

ARTICLE

Electronic Supplementary Information

Microwave-assisted rapid synthesis of titanium phosphate free phosphorous doped  $Ti_3C_2$  MXene with boosted pseudocapacitance

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1. Experimental Methods

1.1. Materials

Pristine  $Ti_3AlC_2$  (99.8%, -385 mesh) was purchased from a china based company through a local vendor technology Co. (China), Hydrochloric acid (HF), Phosphoric acid ( $H_3PO_4$ ), Phytic acid ( $C_6H_{18}O_{24}P_6$ ), Sodium dihydrogen phosphate ( $NaH_2PO_4$ ), sulphuric acid ( $H_2SO_4$ ) as electrolyte were purchased from Merck Chemicals, India limited and used as received. Solvents like N-Methyl-2-Pyrrolidone (NMP) and ethanol are also purchased from Merck Chemicals, India. For producing a suitable binder polyvinylidene fluoride (PVDF) was purchased from Carbon fiber is used as current collector.

1.2. Materials Characterizations

Crystallographic structure and phase information of all the developed samples were analysed by XRD Bruker, D8 DISCOVER semiautomatic diffractometer using Cu K $\alpha$  radiation ( $\lambda = 0.154178$  nm) with a scan speed of  $0.75$  min $^{-1}$  at wide-angle range of  $2\theta$  value  $4$  to  $60^\circ$  where accelerating voltage of  $50$  kV and the emission current of  $\sim 300$  mA was used. The chemical diversities of different doped and undoped material were investigated through X-ray photoelectron spectrometer (SPECS, Germany) with an Mg-K $\alpha$  twin anode X-ray source ( $E = 1253.6$  eV). The binding energies were collected with a reference to the maximum intensity of the C 1s ( $284.6$  eV). Analysis of the spectra was done using CASA XPS software. Scanning electron microscopy was performed in a (Nova Nano SEM 430, Netherland make SEM) to analyze microstructures and morphologies. High resolution transmission electron microscopy was analysed with (HRTEM JEOL JEM-1230 with accelerating voltage of  $120$  kV). FT-IR is used to determine the functional groups in the range of  $500$ -

$4000$  cm $^{-1}$  where the sample was fabricated with KBr. Raman spectra of the synthesized powdered materials were recorded using a WITEC-alpha 300 R Confocal Raman imaging. Powdered materials were on the glass slide for spectra recoding using  $532$  nm laser source with  $50$ - $60$   $\mu$ W power. BET surface area was determined by  $N_2$  adsorption desorption method at liquid nitrogen temperature using Nova 4000e (Quantachrome, USA). Prior to adsorption desorption measurements, the samples were degassed at  $473$  K at  $10^{-3}$  Torr for  $5$  h.

1.3. Electrode fabrication and electrochemical measurements

Electrochemical measurements were carried out in three-electrode cells on a GAMRY work station. In which we use current collectors like nickel foam, carbon cloth, carbon fiber, titanium plate etc. as a working electrode, graphite rod/ Pt as a counter electrode and Ag/AgCl or Hg/Hg $_2$ Cl $_2$  as a reference electrode. In which the working electrodes were prepared by mixing active material (P- $Ti_3C_2$ -MW-PA@1:10), carbon black and 13% PVDF embedded in NMP in a weight ratio of 80:10:10. Addition of adequate amount NMP is required to make slurry of the above mixture which then coated on cleaned carbon fiber and dried under vacuum oven at  $60^\circ$ C overnight to obtain the P-  $Ti_3C_2$  based working electrodes. The electrochemical studies were investigated using cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS), which were performed using GAMRY electrochemical work station. The electrochemical performances of the undoped  $Ti_3C_2$  and P- $Ti_3C_2$  electrodes were evaluated in  $3M$   $H_2SO_4$  filled three-electrode cells. In the three-electrode system, volumetric capacitance  $C_g$  (Fcm $^{-3}$ ), of the electrode through GCD is calculated by the following equation<sup>1,2</sup>:

$$C_g = \frac{I \times \Delta t}{m \times \Delta V}$$

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Where  $I$  (current) (A),  $\Delta t$  (discharge time) (s),  $m$  (mass) (V),  $\Delta V$  (voltage) (V) respectively.

Volumetric capacitance ( $F\text{ cm}^{-3}$ ), energy density ( $E$ ) ( $\text{WhL}^{-1}$ ) and power density ( $P$ ) ( $\text{WL}^{-1}$ ) for the electrode are calculated by the following equations:

$$C_v = C_g \times \rho$$

$$E_v = \frac{C_v \times \Delta V^2}{2 \times 3.6}$$

$$P_v = \frac{3600 \times E_v}{\Delta t}$$

Electrochemical measurements in two electrode systems were also performed with the flexible supercapacitor devices made from the P-Ti<sub>3</sub>C<sub>2</sub>-MW-PA@1:10 and PVA-H<sub>2</sub>SO<sub>4</sub> gel electrolyte. To prepare PVA-H<sub>2</sub>SO<sub>4</sub> gel electrolyte, 1 g of polyvinyl alcohol (PVA) powder was slowly added to dissolve into 10 mL of distilled water, and then the mixture was heated at 90°C under continuous stirring until the solution became clear. Then, 5 mL aqueous H<sub>2</sub>SO<sub>4</sub> (3M) was added dropwise slowly into the above PVA solution under constant stirring to form a gel electrolyte. After that for the preparation of the flexible electrodes, we use the above gel electrolyte and uniformly apply by sandwiching gel as a separator between the two coated P-Ti<sub>3</sub>C<sub>2</sub>-MW-PA@1:10 flexible carbon fiber electrodes in symmetric fashion and then dried adequately for the use in further measurements.

In the two-electrode cell, volumetric capacitance  $C$  ( $F\text{cm}^{-3}$ ) of the electrode in the symmetric ECs is calculated by the following equation<sup>2-5</sup>:

$$C_g = \frac{2 \times I \times \Delta t}{m \times \Delta V}$$

$$C_v = C_g \times \rho$$

Where  $I$  (current) (A),  $\Delta t$  (discharge time) (s),  $m$  (mass) (V),  $\Delta V$  (voltage) (V),  $\rho$  is tap density  $\sim 3.8\text{ gcm}^{-3}$  respectively.

Volumetric energy density ( $E$ ) ( $\text{WhL}^{-1}$ ) and power density ( $P$ ) ( $\text{WL}^{-1}$ ) for the symmetric ECs are calculated by the following equations:

$$E_v = \frac{C_v \times \Delta V^2}{8 \times 3.6}$$

$$P_v = \frac{3600 \times E_v}{\Delta t}$$

where  $\Delta V$  is the voltage range, and  $\Delta t$  is the discharge time.

The Trasatti method was used to differentiate the capacitance contribution from EDL and pseudocapacitive reactions. CV of Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> and P-Ti<sub>3</sub>C<sub>2</sub>-MW-PA@1:10 were first calculated in different scan rate. Then, corresponding areal gravimetric capacitances were calculated based on the following equation<sup>6,7</sup>:

$$C = \frac{S}{2 \times m \times \vartheta \times \Delta V}$$

where  $C$  stands for the gravimetric capacitance (in  $F\text{ g}^{-1}$ ),  $\Delta V$  the potential window (in V),  $m$  is the mass of the electrode,  $S$  the area enclosed by corresponding cyclic voltammograms (in  $\text{AVg}^{-1}$ ) and  $\vartheta$  the scan rate (in  $\text{Vs}^{-1}$ ). Plotting the reciprocal of the gravimetric capacitances ( $C^{-1}$ ) against the square root of scan rates ( $\vartheta^{1/2}$ ) should yield a linear correlation between them, assuming semi-infinite diffusion of ions. Specifically, the correlation can be described by the following equation:

$$C^{-1} = \text{Constant} \times \vartheta^{1/2} + CT^{-1}$$

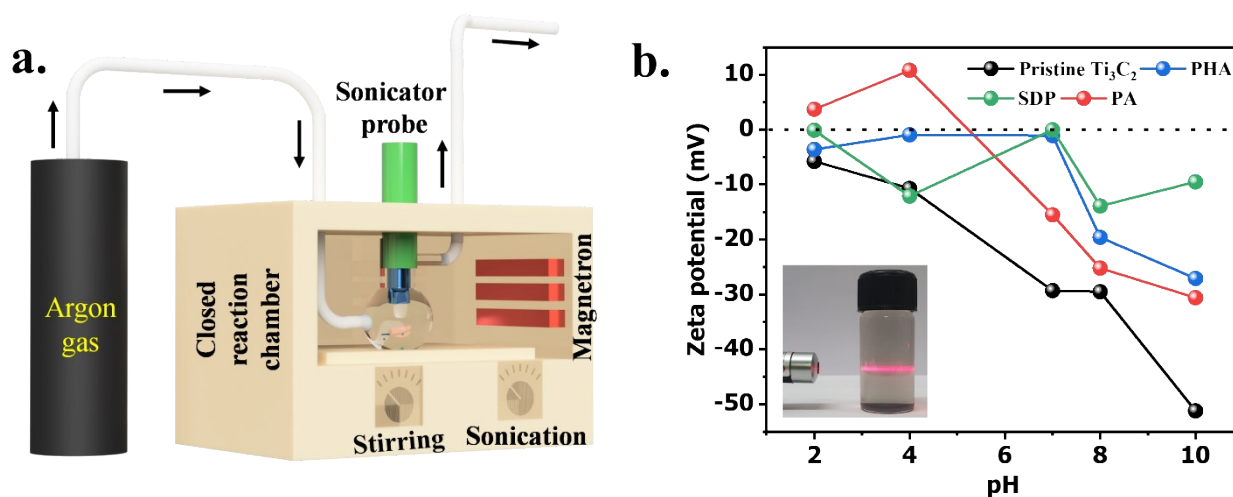
where  $C$ ,  $\vartheta$  and  $CT$  is the experimental gravimetric capacitance, the scan rate and the total capacitance, respectively. The "total capacitance" is equals the sum of EDL and pseudocapacitive. Plotting the gravimetric capacitances ( $C$ ) against the reciprocal of square root of scan rates ( $\vartheta^{1/2}$ ) also give a linear correlation described by the following equation:

$$C = \text{Constant} \times \vartheta^{1/2} + C_{EDL}$$

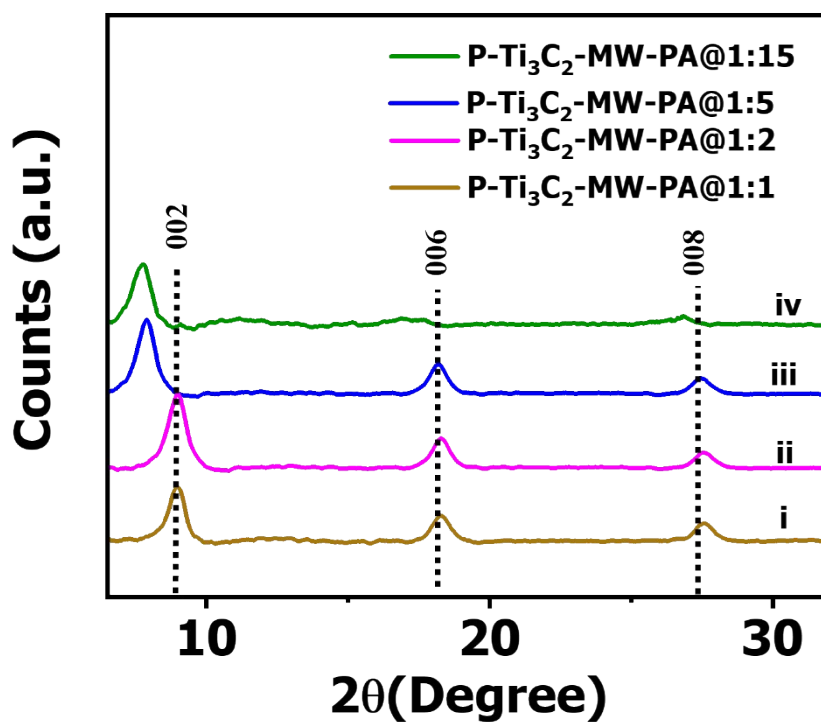
where  $C$ ,  $\vartheta$  and  $C_{EDL}$  is the experimental gravimetric capacitance, the scan rate and the EDLC, respectively. Linear fit the plot and extrapolate the fitting line to y-axis gives the maximum EDL. Subtraction of  $C_{EDL}$  from  $CT$  yields the maximum pseudocapacitance. Finally, the capacitance contribution percentage from EDL capacitance and pseudocapacitance can be calculated by following equation:

$$C_{EDL\%} = \frac{C_{EDL} \times 100}{C_T}$$

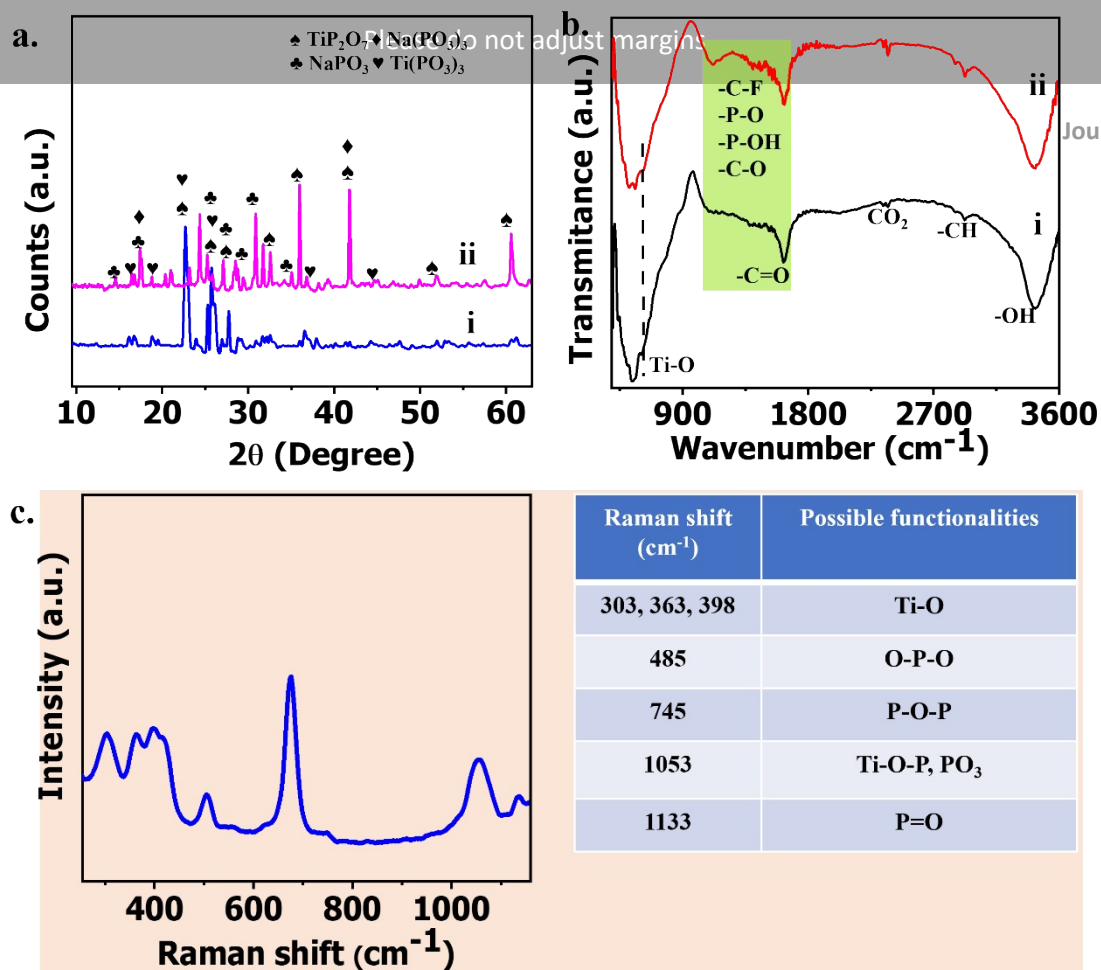
## 2. Supplementary Figureures



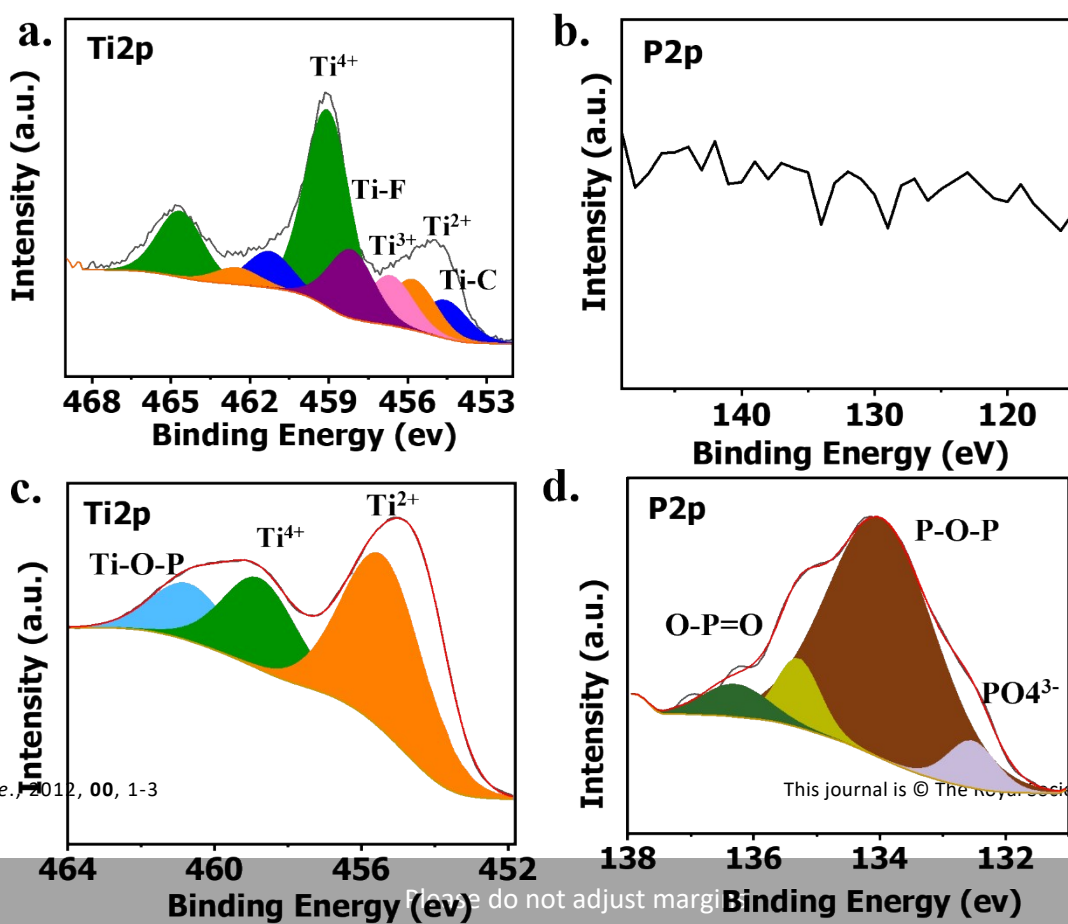
**Figure S1:** (a) One simple sketch of the MW heating chamber and (b) Zeta potential plot of pristine  $Ti_3C_2T_x$  and different doping sources at different pH.



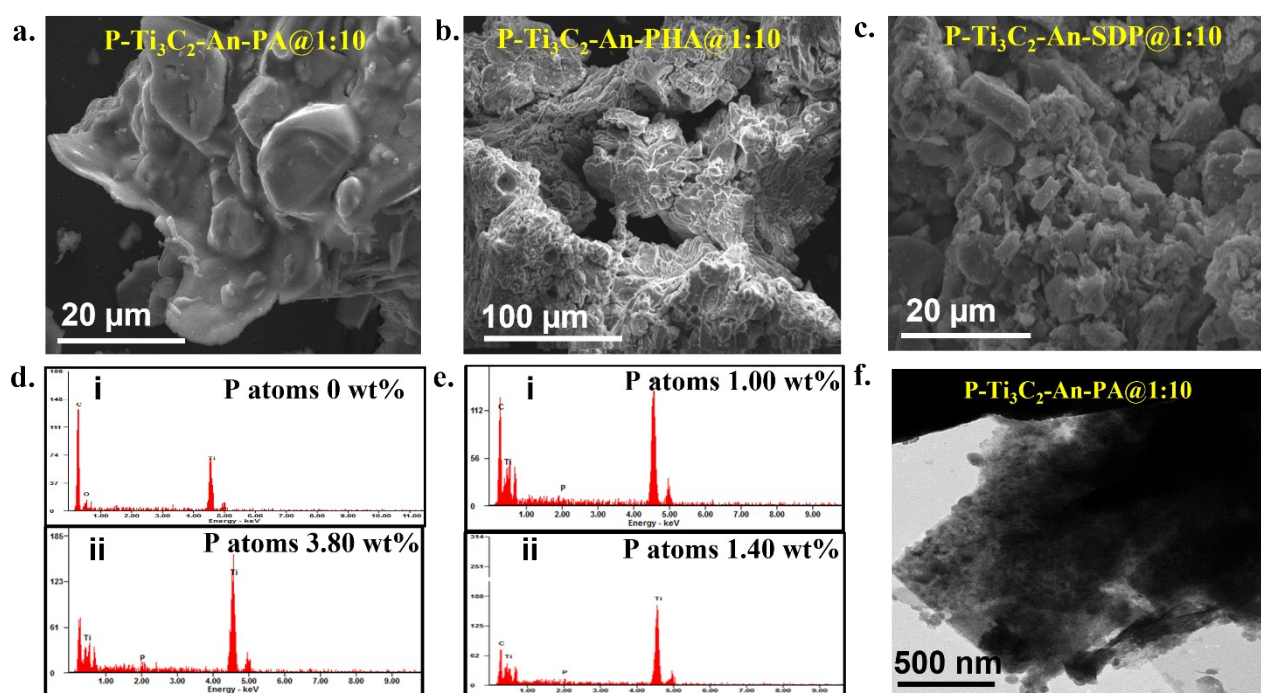
**Figure S2:** XRD of P- $Ti_3C_2$ -MW-PA at different ratios (i) P- $Ti_3C_2$ -MW-PA@1:1, (ii) P- $Ti_3C_2$ -MW-PA@1:2, (iii) P- $Ti_3C_2$ -MW-PA@1:5 and (iv) P- $Ti_3C_2$ -MW-PA@1:15.



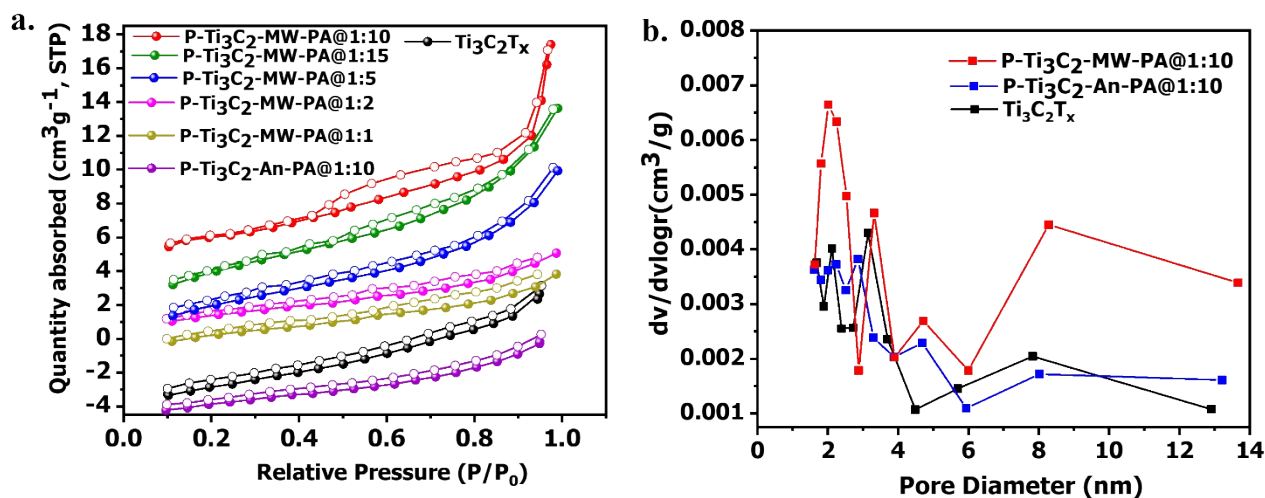
**Figure S3:** (a) XRD of (i) P-Ti<sub>3</sub>C<sub>2</sub>-An-PHA@1:10 and (ii) P-Ti<sub>3</sub>C<sub>2</sub>-An-SDP@1:10; (b) FTIR of (i) Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> and (ii) P-Ti<sub>3</sub>C<sub>2</sub>-MW-PA@1:10; (c) Raman spectra of P-Ti<sub>3</sub>C<sub>2</sub>-An-PA@1:10 with associated Raman shift values and corresponding possible functionalities.



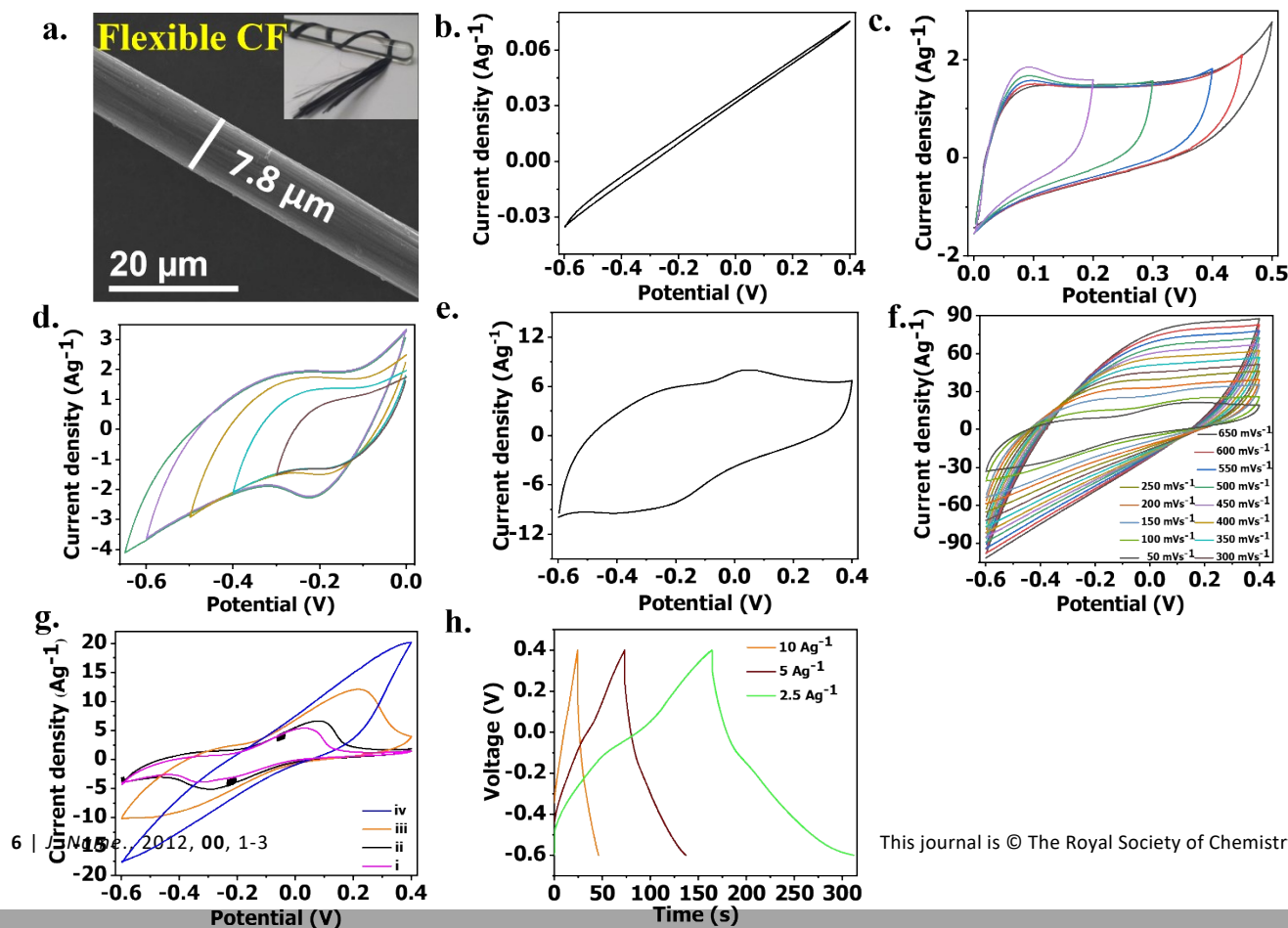
**Figure S4:** (a,b) High resolution XPS of Ti2p and P2p for pristine  $\text{Ti}_3\text{C}_2\text{T}_x$  and (c,d) high resolution XPS of Ti2p and P2p for P- $\text{Ti}_3\text{C}_2\text{-An-PA@1:10}$ .



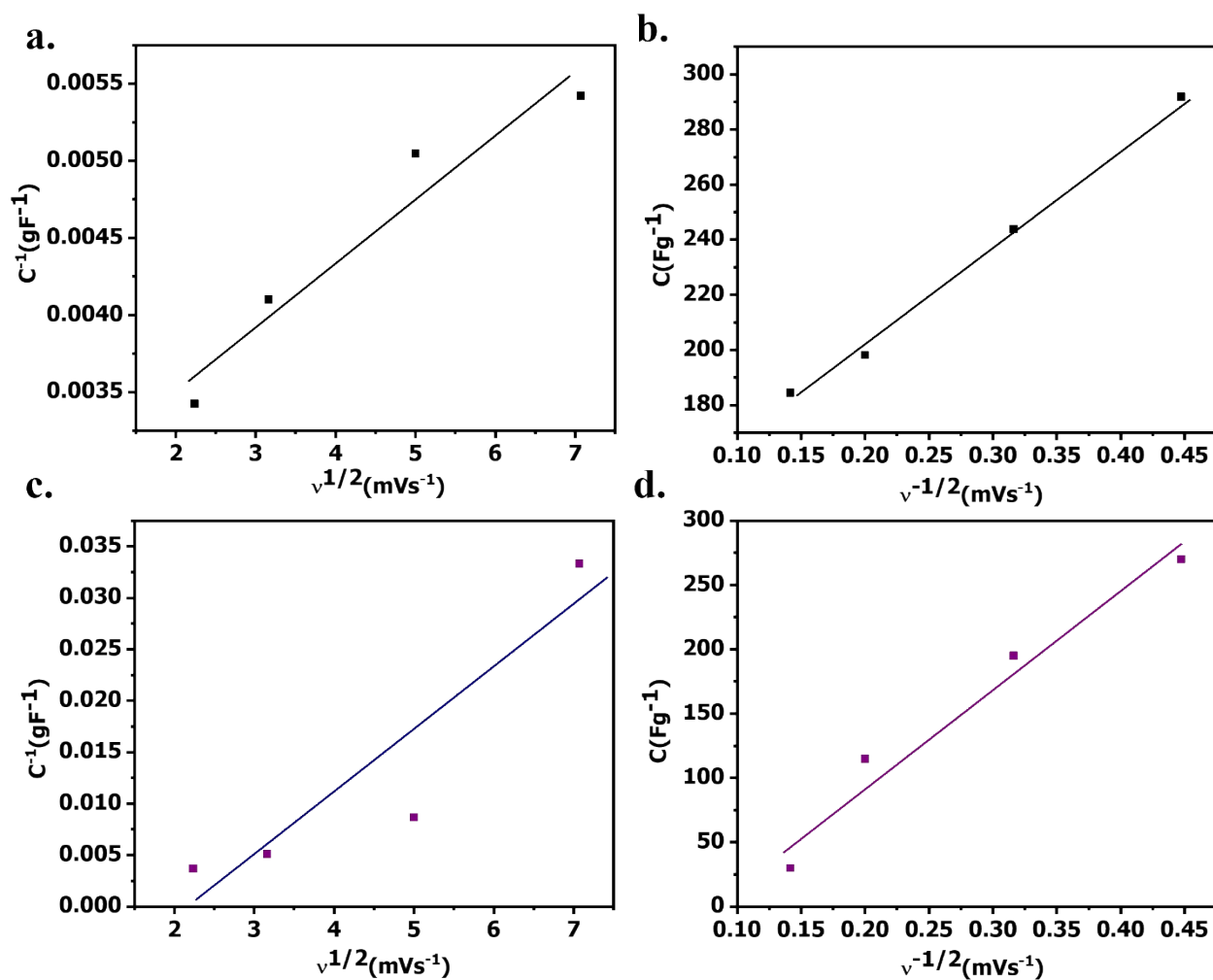
**Figure S5:** SEM images of (a) P-Ti<sub>3</sub>C<sub>2</sub>-An-PA @1:10 prepared at low temperature of 250 °C, (b) P-Ti<sub>3</sub>C<sub>2</sub>-An-PHA@1:10 and (c) P-Ti<sub>3</sub>C<sub>2</sub>-An-SDP@1:10 prepared at 900 °C; (d) EDS spectra of (i) pristine Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> and (ii) P-Ti<sub>3</sub>C<sub>2</sub>-MW-PA@1:10; (e) EDS spectra of (i) P-Ti<sub>3</sub>C<sub>2</sub>-MW-SDP@1:10 and (ii) P-Ti<sub>3</sub>C<sub>2</sub>-MW-PHA@1:10; (f) TEM image for P-Ti<sub>3</sub>C<sub>2</sub>-An-PA@1:10.



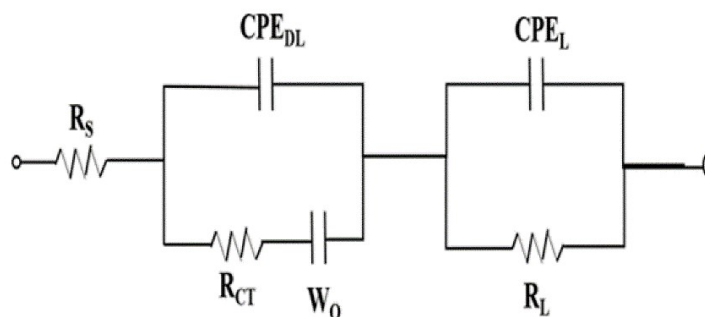
**Figure S6:** (a) N<sub>2</sub> adsorption/desorption isotherm of Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, P-Ti<sub>3</sub>C<sub>2</sub>-An-PA@1:10 and different ratios of P-Ti<sub>3</sub>C<sub>2</sub>-MW-PA (solid circle denotes adsorption and empty circle denotes desorption); (b) BJH pore distribution plot of Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, P-Ti<sub>3</sub>C<sub>2</sub>-An-PA@1:10 and P-Ti<sub>3</sub>C<sub>2</sub>-MW-PA@1:10.



**Figure S7:** (a) SEM image of flexible CF where inset represents its optical appearance and flexibility; (b) CV of bare CF at 5 mV/s; (c,d) CV of P-Ti<sub>3</sub>C<sub>2</sub>-MW-PA@1:10 in different potential window; (e) CV of pristine Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> at 25 mVs<sup>-1</sup>; (f) CV of P-Ti<sub>3</sub>C<sub>2</sub>-MW-PA@1:10 in different scan rate from 50-650 mVs<sup>-1</sup>; (g) CV of P-Ti<sub>3</sub>C<sub>2</sub>-An-PA@1:10 at (i) 5 mVs<sup>-1</sup>, (ii) 10 mVs<sup>-1</sup>, (iii) 25 mVs<sup>-1</sup> and (iv) 50 mVs<sup>-1</sup>; (h) GCD of P-Ti<sub>3</sub>C<sub>2</sub>-MW-PA@1:10 at different current densities.



**Figure S8:** Trasatti's method for (a,b) Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> and (c,d) P-Ti<sub>3</sub>C<sub>2</sub>-An-PA@1:10 (a) inverse capacitance as a function of square root of scan rate; (b) capacitance as a function of inverse square root of scan rate



**Figure S9:** Equivalent electrical circuit corresponding to EIS.

### 3. Supplementary Table

Table S1. Optimization of Conventional annealing for the synthesis of P-Ti<sub>3</sub>C<sub>2</sub>

Parent MXene	Doping source	Ti <sub>3</sub> C <sub>2</sub> :doping source	Variation in annealing temperature and time	Observation
Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub>	PA	1:1	250 °C, 1 hrs.	Phosphatization (formation of phosphate phases) started.
Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub>	PA	1:1	400 °C, 1 hrs.	Phosphatization dominates. And produces compact phosphates.
Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub>	PA	1:1	900 °C, 1 hrs.	
Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub>	PA	1:1	900 °C, 4 hrs.	
Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub>	PA	1:2	900 °C, 1 hrs.	
Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub>	PA	1:5	900 °C, 1 hrs.	
Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub>	PA	1:10	900 °C, 1 hrs.	
Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub>	PHA	1:10	250 °C, 1 hrs.	
Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub>	PHA	1:10	900 °C, 1 hrs.	
Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub>	SDP	1:10	250 °C, 1 hrs.	
Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub>	SDP	1:10	900 °C, 1 hrs.	

Table S2: Comparison of the doping percentages obtained from EDS and XPS of the various doped samples

Doped samples	Doping percentage		
	EDS		XPS
	wt%	at%	at%
P-Ti <sub>3</sub> C <sub>2</sub> -MW-PA@1:15	3.57	3.58	3.75



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P-Ti <sub>3</sub> C <sub>2</sub> -MW-PA@1:10	3.80	3.78	3.77
P-Ti <sub>3</sub> C <sub>2</sub> -MW-PA@1:5	2.79	2.77	2.53
P-Ti <sub>3</sub> C <sub>2</sub> -MW-PA@1:2	1.37	1.35	1.47
P-Ti <sub>3</sub> C <sub>2</sub> -MW-PA@1:1	1.28	1.07	0.91
P-Ti <sub>3</sub> C <sub>2</sub> -MW-SDP@1:10	1.00	1.09	1.02
P-Ti <sub>3</sub> C <sub>2</sub> -MW-PHA@1:10	1.40	1.43	1.37

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