

**Efficient Lithium Storage of Si-Based Anode Enabled by a Dual-Component Protection Strategy**

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Si, as a highly competitive anode material for lithium-ion batteries (LIBs), has gained enormous commercial interests due to its high theoretical capacity, low delithiation potential, and natural abundance. However, its poor cycling stability/electron conductivity seriously restrains its practical applications. To address this problem well, herein, a scalable spray-drying method is explored to construct an ultrastable 3D Si-based composite (designed as Si@C-MX) anode, where the Ti$_3$C$_2$Tx MXene nanosheets (NSs) crump the nano-Si coated uniformly with an ultrathin carbon layer. Synergistically, the coating carbon layer and Ti$_3$C$_2$Tx NSs as the conductive elastomer constrain/buffer the volume expansion of nano-Si, avoid direct contact with the electrolyte, build a continuous electronic network for rapid electron transport, and meanwhile improve mechanical properties of the electrodes. Thanks to the dual protection (i.e., carbon coating and Ti$_3$C$_2$Tx NSs) strategy, the resultant Si@C-MX anode exhibits large reversible capacities, superior rate capability, and long-duration cycle stability. Additionally, the Si@C-MX-based full batteries delivered an energy density of 371.8 Wh kg$^{-1}$ based on the whole device at 123.9 W kg$^{-1}$ and a desirable capacity retention with cycling, which convincingly highlights its promising application in advanced LIBs.

### 1. Introduction

Under the urgent demand for achieving “net-zero emissions systems”,[1] advanced rechargeable lithium-ion batteries (LIBs) with high energy/power and long cycle life need to be developed intensively to meet various energy storage systems, such as electronic devices, electronic vehicles, and even the large-scale grids. Due to the moderate capacity of commercial graphite anode (371.8 mAh g$^{-1}$), the exploration for advanced anode materials for next-generation LIBs becomes especially imperative.[2,3]

Among various candidates, silicon (Si) has attracted considerable attention due to its ultra-high lithium storage capacity (3579 mAh g$^{-1}$, corresponding to Li$_{1.75}$Si at room temperature), low operating potential of 0.4 V (vs Li/Li$^+$), and natural abundance.[4,5] However, the alloying of Si anodes during lithiation, which inevitably leads to $\approx$300% volume expansion of Si itself, easily causes the instable solid electrolyte interphase (SEI) layer, and the pulverization of the active material, thus finally giving rise to the electrode-level failure.[6,7] To address the issues, many methods have been investigated to ameliorate the mechanical instability. Typically, it is a commonly established way by nanosizing Si with various morphologies to improve its electrochemical performance, which can not only accommodates the volume variation but also shortens the diffusion path of lithium ions.[5,8] On the other hand, the carbon coating and/or confinement are considered as another effective strategy for fabricating Si-based electrodes with enhanced electrochemical performance.[9,10] For example, Zheng et al.[9] prepared a series of Si@SiO$_x$/C nanocomposites with carbon coatings of different thicknesses, in which the Si@SiO$_x$/C with the thicker carbon coating has the better cycling stability. However, such single-component protection strategy always cannot satisfy the mechanical requirement of Si during cycling due to less ductile and limited constraint effect of thin carbon layer under the deep cycles.[11,12] In addition, the structural integrity would easily be destroyed during cycling due to the inherently weak interaction between conductive carbon and Si. Therefore, the smart combination of various effective strategies, which utilizes the distinct merits of multicomponent carbon materials with various characteristics, is urgently desired for achieving high-performance Si-based anodes for next-generation LIBs.[13,14]

As a typical graphene-like 2D material, Ti$_3$C$_2$Tx MXene, where $T_x$ represents the functional groups, has evoked a surge of scientific researches towards LIBs due to its attractive lithium-storage ability with superb rate performance and long-term cycling stability.[15,16] Moreover, the Ti$_3$C$_2$Tx itself is eminently suitable as a flexible and conductive matrix as well for many conversion/alloying-type electrodes due to its remarkably electronic conductivity/mechanical properties, large surface area, and abundant functional groups on the surface.[17–20] For instance, Zhang et al.[21] fabricated a MXene/Si@SiO$_x$/C layer-by-layer assembling superstructure by integrating the Stöber method, magnesiothermic reduction, and carbonation, which achieved
competitive electrochemical behaviors for LIBs. However, such a complicated yet costly synthesis process is unfavorable for the mass production at all. As is well known, the spray-drying method, as a well-integrated avenue in the manufacturing process, can provide a facile, rapid, and industrially adaptable fabricated process, resulting in lower fabrication cost and shortened production durations.[22,23] While, many researches, up till now, were mainly focused on the influence of process parameters (temperature, pressure, and droplet size) on specific morphologies of final products.[24,25]

Considering the comprehensive analysis above, herein, a dual-component protection strategy was purposefully explored via a spray-drying method to construct the 3D Si-based composite, in which the Ti3C2T x nanosheets (NSs) crumpled the Si nanoparticles (NPs) coated with the chitosan (CS) derived carbon layer (denoted as Si@C-MX) for LIBs. The uniqueness of the Si@C-MX composite lies in that the moderate carbon layer coating can restrain the volume expansion of Si NPs and avoid direct contact between the electrolyte and Si NPs. On the other hand, the Ti3C2T x NSs substrate serves as the elastomer to provide hierarchical buffer for volume change of Si NPs. The tight connection between the hydroxylated Si NPs, negatively charged —OH terminations on the surface of Ti3C2T x (Figure S1a, Supporting Information). The TEM images (Figure S3a–d, Supporting Information) confirm the uniform distribution of C, Ti, and Si elements in the selected region. All above characteristics corroborate the successful spray-drying synthesis of the flower-ball 3D Si@C-MX, in which the Si NPs with carbon coating are uniformly loaded and encapsulated in the 2D Ti3C2T x NSs, hence building a 3D cross-linked network. For comparison, the other two samples of Si@C and Si-MX are prepared by the same process, which also exhibits the regular flower-ball structures (Figure S2, Supporting Information).

The microstructures of the synthesized samples were evaluated by field-emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). After spray drying, the obtained Si@CS-MX precursor exhibits a unique 3D flower-spherical morphology with highly crumpled Ti3C2T x NSs as the loading matrix (Figure S1a, Supporting Information). The magnified FESEM image (Figure S1b, Supporting Information) shows that the Si@CS NPs with a size of around 100 nm are tightly wrapped by the Ti3C2T x NSs, forming a continuous conductive network. The Si@C-MX specimen, as shown in Figure 1b–d, well inherits the representative morphology of its precursor after being annealed at 600 °C, where the formed Si@C NPs are tightly wrapped in the Ti3C2T x NSs. Further TEM observation (Figure 1e) clearly evidences the existence of the Ti3C2T x NSs at the edge of the flower spheres. The Si NPs, nano-carbon layer, and Ti3C2T x NSs couple with each other, as displayed in the enlarged TEM image (Figure 1f), confirming the co-existence and homogeneously distributed of the three phases. Apparently, the Si@C NPs are evident with a diameter of 100 nm (Figure 1g), which is consistent with the FESEM observations (Figure S1b, Supporting Information; Figure 1d). The high-resolution TEM (HRTEM) image (Figure 1h) visualizes a thin yet uniform carbon layer of about 2.5 nm coating on the surface of Si NPs with discerned lattice fringes. The uniform carbon coating can form a functional region to constrain/buffer the severe volume expansion/contraction due to the alloying/dealloying Si during charge and discharge processes. The well-defined fringes in the regions (i and j) (Figure 1h) are estimated as 0.320 (Figure 1i) and 0.314 nm (Figure 1j), respectively, which correspond to the (111) plane of crystalline Si. The energy-dispersive spectroscopy (EDS) mapping images (Figure 1k) confirm the uniform distributions of C, Ti, and Si elements in the selected region. As regards the Si@C-MX, the new re-

2. Results and Discussion

2.1. Physicochemical and Structural Characteristics

The preparation process of 3D Si@C-MX is schematically illustrated in Figure 1a. Initially, the positively charged CS is spontaneously adsorbed on the Si NPs, which are negatively charged due to the —OH terminated groups on their surface after piranha treatment, forming the nanohybrid (i.e., Si@CS NPs). Then, the resultant Si@CS NPs are located on the surface of Ti3C2T x NSs with a negative charge after the Ti3C2T x NSs suspension is further dropped. After that, the uniform mixture is delivered from the feed pipe to the atomizer of the spray dryer. During the spray-drying process, the increasing surface capillary force originating from the evaporation of water on the surface of Ti3C2T x NSs impels their local deformation. And finally, the highly folded flower balls, namely the Si@CS-MX, are compressed into, which are collected after cyclone. Afterwards, the carbonization of organic CS at high temperature forms amorphous carbon in the annealing process, which constructs a closer connection with the nano Si and Ti3C2T x. Accordingly, the 3D Si@C-MX is successfully prepared.
SiO\textsubscript{x} appeared, but the (002) peak disappears both in the Si@CS-MX and Si@C-MX. It indicates that the certain aggregation of Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x}NSs occurs in the composite and the high-temperature calcination does not destroy the phase structure of Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} and Si. Furthermore, the small broad peaks centering around 21.5° should be ascribed to the contribution from the amorphous carbon.\textsuperscript{[26]} Similar observations are clear as well for the cases of Si@C and Si-MX samples (Figure S5, Supporting Information).

The X-Ray photoelectron spectroscopy (XPS) was further conducted to shed more light on elemental composition and valence states of the Si@C-MX. The full spectrum (Figure 2b) shows the co-existence of Si, C, Ti, O, N, F, and Al, in which the F and Al elements originate from the functional groups and residual Al in the Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x}, respectively, and the N species is introduced by the CS-derived carbon. The high-resolution XPS spectrum of Ti 2p (Figure 2c) is rationally deconvoluted into four pairs of peaks, i.e., Ti (455.0/461.2 eV), Ti\textsuperscript{2+} (456.1/462.0 eV), Ti\textsuperscript{3+} (457.4/462.7 eV), and Ti\textsuperscript{4+} (458.6/464.4 eV).\textsuperscript{[27,28]} The Si 2p spectra of Si@C-MX and Si NPs are comparatively shown in Figure 2d. The fitted peaks at 99.2 eV correspond to the bond of low valence Si, which mainly exists in the pure Si phase, while the peaks located at 103.4 eV are assigned to the high valence Si-O bond, which mainly exists in the SiO\textsubscript{x}.\textsuperscript{[5]} While, no signals for the SiO\textsubscript{x} are detected in the XRD pattern (Figure 2a). It suggests that the amorphous Si-O layer is probably formed on the surface of Si NPs in Si@C-MX sample, which is easily induced by the oxygen-containing functional groups on the surface of Si NPs and Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} NSs over the high-temperature treatment.

The Raman spectra were performed in the different wavelength ranges to investigate the chemical environment of the Si@C-MX sample. The peaks, as displayed in Figure 2e, correspond to the vibration peak of elemental Si. Obviously, compared with pure Si NPs, the peak position exhibits a blue shift (from 511 to 514.7 cm\textsuperscript{-1}) in the Si@C-MX, along with
the decreasing strength. The phenomenon is generally attributed to the phonon conformation/masking effect\[29,30\] due to the thorough carbon coating on the surface of Si NPs, thus affecting the lattice vibration of Si. The presence of the carbon coating was further proved by Raman spectra from 1000 to 1800 cm\(^{-1}\), as collected in Figure 2f. The characteristic D-band (1368 cm\(^{-1}\), i.e., the disordered graphitic structure) and G-band (1595 cm\(^{-1}\), i.e., the \(E_{2g}\) phonon of sp\(^2\) carbon atoms) are apparent coupled with the D\(_{00}\)-band corresponding to amorphous carbon.\[31\] Generally, the integrated area ratio of D-band to G-band \((I_D/I_G)\) represents the graphitization degree of samples. The \(I_D/I_G\) values of Si-MX, Si@C, and Si@C-MX are estimated as 0.94, 1.73, and 1.88, respectively. Besides this, in the spectra of Si@C and Si@C-MX, the strength of D\(_{00}\)-band is larger than that of Si-MX, further revealing the amorphous carbon layer both formed in the products of Si@C and Si@C-MX during annealing.

2.2. Electrochemical Evaluation

As discussed above, the 3D Si@C-MX composite has been successfully prepared through a facile yet industrially adaptable method, which can provide a dual-component protection by the amorphous carbon layer and flexible Ti\(_3\)C\(_2\)T\(_x\) NSs. Besides, the tight 3D cross-linked structure renders an efficient conductive network for efficient electrochemical reactions. Thanks to the appealing dual-component protection, the simultaneous achievements in restraining/buffering the volume change of Si NPs and rapid electron transport/ion transfer during cycling are realized in the Si@C-MX flower-spheres. Thus, the Si@C-MX is highly anticipated with appealing electrochemical Li-storage behaviors. For this, electrochemical evaluations were comprehensively conducted.

Figure 3a demonstrates cyclic voltammetry (CV) curves of Si@C-MX and Si NPs within the potential range of 1.0–3.0 V (vs Li/Li\(^+\)) at a scanning rate of 0.1 mV s\(^{-1}\). Evidently, the CV curves of the Si@C-MX anode show a similar feature to those of the pure Si NPs, featuring the same electrochemical lithium storage processes for the two. In the first cathodic process, the broad peak centering at around 0.5–1.0 V can be attributed to the formation of SEI film,\[11\] owing to the decomposition of electrolyte on the electrode surface and the irreversible lithium ion consumed by the surface functional groups of electrode materials, especially the surface functional groups of Ti\(_3\)C\(_2\)T\(_x\) NSs, which disappears in the second cycle. The sharp reduction peaks starting from 0.5 V mainly correspond to the lithiation of Si phase, which forms the Li\(_x\)Si alloy phase \((0 < x \leq 4.4)\), as described by the following equation

\[
\text{Si} + x\text{Li}^+ + xe^- \leftrightarrow \text{Li}_x\text{Si} \quad (0 < x \leq 4.4)
\]  

The anodic peaks at approximately 0.33 and 0.48 V originate from the two-step dealloying process of Li\(_x\)Si.\[32–34\] During the subsequent second and third cycles of the Si@C-MX (the lower in Figure 3a), the positions of the second anodic peak increase from 0.48 to 0.52 V, and the integrated areas under electrochemical response currents are enhanced with CV cycle prolonging, indicating the slow activation process of the Si@C-MX anode, which is attributed to the amorphization of the crystalline Si due to the large volume expansion during the initial lithium/delithiation process.\[34\] The phenomenon is examined as well for the pure Si NPs (the upper in Figure 3a).
Figure 3b profiles the galvanostatic discharge–charge (GCD) plots of the Si@C-MX at a current density of 0.1 A g\(^{-1}\). Apparently, the lithiation/delithiation platforms appearing in GCD plots well match with the cathodic/anodic peaks in the CV responses (Figure 3a). The Si@C-MX anode delivers high discharge/charge capacities of 1437.8/1186.4 mAh g\(^{-1}\), that is, a high initial Coulombic efficiency (ICE) of 82.5%.

To further investigate the dual-component protection effect in the Si@C-MX anode, rate properties of the Si@C-MX, Si@C, and Si-MX electrodes were carried out firstly in a wide current density range from 0.1 to 10.0 A g\(^{-1}\) (Figure 3c; S6a,b, Supporting Information). Remarkably, the Si@C-MX electrode exhibits average discharge capacities of 1036.2, 1039.8, 959.2, 844.5, 747.0, and 593.9 mAh g\(^{-1}\) at the current densities of 0.1, 0.2, 0.5, 1.0, 2.0, and 5.0 A g\(^{-1}\), respectively. Even at a high current density of 10.0 A g\(^{-1}\), the anode can still obtain a specific capacity of 451.9 mAh g\(^{-1}\). With the current density suddenly going back to 0.1 A g\(^{-1}\), the specific capacity recovers up to 875.4 mAh g\(^{-1}\) (Figure 3c), corroborating the superb rate performance of the Si@C-MX. In addition, the Si@C-MX anode exhibits the smaller voltage drop due to the small polarization even under the ultra-high current density of 10.0 A g\(^{-1}\) than that of Si@C and Si-MX, which confirms the fast reaction kinetics of the Si@C-MX anode due to its favorable electronic/ionic transmission network (Figure S7, Supporting Information). In sharp contrast, as regards Si@C (Figure S6a, Supporting Information) and Si-MX (Figure S6b, Supporting Information) anodes, the reversible capacities of 2475.6 and 2064.5 mAh g\(^{-1}\) are just provided at 0.1 A g\(^{-1}\), respectively, and particularly, the capacities are gained as small as 12.8 and 12.5 mAh g\(^{-1}\) at a large current density of 10.0 A g\(^{-1}\). Additionally, huge gaps from the initial values in capacities of the two electrodes are evidenced when the current density is back to 0.1 A g\(^{-1}\) once again. The high-rate performance of Si@C-MX here should be attributed to the 3D tightly linked conductive network in the composite anode, accelerating the transition of ions and electrons, which can be well supported by the electrochemical impedance spectra (EIS) measurements (Figure 3d,e). After fitted with the circuit diagram (Figure S8, Supporting Information), the charge transfer resistance (R\(_{ct}\)) and internal resistance (R\(_i\)) of the Si@C-MX, Si@C, and Si-MX are collected (Table S1, Supporting Information). The R\(_{ct}\) is derived from the
size of semicircle in the medium-frequency region (Figure 3d), and $R_s$ from the intercepts with the x-axis (Figure 3e). Notably, the Si@C-MX electrode shows the small $R_t$ (121.0 $\Omega$) and $R_s$ (2.0 $\Omega$) due to the highly efficient conductive network from both the uniform coated carbon layer and the Ti$_3$C$_2$T$_x$ NSs matrix, as schematically illustrated in Figure 3f, which is highly conducive to the rapid electrochemical kinetics towards (de) lithiation.

The long-term cycling stabilities of the Si@C-MX, Si@C, and Si-MX electrodes are further examined at the current density of 0.5 A g$^{-1}$, as illustrated in Figure 3g. Although the Si@C and Si-MX electrodes show considerable discharge capacities of 2704.5 and 2518.0 mAh g$^{-1}$, respectively, in the initial discharge process, the capacities decay to 66.4 and 637.4 mAh g$^{-1}$ just after 20 cycles, respectively. More impressively, after 200 uninterrupted cycles, the capacities of the two degrade down to 20.6 and 26.2 mAh g$^{-1}$ for Si@C and Si-MX electrodes, respectively. The crucial reason for the rapid capacity decay of Si@C and Si-MX electrodes should be assigned to the repeated and drastic volume change of Si NPs during cycling, which results in the continuous rupture of Si NPs and the formation of new SEI film, causing the capacity decay and eventually the destruction of the electrodes. By contrast, a high capacity of 803.8 mAh g$^{-1}$ can be obtained by the Si@C-MX after 1000 consecutive cycles. The distinct cycling performance of the Si@C-MX anode can be reasonably attributed to synergistic contributions from both the uniform carbon coating and continuous flexible Ti$_3$C$_2$T$_x$ NSs network, which wrap the Si NPs tightly. It is the "dual insurance" structure, rather than any single one that constrains and buffers the drastic volume change of Si NPs during the charge/discharge process, which can maintain the structural integrity and stabilize the SEI film of the electrode material meanwhile. Therefore, the Si@C-MX anode has obvious advantages compared with other reported Si-based materials (Table S2, Supporting Information).

To gain in-depth insights on the mechanism of dual-component protection originating from both carbon coating layer and Ti$_3$C$_2$T$_x$ NSs in the Si@C-MX electrode, the electrode-level changes of the Si@C, Si-MX, and Si@C-MX in thickness over the lithiation process are purposefully explored, as observed from the cross-section SEM images of the electrodes (Figure 4a–f). The thickness of the active materials loaded on the copper foils of Si@C (Figure 4a), Si-MX (Figure 4c), and Si@C-MX (Figure 4e) is estimated as 17.9, 19.5, and 17.7 $\mu$m, respectively. When discharged to 0.01 V after two charge–discharge cycles, i.e., the full lithiation state, the thickness of electroactive material layer in the Si@C (Figure 4b) and Si-MX (Figure 4d) electrodes expands to 36.6 and 34.4 $\mu$m, respectively, due to the alloying reaction of Si NPs, leading to the volumetric increase by 104.5% and 76.4%, respectively. The hugely swelling of Si@C and Si-MX electrodes in volume verifies that the single-component protection cannot effectively accommodate the capacity decay and eventually the destruction of the electrodes. By contrast, a high capacity of 803.8 mAh g$^{-1}$ can be obtained by the Si@C-MX after 1000 consecutive cycles. The distinct cycling performance of the Si@C-MX anode can be reasonably attributed to synergistic contributions from both.
volume change of Si NPs indeed, which results in the structural crack of the active Si. It will accelerate the formation of new SEI film, consume electrolyte, and reduce active sites, thus causing a rapid decline in electrochemical performance. While for the case Si@C-MX electrode, only 53.1% expansion is observed after lithiation (Figure 4f). Furthermore, the material-level morphology/structure changes after 100 charge–discharge cycles at 0.5 A g⁻¹ are investigated in detail, as shown in Figure 4g–j. Obviously, the single-carbon component or single-Ti₃C₂Tx component protection strategy, namely the Si@C (Figure 4g,h) and Si-MX (Figure 4i,j), is insufficient for inhibiting the volume variation of Si NPs at all, which renders the structural crack, continuous formation of SEI film on the fresh surface, and eventually the pulverization/agglomerate of the active materials after cycling. While, the Si@C-MX electrode (Figure 4k,l) presents a well-preserved morphology capability after long-term cycling at high current density. It is therefore easy to draw a conclusion that the dual-component protection strategy we devised here, namely the tight 3D cross-linked network formed by coated carbon layer and Ti₃C₂Tx NSs can well address the variation issue of Si NPs during cycling, which favors to maintain the structural integrity of the electrode.

In general, it is well established that nanocrystallization, carbon coating, and construction of flexible substrate all can alleviate the volume change of Si anodes during cycling to a certain extent. However, as described above, the unique configuration of the Si@C-MX electrode exhibits optimal electrochemical behaviors among the three. This explicitly means that the interaction between the coating carbon layer and Ti₃C₂Tx, NSs can well address the variation issue of Si NPs during cycling, which favors to maintain the structural integrity of the electrode.

Considering the excellent half-cell electrochemical performance of the Si@C-MX anode itself, the prospective application was further evaluated by the full devices. As schematically depicted in Figure 5a, the full LIBs are assembled with the commercial LiNi₀.₈Co₀.₁Al₀.₁O₂ (NCA) and Si@C-MX as the cathode and anode materials, respectively. As derived from the GCD plots (Figure 5b), the first charge/discharge capacities are

![Figure 5](https://www.advancedsciencenews.com/)

**Figure 5.** (a) Schematic illustration of NCA//Si@C-MX full battery; (b) GCD curves of NCA cathode at the current density of 0.2 A g⁻¹ within the potential range from 3.0 to 4.3 V; (c) Differential capacity versus voltage plots of Si@C-MX anode and NCA cathode; (d) GCD curves and (e) cycling performance of NCA//Si@C-MX full battery at 0.05 A g⁻¹ within the potential range from 2.7 to 4.2 V.
225.0/181.7 mAh g\(^{-1}\) at 0.2 A g\(^{-1}\) in the voltage range of 3–4.3 V (vs Li/Li\(^+\)), corresponding a high ICE of 80.8%. In addition, the NCA cathode still can achieve a reversible discharge capacity of 183.0 mAh g\(^{-1}\), along with a high CE value of 99% in the third cycle. As observed from the differential capacity versus voltage profiles of NCA and Si@C-MX (Figure 5c), the combination of them provides the lithium-ion full cells with an averaging voltage of about 3.5 V. Typically, the constructed Si@C-MX//NCA of them provides the lithium-ion full cells with an averaging voltage (vs Li/Li\(^+\)) of 2.7–4.2 V, coupled with an ICE value of 80%, and an average working voltage of about 3.8 V can be observed (Figure 5d). Typically, the mass loadings of NCA cathode and Si@C-MX anode in the full battery are separately 2.4 and 0.5 mg, which demonstrates a maximum energy density of 371.8 Wh kg\(^{-1}\) at a power density of 123.9 W kg\(^{-1}\) according to the discharge curve by employing the accepted 40% penalty factor to account for the weight of the electrolyte and of the auxiliary components.[39] After 70 charge–discharge cycles at 0.05 A g\(^{-1}\), a discharge capacity of the cathode (Figure 5e) can be maintained as 169.4 mAh g\(^{-1}\) (based on the cathode), along with a desirable capacity retention of 100% and CE of 99.0%, which convincingly highlights its promising application in advanced LIBs as a competitive anode material.

3. Conclusion

In conclusion, in the work, a dual-component protection strategy was smartly developed to construct the advanced Si@C-MX anode by a facile and industrially adaptable spray-drying avenue to address the inherent disadvantages of Si anodes, especially the modest rate performance and cycling stability. The dual-protection strategy here, namely, uniform amorphous carbon coating layer and flexible Ti\(_3\)C\(_2\)T\(_x\) NSs substrate, which ensured the structural integrity during cycling. Furthermore, the strong interaction between Si NPs, amorphous carbon layer, and Ti\(_3\)C\(_2\)T\(_x\) NSs established a highly efficient conductive network for efficient lithium storage. As expected, the Si@C-MX anode exhibited high reversible capacities of 1036.2 mAh g\(^{-1}\) at 0.1 A g\(^{-1}\), and even 451.9 mAh g\(^{-1}\) at a large current density of 10.0 A g\(^{-1}\) and ultra-high stable cycling performance with a retained capacity of 803.8 mAh g\(^{-1}\) after 1000 uninterrupted charge–discharge cycles at 0.5 A g\(^{-1}\). Additionally, the Si@C-MX//NCA full cells delivered a promising energy density of 371.8 Wh kg\(^{-1}\) based on the whole device at a power density of 123.9 W kg\(^{-1}\), which convincingly highlights its promising application in advanced LIBs. The design here provided a competitively commercialized anode platform for next-generation LIBs.

4. Experimental Section

Synthesis of Ti\(_3\)C\(_2\)T\(_x\) NSs: The Ti\(_3\)C\(_2\)T\(_x\) NSs was typically prepared by selective etching of Al from Ti\(_3\)AlC\(_2\) (11 technology, co., LTD) with HCl and LiF, according to our previous work.[40]

Synthesis of Hydroxylated Si NPs: The commercial Si NPs (around 100 nm, Xinnaix metallic materials, co., LTD) was activated by Piranha solution (H\(_2\)SO\(_4\)/H\(_2\)O\(_2\), 7/3, v/v) at 80 °C for 40 min.

Synthesis of Si@C-MX: Firstly, 100 mg of the CS was dissolved in 200 mL of the acetic acid aqueous solution with the concentration of 1% v/v. Then 50 mg of hydroxylated Si NPs were added to the above solution under stirring. After mixing thoroughly, 30 mg of Ti\(_3\)C\(_2\)T\(_x\) NSs were dispersed in the mixture and stirred for 12 h. Finally, the uniform solution was spray-drying by a B-290 spray-dryer (BUCHI, Switzerland). Typically, the above solution was pumped to the spray-drying atomizer through the feed pipe, then atomized into micron size dispersed droplets. Under high temperature air flow (the inlet temperature 220 °C), the droplets are dried and contracted into the Si@CS-MX powder, which was collected by cyclone separator. After further annealed at 600 °C for 2 h under the H\(_2\)/Ar flow at a ramp rate of 1 °C min\(^{-1}\), the Si@CS-MX was completely converted into the Si@C-MX.

Synthesis of Si@C and Si-MX: The synthesis of Si@C and Si-MX was carried out with the same procedure as that for the Si@C-MX, just with the exception of single-phase CS or Ti\(_3\)C\(_2\)T\(_x\) NSs added in the synthesis.

Material Characterization: The crystal structures of the samples were characterized by XRD (Cu K\(_\alpha\) radiation, Rigaku Ultima IV). Raman spectroscopy was performed by Horiba LabRAM HR Evolution (514.5 nm laser). Morphologies and microstructures of samples were carried out using Field-emission scanning electron microscopy (FESEM, JEOL-6300F, 15 kV), TEM/high-resolution TEM (HRTEM), and scanning TEM (STEM) (JEOL JEM 2100 system) with energy dispersive X-ray spectroscopy (EDS). Specific chemical states of elements in the samples were characterized by X-ray photoelectron spectroscopy (XPS, Thermo, Escalab 250xi).

Computational Method: The DFT calculations were carried out with the Perdew–Burke–Ernzerhof (PBE) function within the generalized gradient approximation (CGA) using the Vienna ab initio simulation package (VASP).[41–43] The projector augmented wave (PAW) method was used to describe the electron-ion interaction. The van der Waals (vdW) interaction was described using the DFT-D3.[44] The relatively small supercell, i.e., \(\sqrt{3} \times \sqrt{3} \times 3\) of Ti\(_3\)C\(_2\) and 2 \times 2 of graphene, were chosen for calculation. In addition, the lattice mismatch between Ti\(_3\)C\(_2\) and graphene was within 6.6%. A plane wave basis set with a cut-off energy of 700 eV was used. The Brillouin zone was represented by a Monkhorst-Pack mesh of \(11 \times 11 \times 1\) k-points.[44–46] The convergence criterion of Hellmann–Feynman forces and total energy were 0.01 eV Å\(^{-1}\) and 10\(^{-7}\) eV, respectively. A vacuum region of about 15 Å was adopted to avoid unnecessary interactions.

Electrochemical Measurements: Coin-type cells (CR2032) were fabricated in an argon-filled glove box (MBRAUN, Germany) with oxygen and moisture contents being under 0.5 ppm to evaluate the electrochemical performance of the electrodes. The slurry consisted of the active materials (Si@C-MX, Si@C or Si-MX, 70 wt%), acetylene black (20 wt%), and sodium carboxymethyl cellulose (CMC, 10 wt%) with the water as a solvent. After being coated on the copper foil, the slurry was dried in a vacuum oven at 110 °C. The cathode slurry was fabricated by mixing 80 wt% of commercial LiNi\(_{0.8}\)Co\(_{0.1}\)Al\(_{0.1}\)O\(_2\) (NCA), 10 wt% of acetylene black, and 10 wt% of polyvinylidene fluoride with the N-methyl-2 pyrollidone, and coated on the aluminum foil then dried at 110 °C for 11 h under vacuum. The electrolyte was a solution of 1 M LiPF\(_6\) in the mixture of an ethylene carbonate and diethyl carbonate (1/1, v/v). Lithium foil and Celgard 2400 polypropylene membrane were used as the counter electrode and separator, respectively. The GCD were carried out using a battery testing system (Land CT2001A, Wuhan, China). CV and EIS analysis from 100 kHz to 10 mHz were measured by electrochemical workstation (IviumStat.h, The Netherlands).

Supporting Information

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

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The authors declare no conflict of interest.

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The data that support the findings of this study are available from the corresponding author upon reasonable request.

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carbon coatings, lithium-ion batteries, Si anodes, spray-drying synthesis, Ti$_3$C$_2$T$_x$ nanosheets

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