

Conducting and Lithiophilic MXene/Graphene Framework for High-Capacity, Dendrite-Free Lithium–Metal Anodes

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Supporting Information

ABSTRACT: Li-metal anode is widely acknowledged as the ideal anode for high-energy-density batteries, but seriously hindered by the uncontrollable dendrite growth and infinite volume change. Toward this goal, suitable stable scaffolds for dendrite-free Li anodes with large current density (>5 mA cm^{-2}) and high Li loading (>90%) are highly in demand. Herein, a conductive and lithiophilic three-dimensional (3D) MXene/graphene (MG) framework is demonstrated for a dendrite-free Li-metal anode. Benefiting from its high surface area (259 m² g⁻¹) and lightweight nature with uniformly dispersed lithiophilic MXene nanosheets as Li nucleation sites, the as-formed 3D MG scaffold showcases an ultrahigh Li content (\sim 92% of the theoretical capacity), as



well as strong capabilities in suppressing the Li-dendrite formation and accommodating the volume changes. Consequently, the MG-based electrode exhibits high Coulombic efficiencies (~99%) with a record lifespan up to 2700 h and is stable for 230 cycles at an ultrahigh current density of 20 mA cm⁻². When coupled with Li₄Ti₅O₁₂ or sulfur, the MG-Li/Li₄Ti₅O₁₂ full-cell offers an enhanced capacity of 142 mAh g^{-1} after 450 cycles, while the MG-Li/sulfur cell delivers an improved rate performance, implying the great potential of this 3D MG framework for building long-lifetime, high-energy-density batteries.

KEYWORDS: MXene, Li-metal anode, 3D framework, dendrite-free, graphene

he ever-increasing demands for electric vehicles and portable electronics have accelerated the continuous development of high-energy-density rechargeable batteries.¹⁻³ Lithium (Li) metal possesses an ultrahigh theoretical capacity (3860 mAh g^{-1}) and the lowest redox potential (-3.04 V vs standard hydrogen electrode) compared to other possible candidates, thus has received substantial research focus in the electrochemical energy storage fields.⁴⁻ When matched with high-capacity cathodes such as sulfur (S) and O2, the corresponding theoretical energy densities are predicated to be as high as 2600 Wh kg⁻¹ for Li–S batteries and 11 400 Wh kg⁻¹ for Li–O₂ batteries.^{8–11} However, their commercialization applications have been seriously hindered by the uncontrollable growth of Li dendrites and infinite volume changes during charge-discharge processes.¹²⁻¹

The growth of Li dendrites is known to be influenced by several factors, including (i) inhomogeneous distribution of space-charge and current density on the anode surface, (ii) the chemical and electrochemical reactions between the anode and electrolyte, and (iii) the cracking of the solid electrolyte interphase (SEI).^{15,16} To overcome these issues, a number of strategies have been proposed focusing on either new electrolyte systems (including highly concentrated electrolytes, dual- or ternary-salt electrolytes and additives)¹⁷⁻²⁰ or Libased alloys (e.g., Li-Au, Li-Zn, Li-Al, Li-Si).²¹⁻²⁵ For

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Figure 1. Fabrication and characterization of the 3D MG-Li anode. (a) Schematic illustration of the fabrication process of the 3D MG-Li anode and corresponding photographs of the MGO film, MG film, and MG-Li anode. (b, c) AFM images and height profiles of (b) MXene and (c) GO nanosheets. (d) SEM image of the MG film. Inset is a photograph of the bent MG film. (e) EDS elemental mapping of carbon (red), titanium (green), and fluorine (blue). (f, g) Raman spectra of (f) MXene film, MG aerogels and (g) rGO, MG aerogels. (h) XPS full spectra of MXene and MG aerogels. (i) N_2 adsorption-desorption isotherm of the MG film. Inset is the plot of the pore size distribution. (j) Photographs (top) and corresponding cross-section SEM image (bottom) of the MG-Li anode.

instance, Zhou *et al.* reported on a concentrated ternary-salt electrolyte (LiTFSI-LiNO₃-LiFSI) for a stable Li-metal anode and achieved a high Coulombic efficiency of 99.1%;¹⁷ Xu *et al.* employed LiPF₆ as an additive in a LiTFSI-LiBOB dual-salt electrolyte, and a cyclability of 97.1% capacity was retained after 500 cycles.¹⁸ On the other hand, Nazar *et al.* demonstrated the formation of a Li–Zn (In) alloy, which exhibited a stable performance over 1500 cycles with a Li₄Ti₅O₁₂ cathode.²¹ Aside from these endeavors, designing a stable artificial physical protective barrier also represents a delicate strategy to suppress Li dendrite formation and realize long cycle life batteries.^{26,27} However, these strategies to some extent cannot fully accommodate the infinite volume changes during Li electrochemical cycling, which result in huge internal stress fluctuations and an unstable interface.

On the other side, three-dimensional (3D) hosts with excellent chemical stability and large surface areas are expected to simultaneously suppress the growth of Li dendrites and minimize the volume changes of Li-metal anodes.^{28,29} So far, various 3D porous frameworks based on porous Cu foil,³⁰

nickel foam,^{31,32} and 3D polyimide³³ were reported as effective hosts for Li metal. However, the reported 3D lithium anodes suffer from either a relatively low Li content (<60%) or poor electrical conductivity, limiting the achievable energy density. A 3D conductive carbon framework is thus frequently employed as a lightweight host for Li, especially at a high loading amount. For example, 3D reduced graphene oxide (rGO) film and carbon nanotube (CNT) paper were studied as Li flexible hosts, achieving a capacity up to 3390 mAh g⁻¹ and a mass loading of 80.7%, respectively.^{34,35} Unfortunately, most nanocarbon frameworks are poor in lithiophilicity, leading to inhomogeneous nucleation/deposition processes and loose contact between Li and the host carrier. The subsequent cycling inevitably results in the formation of Li dendrites and "dead Li". This is especially true at a high current density (>5 mA cm⁻²).

To this end, introducing lithiophilic species into 3D highly conductive nanocarbon hosts without compromising the homogeneous nucleation sites is urgently in demand for realizing both high lithium loading and dendrite-free metallic



Figure 2. Mechanism illustration of the MG film for Li deposition. (a) Binding energy of a Li atom with graphene and MXene. (b) Deformation charge density at a Li atom adsorption site of graphene and MXene. (c) Migration paths and (d) corresponding diffusion barrier profile for Li diffusion on MXene. (e) Electrical conductivity of an MG and a pure rGO electrode. (f) Photograph and (g) top SEM images showing nonuniform Li deposition on rGO and MXene guided uniform plating on an MG electrode (1 mAh cm⁻²). An MXene layer is deposited on the upper half of the rGO electrode. (h) Schematic illustrating the mechanism for MG and pure rGO electrodes during the Li plating/striping process. (i) Schematics of the Li adatom on a Li surface with and without electrolytes. The white and yellow areas represent vacuum and electrolyte, respectively. (j, k) Contact angle of an organic electrolyte drop on (j) a MG-Li anode and (k) a bare Li anode at the initial state (top) or 1 min later (bottom).

Li anodes.^{36–38} Particular attention is given to 2D MXene (Ti₃C₂T_x, the most extensively studied MXene), a family of two-dimensional (2D) carbides and nitrides of transition metals (M), where X stands for carbon or nitrogen and T_x represents hydroxyl-, oxygen-, and/or fluorine-terminated groups.^{39,40} The excellent electrical conductivity and abundant lithiophilic functional groups (O, F, and OH) on the MXene surface enable it to be an ideal platform for Li deposition.^{41–44} However, drying and electrode fabrication decreases the achievable lithiophilic sites for Li deposition.^{45,46} Said otherwise, designing a 3D MXene/carbon conductive, lightweight framework with high lithium mass loading and large current density has been proved to be quite difficult.^{47,48}

Herein, we report on a highly conductive, lithiophilic, and lightweight MXene/graphene (MG) framework as the Li scaffold *via* a thermal infusion strategy. Such a 3D MG framework possesses a high surface area (259 m² g⁻¹) and interconnected pore structure, allowing a high Li loading amount while preserving excellent mechanical properties. The structure design in the flexible lithium–metal anode (MG-Li) ensures a capacity up to 3560 mAh g⁻¹ coupled with Coulombic efficiencies (>99%) and cycling stability up to 2700 h in the absence of Li dendrites. The cell can withstand

an extremely high current density of 20.0 mA cm⁻² with very small potential polarization (30 mV). The MG-Li anode also demonstrates improved rate capability and cyclability in the as-assembled full-cell, showcasing promising applications for future long lifetime, high-energy-density batteries.

RESULTS AND DISCUSSION

The fabrication process of the 3D MG-Li anode is schematically shown in Figure 1a. First, the homogeneous mixed suspensions of MXene (Figure S1) and graphene oxide (GO) (ratio of GO and MXene was 3:1) were obtained by highenergy ultrasonication, and then freeze-dried to form 3D freestanding and lightweight MXene/GO (MGO) aerogels, with a mass density of 3.9 mg cm^{-3} . Notably, the introduction of MXene into MGO aerogels greatly improves the mechanical strength (Figure S2).⁴⁹ In this process, the small-size MXene nanosheets (300-500 nm) are uniformly dispersed on the surface of large-size GO nanosheets $(1-5 \ \mu m)$ in 3D aerogels (Figure S3), as observed by transmission electron microscopy (TEM) (Figure S4) and atomic force microscope (AFM) images (Figure 1b,c).50 Second, 3D MGO aerogels were mechanically pressed (at 10 MPa) to prepare layer-stacked MGO films for lithium deposition (Figure S5). Impressively,



Figure 3. Coulombic efficiencies of MG, rGO, and Cu electrodes. (a) Coulombic efficiencies of the MG electrodes with different mass ratios of GO and MXene and a pure GO electrode under a deposition capacity of 0.5 mAh cm⁻² at 0.5 mA cm⁻². (b, c) Coulombic efficiencies of MG, rGO, and Cu foil at a current density of (b) 0.5 mA cm⁻² and (c) 1 mA cm⁻² with the capacity of 2 mAh cm⁻². (d) Coulombic efficiencies of MG and Cu electrodes with increasing current densities from 0.25 to 2.5 mA cm⁻². Li was plated for 1 h at each cycle with a certain current density and then stripped away up to 1.0 V. (e) Long-life Coulombic efficiencies of an MG electrode at a current density of 0.5 mA cm⁻² with a Li deposition amount of 5 mAh cm⁻² for 2700 h. (f) Enlarged plating–stripping curves of MG, rGO, and Cu foil electrodes at 0.5 mA cm⁻². (g) Nyquist plots of MG, rGO, and Cu foil electrodes at pristine cycles. Inset is the relationship between Z' and the square root of the frequency ($\omega^{-1/2}$) in the low-frequency region.

when the MGO film was partially put into contact with molten Li, a spark reaction occurred immediately across the film and realized a rapid reduction of GO, forming a 3D MG interconnected nanoporous framework (Movie S1, Figure 1d).³⁴ In the framework, the single-layer MXene nanosheets homogeneously attach on the surface of graphene, as evidenced by the backscattered scanning electron microscope (SEM) image (Figure S6) and the energy-dispersive spectrometer (EDS) elemental mapping (Figure 1e and Figure \$7). Such a 3D framework is mechanically robust (inset of Figure 1d) and effective in suppressing MXene restacking and oxidation behaviors.⁵¹ X-ray diffraction (XRD) patterns (Figure S8) and Raman spectra (Figure 1f,g) of MG aerogels reveal that MXene and rGO characteristic peaks coexisted in the MG film. X-ray photoelectron spectroscopy (XPS, Figure 1h) indicates that a considrable increasement of O and C in the MG aerogel, which can be explained by the introduction of rGO. Further, the Ti 2p and O 1s core-level XPS spectra reveal that the peaks attributed to $Ti-O_{2-x}F_x$ and $C-Ti-O_x$ in the MG samples become more intense compared to peaks in the MXene film, implying a strong interaction between MXene and rGO. Besides, F 1s signals are clearly detected in both pure MXene and MG (Figure S9), which are expected to play a significant role in the nucleation of metallic Li during plating, as will be discussed later. Based on the Fourier transform infrared spectroscopy (FTIR, Figure S10), it is observed that after the spark reduction reaction the peaks of surface -OH groups have been almost removed, while other peaks attributed to oxygen-containing surface moieties are retained. Beneficial from these oxygen- and fluorine-containing groups, coupled with enhanced lithiophilicity and capillary forces, Li could be readily infused into the nanoporous channels within 1 min by placing the 3D MG aerogel onto the molten media (Movie S1). In a sharp contrast, it is difficult to infuse Li into the pure MXene film (Movie S2). This discrepancy can be fairly attributed to the porosity differences in two samples.

While MG possesses a 3D porous structure with high specific surface area (259 m² g⁻¹, Figure 1i), MXene film is typically compact and thus in lack of necessary nanoporous channels (specific surface area ~0.2 m² g⁻¹, Figure S11) for Li plating. It is noteworthy that, after Li metal was completely stripped from the MG-Li anode, the lithiophilic oxygen-containing groups of rGO are almost removed due to the strong deoxidizing ability of molten Li, indicative of the full transformation of GO into graphene (Figure S12).

For practical pouch and cylindrical cell assembling, good electrode flexibility is critical for the folding or rolling processes.⁵³ Thanks to the mechanically flexible nature and layered structure of MG films (inset of Figure 1d and Figure S13), the pliability of the MG-Li anode (Figure 1j) is significantly enhanced. As a result, the porous chambers of the MG scaffold are uniformly infused by Li with a large thickness of ~500 μ m and ultrahigh lithium mass loading up to 92% without roughening the surface, indicative of extraordinary affinity with Li and high thermal stability of MG aerogels. Furthermore, the thickness and shape of MG-Li anodes can be easily tuned by modifying the thickness and shape of the MG films (Figure S14), showcasing the wide applicability of our proposed strategy for practical applications.

To understand the lithiophilic mechanism of the Li deposition process on the MG film, density functional theory (DFT) calculations were performed to determine the adsorption energy between a Li atom with graphene and MXene clusters (Figure 2a). It is found that the MXene surface exhibits a larger binding energy of -2.93 eV than that of graphene (-2.62 eV), suggesting that the surface of the former is indeed more lithiophilic. Meanwhile, the local charge density between MXene and Li atoms is higher compared to that of graphene–Li (Figure 2b), further indicating stronger interactions when using MXene to anchor Li. Consequently, the well-distributed lithiophilic MXene nanosheet could significantly decrease the electroplating overpotentials and guide the



Figure 4. Electrochemical performance of symmetric cells based on MG-Li, rGO-Li, and bare Li electrodes, respectively. (a) Galvanostatic cycling of symmetric cells based on MG-Li, rGO-Li, and bare Li electrodes with a current density of 3 mA cm⁻² under a stripping/plating capacity of 1 mAh cm⁻². Inset is corresponding detailed voltage profiles of the 100th, 300th, and 700th cycles, respectively. (b) High current density cycling of symmetric cells based on MG-Li, rGO-Li, and bare Li electrodes with a stripping/plating capacity of 1 mAh cm⁻². (c) Galvanostatic cycling of an MG-Li symmetric cell obtained at an ultrahigh current density of 20 mA cm⁻² under a higher capacity of 5 mAh cm⁻². (d) Rate performance of symmetric cells based on the MG-Li, rGO-Li, and bare Li electrodes, respectively. (e) Nyquist plots of the symmetric cells before cycles. (f) Full Li stripping curve of the MG-Li electrode to 0.5 V vs Li⁺/Li. (g) Comparison of gravimetric capacity vs current density and cycle time of the MG-Li anode with currently reported high gravimetric capacity Li composite anodes.

smooth Li deposition across the MG framework. To reflect the rate capability of the Li anode, the mobility of Li atoms on the surface of monolayer MXene was examined by assuming that Li atoms diffuses along the path $i \rightarrow iv$ (Figure 2c). It is found that Li is preferably adsorbed on the positions of both i and iii. That is to say, the C atom sites are more favorable to form a metastable configuration (Figure 2d). Further investigations on the Li diffusion barrier in the case of C-defect and Ti-defect conclude that the Ti-defect influences the Li ion migration energy to a large extent and greatly accelerates the Li ion diffusion (Figure S15).

Adding MXene nanosheets (3600 S cm^{-1}) to the 3D scaffold also greatly improve the electrical conductivity. As seen in Figure 2e, the MG film displays an electrical conductivity of 7.6 S cm⁻¹, almost 3 times higher than that of a pure rGO film (2.6 S cm^{-1}). To illustrate the importance of high electrical conductivity and lithiophilicity of MXene, we fabricated a rGO film electrode with a pure MXene layer coated on half of the rGO surface (Figure 2f). After deposition of 1 mAh cm⁻² Li at a current density of 0.25 mA cm⁻², impressively, the surface of the MXene-modified part was covered by Li without any growth of Li dendrites. On the contrary, irregular Li dendrites were found on the bare rGO

part (Figure 2g and Figure S16).⁵⁴ These results clearly suggest the importance of delicate structure design on highly lithiophilic MXene nanosheets decorated on rGO as preferential Li deposition sites, forming a 3D MG scaffold to suppress the of Li dendrite formation (Figure 2h).

More importantly, as confirmed by DFT calculations in Figure 2i, the energy for Li ion adsorption is much lower when the electrolyte is in contact with the MG-Li surface.⁵⁵ It also found that the contact angle of the electrolyte droplet on the MG-Li significantly decreased to 0° after 1 min (Figure 2j). This is in a sharp contrast to the bare Li, whose contact angle slightly changed to ~16.9° (Figure 2k). The enhanced wettability of the MG-Li anode sufficiently guarantees an uniform distribution of Li ions in the electrode/electrolyte interfaces. As a result, the 3D MG scaffold allows a homogeneous depositon of Li metal.

To examine the effect of MXene on the plating/stripping behaviors, the Coulombic efficiencies of MG aerogels with different mass ratios of MXene to GO were evaluated under a deposition capacity of 0.5 mAh cm⁻² at a current density of 0.5 mA cm⁻². The results are shown in Figure 3a. Apparently, the Coulombic efficiencies of pure rGO aerogels drop quickly to 88% after 35 cycles, possibly because the oxygen-containing

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Figure 5. Morphologies of Li electrodeposition on MG-Li and bare Li anodes under different stages. (a) Voltage profiles of a typical Listripping-plating process at a current density of 2 mA cm⁻² with a capacity of 10 mAh cm⁻² for MG-Li and Li anodes and (b) corresponding thickness at various stages of cycling. #1 corresponds to the stage before cycling, #2 stands for the stage after 50% Li extraction, and #3 represents the stage after Li plating back. (c, d) Cross-section SEM images showing the volume fluctuation and shape change of (c) MG-Li and (d) bare Li anodes at various stages of cycling #1, #2, and #3. Insets are top-view SEM images. (e) Schematic illustration of the microscale Li plating and stripping in 3D MG-Li (top) and bulk Li anodes (bottom).

groups consumed a lot of cyclable Li ions for SEI formation. When the mass ratio of GO to MXene decreases from 5:1 to 3:1, higher and more stable Coulombic efficiencies (98%) as well as longer lifespans are attained. When the MXene content is 50%, the Coulombic efficiencies of the MG decrease to 86% for 85 cycles, implying an optimal MXene content does exist. We selected the ratio of GO to MXene of 3:1 as the optimized condition and conducted the discussion based on this ratio unless specifically noted. The Coulombic efficiencies of the MG electrode reached 98.0% at 0.5 mA cm⁻² for 2 mAh cm⁻² and were maintained at 99.0% after 100 cycles (Figure 3b). The stable cycling performance of the MG-Li anode is in sharp contrast to that of rGO-Li or bare Cu-Li electrodes, which rapidly drop to 78% only after 53 cycles and 18% after 46 cycles, respectively (Figure 3b). The cycling differences of the three electrodes are more pronounced when increasing the current density to 1 mA cm⁻² (Figure 3c) or capacity to 5 mAh cm^{-2} (Figure S17), highlighting the structure design in the realization of long cycle life lithium anodes. The rate performances of MG and Cu electrodes under increased current densities ranging from 0.25 to 2.5 mA cm⁻² at the same plating time of 1 h were also compared. As shown in Figure 3d, the MG electrode still retains highly stable Coulombic efficiencies under a Li deposition capacity of 2.5 mAh cm^{-2} . On the other hand, the Cu electrode fails to maintain stable Coulombic efficiencies when increasing the areal capacity. We further evaluate the rate performance of these two electrodes. Unlike the Cu electrode, which quickly decays as the capacity goes beyond 0.5 mAh cm^{-2} , the MG electrode maintains an excellent stability with stepwise increased capacity from 0.25 to 6 mAh cm^{-2} (Figure S18), coupled with high Coulombic efficiencies of ~99% over 2700 h at 5 mAh cm^{-2} (Figure 3e). To the best of our knowledge, this is the longest cycle time reported under such high Coulombic efficiencies to date. Moreover, the plating overpotential of MG electrode is \sim 36 mV, much lower than that of rGO (62 mV) and Cu (71 mV) electrodes, suggesting the overall ionic transport resistance of MG is the lowest (Figure 3f and Figure S19). This is further confirmed by the electrochemical impedance spectroscopy (EIS), which reveals a much smaller interfacial charge transfer resistance for MG (10.5 Ω) than

those of rGO (27.9 Ω) and Cu (54.1 Ω) electrodes. The Li ion diffusion coefficient of MG, derived from the EIS, is calculated to be 6.99 × 10⁻⁹ cm² s⁻¹, which is higher than those of rGO (1.91 × 10⁻⁹ cm² s⁻¹) and Cu (1.77 × 10⁻⁹ cm² s⁻¹) (Figure 3g), indicative of enhanced Li ion conductivity in the 3D MG framework.⁵⁶

To highlight the advantages of the MG-Li electrode, we compared the long-term voltage profiles of symmetric cells based on MG-Li, rGO-Li, and bare Li foil, respectively. Figure 4a shows that the overpotentials of Li foil and rGO-Li symmetric cells increase sharply after 30 and 90 h, respectively, while flat and consistent voltage profiles for more than 500 h are found in the MG-Li cell. To study the evolution of the voltage profiles in detail, the 100th, 300th, and 700th cycles of the MG-Li cell are further enlarged (insets of Figure 4a). Evidently, a flat voltage plateau (\sim 13 mV) at both the charging and discharging states can be maintained throughout all the cycles. Increasing the current density to 5 mA cm^{-2} , the differences in the cycling stability and overpotential become more pronounced for different cells (Figure 4b). For example, the stripping/plating overpotential for an MG-Li-based symmetric cell is only ~ 25 mV with a stable life over 1000 cycles. However, symmetric cells based on bare Li and rGO-Li electrodes fail quickly with substantial voltage fluctuation at the 28th (~600 mV) and 77th (~428 mV) cycles, respectively (Figure S20). Impressively, our MG-Li electrode also displays an outstanding cycling stability (500 h with a voltage plateau of 18 mV) in a highly active Li-ion battery-based carbonyl electrolyte (1 mA cm⁻², 1 mAh cm⁻², Figure S21). Further increasing the cycling capacity to 5 mAh cm⁻² and ultrahigh current density to 20 mA cm⁻², the voltage curves of the MG-Li cell represent a small hysteresis of only 30 mV without any indication of short circuit up to 120 h (Figure 4c), which has rarely been achieved in earlier studies. The excellent rate performance of the MG-Li symmetric cell is evidenced by the fact that no huge voltage fluctuation is observed when the current density increases from 0.5 to 5 mA cm⁻² at a fixed stripping/plating capacity of 1 mAh cm⁻² (Figure 4d and Figure S22). Correspondingly, the EIS reveals a lower interfacial charge transfer resistance of 31 Ω for MG-Li compared to bare Li (242 Ω) and rGO-Li (60 Ω) (Figure 4e).



Figure 6. Electrochemical performance of full cells based on MG-Li, rGO-Li, and bare Li anode paired with LTO or pure S cathode. (a) Galvanostatic charge and discharge curves obtained at different cycles, (b) cycling stability for 450 cycles tested at 1.0 C (1.0 C = 175 mAh g^{-1} for LTO anode), and (c) rate performance of MG-Li/LTO, rGO-Li/LTO, and bare Li/LTO full cells. (d) Rate capability, (e) galvanostatic charge and discharge curves obtained at the first and 300th cycles, and (f) cycling stability for 300 cycles tested at 0.5 C (1.0 C = 1675 mAh g^{-1} for S cathode) of MG-Li/S, rGO-Li/S, and bare Li/S full cells.

The small charge transport resistance and excellent wettability of the MG-Li electrode (Figure 2j) enable a uniform Li nucleation and guarantee a superior electrochemical performance of symmetric cells. Moreover, the MG-Li delivers a specific capacity up to \sim 3560 mAh g⁻¹ (\sim 92% of the theoretical capacity of metal Li) based on the mass of the whole electrode when charged to 0.5 V (Figure 4f and Table S1). Such a high capacity is mainly attributed to the 3D conducting, stable, interconnected porous structure of MG aerogels (Figure S23). It should be emphasized that the 3D MG-Li has simultaneously achieved an ultrahigh mass capacity of 3560 mAh g^{-1} , ultrahigh cycle rate of 20 mA cm⁻², and long cycle time of 120 h, which is superior to the reported state-ofthe-art composite-Li anodes (Figure 4f, Table S2), such as Ni foam-Li (2061 mAh g^{-1} , 5 mA cm⁻², 40 h),³¹ graphitized carbon fibers-Li (1254 mAh g^{-1} , 4 mA cm⁻², 70 h),⁵⁷ polyimide-Li (2070 mAh g^{-1} , 5 mA cm⁻², 39 h),³³ and carbonized eggplant-Li (3461 mAh g^{-1} , 10 mA cm⁻², 100 L) 58 h).58

To further evaluate the structural stability of MG-Li during galvanostatic cycling, the cells with the same thickness of \sim 500 μ m as bare Li anodes were subjected to a typical Li-strippingplating process at a current density of 2 mA cm⁻² with a fixed capacity of 10 mAh cm⁻². Notably, the MG-Li cell shows a more stable voltage plateau and lower voltage hysteresis (15 mV) than that of a bare Li cell (50 mV), indicative of a superior stable SEI film during cycling and a fast Li deposition process (Figure 5a and Figure S24). To clearly visualize the electrode thickness variation, we further examined the crosssection SEM morphologies of the Li stripping-plating process on MG-Li and bare Li electrodes under different stages of cycling (Figure 5b-d). As expected, after extracting a 10 mAh cm⁻² capacity of Li, the MG-Li anode exhibits a small volume change, and the thickness slightly changes from 510 μ m before cycling to 490 μ m after lithium extraction, then back to 530

 μ m after plating. The overall morphology remains intact, and no observable Li dendrites are found on the electrode (Figure 5c). In sharp contrast, the shape and thickness of the bare Li anode change dramatically from 480 μ m to 210 μ m and back to 410 μ m upon cycling. The huge thickness/volume fluctuation can be fairly attributed to the lack of a stable scaffold, as well as the formation of massive arrays of Li dendrites observed after cycling (Figure 5d and Figure S25). As previously mentioned, the 3D porous MG framework not only offers a stable flexible scaffold to minimize the volume changes for ultrahigh mass-loading Li, but also efficiently dissipates high current density thanks to the evenly distributed lithiophilic MXene in the whole 3D skeleton. As a result, the Li dendrite growth is greatly inhibited (Figure 5e).⁵⁹

To highlight practical applications, we first paired the MG-Li anode with a Li4Ti5O12 (LTO) cathode to assemble the MG-Li/LTO full-cell and compared its electrochemical performance with bare Li/LTO and rGO-Li/LTO cells. All the anodes have a similar thickness (~500 μ m). Figure 6a,b indicate that after 450 cycles the MG-Li/LTO cell maintains 142 mAh g⁻¹ with a high Coulombic efficiency of nearly 100% (Figure S26), while rGO-Li/LTO and Li/LTO decay to 132 and 120 mAh g^{-1} , respectively. Moreover, the MG-Li/LTO cell exhibits a superior rate performance compared with other cells. For example, at 5 and 10 C, the MG-Li/LTO cell shows 141 and 123 mAh g^{-1} , respectively, much higher than those of the rGO-Li/LTO cell (127, 108 mAh g^{-1}) and bare Li/LTO cell (104, 81 mAh g^{-1}), as demonstrated in Figure 6c and Figure S26. This is in line with the EIS results, which reveal a muchreduced interfacial charge transfer resistance for the MG-Li/ LTO (32 Ω) compared to rGO-Li/LTO (61 Ω) and bare Li/ LTO (152 Ω), indicating the MG-Li electrode possesses robust ionic and electronic channels (Figure S28). To demonstrate the advantages of the MG-Li anode for potential Li-S application, we also assembled pouch cells by pairing different anodes with the S cathode; the latter composite electrode was simply prepared by mixing sulfur with carbon black and polyvinylidene fluoride without any further modifications. As shown in Figure 6d and Figure S29, the MG-Li/S cell consistently exhibits an enhanced rate performance with higher capacities than those of rGO-Li/S and Li/S cells, especially at higher current densities. For instance, the MG-Li/S cell delivers 448 and 400 mAh g⁻¹ at 3 and 5 C, respectively, higher than those of rGO-Li/S (384 and 355 mAh $\rm g^{-1})$ and bare Li/S (295 and 242 mAh $\rm g^{-1}).$ After cycling at 0.5 C for 300 times, the MG-Li/S cell still delivers a larger discharge capacity of 795 mAh g^{-1} with high Coulombic efficiency (Figure \$30) and exhibits a higher capacity retention of 54% than those of rGO-Li/S (44%) and bare Li/S cells (only 29%) (Figure 6e,f). In addition, the polarization potential is the lowest in the MG-Li/S cell (188 mV), suggesting improved redox-reaction reversibility benefiting from the litihophilic MXenes and 3D conductive porous scaffold. Nevertheless, all cells showcase rather rapid capacity decay due to the shuttling effect of lithium polysulfides. We believe the MG-Li/S cell performance can be further improved by modifying the cathode part (i.e., introducing LiPS chemisorptive sites) and/or the separator (i.e., coating a physical barrier) to suppress the polysulfide diffusion. However, this is beyond the scope of this work.

For the interesting anode performance endowed by the MG framework, we believe several key factors are playing important roles. First, the 3D lightweight scaffold is suitable for Li-metal melt infusion, increasing the active Li content, and minimizing the infinite volume changes of the Li anode during the stripping and plating process. Second, the interconnected conductive porous structure significantly lowers the local effective current density to form a uniform Li-ion flux and delays the Li dendrite growth rate. Third, the cellular MG scaffold with a micrometer-scale cavity promotes fast electrolyte uptake and stabilizes the as-formed SEI film. Moreover, the well-dispersed lithiophilic MXene nanosheets allow the homogeneous distribution of the electric field and Li nucleation sites, thus guaranteeing the uniform Li plating across the whole framework rather than on the top surface of the electrode. As a result, the formation of Li dendrites and "dead Li" is greatly suppressed.

CONCLUSIONS

In summary, we report on a 3D highly conductive, chemically lithiophilic, and mechanically robust MG framework for a highperformance and dendrite-free Li anode. Owing to the abundant homogeneously dispersed lithiophilic MXene and 3D conductive nanoporous structures in the matrix, the nucleation and growth of metallic Li are well controlled in the 3D MG skeleton. Such a structure design ensures an efficient encapsulation of Li-induced volume change, and improves the current density of the anode electrode. Consequently, the MG achieves an ultrahigh Li content of 92%, high Coulombic efficiency of 99%, and a record lifespan of up to 2700 h at a high capacity of 5 mA h cm^{-2} . Impressively, an ultrahigh current density of 20 mA cm^{-2} and large capacity of 5 mAh cm⁻² are obtained, coupled with long-term cycling stability free of Li dendrite growth. Furthermore, MG-Li anode-based full cells exhibit substantially improved cycling stability and rate performance. This strategy sheds light on the reasonable design of ultrahigh capacity and exceptionally stable metallic Li anodes and is expected to develop next-generation high-safety

and high-energy-density Li-metal batteries, such as Li–S, Li– O_2 , and solid-state batteries.

METHODS

Preparation of 3D MGO Aerogels. $Ti_3C_2T_X$ MXene was prepared from Ti_3AlC_2 by LiF/HCl etchants previously reported,⁶⁰ and GO was synthesized by the modified Hummer's method.⁶¹ After that, the homogeneous solution was obtained by mixing GO (5 mg mL⁻¹) and MXene (10 mg mL⁻¹) solution by sonication for 10 min under an argon flow. The MXene amount was optimized by tuning the mass ratio of GO and MXene from 1:1 to 3:1 and 5:1. Finally, the resulting suspension was freeze-dried for 3 days to obtain 3D MGO aerogels. For comparison, GO aerogels were also prepared without adding MXene, while other steps remained unchanged.

Fabrication of a MG-Li Anode. First, 3D MGO aerogels were pressed at 10 MPa to form 3D MGO films. Then, the MGO films were cut and put into contact with the molten Li in an Ar-filled glovebox with an O_2 and H_2O content below 0.1 ppm. The spark reaction occurred within seconds to partially reduce the MGO films into MG films. Subsequently, the MG film was put on top of the molten Li. Molten Li could steadily climb up and infiltrate the whole inner MG film to afford the MG-Li electrode (see Movie S1). For comparison, the rGO-Li anode was prepared following the above steps except only replacing the MGO film with a GO film.

Material Characterization. The morphology and structure of materials were characterized by SEM (JEOL JSM-7800F), TEM (JEM-2100), AFM (Veeco nanoscope multimode II-D), XPS (Thermo ESCALAB 250Xi equipped with monochromatic Al K α source of 1486.5 eV), FTIR (Bruker, Hyperion 3000), XRD (Empyrean with Cu K α radiation in the 2 θ range from 5° to 90°), thermogravimetric analysis (TGA, SDT Q600 V20.9 Build 20), Raman spectroscopy (LabRAM HR 800 Raman spectrometer, 632 nm), and a Mastersizer 2000 (Malvern Instruments, UK). Nitrogen adsorption and desorption isotherms were carried out to investigate the specific surface area and pore size distribution of the products. Electrical conductivity was measured by a standard four-point probe system (RTS-9).

Electrochemical Measurement. All the cells were assembled with standard CR2025 coin-type cells in an Ar-filled glovebox with O2 and H_2O content below 0.5 ppm. The electrolytes employed were either 1.0 M lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) in a mixture solution of 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) (1:1, vol. ratio) with 1 wt % LiNO₃ as additive or 1 M lithium hexafluorophosphate (LiPF₆) in 1:1 ethylene carbonate (EC)/diethyl carbonate (DEC), about 40 μ L of electrolyte was dropped into each cell, and the polypropylene membrane (Celgard 2700) was used as the separator. MG film, rGO film, or planar Cu was used as the working electrode and Li foil as the counter/reference electrode to evaluate the Coulombic efficiencies. The assembled cells were precycled between 0.01 and 3 V at 100 μ A for five times to stabilize the SEI formation and remove surface contaminations. After that, a certain capacity of Li was deposited onto the current collector and then charged to 1 V (vs Li⁺/Li) to strip the Li at a certain current density for each cycle on a LAND CT2001A battery system. Symmetric cell configurations were assembled with MG-Li, rGO-Li, or bare Li anodes to evaluate the long-time cycling stability. For the full cells, the working electrode contains 80 wt % of active materials (LTO or S), 10 wt % of carbon black, and 10 wt % of polyvinylidene fluoride with N-methyl-2-pyrrolidone as the solvent, and the wellmixed slurry was cast onto carbon-coated Al foil using the doctor blade technique. The cast electrodes were dried under vacuum at 120 °C (LTO) and 55 °C (S) for 12 h. The cathode with an LTO loading of ~2.0 mg cm $^{-2}$ was employed in MG-Li//LTO full cells, using 1.0 M LiPF₆ in EC/DEC (v/v = 1:1) as the electrolyte. The sulfur cathode with a sulfur loading of \sim 1.0 mg cm⁻² was employed in Li–S cells, using LiTFSI in DOL/DME (v/v = 1:1) with 2.0% LiNO₃ as electrolyte in Li–S cells, and about 20 μ L of electrolyte was added into each cell. CV curves were carried out on a CHI 760E electrochemical workstation at a scan rate of 0.1 mV s⁻¹. EIS were carried out using a CHI 760E workstation by applying an ac amplitude of 5 mV over the frequency range of 100 kHz to 0.01 Hz.

Computational Simulation. All calculations have been per-formed with the DMol3 package.⁶² In the framework of DFT, the generalized gradient approximation (GGA) combined with the Perdew-Burke-Enzerhof (PBE) functional was employed to describe the exchange and correlation potential.^{63,64} All the atoms of the calculated systems are allowed to fully relax in order to optimize the adsorption geometries. A double-numerical basis with polarization functions (DNP) is utilized to expand the valence electron functions into a set of numerical atomic orbitals, and the DFT semicore pseudopotential (DSPP) is used when tackling the electron-ion interactions. The k-point mesh in the Monkhorst Pack sampling scheme was set as $1 \times 1 \times 1$.⁶⁵ The Fermi smearing is set to 5.0 \times 10^{-3} Ha (1 Ha = 27.21 eV). For the convergence criteria, the SCF tolerance used was 1.0×10^{-5} eV atom⁻¹, and the maximum force and displacement were set as 5.0 \times 10⁻² eV Å⁻¹ and 2.0 \times 10⁻³ Å, respectively. For the Li ion combined with graphene and MXene, the binding energy (E_a) is defined as the energy difference between the substrate with a Li ion (E_t) and the summation of the Li ion (E_1) and substrate system (E_2) : $E_a = E_1 + E_2 - E_t$. The migration energy is defined as the change of binding energy when the Li ion migrates along the diffusion path on the substrate surface.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsnano.9b07710.

Materials characterization, electrochemical characterization, additional figures, and the table used to perform a comparison of our MG-Li anode with the state-of-theart Li-metal composite anodes (PDF)

Infusing Li into the MG film (Movie: nn9b07710 Si 003.mp4)

Infusing Li into the pure MXene film (Movie: nn9b07710 Si 002.mp4)

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Author Contributions

Z.-S.W. proposed and supervised the overall project. H.D.S. did the fabrication and electrochemical measurement of MG-Li. H.D.S. and Z.S.W. analyzed the data. C.F.Z. prepared the MXene nanosheets. Y.F.D. and P.C.W. participated in the structural characterization of the related materials. P.F.L. did the DFT calculation. H.D.S., C.F.Z., and Z.-S.W. cowrote this paper. All authors commented and have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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