Multiple ambient hydrolysis deposition of tin oxide into nanoporous carbon as a stable anode for Lithium-ion batteries

■ Energy storage

Multiple ambient hydrolysis deposition of tin oxide into nanoporous carbon as a stable anode for Lithium-ion batteries

Vadivukarasi Raju, Xingfeng Wang, Wei Luo, Xiulei Ji*

Abstract: We introduce a novel ambient hydrolysis deposition (AHD) methodology that, for the first time, employs sequential water adsorption followed by a hydrolysis reaction to infiltrate tiny SnO_2 particles inside nanopores of mesoporous carbon in a conformal and controllable manner. The empty space in the SnO_2/C composites can be adjusted by varying the number of AHD cycles. A SnO_2/C composite with an intermediate SnO_2 loading exhibits an initial specific delithiation capacity of 1054 mAh/g as an anode for Li-ion batteries (LIBs). The capacity contribution from SnO_2 in the composite electrode of SnO_2 (1494 mAh/g) when considering that both Sn alloying and SnO_2 conversion reactions are reversible. The composite shows a specific capacity of 573 mAh/g after 300 cycles, one of the most stable cycling performances for the SnO_2/mesoporous carbon composites. Enabled by the controllable AHD coatings, our results demonstrated the importance of the well-tuned empty space in nanostructured composites to accommodate the expansion of electrode active mass during alloying/dealloying and conversion reactions.

Introduction

Intense efforts have been devoted to exploring new electrode materials for Li-ion batteries (LIBs) in pursuing higher energy density and better cycling stability.[1,2] Compared to the conventional graphitic anodes, alloying anodes have attracted much attention due to their high theoretical capacities.[3,4] The primary challenge for alloying anodes is the very large volumetric changes during the Li alloying/dealloying processes, thus causing electrode pulverization and fast capacity fading.[5,6] Among the alloying anodes, SnO_2 is an attractive option due to its high theoretical capacity.[7] During discharge, SnO_2 anodes operate via the following reactions: [8]

$$SnO_2 + 4\,Li^+ + 4\,e^- \rightarrow Sn + 2\,Li_2O \qquad (1)$$

$$Sn + x\,Li^+ + x\,e^- \leftrightarrow Li_xSn\,(x \leq 4.4) \qquad (2)$$

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The theoretical capacity is 782 mAh/g based on the assumption that only the alloying/dealloying reactions are reversible. The value is 1494 mAh/g if the conversion between Sn and SnO_2 is electrochemically reversible. The hurdle for SnO_2 as an anode has been its rapid capacity fading associated to the large Sn volume expansion (up to 259%) during Li^+ insertion.[9] To address this problem, one approach is to downsize the SnO_2 crystallites to minimize the strain during the alloying/dealloying reactions. Various SnO_2 nanostructures[10,11], such as nanotubes,[12] nanosheets,[13] hollow spheres,[14] microboxes [15] and mesoporous SnO_2[16,17] have been investigated. Studies on the correlation between the SnO_2 crystallite sizes and cycling stability revealed that SnO_2 nanoparticles of ~ 3 nm in diameter can exhibit a high capacity with improved cycling.[18] However, maintaining a stable capacity for these single-component SnO_2 nanostructures has been very challenging.

Another approach is to encapsulate SnO_2 or Sn phases into a conducting conduit to accommodate the volumetric change.[19,20] An effective method is to homogenously mix a tin precursor with organic carbon precursor(s) before a carbonization process. Yet, such synthetic route eliminates the possibility of using existing carbon materials that can be potentially desirable.[21] As a result, efforts have been devoted to integrating SnO_2 or Sn into porous carbonaceous materials such as mesoporous carbon,[22] porous graphene[23,24] and carbon nanotubes.[25] To date, a number of infiltration methods, including sonochemical,[26] chemical infiltration,[27] wet-impregnation[28] and sol-gel[29] syntheses, electrostatic self assembly,[30] have been investigated to incorporate active mass into nanoporous frameworks. Most recently, very promising results have been shown on

SnO$_2$/graphene (or N-doped graphene) composites with very high capacities of over 1000 mAh/g and stable cycling.[31,32] Despite the fact that excellent results have been achieved with different unique recipes,[33] a general design principle for porous oxide/carbon composites has not been clearly demonstrated, to the best of our knowledge. This is due to the lack of precise synthetic control to manipulate the loading levels, morphology and dispersing uniformity of the encapsulated metal oxides in a carbon framework.

Herein, we utilize the ambient hydrolysis deposition (AHD) methodology developed in our laboratory for a layer-by-layer deposition of SnO$_2$ by pre-adsorbing water in a nanoporous carbon, CMK-3.[34] Water adsorption in voids has been widely studied to understand the functions of water molecules in life activities of animals and plants.[35,36] It is widely known that nanoporous materials, including nanoporous carbons, can adsorb water spontaneously at ambient conditions. This phenomenon has been investigated experimentally and by simulation work.[37,38] We utilize this important phenomenon to help deposit controllable amounts of SnO$_2$ into a nanoporous carbon through a sequential water adsorption and hydrolysis reactions. We then investigated these tailor-designed materials as anodes for LIBs to address the volume-change challenge for SnO$_2$. A SnO$_2$/carbon composite with an intermediate loading of SnO$_2$ showed great cycling stability for 300 cycles with 573 mAh/g retained at a high current density 200 mA/g.

Results and Discussion

CMK-3, a long-range ordered mesoporous carbon was selected as the model carbon to study the layer-by-layer AHD for a deposition of SnO$_2$ as an anode material for LIBs. Briefly, AHD process involves a pretreatment of carbon with a mild oxidant, such as warm acidic ammonium persulfate (APS), to introduce hydrophilic groups on carbon surface. The obtained sample was designated as APS-CMK. Then, water was adsorbed into the carbon by equilibrating APS-CMK with saturated water vapor at 80 °C for one hour. Finally, the water-loaded sample was soaked in a non-aqueous solution of a tin precursor for one hour. The sample was then filtered in the glovebox. This sample was designated as 1-Sn-CMK. To increase SnO$_2$ loading, the sequential water-loading and hydrolysis process was repeated, and the samples were labeled as 2-Sn-CMK and 3-Sn-CMK.
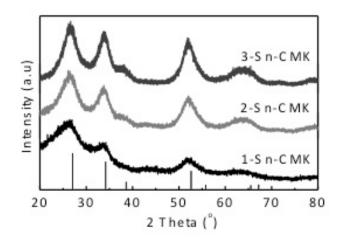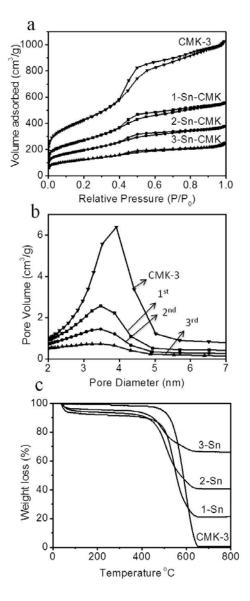

Figure 1. Wide angle XRD patterns of SnO$_2$/C composite after one, two and three cycles of AHD.

Figure 1 shows the X-ray diffraction patterns of samples prepared by first, second and third AHD cycle, respectively. These samples exhibited broad peaks at 25.7°, 33.2°, 36.9°, 50.8° and 62.3°, which can be indexed to (110), (101), (200), (211) and (301) planes of tetragonal SnO$_2$ (JCPDS 41-1445), respectively. These broad peaks suggest the existence of nanosized crystal domains of SnO$_2$. With increasing number of AHD cycles, the intensity of the XRD peaks increases, and the peaks turn slightly sharper, indicating a larger domain size of SnO$_2$ due to layer-by-layer growth. Estimated by Scherrer Equation, the domain size increases from ~2 nm to ~5 nm from the first to the third AHD cycle with corresponding full width half maximum (FWHM) of XXX and XXX, respectively. **Table 1** summarizes the results from surface area and porosity measurements. The N$_2$ sorption isotherms and pore size distribution of the composites are presented in **Figure 2a** and **Figure 2b**, respectively. Treatment of CMK-3 with APS leads to a slight decrease in specific surface area and pore volume. As observed in the low-angle XRD patterns (supplementary **Figure S1**), the long-range order was well maintained. After one AHD cycle, the surface area and the pore volume decreased from 1238 m^2/g and 1.37 cm^3/g from the APS-CMK to 968 m^2/g and 0.962 cm^3/g, respectively. These parameters further decreased after the second and third AHD cycles.

The mass loading of the deposited SnO$_2$ in the composites was measured in air using thermogravimetric analysis (TGA) (**Figure 2c**). The small weight loss below 100 °C can be attributed to water evaporation. Almost no weight loss was observed between 100 °C and 400 °C, demonstrating the thermal stability of the composites in air up to 400 °C. The weight loss from 400 °C to 750 °C is due to carbon combustion. With increasing AHD cycles, the percentage of SnO$_2$ in the composites increases from 21 wt.% to 66 wt.%. When normalized for per gram of carbon, 0.26 g, 0.43 g and 1.30 g of SnO$_2$ was deposited after first, second and third AHD cycle. The dramatic increase of SnO$_2$ deposition in later AHD cycles can be attributed to the enhanced hydrophilic properties of the composite surface after the formation of SnO$_2$ layer.

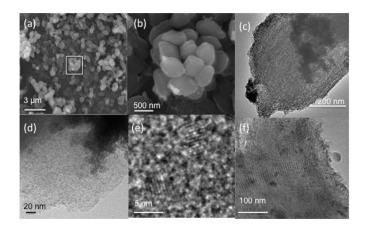| Table 1. Physical characteristics of the samples				
Sample	BET surface area (m^2/g)	Pore diameter (nm)	Pore volume (cm^3/g)	SnO$_2$ (wt%) (TGA)
CMK-3	1270	4.0	1.43	-
APS-CMK	1238	4.0	1.37	-
1-Sn-CMK	968	3.9	0.96	21
2-Sn-CMK	694	3.9	0.57	41
3-Sn-CMK	438	3.8	0.37	66

Figure 2. (a) N_2 adsorption-desorption isotherms of CMK-3, 1-Sn-CMK, 2-Sn-CMK and 3-Sn-CMK, (b) Pore size distribution profiles of pure CMK-3 and the composites after first, second and third AHD cycle, (c) TGA profiles of SnO_2/C composites after first, second and third AHD cycles.

To probe the morphology of the composites, scanning electron microscopy (SEM) and transmission electron microscope (TEM) studies were carried out on SnO_2/C composites (**Figure 3 and Figure S2**). In the SEM images, the absence of SnO_2 nanoparticles indicates the successful loading of SnO_2 into the porous structure of CMK-3. (**Figure 3a and b**). From the TEM images, the fine dispersion of SnO_2 nanoparticles inside the channels of CMK-3 is evident (**Figure 3c**). HR-TEM analysis on 2-Sn-CMK shows the presence crystalline SnO_2 particles embedded in the carbon matrix (**Figure 3d and e**). **Figure 4** shows the high-angle angular dark field (HAADF) scanning TEM (HAADF-STEM) images and the corresponding carbon, oxygen and tin energy dispersive X-ray spectroscopy (EDX) mappings. Combining the information from HAADF-STEM and elemental mapping, it is clear that the SnO_2 nanoparticles in the composite

are of uniform particle size and are homogenously dispersed within the mesoporous channels.[39] EDX also indicated 43 wt.% SnO_2 in the composite, which corroborates the TGA measurements (**Figure S3**).

The electrochemical characteristics of the SnO_2/CMK composites were investigated in coin-style half-cells using lithium-metal foil as the counter electrode and 1.0 M of $LiPF_6$ dissolved in ethylene carbonate and dimethyl carbonate (EC:DMC in the mass ratio of 1:1) as the electrolyte. Note that the specific capacity is calculated based on the total mass of a composite electrode. **Figure 5a** shows the first galvanostatic discharge/charge profiles of the SnO_2/CMK composites cycled

Figure 3. (a) SEM image of 2-Sn-CMK, (b) higher magnification image of the area inside the box in (a), (c) TEM image of 2-Sn-CMK (d) HR-TEM image of 2-Sn-CMK (e) HR-TEM image showing SnO_2 crystallites in 2-Sn-CMK (f) TEM image of 2-Sn-CMK after 300 galvanostatic cycles. Corresponding EDX mapping is shown in the Supporting Information.
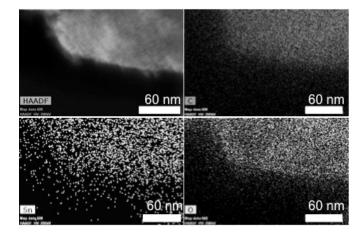

Figure 4. HAADF-STEM image for 2-Sn-CMK and the corresponding elemental mappings of carbon, tin and oxygen, respectively.

between 0.01 V to 2.0 V at a current density of 200 mA/g. For 2-Sn-CMK, the first discharge (lithiation) delivers a capacity of 2675 mAh/g, with a charge (delithiation) capacity of 1054 mAh/g,
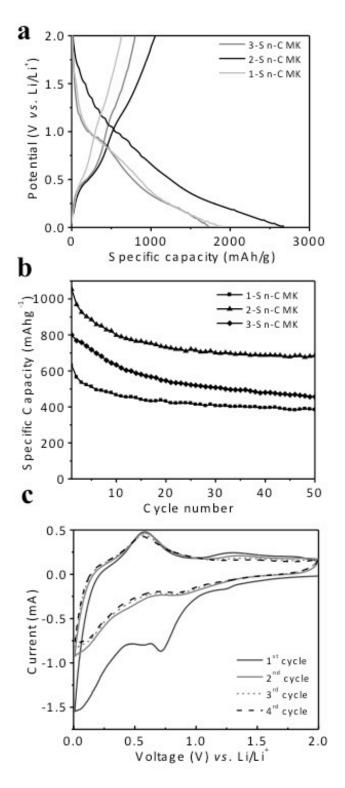
exhibiting a 39% reversible capacity, while 1-Sn-CMK and 3-Sn-CMK have 33% and 46% reversible capacity, respectively. By comparing with the first discharge/charge profiles of APS-CMK with a 22% reversible capacity, one can see that a major portion of the irreversible capacity in the SnO_2/carbon composites is contributed from APS-CMK by forming a solid electrolyte interphase (SEI) layer (Supplementary information **Figure S4**).[40] The reversibility, in fact, increases along higher SnO_2 loading. Certainly, SEI can be formed with the SnO_2 active mass as well, which contributes to the irreversible capacity.

The first delithiation capacity of 2-Sn-CMK, 1054 mAh/g, is much higher than 630 mAh/g for 1-Sn-CMK and 800 mAh/g for 3-Sn-CMK. It is generally accepted that only Li-Sn alloying process for SnO_2 electrodes is reversible, involving 4.4 Li$^+$ per Sn atom, and the theoretical capacity of SnO_2 electrodes is 782 mAh/g. Based on the initial delithiation capacity of APS-CMK (603 mAh/g, **Figure S4)**, the capacity contribution of SnO_2 in the first delithiation capacity of 2-Sn-CMK is 698 mAh/g$_{composite}$. The specific capacity for SnO_2 is calculated to be 1703 mAh/g that is even higher than the theoretical capacity of SnO_2 when 8.4 Li$^+$ is reversibly inserted/deinserted (theoretical capacity of SnO_2: 1494 mAh/g). This surprising result may be due to the synergetic effect between porous carbon and SnO_2 nanoparticles, which might alter and enhance the electrochemical properties of the carbon matrix after SnO_2 deposition. The actual contribution from carbon may be underestimated in the composite. On the other hand, this result indicates that the conversion reaction of SnO_2 into Sn (Equation 1) in 2-Sn-CMK is reversible to a large extent. The actual cause for such a high specific capacity of SnO_2 is currently under investigating in our laboratories. It should be certain that the nanocrystalline nature of SnO_2 and the uniform dispersion of SnO_2 phases in a high surface area matrix would greatly enhance the electrochemical reactivity of SnO_2. Similar observations have been reported for ~ 2-6 nm SnO_2 nanoparticles embedded in graphene matrix, where the contribution from SnO_2 in the graphene composite reaches 94% of its theoretical capacity considering that both alloying and conversion reactions are reversible.[41]
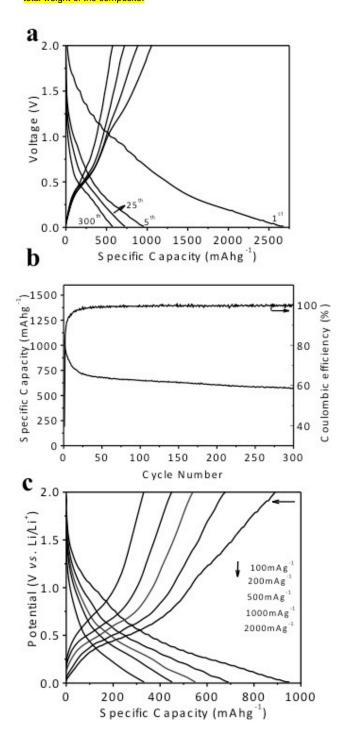
The first 50 charge/discharge cycles were tested at a current density of 200 mA/g for SnO_2/C composites after first, second and third AHD cycles, and the corresponding delithiation capacities are shown in **Figure 5b**. The composite of 2-Sn-CMK demonstrates a higher capacity of 684 mAh/g after 50 cycles. Surprisingly, 3-Sn-CMK shows a smaller capacity of 455 mAh/g and lower capacity retention (57%) after 50 cycles, compared to 2-Sn-CMK (65%). Here, we try to explain this phenomenon by a critical analysis based on the loading of SnO_2 and the available pore volume in the composites for Sn volume expansion. In 2-Sn-CMK, there is 0.695 g of SnO_2 per gram of carbon. According to Equation 1, SnO_2 undergoes a conversion reaction to form Sn and Li_2O, and Sn further alloys with Li$^+$ to form $Li_{4.4}Sn$. Henceforth, it is possible to estimate the volume occupied by $Li_{4.4}Sn$ and Li_2O, if we assume that nano-phases of Sn and Li_2O have the same density as their bulk counterparts. Thus, in 2-Sn-CMK, the SnO_2-derived mass would occupy a volume of 0.402 cm^3/g$_{carbon}$, after the conversion and alloying reactions (assuming a 259 % volume expansion for Sn)[9]. Considering that APS-CMK has a specific pore volume of 1.37 cm^3/g, there would be sufficient pore volume in the 2-Sn-CMK at the end of lithiation for Sn. Similarly, in 3-Sn-CMK, SnO_2-derived mass, after complete conversion and

lithiation reactions, occupies a volume of 1.17 cm^3/g$_{carbon}$. This expansion would fill up 85% of the available pore volume in the

Figure 5. (a) The first-cycle galvanostatic discharge/charge profiles of SnO_2/CMK composites after the first, second and third AHD cycle at a current density of 200 mA/g, (b) Charge capacity cycling data for 1-Sn-CMK, 2-Sn-CMK and 3-Sn-CMK at a current density of 200 mA/g, (c) Cyclic voltammetry profiles of the initial four cycles of 2-Sn-CMK at a scan rate of 0.5 mV s^{-1}. Note that specific capacity is calculated based on the total weight of the composite.

Figure 6. (a) Galvanostatic discharge/charge profiles of 2-Sn-CMK for the 1st, 5th, 25th and 300th cycle, (b) Long-term galvanostatic cycling performance and the corresponding Coulombic efficiency for 2-Sn-CMK at a current density of 200 mA/g, (c) Charge-discharge profiles of 2-Sn-CMK cycled at various current densities. Note that specific capacity is calculated based on the total weight of the composite.

APS-CMK, which may cause a serious strain for alloying and limits electrolyte imbibing. The large capacity difference from composites with different active mass loadings clearly shows the impact from the empty space in the composites on the electrochemical performance of the encapsulated SnO_2. Our results, for the first time, demonstrate the importance of porosity manipulation in nanoporous composites.

Due to its excellent performance, further electrochemistry investigations were carried out for the 2-Sn-CMK. **Figure 5c** shows the cyclic voltammetry (CV) measurements for 2-Sn-CMK at a scanning rate of 0.5 mV/s in the voltage window from 0.01 V to 2.0 V. In the cathodic scan, a large irreversible reduction peak was observed at 0.7 V, which is attributed to the decomposition of SnO_2 into Sn and Li_2O, and also to the formation of SEI on Sn phases and carbon. In the following CV cycles, a cathodic peak at 0.8 still exists, indicative of a certain level of conversion reversibility of SnO_2.[42] A pair of reversible redox peaks at 0.14 V and 0.55 V are assigned to the lithium alloying and dealloying with tin. These observations are in accordance with previous reports of SnO_2-based anodes.[43,44] The largely unchanged peak current intensity, except for the first cycle, indicates good cycling stability of the composite electrode.

Long term galvanostatic cycling was conducted for 2-Sn-CMK between 0.01 V to 2.0 V at current density of 200 mA/g. The charge-discharge profiles of SnO_2/C composite at 1st, 5th, 25th and 300th cycles and the cycling profile are shown in **Figure 6a and 6b**. The coulombic efficiency increased from 85% in the second cycle to 99.6% in the 300th cycle. These results demonstrate the promising cycling stability for SnO_2 supported on mesoporous carbon and can be attributed to the well-managed microstructure of the composites. To further analyze the structural stability, TEM study was carried out on 2-Sn-CMK sample after 300 charge/discharge cycles (**Figure 3f**). From the TEM image, it is evident that mesoporous structure of CMK-3 was well maintained and there is no severe aggregation or agglomeration of SnO_2 particles. The corresponding HAADF scanning TEM image (HAADF-STEM) and EDX mapping of carbon, tin and oxygen reveals the uniform distribution of SnO_2 nanoparticles in the carbon matrix after 300 cycles (**Figure S5**). However, for 3-Sn-CMK after 200 cycles of charge-discharge, there is severe aggregation of SnO_2 particles (**Figure S6**). These results demonstrate the importance of a rigid three-dimensional carbon matrix for homogeneous dispersion of the SnO_2 nanoparticles and the manipulation of empty pore volume to accommodate the huge volume expansion/contraction of the tin nanoparticles during Li insertion/extraction process. Consequently in 2-Sn-CMK, the agglomeration of tin nanoparticles and the cracking or pulverization of electrode material upon prolonged cycling is alleviated, thus maintaining large capacity, high rate capability and cycling stability. Additionally, 3D porous architecture and the short diffusion channels enhance the Li-ion diffusion and accessible pathways to the surface of active materials. The

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obtained specific capacity and the demonstrated number of cycles are higher than previous reports of similar composite with different preparation conditions (Supplementary information Table S1).[45,26] For example, SnO_2 carbon composite hollow spheres exhibited a specific capacity of 473 mAh/g after 50 cycles.[46] Another report for SnO_2 inside mesoporous carbon synthesized via a sonochemical method, showed a specific capacity of 200 mAh/g after 300 cycles.[47] While using a melt injection method to form $OMC-SnO_2$ composites, a specific capacity of 472 mAh/g after 30 cycles was obtained.[48]

Furthermore, the composite of 2-Sn-CMK exhibited excellent rate performance. The rate capability of SnO_2/C composite was investigated at different current rates of 100, 200, 500, 1000 and 2000 mA/g and the charge-discharge profiles are presented in **Figure 6c**. At a current rate of 2000 mA/g, a high capacity of 320 mAh/g was retained. This is higher than the reported rate performance of SnO_2-CNT,[49] carbon coated SnO_2 platelets and SnO_2 embedded in mesoporous carbon.[47] Moreover, even at high current densities high coulombic efficiency of 99% was maintained. The superior rate performance may be attributed to the large porosity within the composite and the conductive carbon framework.

Conclusion

We developed a new layer-by-layer AHD deposition methodology to conformally coat SnO_2 into a nanoporous carbon using sequential water adsorption and hydrolysis reactions. When investigated as anodes for LIBs, the composite with an intermediate loading exhibited stable a stable cycling performance with a capacity of 573 mAh/g retained after 300 cycles. This is superior to the SnO_2/mesoporous carbon composites previously reported. The enhancement is attributed to the fine manipulation of the empty pore volume in the porous composites to accommodate the volume expansion of Sn during alloying/dealloying reactions. We believe that the simple and scalable AHD methodology will potentially have a strong impact in many areas, including energy storage, separation and sensors.

Experimental Section

Materials and Preparation:

CMK-3 was prepared by a nanocasting method following the well-established procedure in the literature by employing SBA-15 as a hard template.

AHD method: Step I: Carbon surface functionalization. CMK-3 was treated with a mild oxidant, an acidic aqueous solution of $(NH_4)_2S_2O_8$, 1.0 M and H_2SO_4, 2 M. The carbon is referred to as APS-CMK. Typically, CMK-3, 0.3 g, was added to a freshly prepared 1.0 M APS acidic solution (30 ml). The mixture was stirred and refluxed at 60 °C for 6 hrs. Then, the solids were filtered, washed with deionized water and dried overnight in an oven at 80 ºC.

Step II: Water loading. Degassed APS-CMK, 50 mg, was allowed to equilibrate in an ambient water vapor/air mixture with 100% relative pressure at 80 ºC for one hour. Later, the sample was poured in to a Petridish and kept at stagnant atmosphere for one more hour.

Step III: Hydrolysis deposition of SnO_2. Water-loaded C-APS was dispersed and soaked for one hour in a dilute solution of Tin (IV) butoxide solvated in 1,3 dioxolane (DOXL) (10 vol%). The solid product was collected by filtration in a glovebox. Samples were heated at 300 ºC under air for 5 hrs.

Characterization methods

X-Ray diffraction (XRD) patterns were collected using a Rigaku Ultima IV Diffractometer with Cu Kα irradiation (λ= 1.5406 Å). The morphology was examined by field emission scanning electron microscopy (FESEM) using an FEI NOVA 230 high resolution SEM with an energy-dispersive X-ray (EDX) attachment. Transmission electron microscopy (TEM) images were recorded by FEI Titan 80-200 TEM. High-angle annular dark field scanning TEM (HAADF-STEM) measurements were carried out on an FEI Titan 80-200 microscope coupled with a HAADF detector and an EDX spectrometer. Nitrogen sorption measurements were performed on Micromeritics TriStar II 3020 analyzer. Thermogravimetric analysis (TGA) was performed using Shimadzu TGA-50 instrument under air from room temperature to 800 °C with a ramping rate of 10 °C min-1.

Assembly and testing of Lithium-ion batteries

Slurries were prepared by mixing 80 wt% active material (SnO_2/C composite), 10 wt% carbon black (Super-P) and 10 wt% polyvinylidene fluoride (PVDF). The mixture was suspended in N-methyl-2-pyrrolidinone (NMP) before casting onto a Cu foil current collector by the doctor blade method. The typical active-mass loading is around 1-1.3 mg/cm^2. Lithium foil anodes were polished in an Ar environment before using as the counter/reference electrode. The electrodes were assembled in to a coin cell in the glovebox. Glass-fiber membrane was used as the separator, and 1 M $LiPF_6$ in ethylene carbonate (EC)/dimethyl carbonate (DMC) as the electrolyte. Galvanostatic cycling was conducted on an Arbin BT2000 system, and cyclic voltammograms (CVs) were collected on a VMP-3 multi-channel workstation at a scanning rate of 0.5 mVs^{-1} at room temperature.

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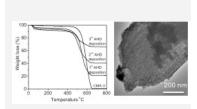
Energy Storage

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Layer-by-layer ambient hydrolysis deposition of tin oxide into nanoporous carbon as a stable anode for Lithium-ion batteries

Novel ambient hydrolysis deposition methodology employs sequential water adsorption and hydrolysis to form tiny SnO_2 nanoparticles inside nanoporous carbon. The SnO_2/C composite materials exhibit superior performance and enhanced cycling stability as anode materials for Lithium-ion batteries.