Encasing Si particles within a versatile TiO$_2$–xF$_x$ layer as an extremely reversible anode for high energy-density lithium-ion battery

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1. Introduction

Technological breakthroughs for lithium-ion batteries (LIBs) mostly depend on the electrode material innovations [1]. Among all the viable anodes, silicon is considered as the most potentially attractive alternative to commercially available graphite anodes due to its natural abundance and superior gravimetric capacity (3579 mA h g$^{-1}$ for the highest lithiated stoichiometry of Li$_{15}$Si$_4$ at room temperature vs. 372 mA h g$^{-1}$ for graphite) [2,3]. Despite the tantalizingly high capacity potential and the economic feasibility, practical implementation of silicon anodes has been hampered by the multifaceted challenges: the silicon accommodates lithium ions upon a solid-state alloying reaction with drastic volume change (300%), the commitment local strain then pulverizes Si at the particle level and deteriorates their physical/electrical contact with both the charge carriers and current collectors at the electrode level [4]. In the meantime, the severe compression/tensile stress, upon the expansion/contraction of Li–Si alloy, ruptures the solid electrolyte interphase (SEI) layer formed at the electrode surface; subsequently the freshly formed Si cracks are exposed to the electrolyte [5,6]. As a result, the cyclability and Coulombic efficiency (CE) of the electrode deteriorate upon sustained cycling. In a full-cell configuration, the Li$^+$ ions would continually be drained out of the cathode, which is the source of Li$^+$ ions, and be irretrievably lost in degradation products forming on the negative electrode due to parasitic reactions; the electrode will ultimately cease to function when the Li$^+$ ion inventory has been depleted [7].

Nanoengineering has enabled a plethora of Si structures which...
have been investigated for their structure-dependent electrochemical properties. Nanoforms with different dimensions, such as nanoparticles [8,9], nanowires/tubes and thin layer sheets [10–12], were proved to be robust in accommodating the stress caused by the volumetric changes. However, the nanostructures have increased area-to-volume ratio which exacerbates the electrolyte decomposition occurring on the initial discharge. Another common strategy is to incorporate around the silicon particles voids or inactive matrix capable of alleviating the mechanical stress [13,14]. The reaction kinetics also hinges on the proper design of the electrical/ionic transport pathways in the electrode [15]. Thus, further processing of the Si nanostructures by incorporating noble metal (Ag, Au, and Pt) particles [16–18], electrolyte reservoir [19,20] or electrically conductive phase was extensively investigated [13,21,22]. For instance, Chen et al. utilized polystyrene to template the synthesis of Si hollow spheres via a magneto-siothermic reduction process; after decoration of the electrically conductive Ag particles, the as-fabricated anode demonstrated a capacity retention of ~93% for 100 cycles at 500 mA g−1 [23]. Liu et al. reported a Si/Carbon composite with the yolk–shell structure with a capacity retention of 83% for 430 cycles (at 460 mA g−1) by etching the pre-coated SiO2 layer with hydrofluoric acid (HF) [24]. However, the approaches used to fabricate hierarchically-structured Si-anodes are tedious from synthetic standpoint as they usually require additional post-treatments and also involve the use of hazardous chemicals like HF [25]. Hence, it is of critical importance to come up with a cost-effective approach that is ideal for mass-production of Si-based anodes with structural attributes mentioned above.

Pioneer studies also invested on the surface chemistry modification of Si particles to improve the interfacial electrode kinetics and the Coulombic efficiency (CE) upon cycling. For example, various coating layers have been introduced to avoid the direct contact between the Si and the electrolyte. For instance, one common method is to develop a conformal carbon coating on the Si structures. However, the thick, amorphous carbon prepared at low pyrolysis temperature exhibited a tendency to irreversibly trap Li+ ions and impede the ionic conductivity. As a result, the cycle stability is undermined [26]. Recently, Wu et al. reported a novel method for the synthesis of polyaniline hydrogel, which encapsulated the Si particles to form electrically conductive network. Although an average CE of ~98.5% (from the 5th cycle onwards) was achieved, the insufficient ionic conductivity of the coating expedited the capacity fading at high-rate cycling [27]. The influence of an ionicly conductive coating, Al2O3 thin layer, in stabilizing the SEI formation on Si anode was also investigated by Li et al. However, the electrode kinetics was impeded as the Li–Al–O phase formed during discharge was electrically insulating [28]. To this end, it is highly desired to realize an ideal design of silicon anode with a multifunctional coating that is mixed conducting (ionically and electrically) and capable of protecting the electrolyte from incessant decomposition during battery operation. Meanwhile the free space should be engineered among the Si particles to relieve the mechanical stress without a rupture of the outer protective layer [28,29].

With the deliberate chemical tailoring from the molecular level, we herein developed an interfacial modification strategy to exploit the full potential of silicon nanoparticles (Si NPs). Analysis of the compositional/phase transitions of the electrode during battery operation further inspired our targeted composite optimization through maximizing the intrinsic properties of each component, i.e. the protective TiO2–xFx coating and the high energy Si NPs. In contrast to integrating various exquisite procedures (hydrothermal/solvothermal or template synthesis) or post-etching treatments together to synergize specific properties, our interfacial modification approach is based on a scalable and straightforward process that enables the simultaneous realization of all the above-mentioned requirements in the versatile TiO2–xFx layer. First of all, fluoride ions (F−) partially substituted lattice oxygen [O] to generate TiF4+(dF−) ions via charge compensation in the anatase TiO2 spinel, which subsequently inject electrons to the conduction band to increase the electrical conductivity [30]; while the TiO2–xFx layer transformed into a lithiated phase (Li0.5TiO2–xFx) at ~1.5 V and eased the ionic conduction (Li+) during the Li–Si alloying reaction. Secondly, the complete TiO2–xFx encasing layer shielded most of the direct contact between the Si NPs and the electrolyte; hence the SEI formation can be spatially confined to outer surface of the TiO2–xFx layer rather than on the individual Si NPs. Lastly, the in-situ etching of the oxide layer by fluoride ions generated the internal voids to dissipate the mechanical stress associated with volume expansion of Si. Galvanostatic tests of the interfacial modified electrodes in both the half-cell vs. Li and full-cell vs. LiFePO4 cathode proved the remarkable cycling performance. Particularly, the Si@TiO2–xFx electrode with the optimized void space and Si/Ti ratio delivers a high areal/volumetric capacities (3.4 mA h cm−2 and 1328 A h L−1), robust cyclability for 800 cycles at 2 A g−1 and satisfactory CE (80% for the 1st cycle and higher than 99.5% from the 10th cycle onwards). More encouragingly, when the Si@TiO2–xFx anode was paired with a 25-μm thick lithium iron phosphate (LiFePO4) cathode in the full-cell prototype, a stable capacity behavior (0.5C) over 100 cycles was obtained. Insights into the electrode evolution occurred during electrochemical cycling were gained by means of hard X-ray photoelectron spectroscopy (HAXPES) and operando X-ray diffraction (XRD). The HAXPES was used to track the voltage-dependent valence changes of Si under the buried interface while operando XRD monitored the phase transformations involving the TiO2–xFx layer during electrochemical testing. Based on these results, we proposed the kinetic boosting mechanism of the TiO2–xFx encapsulation towards a deeper lithiation process of Si upon the repeated alloying/de-alloying process.

2. Results and discussion

The construction of the TiO2–xFx encapsulation layer on commercial Si NPs is schematically illustrated in Fig. 1. To purposely store a native oxide layer on the Si surface, the Si powder was stored in ambient atmosphere at room temperature for 48 h (Process I). The pretreated Si NPs were mixed with sodium carboxymethylcellulose (Na-CMC) binder and a predetermined amount of titanium source (TiF4) in the precursor solution, forming a Ti-CMC complex to wrap the Si NPs (Process II). Specifically, the silanol groups (Si-OH) copiously present on the oxide layer of the Si NPs, interact with the hydroxyl groups on the binder through intermolecular hydrogen bonds when the pH value was adjusted to 7.5. As a result, the Si NPs got wrapped within the polymer [31,32]. The Ti precursor is very hygroscopic and thus hydrolyzes rapidly in water to give an ill-defined and insoluble titanium (IV) hydroxide-fluoride product, described with the equation TiF4+xH2O=Ti(OH)xF4−x+xHF [33]. The hydroxyl functional group of Ti(OH)xF4−x can possibly bind to the carboxylate ion of “Si-impregnated CMC polymer”, as shown in Process II. The fluoride ions in the Ti(OH)xF4−x and HF generated during hydrolysis may further react with the Si NPs etching away the native silicon oxide at the surface. At the final stage, pyrolysis is done in an argon atmosphere (Process III) to crystallize the Ti-complex into a TiOxF2–xFx layer on the Si surface at the completion, into which the interior voids are created in situ through a fluoride etching process. Important features of the Si@TiO2–xFx composites, such as the amount of F-doping, internal porosity and weight ratio of the components can be controlled through changing the
proportions of the Ti precursor, the Na-CMC binder and Si NPs in the precursor mixture (Experimental section).

In order to investigate the effect of composition on the electrochemical performance, different composites consisting of varying amounts of TiO$_2$/C$_0$$_{xFx}$ layer on the Si NPs (Si@TiO$_2$/C$_0$$_{xFx}$) were fabricated with the increasing molar ratio of TiF$_4$ to Si in the precursor solution as 1:3, 1:2, 1:1 and 2:1, respectively. Accordingly, the products were designated as Si@TiO$_2$/C$_0$$_{xFx}$-1, Si@TiO$_2$/C$_0$$_{xFx}$-2, Si@TiO$_2$/C$_0$$_{xFx}$-3 and Si@TiO$_2$/C$_0$$_{xFx}$-4. The field emission scanning electron microscopy (SEM) image of the representative composite, Si@TiO$_2$/C$_0$$_{xFx}$-3, (Fig. 2a) shows the uniform particle distribution without noticeable bulk aggregates. A closer examination of the selected area, shown in Fig. 2b, reveals a continuous coating of a protective layer on the Si NPs with hollow cavities beneath the protective layer (marked with white arrows in Fig. 2b). In Fig. 2c the corresponding energy dispersive X-ray spectroscopy (EDX) element maps of the region of Fig. 2b: the concordance of Si signal with Ti, O and F elemental maps suggests an integrated encapsulation of Si NPs within a Ti-containing protective layer. The two sets of well-defined lattice fringes with spacing of 0.31 nm and 0.19 nm can be seen in the inner region of the composite (marked by the yellow square in the left inset image), which match well with the (111) and (220) planes, respectively, of cubic Si. Additionally, the presence of empty space can be observed (the region with light contrast marked by a white circle in Fig. 2d) in-between the anatase coating and Si NPs, which implies that internal voids have been generated as a result of the in-situ F$^-$ etching of the silica layer. The nitrogen adsorption and desorption isotherms of Si@TiO$_2$/C$_0$$_{xFx}$-3 display a type IV isotherm with type H-1 hysteresis (Fig. S1b) that are characteristic of mesoporous materials [34]. The Barrett-Joyner-Halenda (BJH) pore size distribution ranges broadly from 20 nm to 45 nm (Fig. S1b, inset). A tabular summary of the Brunauer-Emmett-Teller (BET) specific surface area, pore size range and so forth, for the Si@TiO$_2$/C$_0$$_{xFx}$ composites were itemized in Table S1. Notably, the hysteresis loop of the adsorption/desorption curves was successively enlarged from Si@TiO$_2$/C$_0$$_{xFx}$-1 to Si@TiO$_2$/C$_0$$_{xFx}$-4 due to the pronounced capillary condensation effect (Fig. S1b). This tendency synchronizes with the increased BET surface area shown in Table S1 (from 25.6 for Si@TiO$_2$/C$_0$$_{xFx}$-1 to 62.4 m$^2$ g$^{-1}$ for Si@TiO$_2$/C$_0$$_{xFx}$-4), suggesting that the improved mesoporosity originated from the progressive F$^-$ etching process. In stark contrast, the Si@TiO$_2$ composite prepared with the non-fluorine-containing Ti precursor (Titanium isopropoxide, TTIP) only exhibits an intimate coupling of the components, i.e. anatase coating and Si NPs (Fig. S2a and S2b) with the limited surface area (11.8 m$^2$ g$^{-1}$). To elaborate this tangible change of internal voids through the anion etching process, morphological comparison of various Si@TiO$_2$/C$_0$$_{xFx}$ composites was further demonstrated. Compared to the intimate integration of the core shell components in the Si@TiO$_2$/C$_0$$_{xFx}$-1 (Fig. S2c), the Si cores become easily identifiable through the transparent protective coating of the Si@TiO$_2$/C$_0$$_{xFx}$-2 composite (Fig. S2e and 2f) with the inner pores in-
between the protective layer and the Si NPs become visible (marked by arrows in Fig. S2f). While the excessive dosage of TiF4 precursor induces the undue etching of Si, the mesopores spread uniformly across the Si@TiO2-xFx-4 composite without noticeable Si particles left (Fig. S2g). HRTEM image shows the lattice fringes corresponding to the (001) planes of anatase (Fig. S1h). According to previous studies, this anisotropic crystallization of anatase originates from the preferential adsorption of F− on the (001) face and thus inhibits the crystal growth along this orientation [35,36]. For comparison purpose, if no Na-CMC was employed in the precursor solution while keeping all other experimental parameters identical as Si@TiO2-xFx-3, the as-fabricated Si@TiO2-xFx-W/O-CMC composite exhibits a seriously agglomerated Ti species with inhomogeneous encapsulation of Si NPs. This suggests the crucial intermolecular hydrogen bonding effect of the Na-CMC, which bridges the Si NPs and the hydrolyzed Ti(OH)4Fx−x in the

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Fig. 2. (a) SEM image of Si@TiO2-xFx-3 composite at a low magnification; (b) SEM image of Si@TiO2-xFx-3 composite at a higher magnification; (c) EDX element maps of Si, Ti, O, C, F and Na for the area as shown in Figure b; (d) TEM image of Si@TiO2-xFx-3 composite and HRTEM images (inset) of the selected regions, i.e. silicon NPs and TiO2-xFx coating layers; (e) XRD patterns of the commercial Si NPs and various Si@TiO2-xFx composites; (f) Raman spectra of various Si@TiO2-xFx composites.
precursor complex. The X-ray diffraction (XRD) patterns recorded in Fig. 2e show two phases in all Si@TiO2–xFx composites: 1) the characteristic diffraction peaks corresponding to cubic Si with an Fd-3 m space group marked by the black dots (ICSD NO. 51688); and 2) the tetragonal anatase with J41/amd space group (ICSD NO. 9852) marked by the red arrows. For a higher dosage of TiF4 in precursor, the intensities of the diffraction peaks corresponding to Si gradually weakened and broadened, suggesting the reduced size of Si nanocrystalline in the as-fabricated composites. According to the calculation from Debye-Scherrer equation (using the Si (311) diffraction peak), the average crystallite size is estimated as ~94 nm for Si@TiO2–xFx-1, ~71 nm for Si@TiO2–xFx-2, ~48 nm for Si@TiO2–xFx-3 and ~14 nm for Si@TiO2–xFx-4. For the peaks assignable to anatase in the diffraction patterns, additionally, the relative intensity of the (004) peak as compared to the (101) peak increased, reflecting the pronounced (001) facet observed in the microscopic images. Moreover, the diffraction peaks in the Si@TiO2–xFx-W/O-CMC pattern are partially assignable to the TiOF2 phase (ICSD No. 38132), suggesting insufficient oxygen supply from the precursors to form the oxide and thus a phase separation occurred (Fig. 2e, marked by green arrows) [37]. Compositional details of the components were summarized in Table S1. Raman spectroscopy (Fig. 2f) further exhibits the subdued peak that is indexable to Si–Si vibration (519 cm$^{-1}$) from Si@TiO2–xFx-1 to Si@TiO2–xFx-4, this phenomenon echoes with the size reduction of Si nanocrystalline estimated from above Scherer equation. Peak positioned at 144 cm$^{-1}$, corresponding to the E_g mode of anatase TiO2, reveals the intensity reduction as the pronounced F$^-$ doping amount was incorporated within the anatase lattice. Note that this peak almost disappears when most of TiF4 precursor transforms into the dominating TiOF2 phase in the Si@TiO2–xFx-W/O-CMC composites.

High-resolution XPS spectra of various Si@TiO2–xFx composites corroborate the viability of employing F$^-$ doping to modify both the electronic configuration of TiO2 and the interfacial valence of Si. As shown in Fig. 3a, all the F 1$s$ spectra exhibit peaks assignable to two main regions: 1) The F 1$s$ peak at ~688.4–689.0 eV associates with the chemically bonded F in the form of Ti–F–Ti linkages, the formation of which is due to the nucleophilic substitution reaction of [O] in the anatase [38]; and 2) the minor peak at 686 eV suggests the physically adsorbed F$^-$ on the surface of anatase. Previous study has established the significance of controlling the spatial distribution of anionic dopants to modify the electronic configuration of the tetravalent Ti. The interfacial adsorbed anionic dopant cannot contribute to the increased conductivity, neither would interstitial doping wherein anions might even impede the solid-state Li$^+$ diffusivity [39]. As indicated in Table S1 and Fig. 3a, the increased anion dopant mirrors the increased anion dopant, suggesting the generation of Ti$^{3+}$ at the expense of tetravalent Ti in Si@TiO2–xFx-3. Based on the quantitative analysis of the XPS spectra (method described in the experimental section), the atomic ratio of substitutional F to Ti was estimated as 2%, 3.5%, 7% and 13% for Si@TiO2–xFx-1 Si@TiO2–xFx-2, Si@TiO2–xFx-3 and Si@TiO2–xFx-4 composites, respectively; in this regard, the molecular formula TiO$_2$–xFx (x=0.02, 0.035, 0.07 and 0.13) may be written correspondingly (Table S1). The small amount of Ti$^{3+}$ was generated to compensate the charge imbalance when F$^-$ substituted for lattice O$^{2-}$, promoting the electrical conduction by inter-valence electron hopping [40]. Accordingly, as shown in the Si 2p core level spectra in Fig. 3c, the peaks at ~103.9 eV for the tetravalent Si monotonically decreases as the TiO2–xFx coating accumulates (as relative to the peak for the zero-valent Si at ~99.2 eV). This tendency suggests the effective fluoride etching of the oxide during the preparation process. It is noteworthy that the disappearance of the Si peaks in the Si@TiO2–xFx-4 spectrum was due to the signal blocking caused by the thick TiO2–xFx encapsulation layer. On this account, the TiO2–xFx coating layer was expected to modify the interfacial electrochemical process of Si NPs and as such the formation of SEI layer could be mostly restricted to the outer TiO2–xFx layer [30].

Encasing Si NPs in the TiO2–xFx layer along with the in-situ generated voids is expected to buffer the Si volume expansion and
markedly improve the electrode kinetics. To gauge the effect of this strategy on electrochemical performance, galvanostatic cycling tests of various Si@TiO$_2$$_{x}$F$_x$ composites were conducted in pouch-type half cells. At a current density of 500 mA g$^{-1}$, the cyclability of the electrode based on Si NPs (Si ratio was controlled as 52 wt\% in the electrode, which is similar to Si@TiO$_2$$_{x}$F$_{x}$-3) is rather unsatisfactory. It delivered gravimetric capacities of 3482 mAh g$^{-1}$ and 1951 mAh g$^{-1}$ for the first cycle, corresponding to a CE value of 56\% (Fig. S4). Upon continued cycling, the reversible capacity decreased to 820 mAh g$^{-1}$ after 60 cycles with the average CE lower than 95\%. This irreversibility could be attributed to the substantial trapping of lithium ions by silanol groups from the silica surface. As the TiO$_2$ coating amount with the enhanced electrochemical performance after 100 cycles (Fig. 4a). This positive correlation of TiO$_2$$_{x}$F$_x$ coating amount with the enhanced electrochemical performance was further validated in view of the robust cycle behavior of the Si@TiO$_2$$_{x}$F$_{x}$-3. The electrode exhibited a high discharge and charge capacities of 1831 mAh g$^{-1}$ and 1464 mAh g$^{-1}$ during the first cycle, then the reversible capacity experienced a slight increment which finally stabilized at 1620 mAh g$^{-1}$ after 100 cycles. According to the compositional ratio shown in Table S1, the theoretical capacity of the composite was calculated as 1642 mAh g$^{-1}$, indicating the full exploitation of the capacity limit. After calendaring the Si@TiO$_2$$_{x}$F$_{x}$-3 electrode, the mass loading was controlled as 2.1 mg cm$^{-2}$ and the density of electrode layer as 0.72 g cm$^{-3}$. Correspondingly, the areal and volumetric capacities can be estimated as 3.4 mA h cm$^{-2}$ and 1196 Ah L$^{-1}$, respectively. According to the cell stacking model proposed by Obrovac et al. in a recent review, the stack energy density can be roughly calculated as 874 W h L$^{-1}$, or 20\% energy improvement with respect to the conventional LiCoO$_2$/graphite cell with a volumetric capacity of 726 W h L$^{-1}$ as described in the reference [3]. Apparently, two complementary structural features originated from the encapsulation layer contribute to this remarkable cyclability: 1) The interior voids generated in-situ by F$^-$ etching enable the composite electrodes to accommodate the volumetric expansion of Si and retain a mechanically robust structure; and 2) the increased electrical conductivity of the electrodes via the trivalent titanium (Ti$^{3+}$) incorporation in the Si@TiO$_2$$_{x}$F$_x$ composites. Specifically, sheet resistances of Si@TiO$_2$, Si@TiO$_2$$_{x}$F$_{x}$-1, Si@TiO$_2$$_{x}$F$_{x}$-2 and Si@TiO$_2$$_{x}$F$_{x}$-3 were measured by the four-point probe technique as 582, 263, 105, 42 $\Omega$ sq$^{-1}$ respectively. The Si@TiO$_2$$_{x}$F$_{x}$-4 electrode, however, could only deliver a reversible capacity of 925 mAh g$^{-1}$ after 100 cycles in spite of the cycle durability. This lower capacity stems from the excessive weight ratio of TiO$_2$$_{x}$F$_x$ coating amount (68\%), which adversely affects the theoretical capacity of the composite. Hence the TiO$_2$$_{x}$F$_x$ coating has to be optimized to balance various factors, e.g. the appropriate compositional ratio, the complete encapsulation and the adequate interior voids, that collectively harmonize into a mechanical robust structure with the stable electrochemical process at the electrode/electrolyte interface.

Additionally, the pervasive TiO$_2$$_{x}$F$_x$ encapsulation layer has also altered the electrochemical process on the surface of Si and thus minimized the parasitic SEI-forming reactions. For example, the Si@TiO$_2$$_{x}$F$_{x}$-1 electrode exhibits a considerably restrained ICL of 863 mAh h$^{-1}$ as compared to 1531 mA h$^{-1}$ for the Si electrode,

![Fig. 4](image_url) (a) Cycle stability of various Si@TiO$_2$$_{x}$F$_x$ electrodes measured at 500 mA g$^{-1}$; (b) the 1st, 2nd, 10th, 50th, 100th discharge-charge curves for Si@TiO$_2$$_{x}$F$_{x}$-3 composite electrodes; (c) cycling stability of Si@TiO$_2$$_{x}$F$_{x}$-3 electrode at different current densities; (d) long-term cycling performance of Si@TiO$_2$$_{x}$F$_{x}$-3 electrode at 2 A g$^{-1}$.
and the ICL value was further mitigated to 728 mA h g\(^{-1}\) for Si\textsubscript{@}TiO\(_2\)\textsubscript{xFx-2} (Fig. S5a), 366 mA h g\(^{-1}\) for Si\textsubscript{@}TiO\(_2\)\textsubscript{xFx-3} (Fig. 4b) and 249 mA h g\(^{-1}\) for Si\textsubscript{@}TiO\(_2\)\textsubscript{xFx-4} (Fig. S5b), corresponding to their initial CE values as 69%, 80% and 76%, respectively. Notably, the alleviation of irreversibility by the interfacial modification becomes more evident upon continued cycling, as we compared the accumulative ICL between the Si electrode and Si\textsubscript{@}TiO\(_2\)\textsubscript{xFx-3} in Fig. S6. For instance, the difference of ICL at 200 mA g\(^{-1}\) for Si\textsubscript{@}TiO\(_2\)\textsubscript{xFx-3} electrode. Then the current density was increased to 1 A g\(^{-1}\) for Si\textsubscript{@}TiO\(_2\)\textsubscript{xFx-3} electrode. This comparative analysis highlights the effective interfacial modification of the electrode through the spatial confinement of Si NPs within the TiO\(_2\)\textsubscript{xFx} protective layer. It was also observed that the composites with higher TiO\(_2\)\textsubscript{xFx} coating amounts, i.e. Si\textsubscript{@}TiO\(_2\)\textsubscript{xFx-3} and Si\textsubscript{@}TiO\(_2\)\textsubscript{xFx-4}, demonstrated a continual capacity increase which prevails from the 1st to 100th cycle (Fig. 4b and Fig. S5b). As commonly observed in nanosized metal oxide/Li cells, a similar phenomenon was attributed to the reversible formation/dissolution of organic polymeric layer formed by electrolyte decomposition, the gradual establishment of which brings about the extra capacity contribution through a so-called "pseudocapacitance behavior" [41]. However, since the SEI formation was largely restrained by introducing the TiO\(_2\)\textsubscript{xFx} protective layer, some other factors should be accounted for the capacity increase in this particular case, for example, the influence of the TiO\(_2\)\textsubscript{xFx} encapsulation layer on the lithiation process of Si NPs [42]. We will elaborate the detailed mechanism study in the following text.

Since the rate capability determines the output power, it is imperative to investigate the cycle stability under different current densities (Fig. 4c). When cycled at 200 mA g\(^{-1}\), the Si\textsubscript{@}TiO\(_2\)\textsubscript{xFx-3} electrode delivered an initial reversible capacity of 1416 mA h g\(^{-1}\) which gradually increased to 1540 mA h g\(^{-1}\) over the first 20 cycles. Then the current density was increased to 1 A g\(^{-1}\), 1.5 A g\(^{-1}\), 2 A g\(^{-1}\), 3 A g\(^{-1}\) and 4 A g\(^{-1}\) in a stepwise manner for every subsequent 20 cycles, where stable capacities of 1375 mA h g\(^{-1}\), 1194 mA h g\(^{-1}\), 1045 mA h g\(^{-1}\), 854 mA h g\(^{-1}\) and 710 mA h g\(^{-1}\), respectively, were obtained. The dependence of the reversible capacities on the current densities for all the composite electrodes is also summarized in Fig. S7. The capacity differences between the Si\textsubscript{@}TiO\(_2\)\textsubscript{xFx-3} and composites containing lower amounts of TiO\(_2\)\textsubscript{xFx} coating (Si\textsubscript{@}TiO\(_2\)\textsubscript{xFx-1} and Si\textsubscript{@}TiO\(_2\)\textsubscript{xFx-2}) become noticeably larger with increasing current density. In comparison, the Si\textsubscript{@}TiO\(_2\)\textsubscript{xFx-4} composite with the highest TiO\(_2\)\textsubscript{xFx} ratio demonstrates even better capacity retention at the higher rate: the reversible capacity obtained at 4 A g\(^{-1}\) equals to 75% of the value at 200 mA g\(^{-1}\). This comparative analysis further demonstrates the improved rate behavior resulting from the enhanced interfacial kinetics of the charge carrier (electrons and Li\(^+\) ions) transport imparted by the TiO\(_2\)\textsubscript{xFx} coating. The long-term cycling was shown in Fig. 4d, when cycled at the high current density of 2 A g\(^{-1}\). The Si\textsubscript{@}TiO\(_2\)\textsubscript{xFx-3} electrode demonstrated a capacity increase from 1040 to 1240 mA h g\(^{-1}\) upon the first 250 cycles; this trend is similar to the cycle behavior at the lower rate shown in Fig. 4a. The capacity fading in the subsequent cycle averaged out at 0.0018% per cycle and a reversible capacity as high as 1115 mA h g\(^{-1}\) could be still maintained over a total 800 cycles, which corresponds to 90% of its highest reversible capacity. This cycle behavior compares favourably with results reported in the literature. (The comparison with recently reported Si anodes was listed in Table S2.) To make the more informative performance demonstration, we constructed a prototype full cell model through pairing the pre-activated Si\textsubscript{@}TiO\(_2\)\textsubscript{xFx-3} anode (discharged to 0.01 V and re-charged to 2.0 V at 50 mA g\(^{-1}\)) and a LiFePO\(_4\) cathode (25 μm for thickness). At the cycle rate of 0.5 C (85 mA g\(^{-1}\)), charge and discharge capacities for the 1st cycle were recorded as 150 mA h g\(^{-1}\) and 127 mA h g\(^{-1}\) respectively, showing an initial CE of 85% (Fig. 5). Upon continuous cycling, the discharge capacity dropped to 121 mA h g\(^{-1}\) at the 100th cycle, which corresponds to a capacity retention rate of 95%. For comparison, the similar cycle behavior of the LiFePO\(_4\) cathode was demonstrated in Fig. S8. These results suggest that the good CE of the pre-activated Si\textsubscript{@}TiO\(_2\)\textsubscript{xFx-3} electrode (higher than 99% from the 5th cycle onwards) has minimized the irreversible Li\(^+\) consumption from the cathode in the full cell system.

We further investigated the electrochemical process of a Si\textsubscript{@}TiO\(_2\)\textsubscript{xFx-3}/Li pouch cell at a scan rate of 0.5 mV s\(^{-1}\) using cyclic voltammetry (CV). As shown in the 1st CV curve in Fig. 6a, the overlapping cathodic peaks at 1.7 V and 1.5 V vs. Li\(^+/\)Li indicate the multi-step lithiation process of TiO\(_2\)\textsubscript{xFx}: 1) the solid solution formed up to the solubility limit of Li in anatase and 2) the subsequent Li\(^+\) insertion into the vacant octahedral sites of anatase. The anodic peak situated at 2.1 V can be attributed to Li extraction from the anatase crystal structure during the delithiation. The redox peaks were observed to move with cycling and finally stabilized at 1.75 V/2.2 V (marked as A/A\('\)), as a phase allowing for faster movement of charge carriers has formed in the TiO\(_2\)\textsubscript{xFx} layer [39,43]. The pronounced cathodic shoulder peak during the 1st cycle ranging from 1.0V to 0.55V was due to the SEI formation. Two subsequent slopes ranging from 0.3 to 0.1 V (B) and 0.1 to 0.01 V (C) can be associated with the multistep lithiation processes of Si: the initial formation of amorphous lithiated phase (a-Li\(_x\)Si), followed by the solid-state transition of a-Li\(_x\)Si to a deeply lithiated phase, i.e. the metastable crystalline Li\(_x\)Si\(_2\) (c-Li\(_x\)Si\(_2\)) [44]. During the anodic sweep, two characteristic shoulders centered at 0.25 V and 0.4 V are observed, which correspond to the gradual de-alloying processes of the deeply lithiated c-Li\(_x\)Si\(_2\) (B′ and a-Li\(_x\)Si alloy (C), respectively [45,46]. It is intriguing to see that redox couple C/C\('\) becomes more pronounced from 2nd to 30th cycle (marked by the red arrows), probably suggesting that the deep lithiation of Si has been activated as the cycle progressed. This may in return account for the increased retrievable capacity observed in Figs. 4a and d. From the 30th to 100th cycle, the superimpossibility of the CV curves indicates a highly stable electrochemical process for the electrode after the initial kinetic activation. Additionally, we also employed HAXPES to confirm the deeper lithiation of Si in the course of the discharge. HAXPES with the high kinetic energy of 2300 eV was purposely chosen to analyze Si species at the depth beneath the interfacial layer. Fig. 6b shows the Si 2p spectra at various lithiated stages during both the 1st and 50th cycles. In comparison to the 1st cycle, the Si 2p spectra of the Si\textsubscript{@}TiO\(_2\)\textsubscript{xFx-3} electrode for the 50th cycle demonstrates a distinct, negative shift in the binding energies, especially as the
potential was decreased to lower cut-off values, e.g., 0.1 and 0.01 V. This comparative result thus suggests the activation of a deeper lithiation of Si after the initial cycles [47].

The real-time phase transformations of the Si@TiO₂₋ₓFx-3 composite during the lithiation-delithiation process were investigated by Operando XRD. As shown in Fig. 7a, the diffraction peak at 25.3° for anatase (101) gradually shifted toward lower two theta angles as the voltage decreased from the open circuit voltage.

Fig. 6. (a) Cyclic voltammograms of Si@TiO₂₋ₓFx-3 composite at a scan rate of 0.5 mV s⁻¹ from the 1st cycle to the 100th cycle; (b) Si 2p core-level XPS spectra of Si@TiO₂₋ₓFx-3 electrode at various lithiated stages. (Solid lines indicate the spectra at different lithiated stages during the 1st cycle; dot lines indicate the spectra at different lithiated stages during the 50th cycle).

Fig. 7. Operando XRD patterns of the Si@TiO₂₋ₓFx-3 electrode at various lithiation/delithiation stages during (a) the 1st cycle and (b) the 50th cycle at a constant current density of 200 mA g⁻¹.
to 1.0 V (marked by the black arrow). This process corresponds to the faradic Li⁺ insertion into half of the vacant octahedral sites of anatase forming a orthorhombic Li-rich phase of Li₂TiO₂-xFx [48]. This diffraction peak doesn’t exhibit any detectable changes until the electrode was charged back to ~ 2.1 V during the delithiation process. At this potential, the anatase (101) peak shifted back to its original position, indicating the extraction of lithium ions from the Li₂TiO₂-xFx phase. Similar phase transformation of TiO₂-xFx was observed even for the 50th cycle (Fig. 7b) [49]. With the voltage decreasing from 1 V to 0.2 V, the diffraction peak at 28.3° attributed to crystalline Si (c-Si) started to diminish due to the reduced crystallinity of Si. The peak eventually disappeared when the electrode was discharged to 0.1 V through the electrochemical-driven solid-state amorphization process [50]. At this stage, the TiO₂-xFx coating existed in its lithiated form (Li₂TiO₂-xFx), thus acting as a funnel to draw the Li⁺ toward Si particles during the alloying-dealloying process. The enhanced solid-state Li⁺ diffusivity and structural robustness of the electrodes upon interfacial modification were further confirmed by various post-cycling characterizations, including electrochemical impedance spectroscopy (EIS) measurements (Fig. S9) and post-mortem microscopic observations of the electrodes (Fig. S10 and S11) [51, 52]. The detailed analysis was elaborated in the Supporting Information.

### 3. Conclusion

The work presented in this article establishes a versatile TiO₂-xFx protective layer to sheathe the Si NPs via the interplay of interfacial modification technique and the in-situ oxide etching process. With the exquisitely optimized component ratios and internal space engineered into the hierarchical arrangement, the Si@TiO₂-xFx-3 electrode demonstrated a remarkable electrochemical performance in both the half cell and full cell systems upon galvanostatic cycling: high areal capacity (3.4 mA h cm⁻²), excellent cyclability for 800 cycles at 2 A g⁻¹, and CE values of 80% during the first cycle and higher than 99.5% after 10 cycles could be realized for the half cell. When balanced with a 25-μm LiFePO₄ cathode in the full cell model, the good capacity retention of ~95% could be maintained for 100 cycles at 0.5 C. The remarkable cycle performance is considered as the fruits of the multi-functional modification layer as discussed above. Firstly, the optimized void space allowed inner Si NPs to expand freely without rupturing the TiO₂-xFx layer. Secondly, the presence of Ti⁴⁺ due to the substitutional F⁺ doping changed the electronic configuration of anatase, primarily alleviating the electrode resistance. Finally, the coating reduced the direct exposure of Si NPs to the electrolyte, and limited the SEI formation to only the outer protective layer. Furthermore, we employed 1) HAXPES to track the compositional variation at the buried electrode/electrolyte interface and 2) operando XRD to monitor the real-time phase transition of the electrode upon the lithiation process. These results confirmed the kinetic activation of the electrode by forming the lithiated phase Li₃TiO₂-xFx during the alloying/dealloying process of Si. The enhanced kinetics promoted its deeper degree of lithiation and the thus complete exploitation of the electrode to the capacity limit. We believe that this simple interfacial modification approach provides a viable route toward high-performance alloy-type anodes on a commercial scale.

### 4. Material and methods

#### 4.1. Materials

All chemicals were used as received without further purification.

Crystalline Si powder (~100 nm, 99%) was purchased from Alfa Aesar. Titanium (IV) fluoride (TiF₄), titanium (IV) isopropoxide (Ti[OCH(CH₃)₂]₄, 97%), sodium carboxymethyl cellulose (Na-CMC, Aldrich, MW = 250,000, degree of substitution 0.7) and polyvinyl alcohol (PVA, MW = 89,000–98,000, 99%), hydrochloric acid (HCl, 37%) and ethanol (CH₃CH₂OH, 99.5%) were purchased from Sigma-Aldrich. Ultrapure water (Millipore) with a resistivity greater than 18.2 Ω cm was used as the primary solvent.

#### 4.2. Synthesis of Si@TiO₂-xFx composites

In a typical synthesis, oxidative pretreatment was firstly conducted by placing 150 mg Si particles in an ambient atmosphere for 48 h. Subsequently, the pretreated Si particles were dispersed in a 50 mL mixed solvent of ethanol and water (volume ratio is 2:3) at room temperature. After 10 min of magnetic stirring, 40 mg sodium carboxymethyl cellulose was added to the ethanol/water mixed solvent; thereafter, an HCl solution (0.1 M) was added dropwise to the above mixture until the pH value reached ~7.5. Then TiF₄ was added cautiously to the homogeneous solution with the precise control of the predetermined molar ratio of TiF₄ to Si as 1:1. The solution was stirred well while heating at 45°C for 4 h. The composite product was then collected by centrifugation, washed with ethanol and water in turn and subsequently heated at a rate of 3 °C min⁻¹ to 450 °C for 1 h in an argon atmosphere. The as-fabricated composite was designated as Si@TiO₂-xFx-3. When the molar ratio of TiF₄ to Si was changed to 1:3, 1:2 and 2:1 while keeping all other preparation variables the same, the as-fabricated composites were designated as Si@TiO₂-xFx-1, Si@TiO₂-xFx-2, and Si@TiO₂-xFx-4, respectively. When 1.2 mL Ti[OCH(CH₃)₂]₄ was used as the titanium precursor in the preparation instead of TiF₄, the product formed was designated as Si@TiO₂ composite. For the control experiment where no Na-CMC was employed in the precursor solution while keeping all other experimental parameters identical to that of Si@TiO₂-xFx-3, the as-fabricated composite was designated as Si@TiO₂-xFx-W/O-CMC. The mass ratio of Si was analyzed by soaking the Si@TiO₂-xFx composites in a 10% HF solution for 2 h.

#### 4.3. Materials characterization

SEM was performed using a field-emission Zeiss 1550 instrument operated at 10 kV. TEM and high-resolution TEM images were taken with a JEOL JEM-2100F microscope operating at 200 kV and equipped with a Schottky field-emission gun, a Gatan Ultrascan 1000 CCD camera and a Gatan Imaging Filter (Gif Tri-diem 863). XRD of the composites were recorded on a Bruker D8 ADVANCE Diffractometer using Cu Kα radiation. **Operando** XRD analysis was carried out to study the phase transition during the first lithiation/delithiation process, which was performed in a transmission mode using a STOE diffractometer with a position-sensitive detector and Cu Kα radiation with the wavelength (λ) of 1.5406 Å, operating at 45 kV and 40 mA. The BET specific surface areas and pore size distributions of each composite were evaluated at 77 K (in a liquid N₂ bath) using a Micromeritics ASAP 2020 analyzer equipped with the V3.04 E software. The Raman analysis was performed with a Renishaw Ramscope equipped with a Leica DM optical microscope, a CCD camera, and a solid state laser (λ = 532 nm) source. The sheet resistance of various Si@TiO₂-xFx composites was investigated by 4-point probe technique (CMT-SR2000). The measured values were scattered within 10% of the average value, and averaged over five different spots for a specimen.

Precautions were taken for all the XPS measurements conducted on the electrodes at various lithiation stages [47]. To avoid air contamination, a specially-designed stainless-steel sample...
transfer shuttle was used to transport the samples from the glove box to hard x-ray photoelectron spectroscopy. The binding energy was calibrated with the hydrocarbon C 1s peak at 285.0 eV. HAXPES measurements were carried out at BESSY II synchrotron facility (Helmholtz Zentrum Berlin, Germany) where fixed excitation energy of 2300 eV was used (first order lights from respectively the Si (111) and the Si (422) double-crystal monochromator). Considering that 95% of the photoelectron signal comes from a layer thickness equal to three times the inelastic mean free path, the depth of analysis in silicon at 2300 eV is around 12–15 nm beneath the surface. The analyzed area of the samples was a 400 μm diameter disk. The pressure in the analysis chamber was under 10⁻⁸ mbar. Core peaks were analyzed using a nonlinear Shirley-type background, and peak positions and areas were obtained by a weighted least-squares fitting of model curves (70% Gaussian and 30% Lorentzian combination).

Specimens for post-mortem morphological analysis were treated as follows: the composite electrodes were cycled at a current density of 500 mA g⁻¹ for certain cycles and then rested for 24 h. The anode materials were then disassembled from batteries in the glove box followed by washing with 1 mL DMC (dimethyl carbonate). After vacuum drying at 120 °C for 1 h, the samples were mounted on the SEM holder or TEM copper grid in a re-circulating argon glove box (MBRAUN LabMaster 130), and then quickly transferred into the SEM/TEM, reducing the air exposure to less than 3 min.

### 4.4. Electrochemical measurements

The working electrode based on Si NPs was a copper foil current collector coated with a slurry of 50 wt% Si NPs, 15 wt% CMC binder and 35 wt% carbon additive (Super P) in the mixed solvent mixture (1:1, v/v) with 5 wt% CMC additive was used as the electrolyte. The batteries were assembled using the carbon additive in the mixed solvent slurry. The mass loading of these composites was controlled as 2.1 ± 0.3 mg cm⁻². A lithium metal foil was used as the counter electrode and LiPF₆ electrolyte. After vacuum drying at 120 °C for 24 h. The anode materials were then disassembled from batteries, and polyvinylidene fluoride (PVDF) was used as the binder.

Specimens for post-mortem morphological analysis were treated as follows: the composite electrodes were cycled at a current density of 500 mA g⁻¹ for certain cycles and then rested for 24 h. The anode materials were then disassembled from batteries in the glove box followed by washing with 1 mL DMC (dimethyl carbonate). After vacuum drying at 120 °C for 1 h, the samples were mounted on the SEM holder or TEM copper grid in a re-circulating argon glove box (MBRAUN LabMaster 130), and then quickly transferred into the SEM/TEM, reducing the air exposure to less than 3 min.

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### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.nanoen.2016.09.026.

### References

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