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A self-sacrifice template strategy to synthesize Co-LDH/ MXene for lithium-ion batteries

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Experimental details

Synthesis of MXene nanoflakes

1.5 g Ti_3AlC_2 MAX powders immersed in a mixture of LiF (1.5 g) and HCl (9 M, 15 mL), and stirred 24 h at 60℃. The obtained sample was washed by deionized water (DIW) until pH near 7, and then immersed into 500 mL DIW and sonicated for 6 h under argon protection. Finally, the above solution was centrifugated at 3500 rpm for 1 h, then the supernatant was freeze-drying.

Synthesis of ZIF-67/MXene

1 mmol Ti_3C_2 MXene was added in 50 mL DIW, then sonicated 30 min. And 1 mmol $Co(NO_3)_2 \cdot 6H_2O$ and 25 mg CTAB were dissolved in above solution and stirred 30 min at room temperature. Then 50 mL 60 M 2-methylimidazole (2-MI) aqueous solution was added into above mixture solution, stirred 12 h and aged 12 h at room temperature. The solution was centrifugated one time with DIW at 8500 rpm for 5 min. Finally, the sediments were collected and freeze-dried.Synthesis of Co-LDH/MXene.

The Co-LDH/MXene composite was obtained via centrifugating ZIF-67/MXene ten times with DIW and then the sediments were freeze-dried.

For comparison, the ZIF-67 and Co-LDH were obtained via the same process without Ti_3C_2 MXene. And the ZIF-67/Co-LDH/MXene composite was prepared by centrifugating ZIF-67/MXene five times with DIW.

Characterization

The phase composition was analyzed by X-ray diffractometer (XRD, D-MAX 2500, 3-80°, 2°/min). The morphology was analyzed by scanning electron microscopy (SEM, S4800) and transmission electron microscopy (TEM, FEI Talos). The surface chemical state was analyzed by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi). The chemical bonding vibration information was analyzed by Fourier transform infrared spectroscopy (FTIR, EQUINOX55). And the BET analysis is conducted on ASAP2020 HD88, and the temperature is 180℃.

Electrochemical measurements

The working electrode was prepared by mixing active material, acetylene black, and polyvinylidene fluoride in 1-methyl-2-pyrrolidinone with a mass ratio of 8:1:1. The 1 M $LiPF_6$ in a mixture of ethylene carbonate and dimethyl carbonate (1:1 v/v) was electrolyte, and lithium foil was the counter electrode. The 2032-type coin cell was assembled in glove box. And the performance was tested on Battery Testing System (CT-4008, Neware). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurement were conducted on electrochemical workstation (PARSTAT MC). The voltage window is 3 to 0.01 V, the potential amplitude is 5 mV and the frequency ranged from 100 kHz to 0.1 Hz.

Calculations

The b value usually uses to measure the reaction mechanism, which is determined by the scan rate (v) and peak current (i), corresponding to the following formulas:[1]

$$i = av^b \quad \text{(S1)}$$

$$\log(i) = blog(v) + log(a) \quad \text{(S2)}$$

normally, $b = 0.5$ shows that diffusion controls the process, and $b = 1$ shows that the process is controlled by capacitive behavior.

The capacitive contribution (k_1v) and diffusive contribution $(k_2v^{1/2})$ are judged by following formulas:[2]

$$i = k_1v + k_2v^{1/2} \quad \text{(S3)}$$

$$i/v^{1/2} = k_1v^{1/2} + k_2 \quad \text{(S4)}$$

normally, i is current, and $k_1$is the slop of $v^{1/2} - i/v^{1/2}$ plot.

The Li^+ diffusion coefficient (D) is calculated by following formulas:[3]

$$D = R^2T^2(2A^2n^4F^4C^2\sigma^2)^{-1} \quad \text{(S5)}$$

$$Z = R_e + R_{ct} + \sigma\omega^{-1/2} \quad \text{(S6)}$$

normally, *R, T, A, n, F,* and *C* are gas constant, temperature, electrode area, the number of electrons, Faraday constant, and the concentration of Li^+ in electrode materials, respectively. The Warburg factor σ is determined by the slope of $Z \sim \omega^{-1/2}$.

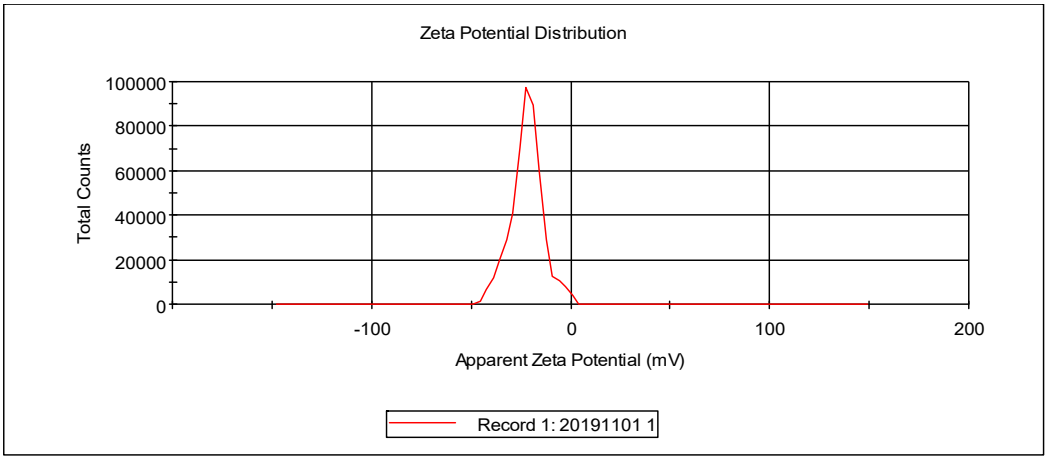

Figure S1. Zeta potential of MXene.

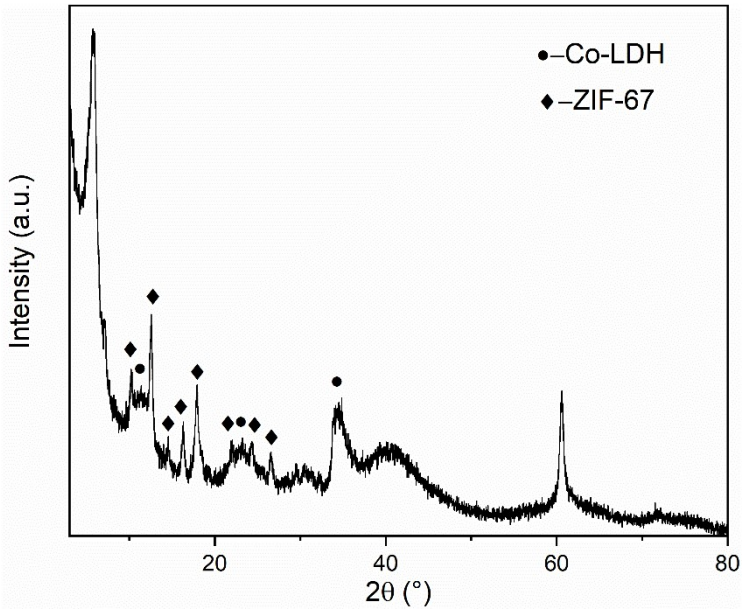

Figure S2. XRD pattern of ZIF-67/Co-LDH/MXene.

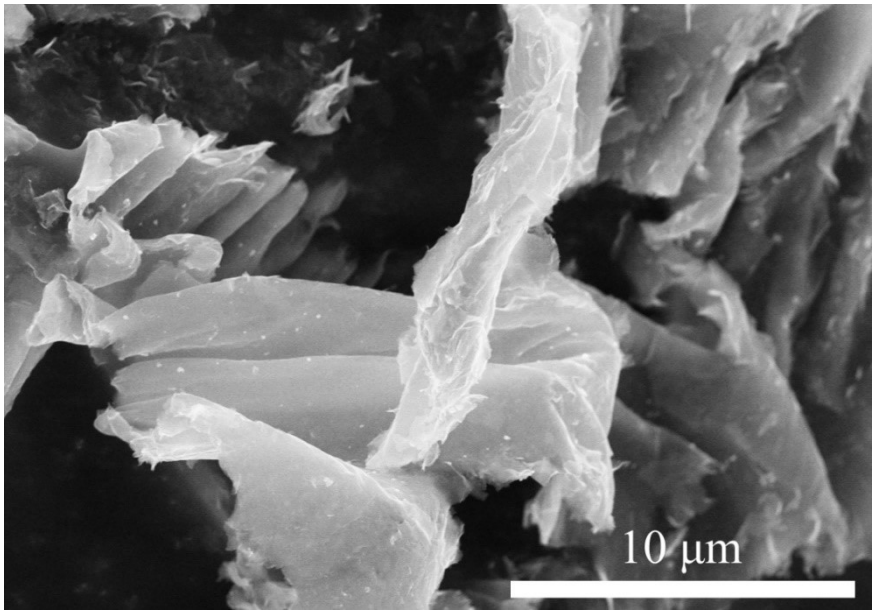

Figure S3. SEM image of MXene.

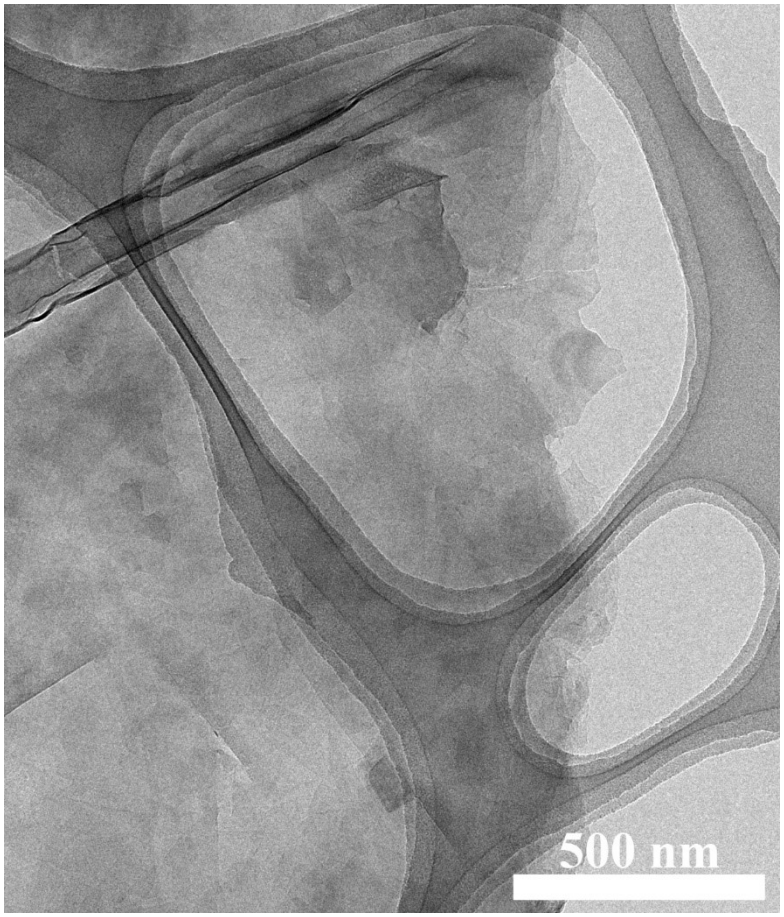

Figure S4. TEM image of MXene.

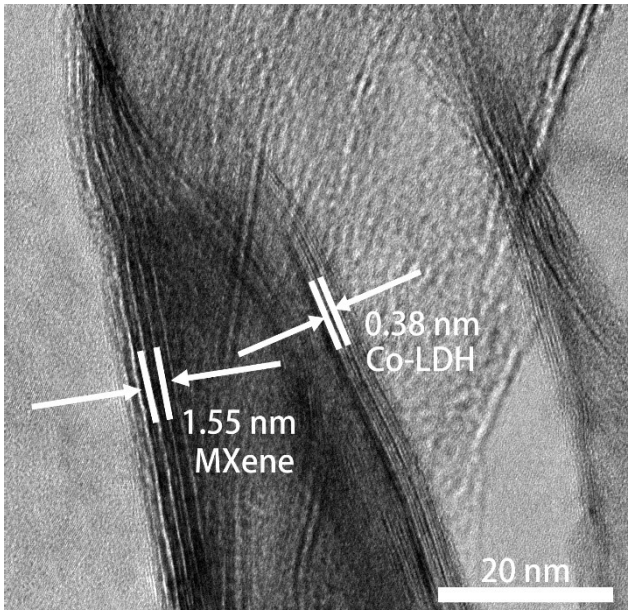

Figure S5. HRTEM image of Co-LDH/MXene.

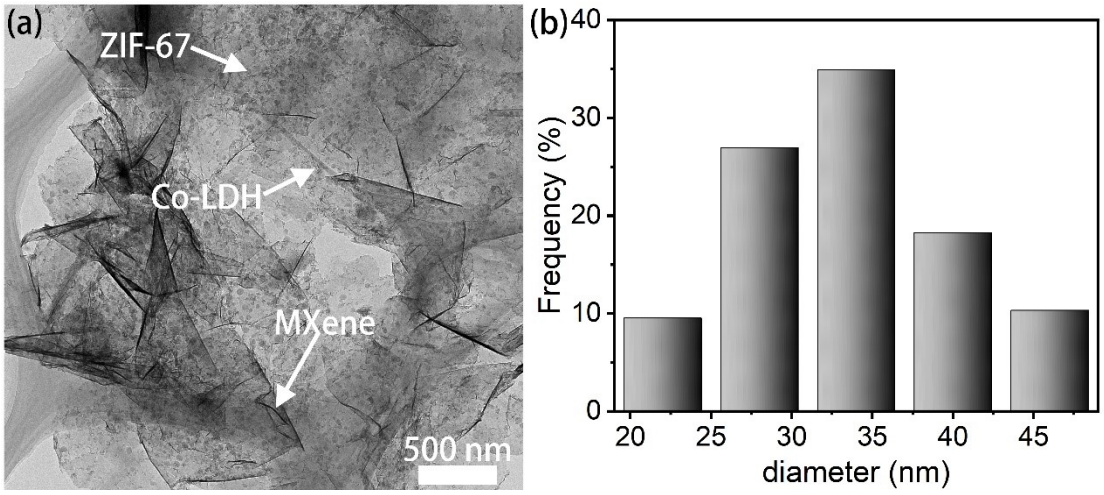

Figure S6. (a) TEM image, and (b) ZIF-67 size distribution of ZIF-67/Co-LDH/MXene.

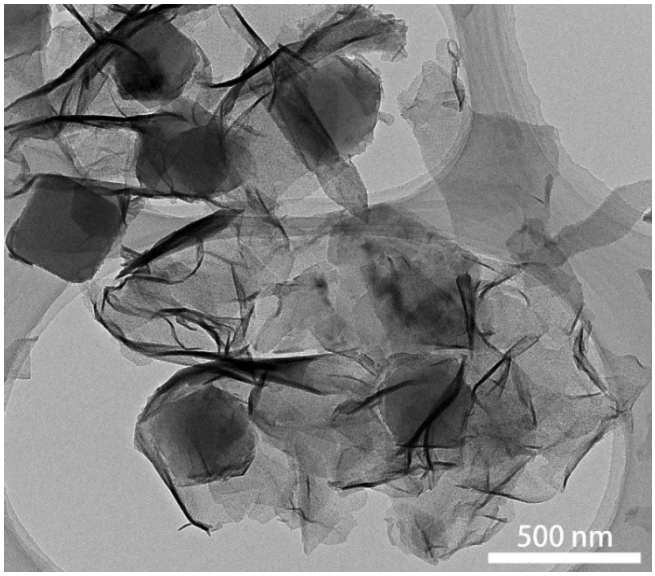

Figure S7. SEM image of ZIF-67/Co-LDH.

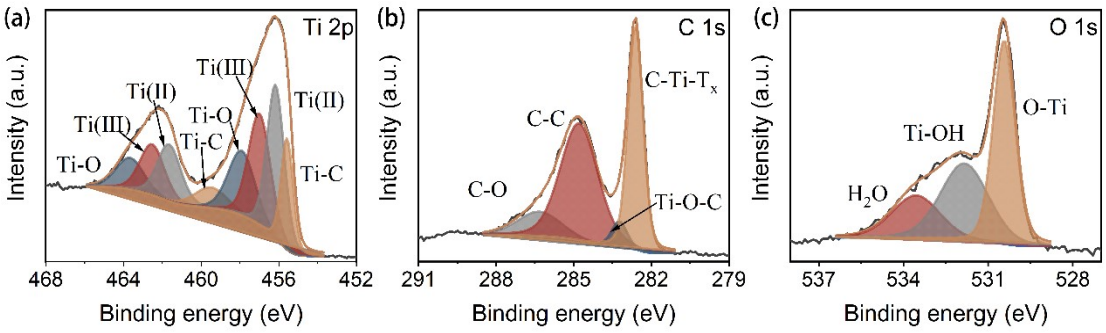

Figure S8. High resolution XPS spectra of MXene (a) Ti 2p, (b) C 1s, and (c) O 1s.

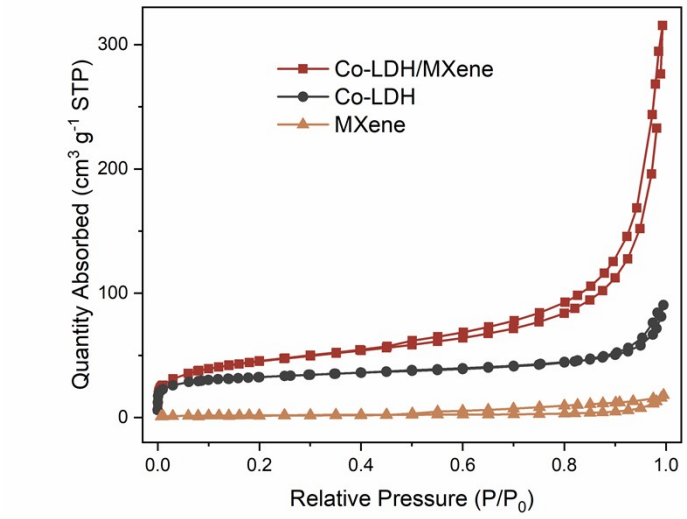

Figure S9. N_2 adsorption-desorption isotherm curves of Co-LDH/MXene, Co-LDH, and MXene.

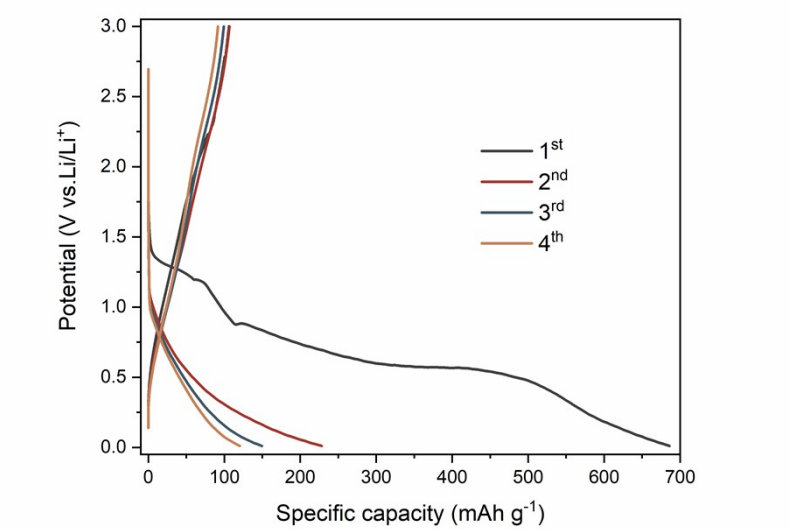

Figure S10. GCD profiles of ZIF-67/MXene.

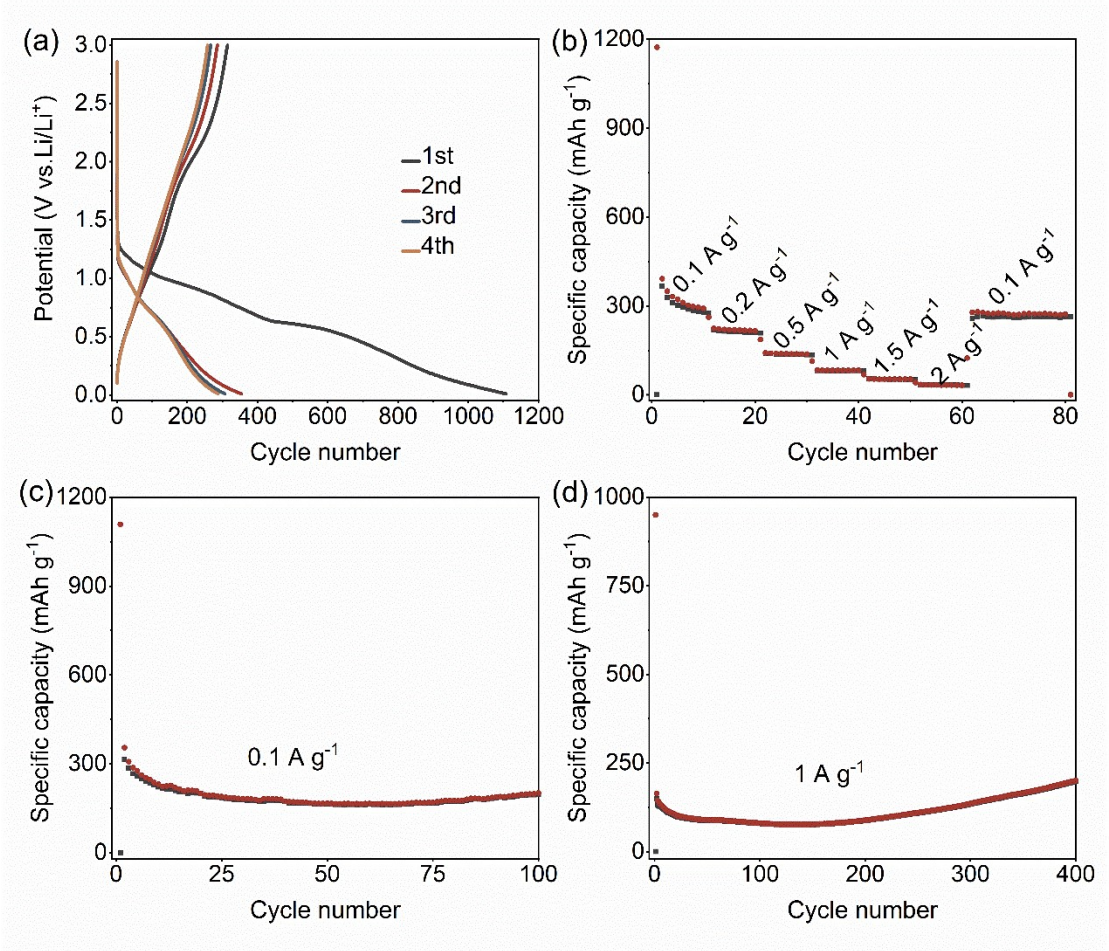

Figure S11. (a) GCD profiles, (b) rate performance, (c) cycle performance at 0.1 A g^{-1}, and (d) cycle performance at 1 A g^{-1} of ZIF-67/Co-LDH/MXene.

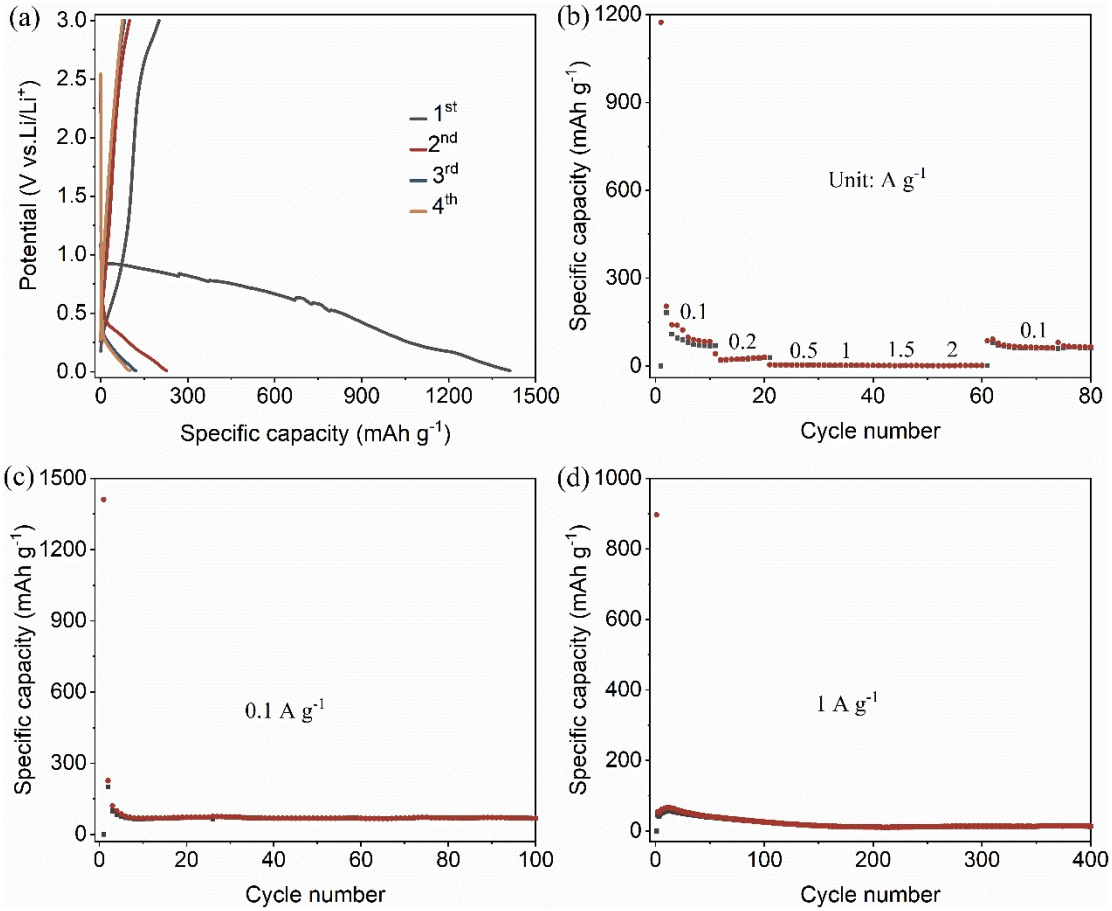

Figure S12. (a) GCD profiles, (b) rate performance, (c) cycle performance at 0.1 A g^{-1}, and (d) cycle performance at 1 A g^{-1} of Co-LDH.

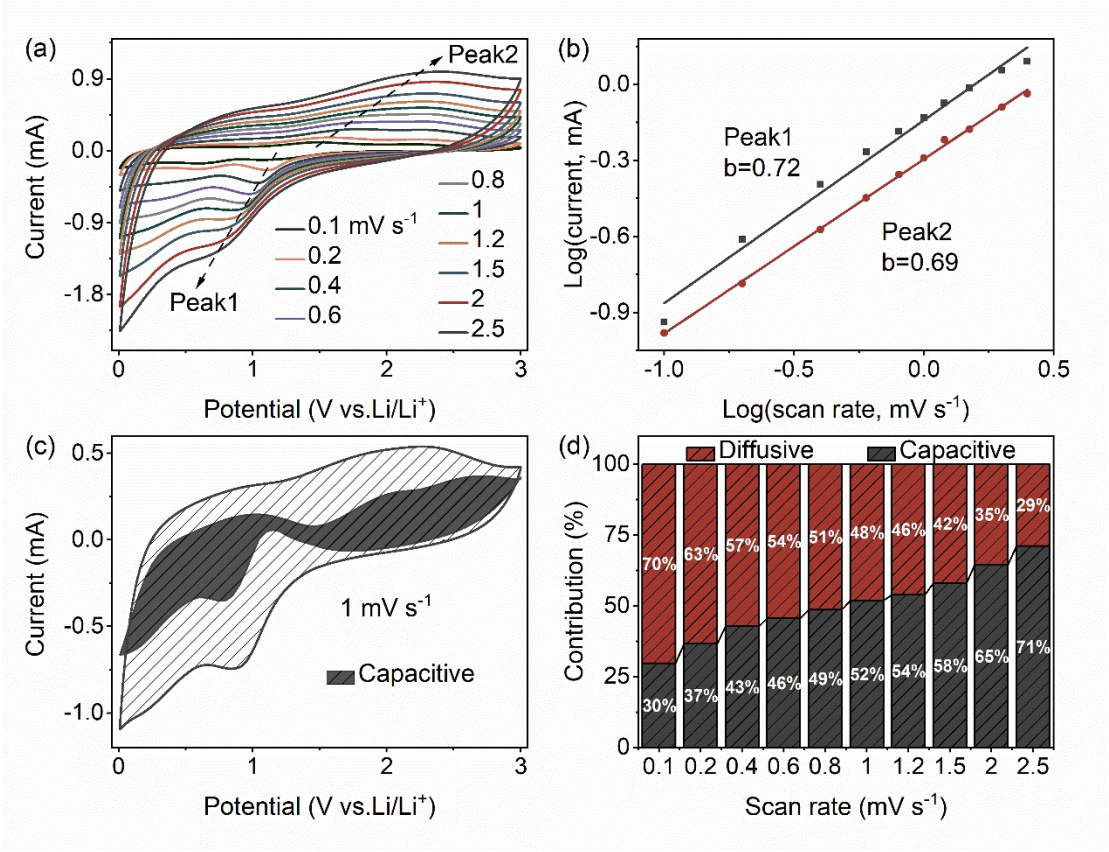

Figure S13. (a) CV curves with scan rate varies from 0.1 to 2.5 mV s^{-1}, (b) $log(i)$ versus $log(v)$ plots, capacitive contribution at (c) 1 mV s^{-1}, and (d) different scan rate of Co-LDH/MXene.

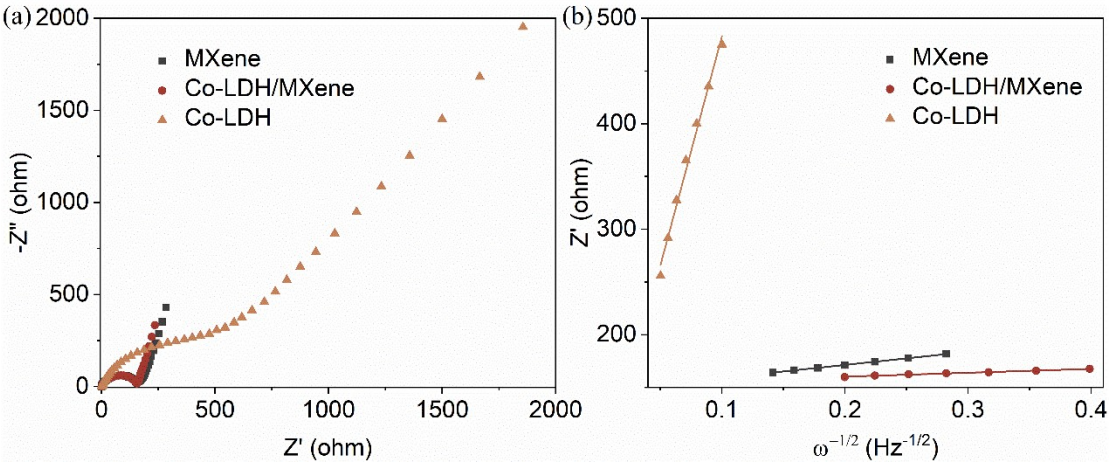

Figure S14. (a) Nyquist plots used for the EIS analysis, and (b) the relationship of the $Z^{'} - \omega^{-1/2}$ curves in the low-frequency region.

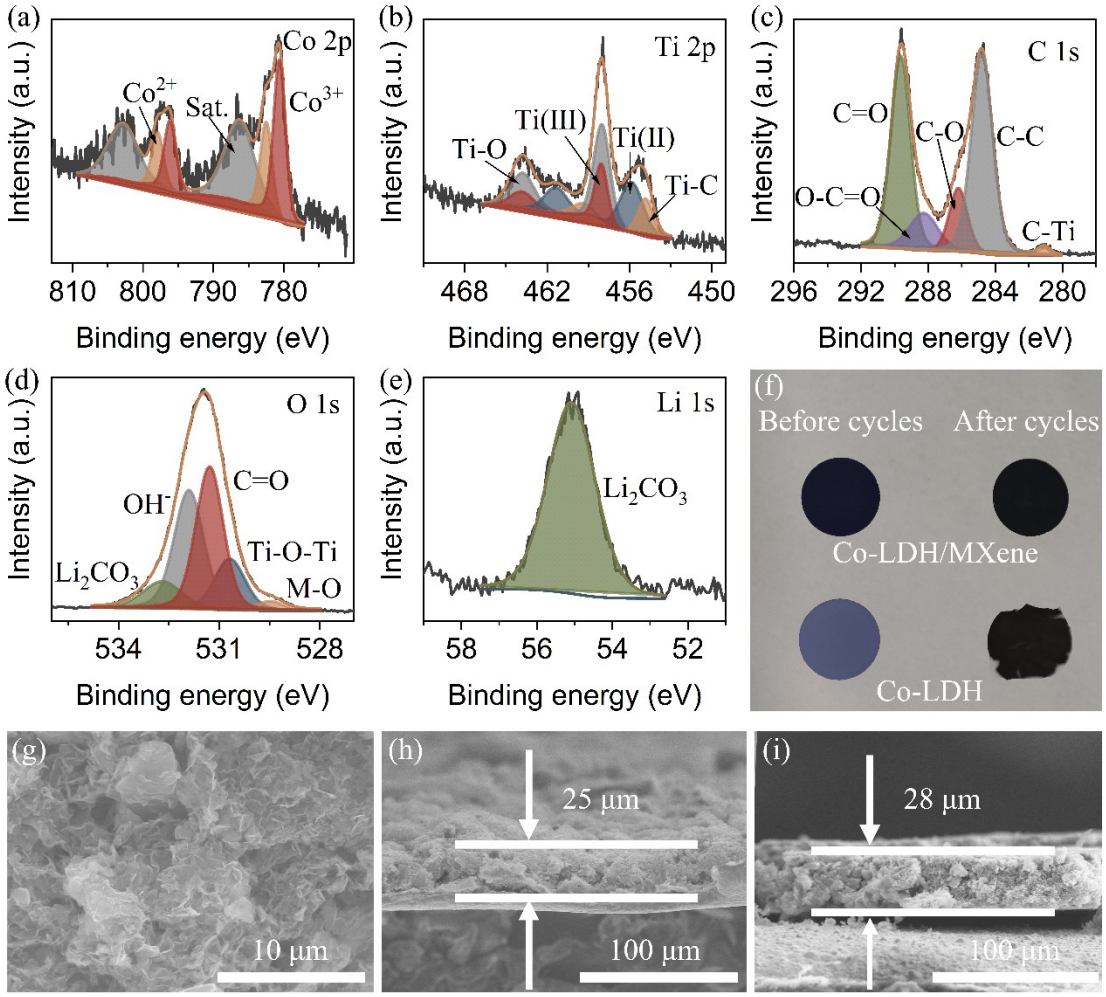

Figure S15. XPS spectrum of Co-LDH/MXene after cycles (a) Co 2p, (b) Ti 2p, (c) C 1s, (d) O 1s, and (e) Li 1s. (f) Photographs of electrodes before and after cycles. (g) SEM image of Co-LDH/MXene electrode after cycles. Cross-sectional SEM images of Co-LDH/MXene (h) before cycles, and (i) after cycles.

References:

1. J.-Y. Tan, J.-T. Su, Y.-J. Wu, C.-L. Huang, P.-Y. Cheng, Y.-A. Chen and S.-Y. Lu, *ACS Sustainable Chemistry & Engineering*, 2021, **9**, 1180-1192.
2. C. Wu, M. Hu, X. Yan, G. Shan, J. Liu and J. Yang, *Energy Storage Materials*, 2021, **36**, 347-354.
3. D. Chen, S. Sun, G. Yu, L. Qin, W. Wang, M. Jiang and J. Chen, *Carbon*, 2020, **166**, 91-100.