Core-shell Si@TiO₂ nanosphere anode by atomic layer deposition for Li-ion batteries

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highlights
- Si nanospheres are precisely coated with TiO₂ by ALD method.
- The Si@TiO₂ composite with a 3 nm TiO₂ layer exhibits the best cycling stability.
- TiO₂ thickness is critical to balance structural stability and conductivity of Si.
- The difference in coating electrode and active material by ALD is also revealed.

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Abstract
Silicon (Si) has been regarded as next-generation anode for high-energy lithium-ion batteries (LiBs) due to its high Li storage capacity (4200 mA h g⁻¹). However, the mechanical degradation and resultant capacity fade critically hinder its practical application. In this regard, we demonstrate that nanocoating of Si spheres with a 3 nm titanium dioxide (TiO₂) layer via atomic layer deposition (ALD) can utmostly balance the high conductivity and the good structural stability to improve the cycling stability of Si core material. The resultant sample, Si@TiO₂-3 nm core–shell nanospheres, exhibits the best electrochemical performance of all with a highest initial Coulombic efficiency and specific charge capacity retention after 50 cycles at 0.1C (82.39% and 1580.3 mA h g⁻¹). In addition to making full advantage of the ALD technique, we believe that our strategy and comprehension in coating the electrode and the active material could provide a useful pathway towards enhancing Si anode material itself and community of LiBs.

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1. Introduction
As one of the most important energy storage devices in the past decades, lithium-ion batteries (LiBs) have been widely applied in cell phones, laptops and other portable electronic devices due to their high energy density and long cycling life [1–5]. Very recently, the increasing demand for high-energy and high-power LiBs in the application of hybrid electric vehicles (HEVs) and electrical vehicles (EVs) has stimulated great interest in advanced electrode materials with much higher energy density, longer cycling life and faster rate capability than the current ones [6,7].

Silicon (Si) is considered as an important anode material for next-generation LiBs owing to its high theoretical capacity of 4200 mA h g⁻¹, which is about ten times higher than that of graphite (372 mA h g⁻¹) [8]. Nevertheless, the repeated Li alloying/de-alloying inevitably leads to a dramatic volume change (~300%), which causes serious particle pulverization, electrical disconnection and fast degradation of structural stability, greatly hindering its widespread application [9–11]. To address this issue, many approaches have been raised through preparation of nanostructured Si and Si-based composites including coating Si surface with a second phase, which have demonstrated superior performances compared with their pristine materials [12–21]. For example, Cui...
et al. proposed a pomegranate-like hierarchical structured Si anode, which effectively tackled the drawbacks of Si [20]. After that, they designed nonfilling carbon-coated porous silicon microparticles, which exhibited excellent cycling stability with high reversible specific capacity (~1500 mAh g⁻¹, 1000 cycles) [21].

Atomic layer deposition (ALD) is a novel thin film growth technique that can deposit uniform and conformal coatings on atomic level, and the thickness of ALD coating layer can be precisely controlled by varying the number of deposition cycles. Until now, significant attention has been drawn to ALD-coating of active materials and electrodes themselves for improved cycling performances with ultrathin metal oxide/nitride layers (e.g., Al₂O₃, TiO₂, TiN, and ZrO₂) [22–34]. These work highlighted the advantages of ALD in atomically-precise thickness control, which offers a facile and unique technique to optimize the thickness of coating layer for optimizing the cycling performances of the employed electrode materials.

The common TiO₂, an ionic conductive and electrochemical active material, has attracted much attention for its robust structural stability against repeated charge/discharge (less than 4%), easy preparation, low polarization, good reversibility and safety performance [35–37]. Furthermore, its small volume change during cycling endows itself as a promising coating layer to prevent electrode crack through particle pulverization. For example, Mitlin et al. demonstrated that TiO₂ thin films overcoating on Si nanowires/tubes electrodes could efficiently improve the lithium storage performances [24,25]. However, such Si electrode materials grown on stainless steel template might have difficulties in large-scale processing. To further elucidate the improvement mechanism and seek commercialized approach of TiO₂ deposited on Si by ALD, Si nanospheres without any template are employed in present work with different thickness of TiO₂ layer coating for investigation. Moreover, it should be pointed out that the transition from one-dimensional nanostructures (nano-wires/tubes) with extremely high aspect ratios to zero-dimensional nanospheres is not trivial and might contribute to a further understanding of the coating technique itself. As a result, it is established that the optimal coating thickness of TiO₂ can balance the conductivity and buffering effect, which explains the improved electrochemical reversibility of the Si@TiO₂ nano core–shell material.

2. Experimental

2.1. Synthesis of Si@TiO₂ nanocomposites

Pristine Si (purity 99.9 wt%, specific surface area 60 m² g⁻¹) was purchased from Shanghai Shuitian Co. Ltd. ALD was performed in a viscous flow reactor (GEMSTAR-6™ Benchtop ALD, Arradiance) at a pressure of ~0.8 Torr. Ultra-high purity N₂ (99.999%) was used as carrier gas at the mass flow rate of 200 scm. TiO₂ ALD coating was performed by alternatively dosing titanium isopropoxide (TTIP, Sigma–Aldrich, 97%) and deionized water at 150 °C. Here the TTIP precursor was contained in a sealed stainless steel bottle at 80 °C to prevent any condensation. The cells were charged and discharged on a battery tester (LAND2001A, China) between 0 and 3.0 V (versus Li/Li⁺) with a current density of 0.1C (1C = 4200 mA g⁻¹) at room temperature. The electrochemical impedance spectroscopy (EIS) measurements were performed over a frequency range from 10 kHz to 10 mHz.

3. Results and discussion

The morphologies of Si and Si@TiO₂ nanocomposites prepared by ALD method were measured by FESEM and HRTEM (Fig. 1a–f). Obviously, pristine Si displays the morphology of smooth and homogeneously distributed spheres with a particle size distribution of 50 ± 2 nm (Fig. 1a). Fig. 1b–e demonstrates the morphologies of TiO₂ overcoated Si spheres with different thickness of 2, 3, 4 and 5 nm, respectively, wherein the uniform TiO₂ coating layers can be clearly observed. A high resolution image of 3-ALD is further shown in Fig. 1f, in which a TiO₂ ALD layer (3 nm) with poor crystallinity were dried at 120 °C for 2 h under vacuum. Coin type cells (CR2032) were assembled in a glove box (MB-10-compact, MBRAUN) under Ar atmosphere, with oxygen and water contents less than 0.5 ppm, where Li metal foil and Whatman glass fiber membrane were used as the counter electrode and separator, and 1 M LiPF₆ dissolved in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) with the volume ratio of 1:1 was used as electrolyte. Before electrochemical tests, the batteries were aged for 24 h to ensure sufficient soakage. The cells were charged and discharged on a battery tester (LANDE2001A, China) between 0 and 3.0 V (versus Li/Li⁺) with a current density of 0.1C (1C = 4200 mA g⁻¹) at room temperature. The electrochemical impedance spectroscopy (EIS) measurements were performed over a frequency range from 10 kHz to 10 mHz.

Fig. 2a displays the XRD patterns of the Si and Si@TiO₂
core–shell structured samples. Obviously, all the diffraction peaks presented in the spectra can be indexed to the phase-pure crystal Si (JCPDS 65–1060), whereas no any other peaks originating from TiO$_2$ can be identified, which implies that the crystallinity and/or the content of the as-deposited TiO$_2$ is low, in line with the observation by HRTEM as shown in Fig. 1 and previous literature [38,39]. In addition, no visible change of Si diffraction peak on Si@TiO$_2$ samples firmly suggests that TiO$_2$ coating layer has little influence on the Si structure.

Raman spectra were also collected to investigate the surface components and structures of the samples (Fig. 2b). In the bottom curve of pristine Si (0-ALD), the strong Raman peaks at 520 and 302 cm$^{-1}$ are assigned to the first-order transverse optical (TO) phonon mode and the 2nd order transverse-acoustic (2 TA) mode of Si, respectively [40]. For the TiO$_2$ coated samples, two distinct features are clearly observed: (i) increase of the characteristic Eg vibration peak intensity of anatase TiO$_2$, locating at 145 cm$^{-1}$ [41], as the thickness increases, being consistent well with the HRTEM observation in Fig. 1; (ii) gradual broadening of the band 520 cm$^{-1}$, which could probably be due to the phonon confinement effect [42,43] and/or a masking effect [43]. Therefore, the combined bulk-sensitive XRD and surface-sensitive Raman results suggest that the
TiO$_2$ coating layers on Si nanoparticles do not influence the bulk crystallinity, though it can introduce subtle composition change on the surface.

XPS measurements were further carried out to elucidate the surface chemical composition before and after TiO$_2$ overcoating. Fig. 3a shows the intensity of Ti 2p peak increases as the thickness of TiO$_2$ increases from 2 to 5 nm while the peaks of Ti 2p$_{1/2}$ and 2p$_{3/2}$ at 464.4 and 458.6 eV [44] remain constant, indicating that the titania ALD films are in the fully oxidized form of TiO$_2$ regardless of its thickness. In the Si 2p region, the pristine Si sample shows two peaks at binding energies of 99.6 and 103.3 eV, corresponding to Si$^0$ and Si$^{4+}$, respectively (Fig. 3b) [45]. This is not surprising since Si is very sensitive to air, by forming a native SiO$_x$ layer. Nevertheless, the SiO$_x$ layer is much thinner compared with the thickness of TiO$_2$ ALD layer, evidenced by the observations in HRTEM image (Fig. 1f), and EDS elemental mapping (Fig. 1g–l). After TiO$_2$ ALD overcoating, the peaks of Si 2p rapidly degrade in their intensities with increased TiO$_2$ thickness (Fig. 3b). In Fig. 3c, the pristine Si sample again shows an O1s binding energy at 532.1 eV, assigned to the oxygen species in the SiO$_x$ [46]. This O1s peak gradually attenuates, while developing a new signal at 529.9 eV, after TiO$_2$ ALD overcoating, originating from oxygen species of the TiO$_2$ layer [47]. Taken together, the development of Ti2p, Si2p and O1s clearly confirms the formation of the Si@TiO$_2$ core–shell structure with precise-thickness control by ALD observed in Fig. 1.

Fig. 4 demonstrates the electrochemical performances of the as-prepared samples. Not surprisingly, bare Si electrode suffers fast capacity decay (Fig. 4a). After coating with 2 nm TiO$_2$, the corresponding 2-ALD electrode exhibits a certain improvement of...
capacity retention. When the TiO$_2$ layer is increased to 3 nm, the 3-ALD electrode demonstrates much increased capacity with desirable retention, which still exhibits 1580.3 mA h g$^{-1}$ after 50 cycles (also seen in Table 1). Careful observation indicates that this electrode only experiences a quick degradation in the initial 10 cycles, and afterwards, the capacity of which remains quite stable. Compared with pristine Si, the 3-ALD electrode obviously shows remarkably improved cycling performance, which could be possibly ascribed to the buffering effect of the TiO$_2$ layer, not only alleviating the huge volume change of Si core during the alloying and de-alloying reaction, also effectively constraining the pulverized Si powder inside the TiO$_2$ shell and thus preventing it cracking from the current collector/electrode, and therefore, enhances the stability of the Si@TiO$_2$ composite. As for the 4-ALD and 5-ALD (not shown, the same as that of 4-ALD) electrodes, the capacity could be barely detected during the cycling. The sharp capacity drop for 4-ALD could be possibly attributed to its much lower electrical conductivity of poor-crystallized TiO$_2$ film [48], which will be discussed later.

The details of charge and discharge curves of 0-ALD and 3-ALD Si@TiO$_2$ electrodes are illustrated in the galvanostatic profiles (Fig. 4b–c). Obviously, after 3 nm TiO$_2$ deposition, the main features of charge/discharge profiles of Si keep unchanged. We can clearly observe the characteristic discharge behavior of Si by showing low voltage plateaus during the first discharge in Fig. 4b–c, which could be assigned to the lithiation of crystalline Si into an amorphous Li$_x$Si phase with a progressively increasing Li content [25]. While the corresponding charge slopes below 0.50 V are related to the Li extraction [10], via de-alloying of amorphous Li$_x$Si phase with different composition [49]. The weak discharge slopes starting at around 1.5 V should be attributed to the formation of solid electrolyte interphase (SEI) film on the surface of the active particles [50], which become less important in the following cycles, leading to some irreversible electrochemical reactions on the surface in the first reduction scan [51,52]. And it can be found that there is a high irreversible capacity loss between the first and fifth discharge down to 0 V, which mainly resulted from some side reactions for SEI formation composed of organic lithium alkylcarbonates, lithium adsorption in the conductive additive carbon black and irreversible electrochemical decomposition of the electrolyte [53–55]. Moreover, no characteristic features of TiO$_2$ can be found around 1.75/1.94 V [56] due to its low content (Fig. 4c). Therefore, the kinetics of Li alloying/de-alloying kinetics process is basically same on the 0-ALD and 3-ALD electrodes. In the following cycles, the charging capacity of pure Si electrode decreases rapidly due to the detrimental pulverization of the Si nanoparticles. For the 3-ALD electrode, it demonstrates much improved reversibility except the similar decay of charging capacity in the initial 10 cycles. After that, it becomes rather stable and the capacity maintains at 1580.3 mA h g$^{-1}$, with a high Coulombic efficiency of 97.97% after 50 cycles. The significantly increased electrochemical reversibility could be attributed to the structural stability after thin TiO$_2$ layer deposition, which constrains the volume change and affords the strain accumulation.

To understand the Li diffusion kinetics, EIS measurements were carried out using the half cells consisting of Si and Si@TiO$_2$ core–shell nanoparticles separately as working electrodes at the state of open circuit voltage, as demonstrated in Fig. 5a. The impedance spectra were analyzed using an equivalent circuit shown in the inset of this figure. The intercept at the $Z_{\text{real}}$ axis in high frequency region corresponds to ohmic resistance ($R_\Omega$), which represents the total resistance of electrolyte, separator, and electrical contacts. The semicircle in the middle frequency range indicates the charge transfer resistance ($R_{ct}$), and the inclined line in the low frequency

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Cycling performances of 0-ALD and 3-ALD electrodes.</th>
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<tbody>
<tr>
<td></td>
<td>0-ALD</td>
</tr>
<tr>
<td>Initial discharge/charge capacities/mA h$^{-1}$</td>
<td>3670.2/2866.1</td>
</tr>
<tr>
<td>Initial coulombic efficiency/%</td>
<td>78.09%</td>
</tr>
<tr>
<td>50$^{th}$ discharge/charge capacities/mA h$^{-1}$</td>
<td>273.3/271.7</td>
</tr>
<tr>
<td>50$^{th}$ coulombic efficiency/%</td>
<td>99.4%</td>
</tr>
<tr>
<td>Capacity retention after 50 cycles/%</td>
<td>9.5%</td>
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Fig. 4. The electrochemical performances of Si nanospheres before and after TiO$_2$ coating: The charge capacity of different electrodes (a), galvanostatic cycling profiles of 0-ALD (b) and 3-ALD (c).
range represents the Warburg impedance. The details of the fitted resistance through the equivalent circuit are listed in Table 2. It can be clearly observed that the solution resistances are similar among the three electrodes. However, the charge transfer resistance, Warburg impedance and total resistance \( R_{\text{tol}} = R_s + R_{\text{ct}} + W_s \) show significant difference, showing the minimum resistances of 52.81, 49.66 and 106.20 \( \Omega \) respectively in 0-ALD electrode, while monotonously raises the values as the increase of TiO2 thickness.

This is not surprising because the native SiOx layer is extremely thin (Figs. 1f–1 and 3) and does not have any considerable impact on the resistance. On the other hand, the poor electrical conductivity of the TiO2 layer due to the poor crystallization [48] (Figs. 1f and 2a) may have an important influence. The resistances of Si and Si@TiO2 core–shell nanoparticles composed electrodes are further visually compared in Fig. 5b. It can be clearly seen that the resistances \( R_{\text{ct}}, W_s \) and \( R_{\text{sol}} \) of the as-prepared samples can be divided into two parts (I and II). In region I, when the TiO2 thickness is less than 3 nm, the resistances increase rather mildly with the TiO2 increase. When the thickness exceeds 3 nm (part II), apparently, the resistances surge sharply. As an intensively studied insulator (bandgap ~ 3.5 eV), it is suggested that the electron tunneling distance of TiO2 is about several nanometers [57], and electron conductivity may degrade rapidly when TiO2 thickness is above this value. In this case, the 3 nm is probably the tunneling distance for the poorly crystallized TiO2, which explains the much declined capacity when its thickness exceeds 3 nm. Above all, the remarkably improved performance on the 3-ALD electrode seems to be achieved by optimizing the electrode structure stability and low resistance of the coating layer. When the TiO2 layer is too thin (<3 nm), it is hard to guarantee the stability of the electrode structure; on the other hand, if it is too thick it will have high resistance, impeding the electron tunneling processes. It should be noted that the optimal thickness of TiO2 on Si nanowire was established to be 10 nm in Ref. 24, far from the 3 nm thickness in this work. The schematic microstructural illustrations between the two works are compared in Fig. 6. Noticeably, Si nanowires in Ref. 24 were grown on 316L stainless steel spacers, which were used as a current collector. In that case, electron might mainly circulate from/to the current collector without passing through the coated TiO2 layer, since a TiO2 overcoating layer with a thickness of 10 nm with a significantly higher resistance is expected based on our results shown in Fig. 5. However, in this work, TiO2 ALD coating on Si nanoparticles was performed before casting on the Cu current collector to prepare the electrode. Apparently, electron transportation has no other choice but to pass through the TiO2 overcoating layer. As a consequence, the thickness of TiO2 overcoating layer could be more sensitive in our case compared with the previous work in Ref. 24 due to the different current flowing pathways, explaining well the large difference of optimized TiO2 thickness.

To further confirm the enhancement of structure stability after TiO2 deposition, the morphologies of 0-ALD and 3-ALD electrodes after 10 complete cycles are unfolded in Fig. 7. It is widely accepted that the main drawback of Si is its large volume expansion/contraction (~300%) upon alloying/de-alloying with lithium, resulting in high mechanical stress, pulverization and loss of electronic contact, which induce severe capacity degradation [58,59]. As can be seen in Fig. 7a, the pristine Si electrode loses its original morphology of homogeneously distributed spheres, degrading to small aggregated particles after only 10 cycles. On the contrary, both morphology and size of 3-ALD Si nanospheres remain almost unchanged, which could be clearly attributed to the buffering effect

Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>( R_s/\Omega )</th>
<th>( R_{\text{ct}}/\Omega )</th>
<th>( W_s/\Omega )</th>
<th>( R_{\text{sol}}/\Omega )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-ALD</td>
<td>3.73</td>
<td>52.81</td>
<td>49.66</td>
<td>106.20</td>
</tr>
<tr>
<td>2-ALD</td>
<td>6.02</td>
<td>58.40</td>
<td>53.87</td>
<td>118.29</td>
</tr>
<tr>
<td>3-ALD</td>
<td>3.11</td>
<td>65.05</td>
<td>55.42</td>
<td>123.58</td>
</tr>
<tr>
<td>4-ALD</td>
<td>5.40</td>
<td>103.10</td>
<td>93.95</td>
<td>202.45</td>
</tr>
<tr>
<td>5-ALD</td>
<td>4.31</td>
<td>125.81</td>
<td>126.4</td>
<td>256.52</td>
</tr>
</tbody>
</table>

Fig. 5. AC impedance spectra of as-assembled cells (a) (inset shows the equivalent circuit) and evolution of resistances with TiO2 increase for Si and Si@TiO2 electrodes at open circuit voltage (b).

Fig. 6. Schematic microstructural illustrations of that of Ref. 24 (a) and this work (b). (Red core: Si material; purple shell: TiO2 layer). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
of TiO$_2$ layer, alleviating the huge volume change of Si during the repeated alloying and de-alloying process. This explains the desirable structure reversibility and electrochemical performance stability in Fig. 4 and Table 1. However, it is rather difficult to distinguish the TiO$_2$ deposition layer in the cycled electrode (Fig. 7b), which could be ascribed to a mixture formation with the SEI layer in the repeated cycling.

4. Conclusions

In conclusion, Si nanoparticle anode material is uniformly coated by TiO$_2$ via ALD with precisely-controlled layer thickness (2, 3, 4, 5 nm). The electrochemical result indicates that TiO$_2$ coating on Si nanoparticles with 3 nm thickness remarkably improves the cycling performance, which delivers a high Coulombic efficiency and charge capacity of 97.97% and 1580.3 mA h g$^{-1}$ after 50 cycles. EIS analysis of the as-prepared samples indicates that TiO$_2$ thickness within 3 nm is beneficial to the desirable conductivity. The morphology characterization after 10 cycles reveals that the TiO$_2$ buffer layer effectively affords the Si volume change inside the spheres during repeated alloying and de-alloying, thus largely suppresses the pulverization and aggregation of Si particles. All these results suggest that the 3 nm is the optimal thickness to take full advantage of the good ionic conductivity and the robust mechanical property of TiO$_2$ layer, which explains the improved electrochemical performances of 3-ALD electrode. Currently, further optimizing the active materials through high flexibility and compatibility ALD modification for the assembly of LIBs is ongoing, including the cathode and anode materials, coating the electrode and the active materials. This work, in principle, endows deep insight in designing, understanding and utilizing ALD modified electrode/active material in next generation rechargeable batteries.

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