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Gallic acid-derived carbon dots intercalated 3D porous $Ti_3C_2T_x$ MX ene for high-capacity supercapacitors

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 $Ti_3C_2T_x$ Mxene shows good promise as an energy storage material. However, two-dimensional MXene materials are easily stacked, which negatively affects the energy density and limits the application of MXene-based supercapacitors. In this paper, a strategy for embedding carbon dots is proposed to address this issue. A three-dimensional structure is formed by cross-linking $Ti_3C_2T_x$ MXene nanosheets with gallic acid (GA), and a subsequent carbonization process is then utilized to prepare a three-dimensional porous carbon dot intercalated $Ti_3C_2T_x$ MXene material. The hydroxyl structures in GA are cross-linked with the hydroxyl structures on the surface of $Ti_3C_2T_x$ under the action of Zn^{2^+} to form a three-dimensional structure. The carbon dots formed by carbonizing the GA are embedded within the $Ti_3C_2T_x$ nanosheets is conducive to the diffusion and transport of electrolyte ions in $Ti_3C_2T_x$ MXene. Consequently, at a scan rate of 2 mV s⁻¹, a $Ti_3C_2T_x$ @Celectrode achieves a high electrochemical gravimetric pecific capacitance (C_x) of 393.7 F g⁻¹. At a higher scan rate of 200 mV s⁻¹, 83.7% capacitance retention is obtained. Moreover, this electrode also shows 90.3% performance retention after 5000 cycles, demonstrating its good cycle stability. Finally, a symmetric supercapacitor was built using carbon cloth and $Ti_3C_2T_x@C$, and at a power density of 153.25Wkg⁻¹, a superb energy density of 21.28Whkg⁻¹is attained. This study offers a facile strategy for effectively preparing MXene electrodes with desirable electrochemical performance.

1. Introduction

MXenes are two-dimensional (2D) materials that have been widely investigated in many fields due to their compelling surface properties and unique structures. For instance, MXene-based materials exhibit high conductivity and good hydrophilicity, indicating their promising potential for catalysis, energy storage, shielding electromagnetic waves, and sensing applications [1,2]. However, the van der Waals forces between the monolayers in MXene structures lead to layer stacking or undesirably narrow layer spacing. When MXenes are used as electrochemical materials, this results in poor electrochemical performance because ion intercalation/deintercalation is inhibited [3-5].

To address this daunting challenge, researchers have investigated a variety of interesting approaches. For instance, a guest material can be introduced as an intermediate layer to generate a porous structure between the MXene layers [6-8]. Jiang's team reports an innovative restricted hydrothermal strategy that combines chemical crosslinking to construct three-dimensional layered porous MXene/reduced graphene oxide (RGO) composite fibers. This well-designed architecture effectively prevents MXene stacking while creating efficient ion transport channels. It is worth noting that thiourea serves as both a chemical crosslinking agent and selective reducing agent, while reduced graphene oxide nanosheets have the physical barrier effect, which

synergically enhances the oxidation resistance of the composite. The optimized composite fiber has excellent electrical conductivity (862.2 S cm⁻¹), mechanical strength (93.1 MPa), and oxidation resistance (90.5% conductivity after 60 days) [9]. Assembling 2D sheets into three-dimensional (3D) morphologies is another effective method for preventing MXene layer stacking [10,11]. Moreover, the self-assembly of 3D porous structures generates an abundance of electrochemically active sites that can be accessed by electrolyte ions [12,13]. Yang's team designed and implemented a layered heterostructure of conductive mesoporous hollow carbon spheres (MHCS) and MXene composite electrodes through simple vacuum filtration without further template removal processes. This direct preparation strategy not only effectively improves the specific surface area of the electrode, but also enhances the abundant surface pores and good electrical conductivity of MHCS, improves the permeability of electrolyte solution, shortens the ion transport path, and thus significantly improves the specific capacitance (395F g⁻¹ at 2 mVs⁻¹) and rate performance (70.9% at 1000 mV s-1) of the electrode. The introduction of carbon nanotubes (CNTs) further improves electrical conductivity and stability while maintaining good flexibility. As a result, MXene/MHCS/CNT films offer high specific capacitance, excellent magnification performance, and excellent cycle stability [11]. However, although three-dimensional structures are conducive to electrolyte ion transport in Ti₃C₂T_x MXene

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electrodes, these structures are not conducive to electron transport between the Ti₃C₂T₂ MXene nanosheets. Due to these factors, new strategies should be developed to prepare three-dimensional porous MXene structures that inhibit the interlayer stacking of Ti₂C₂T MXene nanosheets while guaranteeing rapid electron transport between the nanosheet layers. Due to their small size, carbon dots formed in situ can be easily embedded into the interlayer of MXene, playing a pillarlike role and thus inhibiting the interlayer stacking of MXene. At the same time, due to its high conductivity, it can also serve as an electron transmission channel between MXene layers, thereby enhancing the electron transmission efficiency between MXene layers. Zhang's team proposed a carbon dot-intercalated strategy to prepare flexible MXene thin film electrodes with large ion-accessible active surfaces and high density by gelating and carbonizing calcium alginate (CA) within MXene nanosheets. CA hydrogels are formed in MXene nanosheets and accompanied by evaporation drying, resulting in high density of MXene/CA films. During the carbonization process, CA-derived carbon dots can be embedded into MXene nanosheets, increasing the layer spacing and promoting electrolyte diffusion within MXene films. Thus, MXene films embedded with carbon dots exhibit high capacitance at 3 M H₂SO₄ (1244.6F cm⁻³ at 1 A g⁻¹). Excellent rate performance (662.5 F cm⁻³ at 1000 A g⁻¹) and excellent cycle stability (93.5% capacitance maintained after 30000 cycles). However, it is difficult for polymer materials to completely enter the interlayer of MXene, resulting in an uneven distribution of carbon dots between the MXene layers, and carbon dots derived from small molecular materials can solve this problem [14].

GA is a natural compound containing a catechol structure based on mussel adhesion protein, which shows great potential in the surface coating, modification, and functionalization of different substrates. The small molecule compounds containing phenolic hydroxyl groups can form intermolecular hydrogen bonds with the functional groups (-O,-OH, -F) on the surface of MXene nanosheets. Meanwhile, the phenolic hydroxyl groups on the surface of small molecule compounds and the hydroxyl groups on the surface of MXene nanosheets can be physically cross-linked under the action of divalent metal cations. Therefore, GA coating can effectively maintain the structural stability of MXene and achieve controllable surface functionalization.

In this paper, a carbon dot intercalation strategy is proposed for preparing three-dimensional porous carbon dot-intercalated MXene materials. First, the MXene nanosheets are cross-linked with GA. The hydroxyl groups of GA and the MXene surface are cross-linked under the action of Zn^{2+} , which forms a three-dimensional structure. Then, a carbonization process is employed to generate carbon dots from the GA. These carbon dots are embedded into the MXene nanosheet structure, which increases the layer spacing and promotes electrolyte ion diffusion into the MXene. Thus, the Ti₃C₂T_x@C electrode achieves excellent electrochemical performance, good retention of capacitance at higher scanning rate values, and excellent cycle stability. Moreover, a symmetric supercapacitor prepared using carbon cloth and the Ti₃C₂T_x@C electrode also demonstrates superb energy density. The results in this paper offer a compelling and efficient pathway for obtaining strong electrochemical performance.

2. Materials and Methods

2.1. Materials

Analytical-grade chemicals were used in all experiments without being purified further. Zinc chloride (ZnCl₂), concentrated hydrochloric acid (HCl), and carbon cloth were purchased from China Sinophosphate Chemical Reagent Co., Ltd. The 600 meshTi₃AlC₂ powder was provided by 11 Technology Co., Ltd. (Jilin, China). Gallic acid (C₂H₆O₅) and lithium fluoride (LiF) were obtained from Macklin, Inc.

2.2. $Ti_{3}C_{2}T_{x}$ MXene colloid suspension

The $Ti_3C_2T_x$ MXene was formed by removing the Al from Ti_3AlC_2 powder *via* selective etching. First, a 9 mol/L HCl solution was generated by slowly combining 29.8 mL of concentrated HCl with 10.2 mL of water. Then, 40 mL of this 9 mol/L HCl solution was employed

to dissolve 2 g LiF, and this solution was combined with 1 g Ti_3AlC_2 powder. Next, this mixture was stirred at 40°C for 24 hrs to obtain a slurry. The temperature was maintained with an oil bath. The pH of this slurry was then adjusted to about 6 *via* repeated washing and centrifugation at 7000 rpm. Finally, a $Ti_3C_2T_x$ solution was obtained by ultrasonicating the obtained supernatant under Ar gas for 1 hour and centrifuging at 3500 rpm [15]. The $Ti_3C_2T_x$ colloid solution concentration was 5 mg mL⁻¹, as confirmed by freeze-drying.

2.3. Three-dimensional porous $Ti_3C_2T_x@C$ aerogel

First, 19 mL of the MXene solution (5 mg mL⁻¹) and 1 mL of gallic acid (5 mg mL⁻¹) were combined in a beaker. This combined solution was continuously stirred for 30 minutes. Then, 1 mL ZnCl₂(1 mol/L) was added to the beaker, and stirring was continued for another hour. As a crosslinking agent, Zn^{2+} makes $Ti_3C_2T_x$ and GA physically cross-link, so GA intercalates between the layers of $Ti_3C_2T_x$. Next, centrifugation with deionized water was performed thrice. Finally, $Ti_3C_2T_x@GA$ aerogel was acquired by freeze-drying. The $Ti_3C_2T_x@GA$ was calcined in a tube furnace under Ar gas (500°C, 10°C min⁻¹, 2 hour dwell time). The $Ti_3C_2T_x@C$ aerogel was obtained after natural cooling.

2.4. Flexiblesymmetric supercapacitor

Symmetric supercapacitor devices are prepared by using $Ti_3C_2T_x@C/carbon cloth as both positive and negative electrodes. Two <math>Ti_3C_2T_x@C/carbon cloth electrodes (3 cm × 3 cm)$ were packaged in polyethylene terephthalate (PET), with 3 mol/L polyvinyl alcohol (PVA)/H₂SO₄ gel as electrolyte and water microporous filter membrane as diaphragm material. The $Ti_3C_2T_x@C/carbon cloth electrode is prepared as follows: 8 mg <math>Ti_3C_2T_x@C$ and 80 µL Nafion (as a binder) are dispersed in water/ ethanol solution to prepare the electrode, which is then dripped onto a carbon cloth and dried. The preparation of PVA/H₂SO₄ electrolyte is as follows: Take 20 g of PVA aqueous solution with a mass fraction of 2% (wt), add 3.92 g of sulfuric acid to stir and cool, and then add 5 mg of ammonium persulfate and stir well.

2.5. Characterization

A scanning electron microscope (SEM, Gemini 300, ZEISS) and high-resolution transmission electron microscope (HRTEM, JEOL JEM 2100F) were utilized to view the morphology and microstructure. The surface chemical state and composition were studied with an X-ray photoelectron spectrometer (XPS, AXIS Ultra DLD and AXIS Supra, Kratos). Nitrogen adsorption–desorption analysis was utilized to study the textural properties of each sample (ASAP2460, Micromeritics). Crystal structures were evaluated with an X-ray diffractometer (XRD, Rigaku Ultima IV, Cu K α , 5°/min scan speed).

2.6. Electrochemical tests

Electrode materials were prepared by dispersing 8 mg of active substance with 80 µL Nafionbinder in a water/ethanol solution. Each obtained slurry was coated on a 10 mm glass carbon electrode. The mass of the active material coated on the working electrode is 0.5 mg. Then, a three-electrode Chenhua Chi 760e (Shanghai Chenhua) was used to analyze each prepared electrode. The analysis was performed using working, counter, and reference electrodes (the prepared Ti₂C₂T₂@C electrode, a graphite rod, and Ag/AgCl (1 M KCl), respectively). Cyclic voltammetry (CV) and galvanostatic charge/discharge (GCD) curves were obtained in 3 M H₂SO₄ electrolyte (-0.6 to 0.2 V, vs. Ag/ AgCl). A range of 0.01 Hz to 100 kHz and a fixed potential amplitude of 5 mV were employed for electrochemical impedance spectroscopy (EIS). Finally, a symmetric supercapacitor was built using Ti₃C₂T₂@C/ carbon cloth as both the positive electrode and negative electrode [16]. To prepare this symmetric device, PET was used to encapsulate two $Ti_{3}C_{2}T_{x}@C/carbon$ cloth electrodes. The two electrodes were then separated using a 3 M PVA/H,SO, gel electrolyte.

Gravimetric specific capacitance (C_g) was calculated based on the charge-discharge curves using Eq. (1):

$$C_g = \frac{It}{\Delta Vm} \tag{1}$$

Where I is the gravimetric current (A), t represents the discharge time (s), m is the mass of the working electrode (g), and ΔV is the potential window (V). The value of C_g was also calculated by utilizing the CV curves with Eq. (2):

$$C_{g} = \frac{\int i dV}{2mvV} \tag{2}$$

Where m is the mass of the working electrode (g), v is the potential scan rate (V s⁻¹), V is the potential window (V), and i is the current (A).For calculations involving the symmetric supercapacitor, the total anode+cathode mass was used for the mass of the working electrode. The energy density (E_g) and power density (P_g) of the symmetric supercapacitor were determined using Eqs. (3) and (4):

$$E_{g} = \int IV dt/m \tag{3}$$

$$P_{g} = \frac{E_{g}}{\Delta t}$$
(4)

Where Δt is the discharge time (h) and m is the total working electrode mass (kg).

3. Results and Discussion

The process for preparing porous $Ti_3C_2T_x@C$ aerogel has been shown in Figure 1. First, the Al layer in the Ti_3AlC_2 phase is removed using a LiF/HCl mixture to obtain multilayer $Ti_3C_2T_x$ nanosheets. In this etching step, hydrophilic groups (-F, -O, and -OH) are used to terminate $Ti_3C_2T_x$ [16]. The Ti atoms have different electron gravities than the



Figure 1. Preparation process for obtaining the three-dimensional ${\rm porousTi}_3C_2T_x@$ Caerogel.

O/F atoms, which means that the end of the $Ti_3C_2T_x$ nanosheets carry more charge. Consequently, the $Ti_3C_2T_x$ nanosheets are negatively charged. This provides the $Ti_3C_2T_x$ nanosheets with good water dispersion properties due to electrostatic repulsion [17]. Next, gallic acid solution (GA) is added to the $Ti_3C_2T_x$ MXene suspension and evenly mixed, followed by the addition of $ZnCl_2$ solution. The introduction of Zn^{2+} into the $Ti_3C_2T_x$ MXene@GA suspension breaks its electrostatic balance. At the same time, Zn^{2+} acts as a cross-linker, enabling the formation of a three-dimensional porous $Ti_3C_2T_x$ MXene@GA structure. The obtained $Ti_3C_2T_x@GA$ hydrogel then undergoes freeze-drying to obtain a $Ti_3C_2T_x@GA$ aerogel. Finally, the $Ti_3C_2T_x@C$ aerogel containing intercalated carbon dots is obtained by carbonizing the $Ti_3C_2T_x@GA$ aerogel at 500°C.

In the Figure 2, the surface topography changes caused by pore formation in the $Ti_{a}C_{2}T_{v}MX$ ene that have been shown in Figure 2(a). Large-



Figure 2. SEM micrographs of (a) Ti₃C₂T_x, (b) Ti₃C₂T_x@GA and (c) Ti₃C₂T_x@C. TEM micrographs of (d) Ti₃C₂T_x and (e) Ti₃C₂T_x@C. (f) HRTEM micrographs of Ti₃C₂T_x@C. (g) EDX elemental mapping images of C, Ti, O, F, and Zn for Ti₃C₂T_x@C. EDX: Energy dispersive X-ray spectroscopy.

sized MXene nanosheets with a typical layered structure can be observed. The MXene sheets are oriented in a face-to-face manner, so the Ti₂C₂T MXene has a dense structure, which may limit the availability of active sites for electrolyte ions. In contrast, a three-dimensional macroporous structure (macropore diameters of 5-10 µm) can be observed in the Ti₂C₂T₄@C and Ti₂C₄T₄@GAaerogel (Figure 2b and 2c). Both Ti₂C₅T₄ and Ti₂C₃T₆@C have type-IV nitrogen-desorption isotherms with H₂ hysteresis loops (Figure S1a), indicating mesoporosity. Ti_aC_aT @C has a larger specific surface area than pure Ti₂C₂T₂ ((35.57 vs. 29.69 m²g⁻¹). The barret-joyner-halenda (BJH) pore size distribution of Ti₂C₂T₂@C (Figure S1b) confirms its mesoporosity [18]. The presence of the intercalated carbon dots causes the MXene nanosheets in Ti₂C₂T₂@C to become more disordered. The 3D macroporous structure of Ti₂C₂T @C is attributed to the Zn²⁺ acting as a cross-linking agent for the -OH on the surface of $Ti_3C_2T_x$ and the -OH on GA. This structure facilitates electrolyte penetration and ion accessibility on the surface of the MXene, which is expected to provide superior capacitance and rate performance. The microstructure of the Ti₂C₂T₂@C powder was observed by transmission electron microscope (TEM) (Figure 2e). The carbonized Ti_aC_aT @C nanosheets contain a distribution of many nanometer-sized particles. These nanoparticles are carbon, as indicated by the 0.43 nm lattice spacing (Figure 2f). Thus, Ti₃C₂T₂@C contains intercalated carbon particles. Element mapping demonstrates the uniform distribution of Zn in Ti₂C₂T₂@C (Figure 2g).

XRD was used to evaluate the atomic structures of Ti₂C₂T @C and $Ti_{a}C_{2}T_{a}$, as displayed in Figure 3(a). After etching with LiF-HCl, the (002) peak of the Ti₂AlC₂ MAX phase is shifted to 7.28° (indicating 12.13 Å d-spacing), and the (104) peak vanishes, proving that 2D Ti₂C₂T₂ was successfully synthesized [19]. Compared with $Ti_3C_2T_x$, the (002) peak of the Ti₂C₄T @C aerogel shifts to a lower 20 value by 6.36°(indicating 13.85 Å d-spacing). Thus, Ti₂C₃T₄@C has wider d-spacing, which can be ascribed to the carbon dots intercalated between the Ti₂C₂T₂ MXene nanosheets. This is favorable for making the structure more accessible to the electrolyte [15]. The XPS survey spectra of Ti₂C₂T₂andTi₂C₂T₂@C demonstrate the successful addition of $\hat{Z}n^{2+}$ to Ti₂C₁T₂@C (Figure 3b). The Ti 2p spectra (Figure 3c) show deconvoluted peak pairs at 454.76 and 460.56 eV (Ti-C), 455.46 and 461.24 eV (Ti2+), 456.56 eV and 462.71 eV (Ti³⁺), and 459.03 eV and 464.21 eV (TiO₂) [16]. Due to the presence of Zn²⁺ as a cross-linker, Ti₃C₂T_x@C exhibits stronger Ti²⁺ peaks. The C1s spectrum of $Ti_3C_2T_x@C$ (Figure 3d) has a stronger C-C bond peak than Ti₂C₃T₂, which confirms the large number of carbon dots in Ti₃C₂T₂@C. The O 1s spectrum of Ti₃C₂T₂@C contains a slightly smaller C-Ti-OH bond peak compared to that of $Ti_3C_2T_x$ (Figure 3e), which can also be ascribed to Zn^{2+} cross-linking the -OH on the MXene surface

with the -OH on GA. The Zn 2p spectrum of $Ti_3C_2T_x@C$ confirms that Zn2+ has been successfully inserted into the $Ti_3C_2T_x$ layers (Figure 3f).

The porous, three-dimensional morphology and larger layer spacing of the Ti_aC_aT @C aerogel favors the more rapid transport of electrolyte ions in shorter ion diffusion channels [17,20]. In addition, the numerous carbon dots in $Ti_3C_2T_x@C$ provide excellent electron transport pathways between the $Ti_3C_2T_x$ nanosheets. The CV analysis of the prepared electrodes is exhibited in Figure 4(a). Reversible Faraday pseudocapacitive behavior mainly contributes to the capacitance of Ti₃C₅T₂ and Ti₃C₅T₂@C, as demonstrated by the pair of redox peaks for both materials [21,22]. Ti₃C₂T₂@C has a higher C₂ than Ti₃C₂T₂, as indicated by the larger CV curve area. The GCD analysis of the Ti₂C₂T and Ti₂C₂T @C electrodes is displayed in Figure 4(b). These curves are not linear, indicating that both materials exhibit contributions from Faradaic pseudocapacitance and electric double-layer capacitance [23]. The higher C_{r} of $Ti_{3}C_{2}T_{x}@C$ is confirmed by its longer discharge time. Ti₂C₃T₄@C was further studied by obtaining multiple CV curves at varying scan rate values (Figure 4c). Within 2–100 mVs⁻¹, no significant distortion in the curve shape is observed. Thus, Ti₂C₂T @C has superb rate performance and low internal resistance [16]. Ti₂C₂T₂ (Figure S2a) shows a similar CV curve trend. Moreover, GCD curves acquired at various current density values are also consistent for both samples (Figure 4d and Figure S2b). The calculated C_{a} values of both electrode materials are displayed in Figure 4(e). Ti₃C₂T[°]₂@C displays significantly higher C values than Ti C T at all scan rates (393.7 vs. 315.5 Fg⁻¹ at 2 mVs⁻¹).⁸ This difference is attributed to the three-dimensional porous structure of Ti₃C₂T_x@C, which hinders the stacking of layers, opens more electrodynamically active sites, and promotes faster electrolyte ion transport [18,24]. Additionally, the carbon dots in Ti₃C₂T_x@C act as fast electron transfer channels that accelerate electron transfer between the Ti₂C₂T_v nanosheets. At 200 mVs⁻¹, Ti₂C₂T_v@C still retains a C_a of 329.3 F g^{-1} , while that of Ti₃C₂T_x is only 272.3 Fg⁻¹. The GCD curves acquired in the current density range of 1-100 Ag¹ display a similar trend (Figure 4f). At 1 A g⁻¹, Ti₃C₂T₄@C exhibits a notably high C₂ of 436 Fg⁻¹, and when the current density increases to 100 A g⁻¹, this value only decreases to 292.5 Fg⁻¹. However, the C_a of the Ti₂C₂T_y electrode at 100 Ag⁻¹ declines to 257.5 Fg⁻¹. Therefore, Ti₂C₂T₂@C has better rate performance, which can be explained by three main reasons. First, the self-assembly of the $Ti_3C_2T_x$ sheets with GA via Zn^{2+} cross-linking forms a three-dimensional porous structure, which inhibits Ti₂C₂T₂ layer stacking. This enables the exposure of more electrochemically active sites. Second, the formed Ti₃C₂T_x@C structure facilitates electrolyte ion transport, which ensures excellent rate performance. Third, the carbon dots in Ti₂C₂T₂@C accelerate electron transport between the Ti₂C₂T



Figure 3. (a) X-ray diffractograms of $Ti_3C_2T_x$ and $Ti_3C_2T_x$ @C. (b) XPS survey, (c) Ti 2p, (d) C 1s, (e) O 1s, and (f) Zn 2p spectra of $Ti_3C_2T_x$ and $Ti_3C_2T_x$ @C.



Figure 4. Electrochemical analysis of $Ti_3C_2T_x$ and $Ti_3C_2T_x$ @Celectrodes: (a) CV (5 mV s⁻¹) and (b) GCD (1 A g⁻¹) curves obtained in 3 M H₂SO₄ electrolyte. (c) CV curves of $Ti_3C_2T_x$ @Cat various scan rate values. (d) GCD curves of $Ti_3C_2T_x$ @Cunder different current density values. Rate performance of $Ti_3C_2T_x$ @Celectrodes at different (e) scanning rate and (f) current density values.

nanosheets by providing electron transport paths. A C_g value comparison between this work and other MXene-based electrode materials is shown in Table S1. Compared to these other materials, $Ti_3C_2T_x@C$ has a superb C_g and exceptional rate performance [11,25-27].

[°] A log (i) vs. log(ν) plot was developed to study the charge storage kinetics and distinguish the charge storage mechanisms of Ti₃C₂T₂@C [17]. The peak current was obtained using the following Eq. (5):

$$i = av^b$$
 (5)

Where the variables a and b are obtained by plotting log(i) and log(v). A capacitatively controlled charge storage mechanism is revealed by b = 1, and a diffusion-controlled charge storage process is revealed by b = 0.5 [28]. As displayed in Figure 5(a), the anode peak b value of $Ti_3C_2T_x@C$ is 0.94, while the cathode peak b value is 0.89. Consequently, the storage of charges in $Ti_3C_2T_x@C$ is mainly related to

its fast capacitance behavior. At 20 mVs⁻¹, capacitive control accounts for 82.45% of overall charge storage in the $Ti_3C_2T_x@C$ electrode (Figure 5b). From 2–50 mVs⁻¹, the capacitive control contribution increases from 72.31% to 87.87% with increasing scan rate (Figure 5c). This indicates that the storage of charge in $Ti_3C_2T_x@C$ is primarily governed by Faraday pseudocapacitance behavior rather than a diffusioncontrolled process [29]. The ion diffusion kinetics of the synthesized electrodes were evaluated using EIS. Figure 5(d) exhibits the Nyquist plots of $Ti_3C_2T_x$ and $Ti_3C_2T_x@C$. $Ti_3C_2T_x@C$ has a negligible semicircle, indicating low charge transfer resistance. The equivalent circuit fitting parameters in Table S2 and Table S3 show that $Ti_3C_2T_x@C$ has a lower charge transfer resistance than $Ti_3C_2T_x$. This is mainly because the intercalation of carbon dots in $Ti_3C_2T_x@C$ facilitates electron transfer between the $Ti_3C_2T_x$ anosheets. In addition, the low-frequency linear region of the $Ti_4C_2T_x@C$ Nyquist plot has a higher slope. This is



Figure 5. Electrochemical evaluation of $Ti_3C_2T_x$ @Celectrode: (a) Peak current vs. scan rate log-log plot. (b) Capacitance contributions at 20 mV s⁻¹. (c) Contributions of capacitive control and diffusion control to total capacitance at different scan rate values. (d) Nyquist and (e) Bode plots of $Ti_3C_2T_x$ and $Ti_3C_2T_y$ @C. (f) Cyclic stability of $Ti_3C_3T_y$ @C and $Ti_3C_2T_x$ at 100A g⁻¹.



Figure 6. Performance of $Ti_3C_2T_x@C$ -based symmetric supercapacitor. (a) CV curves at different scanning rate values. (b) GCD curves obtained at different current density values. (c) Rate performance at various scanning rate values. (d) Cycling of $Ti_3C_2T_x@C$ and $Ti_3C_2T_x$ at 50 mV s⁻¹. (e) Comparative Ragone plot. (f) Application of four $Ti_4C_2T_2@C$ -based symmetric supercapacitors in series.

because the 3D porous structure of the Ti₃C₂T_x@C electrode accelerates the transport of electrolyte ions [30]. Bode plots of the Ti₃C₂T_x and Ti₃C₂T_x@C electrode samples are displayed in Figure 5(e). These electrode materials both exhibit phase angles close to -90°, indicating that their capacitive properties are close to the ideal state [31]. The relaxation time constant τ_0 of the Ti₃C₂T_x@C electrode (1.25 s) is shorter than that of the Ti₃C₂T_x electrode (1.84 s), indicating that electrolyte ions are more rapidly transported within Ti₃C₂T_x@C. The Ti₃C₂T_x@C electrode also has excellent cyclic stability (Figure 5f), retaining more than 90.3% of its C_g even after 5,000 cycles, while the C_g of Ti₃C₂T_x only retains 87.6%. To further confirm the stability of the MXene structure, the Ti₃C₂T_x@C electrode that underwent cyclic stability tests was characterized by SEM. After long-term cycling, the porous structure of Ti₃C₂T_x@C collapses to a certain extent, but the basic morphology is still retained (Figure S3).

To investigate the potential for using Ti₂C₂T₂@C in practical applications, a symmetric supercapacitor was prepared [32-39]. CV curves of this symmetric supercapacitor from 2-50 mVs⁻¹ are shown in Figure 6(a). With the increase in scan rate, no significant distortion was observed at 20 mVs⁻¹; however, a significant distortion occurred at 50 mV s⁻¹, indicating that the device has good reversibility and rate performance. A similar trend can be seen in the GCD curves acquired from 1–5 Ag⁻¹ (Figure 6b). The calculated C_{a} values have been shown in Figure 6(c). This symmetric supercapacitor achieves a C_a of 153.25 Fg⁻¹ at 2 mVs⁻¹. Moreover, a C_a of 45.29 Fg⁻¹ is still reached at 50 mVs⁻ ¹. Next, a cycling test was performed at 50 mVs⁻¹ to study the stability of the symmetric supercapacitor (Figure 6d). After 5000 continuous cycles of charging and discharging, 90.1% of the original C_a value is still retained, confirming the good cycle stability of the prepared device. A Ragone plot (Figure 6e) is used to show the gravimetric E_a and P_a values of the symmetric supercapacitor. The highest E_a of 21.28 Whkg⁻¹ is attained at a P_o of 153.25 Wkg⁻¹. Moreover, an E_o of 14.63 Whkg⁻¹ is still retained when P, increases to 526.75 Wkg1. The practical use of this symmetric supercapacitor design was demonstrated by connecting four symmetric supercapacitor devices in series. These devices are capable of successfully lighting an light emitting diode (LED) (Figure 6f).

4. Conclusions

In summary, a three-dimensional porous carbon dot-intercalated ${\rm Ti}_{a}C_{2}T_{x}$ MXene material was prepared by a simple carbon dots

intercalation strategy. The -OH on the Ti₂C₂T₂ MXene nanosheet surface was cross-linked with the -OH on GA under the action of Zn²⁺, forming a three-dimensional structure. Next, Ga-derived carbon dot particles were embedded into the Ti₂C₂T_x MXene via carbonization, leading to larger layer spacing and an active surface accessible to ions. Moreover, these carbon dots acted as excellent electron transport channels, which accelerated electron transport between the Ti₂C₂T MXene nanosheets. Due to this favorable design, the Ti₂C₂T₂@C electrode had a C of 393.7 Fg⁻¹ at 2 mVs⁻¹ and maintained 83.7% of this value at 200° mVs⁻¹. Moreover, the electrode showed 90.3% C retention after 5000 charging and discharging cycles, indicating superb cycle stability. A Ti₃C₂T_x@C/carbon cloth symmetric supercapacitor displayed a high E_e of 21.28 Whkg⁻¹ under a P_e of 153.25 Whkg⁻¹. The results and analysis presented in this study offer a useful approach for efficiently preparing MXene electrodes with high performance. However, due to the limitation of the MXene material preparation process, large-scale manufacturing of Ti₂C₂T₂@C composites has not been possible. In addition, due to the high activity of MXene, it is also necessary to continue to improve the long-term cyclic stability of Ti₃C₂T_x@C composites.

CRediT authorship contribution statement

Qiaonan Yu and Qiang Liu contributed significantly to analysis and project funding support; Zhongliang Liu performed the experiment; Keliang Wu contributed to the conception of the study and wrote the manuscript; Bingke Li performed the methodology; Niuniu Gu design of data analyses and Dongmei Yang provided macro guidance.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Declaration of Generative AI and AI-assisted technologies in the writing process

I acknowledge using generative AI/AI-assisted tools in drafting. Responsibility for originality, accuracy, and ethics remains mine. Work reflects my intent; AI use is transparent.

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Supplementary data

Supplementary data/material includes 3 Figures and 3 Table can be found online at https://dx.doi.org/10.25259/AJC 264 2024.

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