SUPPORTING INFORMATION:

Three-Dimensional Antimony Nanochains for Lithium-ion Storage

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General Information:

¹¹B and ¹H NMR spectra were recorded at room temperature, on a Varian INOVA 300 MHz NMR spectrophotometer. Chemical shifts (δ values) are reported in parts per million relative to BF₃.Et₂O for ¹¹B NMR respectively. Data are reported as: δ value, multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, p=pentet, h=hextet, m=multiplet, br=broad) and integration. All solvents for routine isolation of products were reagent-grade. Sodium borohydride (powder, purity >99% by hydride estimation¹) was purchased in bulk from Dow Chemical Co. (Rohm and Haas). Ammonium sulfate (ACS reagent >99.0%, Fisher Chemical), was powdered prior to use. Tetrahydrofuran (THF, ACS reagent >99.0% containing 0.004% water and 0.025% BHT) was purchased from Sigma-Aldrich. Antimony (III) chloride (Crystalline ACS reagent >99.0%, Alfa Aesar), antimony (III) fluoride (Crystalline ACS reagent >99.8%, Alfa Aesar), polyvinyl alcohol (PVA) 13-23k (ACS reagent 86-89% hydrolyzed, Alfa Aesar), methanol (Anhydrous, Macron), tri-n-octylphosphine (97%, Sigma-Aldrich), oleylamine (98%, Sigma-Aldrich), acetone (ACS reagent >99.0%, Mallinckrodt Chemicals) were purchased from the respective commercial sources and used without further purification. Piperidine borane and triethylamine borane were prepared in accordance with literature reports, and methylamine borane was prepare from the hydrochloride salt of methylamine².

Procedure for the preparation of ammonia-borane³:

Sodium borohydride (SBH) (18.91 g, 0.5 mol, 1 eq.) and powdered ammonia sulfate (66.07 g, 0.5 mol, 1 eq.) were transferred to a dry 2 L round bottom flask containing a large magnetic stir bar. The flask was then cooled in an ice-water bath followed by the addition of 495 mL of reagent-grade tetrahydrofuran. With vigorous stirring 4.5 mL of water was then added dropwise over a period of 5 minutes to limit frothing. Once all water is added the flask is moved to room temperature and stirred vigorously. The reaction is monitored using ¹¹B NMR until completion (~5 h) as judged by the absence of sodium borohydride peaks in the ¹¹B NMR. (Prior to running the ¹¹B NMR experiments, a drop of dimethyl sulfoxide is added to the aliquot to solubilize any sodium borohydride present.) Once complete, the reaction mixture is filtered through celite and the filter cake thoroughly rinsed with tetrahydrofuran. The solvents were removed from the combined filtrates via rotary evaporation, followed by drying *in vacuo* for 12 h to obtain

ammonia borane (AB) as a white solid. A hydride analysis¹ revealed this to be >98% chemically pure.

¹ Brown, H. C. Organic Syntheses Via Boranes, Wiley: New York, **1975**, Chapter 9.

² Ramachandran P. V., Kulkarni A. S., Int. J. Hydrogen Energy, 2017, 42, 1451.

³ Ramachandran P. V., Kulkarni A. S., Zhao Y., Mei J., Chem. COmmun., 2016, 52, 11885.

¹¹B NMR spectroscopic monitoring of ammonia-borane synthesis



1. ¹¹B NMR spectrum of the progress of ammonia-borane synthesis: (a) prior to water addition (SBH: AB, 1:0); (b) 15 min. after addition of water (SBH: AB, 4.4:1.0); (c) 4 h after addition of water (SBH: AB, 0.01:1.00); and (d) 5 h after addition of water (SBH: AB, 0:1).

Characterization of ammonia-borane:

¹H NMR (300 MHz, Tetrahydrofuran-*d8*) δ 4.26 – 3.69 (m, 3H, NH₃), 2.08 – 0.74 (m, 3H, BH₃); ¹¹B NMR (96 MHz, Tetrahydrofuran-*d8*) δ -22.04 (q, J = 95.6 Hz).



2. ¹H NMR (300 MHz, Tetrahydrofuran-*d8*) Ammonia-borane



3. ¹¹B NMR (96 MHz, Tetrahydrofuran-*d*8) Ammonia-borane

Procedure for the preparation of antimony nanoparticles and nanochains⁴

Antimony trichloride (0.080 g, 0.35 mmol, 1 eq.) or antimony salt (0.35 mmol, 1 eq.) was dissolved in 10 mL of deionized water in a 50 mL round bottom flask. Ammonia-borane (0.054 g, 1.75 mmol, 5 equiv.) or reducing agent (1.75 mmol, 5 equiv.) was dissolved in 10 mL of deionized water in a 25 mL round bottom flask. The metal salt/water solution was then quickly added to the ammonia borane/water solution. The flask was then sealed with a rubber septum and kept under nitrogen and stirred at room temperature for 2 h, followed by the addition of 10 mL methanol. The resultant solution was centrifuged, and the supernatant was decanted. The nanoparticles were then dispersed in tri-n-octylphosphine (6.0 mL, 13.5 mmol) and carefully added to a flask containing oleylamine (6.0 g, 50.0 mmol) or other capping agent (for PVA 6.0 g with 10 mL water) kept at 230 °C and stirred for 2 h, after which the reaction was cooled to room temperature, followed by the immediate addition of 10 mL of methanol. The resultant solution was then centrifuged and the supernatant decanted. When using PVA as a capping agent, the solution obtained after methanol addition was added to 100 mL of dichloromethane prior to centrifugation. The nanoparticles were resuspended in acetone. The centrifugation, decantation, and resuspension were repeated twice more and the nanoparticle/acetone solution was transferred to a 20 mL vial and sealed.

Discussion of antimony nanoparticles synthesis via ammonia borane reduction

Our synthesis of antimony nanochains, based on the procedure developed by Revaprasadu and co-workers for the synthesis of alkylamine capped antimony nanoparticles, was modified by the use of ammonia-borane as a reducing agent instead of sodium borohydride. The first stage involves the reduction of antimony trichloride using ammonia-borane, and in the second stage the nanoparticle growth and capping takes place. It has been previously observed^{4,7} that antimony trichloride reduced using sodium borohydride can produce nanoparticles in the same diameter range as produced by the ammonia-borane reduction (10-20 nm). They have also been observed to undergo some self-assembly to higher order nanostructures, particularly when using alkylamine or other capping agents and hot-injection methods. However, the NPs produced with SBH do not form nanoarchitecture to the same extent that was produced when using ammonia-borane as a reducing agent (Figure S1e). It is postulated that the more extensive 3-dimensional nanochain architecture is critical for the results observed during our electrochemical study.

Some mechanistic information for the methods involving NaBH₄ reduction^{4,7}, sodium hydride reduction⁵, and metal amide reduction⁶, has been proposed. The cation of the reducing agent forms a salt with the anion of the metal salt. This happens with a concurrent release of hydrogen gas, the formation of the neutral metal, and usually the production of a secondary byproduct containing the cation of the reducing agent.

Ammonia-borane, a compound with a dative bond between the borane and ammonia moieties, does not contain any 'cationic' species and is expected to undergo a related, but altered mechanism. When antimony trichloride dissolves in water it can be hydrolyzed to form antimony oxychloride and hydrogen chloride as shown in eq. 1 below⁸. It was observed during our synthesis that the pH of the water dramatically decreased after the dissolution of the antimony trichloride (to approximately 1 from 5).

$$SbCl_3 + H_2O \longrightarrow SbOCl + 2 HCl$$
 (1)

Upon combination of the antimony trichloride solution and ammonia-borane solution, there was a vigorous release of hydrogen and an immediate darkening of the mixture, indicative of the reduction of the metal salt. It is assumed that the overall reaction proceeds as in eq. 2.

$$2 \text{ SbCl}_3 + 6 \text{ NH}_3\text{BH}_3 + 18 \text{ H}_2\text{O} \rightarrow 2 \text{ Sb}^0 + 6 \text{ NH}_4\text{CI} + 6 \text{ H}_3\text{BO}_3 + 15 \text{ H}_2$$
 (2)

The hydrogen chloride produced through antimony trichloride hydrolysis is presumed to be involved in two processes, (i) having a role in the formation of the ammonium chloride byproduct by capture of the ammonia released from ammonia borane and (ii) as a driving force for the formation of boric acid, which is the only boron species observed in the reaction mixture prior to the addition of methanol (NMR 4). The ¹¹B NMR spectra matches almost exactly with a commercial sample of boric acid (NMR 5). Previous work by the Ramachandran group has also shown that in the presence of RuCl₃ that ammonia borane is dehydrogenated to produce ammonium tetraborate,⁹ a compound which forms boric acid in the presence of HCl.

Once the water soluble byproducts are removed through centrifugation and water decantation, the reduced antimony is suspended in tri-n-octylphosphine (TOP) and injected into hot (230 °C) oleylamine (OA). The TOP/OA combination acts as a co-surfactants and capping agents, providing an environment which has been shown to be conducive to more controlled and stable nanoparticle growth^{4,10}. The overall schematic for this stage of the nanoparticle synthesis is described in eq. 3.

$$Sb^{0}$$
 + Tri-n-octylphosphine + Oleylamine \rightarrow Capped Sb particles (3)



4. Reaction Solution, prior to the addition of methanol. ¹¹B NMR (96 MHz, water) δ 19.03. (s).



- ⁴ Mntungwa, N.; Khan, M.; Mlowe, S.; Revaprasadu, N., *Mater Lett*, **2015**, *145*, 239.
- ⁵ Houdayer, A. et al., *Materials Chemistry and Physics*, 101 2007, 101, 404.
- ⁶ He, M. et. al., *Chem Mater*, **2015**, *27*, 635.
- ⁷ Mntungwa, N. et al., *Mater Lett.* **2013**, 92, 220.
- ⁸ Greenwood, Norman N.; Earnshaw, Alan (1984). *Chemistry of the Elements*. Oxford: Pergamon Press. pp. 558–571. ISBN 0-08-022057-6
- Ramachandran P V, Gagare P D, Inorganic Chemistry, 2007, 46, 7810.
- ¹⁰He M, Kravchyk K, Walter M, Kovachenko M V. Nano Lett **2014**, 14, 1255.

Effect of the Sb salt, reducing and capping agents on the architecture of Sb nanoparticles





Figure S1. TEM analysis of antimony nanoparticles synthesized using; *antimony salt, reducing agent, capping agent*: (a) SbCl₃, ammonia borane, oleylamine; (b) SbCl₃, methylamine borane, oleylamine; (c) SbCl₃, triethylamine borane, oleylamine; (d) SbCl₃, piperidine borane, oleylamine; (e) SbCl₃, sodium borohydride, oleylamine; (f) SbF₃, ammonia borane, oleylamine; (g) ammonia borane, SbCl₃, PVA.

Analysis of the effect of the Sb salt, reducing and capping agents on the nanoarchitecture

(a) The nanochain architecture is shown nicely in the TEM micrograph and the nanoparticles appear to be uniform. HAADF shows noticeable lower Z, potentially from a surface layer of carbon. Overall the material appears to be composed of single crystals, not polycrystalline. (b) The nanochain architecture is apparent here as well, but the size distribution appears be to more bimodal, with both smaller and larger chains being visible. Numerous hollow pockets or pores can be seen, and overall the bulk material looks to be composed of single crystals with a few regions of polycrystallinity and sharp surface facets. (c) Again, nanochains are apparent, and display a bimodal distribution, but there is a smaller disparity between the two general size categories. A less HAADF intense surface layer is also present, most likely a carbon surface layer. Visible pockets are smaller and less numerous than the previous materials. While low polycrystallinity is again present, with even the corners and turns of the nanochain being within the same zone axis, some small crystals do appear on the surface of the material. (d) The bulk of the volume of this material is presented as large crystals, with only as estimated 20% showing nanochain-like structure. What nanochains are presents are nonuniform is size and appear to have grown on the large crystals. (e) A uniform nanochain is present in this material, and it seems to be clusters of spherical particles with narrow bridges between them. Pockets of varying sizes are again visible, and while small amounts of polycrystallinity appear near the pockets the material looks crystalline overall. A surface layer is again visible, likely an amorphous carbon layer. (f) No nanochain are apparent in this material, only what appear to be agglomerates of massive crystals with small crystals creating a rough surface layer. (g) Large, uniform crystals are present in this material, with a highly polycrystalline surface layer.

Powder XRD, Raman, and EDS spectrographic crystallinity and compositional analysis

The crystalline structure of antimony nanochains were examined using powder X-ray diffraction (XRD) technique equipped with Rigaku diffractometer. Subsequently, the Raman spectroscopic measurement was carried out for structural analysis using a LASER Raman spectrometer.



Figure S2. The crystalline structure and composition of 3D antimony-nanochains investigated using (a) powder X-ray diffraction, (b) Raman spectroscopic measurements, and (c) energy dispersive X-ray spectroscopy.

Transmission electron microscope images

The morphology and 3D antimony nanochains were examined using scanning electron microscopic technique (JEOL NeoScope JCM6000 Benchtop, SEM) and transmission electron microscopy (TEM) at 300 kV on a FEI Titan ETEM 80-300 with the fast Fourier transform (FFT) to further confirmation the crystallographic orientation of antimony nanochains under its simulated diffraction patterns obtained by the CrysTBox software.



Figure S3. Homogeneous morphological investigation of 3D antimony nanochains (a), (b), (c) and crystallinity (d) examined using transmission electron microscopic technique.

High resolution transmission electron microscope images



Figure S4. High resolution transmission electron microscope image displays (a) & (c) the lattice fringes of crystalline antimony and (b) & (d) the corresponding fast Fourier transform of 3D antimony nanochains under the characteristic of zone axis $[0\overline{1}1]$ & $[\overline{4}11]$ of rhombohedral antimony phase, respectively.

Cyclic voltammetric analysis



Figure S5. Cyclic voltammetric analysis of the 3D antimony nanochains anode material between 0.01 - 2.5 V at 0.1 mV s^{-1} using 1 M LiPF₆ in ethylene carbonate (EC) and diethyl carbonate (DEC) in the volume ratio of 1:1 as electrolyte and CelgardTM 2500 separator.

Li-ion insertion into and extraction from antimony nanochains

TEM images of the antimony nanochains demonstrate that the interconnected nano-architecture remains after (de)lithiation process. In the Figure S7 below (a) shows the nanochains prior to lithiation, (b) is while the nanochains are lithiated, and (c) is after delithiation. (a) Large nanochains are visible in this material with some larger crystals also present, and large pockets appear throughout. There are also some parts of the structure which have the appearance of nanochains, but with less intensity than the crystal, possibly the results of antimony leaching into the larger crystals, leaving a less dense structure. (b) This material appears to be mixture of larger crystals and nanochains, and close-up the nanochains show a 'fuzzy', possibly polycrystalline, structure which looks like agglomerated crystals. A low-Z material is covering the particles, most probably binder added during the assembly of the battery cell. (c) The same low-Z material is present, again mostly likely binder present from the battery assembly process. The material also possesses many structures with a hollow appearance, with pockets that are larger and more exaggerated than previous samples. The material has a rougher appearance overall compared to the charged material, but with the same external 'fuzzy', polycrystalline appearance. It is noteworthy that the average particle size shifts towards lower values while going from lithiated to delithatied state. This indicates that the cycling process allows the existence of small nanoparticles within the electrode. Filling the pores of the antimony nanochains with Carbon Super P, which is present in the electrode, could act to stabilize the architecture of the active material.



Figure S6. TEM analysis of (a) pristine, (b) lithiated and (c) delithiated antimony nanochains.

Preparation and physical/chemical characterization of graphene supported antimony

Antimony nanoparticles supported on graphene nanosheets were prepared via impregnation of graphene with antimony acetate solution. Using an antimony:graphene weight ratio of 9, graphene (0.2 grams) and antimony acetate (1.8 grams) were combined in 50 ml of acetic acid. The mixture was then heated at 80 °C overnight to remove the solvent. The resultant material was pyrolyzed at 650 °C for 2 h under inert atmosphere. After pyrolysis antimony nanoparticles supported on graphene were obtained as a dark powder.



Figure S7. Physical and chemical characterization of Sb/Gr composite. (a) XRD pattern; (b,c) TEM micrographs; (d) SEM image; and EDX mapping of (e) carbon and (f) Sb.

Electrochemical impedance spectroscopic analysis



Figure S8. Electrochemical impedance spectroscopy information of 3D antimony nanochains and Sb/Gr before and after 2nd, 100th cycles.