Potassium metal batteries are considered as attractive alternatives beyond lithium-ion batteries. However, uncontrollable dendrite growth on the potassium metal anode has restrained their practical applications. A high-performance potassium anode achieved by confining potassium metal into a titanium-deficient nitrogen-containing MXene/carbon nanotube freestanding scaffold is reported. The high electronic transport and fast potassium diffusion in this scaffold enable reduced local current density and homogeneous ionic flux during plating/stripping processes. Furthermore, as verified by theoretical calculations and experimental investigations, such "potassium-philic" MXene sheets can induce the nucleation of potassium, and guide potassium to uniformly distribute in the scaffold upon cycling. Consequently, the as-developed potassium metal anodes exhibit a dendrite-free morphology with high Coulombic efficiency and long cycle life during plating/stripping processes. Such anodes also deliver significantly improved electrochemical performances in potassium–sulfur batteries compared with bare potassium metal anodes. This work can provide a new avenue for developing potassium metal-based batteries.

Furthermore, the K+/K couple exhibits the lowest redox potential in nonaqueous media (e.g., propylene carbonate) compared with other alkaline metal ions, which endows potassium-based batteries with high operating voltage and energy density.[4] Potassium ions also possess a higher transfer number and ionic conductivity than sodium ions and lithium ions due to potassium's weak Lewis acidity and low desolvation energy, which is expected to facilitate fast diffusion kinetics in batteries.[5] These advantages make potassium-based batteries as high-performance and low-cost rechargeable battery system for large-scale energy storage applications.

Among the anode candidates of potassium-based batteries, K metal has attracted special attention due to its lower potential (~2.93 V vs the standard hydrogen electrode (SHE)) and higher specific capacity (~687 mA h g~\textsuperscript{−1}) compared to other anode materials including carbonaceous, alloying, and intercalation compounds.[6,7] The utilization of K metal anodes can also eliminate ancillary current collectors in anodes, and thus dramatically increase the energy density of batteries. Moreover, K metal anodes enable the application of unpotassiated cathodes for high-energy-density battery systems based on conversion chemistry, e.g., potassium–oxygen (K–O\textsubscript{2}) and potassium–sulfur (K–S) batteries.[8]

However, reversible plating and stripping of K metal in electrolytes remains a major challenge. It is well known that the highly reactive K metal spontaneously reacts with electrolyte compounds to form a solid electrolyte interphase (SEI) on its surface.[9] Due to the "hostless" nature of potassium metal, such an SEI film can be easily broken by mechanical deformation during K deposition/stripping process, which promotes non-uniform ionic flux and leads to the growth of K dendrites.[10] The resulting K dendrites can penetrate the separator, and result in an internal short circuit, causing safety hazards (e.g., combustion and explosion).[11] Furthermore, dendrite growth can expose a large surface area of fresh K metal, leading to a continuous breakdown/re-construction of SEI during cycling, and finally forming isolated electrochemically inactive "dead K." These dramatically decrease the Coulombic efficiency and lifespan of K metal batteries.[6] In the case of K–O\textsubscript{2} and K–S batteries, inhomogeneous K deposition will also enlarge the reaction area with soluble intermediate products (i.e., oxygen species and polysulfides), which aggravates their shuttling and further deteriorates the battery performance.[12]
To date, the research on K metal anodes is still in its infancy. Several works have been reported on restraining dendrite growth on K metal anodes by replacing K metal with a K–Na alloy,[6,13] surface engineering on K metal,[10] or stabilizing the SEI by optimizing liquid electrolyte composition.[14] However, the employment of liquid-state K–Na alloy anodes may induce severe safety concerns. Meanwhile, the surface engineering or electrolyte optimization alone cannot suppress the huge volumetric change during K plating/stripping.[15] In contrast, confining K metal into a 3D matrix is expected to accommodate the volumetric changes at the electrode level, and simultaneously decrease local current density by spreading ion flow laterally, thus blocking the growth of K dendrites.[16] Herein, for the first time, we present a defect-rich and nitrogen-containing MXene (Ti$_{3}$$_{2}$-MXene) labeled as DN-MXene, where T represents surface functional groups, x and y are adjustable numbers)/carbon nanotube (CNT) freestanding scaffold as a K metal host to control nucleation behavior and suppress dendritic growth. This porous scaffold with abundant interconnected voids enables massive loading of metallic K and preserves a constant electrode dimension during plating/stripping. Due to the high electronic transport and fast K ion diffusion,[17] the as-prepared electrode dimension during plating/stripping. Due to the high electronic transport and fast K ion diffusion, the as-prepared scaffold efficiently reduces the effective local current density by spreading ion flow laterally, thus blocking the growth of K dendrites.[16] This elucidates that a small amount of 2D DN-MXene sheets (~20 wt%) added into the skeleton can greatly improve the porosity of the 1D CNT-based scaffold, which is beneficial for the K metal loading that can improve the energy density of K metal-based batteries. Furthermore, the X-ray diffraction (XRD) and Raman results shown in Figure S6 in the Supporting Information confirm the successful preparation of DN-MXene/CNT scaffolds.

Figure 1a illustrates the preparation method of the DN-MXene/CNT freestanding scaffold. Briefly, delaminated DN-MXene sheets (Figure S1, Supporting Information) were obtained by extracting aluminum atoms from MAX precursor (Ti$_3$AlCN) followed by sonication. As shown in the high-resolution N 1s X-ray photoelectron spectroscopy (XPS) spectrum in Figure S2 in the Supporting Information, peaks at ±396.6 and ±397.2 eV can be assigned to the TiCN and N-Ti-Ti$_4$ bonds, respectively, which confirms the formation of the DN-MXene.[18] High-angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) analysis was performed to resolve the crystal structure and defects of the as-prepared Ti$_{3}$$_{2}$-CNT, MXene sheets. Figure 1b presents HAADF-STEM images of DN-MXene sheets. Combined with atomic force microscopy (AFM) result in Figure S3 in the Supporting Information, the as-obtained DN-MXene shows an ultrathin sheet morphology with a thickness of around 2 nm. Noticeably, massive defects, including Ti vacancies and Ti vacancy clusters, appear in DN-MXene sheets. Figure 1c,d shows the simulated and experimental atomic-resolution HAADF-STEM images acquired along the c-axis of the Ti$_{3}$$_{2}$-CNT, MXene sheet, respectively, which are overlaid with the projected atomic structure models. The yellow atoms arranged in a hexagonal pattern directly correspond to the stacked Ti atoms in sublayers. Both simulated and experimental images display slight lattice distortion, compared with N-free titanium carbide MXene in the previously reported literature,[19] which may result from the substitution of carbon by nitrogen in the DN-MXene sublayers.[20] Additionally, abundant Ti vacancies unambiguously exist in the experimental atomic-resolution HAADF-STEM image of the as-obtained Ti$_{3}$$_{2}$-CNT, MXene (Figure 1d), which can benefit K metal deposition when applied in batteries, as discussed below.

After mixing DN-MXene sheets with CNTs, the freestanding scaffolds were prepared by a simple filtration method (Figure 1a, right panel). The top-view (Figure 1e) and cross-sectional (the inset in Figure 1f and Figure S4 (Supporting Information) morphologies of the DN-MXene/CNT scaffold were observed by scanning electron microscopy (SEM). It is clearly observed that CNTs are homogeneously distributed on the DN-MXene sheets, offering a 3D network for high electron-conducting and fast ionic-transport paths. Additionally, the DN-MXene/CNT scaffold with a thickness of ~150 μm presents a porous structure with massive interconnected voids, while the CNT-only scaffolds prepared by same method show relatively dense and compact structure (Figure S5, Supporting Information). This elucidates that a small amount of 2D DN-MXene sheets (~20 wt%) added into the skeleton can greatly improve the porosity of the 1D CNT-based scaffold, which is beneficial for the K metal loading that can improve the energy density of K metal-based batteries. Furthermore, the optical image (left inset of Figure 1f) of the as-prepared DN-MXene/CNT scaffold exhibits excellent bending ability, which makes it a promising flexible host for K metal. After the K infusion, the anode surface presents an obvious metallic luster, indicating the successful loading of metallic K into the porous structure of the scaffold (the right inset of Figure 1f). Furthermore, SEM image of a K@DN-MXene/CNT composite anode verifies that K metal is uniformly distributed in the pores of the scaffold (Figure 1f). The K@DN-MXene/CNT composite anodes prepared by this melt infusion strategy can be directly coupled with K-free cathodes to construct high-performance full batteries.

Density functional theory (DFT) calculations were conducted to further investigate the interaction between K atoms and different scaffolds/current collectors. As shown in Figure 2a–c and Figure S8a–c (Supporting Information), the binding energies of K atoms absorbed on Cu foil, Al foil, and CNT scaffold are calculated to be −0.13, −0.51, and −0.84 eV, respectively. As verified by the discharge profile and XRD results (Figure S9, Supporting Information), K atoms preferably intercalate into the interlayer space of DN-MXene sheets before the plating of K metal, which is consistent with the previous reports.[21] Considering the possible surface functionalities, MXenes terminated with −OH, =O, and −F were modeled.[22] As shown in Figure S10 in the Supporting Information, the binding energies between K-intercalated Ti$_{3}$-CNT, MXenes
and K atoms are 1.91 eV (Ti$_3$CNO$_2$), 1.86 eV (Ti$_3$CN(OH)$_2$), and 1.88 eV (Ti$_3$CNF$_2$), which are larger than their nitrogen-free counterparts (Figure S11, Supporting Information), demonstrating that the substitution of carbon by nitrogen can significantly enhance the interaction with K atoms. Furthermore, when introducing one Ti vacancy into N-containing MXene layer, the binding energies further increase to 2.27 eV (Ti$_{3-x}$CNO$_2$), 2.1 eV (Ti$_{3-x}$CN(OH)$_2$), and 2.04 eV (Ti$_{3-x}$CNF$_2$), which are much larger than those of the Al, Cu, and CNT. This indicates that K atoms prefer to nucleate on the K-intercalated DN-MXene sheets rather than CNTs or other current collectors. Thus, this potassium-philicity of DN-MXene enables the preferential nucleation of K metal during plating, which makes DN-MXene as an ideal “seed point” for the development of dendrite-free metal anode.

To validate the potassium-philic properties of the as-prepared DN-MXene sheets, the nucleation overpotentials of scaffolds/current collectors were tested at a current density of 0.05 mA cm$^{-2}$. All the voltage profiles exhibit a voltage dip at the beginning of K plating, followed by a flat voltage plateau with lower potential. The value of the K metal nucleation overpotential can be defined as the difference between the bottom of the voltage dip and the flat part of the voltage plateau.[23] As shown in Figure 2h, the K nucleation overpotentials of CNT, Cu, and
Al are 33, 65, and 103 mV, respectively. In contrast, the nucleation overpotential of DN-MXene/CNT is much lower (≈6 mV), indicating the reduced resistance for metallic K to nucleate on the as-prepared porous scaffold. This value is also higher than that of N-free Ti$_{3}$-$x$CN$_{2}$ scaffold (Figure S12a, Supporting Information), which is highly consistent with the theoretical calculation results.

The K plating/stripping on different scaffolds and current collectors (DN-MXene/CNT, CNT, Cu, and Al) was further studied by using a two-electrode cell configuration. **Figure 3a** shows the Coulombic efficiencies (the ratio of K stripping capacity to K plating capacity) of the different scaffolds and current collectors in 0.8 M potassium hexafluorophosphate (KPF$_6$) dissolved in ethylene carbonate (EC): diethyl carbonate (DEC) (1:1, v/v). It is noted that all the scaffolds and current collectors present relatively lower Coulombic efficiencies in the initial cycles, which is due to the formation of SEI layer and continuous consumption of electrolyte.[7] Subsequently, the Cu and Al foils exhibit low Coulombic efficiencies (≈50% for Cu and ≈65% for Al) and short lifespans (20 cycles for Cu and 60 cycles for Al), which can be attributed to the dendrite growth and continuous breakdown/reconstruction of SEI layers.[24] CNT scaffolds delivered an average Coulombic efficiency of ≈80% during the cycling process, which could be ascribed to the high specific surface area of the conductive CNT scaffold that significantly reduces local current density.[25] However, the cell using CNT scaffolds still suffers from limited cycling life with Coulombic efficiency dropping dramatically beyond 80 cycles. Noticeably, DN-MXene/CNT scaffolds delivered an average Coulombic efficiency of ≈93.1% and cycling stability (120 cycles), which is also higher than that of N-free MXene/CNT scaffold (Figure S12b, Supporting Information). This indicates that DN-MXene/CNT scaffolds can effectively reduce the local current density, regulate the flux of K ions and suppress...
the growth of the dendrites. The corresponding voltage profiles for K plating/stripping on different scaffolds and current collectors are shown in Figure 3b. The DN-MXene/CNT exhibits a small voltage gap between charge and discharge plateaus (≈0.19 V) compared with those of CNT matrix (≈0.28 V), Al foil (≈0.30 V), and Cu foil (≈0.34 V) at the 20th cycle, indicating the reduced polarization of the as-prepared DN-MXene/CNT scaffolds. Such a small polarization is ascribed to the fact that the DN-MXene can guide homogeneous K plating in the CNT matrix, and therefore suppress the side reactions with electrolyte.

The morphologies of K deposited scaffolds and current collectors were further observed by SEM characterizations. Direct K deposition onto Cu (Figure 3c) and Al (Figure S13a, Supporting Information) foils results in uneven surface and mossy K dendrites. Moreover, as shown in the cross-sectional images, the deposited K metal is highly porous and loose on Cu (Figure S14a, Supporting Information) and Al foils (Figure S14b, Supporting Information), and the thicknesses of the deposited K metal are ≈200 and 160 µm, respectively, far exceeding the theoretical thickness (≈85 µm). When employing CNT scaffolds, the surface of the electrode becomes smoother compared with Cu and Al foils (Figure S13b, Supporting Information). However, an obvious porous structure and mossy dendrites are still observed on the CNT scaffolds (Figure S14c, Supporting Information), which is the result of the direct nucleation of K on the top surface of the CNT scaffold and nonuniform distribution of K ionic flux during cycling. In contrast, K metal is well-confined in the DN-MXene/CNT scaffold with a smooth morphology (Figure 3d). The porous structure of
DN-MXene/CNT scaffold is densely filled with metallic K, and no dendrites can be observed outside the DN-MXene/CNT scaffold (the cross-sectional and mapping images in Figures S14d and S15 in the Supporting Information, respectively). Such a dendrite-free surface morphology can significantly alleviate interfacial side reactions between the metallic K and electrolytes, thus improving the Coulombic efficiency and cycle life. Ex situ SEM characterization was also performed to confirm the nucleation and deposition of K metal on the DN-MXene/CNT scaffold. With plating capacities increasing from 0 to 1, 2.5, and 5 mA h cm\(^{-2}\), it is clearly seen that the K metal is nucleated and deposited inside of the DN-MXene/CNT scaffold (Figure S16, Supporting Information), which is highly consistent with the DFT calculation results in Figure 2. Additionally, the Coulombic efficiency of DN-MXene/CNT scaffold can be further improved to \(\approx 98.6\%\) over 200 cycles by using an optimized electrolyte (0.8 M potassium bis(fluorosulfonyl)imide (KFSI) in EC: DEC (1:1, v/v)) (Figure 3e; Figure S17, Supporting Information), exceeding the previously reported values (Table S1, Supporting Information). This is because the cleavage of the S–F bond of the KFSI salts facilitates the formation of a fluorine-rich SEI layer on K metal anode, which leads to reversible plating/stripping and suppresses dendrites.\(^{[14,27]}\) Therefore, the nucleation guidance from the DN-MXene sheets in the scaffold plays an important role in achieving the dendrite-free surface morphology.

In situ XRD was employed to investigate K deposition on Cu current collectors and DN-MXene/CNT scaffolds during the first plating process. As shown in the in situ XRD patterns (Figure S18, Supporting Information) and the corresponding color plots (Figure 4a), a characteristic diffraction peak at \(\approx 29.6^\circ\) is assigned to the K\(_2\)CO\(_3\) (112) plane (PDF no. 04-010-2694), which is a decomposition product of the electrolyte.\(^{[21]}\) This peak gradually increases in the cell using Cu current collector (Figure 4a), indicating the formation of thick SEI layers due to serious dendrite growth.\(^{[28]}\) In comparison, the K\(_2\)CO\(_3\) (112) peak remains low without obvious change in the cell when using the DN-MXene/CNT scaffold, suggesting that employment of DN-MXene/CNT scaffold can effectively minimize side reactions (Figure 4b). Additionally, Figure S19 in the Supporting Information shows the F 1s XPS spectrum of DN-MXene/CNT scaffold after plating-stripping K metal. A peak at \(\approx 682.8\) eV can be ascribed to the KF in the SEI layer, which is derived from the interaction between K atoms and fluorine terminations of MXene sheets.\(^{[29]}\) Such a fluorine-rich SEI layer endows reversible plating/stripping with higher Coulombic efficiency. Furthermore, the in situ optical microscopy visualization was conducted to study the surface morphologies of Cu current collector and DN-MXene/CNT scaffold during the K metal deposition process. As shown in Figure 4c, mossy K dendrites appear on the surface of Cu current collector during the 30 min plating process, while the surface of DN-MXene/CNT remains smooth and flat, suggesting a dendrite-free potassium surface upon plating. The Sand’s time was further measured by using Cu foil and DN-MXene/CNT scaffold (Figure S20, Supporting Information). The Sand’s time was determined where the apparent voltage divergence occurred due to complete ion depletion and rapid dendrite growth.\(^{[30]}\) The DN-MXene/CNT scaffold delivers a prolonged sand’s time of \(\approx 12\) h, which is 6 times longer than that of Cu foils (\(\approx 2\) h). According to the space charge model\(^{[26]}\) and Equation (1)\(^{[31]}\)

![Figure 4. Mechanism investigation in KPF\(_6\)-based electrolyte. Contour plots of in situ XRD patterns for the K deposited on the a) Cu and b) DN-MXene/CNT scaffold. The corresponding electroplating curves are shown on the left; the high-intensity peak at around 26.8\(^\circ\) is assigned to the Be window. c) In situ optical microscopy visualization of K deposited on the Cu foil scaffold (left panel) and DN-MXene/CNT (right panel) at a current density of 2 mA cm\(^{-2}\).](image-url)
\[ \tau = D \left( \frac{C_0 e \left( \mu_a + \mu_k^+ \right)}{2 \mu_e} \right)^2 \]  

(1)

where \( \tau \) is the Sand's time, which is a time when the K dendrite starts to grow. \( D \) is the diffusion coefficient and \( e \) is the elementary charge. \( C_0 \) is the initial concentration of K salt. \( \mu_a \) and \( \mu_k^+ \) are the anionic and K\(^+\) mobility, respectively, and \( J \) is the effective electrode current density. The increased Sand's time of the DN-MXene/CNT scaffold confirms the fast K\(^+\) transport of scaffold and enhanced specific surface area that reduces the local current density.

To further measure the long-term galvanostatic cycling performance of DN-MXene/CNT scaffolds, symmetric cells were assembled by using two identical K@DN-MXene/CNT electrodes prepared by the melt infusion strategy. Noticeably, the K@DN-MXene/CNT anodes show a higher specific capacity compared to bare K anodes (shown in Figure S21 in the Supporting Information). The symmetric cells with two identical K@CNT electrodes (or two bare K foils) were also assembled for comparison. As presented in Figure 5a, a negative voltage value indicates the K plating, while the positive voltage value refers to K stripping.\(^{[32]}\) The voltage hysteresis of the bare K cell significantly increases from \( \approx 0.62 \) V at the initial cycle to \( \approx 1.13 \) V at 60 h, mainly due to the accumulated thick SEI caused by nonuniform K deposition and dendrite growth. Furthermore, the voltage hysteresis suddenly drops to around \( 0.2 \) V at 75 h, which indicates a short-circuit induced by dendrite growth (inset of Figure 5a,b).\(^{[33]}\) The K@CNT cell shows an average overpotential of \( \approx 0.45 \) V and short-circuits at \( \approx 220 \) h (Figure 5a,b). In contrast, the K@DN-MXene/CNT cell delivers a flat voltage plateau during both K plating and stripping processes (Figure S22, Supporting Information) with a reduced voltage hysteresis of \( \approx 0.3 \) V, which remains steady without obvious oscillation during 300 h cycling (Figure 5b). Additionally, the cycle life of K@DN-MXene/CNT cell can be further improved to...
1000 h in KFSI-based electrolyte (Figure S23, Supporting Information), which validates the excellent reversibility of the DN-MXene/CNT scaffold. Furthermore, the symmetric cell with K@DN-MXene/CNT electrodes also has superior rate performance. The K@DN-MXene/CNT||K@DN-MXene/CNT cell delivered voltage hysteresis of 0.11, 0.16, 0.24, 0.31, 0.40 V, when current densities increase from 0.1 mA cm$^{-2}$ to 0.2, 0.5, 1, and 2 mA cm$^{-2}$, respectively (Figure 5c). These values are much lower than those of K@CNT||K@CNT cells and K||K cells. Therefore, the DN-MXene/CNT scaffold with high electronic conductivity and fast K ion diffusion can effectively reduce local current density and regulate the K metal deposition at high current densities. The electrochemical impedance spectroscopy (EIS) spectra and corresponding simulation results of the symmetric cells after 10 cycles are shown in Figure 5d and Table S2 (Supporting Information). The K@DN-MXene/CNT||K@DN-MXene/CNT cell shows the lowest interfacial resistance among the three symmetric cells, which is in good agreement with their stable cycling performances.

Figure 5e demonstrates a schematic illustration of K metal deposition behaviors on CNT and DN-MXene/CNT scaffolds. For the K@CNT anode, K atoms incline to directly nucleate and plate onto the CNTs randomly during the repeated plating/stripping process. This leads to a porous deposit and dendritic growth outside of the scaffold, thus decreasing the Coulombic efficiency and the cycle life of K@CNT anode (Figure 5e, upper panels). With the introduction of highly electronically conductive DN-MXene sheets into the scaffold, the potassium-philic DN-MXene sheets act as “seed points” to trigger nucleation and guide homogeneous ionic flux during cycling, which results in the uniform K metal deposition without dendrite formation (Figure 5e, lower panels).

As a proof of concept, K–S cells were assembled using the K@DN-MXene/CNT composite as anode and sulfur-polyyacrylonitrile (SPAN) as cathode. To determine the effect of the DN-MXene/CNT scaffold, optically transparent devices were fabricated by immersing a K@DN-MXene/CNT anode (or bare K metal foil) in KPF$_6$-based electrolyte together with the same amount of SPAN powder on the bottom of the vessels. The liquid electrolyte turns yellow after aging for 24 h at room temperature (Figure 6a), and a strong peak at 220–260 nm related to S$_2^-$ and S$_2^{2-}$ appears in the corresponding ultraviolet–visible spectrum.[34] Such a distinct color change implies that the elemental sulfur from the SPAN powder continuously dissolves into the liquid electrolyte, and then electrochemically reacts with K metal to form soluble K polysulfides with dark color. This is consistent with the self-discharge phenomenon observed in batteries.[15] In the device assembled with K@DN-MXene/CNT anode, however, the liquid electrolyte remains clear (Figure 6a) with a much lower polysulfide peak in the UV–vis spectrum (Figure 6a, inset). This verifies that the shuttle effect of soluble polysulfides can be effectively suppressed by employing a DN-MXene/CNT host in K metallic anodes.[16]

Figure 6b shows the rate performances of K–S batteries. Meanwhile, the corresponding voltage profiles are shown in Figure S24 in the Supporting Information. The K@DN-MXene/CNT||SPAN cell exhibits specific capacities of 436, 375, 312, 256, and 193 mA h g$^{-1}$ (based on the mass of sulfur) at current densities of 0.1 C, 0.2 C, 0.5 C, 1 C, and 2 C, respectively. Even at a high current density of 5 C, the cell still maintains a capacity of 113 mA h g$^{-1}$, which is much higher than that of K–S batteries with bare K foils. Figure 6c demonstrates the cycling performances of K–S batteries. The K@DN-MXene/CNT||SPAN cell can deliver an initial discharge capacity of 638 mA h g$^{-1}$ at 0.5 C, which is related to an activation process, including the cleavage of C–S bonds and rearrangement of sulfur atoms (Figure S25a, Supporting Information).[37,38] The corresponding cyclic voltammograms (CV) are shown in Figure S25b in the Supporting Information, in which an irreversible peak at ≈1.25 V can be observed in the first cycle and disappears in the following cycles. Moreover, the peak located at ≈1.79 V can be assigned to the oxidation of the polysulfides during the charge process.[38] The galvanostatic profiles of a K@DN-MXene/CNT||SPAN cell are shown in Figure 6d. The sloping curves during the discharge process are ascribed to the reaction between potassium and sulfur with varying chain lengths.[39] A reversible capacity of 331 mA h g$^{-1}$ was achieved in the subsequent cycles. Even after 500 cycles, a capacity of ≈230 mA h g$^{-1}$ can be retained (Figure 6c). In contrast, K–S batteries with bare K anodes suffer from a severe capacity fading and internal short-circuiting after ≈300 cycles, which is due to the continuous dendrite growth, severe shuttle effect, and electrolyte consumption during plating/stripping of K metal.[40] Noticeably, the K@DN-MXene/CNT||SPAN cell also shows excellent electrochemical performance in KFSI-based electrolyte (Figure S26, Supporting Information).

EIS was measured to study the interfacial behavior of K–S batteries. Figure S27a in the Supporting Information shows the EIS spectra of the K@DN-MXene/CNT||SPAN and bare K||SPAN cells after different numbers of cycles. The obtained EIS spectra can be simulated via an equivalent circuit (Figure S27b, Supporting Information), and the simulation results are presented in Table S3 in the Supporting Information. Notably, the solid/electrolyte interface resistance ($R_I$) of bare K||SPAN cell increases from ≈282 to ≈779 $\Omega$ after 10 cycles, which is associated with the dendrite growth on the K anode and deteriorated SEI film as well as the severe shuttle effect in the batteries. In contrast, after employing the DN-MXene/CNT scaffold, the K–S batteries deliver a lower value of $R_I$ (≈137 $\Omega$ after 1st cycle), which increases slightly to ≈177 $\Omega$ after the 10th cycle. This indicates a stable solid/electrolyte interface and suppressed shuttle effect, which contribute to the excellent long-term cycling stability shown in Figure 6c. Furthermore, the morphologies of K anodes disassembled from K–S batteries after 50 cycles were characterized by SEM (Figure 6e; Figure S28, Supporting Information). It can be observed that the K@DN-MXene/CNT anode after 50 cycles still maintained smooth surface with a low sulfur content of 1.21%. However, numerous dead K metal and porous dendrites were found on the surface of the bare K anode after 50 cycles, and the sulfur content on its surface was as high as 6.87%. These results imply that the DN-MXene/CNT scaffold can not only efficiently suppress the formation of “dead K” and dendrites resulting from the inhomogeneous deposition, but also reduce the reaction area with polysulfides, and therefore restrain the shuttle effect (Figure S29, Supporting Information).
We have rationally designed and prepared a freestanding DN-MXene/CNT scaffold as a matrix for dendrite-free K metallic anodes. Due to the high electronic conductivity and fast K ion diffusion, such DN-MXene/CNT scaffolds can efficiently reduce local current density and facilitate homogeneous K ionic flux, leading to improved rate performance. Furthermore, as validated by DFT calculations and experimental investigations, DN-MXene sheets with potassium-philic characteristic can induce the nucleation of K atoms, therefore suppressing dendritic growth during plating/stripping process. When applying the K@DN-MXene/CNT metal anodes in K–S batteries, the matrix can significantly protect the K metal from the shuttle effect of polysulfides by suppressing dendrite growth, which significantly improves the electrochemical performances of the K–S batteries. This work could open up a new path to inspire the development of K metal anodes and high-performance K-based batteries.

**Experimental Section**

**Synthesis of the Defect-Rich and N-Containing MXene Sheets:** Ti₃AlCN with a particle size of <38 µm was synthesized according to the previous report. Then, 3 g of as-prepared Ti₃AlCN powder was etched in a mixture of 3 g lithium fluoride (LiF, Alfa Aesar) and 30 mL 9 M hydrochloric acid (HCl, Fisher Scientific) at ≈35 °C for 24 h to extract the Al atoms and obtain multilayered Ti₃−ₓCNTₙ suspension. The obtained suspension was repeatedly rinsed with distilled water and centrifuged (3500 rpm) until the pH of the supernatant was higher than 5.

**Preparation of the Freestanding DN-MXene/CNT Scaffold and CNT Scaffold:** The CNTs was purchased from Shenzhen Nanotech Port Co. Ltd., China. DN-MXene/CNT porous scaffold was prepared by a filtration method. Briefly, 10 mL Ti₃−ₓCNTₙ MXene aqueous suspension (~1 mg mL⁻¹) was added dropwise into 40 mL CNT aqueous suspension (~1 mg mL⁻¹). The obtained mixture was then sonicated for 20 min under Ar atmosphere followed by filtration with a Celgard 3501 membrane. Porous DN-MXene/CNT scaffold can be obtained after rinsing with distilled water several times followed by freeze drying. In comparison, the CNT scaffold can be prepared by

![Figure 6. Electrochemical performances of K@DN-MXene/CNT||SPAN and bare K||SPAN K–S batteries in KPF₆-based electrolyte. a) Digital images (shown in inset) and the corresponding UV–vis spectra of liquid electrolytes in optically transparent devices assembled with K@DN-MXene/CNT anode (or bare K foil) and SPAN powder immersed in liquid electrolytes. b) Rate performances of K@DN-MXene/CNT||SPAN and bare K||SPAN K–S batteries. c) Cycling performances of K@DN-MXene/CNT||SPAN and bare K||SPAN K–S batteries at a current density of 0.5 C and d) corresponding discharging-charging profiles at the 2nd cycle and 200th cycle. e) The top-view SEM image of the K@DN-MXene/CNT anode disassembled from a K–S battery after 50 cycles. The elemental mapping and content of sulfur are shown in inset.](image-url)
the same method without adding DN MXene sheets. The weight of the as-fabricated scaffolds was about 4 mg cm\(^{-2}\).

**Preparation of the K@MXene/CNT:** To prepare K@DN-MXene/CNT anodes, a melt-infusion process was performed in an Ar-filled glove box (Universal 2440/750) with a moisture/oxygen concentration below 0.1 ppm. K metal was firstly heated over 70 °C on a hot plate. Subsequently, DN-MXene/CNT matrix was immersed into the molten potassium, held for 20 s, and then cooled to room temperature to obtain K@DN-MXene/CNT anode. The mass loading of K was measured by weighing the mass change before and after melt-infusion process, which was about 70 wt%.

**Characterizations:** The XRD patterns of the as-prepared samples were collected by using Bruker D8 discover XRD with Cu Kα radiation (40 kV and 40 mA). Raman spectra of samples were measured using a Renishaw inVia Raman spectrometer system (Gloucestershire, UK). XPS measurements were performed on a Kratos XASAM-800 spectrometer. The morphology of the samples was observed by field emission scanning electron microscope (FE-SEM; Zeiss Supra 55VP) and HAADF-STEM (JEOL JEM-ARM200) operated at an accelerating voltage of 200 kV. AFM measurements were performed on a Dimension 3100 SPM by using a tapping mode. The specific surface area was determined by the gas sorption technique using a Micromeritics 3Flex analyser based on the Brunauer–Emmett–Teller (BET) method.

**Assembly and Testing of Batteries:** CR2032 coin cells were assembled in an Ar-filled glove box. 0.8 M KPF\(_6\) in EC/DEC (1:1, v/v) or 0.8 M KFSI in EC/DEC (1:1, v/v) was selected as electrolyte. To study the electrochemical deposition of K, different scaffolds and current collectors (DN-MXene/CNT, CNT, Cu foil, and Al foil) were assembled into coin cells with K metal foil as counter/reference electrode and glass fiber membrane (Whatman GF/A) as separator. Before the tests, the cells were activated by discharging to 0.01 V and then charging to 1 V at a current density of 0.5 mA cm\(^{-2}\). Furthermore, various anodes were first plated on different scaffolds at a current density of 0.5 mA cm\(^{-2}\) under a deposition capacity of 1 mA h cm\(^{-2}\) and then stripped to 1 V. To test the specific capacity of the as-prepared K@DN-MXene/CNT anodes, they were assembled into coin cells with Cu foil and glass fiber membrane. The symmetric cells were assembled with two pieces of identical electrodes (K@DN-MXene/CNT, K@CNT or bare K foil), in which the K@CNT anode was prepared by electrodoping 2 mA h cm\(^{-2}\) amount of K onto the CNT scaffold at a current density of 0.5 mA cm\(^{-2}\). Cycling performances were studied by galvanostatic cycling measurement consisting of repeated charge/discharge (1 h) cycles on symmetric cells at a current density of 0.5 mA cm\(^{-2}\). The rate performances were investigated by galvanostatic cycling measurement consisting of repeated charge (1 h)—discharge (1 h) cycles on symmetric cells at various current densities. The in situ optical observations were conducted by using a homemade transparent vessel. The SPAN samples can be obtained by heating the mixture at a range of 10 \(^{5}\) to 10 \(^{7}\) Hz by applying a disturbance amplitude of 5 mV.

**Theoretical Calculations:** All structure relaxation and electronic structure calculations were performed using DFT with the projector-augmented wave method. The exchange-correlation functional of Perdew, Burke, and Enzerhof (PBE) was employed to analyze the exchange and correlation potentials. The cut-off energy level was set as 500 eV, the self-consistent field (SCF) tolerance level was set as 1.0 \(\times 10^{-5}\) au in geometry optimization, while the SCF tolerance was set as 1.0 \(\times 10^{-6}\) for energy calculation. The semiempirical London dispersion corrections of Grimme et al. were applied to account for the van der Waals dispersion interactions.[43]

**Supporting Information**

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

**Conflict of Interest**

The authors declare no conflict of interest.

**Author Contributions**

X.T. and D.Z. contributed equally to this work. X.T., D.Z., Y.G., and G.W. conceived and designed this work. X.T. and D.Z. performed the experiments and wrote the manuscript. P.L. contributed to the DFT calculations. X.G. contributed to the synthesis of MXene materials. H.L., B.S., and K.Y. discussed the results and participated in the preparation of the paper.

**Keywords**

dendrite growth, MXenes, potassium metal anodes, potassium–sulfur batteries, 3D scaffolds
