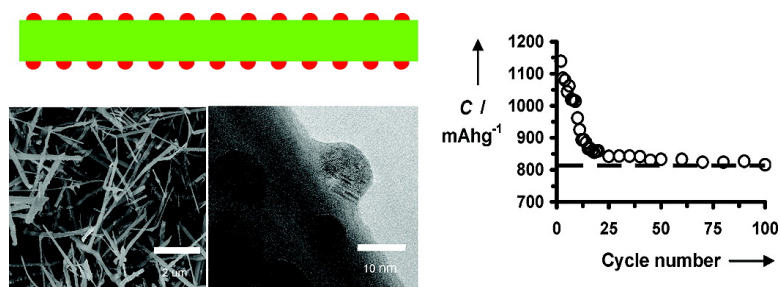


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Hybrid Tin Oxide Nanowires as Stable and High Capacity Anodes for Li-Ion Batteries

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ABSTRACT

In this report, we present a simple and generic concept involving metal nanoclusters supported on metal oxide nanowires as stable and high capacity anode materials for Li-ion batteries. Specifically, SnO₂ nanowires covered with Sn nanoclusters exhibited an exceptional capacity of >800 mAhg⁻¹ over hundred cycles with a low capacity fading of less than 1% per cycle. Post lithiation analyses after 100 cycles show little morphological degradation of the hybrid nanowires. The observed, enhanced stability with high capacity retention is explained with the following: (a) the spacing between Sn nanoclusters on SnO₂ nanowires allowed the volume expansion during Li alloying and dealloying; (b) high available surface area of Sn nanoclusters for Li alloying and dealloying; and (c) the presence of Sn nanoclusters on SnO₂ allowed reversible reaction between Sn and Li₂O to produce both Sn and SnO phases.

One-dimensional, nanowire (NW)-based materials are promising candidates for lithium-ion (Li-ion) battery electrodes due to their faster charge transport, better conducting pathways, and good strain relaxation.¹⁻³ Recently, Si NW arrays⁴ as well as NWs of Co₃O₄,^{5,6} Fe₂O₃,⁷ and SnO₂⁸ in the bulk powder form have shown to retain over 75% of their maximum capacity over 10 charge-discharge cycles. However, their stability over cycling is either unknown or in some cases, capacity fading has been observed after 30-50 cycles.

Of the various metal and metal oxide materials systems, both tin (Sn) and tin oxide (SnO₂)^{9,10} are interesting anode materials for Li-ion batteries because of their semiconducting properties combined with high capacity (Sn, 994 mAhg⁻¹ and SnO₂, 781 mAhg⁻¹)^{11,12} compared to that of graphite (372 mAhg⁻¹). However, significant capacity fading with cycling is a problem specifically with metal oxide based materials due to enormous volume changes during Li alloying and dealloying leading to metal segregation and crystallographic deformation,¹³ which in the case of Sn is as high as 259%.¹⁴ So, there has been a recent interest in investigating the use of nanowire-based oxide materials to improve the capacity.

Recent studies showed that the SnO₂ nanowires and heterostructured SnO₂/In₂O₃ nanowires retain a capacity of

~700 mAhg⁻¹ up to 15 cycles^{8,15} but quickly fade to ~300 mAhg⁻¹ after 50 cycles.¹⁶ Similarly, SnO₂ nanorods have been shown to retain a capacity of ~400 mAhg⁻¹ after 60 cycles.¹⁷ An amorphous tin-based oxide has shown a capacity retention of ~650 mAhg⁻¹ after the first cycle and significantly low fading up to 100 cycles.¹⁰ Also, Sn/SnO₂ particle composites have been tested with capacity retention of 549 mAhg⁻¹ after 40 cycles.¹⁸ All the above studies using nanoscale tin oxide-based materials report low capacities ranging from 300 to ~620 mAhg⁻¹ after 50 cycles. Therefore, it is important to develop strategies to increase the stability of nanoscale metal/metal oxide systems with high capacity retention.

Herein, we present a unique and simple generic design of hybrid structures involving metal nanoclusters covered metal oxide nanowires as stable anode materials with high reversible capacity. Although, the present study demonstrates the above concept with Sn and SnO₂ material system, it can be extended to a wide range of metal oxides, nitrides, and other semiconductors such as Si and Ge. For the present study, gram quantities of tin oxide nanowires are synthesized using a process that uses direct oxidation of tin powder in a microwave plasma. The resulting tin oxide nanowires are free of any foreign metal contamination that otherwise may hinder their electrochemical performance.

Experimental Section. SnO₂ nanowires were synthesized by reacting Sn metal powders directly in the gas phase with

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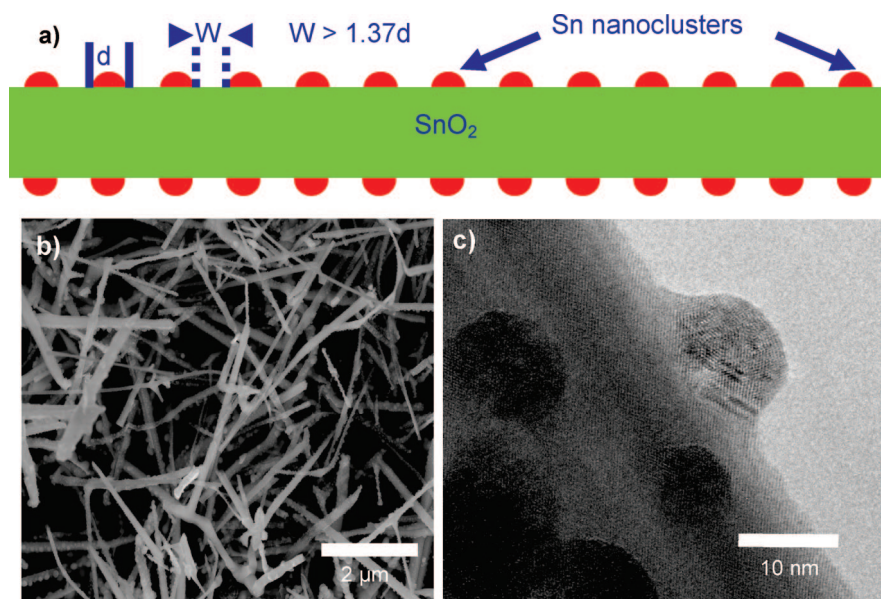


Figure 1. The concept of engineered metal nanocluster covered metal oxide nanowires. (a) Schematic showing evenly spread out Sn nanoclusters on a SnO₂ nanowire surface with spacing dependent on the droplet diameter. (b) A low-magnification SEM image showing a network of Sn-nanocluster-covered SnO₂ nanowires. (c) An HRTEM image showing well-spaced crystalline Sn nanoclusters on the nanowire periphery.

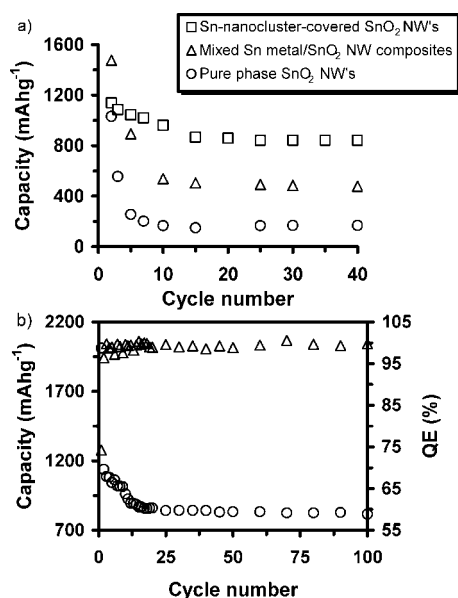


Figure 2. Electrochemical measurements of SnO₂ nanowire-based materials. (a) Cyclic performance comparison of (i) Sn-nanocluster-covered SnO₂ nanowires, (ii) SnO₂ nanowires with dispersed Sn metal, and (iii) pure SnO₂ nanowires measured between 0 to 2.2 V. Results are shown from the second cycle to the 40th cycle. (b) Capacity fading for the hybrid structures under the same conditions showing exceptional reversibility. Columbic efficiency of each cycle is also presented on the secondary y-axis in the right. QE = Columbic efficiency.

oxygen containing plasma without the use of a substrate in a microwave (MW) plasma jet reactor at a power of 2 kW. This process is discussed in detail elsewhere.¹⁹ The as-synthesized SnO₂ nanowires were purified by dispersing them in 1-methoxy 2-propanol followed by gravity sedimentation. Pure SnO₂ nanowires were exposed to H₂ plasma in a microwave chemical vapor deposition reactor at a power of

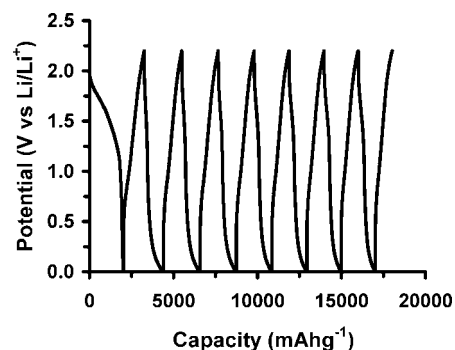


Figure 3. The voltage-capacity curves of the hybrid structures for the first eight cycles between 0 to 2.2 V performed at a rate of 100 mA g⁻¹ and room temperature.

500 W for 15 min to obtain the Sn-nanocluster-covered SnO₂ nanowires. All the samples were characterized using field emission scanning electron microscopy (FE-SEM) (FEI Nova 600), X-ray diffraction (XRD) (Bruker D8 Discover), and transmission electron microscopy (TEM) (Tecnai F20 FEI TEM with a Gatan 2002 GIF system). The material for the working electrode was prepared by spreading the SnO₂ nanowire-based material uniformly on a platinum foil by applying pressure. The electrodes were made by mixing the SnO₂ nanowire-based material with carbon black and a poly(vinylidene fluoride) binder in a weight ratio of 80:10:10, respectively, in a 1-methyl-2-pyrrolidone solvent and then spreading it onto platinum foil. A three electrode cell with the SnO₂ nanowire electrode as the working electrode and lithium foil as both the reference and auxiliary (counter) electrodes was used. The electrolyte consisted of 1 M LiPF₆ in a 1:1 (volume) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC). The electrochemical measurements were performed using eDAQ e-corder and potentiostat in the voltage range of 0 to 2.2 V.

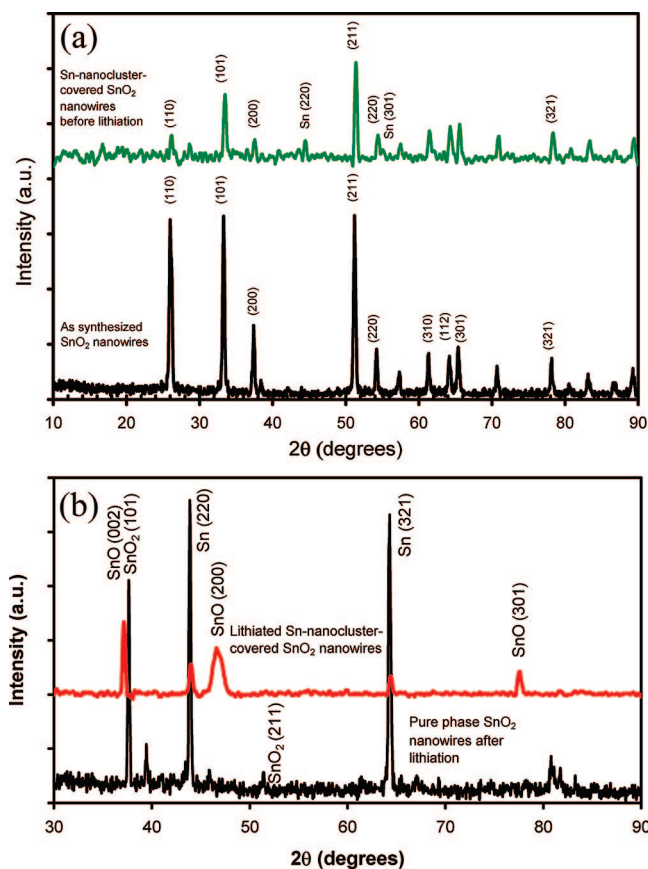


Figure 4. X-ray diffraction spectra of (a) as-synthesized SnO₂ nanowires and as-synthesized, Sn-nanocluster-covered SnO₂ nanowires and (b) lithiated pure phase SnO₂ nanowires and lithiated Sn-nanocluster-covered SnO₂ nanowires.

Results and Discussion. The design principle for the proposed hybrid structures is that the SnO₂ nanowires are covered with Sn nanoclusters with spacing ~ 1.4 times the diameter of each cluster as shown in Figure 1a. The spacing is necessary to accommodate the volume expansion of Sn clusters during alloying thereby preventing the Sn agglomeration. The faster electron transport through the underlying SnO₂ nanowires is expected to allow for efficient Li alloying and dealloying while the exposed Sn nanoclusters and SnO₂ nanowire surfaces serve as Li alloying sites. The SEM image in Figure 1b distinctly shows the Sn-nanocluster-covered SnO₂ nanowires with diameters ranging from 30–100 nm and a few microns long. The as-synthesized SnO₂ nanowires were reduced using H₂ plasma exposure producing nanometer-sized Sn clusters on the nanowire surfaces. The H₂ plasma exposure also reduced the nanowire diameters from 50–200 nm range to 30–100 nm range. See Figure 1c for a high resolution TEM image showing a SnO₂ nanowire covered with 15 nm sized, crystalline Sn nanoclusters evenly spaced from each other.

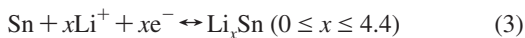
All materials systems are tested using anodic measurements over a potential window of 0 to 2.2 V (versus Li/Li⁺). The data using pure SnO₂ nanowires showed a high initial capacity of 2400 mAhg⁻¹ but severe capacity degradation occurred within the next 15 cycles leading to a reversible capacity of 166 mAhg⁻¹ after 40 cycles as shown in Figure

2a. In comparison, Sn-nanocluster-covered SnO₂ nanowires exhibited a reversible capacity of 845 mAhg⁻¹ after 40 cycles as shown in Figure 2b. Other types of Sn/SnO₂ composite nanowire systems (metal Sn nanoclusters distributed in between the SnO₂ nanowire networks) showed an initial capacity of 2800 mAhg⁻¹ with a final reversible capacity of 490 mAhg⁻¹ after 40 cycles. This result is similar to that obtained in prior studies using Sn/SnO₂ composites.¹⁸

Figure 2b depicts the discharge specific capacity and the columbic efficiency with cycling at 100 mA g⁻¹ current density, demonstrating for the first time that the mechanical stability of the material can be sustained for up to 100 cycles with an exceptional reversible capacity of 814 mAhg⁻¹. The hybrid structures show an initial irreversible capacity of 413 mAhg⁻¹, which accounts to a columbic efficiency of 74%, notably the highest reported until now in SnO₂ systems. See the secondary axis in Figure 2b. The columbic efficiency in the subsequent cycles is shown to be over 98%. The capacity fading at a rate of $\sim 1.3\%$ for the initial 15 cycles and $\sim 0.8\%$ after the 15th cycle is considerably lower than that reported for other nanoscale SnO₂ material systems.^{8,16} The reasons for enhanced capacity retention and Coulombic efficiency could be attributed to their high surface area to volume ratio which increases the net amount of Li alloying and dealloying. Figure 3 shows the initial charge and discharge curves of the hybrid SnO₂ structures in a potential window of 0 to 2.2 V. High discharge capacity of 2013 mAhg⁻¹ in the first cycle is attributed to the fact that Li intercalates into SnO₂ during the first cycle followed by the subsequent alloying of Li with Sn forming a Li_xSn alloy, which corresponds to the plateau observed below 0.5 V in the charge–discharge curves. For pure phase SnO₂ nanowires, rapid capacity degradation is observed with cycling and capacity retention of 166 mAhg⁻¹ is obtained after 40 cycles. The XRD and SEM characterization of the material after cycling showed that the SnO₂ NWs reduce completely to Sn while destroying the nanowire morphology. These observations about severe degradation of nanowire morphology and reduction in the capacity are consistent with prior studies involving SnO₂ and other metal oxide nanowires.^{8,15,16} In some cases, the as-synthesized SnO₂ nanowire samples have exhibited capacity retention over a range of values (166–300 mAhg⁻¹), which is possibly due to the presence of some excess Sn metal on nanowire surfaces similar to our hybrid nanowire systems. Complete reduction of the SnO₂ nanowires at various microwave powers yielded Sn crystals of varying diameters rather than Sn nanowires. SEM image of the completely reduced system is shown in the Supporting Information. The performance of Sn thin films as anodes has been studied before²⁰ and performs similarly to that of pure phase SnO₂ system, that is, the capacity fades quickly to about 200 mAhg⁻¹ in 20 cycles.

The stability of the Sn-nanocluster-covered SnO₂ nanowires could possibly be explained with the following Li alloying mechanism:²¹





The reaction of SnO₂ with Li ions, electrolyte decomposition, and solid electrolyte interface formation are believed to be the reasons for large irreversible capacity during the first cycle. In the case of pure SnO₂ materials including nanowires, the reduction of SnO₂ to Sn takes place in the first cycle. Repeated cycling induces enormous volume changes in Sn that tends to expand and coalesce with the nearby Sn atoms, leading to large agglomerates, thus reducing the available surface area for the Li-ion storage capacity of the material and eventually destroys the pure oxide nanowire structure.

In the case of our hybrid structures involving Sn-nanocluster-covered SnO₂ nanowires, the spacing between clusters was adequate enough to accommodate the volume changes induced by the lithiation process, preventing agglomeration thus explaining high capacity even after hundred charge–discharge cycles. In addition, the underlying nanowires must retain both morphology and conductivity for the observed stability with cycling. So, the XRD spectra were obtained for both pure phase and Sn-nanocluster-covered SnO₂ nanowire samples after they were subjected to several charge–discharge cycles. Figure 4a depicts the XRD spectra of as-synthesized rutile phase SnO₂ nanowires and Sn-nanocluster-covered SnO₂ nanowires. Figure 4b shows the XRD spectra of both pure phase and Sn-nanocluster-covered SnO₂ nanowires after 25 and 100 charge and discharge cycles, respectively. After lithiation, the majority of the SnO₂

nanowires get completely converted into Sn phase in the case of pure SnO₂ nanowire samples along with unreacted SnO₂ phases. In comparison, the Sn-nanocluster-covered SnO₂ nanowires after hundred charge–discharge cycles show the presence of SnO phase in addition to Sn phases. The observed, small peak shifts with both SnO (301) and SnO (002) peaks toward the lower diffraction angle indicate that the observed SnO phase might be a lithiated SnO phase. The observed capacity retention can be attributed to the presence of Sn as well as SnO phase. The SnO phase is formed as a result of the reversibility of eq 3 in which the nanoscale Sn domains can decompose the Li₂O, which is otherwise irreversible. This reversibility gives rise to the formation of SnO nanodomains from Sn-nanosized particles during the delithiation process. Such nanodomains are clearly seen to be present in an amorphous matrix within the nanowires after they were subjected to 100 charge–discharge cycles. See the high-resolution TEM (HRTEM) image in Figure 5b. The reversibility of the metal particles to metal oxides by the decomposition of Li₂O in nanosized domains was shown to be feasible in other reports.^{1,6}

The SEM image in Figure 5a distinctly shows unblemished hybrid nanowires after 100 charge–discharge cycles. However, the image shows the enlarged Sn nanoclusters on the nanowire periphery that is due to the volume expansion of Sn as well as the Sn segregation from the interior of the nanowire. The proposed reversibility with the Sn nanocluster-covered SnO₂ nanowires is schematically illustrated in Figure

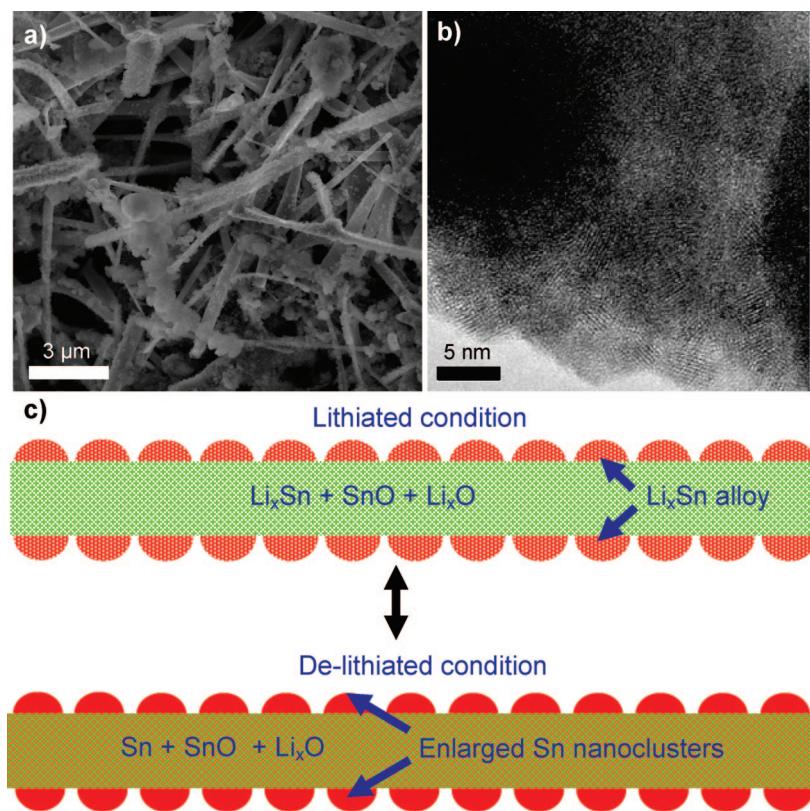


Figure 5. Characterization of hybrid structures after 100 cycles of charge and discharge. (a) SEM image of hybrid nanowires. (b) HRTEM image of the Sn nanocluster-covered SnO₂ nanowires. (c) A schematic illustrating the reversible Li alloying and dealloying steps in the Sn-nanocluster-covered-SnO₂ nanowires.

5c. As shown in the schematic, the nanowire is composed of SnO and Li_xO in which SnO promotes the electronic conductivity while the Li_xO phase promotes the Li-ion migration during Li alloying and dealloying stages as well as prevents further Sn agglomeration inside the nanowire.¹⁸ Hence, the nanowire morphology is retained after several cycles avoiding major structural changes. The SnO phase could also arise due to the slightly reversible nature of the reaction in eq 2 during the dealloying process, that is, the faster kinetics for SnO formation compared to SnO_2 .^{22,23}

Conclusions. In summary, a new class of hybrid structures involving SnO_2 nanowires decorated with well-separated Sn nanoclusters exhibit a reversible storage capacity greater than 800 mAhg^{-1} over 100 cycles. These hybrid structures with improved stable capacity better relieve the stresses associated with volume changes compared to the pure phase SnO_2 nanowires. The capacity fading after the first few cycles is the lowest at less than 1% per cycle. Post-lithiated samples show the intact hybrid structure after 100 cycles. The proposed new concept could be applied to other nanoscale metal oxide, nitride systems including Co_3O_4 ($\sim 900 \text{ mAhg}^{-1}$)¹ and other material systems, such as Si,⁴ leading to stable and high capacity Li-ion batteries and could lead to major advancements in portable power applications.

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Supporting Information Available: The details of the pure phase SnO_2 nanowire electrode performance including the electrochemical testing (capacity curves), postlithiation characterization (SEM and XRD) are included. The XRD peak analysis of the postlithiated Sn-nanocluster-covered SnO_2 electrode is also presented. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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