1. Experimental Procedures

1.1 Materials

Ferric acetylacetonate, cobalt acetylacetone, oleic acid, oleylamine and benzyl ether were purchased from Sigma-aldrich. Ti₃AlC₂ powders were purchased from 11 technology Co., Ltd. Hydrochloric acid (HCl) and lithium fluoride (LiF) were from Sinopharm Chemical Reagent Co., Ltd.

1.2 Synthesis of MXene flake colloidal solution

Multilayer Ti₃C₂Tx MXene powders were synthesized by etching Ti₃AlC₂ MAX phase powders (with a particle size <38 μm), as described in the previous report. First, 1g Ti₃AlC₂ powders was immersed in a mixture solution of 1g lithium fluoride (LiF) and 20 mL hydrochloric acid (HCl) at 30 °C. Then, the suspension was stirred at a speed of 700 rpm for 18 h. Afterward, the solution was decanted and the solids were filtered. Fresh deionized (DI) water was then added to wash the obtained powder several times until the pH value of liquid was higher than 5. To obtain few- and/or single-layer flakes, the multilayer Ti₃C₂Tx powders were delaminated via sonifier cell disrupter. In this case, the multilayer Ti₃C₂Tx powders aqueous solution with a weight ratio of multilayer Ti₃C₂Tx: H₂O of 1:100 were strongly sonicated under flowing argon for 2 h, and then centrifuged at 3500 rpm for 30 min to obtain the supernatant containing Ti₃C₂Tx flakes, henceforth referred to as the MXene colloidal solution (0.5 mg/mL).

1.3 Synthesis of CoFe₂O₄ nanoparticles (NPs)

2 mmol Ferric acetylacetonate, 1 mmol cobalt acetylacetone, 4 mL oleic acid, 4 mL oleylamine and 20 mL benzyl ether were mixed and magnetically stirred for 30 min under a flow of argon at room temperature (RT). The solution was heated to 120 °C for 30 min and
then to 200 °C at a heating rate of 5 °C/min and was kept at the temperature for 2 h. The solution was further heated to 290 °C with a heating rate of 5 °C/min and was kept at this temperature for 0.5 h. The heating source was removed, and the solution was cooled to RT, after which the solution was exposed to air. The black product was precipitated by adding ethanol, and separated by centrifugation. The dark-yellow supernatant was discarded. Finally, the CoFe$_2$O$_4$ NPs were dried overnight in vacuum.

1.4 Manufacturing of MXene&CoFe$_2$O$_4$ hybrid 3D electrode

To obtain the MXene&CoFe$_2$O$_4$ hybrid 3D electrodes, 10 mg CoFe$_2$O$_4$ NPs was mixed with 10 mL Ti$_3$C$_2$Tx flake colloidal solution, the mass ratio of Ti$_3$C$_2$Tx to CoFe$_2$O$_4$ NPs was controlled at 1:2. The mixture was then sonicated for 10 min to ensure an uniform dispersion of Ti$_3$C$_2$Tx flakes and CoFe$_2$O$_4$ NPs in the solution. After that, the mixture colloidal solution was filtered through a polypropylene membrane with 0.45 µm pore to yield a film as an active material. Then the other 5 mL (2.5 mg) Ti$_3$C$_2$Tx flake colloidal solution was filtered to form a film as a current collector on the aforementioned film. The hybrid film was dried under the infrared light for 10 min and peeled off from the polypropylene membrane, yielding a flexible freestanding MXene&CoFe$_2$O$_4$ hybrid 3D electrode.

1.5 Characterization

Powder X-ray diffraction (XRD) data were recorded using a Rigaku D/Max-2500 diffractometer with graphite monochromatized CuKα radiation ($\lambda=0.15406$ nm) at 40 kV, 200 mA. The morphology and structures of the as-prepared samples were determined with an FEI Nova Nano 450 field emission scanning electron microscope (FE-SEM) at an accelerating voltage of 15 kV, FEI Tecnai G$^2$ Spirit (120 kV) and FEI Tecnai G$^2$ F20 (200 kV) high resolution transmission electron microscopes (HR-TEM). Energy-dispersive X-ray spectroscopy (EDX) analysis of the samples was also carried out during SEM measurements.
to perform the elemental analysis of the samples. The electronic conductivity of the film electrodes, which were tailored to $20 \times 20 \text{ mm}^2$, was measured by HMS-5000 Hall effect measurement system (ECOPIA, Korea) and the thickness was measured by the cross-section SEM images. The water contact angles were tested by OCA20 contact angle system (Dataphysics, Germany). Chemical composition and oxidation state of the samples were further analyzed using high-resolution XPS with monochromated Al $K\alpha$ radiation ($h\nu=1486.6$ eV). Binding energies were referenced to the C 1$s$ peak of (C–C, C–H) bond, which was set at 284.8 eV. X-ray absorption spectra (XAS) of Fe K edge and Co K edge were collected at Beijing Synchrotron Radiation Facility (BSRF) on beamline 1W1B. All the data were collected with transmission mode at ambient temperature. X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) were analyzed by ATHENA software package.

1.6 Electrochemical Characterization

The working electrodes were the prefabricated MXene&CoFe$_2$O$_4$ hybrid 3D electrodes, cells were assembled into coin cells (CR 2032) in which Li sheets were used as the counter and reference electrodes. The electrolyte was 1 M LiPF$_6$ in a mixture of ethylene carbonate (EC)/dimethy carbonate (DEC)/ethyl methyl carbonate (EMC) in a 1:1:1 volume ratio. In addition, copper conducting resin was employed for enhancing contact between the flexible electrode and the electrode shell. The cells were assembled in an argon-filled glove box (MBRAUN) with the concentrations of moisture and oxygen below 0.5 ppm. In order to make the comparison, the CoFe$_2$O$_4$ electrodes were prepared by mixing CoFe$_2$O$_4$ powders with Super P carbon black, and polyvinylidene fluoride (PVDF) binder in N-methyl-2-pyrrolidinone (NMP) with a weight ratio of 8:1:1 and the resulting slurry were pasted on a copper foil and then dried at 120 °C in vacuum. Cyclic voltammetry (CV) was performed on
an Electrochemical Workstation (VMP3, Bio-logic Science Instruments) from 0.05 to 3 V versus Li/Li$^+$ at 0.5 mV/s. Galvanostatic charge/discharge (GCD) measurements were carried out using a LAND battery tester (Wuhan LANHE, China), two same cells were employed for confirmation. Electrochemical impedance spectroscopy (EIS) tests were also measured on a VMP3 electrochemistry workstation in the frequency range of 200 kHz to 10 mHz with AC voltage amplitude of 10 mV at open circuit potential.
2. Figures and Tables

![Hysteresis loops of CoFe$_2$O$_4$ NPs.](image)

**Fig. S1.** Hysteresis loops of CoFe$_2$O$_4$ NPs.
**Fig. S2.** Water contact angles of the positive and negative sides of the MXene&CoFe$_2$O$_4$ electrode.
Fig. S3. (a) Cyclic voltammetry curves of CoFe$_2$O$_4$ electrode and (b) MXene&CoFe$_2$O$_4$ hybrid 3D electrode.
Fig. S4. Long term cycle test result of the Ti$_3$C$_2$Tx MXene at a current rate of 1 C (1C=320 mAh/g).
Fig. S5. XRD patterns of (a) MXene&CoFe$_2$O$_4$ and (b) CoFe$_2$O$_4$ after cycles.
Fig. S6. XANES spectra (a) Co and (b) Fe, the Fourier transforms (FT) of EXAFS spectra.
In order to further explain the high performance of the hybrid electrode. Co and Fe were chosen as the characteristics for investigation. The XANES spectra of Co show the main absorption peaks shifted to higher energies after cycles. However, the position of Fe still located at the initial one. The reason may be attributed to that Co holds a higher activity than Fe, and the electrons lost. The ATHENA software package was used to conduct data processing for Fourier transforms. The intensity ratio of Co-O and Co-Fe peaks before cycles is lower than 1, however, the ratio after cycles is > 1. A similar trend happened on the ratio of Fe-O and Fe-Co. It may be due to the occurrence of a phase transition in CoFe$_2$O$_4$ via the equation: \[ \text{CoFe}_2\text{O}_4 + 8\text{Li}^+ + 8\text{e}^- \rightarrow \text{Co} + 2\text{Fe} + 4\text{Li}_2\text{O}. \] The bonds were broken upon the electrochemical process. Compared with the peaks of both Fe and Co at 4 to 6 Å, only the intensity of the peaks for CoFe$_2$O$_4$-C is extremely low. The low peaks indicated there are no adjacent atoms. It is inferred that the interval may lead to a bad charge/electron conductivity.
Fig. S7. Comparison of the high resolution XPS spectra of Co, Fe, O, Ti and survey spectra for MXene&CoFe₂O₄ and CoFe₂O₄ before and after cycles.
Fig. S8. HRTEM images of MXene\&CoFe$_2$O$_4$ at 3 V, CoO (JCPDS#43-1004), Fe$_2$O$_3$ (JCPDS#39-1346).
Fig. S9. HRTEM images of CoFe$_2$O$_4$ at 3 V, Fe (JCPDS#87-0722).
Fig. S10. HRTEM images of MXene\&CoFe$_2$O$_4$ at 0 V, Co (JCPDS#15-0806).
Fig. S11. HRTEM images of CoFe$_2$O$_4$ at 0 V, CoFe$_2$O$_4$ (JCPDS#22-1086).
Fig. S12. TEM images of MXene&CoFe$_2$O$_4$ and CoFe$_2$O$_4$ at 0/3 V.

Fig. S13. (a) Digital image and (b) SEM image of the MXene&CoFe$_2$O$_4$ electrode after the cycle test.

In order to further investigate the hybrid electrode. The half cell was disassembled. Due to the wettability between the electrode and the electrolyte, the hybrid electrode cannot be separated from the stainless steel battery shell. The SEM image of the MXene&CoFe$_2$O$_4$ electrode shows some cracks, which can be attributed to the charge-discharge process over a long period of time. However, the electrode remains with a complete surface.
Fig. S14. SEM images of the MXene&CoFe$_2$O$_4$ electrode after the cycle test and the corresponding elemental maps.

Fig. S14 shows the enlarged SEM image and the corresponding elemental maps. The surface of MXene&CoFe$_2$O$_4$ electrode is covered by MXene flakes and SEI films. The elemental maps indicated that Fe, Co, and Ti are uniformly distributed throughout the electrodes. Moreover, the elemental maps of P was indicative of the residual electrolyte.