Honeycomb-like hierarchical porous silicon composites with dual protection for ultrastable Li-ion battery anodes

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Abstract
Silicon offers a high theoretical specific capacity for anodic lithium storage. However, its applications are hindered by the electrode instability caused by the sharp volume change, and the limited rate performance resulted from the insulating property. Herein, we introduce a facile and fast method of preparing honeycomb-like silicon-based anodes (MXene-Si@C) with porous structure using MXene and carbon-coated silicon. The dual protection from both the surface coating and as-formed interlayered vacant spaces ameliorate the volume expansion of the silicon and thus reinforce the mechanical stability of the electrode. In addition, the highly conducting MXene and the surface carbon coating form a hierarchical and consecutive electron-conducting network with evidently reduced resistance. With this proposed composite, a high average Coulombic efficiency of 99.73% and high capacity retention of 82.4% after 300 cycles at 1 A/g can be achieved even with an areal loading around 1.5 mg/cm². Coupled with an NCM523 cathode, the proof-of-concept full cell delivers a high capacity of 164.2 mAh/g with an extremely high energy density of 574 Wh/kg (based on the mass of the electrode materials) at 0.2 C and an excellent cyclability at 0.5 C of 100 cycles with decent capacity retention (80.28%).

KEYWORDS
Cycling stability, lithium-ion battery, self-assembly, silicon-based anode, Ti₃C₂MXene

1 | INTRODUCTION

Silicon gains huge attention for its high-specific capacity of 3579 mAh/g after full lithiation to Li₃.₇₅Si and low lithiation voltage plateau (~370 mV vs. Li/Li⁺). Therefore, silicon-based anodes are widely regarded as one of the most promising candidates for next-generation lithium-ion batteries (LIBs) when coupling with high-voltage cathodes. However, their performance may not be well retained during cycling due to the extremely sharp volume change (>300% when fully lithiated), causing electrode pulverization and detachment from the current collector. Meanwhile, both the electrically and the ionically insulating properties of silicon usually render unsatisfactory electrochemical performance.
reaction kinetics, limiting the rate performance of silicon-based anodes.

Tactics for these challenges could be generally divided into several categories, ranging from electrode structure design, electrolyte innovation, binder development, surface coating, and so forth. Among those strategies, electrode structure designs, where internal spared spaces and stable electron-conducting frameworks are created, have been proven effective to promote the performance of silicon anode. For example, yolk-shell silicon-carbon composite (Si@C) and Si–titanium oxide (Si@TiO₂) composite demonstrated hugely improved ionic transportation through the electrode and achieved excellent cycling stability compared with bare Si. Agyeman et al. also reported a sandwich structure comprising rGO wrapped Si@C to confine carbon decorated SiNPs among layered graphene through covalent bonds, leading to a stable cycling performance of the Si-based anode. Similarly, internal hollow spaces with an Si outer shell were also reported effective for accommodating the volume expansion. However, the formation of these inner hollow spaces is usually based on the template-sacrifice method through metal-assisted (Al/Mg) thermal-reduction followed by repeated acid etching using HCl or HF. Though some innovative structures may be realized through the complicated synthesis routine, the huge time and energy consumption, the low yield of final products and inevitable impurities like Mg₂Si discourage it from practical use. In addition, previously reported Si-based anodes usually come at the cost of largely reducing the tap density and only show their structural superiority with small areal mass loadings. Based on the above-mentioned considerations, an “expressway” with simplicity and scalability meanwhile able to equip silicon-based anode with both consecutive conducting framework and expansion-tolerating structure is urged in view of practical applications.

Titanium carbide (Ti₃C₂) MXene has gained massive attention for its rich surface functional groups, mechanical properties, conductivities, hydrophilicity, and many untapped potentials. In-plane conductivity of MXene reaches around 6500 S/cm, which is among the most conductive 2D materials, and mechanically excellent properties like extremely high Young’s modulus of MXenes (up to 0.33 TPa) qualify them as robust and conducting framework for Si-based anode.

To take the baton from previous studies, here we present a highly stable honeycomb-like structure of Si-based anode realized by aqueous self-assembly using MXene flakes. With rich fluorine and hydroxyl terminations on the surface, MXene shows hydrophilicity thus could be well dispersed in water to form a homogeneous colloidal solution and so are the Si nanoparticles and Si@C, making them eligible for solution processible in an aqueous environment. The proposed aqueous self-assembly is driven by electrostatic interaction between negatively charged MXene (zeta potential: down to -53.6 mV) and positively charged Si@C particles pre-processed by polydiallyldimethylammonium chloride (PDDA). The carbon layer outside the Si spheres could not only serve as buffer layer as massively reported but also provides more sites for surfactant adsorptions and boost the process of self-assembly compared to uncoated Si. In addition, the contact between nano-Si and MXene can be enhanced by the carbon coating due to the enhanced interactions. Consequently, an internally hierarchical and consecutive conducting network with ample inner hollow space is built inside the “honeycomb.” Furthermore, the MXene nanoflakes function as walls and alleviate autonomous aggregation of Si-based particles, thus preventing lithium-source exhaustion. As a result, the developed MXene-Si@C anode achieves excellent cycling and rate performance. At a current density of 1 A/g, it delivers a high initial specific capacity of 1112.8 mAh/g, with retention of 82.4% after 300 cycles. Notably, under a large mass loading of 2.1 mg/cm², a high areal specific capacity of 2.5 mAh/cm² can be maintained even after 100 cycles. Furthermore, the full cell coupling the MXene-Si@C anode with the NCM523 cathode demonstrates an extremely high-energy density of 574 Wh/kg when discharged at 0.2 C, and an excellent rate capability and long cycle life for near 100 cycles at 0.5 C with retention over 80%, both of which validate its potential in practical use. The pouch-cell with this full-cell configuration could power the LED lights and work under different bending situations. Moreover, the wide applicability of this aqueous fabrication of Si-based anode could be promoted to other 2D materials like GO, which are similarly able to form miscible suspensions in aqueous solutions, as supported by the same synthesis routine of GO-Si@C (assembled from GO and Si@C) anodes with improved cycling stabilities.

## 2 RESULTS AND DISCUSSION

### 2.1 Characterization

Figure 1A schematically illustrates the overall fabrication workflow of the honeycomb-like MXene-Si@C along with the photo of the products. Silicon nanoparticles (SiNPs) are coated with porous carbon layers in a conventional pyrolysis method as depicted in the experimental section. The as-coated carbon layer could not only provide better electron conductivity than intrinsically insulating Si but also increase the active adsorption pore sites due to its mesoporous structure, thus providing more effective adsorption sites for ionic...
surfactant PDDA. PDDA functions as an ionic surfactant, endowing the particles with a positively charged surface layer. Meanwhile, the delaminated MXene, acquired by etching Ti$_3$AlC$_2$ MAX phase with lithium fluoride in acid solution, is equipped with rich negatively charged surface groups (–OH, –O, or –F). Therefore, the as-prepared MXene shows a minus zeta potential. The distinctively opposite surface charge properties lay the basis for an extremely strong electrostatic interaction. Once these two oppositely charged components are mixed, flocculation instantaneously forms within several seconds, where the Si@C nanoparticles are closely packed among the interlayers of MXene flakes. The product, marked as MXene-Si@C, is also shown in Figure S1.

For comparison, the pure silicon (i.e., without carbon coating) similarly processed by PDDA, denoted as MXene-Si, undergoes a far slower process (around 10 min or more) of flocculating due to much fewer absorbed surfactant, and its optical image is shown in Figure S2.

The SEM image in Figure 2A presents the structure of MXene-Si@C, where Si@C nanoparticles are packed into a consecutive network composed of MXene flakes, providing enough buffer zones for the particle expansion/contraction. The as-formed pores shown in the SEM image is quite similar to a honeycomb-like structure as shown in Figure 1A (with more specific details in Figure S13), which may not only offer internal space for tolerating the expansion of particles but also provides a locally interconnected path for electrolyte infusion, therefore, sterically overcoming the cumbersome kinetics of the electrode. The energy-dispersive X-ray spectroscopy (EDS) in Figure S12 shows a uniform distribution of silicon particles in the MXene-Si@C. In addition, evident signals of fluorine are observed together with the Ti element as expected. The TEM images in Figure 2B, C also

![Diagram of surfactant PDDA and MXene-Si@C](image-url)
present that Si@C nanoparticles are wrapped by layers of the MXene, which is in accordance with the SEM images.

The carbon layers shown in HRTEM present a chaotic atom arrangement with a scale around 5–10 nm, suggesting a low degree of graphitization, which is also evidenced by the low \( I_G/I_D \) ratio from the Raman spectroscopy (Figure 3C). Between the crystalline silicon and amorphous carbon, there is a transition region with slighter contrast than the dark crystalline area of Si, which represents an intrinsically formed SiO\( \text{_x} \) layer, as typically reported in previous literature.\(^{29}\)

The nitrogen adsorption-desorption isotherms in Figure 2D indicate a decrease of the BET surface area from 51.07 m\(^2\)/g of Si@C to 28.20 m\(^2\)/g of MXene-Si@C. This might be partially attributed to the fact that the introduction of MXene nanoflakes lowers the mass portion of the carbon coating. Meanwhile, some active mesopore sites of the coated carbon layer are covered by MXenes or some unremoved glutinous PDDA. The pore width distribution of these two samples is exhibited in Figure 2E. Though with reduced specific surface areas, the MXene-Si@C owns a larger average pore width as well as more macropores with a width larger than 50 nm, which would serve as better sites for accommodating the expansion of nanosized silicon.

The X-ray diffraction (XRD) shown in Figure 2G shows a typical pattern of pristine Si crystals (the gray pattern), where the peaks from left to right corresponds to plane indices (111), (220), (311), (400), (331), and (422), respectively.\(^{19}\) In contrast, the pattern of Si@C shows an obvious amorphous bulge at 2\( \theta \) of 22.5° due to the amorphous carbon layer. The MXene alone shows a
strong signal of the (002) plane at 2θ of 7.5°, presenting a downshift compared with the typical main peak of the Ti₃C₂Tₓ due to the larger interlayer spacing in the few layer MXene. However, self-assembled MXene-Si@C samples merely show the weak signal in the same position. This is probably because only a trace amount of the MXene is incorporated and part of them are oxidized during the synthesis workflow, which are commonly found in the self-assembled composite.

The Raman test is carried out to verify the formation of low-crystallinity carbon coating of Si@C, of which the I_D/I_G = 1.013, indicating abundant defects or vacancies in the carbon coating of Si@C (Figure 2F). Such a defect-rich carbon layer is expected to provide short immigration pathways for Li⁺ and active sites for fast lithiation/delithiation. The peaks for Si-containing anode around 517.2 cm⁻¹ are typical for crystalline silicon. Fourier-transform infrared (FT-IR) spectroscopy is carried out to further evidence the bonds and functional groups (Figure 2H). The absorption peaks at 540 cm⁻¹ represent the Si–O–Si vibration mode, while the peaks at 1270 cm⁻¹ is ascribed to the stretching of Si–O–Si bond. The evident absorption peaks of MXene-Si and MXene-Si@C at 1710 cm⁻¹ are ascribed to the stretching of Si–O–Si bond. The evident absorption peaks of MXene-Si and MXene-Si@C at 1710 cm⁻¹ are ascribed to the C=O bond vibration of MXene. Meanwhile, the Ti–O–Ti bond vibration is indicated by the peaks at 1580 cm⁻¹, indicating oxidation of MXene into TiO₂. For the self-assembled MXene-Si@C and MXene-Si, the FT-IR results also show a slight absorption at the position of 3500 cm⁻¹ and 3580 cm⁻¹, which should be assigned to the O–H bonds from Si–OH and Ti–OH, respectively. For the MXene-Si, there occurs an absorption peak at 950 cm⁻¹ ascribing to Ti–O–Si bonds, which
indicates a chemical bonding based combination between SiNPs and MXenes instead of bare physical interaction, of which the signal is not detectable for the spectra of MXene-Si@C. This supports our assumption that the electrostatic self-assembly is very weak between PDDA processed SiNPs and MXene flakes, of which the product is more membrane-like after vacuum filtration. Besides this, the TGA results in Figure 21 show that the portion of Si in the Si@C composite is about 77.2%, while the weight ratio of the MXene flake to the Si@C is 1:4. Thus, the weight percentage of the pure Si inside the MXene-Si@C is estimated to be around 61.7%, while the carbon and the MXene flakes initially take up for around 18.2%, and 20.0%, respectively.

2.2 | Electrochemical performance

Cyclic voltammetry test of MXene-Si@C is shown in Figure 3A. The first cathodic scan shows a current plateau different from later cycles at 0.46 V, which indicates the signal of SEI formation and correlates to a linear variation region before the voltage plateau in the first discharge curve in Figure 3D. In addition, a peak occurs around 0.10 V with a sharp current increase, which is different from the cathodic peak position of later cycles (~0.18 V). This can be ascribed to the crystalline Si reversibly transforming into amorphous Li15Si4. In the later cycles, a crescendo of peak current is observed of the whole electrode during the repeated scan.33

The rate capability tests of all electrodes were carried out at 0.2, 0.5, 1.0, 2.0, and 5.0 A/g, respectively (Figure 3B). The pristine Si anode shows the highest capacity at a small current of 0.2 A/g (~2300 mAh/g), while it delivers a poor performance when the current density reaches 1.0 A/g. As for the Si@C anode, though the conductive carbon coating indeed improves the rate performance due to the enhanced ion and electron conductivities, its cycling performance under each current density is not stable, and it shows inferior capacity compared to the MXene-Si@C when the current density reaches 1.0 A/g due to the lack of interconnected porous structures for accelerating ion migration in electrolyte and void space for accommodating volume expansion. By contrast, the as-prepared MXene-Si@C anode demonstrates specific capacities of 1527.1, 1267.7, 1089.4, 871.1, and 644.7 mAh/g at each corresponding current density, respectively, showing the best capacity retention when current soars. After the current density bounces back to 0.2 A/g, the specific capacity recovers to 1461.6 mAh/g, which indicates an excellent rate performance as well the stability of the anode.

This high utilization at large current densities and well-maintained capacity after restoring current to 0.2 A/g may be attributed to the largely reduced charge transfer resistance ($R_{ct}$) as indicated by the EIS plots in Figure 3C.37 It can be found that the MXene-Si@C electrode exhibits the lowest charge transfer resistance compared to the Si@C and pristine Si electrodes. This can be explained as follows. First, a more conductive electrical contact is achieved between the Si@C and the MXene-derived wrinkled network, enabling faster interfacial charge transfer and, therefore, greatly boosting the fast electrochemical reaction of the Si anode. Additionally, the larger macroscopic pores within the MXene-Si@C electrode could facilitate the electrolyte infusion for achieving a homogeneous Li-ion distribution along the through-thickness direction.

The charge–discharge profiles of MXene-Si@C of the first three cycles and the 85th cycle at 0.2 A/g are shown in Figure 3D. The initial coulombic efficiency (ICE) is 77.87% with initial discharge and charge capacity of 1939.1 and 1510.1 mAh/g, respectively. Inevitable capacity loss in the first discharge process mainly correlates to the SEI formation on the electrolyte–electrode interface. After 85 cycles at small current of 0.2 A/g, the MXene-Si@C electrode retains a specific capacity of 1330.5 mAh/g (88.11% of the initial charge capacity). In contrast, the pristine Si anode, though with a much higher initial capacity of 2703.3 and 2237.8 mAh/g during the first lithiation and delithiation, respectively, shows a much lower capacity retention of 1152.4 mAh/g (59.46% of the initial charge capacity) after same cycles at 0.2 A/g (Figure S4). The structural superiority of our designed MXene-Si@C is even more evident when the loading is increased to 2.1 mg/cm² (initial areal capacity ~3 mAh/cm²) as shown in Figure S3. The MXene-Si@C electrode maintains a capacity around 2.4 mAh/cm² (retention rate ~80%) after 100 cycles at 0.2 A/g, which further demonstrate the potential for its practical use. Moreover, the MXene-Si@C anode is also tested at 0.4 A/g, showing better cycling stability than pristine silicon and Si@C anodes for the long term (cycle number >100 [Figure S5]).

To further explore the advantages of the self-assembled MXene-Si@C when cycled at large-current densities, cycling tests are carried out at a high-current density of 1 A/g (Figure 3E). The pristine Si shows a sudden capacity drop at 1 A/g and breaks down (which means showing no charge/discharge capacity) at 2 A/g (Figure 3B). The sluggish reaction kinetics and the electron-insulating pack of the pristine Si anode result in an extremely large overpotential when large current densities are applied, leading to negligible charge/discharge capacities. Coating Si with a thin carbon layer (Si@C) can homogenize Li⁺ ion distribution and promote the
overall conductivity of electrons, thereby promoting rate capabilities and cyclability at large current densities. However, the Si@C still suffers fierce capacity decay for over 50% after around 100 cycles, which is far from satisfactory. By comparison, even at a large current density of 1 A/g, the MXene-Si@C still delivers a reversible specific capacity of 983.5, 942.0, and 917.7 mAh/g after 100, 200, and 300 cycles, respectively, corresponding to a capacity retention of 82.4% after 300 cycles, indicating superior cycling stability benefiting from the structural stability. Moreover, even at 2 A/g, the MXene-Si@C still presents satisfactory capacity retention over 80% after 200 cycles (Figure S6), further demonstrating the excellence of both the cyclability and rate capability embodied by the self-assembled structure. Therefore, based on the comparative results given by above stated multidimensional tests of the electrochemical performance, it is reasonable to assert such a structure rendered by self-assembly could not only promote the reaction kinetics for a better rate performance but also largely address the stability issue of Si-based anodes aroused by volume expansion. Table S1 lists recent studies of the Si-based anode in the open literature. The MXene-Si@C in this study shows superior cycling stability and is among the highest areal capacity loading (in mAh/cm²). Furthermore, to demonstrate the wide applicability of this aqueous fabrication, the GO-Si@C electrodes are fabricated based on the self-assembly method, and their cycling stability shows great improvements compared to the pristine Si (Figure S8).

A deeper insight into the structural stability is presented by the EIS results at different cycles. The EIS of the MXene-Si@C electrode is tested after 10, 100 cycles at 1 A/g, respectively, to observe the impedance variation. As shown in Figure S11, Rct of the MXene-Si@C electrode decreased a lot after 10 cycles, which may be attributed to the activation of the whole electrode. After 100 cycles at 1 A/g, a bounce-back of both the SEI resistance (RSEI) and charge transfer resistance (Rct) occurs, indicating a less conducting SEI and a weakened electrical contact between the Si-based nanoparticles and the conducting components during the repetitive volume variation. However, the Rct after 100 cycles remains at a rather low level, indicating a well-maintained high rate of Li-ion diffusion benefited from the self-assembled network.

Postmortem observations and characterizations are carried out to further validate the structural superiority of the MXene-Si@C over the pristine Si and Si@C. As shown in the optical photos in Figure 3F–H, after disassembling the coin cells, the MXene-Si@C shows no change in surficial morphology after 50 cycles at 0.4 A/g, while for the pristine Si electrode and Si@C electrodes, obvious and slight pulverizations are observed, respectively. The SEM images reveal thorough damage of the pristine Si anode caused by repeated swelling of the whole electrode. For the Si@C anode, even though the electrode integrity is better maintained compared to the pristine Si anode, cracks spreading along the pristine Si are still obvious, resulting in the accelerated cycling deterioration in later 55 cycles (Figure S5). However, experiencing even longer cycles than the contrast groups (Si and Si@C anodes), the MXene-Si@C anode shows seemingly intact surfaces without huge cracks, proving a mechanically stable structure. In addition, postmortem XPS results could also serve as evidence of the structural stabilities. A specific distinction in XPS (F 1s) spectra between cycled MXene-Si@C, Si@C, and pristine Si electrodes is shown in Figure 4, where the green peak is assigned to the organic components (with C–F and Si–O–F bonds, usually >688.5 eV), while the purple one to the inorganics (LiF, Li2PO3F, or TiO2F2). It is evident that, compared to the pristine Si and Si@C, the SEI of MXene-Si@C electrode after anatomy has a weaker signal of organic compositions, which mainly arises from the decomposition of the electrolyte solvents. Also, for the MXene-Si@C, there is a quick decrease of the peak green, which indicates less tendency of the carbonate solvent to decompose, while the pristine Si shows no monotonicity of the organic signals as the more serious problem of structural stability would expose more fresh-Si surfaces to the electrolytes and triggering relentless decomposition of solvent. These comparative characterization results combined with the cycling performance prove that the self-assembled MXene-Si@C anode shows well improved structural and electrochemical stability and is qualified for long-term cycling.

In practical applications, especially for the thriving electric vehicles, the NCMs Li[Ni0.5Co0.2Mn0.3]O2 are often utilized as cathode for the sake of energy density promotion due to its high working voltage, high-specific capacity, and low manufacturing cost. Here, the NCM523 cathode is chosen to couple the MXene-Si@C anode. To fully utilize the advantage of NCM cathodes and promote the ICE of full cell, prelithiation of the anode is carried out before battery assembly. The MXene-Si@C||NCM523 full cell is tested with a cutoff voltage of 4.25 V. Rate capability of the full cell is tested at 0.5, 1.0, 2.0, 5.0, and 10.0 C (where 1 C = 150 mAh/g) shows specific capacities of 147.9, 139.2, 128.5, 112.9, and 85.8 mAh/g, respectively, which is comparable with the results measured in Li||NCM523 cells with an excessive amount of Li (Figure S7).

This result indicates an adorable reaction kinetics and high reversibility of the as-synthesized Si-based anode. Moreover, the cycling performance of the MXene-Si@C||
NCM523 cell is tested at 0.5 C (Figure 5D). Initially, the full cell at 0.2 C for preactivation shows a high-specific capacity of 164.2 mAh/g and the corresponding energy density reaches a value of 574 Wh/kg (based on the mass of electrode materials), which is among the most outstanding ones in reported works. In addition, the pouch-cell level energy density is calculated as shown in Table S2. In later cycles at 0.5 C, a specific capacity of 146.1 mAh/g is shown, and 117.3 mAh/g is retained after 100 cycles, equivalent to a high capacity retention of 80.28%. Even after 150 cycles, over 70% of the initial capacity is still maintained. It is worth mentioning that there appears accelerated capacity degradation after 55 cycles, as denoted in the cycling plot, which might be ascribed to the increase of impedance and collapse of layered NCM structure triggered by Li₂CO₃ impurity phase, NiO, and spinel LiNi₂O₄, as reported in other works. The specific capacity of the NCM523 in the full cell is close to that in Li||NCM523 half-cell, which justifies a complete capacity utilization and structural stability of the MXene-Si@C anode. Furthermore, based on the full-cell configuration, a pouch cell consisting of an MXene-Si@C anode and NCM523 cathode is assembled, which could easily and stably power the LED light even at different bending conditions (Figure 5F), which can partially be ascribed to the aforementioned enhanced stability of the electrode. All those results of full-cell tests demonstrate the strong feasibility of the as-prepared MXene-Si@C anodes for practical applications.

**Figure 4** (A) XPS results with the depth profile of different anodes after 50 cycles; (B) schematics illustration of the less-formed SEI and enhanced electrode stability of MXene-Si@C.
3 | CONCLUSIONS

This study presented a honeycomb-like structure of Si-based anode realized by aqueous self-assembly between MXene and Si-based nanoparticles. Such an approach is proven to be highly effective to achieve excellent cycling stability and rate capability of the Si-based anode, as supported by results of both the half-cell and the full-cell tests. The as-synthesized MXene-Si@C shows an initial capacity of 1112.8 mAh/g at 1 A/g with reasonable loadings. The feasibility of our designed MXene-Si@C is demonstrated through the MXene-Si@C||NCM523 full cell with reasonable areal mass loadings, which donates a high-energy-density of 574 Wh/kg at 0.2 C, and could be well operated at 0.5 C for 100 cycles with decent capacity retention (>80%). The pouch-cell is assembled with the MXene-Si@C anode and NCM523 is demonstrated with good mechanical stability of the electrode. In a nutshell, a highly efficient and scalable method is proposed for the fabrication of a highly stable Si-based anode in LIBs. This fabrication process could be popularized to other two-dimensional materials and nanoparticles, therefore, offering a new avenue in achieving high-performance electrodes for effective Li-ion storage in the future.

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CONFLICT OF INTERESTS
The authors declare no conflict of interest.
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