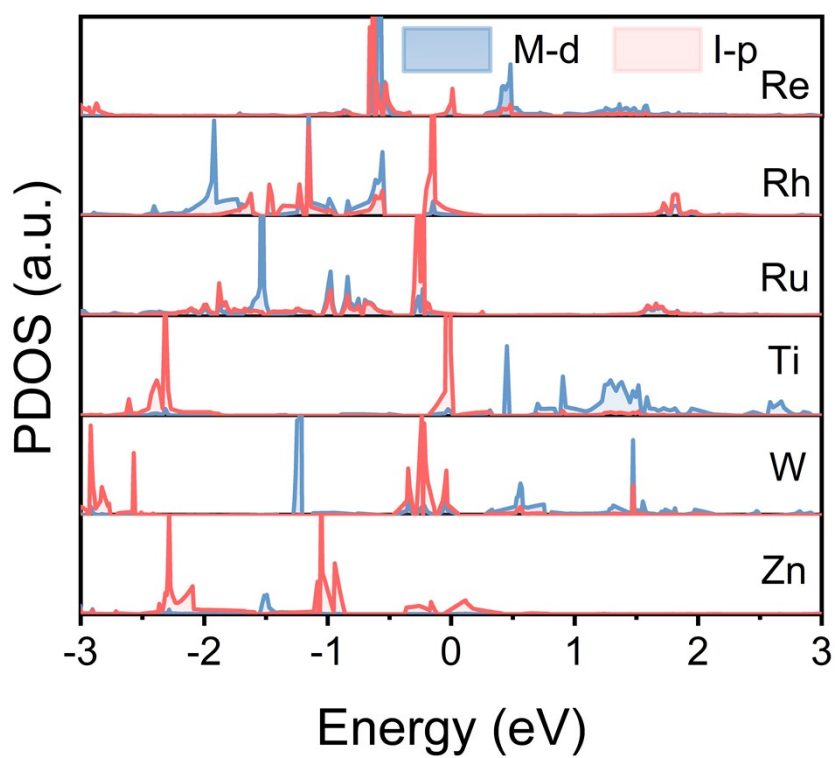


Figure S3. PDOS between the p orbital of I and d orbital of M-NC (M = Re, Rh, Ti, W, and Zn).

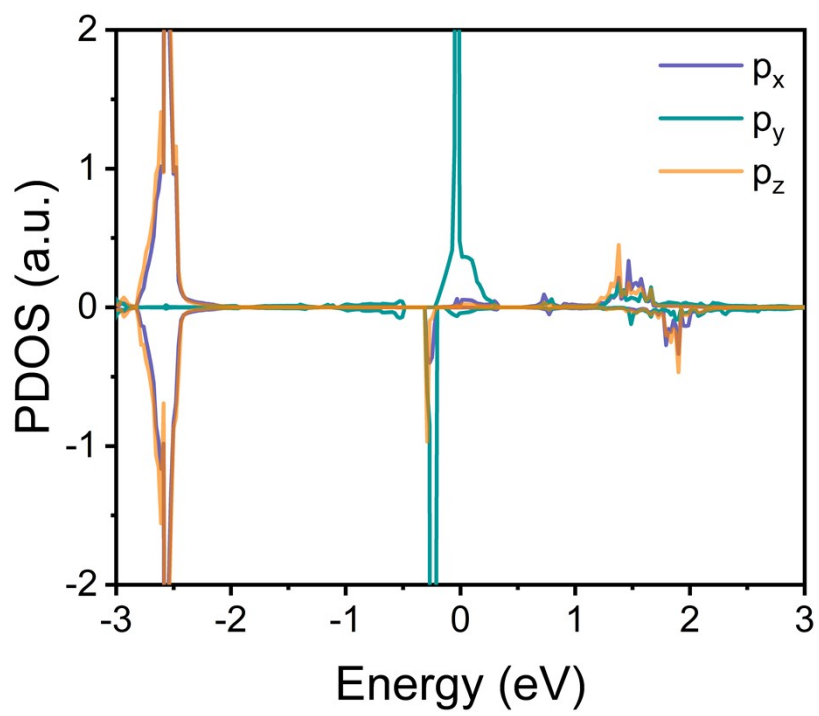


Figure S4. PDOS of I-p orbitals.

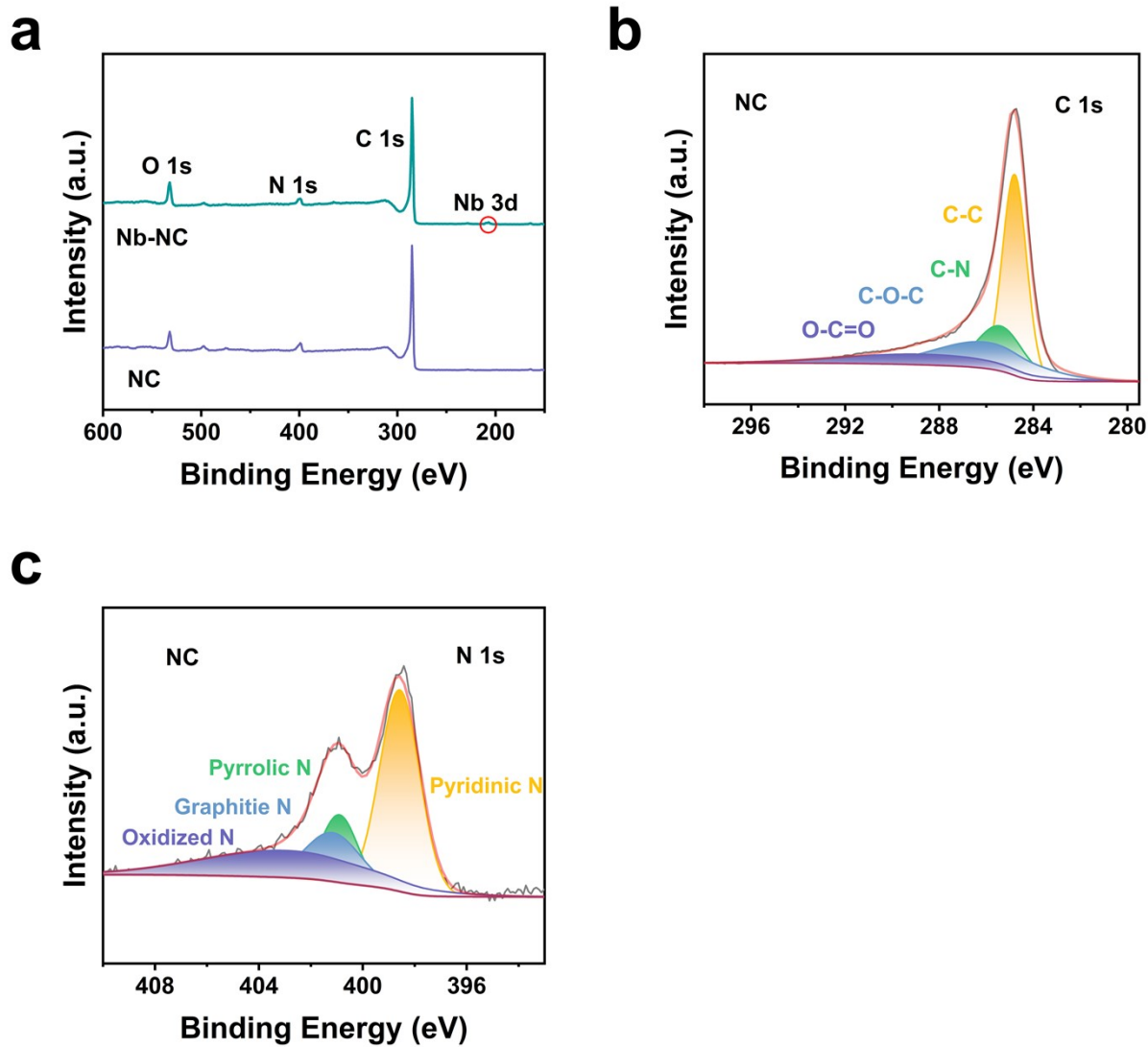


Figure S5. a) XPS survey spectra for NC and Nb-NC powder. XPS high-resolution spectra of b) C 1s and c) N 1s for NC.

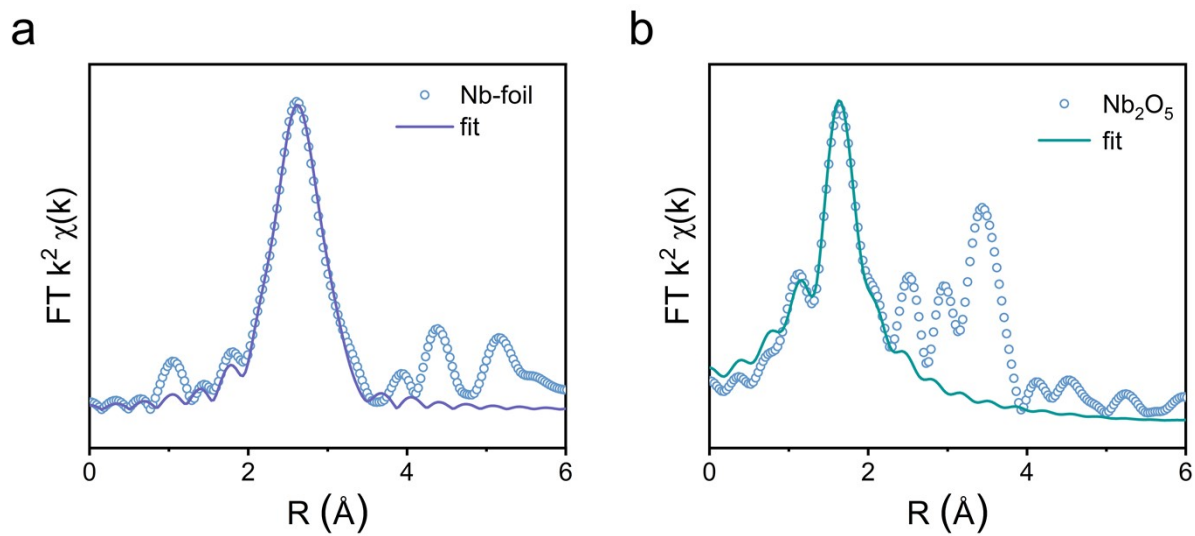


Figure S6. EXAFS spectra and the curve-fit in R-space for a) Nb-foil and b) Nb_2O_5 .

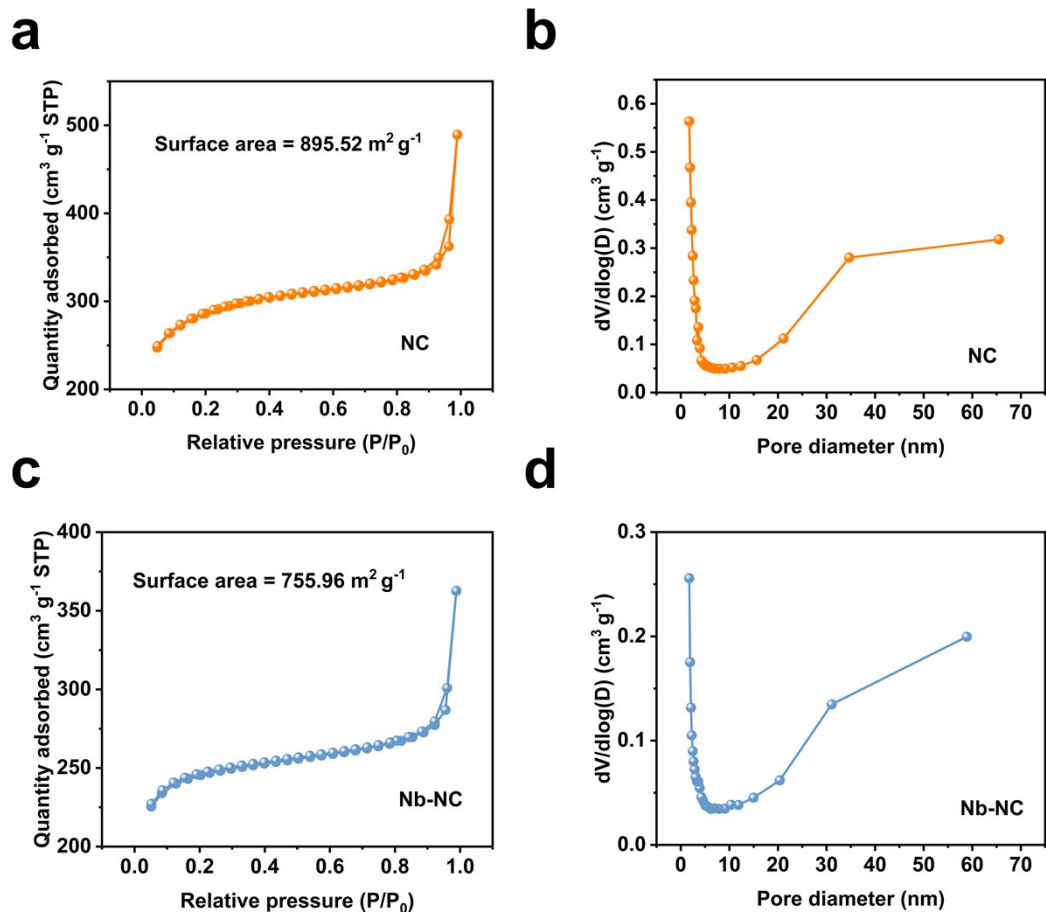


Figure S7 a) Nitrogen adsorption-desorption curve and b) pore size distribution curve for NC.
 c) Nitrogen adsorption-desorption curve and d) pore size distribution curve for Nb-NC.

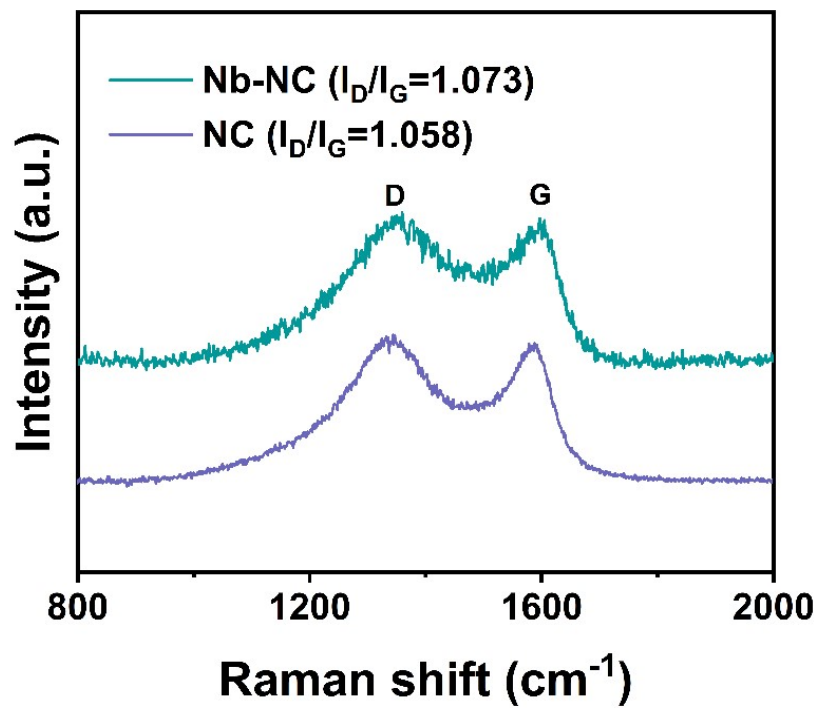


Figure S8. Raman spectrum of NC and Nb-NC powders.

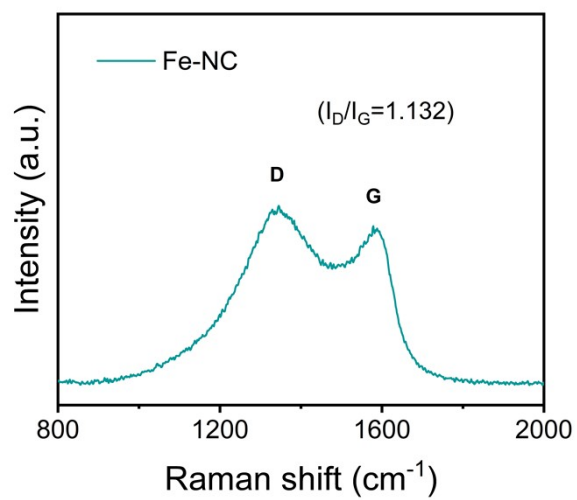


Figure S9. Raman spectrum of Fe-NC powders.

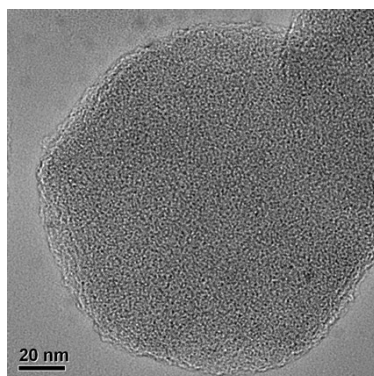


Figure S10. TEM images of Fe-NC powder.



Figure S11. Optical picture of NC-Nb/I₂ cathode

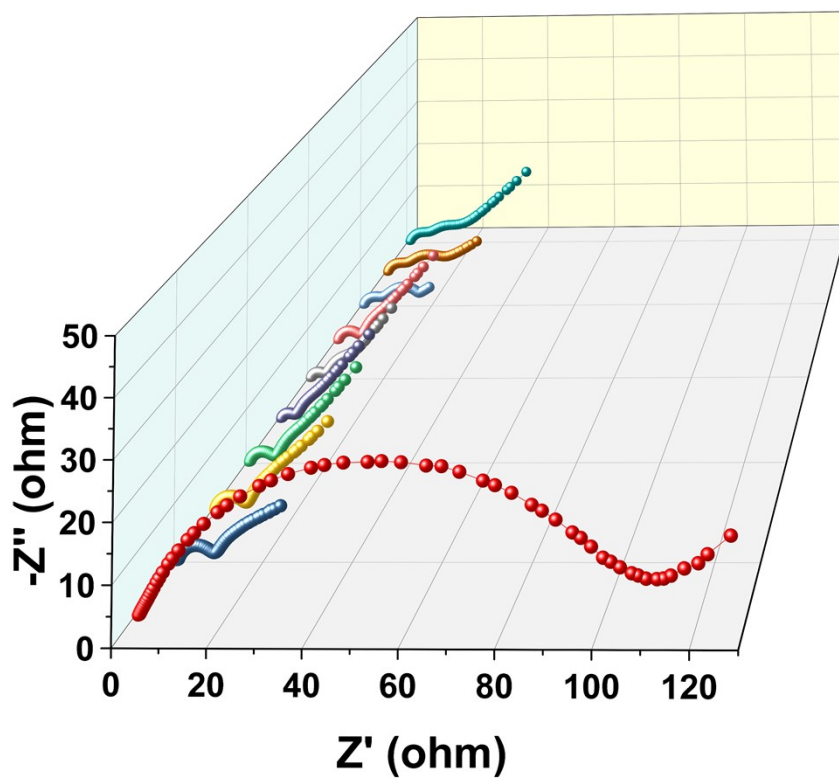


Figure S12. In situ EIS characterization of NC/I₂ during charge-discharge process.

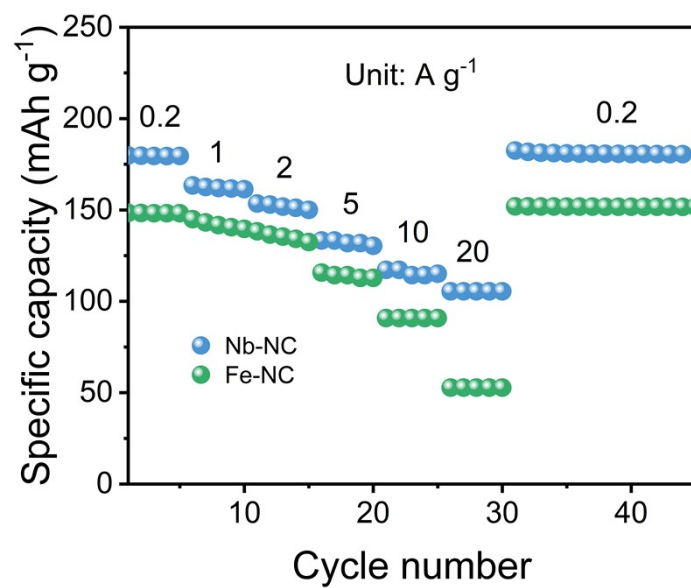


Figure S13. Rate performance of Zn-I₂ batteries with Nb-NC/I₂ and Fe-NC/I₂ cathodes.

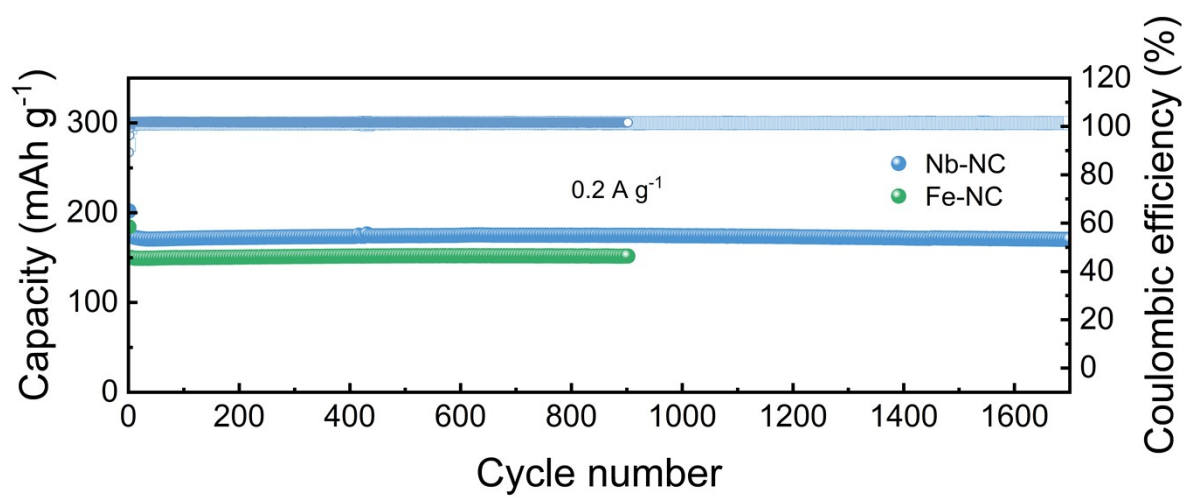


Figure S14. Long cycle performance test of Zn-I₂ batteries with NC/I₂ and Nb-NC/I₂ electrodes at a current density of 0.2 A g⁻¹.

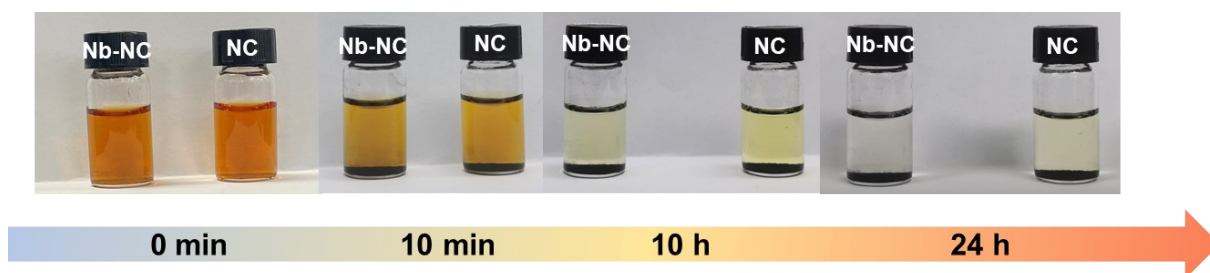


Figure S15. Optical photographs of NC and Nb-NC in $Zn(I_3)_2$ solution over time.

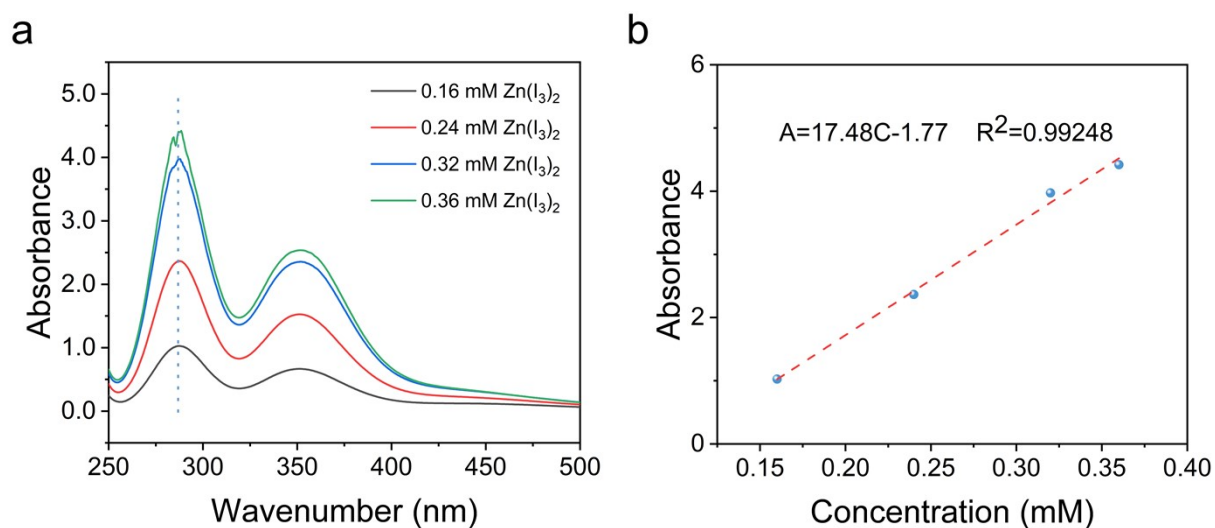


Figure S16. (a) The UV-vis spectra of I_3^- solutions with different concentrations. (b) The corresponding standard plots revealing the relationship between concentration and absorbance.

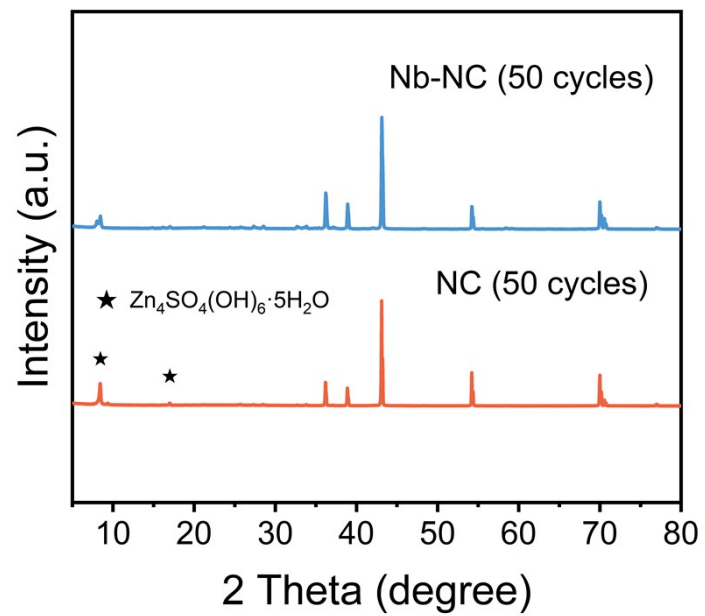


Figure S17. XRD pattern of Zn anode after 50 cycles in Zn||Nb-NC/I₂ battery and Zn||NC/I₂ battery.

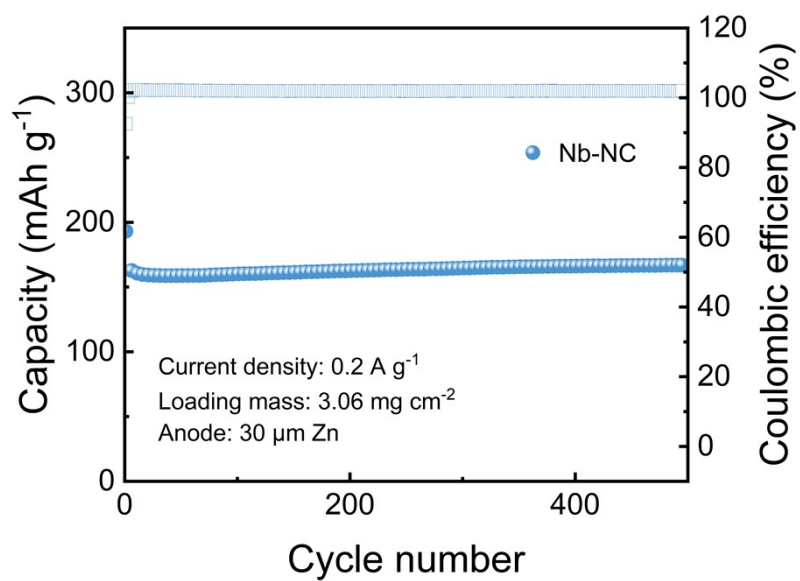


Figure S18. Cycle performance test of Zn-I₂ batteries with a 30 μm Zn anode and Nb-NC/I₂ electrodes at a current density of 0.2 A g⁻¹.

Table S1. d-band center up and d-band center down of M-MC (M= Co, Cu, Fe, Nb, Ni, Re, Rh, Ru, Ti, W, and Zn).

	d-band center up (eV)	d-band center down (eV)
Co-NC	-0.668	-0.668
Cu-NC	-3.599	-4.496
Fe-NC	-2.858	0.045
Mo-NC	-1.342	0.543
Nb-NC	0.271	1.185
Ni-NC	-2.351	-2.348
Re-NC	-1.234	-1.228
Rh-NC	-1.557	-1.555
Ru-NC	-1.519	-0.362
Ti-NC	0.599	0.534
W-NC	-1.257	-0.596
Zn-NC	-5.868	-5.899

Table S2. EXAFS fitting parameters at the Nb K-edge for various samples. ($S_0^2=0.9$)

Sample	Shell	CN ^a	R(\AA) ^b	$\sigma^2(\text{\AA}^2)$ ^c	$\Delta E_0(\text{eV})$ ^d	R factor
Nb-foil	Nb-Nb1	8	2.85±0.01	0.0063	4.8±0.9	0.0083
	Nb-Nb2	6	3.25±0.01	0.0066		
Nb-2	Nb-O1	1	1.81±0.01	0.0047	6.0±1.2	0.0055
	Nb-O2	4	2.06±0.01	0.0065		
	Nb-O3	1	2.23±0.01	0.0030		
Nb-1	Nb-N	4.0±0.5	2.08±0.01	0.0020	-9.4±1.9	0.0189

^aCN: coordination numbers; ^bR: bond distance; ^c σ^2 : Debye-Waller factors; ^d ΔE_0 : the inner potential correction. R factor: goodness of fit.

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