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

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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 0.1 C (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.

Key words: Silicon nanospheres; Titanium dioxide overcoating; Atomic layer deposition (ALD); Cycling performance; Buffering effect

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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 ($\sim 1500 \text{ mA h g}^{-1}$, 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.* Al_2O_3 , TiO_2 , TiN and ZrO_2) [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 TiO_2 , 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 TiO_2 thin films overcoating

on Si nano-wires/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, Arradance) 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 sccm. 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, and the inlet lines were kept at 120 °C to prevent any condensation. The timing sequence of TiO₂ ALD was 10, 300, 4, and 300 sec for TTIP dose time, N₂ purge time, water dose time, and N₂ purge time, respectively (10-300-4-300). TiO₂ ALD

was deposited on the silicon spheres with different cycle numbers to obtain TiO₂ coated Si nanospheres with the thickness of 2, 3, 4, and 5 nm (named as 2-ALD, 3-ALD, 4-ALD and 5-ALD, respectively; and the pristine Si is labeled as 0-ALD for comparison).

2.2 Physical characteristics

X-ray diffraction (XRD) measurements were performed on a diffractometer (DX-2700, Fangyuan) with Cu K α radiation ($\lambda = 1.54145 \text{ \AA}$). Raman spectra were recorded on a Raman spectrometer (RM-1000, Renishaw) using 632.8 nm He-Ne laser as irradiation source. In the experiment, the laser power was maintained at the same low value of $1 \times 10^4 \text{ W cm}^{-2}$ for all the samples. Surface-sensitive X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Electron Corporation spectrometer with an Al K α (1486.6 eV) radiation. Surface morphology and microstructure of samples were characterized by field-emission scanning electron microscopy (FESEM, JSM-7001F, JEOL) and high resolution transmission electron microscopy (HRTEM, JEM-2010, JEOL). While characterizations of the 3-ALD samples were more carefully carried out on an aberration-corrected high-angle annular dark-field scanning TEM (HAADF-STEM) instrument at 200 kV (JEOL-2010F). Meanwhile, energy-dispersive X-ray (EDX) spectroscopy was also collected on the same equipment. To investigate the microstructures of different electrodes after electrochemical test, the cycled electrodes were taken out from the cells and repeatedly rinsed with dimethyl carbonate (DMC) and then dried under vacuum in a mini chamber of glove box before carefully transferred into the chamber of HRTEM.

2.3 Electrochemical characteristics

For the fabrication of electrodes, 70 *wt.*% of active material was mixed with 15 *wt.*% of acetylene black (Super-P, 3M Carbon) and 15 *wt.*% of binder (Sodium alginate, Sigma-Aldrich). The electrodes were dried at 120 °C for 12 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 (LAND2001A, China) between 0 and 3.0 V (versus Li/Li⁺) with a current density of 0.1 C (1 C = 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 and well crystallized Si sphere in (111) direction are observed. Surprisingly, the “native” silicon oxide (SiO_x) layer between the Si core and TiO₂ shell is not observed under the current resolution, implying

that its thickness could be extremely thin if existed. The morphology and composition of the 3-ALD sample were further studied using HAADF-STEM, along with EDX elemental mapping as shown in Fig. 1g-l. The pronounced signals of Ti and O near the surface clearly demonstrate a Si@TiO₂ core-shell structure, in good agreement with the observations in Fig. 1b-f. However, the presence of “native” SiO_x layer is not detectable, again implying that its thickness could be extremely thin.

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 TiO₂ can be identified, which implies that the crystallinity and/or the content of the as-deposited TiO₂ is low, in line with the observation by HRTEM as shown in Fig. 1 and previous literatures [38,39]. In addition, no visible change of Si diffraction peak on Si@TiO₂ samples firmly suggests that TiO₂ 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 (2TA) mode of Si, respectively [40]. For the TiO₂ coated samples, two distinct features are clearly observed: (i) increase of the characteristic E_g vibration peak intensity of anatase TiO₂, 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 TiO₂ 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 TiO₂ overcoating. Fig. 3a shows the intensity of Ti 2p peak increases as the thickness of TiO₂ 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 TiO₂ 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 Si⁰ and Si⁴⁺, 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 TiO₂ ALD layer, evidenced by the observations in HRTEM image (Fig. 1f), and EDS elemental mapping (Fig. 1g-l). After TiO₂ ALD overcoating, the peaks of Si 2p rapidly degrade in their intensities with increased TiO₂ 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 TiO₂ ALD overcoating, originating from oxygen species of the TiO₂ layer [47]. Taken together, the development of Ti2p, Si2p and O1s clearly confirms the formation of the Si@TiO₂ 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 TiO₂, the corresponding 2-ALD electrode exhibits a certain improvement of capacity retention. When the TiO₂

layer is increased to 3 nm, the 3-ALD electrode demonstrates much increased capacity with desirable retention, which still exhibits $1580.3 \text{ mA h g}^{-1}$ 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_xSi phase with a progressively increasing Li content at lower voltage [\[25\]](#). While the corresponding charge slopes below 0.50 V are related to the Li extraction [\[10\]](#), via de-alloying of amorphous Li_ySi 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 $1580.3 \text{ mA h g}^{-1}$, 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_{real} axis in high frequency region corresponds to ohmic resistance (R_s), 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 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 ($R_{tot} = R_s + R_{ct} + W_s$) show significant difference, showing the minimum resistances of 52.81, 49.66 and 106.20 Ω respectively in 0-ALD electrode, while monotonously raises the values as the increase of TiO_2 thickness. This is not surprising because the native SiO_x layer is extremely thin (Figs. 1f-l and 3) and does not have any considerable impact on the resistance. On the other hand, the poor electrical conductivity of the TiO_2 layer due to the poor crystallization [48] (Figs. 1f and 2a) may have an important influence. The resistances of Si and Si@ TiO_2 core-shell nanoparticles composed electrodes are further visually compared in Figure 5b. It can be clearly seen that the resistances (R_{ct} , R_w and R_{tot}) of the as-prepared samples can be divided into two parts (I and II). In region I, when the TiO_2 thickness is less than 3 nm, the resistances increase rather mildly with the TiO_2 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 TiO_2 is about several nanometers [57], and electron conductivity may degrade rapidly when TiO_2 thickness is above this value. In this case, the 3 nm is probably the tunneling distance for the poorly crystallized TiO_2 , 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 TiO_2 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 TiO_2 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 TiO_2 layer, since a TiO_2 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, TiO_2 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 TiO_2 overcoating layer. As a consequence, the thickness of TiO_2 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 TiO_2 thickness.

To further confirm the enhancement of structure stability after TiO_2 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 ($\sim 300\%$) 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 of TiO₂ 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 TiO₂ 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 TiO₂ *via* ALD with precisely-controlled layer thickness (2, 3, 4, 5 nm). The electrochemical result indicates that TiO₂ 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 TiO₂ thickness within 3 nm is beneficial to the desirable conductivity. The morphology characterization after 10 cycles reveals that the TiO₂ 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 TiO₂ 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.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (50902044, 21473169, and 51402283), the 863 Program of China (2015AA034201), the State Scholarship Fund from China Scholarship Council (201308410027), the Program for Science & Technology Innovation Talents in Universities of Henan Province, China (16HASTIT042), and the Recruitment Program of Global Youth Experts, the Scientific Research Foundation for the Returned Overseas Chinese Scholars, and the U.S. Department of Energy's Office of Basic Energy Science, Division of Materials Sciences and Engineering, under contract with UT-Battelle, LLC (SD).

References

- [1] M. Armand, J.M. Tarascon, *Nature* 451 (2008) 652–657.
- [2] M. Sathiya, A.M. Abakumov, D. Foix, G. Rousse, K. Ramesha, M. Saubanère, M.L. Doublet, H. Vezin, C.P. Laisa, A.S. Prakash, D. Gonbeau, G. VanTendeloo, J.M. Tarascon, *Nat. Mater.* 14 (2015) 230–238.
- [3] C.X. Zu, H. Li, *Energy Environ. Sci.* 4 (2011) 2614–2624.
- [4] D. Deng, M.G. Kim, J.Y. Lee, J. Cho, *Energy Environ. Sci.* 2 (2009) 818–837.
- [5] Q. Zhang, Y. Wang, Z.W. Seh, Z. Fu, R. Zhang, Y. Cui, *Nano Lett.* 15 (2015) 3780–3786.

- [6] H. Wu, G. Chan, J.W. Choi, I. Ryu, Y. Yao, M.T. McDowell, S.W. Lee, A. Jackson, Y. Yang, L. Hu, Y. Cui, *Nat. Nanotechnol.* 7 (2012) 309–314.
- [7] M.M. Thackeray, C. Wolverton, E.D. Isaacs, *Energy Environ. Sci.* 5 (2012) 7854–7863.
- [8] C.K. Chan, H.L. Peng, G. Liu, K. McIlwrath, X.F. Zhang, R.A. Huggins, Y. Cui, *Nat. Nanotechnol.* 3 (2008) 31–35.
- [9] T. Song, L.B. Hu, U. Paik, *Phys. Chem. Lett.* 5 (2014) 720–731.
- [10] I. Kovalenko, B. Zdyrko, A. Magasinski, B. Hertzberg, Z. Milicev, R. Burtovyy, I. Luzinov, G. Yushin, *Science* 334 (2011) 75–79.
- [11] D.S. Jung, M.H. Ryou, J.W. Choi, *PNAS* 110 (2013) 12229–12234.
- [12] M. Ebner, F. Marone, M. Stampanoni, V. Wood, *Science* 342 (2013) 716–720.
- [13] H. Wu, G.Y. Zheng, N. Liu, Y. Cui, *Nano Lett.* 12 (2012) 904–909.
- [14] H. Kim, M. Seo, M.H. Park, J. Cho, *Angew. Chem. Int. Ed.* 49 (2010) 2146–2149.
- [15] T. Song, J.L. Xia, J.H. Lee, D.H. Lee, M.S. Kwon, J.M. Choi, J. Wu, S.K. Doo, H. Chang, W.I. Park, D.S. Zang, H. Kim, Y.G. Huang, K.C. Hwang, J.A. Rogers, U. Paik, *Nano Lett.* 10 (2010) 1710–1716.
- [16] Y. Yao, M.T. McDowell, I. Ryu, H. Wu, N.A. Liu, L.B. Hu, W.D. Nix, Y. Cui, *Nano Lett.* 11 (2011) 2949–2954.
- [17] A. Magasinski, P. Dixon, B. Hertzberg, A. Kvit, J. Ayala, G. Yushin, *Nat. Mater.* 9 (2010) 353–358.
- [18] Y. H. Wang, Y. He, R. J. Xiao, H. Li, K. E. Aifantis, X. J. Huang, *J. Power Sources* 202 (2012)

236–245.

[19] H. Li, X.J. Huang, L.Q. Chen, Z.G. Wu, Y. Liang, *Electrochem. Solid-State Lett.* 2 (1999) 547–549.

[20] N. Liu, Z.D. Lu, J. Zhao, T.M. McDowell, H.W. Lee, W.T. Zhao, Y. Cui, *Nat. Nanotech.* 9 (2014) 187–192.

[21] Z.D. Lu, N. Liu, H.W. Lee, J. Zhao, W.Y. Li, Y.Z. Li, Y. Cui, *ACS Nano* 9 (2015) 2540–2547.

[22] Y. He, X.Q. Yu, Y.H. Wang, H. Li, X.J. Huang, *Adv. Mater.* 23 (2011) 4938–4941.

[23] X.F. Li, J. Liu, M.N. Banis, A. Lushington, R. Li, M. Cai, X.L. Sun, *Energy Environ. Sci.* 7 (2014) 768–778.

[24] E.M. Lotfabad, P. Kalisvaart, K. Cui, A. Kohandehghan, M. Kupsta, B. Olsen, D. Mitlin, *Phys. Chem. Chem. Phys.* 15 (2013) 13646–13657.

[25] E.M. Lotfabad, P. Kalisvaart, A. Kohandehghan, K. Cui, M. Kupsta, B. Farbod, D. Mitlin, *J. Mater. Chem. A* 2 (2014) 2504–2516.

[26] X.F. Li, J. Liu, X.B. Meng, Y.J. Tang, N.B. Mohammad, J.L. Yang, Y.H. Hu, R.Y. Li, M. Cai, X.L. Sun, *J. Power Sources* 247 (2014) 54–57.

[27] J.C. Li, X.C. Xiao, Y.T. Cheng, W.V. Mark, *J. Phys. Chem. Lett.* 4 (2013) 3387–3393.

[28] I.D. Scott, Y.S. Jung, A.S. Cavanagh, Y.F. Yan, A.C. Dillon, S.M. George, S.H. Lee, *Nano Lett.* 11 (2011) 414–418.

[29] Y.S. Jung, A.S. Cavanagh, L. Gedvilas, N.E. Widjonarko, I.D. Scott, S.H. Lee, G.H. Kim, S.M. George, A.C. Dillon, *Adv. Energy Mater.* 2 (2012) 1022–1027.

- [30] Y.S. Jung, A.S. Cavanagh, L.A. Riley, S.H. Kang, A.C. Dillon, M.D. Groner, S.M. George, S.H. Lee, *Adv. Mater.* 22 (2010) 2172–2176.
- [31] L.A. Riley, S.V. Atta, A.S. Cavanagh, Y.F. Yan, S.M. George, P. Liu, A.C. Dillon, S.H. Lee, *J. Power Sources* 196 (2011) 3317–3324.
- [32] L.A. Riley, A.S. Cavanagh, S.M. George, S.H. Lee, A.C. Dillon, *Electrochem. Solid-State Lett.* 14 (2011) A29–A31.
- [33] L.A. Riley, A.S. Cavanagh, S.M. George, Y.S. Jung, Y.F. Yan, S.H. Lee, A.C. Dillon, *Chem. Phys. Chem.* 11 (2010) 2124–2130.
- [34] J.Q. Zhao, Y. Wang, *Nano Energy* 2 (2013) 882–889.
- [35] J.S. Chen, X.W. Lou, *Mater. Today* 15 (2012) 246–254.
- [36] N.D. Petkovich, S.G. Rudisill, B.E. Wilson, A. Mukherjee, A. Stein, *Inorg. Chem.* 53 (2014) 1100–1112.
- [37] G. Armstrong, A.R. Armstrong, P.G. Bruce, P. Reale, B. Scrosati, *Adv. Mater.* 18 (2006) 2597–2600.
- [38] J. Aarik, A. Aidla, T. Uustare, V. Sammelselg, *J. Cryst. Growth* 148 (1995) 268–275.
- [39] W.D. Kim, G.W. Hwang, O.S. Kwon, S.K. Kim, M. Cho, D.S. Jeong, S.W. Lee, M.H. Seo, C.S. Hwang, Y.S. Min, J. Cho, *J. Electrochem. Soc.* 152 (2005) C552–C559.
- [40] R. Wang, G. Zhou, Y. Liu, S. Pan, H. Zhang, D. Yu, Z. Zhang, *Phys. Rev. B* 61 (2000) 16827–16832.
- [41] F. Tian, Y. Zhang, J. Zhang, C. Pan, *J. Phys. Chem. C* 116 (2012) 7515–7519.

- [42] C. Meier, S. Luttjohann, V.G. Kravets, H. Nienhaus, A. Lorke, H. Wiggers, *Physica E* 32 (2006) 155–158.
- [43] Y.S. Hu, R.D. Cakan, M.M. Titirici, J.O. Müller, R. Schlögl, M. Antonietti, J. Maier, *Angew. Chem. Int. Ed.* 47 (2008) 1645–1649.
- [44] N. Kruse, S. Chenakin, *Appl. Catal. A: General* 391 (2011) 367–376.
- [45] R.A. Alfonsetti, G.D. Simone, L. Lozzi, M. Passacantando, P. Picozzi, S. Santucci, *Surf. Interface Anal.* 22 (1994) 89–92.
- [46] W.L. Zhang, S. Zhang, M. Yang, T.P. Chen, *J. Phys. Chem. C* 114 (2010) 2414–2418.
- [47] A.O.T. Patrocínio, E.B. Paniago, R.M. Paniago, N.Y.M. Iha, *Appl. Surf. Sci.* 254 (2008) 1874–1879.
- [48] S. Won, S. Go, W. Lee, K. Jeong, H. Jung, C. Lee, E. Lee, J. Lee, *Met. Mater. Int.* 14 (2008) 759–765.
- [49] V.L. Chevrier, H.M. Dahn, J.R. Dahn, *J. Electrochem. Soc.* 158 (2011) A1207–A1210.
- [50] B.D. Polat, O. Keles, K. Amine, *Nano Lett.* 15 (2015) 6702–6708.
- [51] L. Aldon, P. Kubiak, A. Picard, J.C. Jumas, J.O. Fourcade, *Chem. Mater.* 18 (2006) 1401–1406.
- [52] J.Y. Zheng, H. Zheng, R. Wang, L.B. Ben, W.W. Lu, L.W. Chen, L.Q. Chen, H. Li, *Phys. Chem. Chem. Phys.* 16 (2014) 13229–13238.
- [53] T.F. Yi, J. Mei, Y.R. Zhu, Z.K. Fang, *Chem. Commun.* 51 (2015) 14050–14053.
- [54] T.F. Yi, Y. Xie, Y.R. Zhu, R.S. Zhu, H. Shen, *J. Power Sources* 222 (2013) 448–454.
- [55] T.F. Yi, S.Y. Yang, Y. Xie, *J. Mater. Chem. A* 3 (2015) 5750–5777.

[56] Y. Yang, Y. Bai, S. Zhao, Q. Chang, W. Zhang, J. Alloys Compd. 579 (2013) 7–11.

[57] G. Serrano, B. Bonanni, T. Kosmala, M.D. Giovannantonio, U. Diebold, K. Wandelt, C. Goletti, Beilstein J. Nanotechnol. 6 (2015) 438–443.

[58] X. Meng, X.Q. Yang, X. Sun, Adv. Mater. 24 (2012) 3589–3615.

[59] T. Song, D.H. Lee, M.S. Kwon, J.M. Choi, H. Han, S.G. Doo, H. Chang, W. Park, W. Sigmund, H. Kim, U. Paik, J. Mater. Chem. 21 (2011) 12619–12621.

Table 1. Cycling performances of 0-ALD and 3-ALD electrodes.

	0-ALD	3-ALD
Initial discharge/charge capacities/ mA h g^{-1}	3670.2/2866.1	4346.3/3580.8
Initial Coulombic efficiency/%	78.09%	80.82
50 th discharge/charge capacities/ mA h g^{-1}	273.3/271.7	1613.0/1580.3
50 th Coulombic efficiency/%	99.4%	97.97
Capacity retention after 50 cycles/%	9.5%	44.1%

Table 2. Fitting results of EIS data for the as-assembled cells.

Sample	$R_s /$ (Ω)	$R_{ct} /$ (Ω)	$W_s /$ (Ω)	$R_{tol} /$ (Ω)
0-ALD	3.73	52.81	49.66	106.20
2-ALD	6.02	58.40	53.87	118.29
3-ALD	3.11	65.05	55.42	123.58
4-ALD	5.40	103.10	93.95	202.45
5-ALD	4.31	125.81	126.4	256.52

Figure captions

Figure 1. FESEM images of pristine Si (0-ALD) sample (a) and TEM images of 0-ALD (inset of a), 2-ALD (b), 3-ALD (c), 4-ALD (d), 5-ALD (e) and HRTEM image of 3-ALD (f). HAADF STEM image (g) and elemental mapping for Ti, Si, O analysis for the as-prepared 3-ALD sample (h-l).

Figure 2. XRD patterns (a) and Raman spectra (b) of Si nanoparticles before and after TiO_2 coating by ALD.

Figure 3. Binding energy profiles of (a) Ti 2p, (b) Si 2p and (c) O 1s of Si nanoparticles before and after TiO_2 coating by ALD.

Figure 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).

Figure 5. AC impedance spectra of as-assembled cells (a) (inset shows the equivalent circuit) and evolution of resistances with TiO_2 increase for Si and Si@TiO_2 electrodes at open circuit voltage (b).

Figure 6. Schematic microstructural illustrations of that of Ref. 24 (a) and this work (b). (Red core: Si material; purple shell: TiO_2 layer)

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