Hollow MXene Spheres and 3D Macroporous MXene Frameworks for Na-Ion Storage

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A family of 2D transition metal carbides and nitrides (MXenes) has been attracting increasing attention since their discovery in 2011.[1a] MXenes are synthesized by selective extraction of the “A” element (such as Al and Ga) from their parent MAX phases. They have a general formula M_{n+1}AX_n, where M stands for an early transition metal (such as Ti, V, Nb, and Mo), X stands for C and/or N, and T represents various surface terminations (OH, O, and/or F groups).[1a] The unique structure and surface chemistry render MXenes a combination of properties such as metallic conductivity, a hydrophilic surface, and good mechanical stability.[1c-2] These superior properties distinguish MXenes from other 2D materials and make them promising candidates for energy storage,[3] nanocomposites,[4,5] transparent conductor,[5] separation membranes,[6] catalysis,[7] electromagnetic interference shielding,[8] sensors,[9] and biomedical[10] applications.

So far, applications of MXenes in electrical energy storage have attracted the most interest.[13-14] MXene-based electrodes with varied chemistry and structures showed competitive performance in electrochemical capacitors,[1d,11] Li/Na-ion batteries,[1c,12] and Li–S batteries.[1c,12] However, similar to other 2D materials, the performance of MXenes is still hindered by their tendency to stack or aggregate, which limits the ionic transport through the electrodes. In order to fully utilize their electrochemical performance, strategies including creating porous structures and introducing interlayer spacers to MXene sheets were proposed. For example, Li-ion storage capacity was increased by a factor of 4 after creating mesopores in MXene nanosheets, along with an impressive rate performance.[13] Using the ab initio density functional theory calculations, Yu’s group demonstrated that the enlarged interlayer distance of Ti_{3}C_{2}T_{x} MXene enables the stable multilayer Na-ion adsorption and therefore significantly enhances its theoretical capacity.[14] Experimentally, the increase in interlayer spacing of MXenes achieved by the introduction of interlayer spacers, such as nanocarbons,[15] polymers,[16] metal oxide nanoparticles,[17] and large ions,[18] has led to significantly improved energy storage capability as well.

Recent reports and reviews have suggested that the integration of 2D materials into 3D macroscopic structures, such as porous films, scaffolds, and networks, could provide a good solution to the issue of poor ionic and electronic transport in electrode materials, thereby resulting in high-performance devices.[19] In particular, 3D macroporous graphene frameworks have been produced by integrating graphene materials with polymers and self-assembly, offering significantly enhanced performance in applications in energy, environment, sensing, and biological fields.[20] The same is true for other 2D materials like molybdenum disulfide (MoS_2).[21] Among different strategies for the construction of 3D macroporous architectures, the...
template approach is the most promising and attractive due to its ability to produce well-defined and shaped architectures.\[22\]

In this communication, we report on processing 2D transition metal carbides (MXenes) into 3D macroporous frameworks via sacrificial poly(methyl methacrylate) (PMMA) spherical templates. Electrochemical performance of the 3D macroporous MXene frameworks was assessed by their Na-ion storage capacity, which has been receiving increasing interest as an alternative to the current Li-ion batteries due to its suitable energy density, low cost, and the abundance of sodium salts in nature.\[23\]

A schematic of the preparation procedure is depicted in Figure 1. To capitalize on the strong interaction between MXene flakes and PMMA spheres, individual hollow MXene flakes were fabricated first. Upon mixing the two solutions, MXene flakes spontaneously wrap around the surface of PMMA spheres, driven by the interaction between their surface hydroxyl groups (Figure 1a–c). MXene/PMMA spheres can be separated from the solution by centrifugation (Figure 1c). By thermal evaporation at 450 °C, PMMA is removed, leading to the formation of self-supporting, hollow MXene spheres (Figure 1d). In order to make a free-standing film, PMMA/MXene spheres were vacuum-filtered (Figure 1e), followed by thermal evaporation at 450 °C to remove the PMMA. A flexible and conductive 3D macroporous MXene architecture is obtained after that (Figure 1f), which is expected to be a promising candidate as a high-performance electrode in energy storage devices.

Figure 2a,b shows the morphologies of PMMA spheres and Ti₃C₂Tx MXene flakes. The PMMA spheres are of 2–3 μm in diameter with a rough surface. The Ti₃C₂Tx flakes have a lateral size of several micrometers and a thickness of ≈1 nm. The scanning electron microscopy (SEM) image in Figure 2c shows the Ti₃C₂Tx/PMMA hybrid spheres with a smoother surface than the PMMA precursors due to the wrapping of Ti₃C₂Tx flakes. Self-supporting, hollow Ti₃C₂Tx spheres were obtained after the thermal evaporation of PMMA (Figure 2d). As shown in Figure 2e,f, these hollow spheres have good electron transparency, indicating thin walls consisting of few layers of Ti₃C₂Tx. Note that such self-supporting hollow spheres can be easily obtained from graphene but were reported as difficult to make from 2D MoS₂ flakes due to their inherent rigidity. These hollow MXene spheres can be easily dispersed in solvents, such as water and ethanol, by sonication, which was demonstrated by the images of well-dispersed hollow spheres obtained on a mica substrate after drying one drop of the corresponding suspension (Figure S1, Supporting Information), indicating their potential use in the environmental, biological, and biomedical applications.

As described above in Figure 1e, the Ti₃C₂Tx/PMMA hybrid spheres can be assembled into a free-standing film by a vacuum-assisted filtration process (Figure S2, Supporting Information). After thermal annealing at 450 °C in Ar, flexible macroporous Ti₃C₂Tx films were obtained (Figure 3a). Figure 3b shows the thermogravimetric analysis (TGA) curves of the PMMA and Ti₃C₂Tx/PMMA hybrids. It is obvious that PMMA was completely evaporated at temperatures higher than 400 °C. For the Ti₃C₂Tx/PMMA hybrid film, ≈80% of the weight was lost, indicating that the mass ratio of PMMA: Ti₃C₂Tx was around 4:1. The small weight jump at ≈400 °C in the TGA curve of the hybrid can be ascribed to the oxidation of Ti₃C₂Tx by its oxygen-containing functional groups or the decomposition products of PMMA. The cross-sectional SEM image shown in Figure 3c reveals that the macroporous film is composed of a large number of Ti₃C₂Tx hollow spheres, forming a 3D framework. The film has a thickness of ≈13 μm, about an order of magnitude larger than the film of a similar weight (=5 mg) built of compactly stacked Ti₃C₂Tx flakes (Figure S3, Supporting Information). This results in a decrease in the film packing density from 3.8 g cm⁻³ for the compact film to ≈0.4 g cm⁻³ for the macroporous film. The electrical conductivity of the macroporous Ti₃C₂Tx film was measured to be ≈200 S cm⁻¹, which is smaller than the conductivity of the compact Ti₃C₂Tx films\[22\] but much higher than that of a 3D graphene film with a similar structure (≈12 S cm⁻¹).\[22\]

The stacking of hollow Ti₃C₂Tx spheres promotes the roughness of the macroporous film surface, leading to a good hydrophobicity with a large water contact angle of 135° due to the lotus effect (Figure 3e).\[24\] This distinguishes the surface property of the macroporous films as compared to the compact ones, which usually exhibit a water contact angle of ≈35° (Figure 3f).
The interfacial structure between neighboring Ti$_3$C$_2$Tx hollow spheres is shown in Figure 3g. A good contact between spheres is evident therein, which is probably contributed by the van der Waals interactions and hydrogen bonds between neighboring 2D Ti$_3$C$_2$Tx flakes. This is crucial for the construction of robust and conductive 3D frameworks. Note that hollow MXene spheres are tunable in size and their wall thickness. For example, the wall thickness of the Ti$_3$C$_2$Tx hollow spheres and flexibility of the 3D macroporous films can be easily tuned by the mass ratio of the PMMA to Ti$_3$C$_2$Tx, such as (002) peaks for MXenes are observed for all of these films. The compact and 3D macroporous Ti$_3$C$_2$Tx films show a similar c-lattice parameter (c-LP) of ~27.3 Å, with their (002) peaks located at ~6.4°. However, a larger full width at half maximum of the macroporous films and the disappearance of higher order of (00l) peaks for MXenes, such as (004) and (006) peaks, can be attributed to the bending of the flakes due to the introduction of the macroporous architecture and their random orientation in the film. The absence of peaks for transition metal oxides in the patterns of macroporous films demonstrates a good retention of the MXene flakes after annealing with no oxidation. This is confirmed by the transmission electron microscopy (TEM) image of the annealed Ti$_3$C$_2$Tx flakes and the corresponding selected area electron diffraction pattern (Figure S6, Supporting Information). The 3D Mo$_2$CTx film shows a c-LP of 22.8 Å. The (002) peak for 3D V$_2$CTx film splits into two peaks, which show c-LPs of 40.2 and 32.4 Å, respectively. The exact reason for larger interlayer spacing and two (002) peaks in the 3D V$_2$CTx film is not clear at the moment. It can possibly be explained by the presence of adsorbed water or carbonized residues of organic molecules in the film, due to a different delamination method that was used for V$_2$CTx (see Supporting Information).

The combination of good conductivity and macroporous structure of the 3D macroporous MXene films makes them promising candidates for Na-ion storage and other electrochemical applications. Also, it is important to note that the MXenes exhibit a pseudocapacitive Na-ion storage mechanism, which renders them a higher Na-ion capacity than double-layer electrodes and a higher rate capability relative to bulk Faradic electrodes. Herein, the free-standing and binder-free films
were directly used as anodes without any current collectors and their electrochemical performance was tested in a two-electrode cell with Na foil as the counter and reference electrode. The cyclic voltammetry (CV) profiles of the 3D MXene films are shown in Figure 4a and Figure S7 (Supporting Information). A pair of cathodic/anodic peaks located at around 0.8/1.4 V versus Na/Na$^+$, corresponding to the Na$^+$ insertion/extraction from the electrodes, are observed (Figure 4a). Their broadness indicates a nondiffusion limited and pseudocapacitive mechanism of Na-ion storage at the surface of MXene flakes, which is in good agreement with previous studies on MXenes.$^{[3c,12c]}$ For all three 3D MXene film electrodes, irreversible cathodic peaks are observed in the first cycle of CVs, which can be attributed to the formation of a solid electrolyte interface as well as the irreversible reaction of Na ions with the surface functional groups (F, OH, and O) and/or water molecules confined between MXene flakes (Figure S7, Supporting Information).$^{[3c,12c,27]}$ Figure 4b compares the rate performance of the three different

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Figure 3. a) Digital image showing the flexibility of a 3D macroporous Ti$_3$C$_2$T$_x$ film. b) TGA curves of pure PMMA spheres and a Ti$_3$C$_2$T$_x$/PMMA hybrid film under Ar. c) Cross-sectional and d) top-view SEM images of the 3D macroporous Ti$_3$C$_2$T$_x$ film. Water contact angles of the e) 3D macroporous Ti$_3$C$_2$T$_x$ film and f) a compact Ti$_3$C$_2$T$_x$ film. g) TEM image showing the interfacial structure between two neighboring Ti$_3$C$_2$T$_x$ hollow spheres in the 3D film. Cross-sectional SEM image of the 3D macroporous h) V$_2$CT$_x$ and i) Mo$_2$CT$_x$ films. j) Comparison of XRD patterns of a compact Ti$_3$C$_2$T$_x$ film and the 3D macroporous MXene films.
3D MXene films. At 0.25 C, the Mo$_2$CT$_x$ film achieved a reversible capacity of ≈370 mAh g$^{-1}$, compared with ≈330 and 340 mAh g$^{-1}$ for the Ti$_3$C$_2$T$_x$ and V$_2$CT$_x$ film electrodes, respectively. All these films exhibited excellent capacity retention with increasing current rates. At a high current rate of 25 C, the Ti$_3$C$_2$T$_x$, Mo$_2$CT$_x$, and V$_2$CT$_x$ retained a capacity of 120, 125, and 170 mAh g$^{-1}$, respectively. It was noticed that the V$_2$CT$_x$ exhibited the best rate performance among the three 3D films, which is ascribed to its largest interlayer spacing. The charge–discharge curves at different current rates for the 3D Ti$_3$C$_2$T$_x$ film electrode are shown in Figure 4c. At 0.25 C, the presence of charge–discharge plateaus at 0.8/1.4 V corresponds well with the broad redox peaks in CV curves shown in Figure 4a. These features disappear at higher current rates, which confirms the pseudocapacitive Na-ion storage mechanism in MXenes.$^{[3c]}$ Similar phenomena are also observed for 3D V$_2$CT$_x$ and Mo$_2$CT$_x$ film electrodes (Figure S7, Supporting Information), making them promising for Na-ion capacitor applications.

Comparison of the Na-ion storage capability of the 3D macroporous MXene film electrodes with other reported materials is shown in Figure 4d. These 3D MXene films showed better gravimetric performance than many other reported materials, including banana peels-derived carbon materials,$^{[28]}$ porous carbon nanofibers,$^{[29]}$ MoS$_2$/graphene papers,$^{[23c]}$ etc. At low current densities, the 3D MXene films showed capacities comparable with the banana peels-derived carbon materials. However, they outperformed all other materials in the rate performance due to their excellent electrical conductivity and
macroporous structure. In particular, much better Na-ion gravimetric storage capability is achieved by the 3D macroporous Ti\textsubscript{3}C\textsubscript{2}Tx films in comparison to multilayer Ti\textsubscript{3}C\textsubscript{2}Tx particles\cite{k} and porous Ti\textsubscript{3}C\textsubscript{2}Tx/CNT hybrid films,\cite{l} revealing the advantage of the 3D macroporous architecture. While the macroporous structure will lead to a somewhat lower volumetric capacity, elimination of binder, conductive additives, and metal current collector will, at least partially, compensate for it.

Figure 4e shows the 1000-cycle stability of the 3D macroporous MXene film electrodes at 2.5 C. The initial discharge capacities for Ti\textsubscript{3}C\textsubscript{2}Tx, V\textsubscript{2}CT\textsubscript{x}, and Mo\textsubscript{2}CT\textsubscript{x} were 390, 470, and 400 mA h g\textsuperscript{-1}, respectively. The reversible capacities retained by these film electrodes were 210, 260, and 210 mA h g\textsuperscript{-1}, with corresponding first-cycle Coulombic efficiencies as 53.8%, 55.3%, and 51.2%, respectively, which were higher than the previously reported Ti\textsubscript{3}C\textsubscript{2}Tx film electrode (40%)\cite{m} As discussed above, the initial irreversible capacities were mainly attributed to the irreversible reaction between MXene flakes and the electrolyte.\cite{n, o, p} Some improvement in Coulombic efficiency here can be attributed to the partial removal of MXene surface functional groups by thermal annealing during the manufacturing process. Further improvement can be achieved by optimizing the surface chemistry of MXenes. The 3D Mo\textsubscript{2}CT\textsubscript{x} and V\textsubscript{2}CT\textsubscript{x} film electrodes exhibited a gradual increase in capacity during the first 300 cycles, while the capacity for Ti\textsubscript{3}C\textsubscript{2}Tx electrode kept increasing until after 700 cycles. This can be ascribed to the improved electrolyte accessibility to active sites caused by the macroporous structure. The latter was dried in air at room temperature for 10 min and peeled off from the polypropylene membrane, yielding a flexible freestanding Ti\textsubscript{3}C\textsubscript{2}Tx/PMMa hybrid film. The composite film was annealed at 450 °C for 1 h under flowing argon to remove the PMMA, leaving Ti\textsubscript{3}C\textsubscript{2}Tx hollow spheres. The Ti\textsubscript{3}C\textsubscript{2}Tx hollow spheres were stable and could be easily dispersed in solvents such as water and ethanol, suggesting good contacts between spheres and metallic conductivity of Ti\textsubscript{3}C\textsubscript{2}Tx. These 3D macroporous MXene films were directly used as anodes for Na-ion storage, properties, the as-prepared 3D macroporous MXene films were cut into self-supported electrodes. CR2032-type coin cells were assembled in an argon-filled glove box using the macroporous MXene film electrode as the working electrode and Na foil as the reference and counter electrode, which were electronically separated by a glass microfiber (Whatman) saturated with an electrolyte. The loading of MXene film electrodes was measured between 0.01 and 3.0 V versus Na\textsuperscript{+}/Na using an Arbin system (Arbin BT-2143-11U, College Station, TX, USA). CV measurements were conducted by using a VMP3 potentiostat (Biologic, France) and was measured between 0.01 and 3.0 V versus Na\textsuperscript{+}/Na at a scan rate of 0.1 mV s\textsuperscript{-1}

Other information on the synthesis and delamination of Ti\textsubscript{3}C\textsubscript{2}Tx, V\textsubscript{2}CT\textsubscript{x}, and Mo\textsubscript{2}CT\textsubscript{x} MXenes, synthesis of PMMA spheres, and characterization techniques can be found in the Supporting Information.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

3D frameworks, hollow spheres, MXene, Na-ion storage, templates