3D hierarchical Ti$_3$C$_2$/TiO$_2$ composite via in situ oxidation for improved lithium-ion storage†

Jianlin Zhang,†‡ Shan Wei,‡ Qingyun Miao, Huihui Yue, Xuxia Meng, Fei Wang‡* and Naitao Yang‡*

To address the intrinsic limitations of both TiO$_2$ and MXenes, we propose an effective strategy for the engineering of a 3D Ti$_3$C$_2$/TiO$_2$ nanorod hybrid, where the in situ synthesized TiO$_2$ nanorods are homogeneously decorated onto the surface of 3D Ti$_3$C$_2$ MXene via simple oxidation. As the LIB anode, it demonstrates exceptional long-term cycling stability with a specific capacity of 384.1 mA h g$^{-1}$ after 600 cycles at 1.0 A g$^{-1}$.

Nowadays, in the quest for anode alternatives, titanium dioxide (TiO$_2$) stands out with its higher Li$^+$ intercalation potential (1.7 V vs. Li$^+$/Li), ultrastable structure, cost-effectiveness, and minimal volume change (<4%), rendering it a highly promising anode material for LIBs.¹,² Nevertheless, the poor intrinsic electrical conductivity and low Li$^+$ migration rate of pristine TiO$_2$ impede its practical application. Addressing these challenges involves designing TiO$_2$ nanomaterials and integrating them with different carbonaceous substrates to enhance electron and ion transfer, while also providing a robust framework to accommodate stress during the lithiation/delithiation process.³

Currently, Ti$_3$C$_2$T$_x$ MXene is one of the most well-known MXenes, including its exceptional electrical conductivity, high surface area, tunable surface chemistry, and pseudocapacitive energy storage mechanisms, rendering it highly promising as a fast-charging anode for metal ion storage.⁴–⁶ Wang et al. described a unique hybrid architecture TiO$_2$/Ti$_3$C$_2$T$_x$ for ultrafast storage, prepared by self-assembly between positively charged TiO$_2$ spheres and negatively charged Ti$_3$C$_2$T$_x$ nanosheets.⁷ However, the reported method for synthesizing TiO$_2$/MXene structures typically involves two steps: (1) the synthesis of metal oxides and (2) the deposition of MXene.⁷,⁸ The preparation of related composites typically entails complex procedures leading to weak bonding interactions between TiO$_2$ materials and MXene layers.

Hence, there is a critical need to seek a straightforward technology of TiO$_2$-MXene composites with improved electrochemical properties.

The in situ conversion of Ti$_3$C$_2$T$_x$ into corresponding transition metal oxides (TiO$_2$) within the interlayers has been introduced,⁹,¹⁰ where the hybrid heterostructure not only mitigates the volume variation of TiO$_2$ but also prevents the stacking of Ti$_3$C$_2$T$_x$ nanosheets, seamlessly integrating the metallic conductivity of Ti$_3$C$_2$T$_x$ with the high capacity properties of metal oxide TiO$_2$.¹¹,¹² Li et al. have fabricated TiO$_2$ nanoparticles uniformly dispersing on the Ti$_3$C$_2$ flake surface to create a TiO$_2$/Ti$_3$C$_2$ nanocomposite through a one-step ethanol-thermal approach, which resulted in the reversible specific capacity of 257.3 mA h g$^{-1}$ at 50 mA g$^{-1}$.¹³ Importantly, the composite materials formed by in situ surface oxidation typically feature tight interfacial coupling between Ti$_3$C$_2$T$_x$ MXene and the active material TiO$_2$, thereby leading to superior electrochemical properties of the Ti$_3$C$_2$T$_x$/TiO$_2$ MXene composites.¹⁴

Herein, we employ in situ oxidation to engineer Ti$_3$C$_2$/TiO$_2$ composites with diverse morphologies, as illustrated in Scheme 1. Briefly, an aqueous dispersion of few-layered Ti$_3$C$_2$T$_x$ MXene was prepared by selectively exfoliating the Al layers from Ti$_3$AlC$_2$ MAX powder via a modified etching tactic involving a concentrated HCl solution enriched with LiF, followed by ultrasound peeling. Subsequently, the homogeneous suspension of Ti$_3$C$_2$T$_x$ MXene sheets promptly induced sedimentation upon the introduction of the melamine formaldehyde sphere (MFS), due to the electrostatic interactions between the cationic MFS spheres and the anionic surface of the MXene nanosheets, resulting in the assembly of an MXene-MFS network.¹⁵ The MFS was progressively eliminated through a thermal annealing procedure, eventually resulting in the formation of a 3D porous and hollow framework. After one-step in situ high-temperature thermal oxidation in N$_2$, TiO$_2$ nanorods wrapped by the 3D Ti$_3$C$_2$ MXene were produced (denoted as 3D Ti$_3$C$_2$/TiO$_2$), while preserving the 3D porous structure. In comparison, annealed 2D Ti$_3$C$_2$T$_x$ MXene resulted in TiO$_2$ nanorods grown on the 2D layer surface (denoted as 2D Ti$_3$C$_2$/TiO$_2$). When 2D or 3D Ti$_3$C$_2$
MXene was subjected to heat treatment in an air atmosphere, Ti$_3$C$_2$ MXene completely transformed into TiO$_2$ nanoparticles accordingly (denoted as 2D TiO$_2$ and 3D TiO$_2$).

The crystallographic form of the synthesized samples was investigated by powder X-ray diffraction (PXRD). As depicted in Fig. 1a, the (002) peak of Ti$_3$C$_2$T$_x$ MXene around 6.9° appeared after the etching of the Ti$_3$AlC$_2$ MAX phase by the LiF/HCl solution, indicating the successful removal of Al layers.\(^16\) The XRD pattern of the Ti$_3$C$_2$T$_x$/MFS hybrid after being self-assembled in a 3D wrinkle structure shows that the characteristic (002) peak of Ti$_3$C$_2$T$_x$ is also observed, but shifts toward a smaller angle (6.3°), suggesting a larger interlayer spacing of MXene due to the pyrolysis of the MFS templates. Importantly, the engineered 3D hybrid networks have been demonstrated to effectively mitigate the self-stacking tendency of the 2D Ti$_3$C$_2$T$_x$ flakes. Subsequently, the as-synthesized 2D or 3D Ti$_3$C$_2$ MXene nanosheets were in situ oxidized to form TiO$_2$ nanomaterials on the MXenes, yielding the derived TiO$_2$-based anode. The diffraction patterns of 2D TiO$_2$, 2D Ti$_3$C$_2$/TiO$_2$, 3D TiO$_2$, and 3D Ti$_3$C$_2$/TiO$_2$ reveal sharp peaks at 25.28°, 37.80°, and 48.05°, attributed to the (101), (004), and (200) crystallographic planes of anatase-structured TiO$_2$ (JCPDS no. 21-1272). Additionally, characteristic peaks for the (110), (101), (211), and (301) planes of the rutile phase of TiO$_2$ (JCPDS no. 21-1276) are observed at 27.44°, 36.08°, 54.32°, and 69.01°, respectively, suggesting the coexistence of diffraction peaks for both anatase and rutile TiO$_2$.\(^17\) Furthermore, the characteristic diffraction peaks for Ti$_3$C$_2$ MXene still appear in the 2D Ti$_3$C$_2$/TiO$_2$ and 3D Ti$_3$C$_2$/TiO$_2$ nanoarchitecture derived from calcination under a nitrogen atmosphere,\(^14,18\) confirming the coexistence of TiO$_2$ nanomaterial and Ti$_3$C$_2$ MXene. Conversely, samples calcined under high-temperature treatment in an air atmosphere only have the characteristic peak of TiO$_2$, indicating that the MXene precursor was oxidized into TiO$_2$ materials.\(^19\) This finding indicates the successful fabrication of a TiO$_2$/Ti$_3$C$_2$ MXene composite with various structures via effective partial thermal oxidation of the Ti layer in Ti$_3$C$_2$ MXene at high temperatures.

The bulk Ti$_3$AlC$_2$ phase transformed into an accordion-like multilayered Ti$_3$C$_2$ MXene through acid etching (Fig. S1a, ESI† and Fig. 1b), indicating the effective etching of the MAX.\(^20,21\) The few-layered Ti$_3$C$_2$ MXene surface, enriched with functional groups such as –OH, –O, and –F, was achieved through subsequent ultrasonic exfoliation (Fig. S1c, ESI†). The introduction of MFS (Fig. S1d, ESI†) facilitated electrostatic interactions, spontaneously leading to the self-assembly of the 2D layer structure into a 3D fold structure (Fig. S1e, ESI†). Subsequently, a 3D honeycomb-like architecture was obtained through the decomposition of the MFS templates (Fig. S1f, ESI†), which offer sufficient diffusion pathways for electron and ion transfer and effectively minimize the polarization of the electrode. Ultimately, Ti$_3$C$_2$/TiO$_2$ was synthesized through the heat treatment of Ti$_3$C$_2$ MXene nanosheets in different atmospheres. Clearly, TiO$_2$ nanoparticles are closely connected forming the 2D nanoflakes, and the stacked layers of Ti$_3$C$_2$ disappear (Fig. 2a and Fig. S2a, ESI†), which due to the typical layered T$_x$C$_3$ nanosheets offers a suitable derivative template to regulate the growth of TiO$_2$ nanocrystals.\(^19\) Fig. 2b and Fig. S2d (ESI†) depict the growth of TiO$_2$ nanorods on the surface of 2D Ti$_3$C$_2$ during the heating process under a nitrogen atmosphere. As observed in Fig. 2c and Fig. S2g (ESI†), well-aggregated nanoparticles of TiO$_2$ are derived from the complete oxidation of the 3D Ti$_3$C$_2$. In Fig. 2d and 3a, the generated thick nanorods of TiO$_2$ appear on the surface of the 3D Ti$_3$C$_2$. The lattice fringes measured at 0.35 nm and 0.21 nm correspond to the anatase-structured TiO$_2$ (101) planes and rutile-structured TiO$_2$ (111) planes, respectively (Fig. S3b, ESI†). The novel structure of 3D Ti$_3$C$_2$/TiO$_2$ not only promotes the charge transfer between the TiO$_2$ nanocrystals but also validly buffers the volume variation of TiO$_2$ along the widthwise direction in the charge/discharge process. Besides, according to elemental mapping images (Fig. S3c, ESI†), the 3D Ti$_3$C$_2$/TiO$_2$ architecture is mainly composed of C, O, N, and Ti elements. In brief, the above
The incorporation of graphitic carbon enhances the conductivity, which boosts the formation of TiO$_2$ nanorods grown on the three-dimensional Ti$_3$C$_2$ MXene. The rise in the specific surface area could be ascribed to the transformation of Ti$_3$C$_2$ MXene into TiO$_2$ nanomaterials. The specific surface area of TiO$_2$, Ti$_3$C$_2$/TiO$_2$, and 3D Ti$_3$C$_2$/TiO$_2$ are around 27.8, 18.9, and 12.3 m$^2$/g, respectively.

The survey spectrum of 3D Ti$_3$C$_2$/TiO$_2$ confirms the existence of C, O, N, and Ti elements, demonstrating the N-doping of the 3D Ti$_3$C$_2$ MXene during the carbonization process of melamine–formaldehyde (MFS) spheres. In Fig. 1e, the C1s peak at 284.8 eV contributes to C–C bonds, while the other peaks appearing at 281.4, 286.3, and 289.6 eV belong to C–Ti, C–O, and C=O, respectively. The O1s peaks in Fig. 1g are observed at 530.0 and 531.4, representing Ti–O and C–O bonds, respectively. In the XPS spectra of N1s (Fig. 1h), the peaks can be related to Ti–N (396.9 eV), pyridinic N (397.5 eV) and pyridinic N (401.6 eV). The Ti2p spectra (Fig. 1i) consist of six characteristic peaks as three doublets of de-convoluted peaks centered at 457.1/462.8, 458.6/464.6, and 460.3/466.2 eV assigned to the Ti$^{2+}$, Ti$^{3+}$ and Ti$^{4+}$, respectively.23 The high valence state (Ti$^{4+}$) of Ti species of 2D TiO$_2$ and 3D TiO$_2$ shows an increasing trend because of the oxidation of a low valence state (Ti$^{2+}$ or Ti$^{3+}$) in the air atmosphere (Fig. S4a–c, ESI†).

To assess the comprehensive structural merits of the synthesized hybrid structure applied as the anode material for LIBs, the electrochemical performance of the corresponding materials is investigated. A cathodic peak at 0.70 V and an anodic peak at 0.95 V are both illustrated in the first cycle in the curves of the 3D Ti$_3$C$_2$/TiO$_2$ (Fig. 3a) and 2D Ti$_3$C$_2$/TiO$_2$ (Fig. S2b, ESI†), corresponding to the Li$^+$ intercalation and deintercalation within the interlayers of Ti$_3$C$_2$.20 Besides, a broad peak at 1.0 V in the first scan is assigned to the generated solid electrolyte mesophase (SEI) and the irreversible loss of the electrolyte. Additionally, the peaks at 1.7 and 2.2 V relate to the redox reaction of TiO$_2$ materials (Fig. S4d and f, ESI†). Moreover, after the first cycle, subsequent CV curves almost overlapped, certifying that the hybrid 3D Ti$_3$C$_2$/TiO$_2$ and 2D Ti$_3$C$_2$/TiO$_2$ electrodes show high electrochemical reversibility and stability in the process of the insertion/extraction of electrolyte ions for enhanced lithium storage performance.15 To delve into the kinetic capabilities of 3D Ti$_3$C$_2$/TiO$_2$, the CV curves at different sweep speeds were conducted (Fig. S5a, ESI†). The capacitive contribution of 3D Ti$_3$C$_2$/TiO$_2$ increases with the sweep rate, culminating in a dominance of 89.4% of the total capacity at the 1.0 mV s$^{-1}$ sweep rate (Fig. S5c and d, ESI†). The charge/discharge curves of the 3D Ti$_3$C$_2$/TiO$_2$ process have a higher initial discharge and charge capacity of 1516.3 and 864.0 mA h g$^{-1}$ than the other samples (Fig. 3b) due to its successful construction of TiO$_2$ nanorod-doped 3D porous Ti$_3$C$_2$ MXene. The initial Coulombic efficiency (ICE) of the 3D Ti$_3$C$_2$/TiO$_2$ is calculated as 57.0%, where the irreversible capacity loss is owing to the unstable SEI formation.24 Meanwhile, the inferior ICEs of 50.6%, 28.7% and 29.6% (charge/discharge capacities of 179.0/347.9, 338.6/1177.5, 120.2/405.4 mA h g$^{-1}$) are observed for the 2D Ti$_3$C$_2$/TiO$_2$, 2D TiO$_2$ and 3D TiO$_2$, respectively.

Fig. 3c depicts the rate performances of the four samples, wherein the 3D Ti$_3$C$_2$/TiO$_2$ clearly demonstrates superior Li$^+$ transport rate compared to the other three samples in all rate capability tests, attributable to its conductive 3D porous structure to support shorter charge transportation pathways, thereby enhancing the rate capability.15,25 More strikingly, the 3D Ti$_3$C$_2$/TiO$_2$ electrode achieves satisfactory capacity retention with discharge capacities of 287.8, 186.3, 157.9, 126.3, 93.8, and 73.3 mA h g$^{-1}$ at various current densities from 0.1 to 0.3, 0.5,
1.0, 2.0 and 3.0 A g⁻¹, respectively. Even when the current density switches back to the initial 0.1 A g⁻¹, the specific capacity of 208.2 mA h g⁻¹ was still realized, signifying the excellent capability to sustain long repeated lithiation/delithiation behavior of the 3D Ti₃C₂/TiO₂ material.⁶,²⁶ Fig. 3d further compares the long-term cycling stability for the four samples evaluated at 1.0 A g⁻¹. The 3D Ti₃C₂/TiO₂ displays a higher specific capacity of 384.1 mA h g⁻¹ even after 600 cycles at 1.0 A g⁻¹ than the 2D Ti₃C₂/TiO₂, 2D TiO₂ and 3D TiO₂. TiO₂ nanorods grown on the surface of 2D or 3D Ti₃C₂ MXene can efficiently relieve the tension of MXene sheets and reduce the contact between the surface defects of MXene sheets and electrolyte, greatly enhancing the discharging capacity of the composites. However, for 2D or 3D TiO₂, excessive TiO₂ nanoparticles are inclined to aggregate, leading to lower discharging capacity. Remarkably, the discharging capacity of the 3D Ti₃C₂/TiO₂ shows an obvious increase upon cycling, primarily attributed to the continuous activation of Li⁺ storage sites of the active material during cycling.¹⁶ Meanwhile, the repeated Li⁺ insertion/extraction brings the expansion of the 3D Ti₃C₂ interlayer spacing, providing more favorable active sites for anion and electron transportation. Impressively, nearly ~100% Coulombic efficiency is well maintained for the 3D Ti₃C₂/TiO₂ nanocomposites after 600 consecutive cycles. Electrochemical impedance spectroscopy (EIS, Fig. 3e) further confirms the lower electron transfer resistance (Rct) and higher lithium ion diffusion coefficient (1.31 × 10⁻¹³ cm² s⁻¹) of the 3D Ti₃C₂/TiO₂ composite (37.044 Ω) compared to 2D Ti₃C₂/TiO₂ (94.938 Ω), 2D TiO₂ (146.05 Ω) and 3D TiO₂ (129.59 Ω), ascribed to its 3D conductive MXene framework offering increased surface area and shorter diffusion pathways to improve the ionic transport kinetics [Fig. S6, ESI†].²⁶ Consequently, the 3D Ti₃C₂/TiO₂ composite demonstrates enhanced cycling durability in LIBs compared to other materials reported previously (Table S1, ESI†).

In summary, we present a straightforward in situ derivatization strategy to synthesize the porous hierarchical 3D Ti₃C₂/TiO₂ nanorod architecture as an anode material for enhanced lithium-ion storage capability. The nanohybrid was obtained by utilizing MFS as the template to fabricate a 3D honeycomb-like Ti₃C₂–MXene followed by carbonization under a nitrogen atmosphere. During this process, the high-temperature thermal instability of the Ti₃C₂–MXene substrate promotes the transformation of the Ti layer on the MXene surface into 1D TiO₂ nanorods. The 1D TiO₂ nanorods, encapsulating the surface of the 3D Ti₃C₂ preserve the MXene layers from structural collapse. Moreover, the internal MXene matrix acts as a conductive scaffold, enhancing the conductivity of TiO₂ nanorods in favor of the competitive electrochemical property of the composites. Therefore, the hierarchical 3D Ti₃C₂/TiO₂ architecture indicates superior rate performances and outstanding cyclic stability. This work provides further opportunities for transition metal oxide-based materials for energy storage applications.

This work was supported by the National Natural Science Foundation of China (21978157), the Natural Science Foundation of Shandong Province (ZR2022Q0839 and ZR2023MB093) and the Key Development Project of Shandong Province (2022CXGC020310).

Data availability
The data supporting this article have been included as part of the ESL.

Conflicts of interest
There are no conflicts to declare.

Notes and references