



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

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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 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 TiO_2 deposited on Si by ALD, Si nanospheres without any template are employed in present work with different thickness of TiO_2 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 TiO_2 can balance the conductivity and buffering effect, which explains the improved electrochemical reversibility of the Si@ TiO_2 nano core–shell material.

2. Experimental

2.1. Synthesis of Si@ TiO_2 nanocomposites

Pristine Si (purity 99.9 wt%, specific surface area $60 \text{ m}^2 \text{ g}^{-1}$) 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 N_2 (99.999%) was used as carrier gas at the mass flow rate of 200 sccm. TiO_2 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 TiO_2 ALD was 10, 300, 4, and 300 s for TTIP dose time, N_2 purge time, water dose time, and N_2 purge time, respectively (10-300-4-300). TiO_2 ALD was deposited on the silicon spheres with different cycle numbers to obtain TiO_2 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 $\text{Cu K}\alpha$ 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 $\text{K}\alpha$ (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 LiPF_6 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 0.1C ($1\text{C} = 4200 \text{ mA g}^{-1}$) 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@ TiO_2 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 $50 \pm 2 \text{ nm}$ (Fig. 1a). Fig. 1b–e demonstrates the morphologies of TiO_2 overcoated Si spheres with different thickness of 2, 3, 4 and 5 nm, respectively, wherein the uniform TiO_2 coating layers can be clearly observed. A high resolution image of 3-ALD is further shown in Fig. 1f, in which a TiO_2 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 TiO_2 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@ TiO_2 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@ TiO_2

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