Electronic Supplementary Material (ESI) for Nanoscale.
This journal is © The Royal Society of Chemistry 2014

Electronic Supplementary Information (ESI) for

Monodisperse SnSb Nanocrystals for Li-ion and Na-ion Battery Anodes: Synergy and Dissonance Between Sn and Sb

by Meng He,[†,‡] Marc Walter, [†,‡] Kostiantyn V. Kravchyk, [†,‡] Rolf Erni,[#] Roland Widmer,[§] and Maksym V. Kovalenko*[†,‡]

[†] Laboratory of Inorganic Chemistry, Department of Chemistry and Applied Biosciences, ETH Zürich, CH-8093 Zürich, Switzerland

[‡] Laboratory for Thin Films and Photovoltaics, Empa – Swiss Federal Laboratories for Materials Science and Technology, CH-8600 Dübendorf, Switzerland

[#] Electron Microscopy Center, Empa – Swiss Federal Laboratories for Materials Science and Technology, CH-8600 Dübendorf, Switzerland

[§]Nanotech@surfaces Laboratory, Empa – Swiss Federal Laboratories for Materials Science and Technology, CH-8600 Dübendorf, Switzerland

[*]E-mail: mvkovalenko@ethz.ch

Materials and Methods.

Chemicals. Oleylamine (OLA, techn., TCI), toluene (99.9%, Sigma-Aldrich), toluene dried (≥99.9%, max. 0.005% H_2O, VWR Merck), ethanol (≥99.9%, Scharlau), oleic acid (OA, 90%, Aldrich), tin (II) chloride ($SnCl_2$, anhydrous, ABCR), antimony (III) chloride ($SbCl_3$, 99.999%, ABCR), lithium bis(trimethylsilyl)amide ($LiN(SiMe_3)_2$, 97 %, Sigma-Aldrich), 1-dodecanethiol (Sigma-Aldrich), diisobutylaluminum hydride (DIBAH, 1M in toluene, Sigma-Aldrich), hydrazine (Gerling Holz+Co) and acetonitrile (dried, Merck) were used as received. OLA was dried at 100 ℃ under vacuum overnight.

Battery components. Carbon black (Super C65, TIMCAL), carboxymethyl cellulose (CMC, Grade: 2200, Lot No. B1118282, Daicel Fine Chem Ltd.), 1 M solution of $LiPF_6$ in ethylene carbonate/dimethyl carbonate (EC/DMC, Novolyte), $NaClO_4$ (98%, Alfa Aesar), propylene carbonate (BASF, battery grade), 4-fluoro-1,3-dioxolan-2-one (FEC, >98.0%, TCI), Celgard separator (Celgard 2400, 25µm microporous monolayer polypropylene membrane, Celgard Inc. USA), glass microfiber separator (GF/D, Cat No.1823-257, Whatman), Cu foil (9µm, MTI Corporation).

Synthesis of SnSb NCs. $SnCl_2$ (0.25 mmol, ~0.048g) and dried OLA (10 mL) were mixed in a glovebox and via syringe added into a 50-mL three neck flask and kept under vacuum for ~45 minutes at 100°C. Meanwhile, $LiN(SiMe_3)_2$ (3.6mmol, ~0.6g) and $SbCl_3$ (0.25mmol, ~0.055g) were separately dissolved in 1 mL of anhydrous toluene. The temperature was raised to 210°C under nitrogen, followed by the injection of $LiN(SiMe_3)_2$ solution and, 10s later, DIBAH (0.6 mL, 1M in toluene). After another 10 sec, $SbCl_3$ solution was injected as well. The reaction mixture was held for 6 hours at 210°C. Finally, the reaction was quickly quenched by cooling with an ice-water bath together with the injection of anhydrous toluene (12mL) at around 100°C. Upon cooling, 1-dodecanthiol (~0.4mL) and oleic acid (~0.4mL) were added at around 50°C. After cooling, SnSb NCs were precipitated by adding ethanol (~60 mL), followed by centrifugation at 6500 rpm for 4 min. Then SnSb NCs were redispersed in toluene (12 mL) containing oleic acid (~0.25 mL), and then precipitated by ethanol (12 mL) and centrifuged at 6000 rpm for 1 min. Finally, SnSb NCs were dispersed in common nonpolar solvents such as chloroform or toluene and stored in the fridge.

Ligand removal. In order to remove the organic capping ligands, NCs were precipitated with EtOH, centrifuged and redispersed in a solution of 0.8 mL hydrazine in 25 mL anhydrous acetonitrile. The suspension was stirred at room temperature for two hours. After centrifugation, the precipitate was washed three times with acetonitrile (~20 mL) to remove residual hydrazine and dried for 12 h at room temperature under vacuum.

Assembly and testing of Li- and Na-ion half-cells. Electrodes were prepared by ball-milling the respective ligand-free NCs (SnSb, Sn, or Sb, 64 wt.%) with carbon black (21 wt.%) and CMC binder (15 wt%) in water for 1 hour and casting the hereby obtained slurry onto Cu foil. The current collectors were then dried for 12h at 80°C. Homemade, reusable coin-type cells were assembled in an argon-filled glove box ($O_2 < 1$ ppm, $H_2O < 1$ ppm) using two layers of separators (Celgard and glass fiber) for LIBs and one layer separator (glass fiber) for SIBs. Elemental lithium or sodium served as both reference and counter electrodes. As electrolytes, 1 M $LiPF_6$ in EC:DMC (1:1 by wt.) was used for Li-ion batteries and 1 M $NaClO_4$ in PC for Na-ion batteries. To improve cycling stability 3% of FEC were added to both electrolytes. Cells were cycled between 0.02 – 1.5 V on a MPG2 multi-channel workstation (Bio-Logic). The obtained capacities were normalized to the mass of NCs.

Characterization. Transmission Electron Microscopy (TEM) images were obtained with a Philips CM30 TEM microscope at a voltage of 300 kV. Carbon-coated TEM grids from Ted-Pella were used as substrates. Average size and size distribution were obtained from more than 100 NCs in the TEM images using Nano Measurer software (http://nano-measurer.software.informer.com). EDX-STEM elemental mapping were performed on JEOL 2200FS at a voltage of 200 kV. Wide-angle powder X-ray diffraction (XRD) spectra were collected on STOE STADI P powder X-ray diffractometer. EDX elemental analysis was performed on Hitachi S-4800 SEM microscope. Elemental analysis was also performed by Bachema analytical laboratories (http://www.bachema.ch/) using inductively coupled plasma optical emission spectrometry (ICP-OES). X-ray photoelectron spectroscopy (XPS) measurements were carried out using Al K_α X-ray radiation.

Table S1. Results of ICP-OES measurements

Elements	Sample **before** ligand removal	Sample **after** ligand removal
Antimony (dissolved)	1.080 mg/L	2.800 mg/L
Tin (dissolved)	1.590 mg/L	4.140 mg/L

The atomic ratio (Sb:Sn) of the Sn-Sb alloy is calculated to be **0.6622** (sample before ligand removal) and **0.6594** (sample after ligand removal) corresponding to Sn_3Sb_2 or $Sn_{0.6}Sb_{0.4}$.

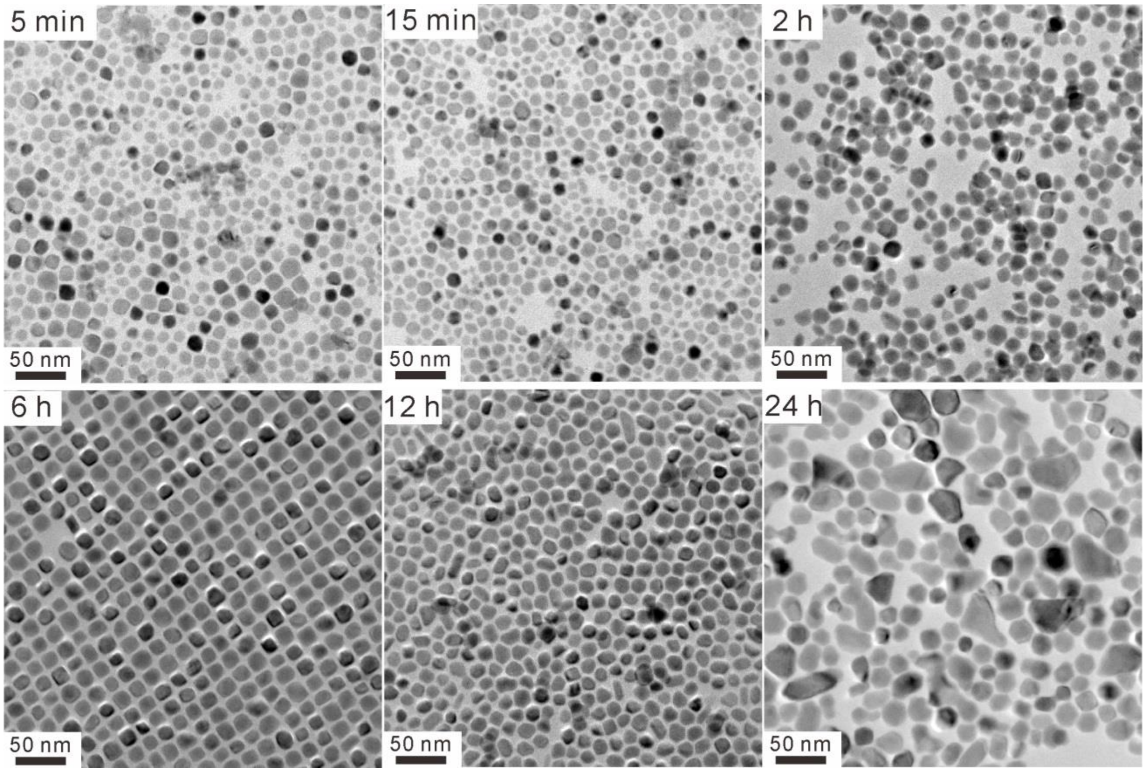

Figure S1. TEM images showing the morphology and size evolution of SnSb NCs during the synthesis.

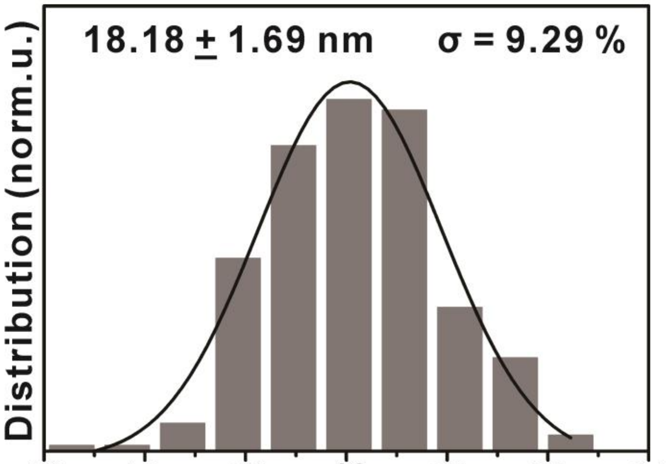

Figure S2. Size-distribution histogram corresponding to the TEM image in the main text (Figure 1, growth time of 6 hours).

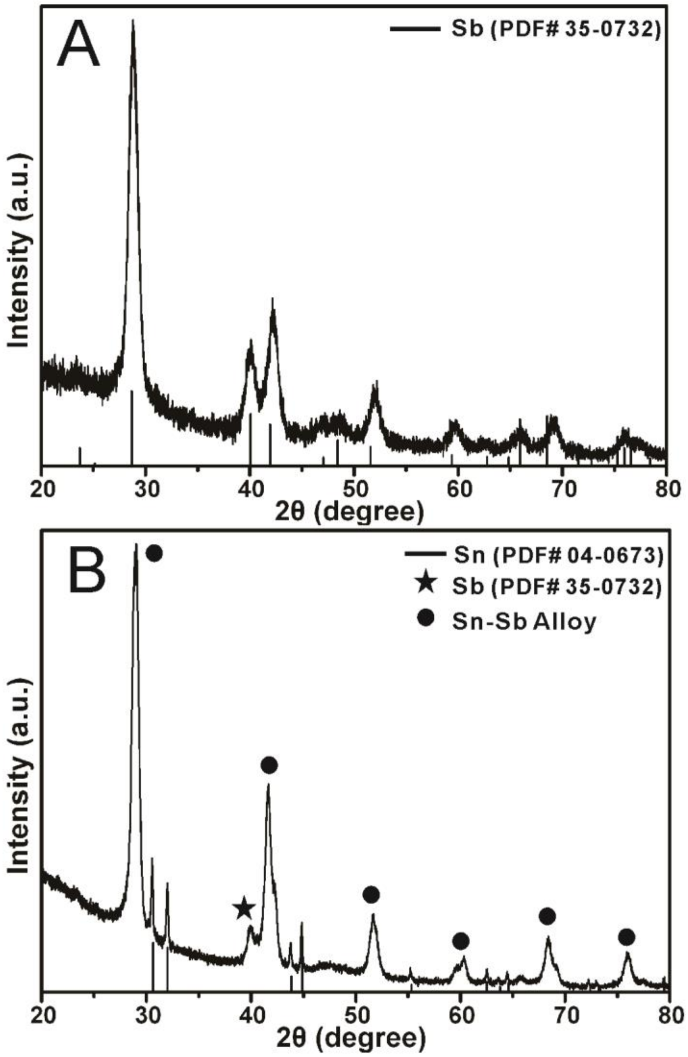

Figure S3. Powder XRD patterns of samples obtained by (A) simultaneous injection of $SbCl_3$ and $SnCl_2$; (B) with prolonged growing time (45 min) for Sn seeds before $SbCl_3$ injection. Such extended growth time of Sn seeds hampers the subsequent diffusion of Sb into the Sn lattice and consequently a mixture of Sn and Sn-Sb alloys was obtained. Thus it is essential to limit the delay between injections to minimum (10-20s) in order to maintain small initial size of Sn seeds (ca. 10nm), while the following growth occurs presumably via co-deposition of Sn and Sb.

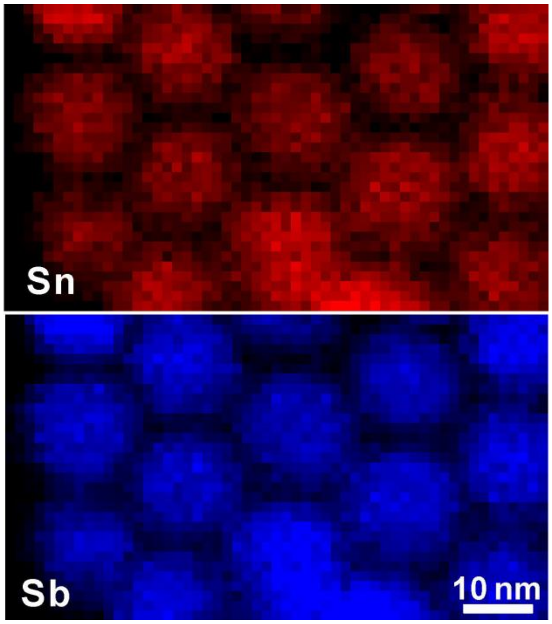

Figure S4. EDX-STEM elemental maps of SnSb NCs.

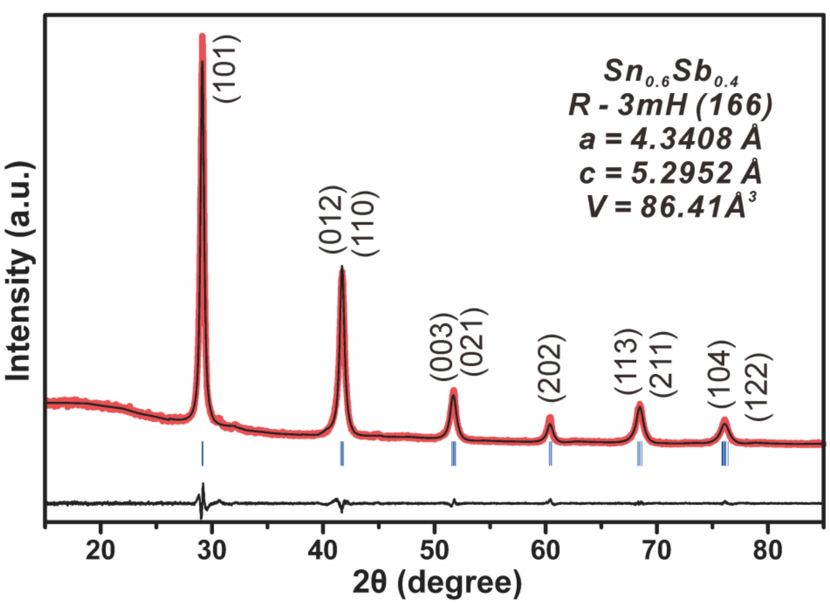

Figure S5. XRD pattern of SnSb NCs along with Rietveld refinement in rhombohedral setting (red curve-experiment; black curve - fit). Expected line-splitting is invisible due to peak broadening caused by the small particle size. Refinement parameters were:

Pattern				Phase	
Chi2	Rp	Rwp	Rexp	Rbragg	RF
2.03	13.5	11.3	7.94	0.881	0.6064

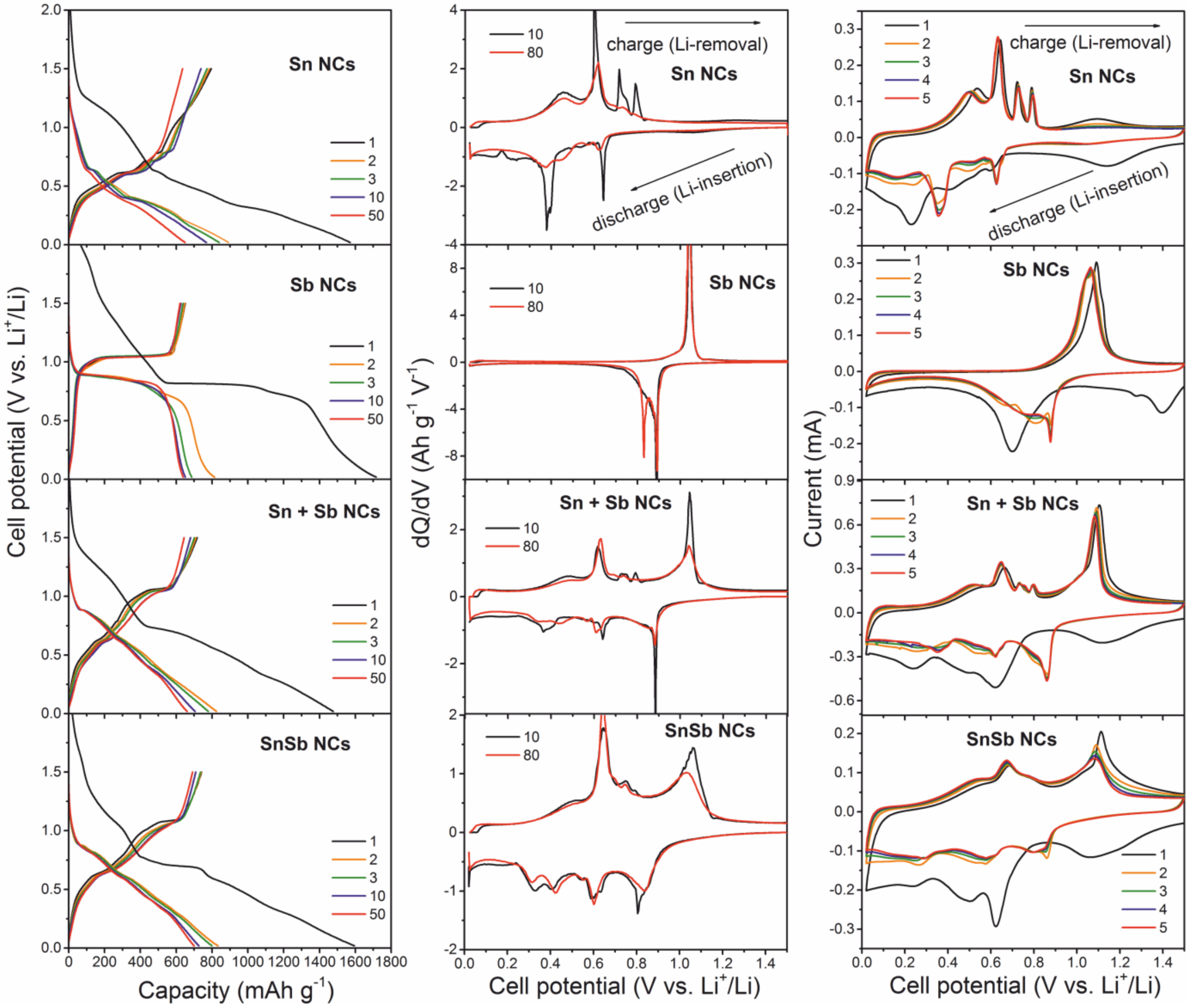

Figure S6. Li-ion half-cells using SnSb, Sb or Sn NCs as anode materials: galvanostatic discharge and charge curves (left panel) and corresponding dQ/dV plots (middle panel). Right panel shows cyclic voltammograms for the initial five charge-discharge cycles (scan rate = 0.1 mV s^{-1}), which are very similar to the early-stage dQ/dV plots.

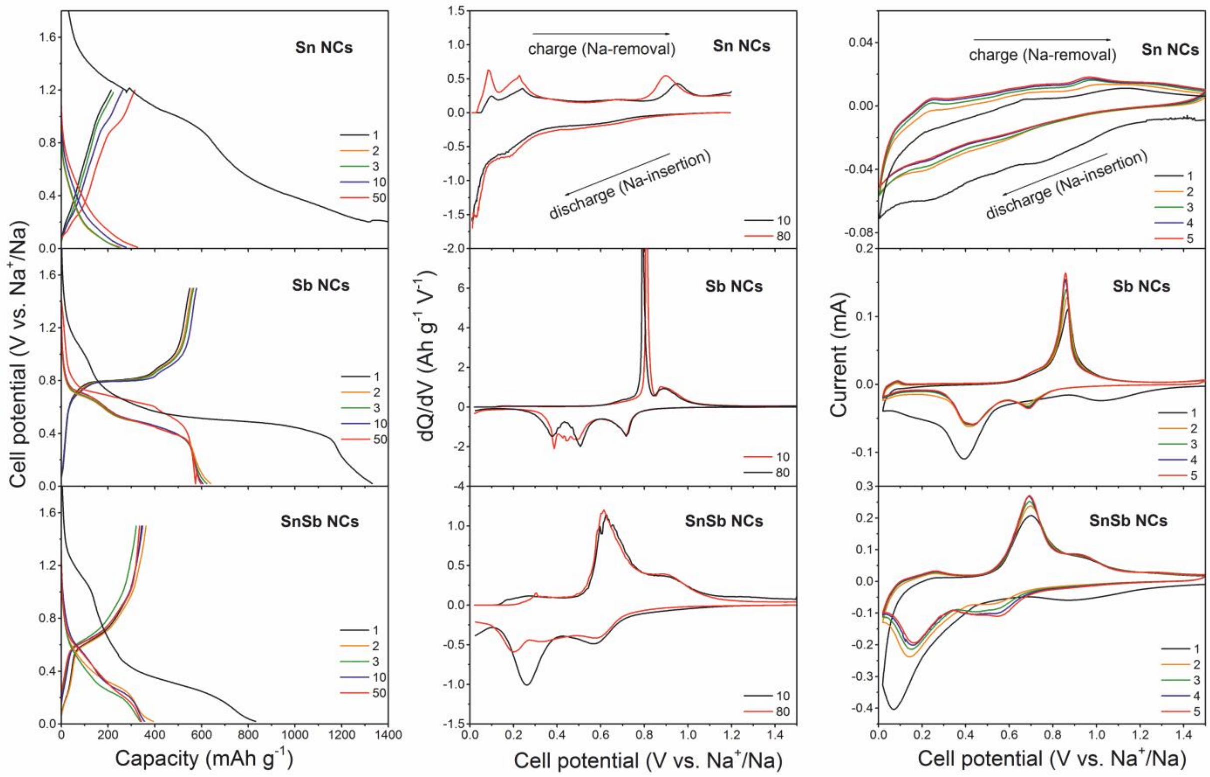

Figure S7. Na-ion half-cells using SnSb, Sb or Sn NCs as anode materials: galvanostatic discharge and charge curves (left panel) and corresponding dQ/dV plots (middle panel). Right panel shows cyclic voltammograms for the initial five charge-discharge cycles (scan rate = 0.1 mV s^{-1}), which are very similar to the early-stage dQ/dV plots.

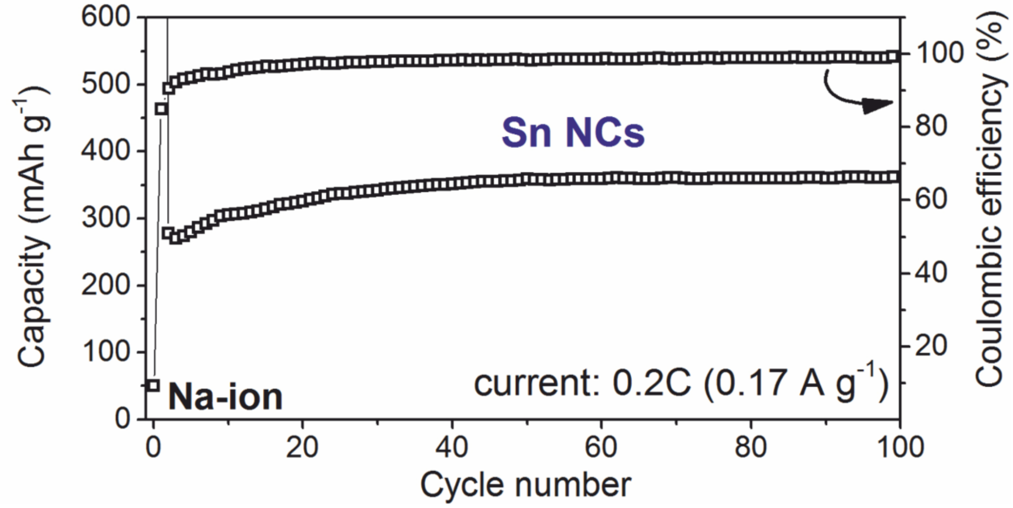

Figure S8. Galvanostatic cycling of a Na-ion half-cell comprising 20 nm Sn NCs as anode material (electrode composition: 30% Sn NCs, 45% CB, 25% CMC; potential window: 0.01-1.2 V).

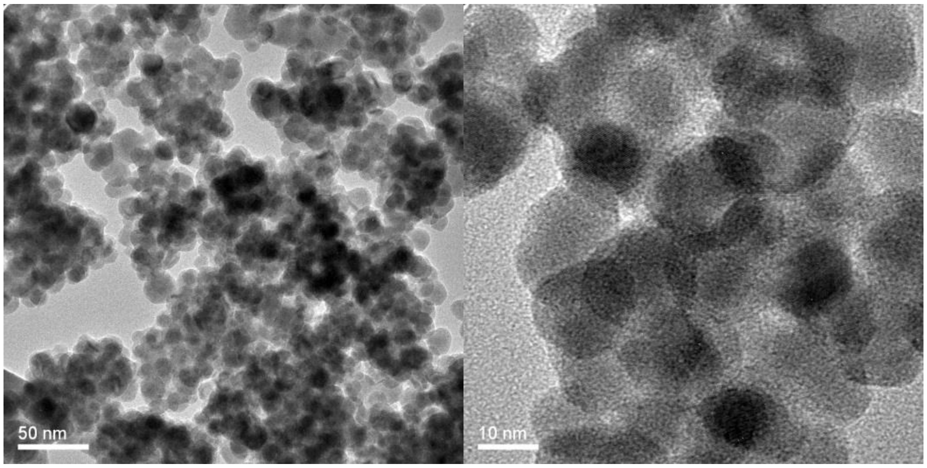

Figure S9. TEM-images of SnSb NCs after ligand removal.

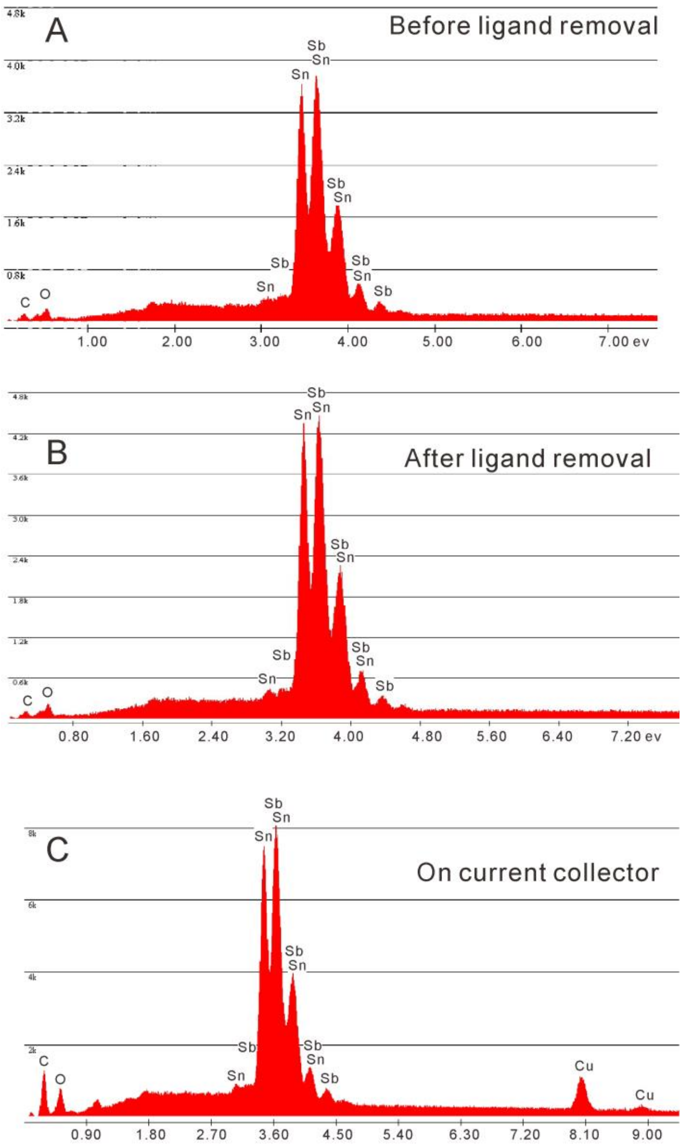

Figure S10. EDX-Spectra of SnSb NCs before (A), after (B) ligand removal and as electrodes with CB and CMC on Cu-current collectors.

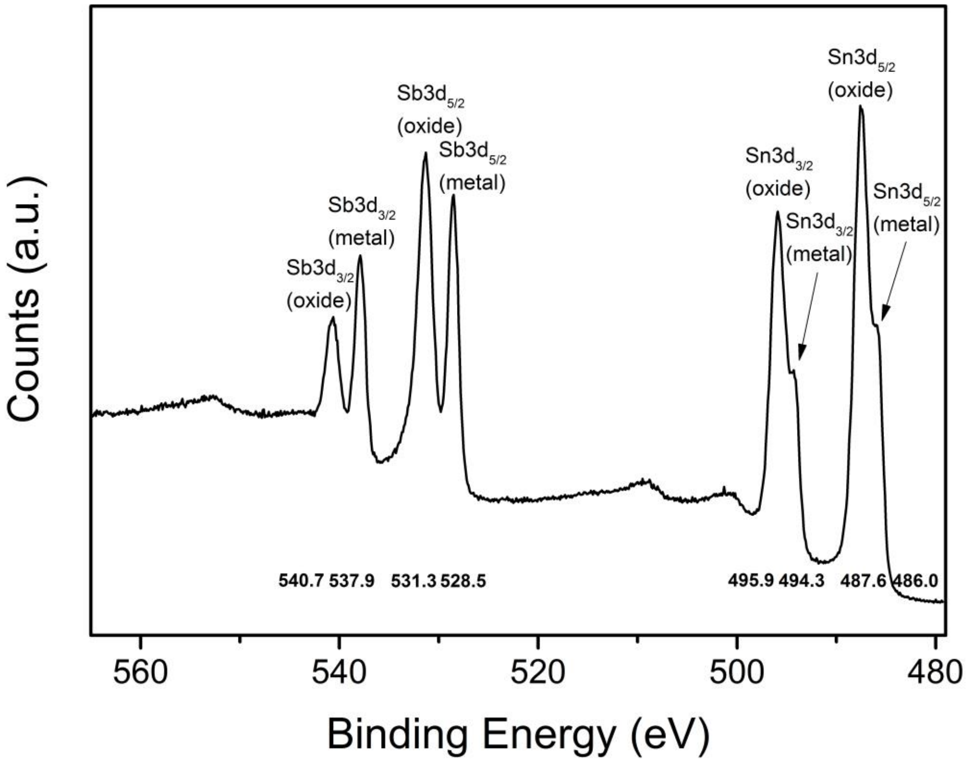

Figure S11. XPS-Spectra of SnSb NCs after ligand removal. Peaks were assigned according to XPS databases (www.lasurface.com/database/elementxps.php; http://srdata.nist.gov/xps/; access date October 2014).