

Supporting information

Experiment

1.1 Preparation of materials

1.1.1 Synthesis of active materials

Here, we denote $K_{0.1}Na_{2.95}V_{1.95}Co_{0.05}(PO_4)_3@MXene$, $K_{0.1}Na_{2.95}V_{1.95}Co_{0.05}(PO_4)_3$ and $Na_3V_2(PO_4)_3$ as $KC05@MX$, $KC05$ and NVP , respectively. All the active materials were synthesized by a sol-gel method with subsequent treatment of freeze-drying and calcination. Take the preparation of $KC05@MX$ as an example, the other samples were prepared follow the same procedure without $MXene$ or $MXene$, KH_2PO_4 , $Co(NO_3)_2 \cdot 6H_2O$, $CH_3COONa \cdot 3H_2O$ for $KC05$ or NVP , respectively.

The preparation of $KC05@MX$ sample, are conducted under N_2 atmosphere the whole procedure, as shown in Fig.1, NH_4VO_3 , oxalic acid, NaH_2PO_4 , KH_2PO_4 , $Co(NO_3)_2 \cdot 6H_2O$, $CH_3COONa \cdot 3H_2O$ and $MXene$ dispersion liquid were used as starting reagents. Aiming to gain a $KC05@MX$ composite materials with the $MXene$ mass content of 4.7% (0.15 g MX + 3 g $KC05$). Firstly, the stoichiometric amounts of NH_4VO_3 (1.4913 g) and $Co(NO_3)_2 \cdot 6H_2O$ (0.0951 g) were put into flask with 60 mL H_2O in it, and a yellow homogenous solution was obtained under continuous stirring at 80 °C. Simultaneously, the oxalic acid solution, obtained by resolving 4.945 g oxalic acid into 20mL H_2O , was dropwise added into the yellow solvent with the color changed to blue. Subsequently, the stoichiometric amounts of KH_2PO_4 (0.0889 g), $CH_3COONa \cdot 3H_2O$ (0.0445 g) and NaH_2PO_4 (2.2745 g) were added into the system,

and the MXene dispersion liquid (40mL, 3.74mg mL⁻¹) was poured into the flask, under vigorously stirring at 80 °C for approximately 1h, the mixture turned into a gel. Finally, the obtained gel was freeze-dried for 24 h and the obtained powders were calcined in a tube furnace under N₂ atmosphere at 450 °C and 700 °C for 4h and 6 h, respectively, to produce KC05@MX sample.

1.1.2 Synthesis of MXene material

As for the obtain of the MXene dispersion solution, is the dispersed solution of Ti₃C₂T_x nanosheets, which were prepared through etching the Ti₃AlC₂ MAX phase in the corrosive solution (2 g LiF resolved in 40 mL 9M HCl). Firstly, the Ti₃AlC₂ MAX phase precursor (2 g) was added to this corrosive solution under 35°C with stirring for 24 h. The Al layers were removed in the etched processes. The resulted mixed solution was washed through centrifugation (until the supernatant pH is 6) and subsequent ultrasonication (in ethanol for 1 h under N₂ atmosphere and low temperature). Finally, after centrifugation at 3500 rpm, the Ti₃C₂T_x solution, which is named as MXene dispersion solution, is obtained with the concentration of 3.74 mg mL⁻¹.

1.1.3 Synthesis of Bi₂Se₃

Bi₂Se₃ samples were prepared via liquid-phase chemical synthesis. Firstly, 1 g of polyvinylpyrrolidone (PVP) and 0.902 g Bi(NO₃)₃•5H₂O were added to the solution and vigorously stirred, followed by 1-h sonication to form a uniform solution (solution A). Furthermore, 0.195 g of selenide (Se) powder and 0.192 g of NaBH₄ were mixed in 8 mL of water under argon (Ar) atmosphere and stirred until the solution became clear (solution B). Solution A was poured into a three-neck flask and heated to 160 °C under

Ar atmosphere. Then, 4 mL of solution B was injected into it. After 15 min, the products were collected by centrifugation, washed several times with deionized water, and then freeze-dried in a vacuum. Finally, Bi₂Se₃ samples were obtained by annealing at 400 °C for 2 h under N₂ atmosphere.

1.2 Characterization of active materials

The crystal structure was detected on X-ray powder diffraction (XRD, Ultima IV diffractometer) equipment, the XRD patterns were recorded with the angle range of 10-80° under the speed of 10° min⁻¹ and the step of 0.02°. The scanning electron microscope (SEM, SU8010) and transmission electron microscope (TEM, Tecnai G2 F20 S-TWIN TMP) characterization means were performed to reveal the morphological and microstructural of samples. The chemical state of V, K, and Co elements in KC05@MX was confirmed via X-ray photoelectron microscopy (XPS, ESCALAB 250X). Raman spectrum demonstrated the degree of graphitization of KC05@MX. The N₂ adsorption and desorption isotherm was drawn in the AJWGB, BK122W instrument, characterized the superficial area of samples. The small variation of each doping concentration is determined by inductively coupled plasma-mass spectrometer (ICP-MS) using NexION™350D, PerkinElmer. Thermogravimetric analysis (TGA, Mettler-Toledo) was employed to further calculate the mass ratio of each part in the hybrid KC05@MX material.

1.3 Battery Assembly and Electrode Formation

For characterizing the electrochemical properties of active materials, we have assembled, in argon glove box, both the half-cell (2016-type) and asymmetric full-cell

(2025-type), which are both consist of cathode, electrolyte, separator and counter electrode. Specifically, the primary difference between them is the counter electrode of the half-cell and full-cell is Na and Bi₂Se₃, respectively. And the separator is Celgard 2400 membrane and glass separator for half-cell and full-cell, respectively. Except, the electrolyte is the same, which is the EC/DEC solution containing 1 M NaClO₄ and 5% FEC. What's more, the cathode was produced by coating Al foil with slurry, which was prepared by mixing active materials (all samples), conductive agent (acetylene black) and binder (PVDF) together in NMP solution with the mass ratio of 7:2:1 (specific mass is 0.21 g: 0.06 g: 0.03 g). Subsequently, drying it in vacuum under 45 °C for 4 h and 120 °C for 12 h. Finally, the resulted electrode slice was punched into disks with a diameter of 16mm and the loading density of each piece was 1.5 mg cm⁻² averagely.

1.4 Electrochemical test

There were some means have been applied to estimate the electrochemical performance of all samples, the galvanostatic charge/discharge (GCD) and galvanostatic intermittent titration technique (GITT) profiles were recorded, on a LAND equipment at room temperature, with the voltage window of 2.3-4.1 V (Potential vs. Na⁺/Na) at various current density. Moreover, the kinetic characteristics of KC05@MX electrodes were detected using an electrochemical workstation (IVIUMnSTAT). Cyclic voltammetry (CV) curves were tested at varying scan rates at 0.1, 0.2, 0.5, 1, 2 and 5 mV s⁻¹ with the voltage window of 2.3-4.1 V (Potential vs. Na⁺/Na). The electrochemical impedance spectroscopy (EIS) means were operated with the frequency range of 10 mHz-100 M Hz.

2. Result data

Table.S1 Cell data obtained from Rietveld refined KC05@MX materials by GSAS program.

Atom	Type	Wyckoff	X/a	Y/b	Z/c	Occupancy
Na1	Na	6b	0.000000	0.000000	0.000000	0.7690
Na2	Na	18e	0.635100	0.000000	0.250000	0.7190
K	K	6b	0.000000	0.000000	0.000000	0.0890
V	V	12c	0.000000	0.000000	0.148109	0.9750
Co	Co	12c	0.000000	0.000000	0.148109	0.0250
O1	O	36f	0.192500	0.169000	0.090000	1.0000
O2	O	36f	0.031400	0.208000	0.194000	1.0000
P	P	18e	0.290500	0.000000	0.250000	1.0000

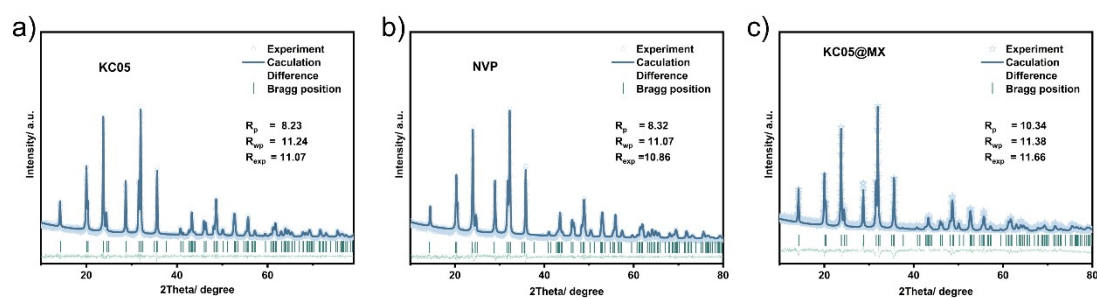


Fig.S1 The refined curves of KC05(a) and NVP (b). (c) The Rietveld refined result of KC05@MX.

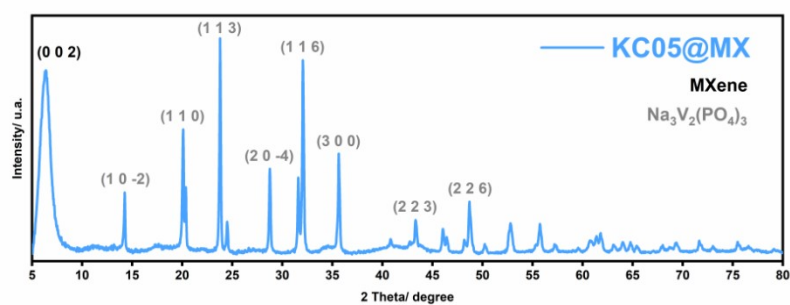


Fig.S2 XRD pattern of KC05@MX sample.

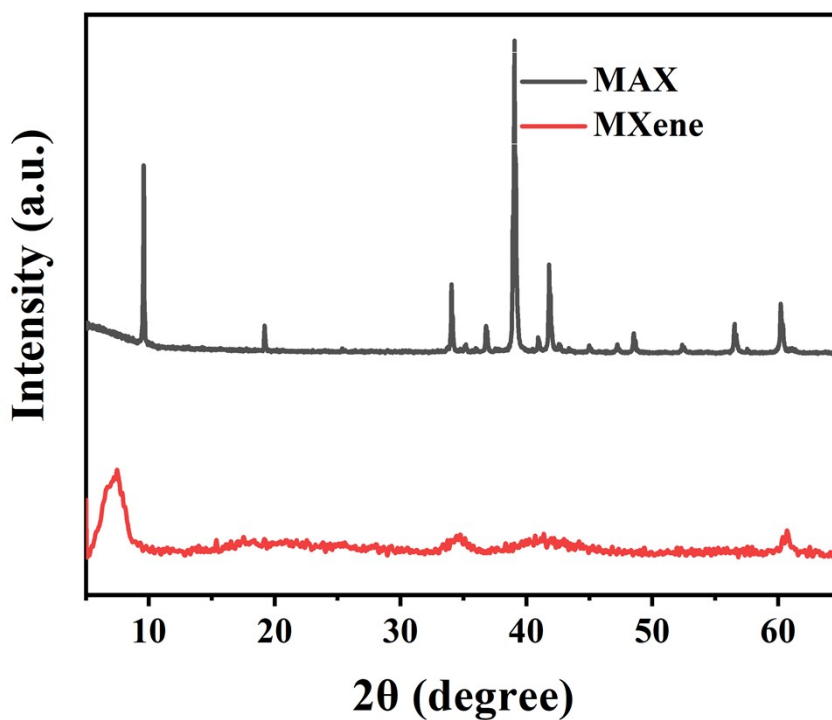


Fig.S3 XRD patterns of MAX and MXene.

Table. S2 Chemical compositions of all samples.

Sample name	Target composition	Measured composition
NVP	$\text{Na}_3\text{V}_2(\text{PO}_4)_3$	$\text{Na}_{2.99}\text{V}_{1.98}(\text{P}_{0.99}\text{O}_{4-x})_{2.98}$
KC0.05	$\text{K}_{0.1}\text{Na}_{2.95}\text{V}_{1.95}\text{Co}_{0.05}(\text{PO}_4)_3$	$\text{K}_{0.09}\text{Na}_{2.93}\text{V}_{1.94}\text{Co}_{0.04}(\text{P}_{0.99}\text{O}_{4-x})_{2.99}$
KC0.05@MX	$\text{K}_{0.1}\text{Na}_{2.95}\text{V}_{1.95}\text{Co}_{0.05}(\text{PO}_4)_3/\text{Ti}_3\text{C}_2\text{T}_x$	$\text{K}_{0.09}\text{Na}_{2.95}\text{V}_{1.94}\text{Co}_{0.04}(\text{P}_{0.99}\text{O}_{4-x})_3/\text{Ti}_{2.98}\text{C}_{2-x}\text{T}_x$

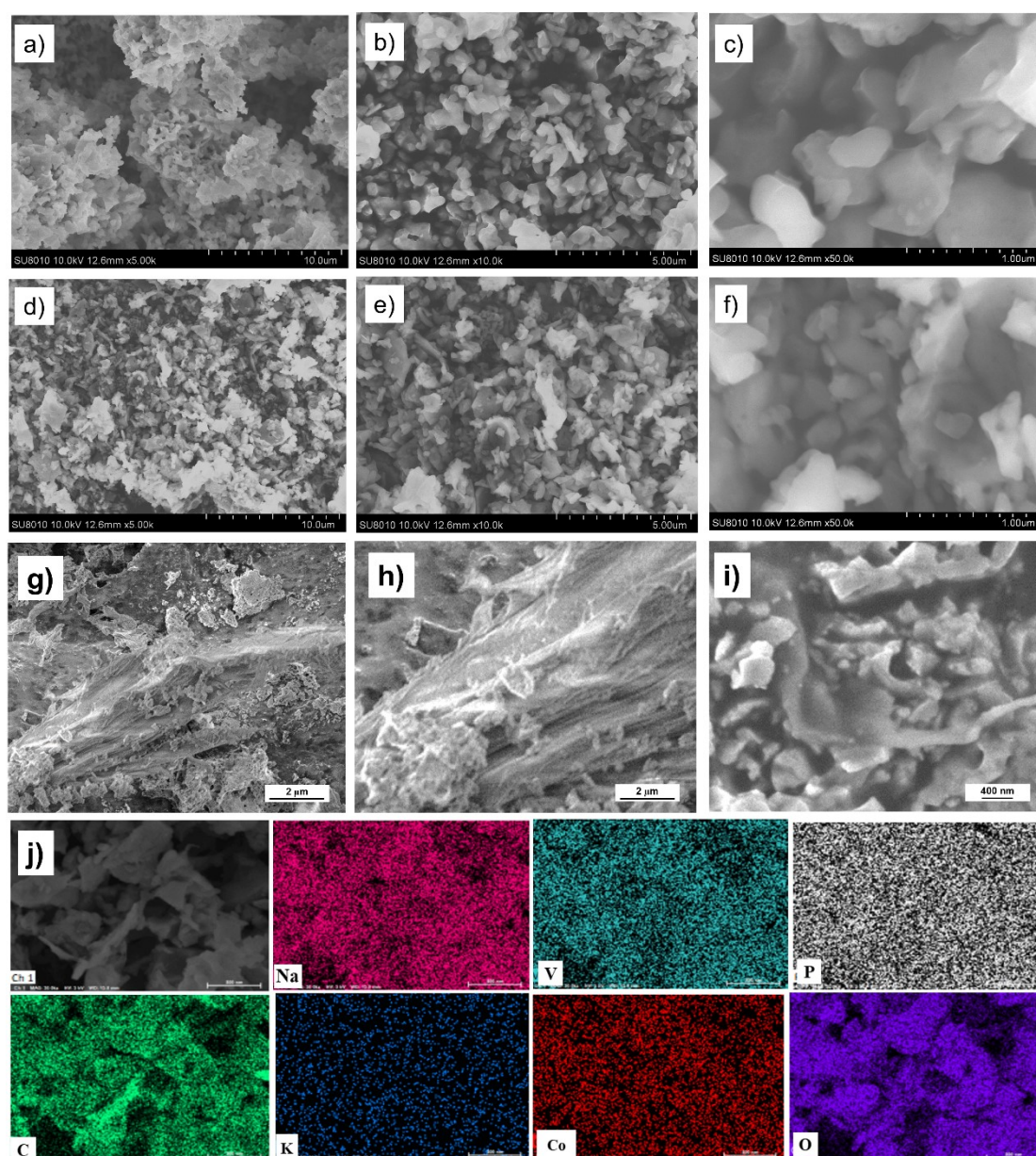


Fig.S4 SEM images at different amplification ratio of NVP (a-c), KC05 (d-f) and KC05@MX (g-i).

(j)The EDS image of KC05@MX and the element mapping of Na, V, P, C, K, Co and O.

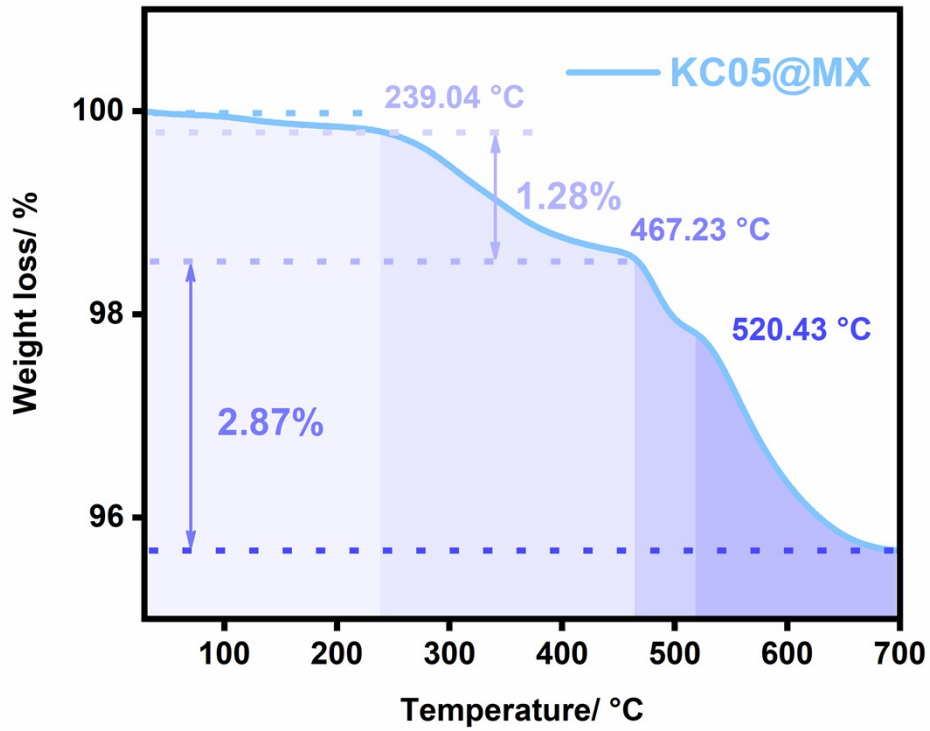


Fig.S5 TGA curve of KC05@MX at air from 50 to 700 °C

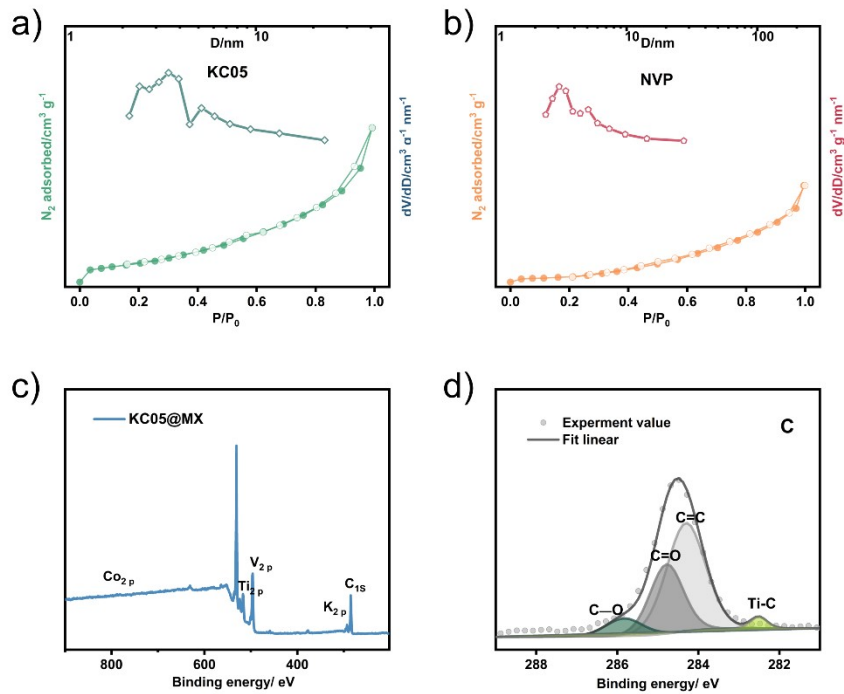


Fig.S6 The N₂ adsorption-desorption isotherms and pore distribution of KC05 (a) and NVP (b). The

XPS survey spectrum (c) and the high resolution C_{1s} spectrum (d) of KC05@MX sample.

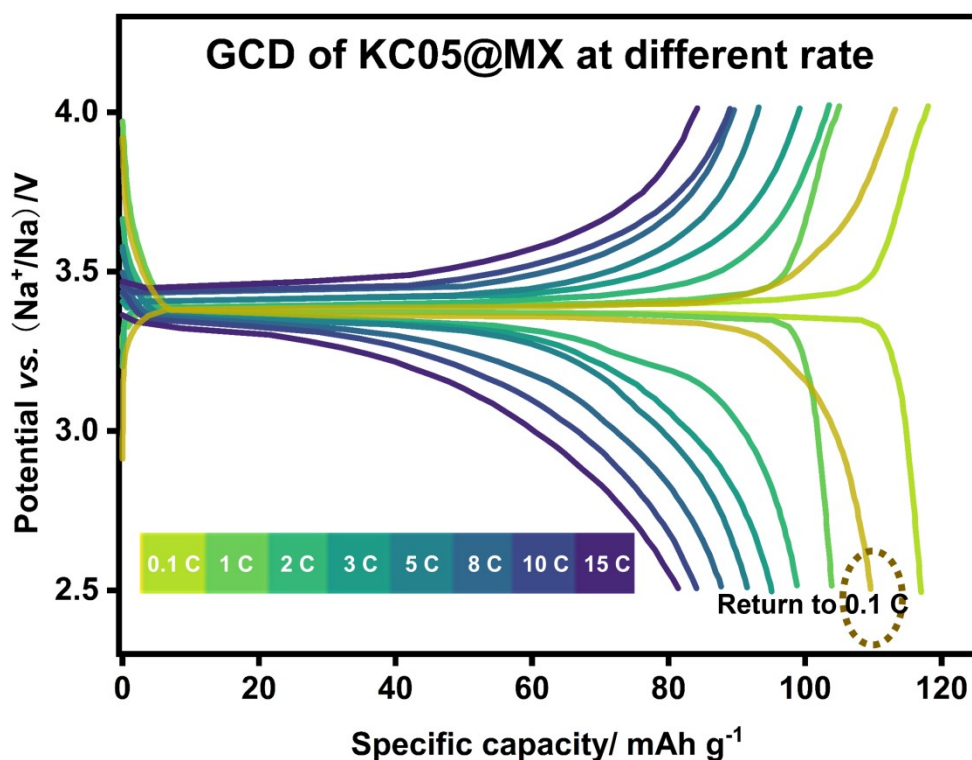


Fig.S7 GCD curves of KC05@MX at different rate.

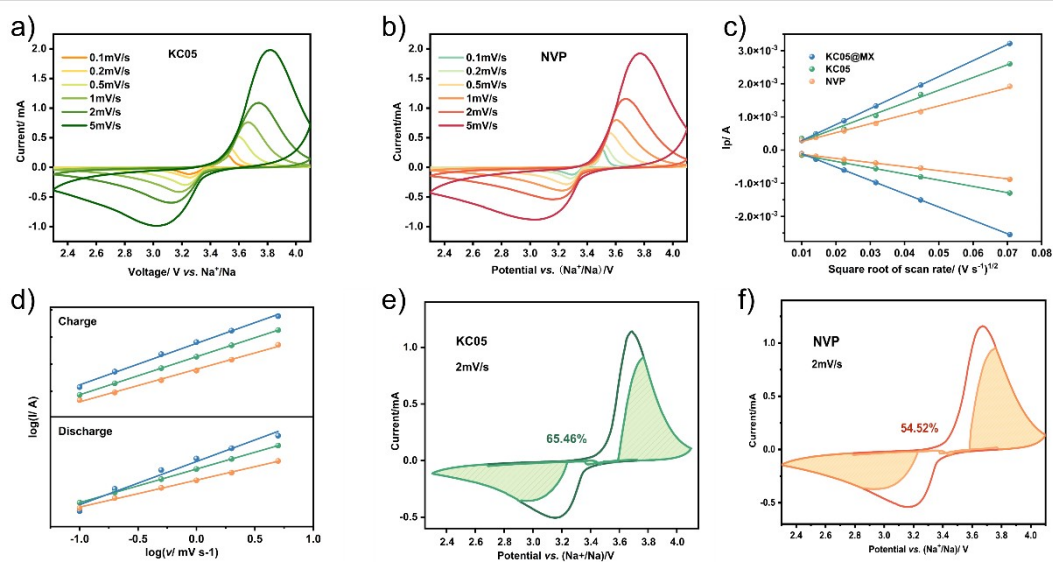


Fig.S8 The CV profiles under various scan rate of KC05(a) and NVP (b). (c) The ' I_p vs. $v^{1/2}$ ' curves of three electrodes. (d) The ' $\log I$ vs. $\log v$ ' profiles of all electrodes. The Quantitative analysis capacitive contribution of KC05 (e) and NVP (f).

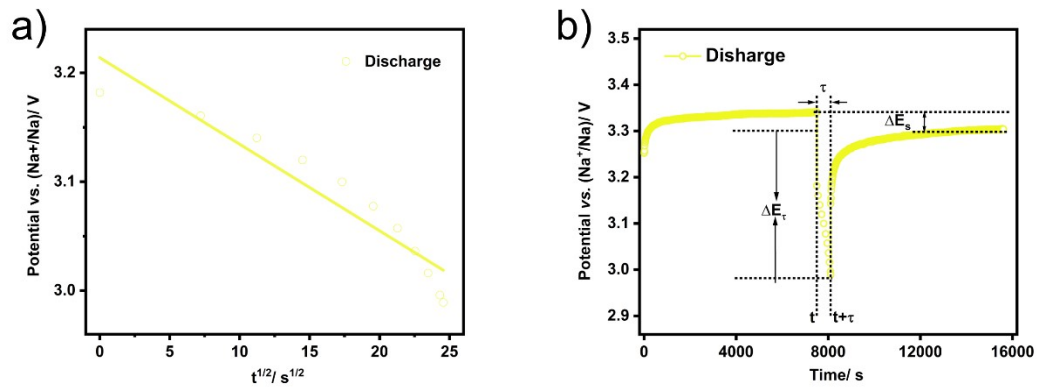


Fig.S9 The 'V vs $\tau^{1/2}$ ' fitting curve (a) and the 'Potential vs Time' (b) curve in a single period during the discharge process of KC05@MX.

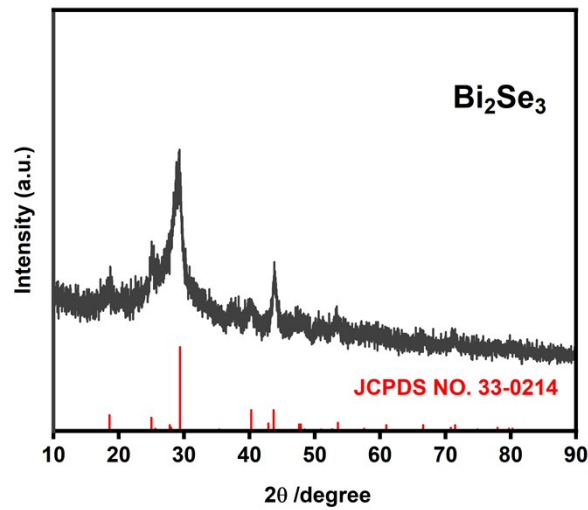


Fig.S10 XRD pattern of Bi₂Se₃ sample.

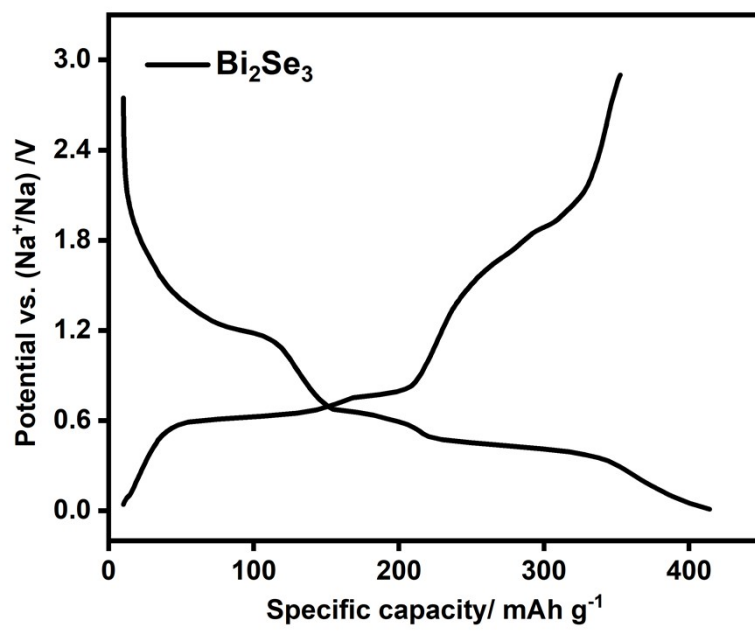


Fig.S11 GCD curve of Bi₂Se₃ sample.