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Polymer-MXene Composite Films formed by MXene-facilitated Electrochemical Polymerization for Flexible Solid-State Microsupercapacitors

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Abstract:

Materials with tailored properties are crucial for high performance electronics applications. Hybrid materials composed of inorganic and organic components can possess unique merits for broad application by synergy between the advantages the respective material type offers. Here we demonstrate a novel electrochemical polymerization (EP) enabled by a 2D transition metal carbide MXene for obtaining conjugated polymer-MXene composite films deposited on conducting

substrates without using traditional electrolytes, indispensable compounds for commonly electrochemical polymerization. The universality of the process provides a novel approach for EP allowing fast facile process for obtaining different new polymer/MXene composites with controlled thickness and micro-pattern. Furthermore, high performance microsupercapacitors and asymmetric microsupercapacitors are realized based on the excellent composites benefiting from higher areal capacitance, better rate capabilities and lower contact resistance than conventional electropolymerized polymers. The AMSCs exhibit a maximum areal capacitance of 69.5 mF cm^{-2} , an ultrahigh volumetric energy density ($250.1 \text{ mWh cm}^{-3}$) at 1.6 V, and excellent cycling stability up to 10000 cycles. The excellent electrochemical properties of the composite polymerized with MXene suggest a great potential of the method for various energy storage applications.

1. Introduction

Conductive polymers are recognized as a class of organic materials with unique advantages over inorganic solids, including low cost, easy processing, compatibility and tunable intrinsic properties (electronic, optical, conductivity and stability) [1-3], which make them good candidates in a wide range of application areas, such as smart windows [4], thermoelectrics [5], biosensors [6], corrosion protection [7], light-emitting diodes [8] and energy storage devices [9-11]. In recent years, many different synthetic methods for conductive polymers under mild conditions have been developed, which vastly extends the possibility to advance the fabrication process for energy storage devices [12-15]. In situ electrochemical polymerization (EP) shows unique advantages as the coupling reaction occurs in the electrolyte solution and the conductive polymer film is deposited directly on the destination electrode in one step [16-20]. The growth rate and thickness of the polymer film can be easily modulated by controlling the applied potential (or current density) and the total amount of charge passed through the cell, respectively [21]. The electrolyte

solution of EP generally contains three components: solvent, supporting electrolyte, and monomer [22]. However, the supporting electrolyte is an indispensable part that plays a vital role in electrochemical polymerization process. During the EP process, electrolyte ions will act as counter ions trace doped into the polymer film, which then obtain the organically conductive polymer with excellent performance and variable conductivity. At present, it is impossible to obtain an organic-inorganic composite film in one-step by the EP method which will severely limits the application of EP for composite films despite the inherent advantages.

MXenes, discovered in 2011, is a comparatively new class of 2D transition metal carbides, carbonitrides and nitrides [23]. They are produced by etching the ‘A’ layers from their ternary carbides precursors, so called MAX phases [24], where M is a transition metal, A is an A-group element such as Al, Ga or Si, and X is C and/or N [25-26]. The most studied MXene to date is $\text{Ti}_3\text{C}_2\text{T}_x$ (in short Ti_3C_2), where T_x represents surface terminations, typically O, OH and/or F [27-28]. Most recently, a new type of MAX phase, *i*-MAX, was discovered, realizing a MXene with in-plane vacancy ordering [29-30]. Apart from exhibiting a high conductivity, the first vacancy MXene, $\text{Mo}_{1.33}\text{C}$, has shown a high potential for supercapacitor applications [30-31]. Recently, using spontaneous electron transfer between MXene and organic monomer to promote the polymerization of organic monomers and form a composite film [32-33] and preparation of composite films by physical mixing of MXene and a conducting polymer [31] have achieved great success. However, these methods take a long time and cannot directly result in a patterned composite film in one step, which then had to be obtained by vacuum filtration. In a colloidal solution, typically negatively charged MXene [32-34] is very similar to electrolyte ions. If MXene is introduced into the EP process, which can act as counter ions by self-assemble with positively charged conductive polymer chain to form a molecular-level contact MXene-doped conductive

polymer film in one step with high efficiency on the electrode surface. The MXene-doped conductive polymer could potentially provide an electrode architecture with improved performance for energy storage devices.

Herein, we demonstrate a novel *in situ* electrochemical polymerization process of 2D MXene-doped conductive polymer films enabled by MXene without use of conventional electrolytes. During the EP process, the colloidal solution of MXene not only provides a highly conductive solvent, but also simultaneously self-assembles into the polymer film during the polymerization process with high doping content compared to conventional electrolytes to form a molecular-level conjugated polymer-MXene composite films (Figure 1A). Furthermore, high performance solid state microsupercapacitors (MSCs) based on the composite films are realized, which exhibit excellent rate performance, great cycling stability, and ultrahigh energy density. Moreover, in order to further increase the cell voltage and energy density, asymmetric microsupercapacitors (AMSCs) are constructed based on the *in situ* EP composite films and MnO_2 , achieving a high energy density of $250.1 \text{ mWh cm}^{-3}$ and power density of 32.9 W cm^{-3} at 1.6 V (larger than that of commercial batteries for powering low power consumption electronics). In addition, the AMSCs show excellent cycle stability up to 10000 cycles.

2. Experimental Section

2.1 Synthesis of the $\text{Mo}_{1.33}\text{C}$ MXene

$\text{Mo}_{1.33}\text{C}$ was synthesized by etching $(\text{Mo}_{2/3}\text{Sc}_{1/3})_2\text{AlC}$ *i*-MAX phase with HF as previously reported [30]. Briefly, one gram of the $(\text{Mo}_{2/3}\text{Sc}_{1/3})_2\text{AlC}$ *i*-MAX phase powder was added to 20 ml 48% HF, stirring for 24 h at room temperature. After the reaction, the product was washed with deionized water. After washing, multilayer MXene was delaminated into single/few layer MXene by intercalating with TBAOH. 10 mL 40% TBAOH water solution was added to the multilayer

MXene, which was shaken for manually for 5 min. Extra TBAOH was removed by centrifuging at 5000 r.p.m for 5 min and by (three times) carefully rinsing with water. Then, water was added to the intercalated powder and the mixture shaken for 5min, for delamination into single- or few-layered MXene. Finally, homogeneous delaminated $\text{Mo}_{1.33}\text{C}$ MXene was obtained by centrifuging for 30 min at 3500 r.p.m.

2.2 Synthesis of the $\text{Ti}_3\text{C}_2\text{T}_x$ MXene

$\text{Ti}_3\text{C}_2\text{T}_x$ was synthesized by etching Ti_3AlC_2 MAX phase with LiF/HCl as previously reported [56]. Briefly, LiF (1 g) and HCl (20 mL, 9 M) were mixed by stirring in a Teflon vessel. Then, Ti_3AlC_2 powder (1 g) was slowly added into the mixture and were kept for 24 h at 35 °C under stirring. After the reaction, the product was repeatedly washed with deionized water and centrifuged at 3500 rpm for 5 min. Finally, the homogeneous delaminated $\text{Ti}_3\text{C}_2\text{T}_x$ supernatant was obtained by sonicating under Ar flow and followed by centrifugation for 1 h at 3500 rpm.

2.3 Fabrication of electrochemical polymerization films on patterned substrate

First, the patterned conductive substrate was made by photolithography. After cleaning with acetone, ethanol, and deionized water, the patterned conductive substrate was immersed in different forms of mixed solution. The electrochemical polymerization was then carried out in a three-electrode configuration, where the platinum sheet and Ag/AgCl in 1 M KCl serve as the counter electrode and reference electrode, respectively. The E-M was obtained in 20 ml aqueous solution containing 2 mg $\text{Mo}_{1.33}\text{C}$ and 20 μl EDOT monomer under constant voltage of 1.1 V and keep for 30 min. For Py-M, in 20 ml aqueous solution containing 2 mg $\text{Mo}_{1.33}\text{C}$ and 20 μl Pyrrole monomer under constant voltage of 1.0 V for 30 min. For E-T and Py-T, the same conditions were used, only replacing $\text{Mo}_{1.33}\text{C}$ with $\text{Ti}_3\text{C}_2\text{T}_x$. For comparison, the PEDOT was synthesized by using an electrolyte of 0.1 M Na_2SO_4 under constant voltage of 1.1 V for 30 min. The PPy was

synthesized by using the electrolyte of 0.1 M SDBS under constant voltage of 0.8 V for 100 s. The MnO_2 was grown in an aqueous solution containing 0.2 M $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and 0.2 M Na_2SO_4 using constant voltage of 1.0 V. After electrochemical polymerization, the as-fabricated films were rinsed in deionized water several times.

2.4 Fabrication of the Flexible Solid-State AMSCs

AMSCs were fabricated through the assembly of an E-M film and a MnO_2 film by selective electrodeposition with a solid-state PVA/LiCl electrolyte. First, 1 g LiCl was mixed with 10 mL of deionized water, and 1 g of PVA was added. The whole mixture was stirred under 85 °C until the mixture becomes clear. Then, the solution was kept at 85 °C without stirring. Second, the gel electrolyte was carefully casted on the interdigital pattern area and left in air for 1 h at room temperature to evaporate excess water.

2.5 Materials- and electrochemical characterization

The electrochemical tests are performed using a VSP potentiostat (Bio-Logic, France). The impedance measurements are performed with a 5 mV amplitude in a frequency range from 100 mHz to 100 kHz at open-circuit potential. The morphology and microstructure of the different electrodes were investigated by means of field emission scanning electron microscopy (LEO 1550 Gemini) equipped with energy dispersive spectroscopy (EDS). XPS measurements were performed using monochromatic Al-K α (1,486.6 eV) radiation in a Kratos AXIS Ultra DLD system and a Scienta SES200 system. Transmission electron microscopy was performed in the Linköping double corrected FEI Titan³ 60-300, operated at 300 kV. The samples for TEM were prepared by dispersion of fine particles onto Holey-Carbon TEM grids.

3. Results and Discussion

3.1 Polymer-MXene composite films formed by MXene-facilitated electrochemical polymerization

In this work, to demonstrate the electrochemical polymerization of organic monomers enabled by 2D MXene without use of conventional electrolytes, the Mo_{1.33}C MXene was mixed with EDOT in an aqueous solution. The electrochemical behavior of the EDOT and Mo_{1.33}C MXene mixture (E-M) was investigated by cyclic voltammetry (CV) as shown in Figure 1B. From the CV in the potential sweep between -0.1 and 1.0 V, two broad redox peaks were observed which are similar to those of EDOT in Na₂SO₄ electrolyte solution (E-N) (Figure S1). In the successive cycles the peak current increased, indicating coupling between the EDOT radical cations and the growth of the film on the electrode [13,35,36]. We cannot, however, form a polymer film in EDOT aqueous solution without MXene/conventional electrolyte (Figure S1B). Interestingly, EDOT with the Mo_{1.33}C MXene can be oxidized at relatively lower potentials ($E_{\text{onset}} = 0.76 \text{ V vs. Ag/AgCl}$) compared to the EDOT with Na₂SO₄ electrolyte ($E_{\text{onset}} = 0.89 \text{ V vs. Ag/AgCl}$). This is due to the anomalous surface charges and edge defects of MXenes. In addition, we found a thicker PEDOT EP film could be more easily prepared in MXene solution than in Na₂SO₄ electrolyte. This indicates that Mo_{1.33}C MXene can more effectively facilitate the polymerization of EDOT.

To demonstrate the universality of the MXene-facilitated electrochemical polymerization, we investigated Mo_{1.33}C MXene with Pyrrole (P-M) and Ti₃C₂ MXene with EDOT (E-T) or pyrrole (P-T). In all cases, the composite films were successfully deposited on the electrode. The CV curves for Mo_{1.33}C MXene with Pyrrole and Ti₃C₂ MXene with EDOT or pyrrole are shown in Figure S1, together with PEDOT prepared in Na₂SO₄ electrolyte and PPy prepared in SDBS electrolyte (P-S) for comparison. In addition, the zeta potential of the MXene solution was not significantly changed by the addition of organic monomers, which means that the mixed colloidal solution can maintain a good stability (Table S1 and Figure S2).

Conventional electrolytes are very important components for providing an electrically conductive environment and doped into the polymer film as counter ions during electrochemical polymerization. Generally, electrochemical polymerization cannot take place without the participation of electrolytes. Differently with common electrochemical polymerization, the method we demonstrate here could be schematically illustrated in Figure 1C. First, negatively charged MXene (Ti_3C_2 , $\text{Mo}_{1.33}\text{C}$) provided an electrolyte-like conductive environment in a stable dispersion mixed solution with organic monomers (Pyrrole, EDOT). Then, in the process of electrochemical polymerization, the organic monomers would lose electrons to an electrode form cationic radicals, which couple to each other and form polymer chains. Meanwhile, the negatively charged MXene would moves toward the working electrode driven by an electric field and doped into the polymer chains with a high content to form a complex film in the cationic radical coupling process. The composites with a conductive polymer as a host penetrated by MXene not only possess higher conductivity than the pristine polymer film (Figure S3,4), but also greatly improve the electrochemical performance of the conductive polymer film as shown in Figure S5-11.

Scanning electron microscopy (SEM) images of the four films (E-N, E-M, P-S, P-M) are shown in Figure 2 and Figure S12-14. The SEM micrographs show the change in morphology corresponding to different solution components. The PEDOT prepared in Na_2SO_4 electrolyte was uniformly coated onto the substrate with a random nanoflake morphology (Figure S12A). The electrodeposited PEDOT with $\text{Mo}_{1.33}\text{C}$ shows a nanosphere-shaped architecture (Figure 2A). For pyrrole, the morphology changed from a closely packed nanorod structure (Figure S12B) prepared from SDBS electrolyte to a nanosphere-shaped structure (Figure 2B) prepared from $\text{Mo}_{1.33}\text{C}$. The 3D structure of the E-M and P-M electrodes were further analyzed using cross-sectional SEM (Figure 2C, D). Both E-M and P-M shows a 3D porous structure composed of nanospheres (Figure

S15). To further investigate the structure of the polymer-MXene composite, aberration corrected transmission electron microscopy (TEM) was applied. Figure 2E, F shows overview (inset) and high-resolution images of the E-M and P-M, respectively. The overview of the E-M structure identifies a particle with rounded features, similar to the particles observed by SEM. The corresponding high-resolution image of the particle edge shows bundles of parallel lines running along the outline of the particle edge. Each line can be interpreted as a single sheet of MXene (thickness about 1.1 nm, Figure S16). These lines form loops, which suggests that few layer thick MXene form closed, approximately spherical shells that enclose the PEDOT (as schematic in Figure 1A). Correspondingly, the polymer-MXene composite overview shows a structure that locally forms spherical particles, though the majority of the structure appears as sheets. The high-resolution image additionally identifies few-layer MXene closed loops. However, the structure is typically flatter and with smaller dimensions compared to the MXene/PEDOT shells. The MXene shells in the vicinity of the local spherical particles are composed of thicker (multiple) MXene layers.

The X-ray photoelectron spectroscopy (XPS) data shown in Figure 3A-C (see also Figure S17) confirm the incorporation of $\text{Mo}_{1.33}\text{C}$ MXene into the polymer films during the electrochemical polymerization. In addition, energy dispersive X-ray spectroscopy (EDX) elemental mapping was used to study the distribution of polymer-MXene (Figure 3D,E). EDX mapping of Mo confirms a homogeneous distribution of $\text{Mo}_{1.33}\text{C}$ MXene throughout the 3D polymer framework (see also Figure S18). The corresponding polymers of EDOT and Pyrrole prepared in MXene solution were confirmed by Fourier Transform Infrared Spectrometer (FT-IR) and absorption spectra (Figure S19 and 20). Based on the above results, we conclude that we have successfully obtained a

polymer-MXene composite with a 3D porous structure by in situ electrodeposition in a solution of organic monomers (EDOT, Pyrrole) and MXenes.

3.2 Electrochemical performance of polymer-MXene composite films

For energy storage, nanosphere structures with plenty of pores will be beneficial for the infiltration and diffusion of the electrolyte, thus likely improving the capacitance. In addition, the nanosphere structure will help to resolve potential stagnant ion transport, which is one of the main challenges for pseudocapacitive materials [37-39]. Moreover, the dopant of MXene will further improve the conductivity and capacitance of the polymers (Figure S3,4). Steps for fabricating in-plane solid state MSCs by in situ EP on a predesigned patterned substrate are shown in Figure S5. First, a piece of ITO was selectively etched to form a pattern of predesigned interdigitated electrodes by photolithography. Note that this method can be applied to any conductive substrate to prepare a variety of patterned electrodes. Subsequently, polymer-MXene MSCs were fabricated through a facile *in situ* electrochemical polymerization process. The electrochemical performance of the E-M and P-M MSCs were investigated in a two-electrode configuration. MSCs based on E-N and P-S were examined for comparison. Cyclic voltammograms (CVs), at a scan rate of 50 mV s⁻¹, of the four polymer-based MSCs are shown in Figure 4 A and B. Typical rectangle-like CV curves were obtained for all of them. The CV curves of all MSCs devices at different scan rates are shown in Figure S6-11. The electrode material prepared in MXenes solution have much higher areal capacitance compared to the polymer prepared in conventional electrolytes. This could be attributed to the high-capacitance MXene, as well as the 3D porous structure that increase the accessibility of the active electrode materials, thus increasing the capacitance. Typical CV curves of the E-M MSCs at different scan rates are shown in Figure 4C, exhibiting a good rectangular shapes up to 200 mV s⁻¹, which indicates a low resistance and good reversibility. Isosceles triangle

shaped charge–discharge curves indicate good reversibility of the E-M MSCs at different current densities, as shown in Figure 4D, which is in good agreement with the CV curves. In addition, the E-M MSCs shows better coulombic efficiency than E-N MSCs.

The areal capacitances at different current density for the four MSCs are shown in Figure 4E. The E-M MSCs exhibits an areal capacitance of 47.4 mF cm^{-2} at 0.2 mA cm^{-2} , maintaining 44.1 mF cm^{-2} at 4 mA cm^{-2} , with only a 7% decrease. For E-T MSCs (Figure S10), areal capacitance values as high as 40.0 mF cm^{-2} at a current density of 0.2 mA cm^{-2} are observed, with a good 89% capacitance retention at a high current density of 4 mA cm^{-2} . In contrast, the E-N MSCs shows only a 4.1 mF cm^{-2} capacitance at $20 \text{ } \mu\text{A cm}^{-2}$, which decreases to 0.48 mF cm^{-2} at 0.2 mA cm^{-2} , with only a 12% retention. The increased capacitance and rate performance are also reflected in the pyrrole-based MSCs. The increased capacitance and excellent rate-capabilities based on the polymer-MXene MSCs are possibly attributed to the superior electrical conductivity of the polymer-MXene composite films and fast ion transport in the 3D nanopores structure formed from *in situ* EP in mixtures of organic monomers and MXene. During the electrochemical polymerization process, the MXene self-assembles into a nanosphere structure that can effectively promote the electron transfer between the polymer and the MXene. The high-conductivity MXene shell formed on the outer periphery of interconnected nanosphere structures further promotes electron transport inside the film (as inset of Figure 1A upper right), realizing high capacitance and excellent rate-capabilities, in stark contrast to the insulating PSS shells of the prototypical PEDOT:PSS conducting polymer films [40-41]. The electrochemical capacitive behavior of the four MSCs was further investigated by electrochemical impedance spectroscopy (EIS), as shown in Figure 4F. It can be seen that the complex plane plots of E-M MSCs and P-M MSCs show a larger slope, close to 90° , compared to E-N and P-S MSCs at low frequency, which indicates fast

ion diffusion. At high frequency, see inset in Figure 4F, E-M shows a smaller charge-transport semicircle than that of E-N MSC. This is consistent with the result of in-situ conductivity measurements, where the conductivity of the composite film (E-M and P-M) is found to be higher than that of a pristine polymer film (E-N and P-S) (Figure S3).

3.3 Electrochemical performance of asymmetric microsupercapacitor

Among the various transition metal oxide materials, MnO_2 has been used widely as an energy storage electrode material owing to its remarkable theoretical specific capacitance ($\sim 1375 \text{ F g}^{-1}$), and being environmentally friendly, earth-abundant, and of low cost [38,42,43]. Considering the high pseudocapacitance of the MnO_2 electrode and the excellent rate-capabilities of the E-M electrode, a flexible solid-state asymmetric microsupercapacitor (AMSC) device was assembled by *in situ* EP using E-M as the negative electrode and MnO_2 as the positive electrode, as schematically illustrated in Figure S5. Charge balance between the two electrodes was achieved by controlling the deposition time of MnO_2 at the positive electrode and the thickness of the E-M film at the negative electrode (Figure 5A). Finally, an operating potential window of up to 1.6 V was achieved for the AMSCs, which should yield a high energy density, and is the widest voltage window reported to date for MXene-based supercapacitors [44]. In addition, the cell voltage of this AMSCs device can be tuned from 1.0 to 2.0 V, as shown in Figure 5B. The performance of the all-solid-state AMSCs was investigated through CV curves at various scan rates under 1.6 V. As shown in Figure 5C, the shape of the CV curves remains pseudorectangular even at very high scan rate of 1000 mV s^{-1} , which indicates a low resistance and fast charge-discharge properties. Galvanostatic charge/discharge curves of the full device with different current density between 0.0 and 1.6 V are shown in Figure 5D. The linear slope and triangular shape indicate good reversibility of the charge/discharge process, which is consistent with the CV curves. The current density

dependence of the capacitance of the AMSCs is shown in Figure 5E. A high areal capacitance of 69.5 mF cm^{-2} (636.9 F cm^{-3}) can be achieved at 0.5 mA cm^{-2} . Similar to the results of E-M MSCs, the AMSCs device also demonstrates a remarkable rate capability with capacitance retention of 61% as the current density increases from 0.5 to 4 mA cm^{-2} . Long cycle life is another important feature of commercially viable supercapacitors. Therefore, the cycling stability of the AMSCs was investigated by galvanostatic charge/discharge tests at a current of 1.5 mA cm^{-2} (Figure 5F). Indeed, the asymmetric supercapacitor is very stable as it maintains over 92% of its original capacity after 10000 charge/discharge cycles. The EIS of the AMSCs demonstrates a slight increase of the internal resistance and the microscopic appearance of the electrode materials has hardly changed after 10000 cycles (Figure S25,26).

In addition, the AMSCs shows exceptional electrochemical stability under different bending angles. No significant deviation of the CV curves was observed when the bending angle changed from 0° to 180° , displaying excellent capacitance stability at different bending curvatures (Figure 6A). To meet the high voltage or capacitance requirements, supercapacitors are often put into a bank of cells connected together in series or in parallel. CV and GCD measurement (Figure 6B, C) shows that the discharge time of AMSCs connected in parallel is twice as long as that of a single one within the same voltage window of 1.6 V . Meanwhile, the output voltage of two devices connected in series is doubled. These results suggest that the fabricated devices have good reproducibility and can be well managed for practical power applications. The achieved high specific capacitance, outstanding rate capability, and tunable voltage window in AMSCs will pave the way for polymer-MXene based supercapacitors for high-level energy and power applications. The volumetric energy and power densities of different types of MSCs, as well as a comparison with previously reported MSCs devices, are plotted in the Ragone plot as shown in Figure 6D. For

AMSCs, a maximum energy density of 250.1 mWh cm⁻³ can be obtained at a specific power density of 1.87 W cm⁻³. Importantly, the energy density remains 138.4 mWh cm⁻³ at a high power density of 32.9 W cm⁻³. The good retention of the high energy density also occurs in the polymer-MXene based MSCs. The E-M MSCs exhibits energy density values in the range of 18.7-20 mWh cm⁻³ with a corresponding power density in the range of 0.4-8.3 W cm⁻³. For P-M, the energy density changes from 5.9 to 11.6 mWh cm⁻³ with a power density in the range of 0.3-6.8 W cm⁻³. These values are better than MSCs based on other materials, including carbon materials (0.15-9 mWh cm⁻³) [45-49], transition metal oxides/hydroxides/carbides (1-5 mWh cm⁻³) [50-55] and conducting polymers (5-11 mWh cm⁻³) [56-57] manufactured through various technologies.

4. Conclusions

In summary, we developed a simple, green, and scalable method for synthesizing high quality conjugated polymer-MXene composites by in situ EP from the mixture of organic monomers and MXene without additional electrolyte. Patterned composite films with microstructures can be achieved on any conductive substrates by one step in-situ polymerization and the film thickness can be controlled by manipulating the amount of applied current on the electrode. The MSCs based on the unique interconnected 3D porous structure composed of polymer-MXene composite nanospheres realize excellent pseudocapacitance (47.4 mF cm⁻²) and ultrahigh energy capability (20.05 mWh cm⁻³). The polymer-MXene composite structure also improves the stability and rate performance of the MSCs significantly. Furthermore, by constructing an AMSCs with MnO₂, the operating voltage increases up to 1.6 V, the areal capacitance achieved 69.5 mF cm⁻² and energy density up to 250.1 mWh cm⁻³. Our study opens a new avenue for convenient fabrication of polymer-MXene composite materials by electrochemical polymerization with greatly enhanced electrochemical performance, unfolding exciting opportunities in a wide range of mobile power

supply applications including micro-portable electronics, electromechanical systems, and nanorobots.

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Figures and captions:

Figure 1. Schematic illustration. (a) The scheme for electrochemical polymerization of conjugated polymer-MXene composite nanospheres. (b) CV for the electrochemical polymerization of EDOT facilitated by MXene at the scan rate of 50 mV s⁻¹ (0.1 mg ml⁻¹ Mo_{1.33}C and 1 μl ml⁻¹ EDOT monomer in H₂O). (c) Schematic diagram of MXene-facilitated electrochemical polymerization mechanism.

Figure 2. Morphology of conjugated polymer-MXene complex. SEM image of (A) PEDOT prepared in $\text{Mo}_{1.33}\text{C}$ (E-M); (B) PPy prepared in $\text{Mo}_{1.33}\text{C}$ (P-M); cross-sectional SEM image of (C) E-M and (D) P-M; HRTEM image of E-M (E, inset: the overview image of E-M) and P-M (F, inset: the overview image of P-M).

Figure 3. Distribution of MXene in complex. Mo 3d XPS spectra of (A) pristine $\text{Mo}_{1.33}\text{C}$, (B) E-M and (C) P-M; EDS elemental mapping of cross-sectional (D) E-M and (E) P-M.

Figure 4. Electrochemical performance of microsupercapacitors. A) Comparison of CV curves of E-N MSCs and E-M MSCs tested under the scan rates of 50 mV s⁻¹, B) Comparison of CV curves of P-S MSCs and P-M MSCs tested under the scan rates of 50 mV s⁻¹, C) Detailed CV curves of the E-M MSCs tested under different scan rates, D) Galvanostatic charging/discharging curves of the E-M MSCs with different current densities, E) Comparison of areal capacitances of E-N, E-M, P-S and P-M at different current density, F) Nyquist plot of the device tested at the open-circuit potential within the frequency range from 10⁻¹ to 10⁵ Hz. The above inset shows the enlarged plot in the high-frequency region. The following inset show the Nyquist plot of P-S.

Figure 5. Performance of the asymmetric microsupercapacitors up to 1.6 V. (A) Comparison of CV curves collected for E-M and MnO_2 electrodes at a scan rate of 100 mV s^{-1} . (B) CV curves of the AMSCs device collected at different voltage windows. (C) Areal specific capacitance of AMSCs device at different scan rate. (D) Galvanostatic charge/discharge curves of AMSCs at different current densities. (E) Areal specific capacitance of AMSCs at different current density. (F) Long-term charge-discharge cycling performance of the AMSCs device. Inset: Changes of galvanostatic charge/discharge curves of AMSCs device before and after 10000 cycles.

Figure 6. (A) CV curves of the AMSCs device bended with different angles at 100 mV s⁻¹. Inset: Optical image of the flexible AMSCs. (B) CV curves of AMSCs devices connected in series and in parallel at a scan rate of 100 mV s⁻¹. A single device is shown for comparison. C) GCD curves of AMSCs devices connected in series and in parallel at a current density of 1 mA cm⁻². (D) Energy and power density of the MSCs devices and AMSCs device compared with previously reported devices.

TOC Graphic

Polymer-MXene Composite Films formed by MXene-facilitated Electrochemical Polymerization for Flexible Solid-State Microsupercapacitors

Keywords: MXene; electrochemical polymerization; conjugated polymer; composite film; microsupercapacitors

Supporting Information

Polymer-MXene Composite Films formed by MXene-facilitated Electrochemical Polymerization for Flexible Solid-State Microsupercapacitors

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Apparatuses. The electrochemical tests are performed using a VSP potentiostat (Bio-Logic, France). The impedance measurements are performed with a 5 mV amplitude in a frequency range from 100 mHz to 100 kHz at open-circuit potential. The morphology and microstructure of the different electrodes were investigated by means of field emission scanning electron microscopy (LEO 1550 Gemini) equipped with energy dispersive spectroscopy (EDS). XPS measurements were performed using monochromatic Al-K α (1,486.6 eV) radiation in a Kratos AXIS Ultra DLD system and a Scienta SES200 system. Transmission electron microscopy was performed in the Linköping double corrected FEI Titan³ 60-300, operated at 300 kV. The samples for TEM were prepared by dispersion of fine particles onto Holey-Carbon TEM grids. Spectroelectrochemical studies were carried out on a Cary 50 UV-vis-NIR spectrophotometer under computer control. The zeta potential were measurement by Malvern Zetasizer Nano ZS Analyzer. The samples were prepare by ultrasound to form a homogeneous dilute solution. Infrared spectra were recorded using a Bruker Vertex 70 Fourier transform infrared (FT-IR) spectrometer with samples in KBr pellets. Thermogravimetric analysis (TGA) was performed with a Pyris Diamond TG/DTA thermal analyzer (Perkin-Elmer) under a Argon stream at the heating rate of 10 K min⁻¹. AFM was used to study the thickness of Mo_{0.33}C films at ambient

conditions (room temperature in a lab) using a Veeco DI Dimension 3100 scanning probe microscope, equipped with the Nanoscope IV electronics. The measurements were performed in tapping mode using Si tips (PPPNCHR-50 from Nanosensors) with a tip radius of curvature <7 nm. Nitrogen adsorption isotherms of E-M and P-M were measured at 77 K using an ASAP 2020 instrument (Micromeritics U.S.). The total surface area was calculated with the BET method, and the pore size distribution data were calculated using the BJH and DFT methods based on the adsorption and desorption data.

Calculations. The capacitance was calculated from the galvanostatic charge/discharge curves at different current densities using the formula using the following equation:

$$C_{device} = \frac{i}{dE/dt} \quad (1)$$

where i is the current applied (in amps, A), and dE/dt is the slope of the discharge curve (in volts per second, V/s). Specific capacitances were calculated based on the area and the volume of the device stack according to the following equations:

$$C_A = \frac{C_{device}}{A} \quad (2)$$

$$C_v = \frac{C_{device}}{V} \quad (3)$$

where C_A is the areal capacitance in mF cm⁻², C_v is the volumetric capacitance in F cm⁻³. A and V refer to the area (cm²) and the volume (cm³) of the active material on both electrodes, respectively.

The energy density of each device was obtained from the formula given in Equation (4):

$$E = \frac{1000}{2 \times 3600} C_v \Delta E^2 \quad (4)$$

where E is the energy density in Wh cm^{-3} , C_v is the volumetric capacitance obtained from galvanostatic charge/discharge curves using Equation (3) in F cm^{-3} and ΔE is the operating voltage window in volts.

The power density of each device was calculated using the equation:

$$P = \frac{E}{t} \quad (5)$$

where P is the power density in W cm^{-3} and t is the discharge time in hours.

Asymmetric cells. In order to achieve optimal performance with asymmetric supercapacitors, there should be a charge balance between the positive and negative electrodes. The charge stored by each electrode depends on its volumetric capacitance ($C_{v(\text{electrode})}$), volume of the electrode (V), and the potential window in which the material operates (ΔE).

$$q = C_{v(\text{electrode})} \times V \times \Delta E \quad (6)$$

To attain the charge balance, the following condition must be satisfied

$$q_+ = q_- \quad (7)$$

$$\frac{V_+}{V_-} = \frac{C_{v(\text{electrode})-} \times \Delta E_-}{C_{v(\text{electrode})+} \times \Delta E_+} \quad (8)$$

1. Electrochemical polymerization Behavior in Different Mixture Composition

Figure S1. CV for the electrochemical polymerization of different mixture composition at the scan rate of 50 mV s⁻¹. (A) 0.1 M Na₂SO₄ and 1 μl ml⁻¹ EDOT monomer in H₂O, (B) 1 μl ml⁻¹ EDOT monomer in H₂O, (C) 0.1 M TBAOH and 1 μl ml⁻¹ EDOT monomer in H₂O, (D) 0.1 mg ml⁻¹ Ti₃C₂T_x and 1 μl ml⁻¹ EDOT monomer in H₂O, (E) 0.1 M SDBS and 1 μl ml⁻¹ Pyrrole monomer in H₂O, (F) 0.1 mg ml⁻¹ Mo_{1.33}C and 1 μl ml⁻¹ Pyrrole monomer in H₂O, (G) 0.1 mg ml⁻¹ Ti₃C₂T_x and 1 μl ml⁻¹ Pyrrole monomer in H₂O.

The electrochemical behavior of different mixture compositions was investigated by the cyclic voltammetry (CV) method as shown in Figure S1. For EDOT with an electrolyte of Na₂SO₄, the representative current growth revealing the electrochemical performance of monomers and the formation of corresponding polymers is depicted in Figure S1A. The same electrochemical polymerization behavior also appears in EDOT with MXene (Mo_{1.33}C and Ti₃C₂T_x) without electrolyte (Figure 1B and Figure S1D). In this case, we can successfully deposit EP films on the working electrode. This indicated that MXene can effectively promote the electrochemical polymerization of EDOT. To further demonstrate the function of MXene in electrochemical polymerization, the CV method was carried out for EDOT in aqueous solution without electrolyte or MXene, as shown in Figure S1B. The current is significantly reduced compared to electrolyte/MXene cases, and no obvious redox peaks or current growth follow the progress of CV. There also is no EP film observed on the working electrode. This indicates that the electrochemical polymerization of EDOT cannot be carried out in absence of an electrolyte. For Mo_{1.33}C, TBAOH was used during the intercalation. In order to exclude the impact of residual TBAOH, CV was carried out for EDOT with TBAOH, where the current growth or the EP film is not observed. We also demonstrate that polypyrrole can be obtained through EP of the monomer using MXene (Mo_{1.33}C and Ti₃C₂). The above result shows that MXene can effectively promote electrochemical polymerization, replacing conventional electrolytes.

2. Zeta potential of the Different Mixture Composition

Table S1. The Zeta potential of different sample.

Sample	M	M-E	M-P	T	T-E	T-P
Zeta Potential (mV)	-40.1	-41.5	-43.1	-42.0	-40.6	-41.2

Figure S2. Digital photographs of the (A) $\text{Mo}_{1.33}\text{C}$, (B) $\text{Mo}_{1.33}\text{C}+\text{EDOT}$, (C) $\text{Mo}_{1.33}\text{C}+\text{Pyrrole}$, (D) Ti_3C_2 , (E) $\text{Ti}_3\text{C}_2+\text{EDOT}$ and (F) $\text{Ti}_3\text{C}_2+\text{Pyrrole}$ colloids, all displaying a clear Tyndall scattering effect with laser light.

From the Table S1, the surfaces of the $\text{Mo}_{1.33}\text{C}$ and Ti_3C_2 sheets are both shown to be negatively charged with a zeta-potential of -40.1 mV and -42.0 mV , respectively. A simple mixing of the MXene and organic monomers yields a homogeneous dispersion with no observation of apparent precipitation even after storing without stirring for weeks. The zeta potential of the MXene solution did not significantly change by mixing MXene with organic monomers, suggesting that the mixed colloidal solution can maintain good stability. Figure S2 shows the optical images of the obtained dispersions with the observation of a strong Tyndall scattering effect when directing a side-incident light beam on the colloidal dispersions. Delaminated nanosheets are responsible for this phenomenon.

3. Electrical performance of sample

Figure S3. Conductance changes at different potentials for E-N, E-M, P-S, P-M, P-T and E-T.

The *in situ* conductivity measurements has been carried out using a four-terminal setup. The microelectrochemical setup consists of two working interdigitated electrodes with an applied constant bias (0.05 V) connected by the EP film channel. Ag/AgCl was used as reference electrode, while a Pt wire was used as the counter electrode and 0.1 M LiCl was electrolyte. Cyclic voltammetry measurements were performed by retaining a bias between the two working electrode of 0.05 V. A constant bias ($E = -0.05$ V) has been applied between the two working electrodes to produce a current flow in the channel, which dominates the observed voltammetric response. The recorded currents have then been divided by the applied bias, to produce a conductance (C) response as function of the applied voltage (vs Ag/AgCl). Conductivity (σ) has then been calculated as: $\sigma = C \times L/A$, where A is the cross-sectional area and L is the channel length.

Figure S4. I-V curves of E-N, E-M, E-T, P-S, P-M, and P-T.

4. Electrochemical Performance of Symmetric Microsupercapacitors.

Figure S5. Schematic procedure for the fabrication of microsupercapacitors.

Figure S6. Electrochemical performance of E-Na symmetric Microsupercapacitors. (A) areal capacitance of E-Na MSCs at different scan rate. (B) Galvanostatic charge/discharge curves of E-Na MSCs at different current densities. (C) Rate performances of E-Na MSCs at different current density. (D) Electrochemical impedance spectroscopy data of E-Na MSCs tested at the open-circuit potential within the frequency range from 10^{-1} to 10^5 Hz. (E) Long-term charge–discharge cycling performance of the E-Na MSCs device. Inset: The comparison of GCD curves before and after cycling test. (F) The comparison of EIS spectra before and after cycling test. Inset: the enlarged plot in the high frequency region.

Figure S7. Electrochemical performance of E-M symmetric Microsupercapacitors. (A) areal capacitance of E-M MSCs at different scan rate. (B) Galvanostatic charge/discharge curves of E-M MSCs at different current densities. (C) Rate performances of E-M MSCs at different current density. (D) Electrochemical impedance spectroscopy data of E-M MSCs tested at the open-circuit potential within the frequency range from 10^{-1} to 10^5 Hz. The inset shows the enlarged plot in the high frequency region. (E) Long-term charge–discharge cycling performance of the E-M MSCs device. Inset: The comparison of GCD curves before and after cycling test. (F) The comparison of EIS spectra before and after cycling test. Inset: the enlarged plot in the high frequency region.

Figure S8. Electrochemical performance of P-SDBS symmetric Microsupercapacitors. (A) Areal capacitance of P-SDBS MSCs at different scan rate. (B) Galvanostatic charge/discharge curves of P-SDBS MSCs at different current densities. (C) Rate performances of P-SDBS MSCs at different current density. (D) Electrochemical impedance spectroscopy data of P-SDBS MSCs tested at the open-circuit potential within the frequency range from 10^{-1} to 10^5 Hz. (E) Long-term charge–discharge cycling performance of the Py-SDBS MSCs device. Inset: The comparison of GCD curves before and after cycling test. (F) The comparison of EIS spectra before and after cycling test.

Figure S9. Electrochemical performance of P-M symmetric Microsupercapacitors. (A) Areal capacitance of P-M MSCs at different scan rate. (B) Galvanostatic charge/discharge curves of P-M MSCs at different current densities. (C) Rate performances of P-M MSCs at different current density. (D) Electrochemical impedance spectroscopy data of P-M MSCs tested at the open-circuit potential within the frequency range from 10^{-1} to 10^5 Hz. (E) Long-term charge–discharge cycling performance of the P-M MSCs device. Inset: The comparison of GCD curves before and after cycling test. (F) The comparison of EIS spectra before and after cycling test. Inset: the enlarged plot in the high frequency region.

Figure S10. Electrochemical performance of E-T symmetric Microsupercapacitors. (A) Areal capacitance of E-T MSCs at different scan rate. (B) Galvanostatic charge/discharge curves of E-T MSCs at different current densities. (C) Rate performances of E-T MSCs at different current density. (D) Electrochemical impedance spectroscopy data of E-T MSCs tested at the open-circuit potential within the frequency range from 10^{-1} to 10^5 Hz.

current density. (D) Electrochemical impedance spectroscopy data of E-T MSCs tested at the open-circuit potential within the frequency range from 10^{-1} to 10^5 Hz.

Figure S11. Electrochemical performance of P-T symmetric Microsupercapacitors. (A) Areal capacitance of P-T MSCs at different scan rate. (B) Galvanostatic charge/discharge curves of P-T MSCs at different current densities. (C) Rate performances of P-T MSCs at different current density. (D) Electrochemical impedance spectroscopy data of P-T MSCs tested at the open-circuit potential within the frequency range from 10^{-1} to 10^5 Hz.

5. SEM of the E-N, P-S, E-T and P-T

Figure S12. SEM image of (A) PEDOT prepared in Na_2SO_4 electrolyte (E-N), (B) PPy prepared in SDBS electrolyte (P-S).

Figure S13. (A, B) SEM image of PEDOT prepared in Ti_3C_2 (E-T) film. (C) SEM image of the cross section of E-T film.

Figure S14. (A) SEM image of PPy prepared in Ti_3C_2 (P-T) film. (C) SEM image of the cross section of P-T film.

6. Nitrogen sorption isotherm measurements

Figure S15. Nitrogen adsorption–desorption isotherm of the E-M film (A) and P-M film (C). DFT pore size distribution of the E-M film (B) and P-M film (D).

We conducted Nitrogen sorption isotherm measurements to investigate the porosity of the E-M and P-M films and observed that these films were highly porous. The Brunauer-Emmett-Teller (BET) surface area of E-M film was evaluated to be as high as $930 \text{ m}^2 \text{ g}^{-1}$. The pore-size distribution profile of E-M film revealed that the main pore size was 1.3 nm and the pore size of the distribution was about 5–40 nm (Figure S15B). The P-M film exhibited a BET surface area of $860 \text{ m}^2 \text{ g}^{-1}$. Using the nonlocal density function theory method, the pore size distribution of the P-M film was calculated to be about 3–200 nm (Figure S15D) based on the adsorption and desorption data. These pores may form from the gap between the nanospheres of EP films, and corresponding to the free volume in polymer physics that makes small molecules such as gas, the anions diffuse freely in the region that is very deep from the polymer surface. However, for traditional conductive polymers, there are some π – π aggregates in the polymer chains, preventing

interaction between electrolyte anions with polymer segments inside the aggregate, which yields low electrochemical performance. The introduction of MXene to the skeletal structure of conductive polymers will increase molecular spacing and facilitate the movement of the dopant ions into every electroactive site. Finally, the electrochemical properties of the composite film could be enhanced. This indicated that the microporous structure with the increased distance between the molecules would be advantageous for electrolyte ion migration, facilitating the doping and dedoping process, resulting in improved capacitance performance.

7. AFM and TEM of single layer

From the section TEM image of multilayer $\text{Mo}_{1.33}\text{C}$ (Figure S16A), we can deduce that the lattice spacing of each layer is approximately about 1.1 nm, consistent with the thickness of the single layer MXene obtained in the AFM measurements (Figure S16B).

Figure S16. (A) The side view TEM image of multilayer $\text{Mo}_{1.33}\text{C}$ MXene flake, (B) AFM of single layer $\text{Mo}_{1.33}\text{C}$ MXene.

8. High-resolution core-level XPS

Figure S17. High-resolution XPS spectra of (A) Mo_{1.33}C, (B) Ti₃C₂, (C) E-Na, (D) P-SDBS, (E) E-M, (F) E-T, (G) Py-M, (H) Py-T.

From the Mo 3d, Ti 2p regions, peaks for MXene are identified, labeled in the figures as C-Mo-T_x in Mo 3d (Mo_{1.33}CT_x) and (OH,O)-Ti-C, (OH,O)-Ti²⁺-C, (OH,O)-Ti³⁺-C and F-Ti-C for Ti 2p region (Ti₃C₂T_x) after polymerization the peaks identified for MXene are reduced and the peaks identified for oxides are increased this is more apparent in the Mo_{1.33}CT_x case^{3,4}.

The spectra measured for the MXenes with polymers show features from the MXene (Mo 3d and Ti 2p) as well as the C 1s regions also the polymer is shown from the S 2p region in the PEDOT and N 1s region in the polypyrrole. It is confirm the incorporation of MXenes into the polymer films during the electrochemical polymerization process.

9. EDS of the sample

Figure S18. The surface EDS elemental mapping images of (A) E-M (C, O, S, Mo) and (B) P-M (C, N, Mo).

10. UV and FT-IR of sample

Figure S19. The FT-IR spectra of (A) EDOT and corresponding polymer, (B) pyrrole and corresponding polymer.

Figure S20. Absorption spectra of (A) EDOT and corresponding polymer, (B) pyrrole and corresponding polymer.

11. The content of composite film component

Figure S21. Thermogravimetric analysis curves of Mo_{0.33}C, PEDOT, PPy, E-M and P-M films under an Argon atmosphere.

Figure S22. EDX spectrum of E-M (A) and P-M (B).

In order to investigate the content of MXene and polymer in the polymer/MXene composite, we conducted thermogravimetric analysis (TG) and EDX experiments. For the composite films, the MXene is only doped into polymer during the electrochemical polymerization of monomer, and there is no chemical reaction with polymer. Therefore, we assume that in the composite film, the thermal weight loss process of MXene and polymer does not affect each other. From the TG curve, we can calculate that the content of MXene in the E-M and P-M composite film is 24.6% and 30.6%, respectively. In addition, from the results of EDX of E-M and P-M, the content of MXene in the E-M and P-M composite film is 23.5% and 32%, in consistent with the results of TG.

12. Electrochemical Performance of MnO₂-based Microsupercapacitors

Figure S23. Electrochemical performance of MnO₂ symmetric Microsupercapacitors A) detailed CV curves of the MnO₂ MSCs tested under different scan rates, B) the galvanostatic charging/discharging curves of the MnO₂ MSCs with different current densities, C) The areal capacitances of MnO₂ MSCs at different current density, D) Nyquist plot of the device tested at the open-circuit potential within the frequency range from 10⁻¹ to 10⁵ Hz. The above inset shows the enlarged plot in the high-frequency region.

The electrochemical performance of the MnO₂ MSCs were investigated in a two-electrode configuration. Typical CV curves of the MnO₂ MSCs at different scan rates are shown in Figure S23A, exhibiting a good rectangular shape up to 500 mV s⁻¹, which indicates a low resistance and good reversibility. Isosceles triangle shaped charge-discharge curves indicate good reversibility of the MnO₂ MSCs at different current densities, as shown in Figure S23B, which is in good agreement with the CV curves. The areal capacitances at different current density for MnO₂ MSCs are shown in Figure S23C. The MnO₂ MSCs exhibits an areal capacitance of 39.1 mF cm⁻² at 0.2 mA cm⁻², maintaining 22.7 mF cm⁻² at 4 mA cm⁻². The electrochemical

capacitive behavior of the MnO_2 MSCs was further investigated by electrochemical impedance spectroscopy (EIS), as shown in Figure S23D. It can be seen that the complex plane plots of MnO_2 MSCs show a larger slope at low frequency, which indicates fast ion diffusion. At high frequency, see inset in Figure S23D, MSCs shows a smaller charge-transport semicircle which indicates a rapid electron transfer inside the MnO_2 film.

13. SEM of EP MnO_2

Figure S24. (A) High-magnification SEM image of the MnO_2 . SEM image (B) and corresponding elemental mapping images of O (C), and Mn (D).

14. Electrochemical performance and stability of AMSCs

Figure S25. Changes of the Nyquist plots of AMSCs device before and after 10000 cycles at a current of 1.5 mA cm^{-2} .

Figure S26. Cross-sectional SEM image of the device after cycling test. (A) E-M, (C) MnO_2 . The left side SEM image (B, D) is an enlarged view of the active materials part of the device.

After cycling, the AMSCs devices were studied by SEM and the cross-sectional SEM images of the device ((A) E-M, (C) MnO_2) were shown in Figure S26. After 10000 cycles, the morphology of the E-M almost maintain the nanosphere structures as before the cycling (part of the electrolyte penetrates into the E-M film), indicating that the EP composite film were

effectively stabilized by the infiltration of MXene. In addition, MnO₂ also maintained the microstructure after stability testing.

Figure S27. Self-discharge behaviour of AMSCs device

Table S2. The capacitance performance of MSCs at different current density.

Current density (mA cm ⁻²)	E-M		P-M		AMSCs	
	C _A (mF cm ⁻²)	C _V (F cm ⁻³)	C _A (mF cm ⁻²)	C _V (F cm ⁻³)	C _A (mF cm ⁻²)	C _V (F cm ⁻³)
0.2	47.4	225.6	26.7	333.9	71.2	652.5
0.5	47.3	224.9	26.3	328.4	69.5	636.9
1.0	47.4	223.9	19.5	243.9	60	549.9
1.5	46.6	221.6	18.6	232.5	56.4	516.9
2.0	45.7	217.7	16.3	203.1	49.4	452.7
3.0	44.8	213.0	15.7	196.1	42.5	389.5
4.0	44.0	209.7	13.5	169.3	42.4	388.6

Table S3. Electrochemical performance of microsupercapacitors featuring a variety of electrodes materials such as MXene, Graphene, polymers, MnO₂ and their hybrid materials.

Electrode Materials	Potential/V	electrolyte	C _A /mF cm ⁻²	E/mW h cm ⁻³	P/W cm ⁻³	Ref.
Ti ₃ C ₂ T _x	0-0.6	PVA/H ₂ SO ₄	27	18	0.7	5
PANI	0-0.8	PVA/H ₂ SO ₄	20.4	7.4	8	6
LSG/MnO ₂	0-0.9	1.0 M Na ₂ SO ₄	384	8000	10.3	7
LSG	0-0.8	PVA/H ₃ PO ₄	8.19	5.1	2.4	8

SWCNT	0-0.8	PVA-H ₃ PO ₄	0.521	0.18	11	9
PPy	0-0.5	PVA/H ₂ SO ₄	8.15	15.25	0.89	10
N-doped MGFs	0-3.0	EMIBF ₄ / PVDF-HFP	306.3	0.957	15	11
Ni@MnO ₂	0-0.8	PVA/CH ₃ CO OLi	52.6	11.1	39.6	12
rGO//Ti ₃ C ₂ T _x	0-1.0	PVA/H ₂ SO ₄	2.4	8.6	0.2	13
Ti ₃ C ₂ T _x	0-0.6	PVA/H ₂ SO ₄	61	10.8	4.7	14
Graphene/ MnO ₂ /Silver Nanowire	0-0.9	0.5 M Na ₂ SO ₄	35.2	2.3	0.16 2	15
E-M//MnO₂	0-1.6	PVA/LiCl	69.45	250.1	32.9	This work

C_A: areal capacitance; E: energy density; P: power density; PANI: polyaniline; PPy: polypyrrole; EMIBF₄: 1-ethyl-3-methylimidazolium tetrafluoroborate; PVDF-HFP: poly(vinylidene fluoride-co-hexafluoropropylene); LSG: laser-scribed graphene; SWCNT: single-walled carbon nanotubes; MGFs: microfluidic-directed graphene fibers; rGO: reduced graphene oxide; E-M: PEDOT-Mo_{1.33}C composite film.

Table S4. Comparison of our current work with the published two articles.

	Current work	Article in JMCA ¹⁶	Article in Adv. Funct. Mater. ¹⁷
Reactants	MXene (Mo _{1.33} C, Ti ₃ C ₂ T _x) and monomers (EDOT, Pyrrole)	Ti ₃ C ₂ T _x and monomer EDOT	Mo _{1.33} C and polymer PEDOT:PSS
Apply electric field	Yes	No	No
Polymerization method	Electrochemical polymerization	charge-transfer-induced polymerization	No
Complex formation by	Electrochemical reaction	Chemical reaction	Physical mix
Time	Short (~ 30 min)	Long (~24 h)	Long (~24 h)
Main component in final products	Polymer (~70%)	Ti ₃ C ₂ T _x (~95%)	Mo _{1.33} C (~90%)
Composite film formation method	In situ electrochemical polymerization	Vacuum filtration	Vacuum filtration
Possibility to obtain Pattern in μm	Yes	No	No

Application	Microsupercapacitors	Lithium ion storage	Supercapacitors
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Overall, the method demonstrated in current manuscript is very different from the methods reported in the above two articles and has unique advantages. In addition, the universality of the method (MXene can promote the electrochemical polymerization of organic monomers without use of traditional electrolytes) was studied in the manuscript by choosing two classic organic monomers (Pyrrole and EDOT) and MXene ($\text{Mo}_{1.33}\text{C}$, $\text{Ti}_3\text{C}_2\text{T}_x$), which shows that the method is universal and not limited to a specific monomer.

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