

**Achieving high-rate and high energy density in all-solid-state flexible asymmetric
pseudocapacitor through the synergistic design of binder-free 3D ZnCo₂O₄ nano
polyhedrons and 2D layered Ti₃C₂T_x-MXenes**

Muhammad Sufyan Javed^{a,b,*}, Hang Lei^a, Hidayat Ullah Shah^c, Sumreen Asim^d, Rizwan Raza^b,
Wenjie Mai^{a*}

*^aSiyuan Laboratory, Guangdong Provincial Engineering Technology Research Center of Vacuum
Coating Technologies and New Energy Materials, Department of Physics, Jinan University,
Guangzhou 510632, P. R. China*

*^bDepartment of Physics, COMSATS University Islamabad, Lahore Campus, Lahore 54000,
Pakistan*

*^cDepartment of Physics, University of Science and Technology Bannu Khyber pakhtunkhwa
28100, Pakistan*

*^dDepartment of Chemistry, Khwaja Fareed University of Engineering and Information Technology, RYK-
64200, Pakistan*

Corresponding authors

safisabri@gmail.com (M.S. Javed)

wenjiemai@gmail.com (W. Mai)

1. Experimental section

All the chemicals were analytical grade and used without further purification. Zinc chloride (ZnCl_2), cobalt chloride ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$), potassium hydroxide (KOH), Urea ($\text{CH}_4\text{N}_2\text{O}$), sodium fluoride (NaF), max phase powder of layered ternary carbide (Ti_3AlC_2), hydrochloric acid (HCl), lithium fluoride (LiF) and ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$) ethanol, methanol and polyvinyl alcohol (PVA) were purchased from Aladdin Chemicals suppliers and manufacturers. The Millipore purified water was used throughout all experiments.

1.1 3D ZnCo_2O_4 nano polyhedrons

In a typical run of experiment for the synthesis of ZnCo_2O_4 nano polyhedrons, 2 mmol of zinc chloride, 4 mmol of cobalt chloride, 1 mmol of sodium fluoride and 3 mmol of urea were mixed in the mixture of 20 mL of deionized water and 20 mL of ethylene glycol for 2 h to get a homogeneous solution. Meanwhile, pieces of carbon fibre textile (CFT) with desired dimensions were thoroughly soaked in H_2SO_4 : HCl, 50/50 % for 24 h to increase the hydrophobicity of the substrates after that they were cleaned with ethanol and water. Afterwards, a mixed solution of the metal precursor and pieces of cleansed CFT were hanged in Teflon autoclaves with a capacity of 50 mL (one Teflon contain only one piece of CFT to control the mass loading density on each CFT piece). After that, the Teflon-lined-autoclaves were moved to a preheated furnace at 180 °C for 20 h. After the completion of the hydrothermal reaction, the autoclaves were endorsed natural cooling to room temperature; the obtained ZCO@CFT precursors were thoroughly washed with deionized water, acetone and dried at 90 °C for 12 h. In the last step, the ZCO@CFT precursors were sintered at 350 °C for 2h in an air atmosphere to get the well-crystallized product with a pure phase of ZnCo_2O_4 . The mass loading density was 1.25 mg cm^{-2} , which was carefully calculated by the difference between pristine CFT and ZCO@CFT .

1.2 Synthesis of delaminated 2D-Ti₃C₂T_x (MXene)

Max phase powder of layered ternary carbide (Ti₃AlC₂) with particle size < 50 μm was used to synthesised the delaminated 2D-Ti₃C₂T_x (MXene) according to the selective etching the Al layers from Ti₃AlC₂ in a mixed solution of hydrochloric acid and lithium fluoride. In a typical run, the etching solution was arranged by mixing the 1.0 g of LiF into 10 M HCl in 30 mL of deionised water and stirred for 10 min. After that, 1.5 g of Ti₃AlC₂ max phase powder was slowly added to the etching solution at room temperature and kept the system stirring for 24 h. The acidic solution was washed with deionised water until pH reach to 6 using centrifugation at 4000 rpm (10 min per cycle). The obtained product was sonicated for 2 h and dried in a vacuum oven at 90 °C for 24 h prior to use as anode material for SC.

1.3 Fabrication of electrodes

The annealed ZCO@CFT was directly used to test as single electrode without any further processioning as a binder-free self-supported cathode material. The anode material was prepared by mixing the Ti₃C₂T_x powder (90 %) and Polyvinylidene fluoride (PVDF) (10 %) in N-Methyl-2-pyrrolidone (NMP) and stirred until the mixture has become homogenous. The obtained mixture was pasted on the CFT and dried at 60 °C prior to use and denoted as MXene@CFT. The active working area of the electrode was chosen to 1×1 cm². The mass loading density was 1.25 mg cm⁻², which was carefully calculated by the difference between pristine and Ti₃C₂T_x coated CFT.

1.4 Optimization of mass loading densities

The optimization of mass loading densities of positive and negative electrodes was controlled as follow: We performed a number of experiments to control active mass loading density on CFT and it is optimized as follow: 2 mmol of zinc chloride, 4 mmol of cobalt chloride, 1 mmol of sodium

fluoride and 3 mmol of urea were mixed in the mixture of 20 mL of deionized water and 20 mL of ethylene glycol. By this amount of reactants we obtained the mass loading density of 1.15~1.25 mg cm⁻², which was carefully calculated by the difference between pristine CFT and ZCO@CFT. (only one piece of CFT with dimension of 2×4 cm² was put into autoclave). To obtain the accuracy, we cut at least 10-15 pieces of ZCO@CFT with dimensions of 1×1 cm² and choose the electrode for testing which exactly has 1.25 mg cm⁻² mass loading density. The mass loading density can be tuned by varying the amount of reactants; for example, we obtained 0.8~0.85 mg cm⁻² by reducing the amount of reactants to half as compared to above one and used 30 mL autoclave with only one piece of CFT with dimension 2×4 cm².

For negative electrode, it was prepared by slurry casting method and it is easy to control the mass loading density. Typically, we prepared the MXene@CFT electrode with 1.0~1.2 mg cm⁻² by coating the 200 μm thick layer and by increasing the thickness of the layer mass loading density can be increase. The procedure for preparing the slurry was mentioned in Supporting Information section 1.3. The mass loading densities for the fabrication of device was optimized based on the charge balance theory.

1.5 Fabrication of flexible asymmetric supercapacitors

All-solid-state asymmetric SCs were fabricated using ZCO@CFT as a positive and MXene@CFT as negative electrodes with KOH/PVA solid-state jelly electrolyte, and a piece of Whatman filter paper (8 μm thickness) was served as a separator. The mass loading densities on both electrodes were balanced using mass balance theory to obtain the high precision in the results. The typical mass loading densities on both electrodes was not more than 5 mg cm⁻² for ZCO||MXene-ASC. The KOH/PVA solid-state electrolyte was prepared by mixing 1.6 g KOH first in 5 mL deionised

water and 6 g PVA in 60 mL deionised water and after that mixed both solutions, and heated at 90 °C until the mixture became the clear homogenous solution. The KOH/PVA was stirred continuously for 2 h at room temperature to remove the air bubbles.

1.6 Electrochemical Measurements and calculations

The electrochemical measurements of single electrodes were conducted in a three-electrode system using KOH as an aqueous basic electrolyte, Ag/AgCl as a reference electrode, and a platinum plate as a counter electrode. Cyclic Voltammetry (CV) and galvanostatic charge/discharge (GCD) tests for both two and three-electrode systems were recorded using electrochemical workstation (CHI 660E, China). Electrochemical impedance spectroscopy (EIS) measurements were investigated under A.C. signal of voltage (5 mV) in the frequency range of 0.01-100 kHz. Each electrochemical test in three and two electrode systems was performed three times to confirm the reproducibility of the results. The specific capacitance in the three-electrode system (C_s), specific capacitance in the two-electrode system (C_{cell}), energy density (E) and power density (P) of ZCO||MXene-ASC were computed based on the total mass of both electrode materials using the following equations.

$$C_s = \frac{\int I dt}{m(V_f - V_i)} \quad (1)$$

$$C_a = \frac{\int I dt}{A(V_f - V_i)} \quad (2)$$

$$C_{cell} = \frac{\int I dt}{M(V_f - V_i)} \quad (3)$$

$$E = \frac{\int I dt}{M \times 3.6} \quad (4)$$

$$P = \frac{E}{\Delta t_d} \times 3600 \quad (5)$$

Where, C_s , C_{cell} ($F g^{-1}$) and C_a ($F cm^{-2}$) are the specific and areal capacitance of single electrode and ZCO||MXene-ASC, respectively; $\int I dt$ is the area under discharge curve; m (g) is the mass of active material on a single electrode; A (cm^2) is the area of the working electrode; $\Delta V = V_f - V_i$ is the potential window; M (g) is the total mass of positive and negative electrode materials for SSC; P ($W kg^{-1}$) is the power density; E ($Wh kg^{-1}$); Δt_d is the discharging time (s).

1.7 Material characterisation

X-ray diffraction (XRD) was acquired with a Rigaku, MiniFlex600, CuK α radiation ($\lambda = 1.54065$ Å). The X-ray Photoelectron Spectroscopy was carried out using XPS, Ulvac-Phi, PHI X-tool. Surface morphologies of the products were examined by field emission scanning electron microscopy (SEM, ZEISS ULTRA 55) and transmission electron microscopy (TEM, JEOL 2100F, 200 kV). The BET specific surface area was determined using N₂ adsorption/desorption isotherm measurements by multipoint Brunauer-Emmett-Teller (BET) method with Quantachrome Instrument (version 5.12) and pore size distribution was computed by Barret-Joyner-Halenda (BJH) method.

Supporting Figures (S1-S9)

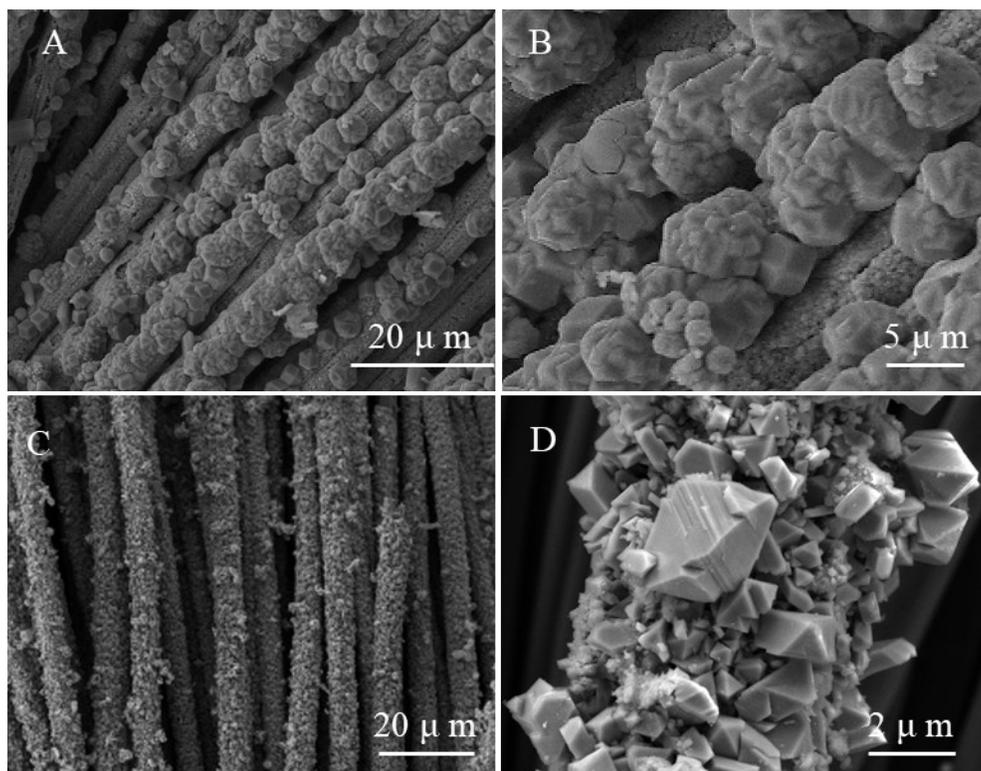


Fig. S1. (A-B) Low and high resolution FESEM images of Zn₂CoO₄@CFT and (C-D) Low and high resolution FESEM images of Zn_{1.5}Co_{1.5}O₄@CFT.

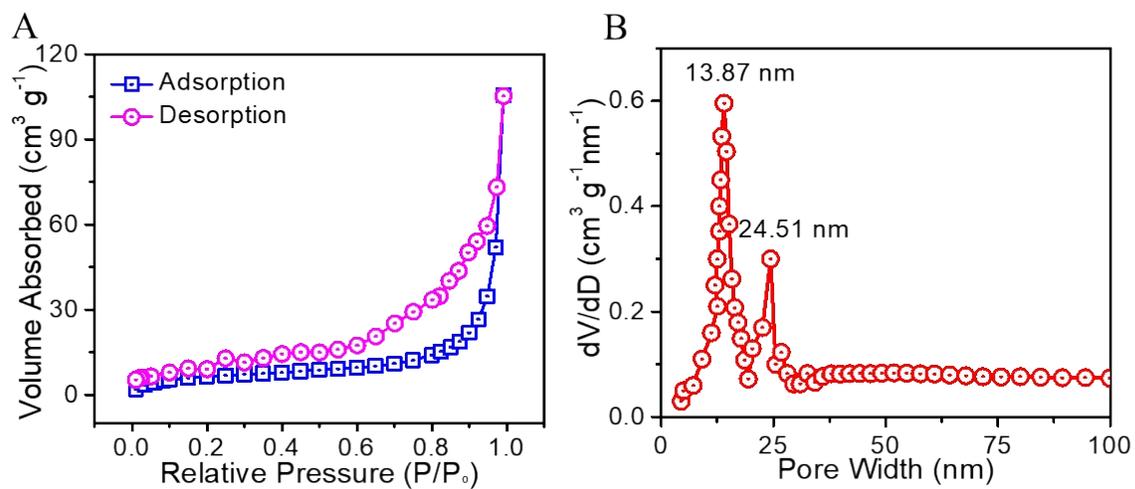


Fig. S2. (A) BET N₂ adsorption-desorption analysis (B) pore size distributions of the ZnCo₂O₄ polyhedrons calculated by BJH method.

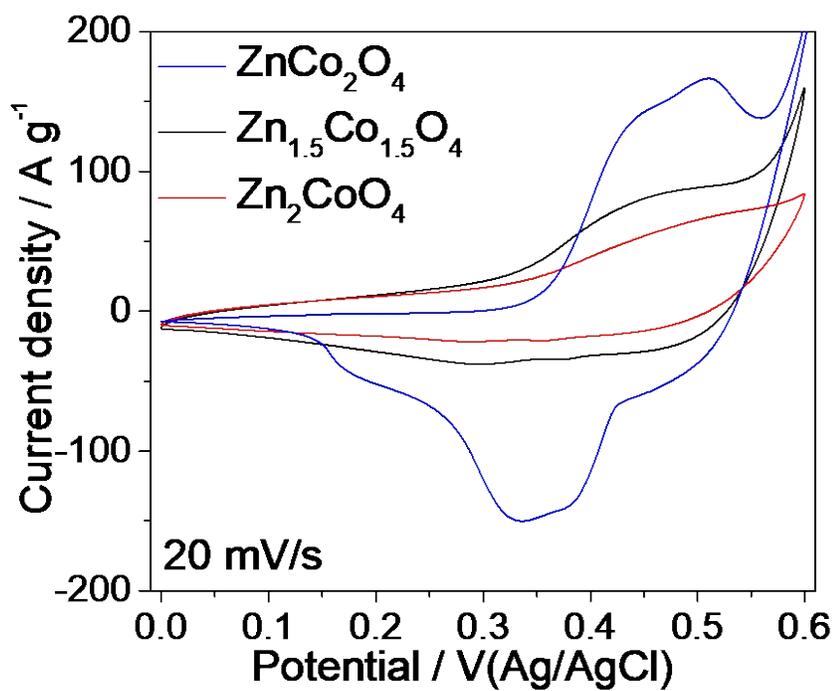


Fig. S3: Concentration dependent electrochemical performance of Zn/Co@CFT electrodes

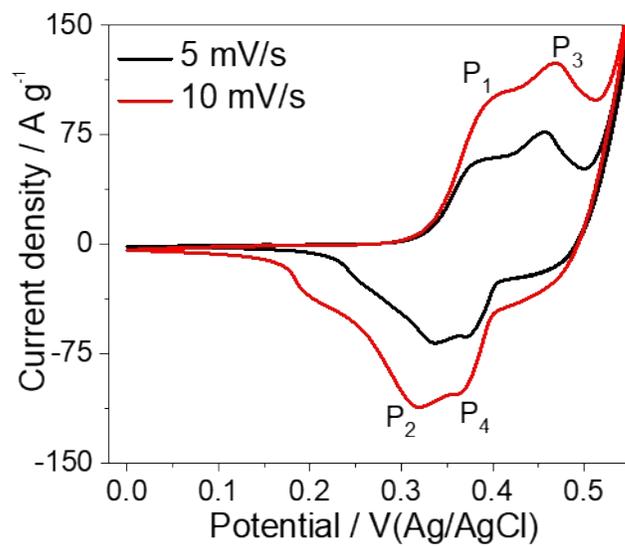


Fig. S4. CV curves of ZCO@CFT electrode at low scan rates

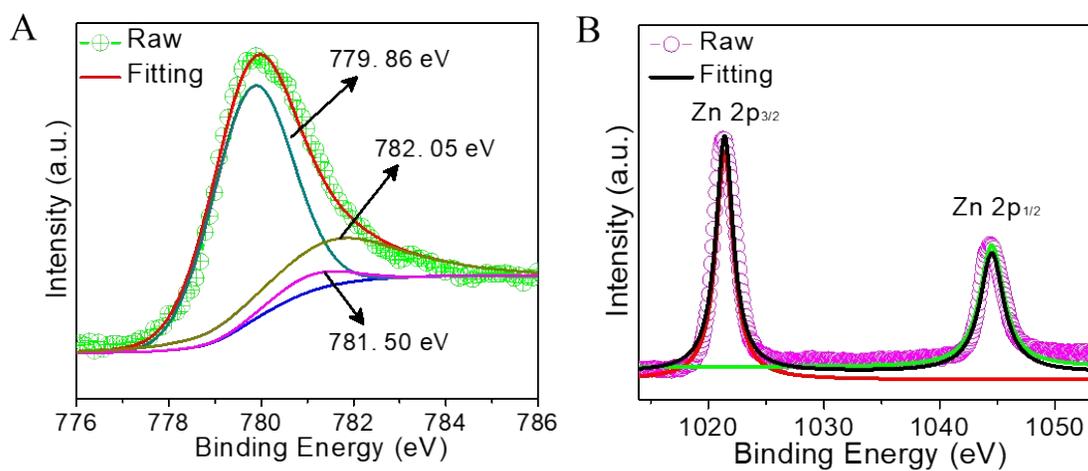


Fig. S5. (A) High-resolution XPS spectra of Co 2p_{3/2} and (B) High-resolution XPS spectra of Zn 2p of ZCO@CFT electrode after running for 100 cycles.

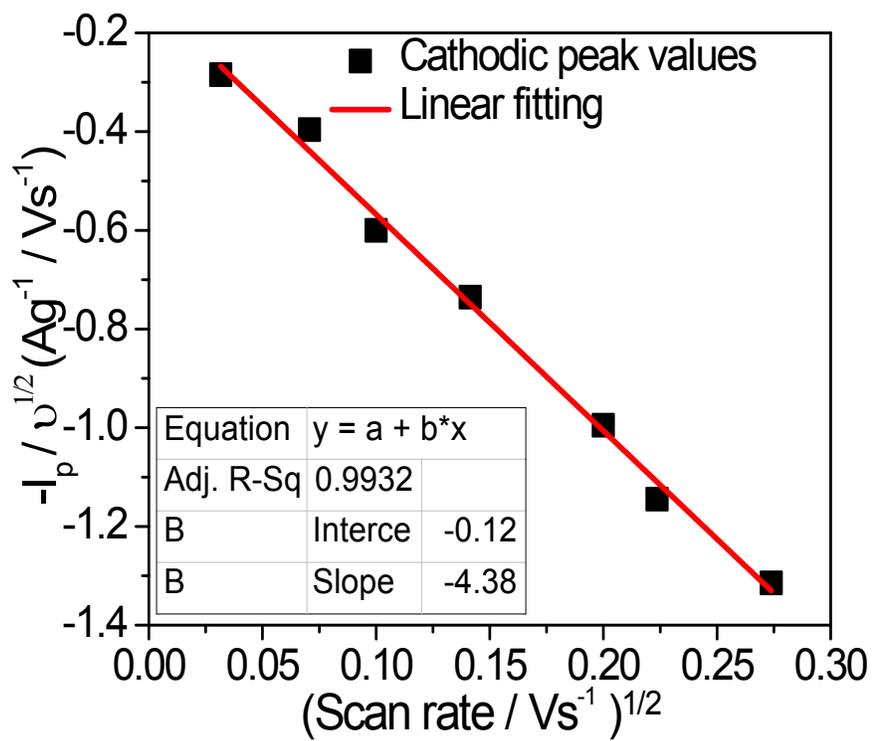


Fig. S6. Plot for calculating the values of p and q constants ZCO@CFT electrode

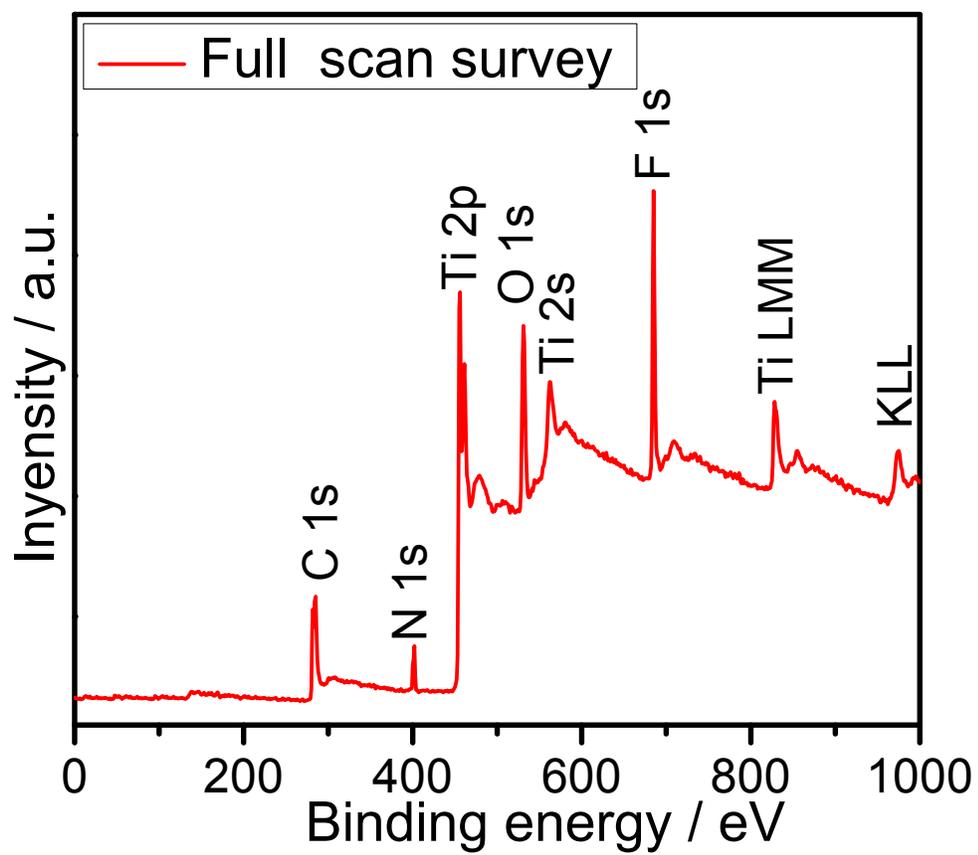


Fig. S7: XPS full scan survey of $\text{Ti}_3\text{C}_2\text{T}_x$ -MXene

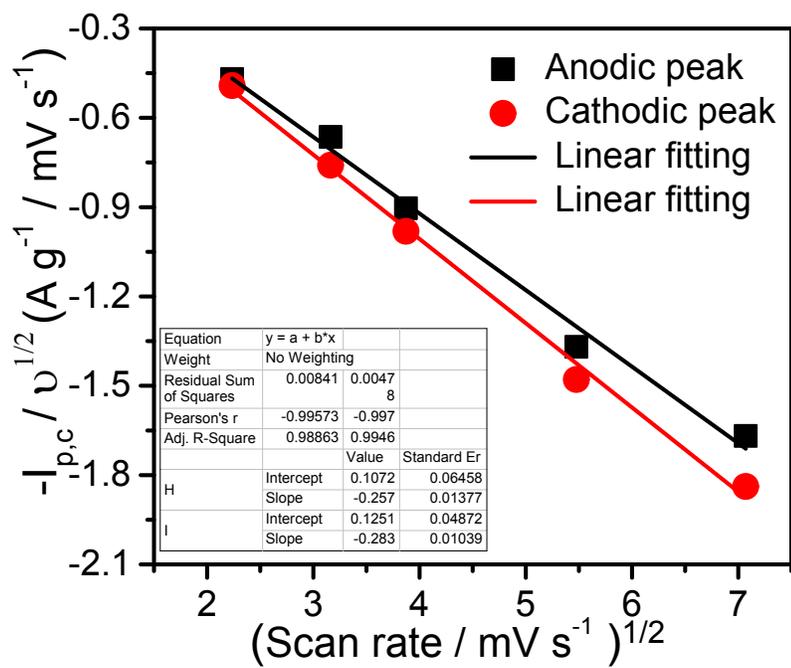


Fig. S8. Plot for calculating the values of p and q constants for MXene@CFT electrode

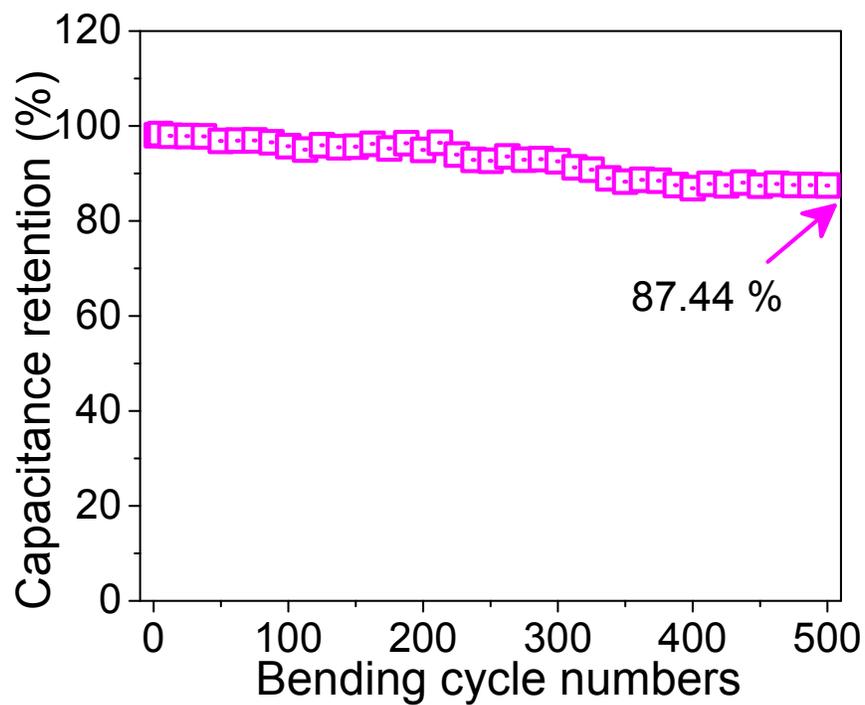


Fig. S9. Bending cycles versus capacitance retention for ZCO||MXene-ASC.