Amorphous Ultrathin SnO₂ Films by Atomic Layer Deposition on Graphene Network as Highly Stable Anodes for Lithium-Ion Batteries

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Supporting Information

ABSTRACT: Amorphous SnO₂ (a-SnO₂) thin films were conformally coated onto the surface of reduced graphene oxide (G) using atomic layer deposition (ALD). The electrochemical characteristics of the a-SnO₂/G nanocomposites were then determined using cyclic voltammetry and galvanostatic charge/discharge curves. Because the SnO₂ ALD films were ultrathin and amorphous, the impact of the large volume expansion of SnO₂ upon cycling was greatly reduced. With as few as five formation cycles best reported in the literature, a-SnO₂/G nanocomposites reached stable capacities of 800 mAh g⁻¹ at 100 mA g⁻¹ and 450 mAh g⁻¹ at 1000 mA g⁻¹. The capacity from a-SnO₂ is higher than the bulk theoretical values. The extra capacity is attributed to additional interfacial charge storage resulting from the high surface area of the a-SnO₂/G nanocomposites. These results demonstrate that metal oxide ALD on high surface area conducting carbon substrates can be used to fabricate high power and high capacity electrode materials for lithium-ion batteries.

KEYWORDS: atomic layer deposition, critical size, conformal, amorphous SnO₂, interfacial capacity

INTRODUCTION

The development of portable electronic devices and hybrid electric cars requires advanced lithium-ion batteries (LIBs) with large energy densities, fast rate capabilities, prolonged lifetime, and low cost. However, the current commercial graphite anode has a low gravimetric capacity of 372 mAh g⁻¹, which leads to a limited energy output density of LIBs.¹ Transition metal oxides with higher theoretical capacities (>600 mAh g⁻¹) have been exploited as alternative anode materials including Fe₂O₃/Fe₂O₅,²–⁴ Co₃O₄/CoO,⁵–⁷ Mn₃O₄,⁹ NiO,¹⁰ MoO₃/MoO₂,¹¹,¹² and CuO.¹³ Si, Sn, Ge, and Al form alloys with Li and are also being considered. Among them, Sn-based material is the only commercialized anode in the market. However, Co has to be added as 1:1 ratio into composites to reach satisfying performance.¹⁴ To prevent using expensive Co, SnO₂ has become an alternative anode and attracted much attention these years.¹⁵–¹⁷

The reaction of Li with SnO₂ consists of two steps. The first step is irreversible and produces Li₂O and Sn, then a series of tin–lithium alloys forms in the second step (reactions 1 and 2):¹⁸

\[ \text{SnO}_2 + 4\text{Li}^+ + 4e^- \rightarrow \text{Sn} + 2\text{Li}_2\text{O} \quad \text{irreversible} \]  

(1)

\[ \text{Sn} + x\text{Li}^+ + xe^- \leftrightarrow \text{Li}_x\text{Sn} \quad (0 \leq x \leq 4.4) \quad \text{reversible} \]  

(2)

A series of Li–Sn alloys (Li₃Sn₄, Li₅Sn₇, Li₅Sn₂, Li₇Sn₃, Li₉Sn₅, LiₓSnᵥ and LiₓSn₃) are formed between 0 and 0.6 V versus Li/Li⁺.¹⁹ The highest theoretical capacity for Li–Sn alloy can reach 782 mAh g⁻¹ (Li₁₂Sn₃). However, it also brings a 250% volume change,²⁰ which results in electrode pulverization and eventually capacity fading.¹⁹,²¹ The common strategy is to grow SnO₂ nanoparticles on surface of carbonaceous substrates, such as graphene and carbon nanotubes, or design novel nanostructured SnO₂. Although these routines can greatly improve performance of SnO₂, it usually requires the 15–30
cycles to reach stable capacities. This is because large SnO$_2$ nanostructure breaks down into its critical size (≅3 nm) and eventually form a stable solid–electrolyte interphase (SEI). This process continuously consumes precious lithium from the cathode, which causes a deteriorated performance in a full cell. Although the initial coulombic efficiency (CE) can be improved by adding surface-stabilized lithium metal powders, it cannot provide enough lithium reservoir for a long formation process without sacrificing safety and energy density. Therefore, if SnO$_2$ should to be considered as an alternative to the commercial graphite anode, it is critical to reduce formation cycles down to several cycles, ideally, one cycle.

Atomic layer deposition (ALD) is an important thin film growth technique that utilizes sequential self-limiting surface reactions to deposit ultrathin films with Ångstrom-level control. In addition, the chemical reactions in ALD form excellent building block to tolerant volume change during two-dimensional sheet structure of graphene provides an uniformity along surfaces of graphene network by ALD. The processing can precisely control the size, morphology, and crystallinity on cycling stability. Therefore, ALD is an ideal tool to deposit SnO$_2$ nanostructure under its critical size and with desired morphology.

In this work, we reported the synthesis of aSnO$_2$ thin film uniformly along surfaces of graphene network by ALD. The two-dimensional sheet structure of graphene provides an excellent building block to tolerant volume change during charge/discharge. Compared to the previously reported ALD SnO$_2$/G anode, a different Sn precursor and deposition process were chosen, which gave much improved cycling performance. Within five formation cycles, SnO$_2$/G anode reached its stability. In addition, we also discussed the extra capacity contributed from grain boundary and the effect of crystallinity on cycling stability.

**EXPERIMENTAL DETAILS**

Graphene sheets were produced by thermal exfoliation of the as-synthesized GO powders. Details of the graphene synthesis can be found in our previous publications. SnO$_2$ ALD was grown directly on graphene powders using a rotary ALD reactor. Specifically, tetrakis(dimethylamino) tin (TDMASn, Gelest, > 95% purity) and high-performance liquid chromatography (HPLC) grade water (H$_2$O, Aldrich) were used in this work. The TDMASn was held in a stainless steel bubbler maintained at 65 °C. SnO$_2$ ALD was performed at 150 °C using alternating TDMASn and H$_2$O exposures in an ABAB$_n$ sequence:

\[
\begin{align*}
\text{OH}_4^+\text{Sn(DMA)}_4 & \rightarrow (\text{O})_x\text{Sn(DMA)}_{4-x} + x\text{HDMA} \\
(\text{O})_x\text{Sn(DMA)}_{4-x} + 2\text{H}_2\text{O}_2 & \rightarrow \text{O}_x\text{Sn(OH)}_{4-x} + (4 - x)\text{HDMA} + \text{O}_2
\end{align*}
\]

where the asterisks represent the surface species. The typical growth rate for the SnO$_2$ ALD chemistry is ≅0.6 Å per cycle, and thus the thickness of SnO$_2$ film can be well controlled at the nanometer scale by ALD cycles. The SnO$_2$ ALD reaction sequence was: (i) TDMASn dose to 1.0 Torr; (ii) evacuation of reaction products and excess TDMASn with N$_2$ purging; (iii) H$_2$O dose to 1.0 Torr; and (iv) evacuation of reaction products and excess H$_2$O with N$_2$ purging.

The phase, crystallinity, and microstructure of the ALD SnO$_2$ were characterized by X-ray diffraction (XRD) using PAN analytical X-ray diffraction system, scanning electron microscopy (SEM) by a Carl Zeiss Ultra 1540 Dual Beam FIB/SEM System, and a transmission electron microscopy (TEM) using a JEOL JEM-2100 instrument, operated at 200 kV. X-ray photoelectron spectroscopy (XPS) was performed using a PHI 5000 Versa Probe system. The surface area and pore size distribution were measured using a Quantachrome AUTOSORB-1 instrument, with the samples heated at 150 °C under vacuum for 12 h before testing. Thermogravimetric analysis (TGA) was performed in air from 30 to 700 °C at a heating rate of 10 °C/min in a TA Instrument TGA-Q50.

The electrodes were made by mixing SnO$_2$/G nanocomposites with polyvinylidene fluoride (PVDF) and carbon black at a weight ratio of 75:15:10 in 1-methyl-2-pyrrolidinone solvent. The slurry was coated on copper foil by blade and dried under vacuum at 80 °C overnight. All of the cells were assembled in an argon-filled drybox with Li metal as the negative electrode. A Celgard separator 2340 and 1 M LiPF$_6$ electrolyte solution in 1:1 w/w ethylene carbonate and diethyl carbonate (Novolyte) were used to fabricate the coin cells. Cyclic voltammetry (CV) measurement was carried out using a potentiostat VersaSTAT 4 (Princeton Applied Research) at a scan rate of 0.5 mV s$^{-1}$. Galvanostatic charge/discharge cycles were performed at a voltage range of 3–0.01 V using an Arbin BT 2000 testing station. The mass loading of SnO$_2$/G nanocomposites is ≅1–2 mg/cm$^2$.

**RESULTS AND DISCUSSION**

Graphene nanosheets were prepared by thermal exfoliation of graphite oxide, and therefore defects and residual oxygen functional groups inevitably existed in the structure of graphene. These defective sites serve as the initial nucleation sites for the controllable growth of SnO$_2$ by ALD. However, the difficulty of the total removal water from high surface area may cause a little CVD growth, leading to thin film growth instead of particles. The large distribution of mesoporous structure developed upon thermal exfoliation allows the gas phase ALD precursors to diffuse into the internal structures of G, which results in uniform SnO$_2$ film along surface of 3-D graphene matrix.

As observed from SEM analysis (Figure 1), the SnO$_2$ film is uniformly anchored along the porous network of wrinkled graphene. No SnO$_2$ particles can be seen. The highly dense coverage of surface defects (carboxyl or hydroxyl groups) on graphene allows the uniform surface interaction with ALD precursors. The high-resolution TEM image (not shown) did not observe any nanoparticles and crystalline structures. It is very difficult to distinguish amorphous SnO$_2$ film from graphene sheets due to lack of lattice contrast. The graphene sheets synthesized by graphite oxidation followed by thermal exfoliation and reduction were evaluated using Raman
spectroscopy. The D- and G-bands of graphene and the prominent D-band (∼1350 cm\(^{-1}\)) to G-band (∼1580 cm\(^{-1}\)) ratio reveal that there are structure disorders and defects caused by the extensive oxidation in making graphite oxides.\textsuperscript{35,36} A more detailed study can be found in our previous work.\textsuperscript{37}

TGA measurement as shown in Figure S1 in Supporting Information indicates that the mass percentage of SnO\(_2\) in the composites reaches 53% for 50 ALD cycles. The high mass loading of active material is critical to realize the feasibility of using ALD for large-scale nanocomposite powder production. Here, we adapted static dosing ALD precursors instead of flow-type ALD since static dosing can reach much higher reactant utilization efficiency and allow coating high surface area substrates such as graphene and CNTs powder.\textsuperscript{32} Our results indicate that more than 50 wt % of active materials can be achieved with less than 50 ALD cycles. The greatly reduced ALD deposition time and cost, along with maximized precursor utilization efficiency, make ALD possible for large-scale powder production. At this time, we have the capability of synthesizing nanocomposites in a batch quantity of 10 g of powder per ALD run at a lab scale.

The nitrogen adsorption/desorption isotherms of SnO\(_2\)/G composites together with the pore size distribution, derived based on the density functional theory (DFT) model, are shown in Figure S2. The sample displays the typical type IV isotherm with a large hysteresis loop, demonstrating that the significant amount of mesopores, which initially existed in the graphene,\textsuperscript{32} were preserved after ALD deposition. The broad pore distributions from 3–35 nm almost remain intact after deposition, resulting from the unique self-limiting reaction of ALD. Such open structure is expected to provide easy access of electrolytes and facilitate the fast Li-ion diffusion when used as a potential LIB material. The specific surface area is 240 m\(^2\)/g for 50 ALD cycles SnO\(_2\)/G composites, compared to 450 m\(^2\)/g for pristine graphene. The reduced surface area is a result of the overall reduction in specific area with increased mass loading of SnO\(_2\). Figure 2, panel a shows the XPS spectrum of the SnO\(_2\)/G composites, which reveals the presence of carbon, oxygen, and tin. The Sn 3d regions with two peaks centered at 494.9 and 486.5 eV (Figure 2b) indicate the existence of Sn(IV). These XPS results verify the presence of SnO\(_2\) on graphene.

Electrodes made with the SnO\(_2\)/G nanocomposites were tested in coin cells with lithium metal as a counter electrode. Cyclic voltammograms of SnO\(_2\)/G nanocomposites were measured between 0.01 and 3 V at a scan rate of 0.5 mV/s. Figure S3 shows the first and fifth cycle of CV of SnO\(_2\)/G nanocomposite electrode. In the first cycle, the first two reduction peaks at ∼1.2 and 0.8 V are observed and can be ascribed to the reduction of SnO\(_2\) to Sn\textsuperscript{38} and formation of SEI.\textsuperscript{39} The peaks around 0.5 V and below are assigned to the formation of Li–Sn alloy. The broad peak at ∼0.5 V is an overlap of delithiation reaction of LiSn alloy.\textsuperscript{40} The high current response near 0 V indicates the lithium intercalation into the graphene backbone.\textsuperscript{5,8} In the subsequent anodic scans, the peak at ∼0.6 V corresponds to a series of dealloying of LiSn. The peak at ∼1.2 V is believed to be due to lithium extraction from carbon.\textsuperscript{26} There are also some literatures ascribing this peak to reform SnO\(_2\) from Sn and Li\textsubscript{2}O.\textsuperscript{41} The CV curves also show good reproducibility in the fifth cycle, suggesting a high reversibility of the lithium and SnO\(_2\) reaction.

Figure 3 presents the voltage profiles of SnO\(_2\)/G composites for the first five cycles at a current density of 100 mA g\(^{-1}\). The initial discharge capacity is 1250 mAh g\(^{-1}\) due to formation of SEI and Li\textsubscript{2}O. The charge capacity is 730 mAh g\(^{-1}\), corresponding to an initial coulombic efficiency of ∼60%. From the second cycle, the discharge curves are almost overlapped. No obvious plateau was seen during discharging, but two voltage plateaus at ∼0.6 and 1.2 V were observed from the charging curves, consistent with CV analysis.

Excellent rate performance has been achieved using 50 ALD cycle SnO\(_2\)/G nanocomposites, as shown in Figure 4, panel a, at various current densities. The cell has been continuously cycled without any rest between different rates. A high capacity ∼800 mAh g\(^{-1}\) is obtained at 100 mA g\(^{-1}\). SnO\(_2\)/G nanocomposites are able to maintain ∼500 mAh g\(^{-1}\) capacity even when the current density is increased to 1000 mA g\(^{-1}\), retaining ∼63% of its discharge capacity at 100 mA g\(^{-1}\). This is much higher than the capacity of graphite, which can only
Figure 4. (a) Rate performance of SnO2/G composites at various current densities; (b) rate performance of SnO2 contribution only at various current densities; (c) cycling performance and CE of SnO2/G composites at 1000 mA g⁻¹.

preserve ~30% of its original capacity at a rate of ~1000 mA g⁻¹. The specific capacity of a-SnO2 is calculated by subtracting the graphene contributions from the nano-composites shown in Figure 4, panel b. The actual contribution of the graphene in the evaluation of the SnO2 ALD-coated graphene electrodes could be even lower because the graphene is completely covered with SnO2 ALD films.

We also studied the long-term stability of SnO2/G at fast charge/discharge rates. Figure 4, panel c shows the cycling performance of SnO2/G at 1 A g⁻¹. The first five cycles were stabilized at 100 mA g⁻¹ to ensure the enough activation and formation of stable SEI. After 200 cycles, the capacity retention was ~92%, and SnO2/G can still deliver a reversible capacity of 410 mAh g⁻¹ and maintain the CE over 99.5%. We would like to point out that at ~110 cycles, the sudden capacity drop is caused by a power outage. After the process resumed, the capacity shows no decay until the 200th cycle. Therefore, we believe the actual capacity retention should be higher than 92%. We attribute the good rate performance to the synergistic effect of amorphous thin film morphology of SnO2 and conductive 3-D graphene matrix, which ensure fast lithium-ion diffusion and electron transfer.

The excellent electrochemical performance of SnO2/G nanocomposites can be attributed to several potential factors: (1) ALD allows for the deposition of SnO2 film under the critical size below which the pulverization of large SnO2 nanoparticles (250% volume expansion/contraction during discharge/charge processes) can be greatly mitigated; (2) ultrathin SnO2 film shortens the Li⁺ diffusion path, resulting in a very impressive rate performance; (3) the 3-D structure of SnO2/G nanocomposites greatly enhances lithium diffusion and electron conduction; (4) the excellent mechanical properties of graphene can accommodate the large volume change of SnO2; and (5) the chemical bonding between SnO2 and graphene prevents the aggregation of nanoparticles during cycling.

Five formation cycles for Sn-based anodes are comparable to the commercial graphite and to our best knowledge, is the best reported in the literature summarized in Table 1. The short formation cycle is critical for SnO2-based anode in a full cell. The common cause for long formation cycles is due to SEI formation and lack of stable electrode structure. When the anode’s volume changes during charge/discharge, the fresh surface is continuously exposed to the electrolyte, which causes irreversible loss until the structure reaches equilibrium and a stable SEI is formed. ALD can ensure film and nanoparticles under their critical size (~3 nm) so the volume expansion is much less dramatic compared to larger particles size reported by other techniques. In addition, carbonaceous materials with large surface areas tend to form significant amount of SEI at the defects and edge plane. For example, graphene’s oxygen-containing surface functional groups are very reactive and can oxidize the electrolyte and consequently induce electrochemical instability in the electrode. For wet-chemistry based synthesis, SnO2 is prone to nucleate on those defect sites and edge plane as well; however, it is impossible to completely cover them. In contrast, because of its separated gas phase reaction, those sites can easily attract ALD precursors and form complete coverage on defects and edge, reducing the irreversible loss and formation cycles.

SnO2 ALD for lithium anode was previously reported by using SnCl4 and H₂O as precursors. It has the highest capacity of 793 mAh g⁻¹ at 400 mA g⁻¹. However, its capacity decreases until the 10th cycle and then keeps increasing for 200 cycles. No stable capacity can be observed. We believe this is probably due to the different ALD chemistry. Our group has shown that SnCl4 and H₂O form very low quality of SnO2 films at 200 °C with a high percentage of Cl residue. The Cl residue may further form LiCl with Li⁺, which causes irreversible lithium loss and long formation cycles. In addition, a thicker film had to be formed to cover the surface of graphene conformally in that literature. The gradually increased capacity phenomenon was also observed in many other literatures. However, we believe this phenomenon may cause more concerns than its benefits. A full cell consists of a pair of matched cathode and anode, which should provide the same energy (Ah). To prevent lithium plating and improve the safety, the anode has to be carefully calculated to accommodate lithium provided by the cathode. The gradually increased capacity makes it impossible to use in a battery, although some amazing capacities are reported. If any other material is considered as an alternative to graphite anode, a stable capacity should be reached within several cycles, ideally less than five.
Research Article

Table 1. Comparison of Different SnO₂ Anode Reported in Literature with This Work

<table>
<thead>
<tr>
<th>materials</th>
<th>highest capacity</th>
<th>formation cycle number</th>
<th>initial Coulombic efficiency</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO₂/graphene</td>
<td>840 mA h g⁻¹ at 67 mA g⁻¹</td>
<td>~15</td>
<td>58%</td>
<td>55</td>
</tr>
<tr>
<td>SnO₂/graphene</td>
<td>635 mA h g⁻¹ at 60 mA g⁻¹</td>
<td>~30</td>
<td>44%</td>
<td>56</td>
</tr>
<tr>
<td>SnO₂/ferrocene-encapsulated SWCNT</td>
<td>905 mA h g⁻¹ at 150 mA g⁻¹</td>
<td>~15</td>
<td>60%</td>
<td>57</td>
</tr>
<tr>
<td>SnO₂/graphene</td>
<td>570 mA h g⁻¹ at 50 mA g⁻¹</td>
<td>~30</td>
<td>43%</td>
<td>16</td>
</tr>
<tr>
<td>Sn₀/substituted N-doped graphene</td>
<td>1346 mA h g⁻¹ at 500 mA g⁻¹</td>
<td>capacity decreases for ~25 cycles and then increases until 500 cycles</td>
<td>61.3%</td>
<td>58</td>
</tr>
<tr>
<td>nano-Sn/C</td>
<td>710 mA h g⁻¹ at 200 mA g⁻¹</td>
<td>~20</td>
<td>69%</td>
<td>40</td>
</tr>
<tr>
<td>SnO₂/G</td>
<td>718 mA h g⁻¹ at 100 mA g⁻¹</td>
<td>~25</td>
<td>68%</td>
<td>59</td>
</tr>
<tr>
<td>SnO₂/MWCNT</td>
<td>420 mA h g⁻¹ at 156 mA g⁻¹</td>
<td>~60</td>
<td>56%</td>
<td>60</td>
</tr>
<tr>
<td>Sn-core/carbon-sheath nanocable</td>
<td>630 mA h g⁻¹ at 100 mA g⁻¹</td>
<td>~50</td>
<td>66.9%</td>
<td>61</td>
</tr>
<tr>
<td>interconnected SnO₂ nanoparticles</td>
<td>778 mA h g⁻¹ at 78 mA g⁻¹</td>
<td>~20</td>
<td>50%</td>
<td>62</td>
</tr>
<tr>
<td>ultrasmall SnO₂ particles in micro/mesoporous carbon</td>
<td>560 mA h⁻¹ at 1400 mA g⁻¹</td>
<td>~30</td>
<td>44%</td>
<td>63</td>
</tr>
<tr>
<td>Sn anchored on graphene</td>
<td>1022 mA h g⁻¹ at 200 mA g⁻¹</td>
<td>~100</td>
<td>69%</td>
<td>64</td>
</tr>
<tr>
<td>bowl-like SnO₂@carbon hollow particles</td>
<td>1282 mA h g⁻¹ at 100 mA g⁻¹</td>
<td>~15</td>
<td>68.4%</td>
<td>65</td>
</tr>
<tr>
<td>SnO₂ nanowires coated with ALD TiO₂</td>
<td>883 mA h g⁻¹ at 100 mA g⁻¹</td>
<td>~50</td>
<td>67.7%</td>
<td>66</td>
</tr>
<tr>
<td>SnO₂/G with ALD HfO₃</td>
<td>853 mA h g⁻¹ at 150 mA g⁻¹</td>
<td>~40</td>
<td>61.7%</td>
<td>67</td>
</tr>
<tr>
<td>SnO₂/graphene by ALD</td>
<td>793 mA h g⁻¹ at 400 mA g⁻¹</td>
<td>capacity decreases for ~10 cycles, increases for 200 cycles, and decreases until 400 cycles</td>
<td>49.5%</td>
<td>28</td>
</tr>
<tr>
<td>SnO₂/graphene by ALD</td>
<td>800 mA h g⁻¹ at 100 mA g⁻¹</td>
<td>~5; stable for at least 200 cycles</td>
<td>60%</td>
<td>this work</td>
</tr>
</tbody>
</table>

Another important issue studied in this work is where the high capacity of SnO₂ comes. So far, there are two possible explanations: (1) reversible reaction from Sn to SnO₂, which gives a total theoretical capacity of 1494 mAh g⁻¹; or (2) interfacial storage at grain boundaries. The evidence for the first explanation is the peak at ~1.2 V from CV analysis. However, there is a strong argument against this hypothesis that metallic Sn/carbon composites also have the same peak. To further understand the possible source for this extra capacity, we intentionally created oxygen vacancy to form SnOᵥ, which consists of SnO₂, SnO, and Sn. If the first step is indeed reversible, then decreasing oxygen content will reduce the contribution from the first reaction step to the total capacity. We expect SnO₂ to have lower capacity than SnO₂ if the first step is reversible. In this experiment, we annealed as-grown SnO₂/G nanocomposite in H₂ atmosphere at 300 and 400 °C for 2 h. XRD in Figure 5 shows that as-grown SnO₂/G has amorphous structure. After annealing 300 °C in H₂, SnO₂ peaks become more profound, indicating an improved crystalline structure. A slight weight loss was also observed due to oxygen loss. After 400 °C annealing with H₂, SnO₂/G became a mixture of SnO₂, SnO and metallic Sn. We tested their rate performances using the same conditions as amorphous SnO₂/G in Figure 6. The capacities of annealed samples were almost overlapped with amorphous SnO₂/G, but with a slightly degraded cycling stability. This result indicates the total capacity from SnO₂ is independent of its oxygen content. Therefore, the first reaction step should not be reversible. We believe that the extra capacity from our system is probably due to interfacial storage. Maier et al. describe a phenomenon upon which lithium ions collect at grain boundaries, which results in...
both battery and capacitor-like properties. There have been quite a few studies of SnO2 for supercapacitors. A high capacity of 363 F g\(^{-1}\) was reported for SnO2 smaller than 10 nm recently. However, to achieve reversible interfacial formation of SnO2 from Sn and Li2O. The ALD process represents an innovative approach to synthesize advanced metal oxide-based electrodes for stable and high-performance LIBs. By subtracting the graphene contribution from the composites, surface of graphene by ALD. ALD allows depositing SnO\(_2\) under its critical size with controlled morphology and minimal volume change. In addition, amorphous structure shows better capacity retention due to its isotropic volume expansion compared to directional volume expansion of crystalline structure. This is consistent with conclusions from the literature.28,33,54

**CONCLUSION**

We have successfully synthesized SnO\(_2\) thin film along the surface of graphene by ALD. ALD allows depositing SnO\(_2\) under its critical size with controlled morphology and crystallinity, which give exceptional electrochemical performance. Fifty ALD cycles of SnO\(_2\)/G exhibit a stable capacity of 800 mAh g\(^{-1}\) at 100 mA g\(^{-1}\) and 450 mAh g\(^{-1}\) at 1000 mA g\(^{-1}\). By subtracting the graphene contribution from the composites, SnO\(_2\) displays an unprecedented specific capacity of 1200 mAh g\(^{-1}\), higher than the theoretical capacity. The long cycling test under 1000 mA g\(^{-1}\) shows a very stable lifetime and nearly 100% CE. More importantly, SnO\(_2\)/G nanocomposites show much shorter formation cycles compared to nanostructured SnO\(_2\) synthesized by other techniques. To our best knowledge, our SnO\(_2\)/G nanocomposites reach the stable capacity with the least formation cycles reported in the literature. We believe that fewer formation cycles are more critical to realize Sn-based anodes than simply attempting high capacity and rate performance. H\(_2\) annealing test indicates the extra capacity from SnO\(_2\) is probably due to interfacial storage instead of reformation of SnO\(_2\) from Sn and Li\(_2\)O. The ALD process represents an innovative approach to synthesize advanced metal oxide-based electrodes for stable and high-performance LIBs.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b08719.

Figure of TGA of ALD SnO\(_2\)/G composites; figure of Nitrogen adsorption/desorption isotherms of SnO\(_2\)/G composites and DFT pore size distribution; figure of CV curves of 50 ALD cycle SnO\(_2\)/G composite at the first and fifth cycle (PDF)

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**Notes**

The authors declare no competing financial interest.

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**REFERENCES**


(37) Ban, C. M.; Xie, M.; Sun, X.; Travis, J. J.; Wang, G. K.; Sun, H. T.; Dillon, A. C.; Lian, J.; George, S. M. Atomic Layer Deposition of Amorphous TiO2 on Graphene as an Anode for Li-Ion Batteries. Nanotechnology 2013, 24 (42), 424002.


(64) Qin, J.; He, C. N.; Zhao, N. Q.; Wang, Z. Y.; Shi, C. S.; Liu, E. Z.; Li, J. Graphene Networks Anchored with Sn@Graphene as Lithium Ion Battery Anode. *ACS Nano* 2014, 8 (2), 1728−1738.

