Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information for

Monodisperse $CoSn_2$ and $FeSn_2$ nanocrystals as high-performance anode materials for lithium-ion batteries

Shutao Wang, ‡[a,b] Meng He, ‡[a,b] Marc Walter,[a,b] Frank Krumeich,[a]
Kostiantyn V. Kravchyk,[a,b] and Maksym V. Kovalenko*[a,b]

S. Wang, M. He, M. Walter, Dr. K.V. Kravchyk, Dr. F. Krumeich, Prof. Dr. M. V. Kovalenko
[a] Department of Chemistry and Applied Biosciences
ETH Zürich – Swiss Federal Institute of Technology Zürich
Vladimir Prelog Weg 1, 8093 Zürich (Switzerland)
and
[b] Empa-Swiss Federal Laboratories for Materials Science and Technology
Laboratory for thin films and photovoltaics
Überlandstrasse 129, 8600 Dübendorf, (Switzerland)
‡ These authors contributed equally.
[*] Prof. Dr. Maksym V. Kovalenko
E-mail: mvkovalenko@ethz.ch

Materials and Methods

I. Materials

Chemicals and solvents. Cobalt (II) chloride (99.99%, Aldrich), tin (II) chloride (anhydrous, ABCR), lithium diisopropylamide ($LiN(iPr)_2$, 97%, Sigma-Aldrich), lithium bis(trimethylsilyl)amide ($LiN(SiMe_3)_2$, 97 %, Sigma-Aldrich), oleic acid (OA, 90%, Aldrich), toluene (99.9%, Sigma-Aldrich), ethanol (≥99.9%, Scharlau), hydrazine (Gerling Holz+Co) and acetonitrile (Sigma-Aldrich) were used as received. Oleylamine (OLA, 90%, ACROS) was dried prior to use at 100 °C under vacuum overnight.

Battery components. Carbon black (Super C65, TIMCAL), carboxymethyl cellulose (CMC, Grade: 2200, lot No. B1118282, Daicel Fine Chem Ltd.), 1M solution of $LiPF_6$ in ethylene carbonate/dimethyl carbonate (EC/DMC, Novolyte), 4-fluoro-1,3-dioxolan-2-one (FEC, >98.0%, TCI), Celgard separator (Celgard 2320, 20µm microporous trilayer membrane PP/PE/PP, Celgard Inc. USA).

II. Methods

Synthesis of $CoSn_2$ NCs. In a typical synthesis of *ca*. 10 nm $CoSn_2$ NCs, dried OLA (13 mL) was mixed with $CoCl_2$ (0.033 g, 0.25 mmol) in a 50-mL three neck flask, and then additionally dried under vacuum (45 minutes at 120 ºC), heated to 270ºC under nitrogen, followed by the injection of $LiN(iPr)_2$ solution (3.6 mmol, 0.38 g, in 2 mL of OLA) and, after 30s, 0.5 mmol of $SnCl_2$ (0.095 g, in 3 mL of OLA). The reaction mixture was held for 4 h at this temperature. Finally, the reaction was quickly quenched by the combined effect of the cooling with an ice-water bath together with the injection of anhydrous toluene (12 mL) into a crude solution at around 150 °C. Upon cooling, oleic acid (0.4 mL) was added at around 50 °C. After cooling, $CoSn_2$ NCs were precipitated by adding ethanol (60 mL), followed by centrifugation at 8500 rpm for 4 min. Then $CoSn_2$ NCs were redispersed in toluene (12 mL) containing oleic acid (0.25 mL), and then precipitated by ethanol (12 mL) and centrifuged at 8000 rpm for 1 min. Finally, $CoSn_2$ NCs were dispersed in common nonpolar solvents such as chloroform or toluene and stored in the fridge.

Table S1. Experimental conditions for $CoSn_2$ NCs synthesis.

#	OLA, mL	$CoCl_2$, mmol	T(inj), ℃	$LiN(iPr)_2$, mmol	$SnCl_3$, mmol	Reaction time, h	Mean size, nm	S, %
1	13	0.25	210	3.6	0.5	4	5	9.93
2	13	0.25	270	3.6	0.5	4	13	9.6

Synthesis of $FeSn_2$ NCs. In a typical synthesis of *ca*. 12 nm $FeSn_2$ NCs, dried OLA (12 mL) was mixed with of $FeCl_2$ (0.021 g, 0.167 mmol) in a 50-mL three neck flask, additionally dried under vacuum (45 minutes at 120 ºC), heated to 330 ºC under nitrogen, followed by the injection of $LiN(iPr)_2$ solution (3.6 mmol, 0.38 g, in 2 mL of OLA) and, after 30s, 0.25 mmol of $SnCl_2$ (0.048 g, in 3 mL of OLA). The reaction mixture was held for 15 min at this temperature. Finally, the reaction was quickly quenched by cooling with an ice-water bath together with the injection of anhydrous toluene (12 mL) at around 150 °C. Upon cooling, oleic acid (0.4 mL) was added at around 50°C. After cooling, $FeSn_2$ NCs were precipitated by adding ethanol (~60 mL), followed by centrifugation at 8500 rpm for 4 min. Then $FeSn_2$ NCs were redispersed in toluene (12 mL) containing oleic acid (0.25 mL), and then precipitated by ethanol (12 mL) and centrifuged at 8000 rpm for 1 min. Finally, $FeSn_2$ NCs were dispersed in common nonpolar solvents such as chloroform or toluene and stored in the fridge.

Synthesis of Sn nanoparticles. Sn NCs were synthesized and purified according to the previously published procedure of Kravchyk *et al*. [*J. Am. Chem. Soc.*, 2013, **135**, 4199-4202.].

Ligand removal. In order to remove the organic capping ligands, NCs were precipitated with ethanol, centrifuged and redispersed in a solution of 0.8 mL hydrazine in 25 mL anhydrous acetonitrile. The suspension was stirred at room temperature for 2 h. After centrifugation (8000 rpm, 4 min), the precipitate was washed three times with acetonitrile (20 mL) to remove residual hydrazine. Finally, NCs were separated from the solution by centrifugation (8000 rpm, 4 min) and dried for 12 h at room temperature under vacuum.

Assembly and testing of Li-ion half cells. Electrodes were prepared as follows: the respective NCs after ligand removal, carbon black, and CMC binder were mixed in the weight ratio of

64:21:15 for 1 h by ball-milling with deionized water as solvent. Carbon black (Super C65, TIMCAL) was used as a conductive additive. The slurry was coated onto Cu foil. The current collectors were dried at room temperature for 12 h and then for 12 h under vacuum at 80°C. Coin-type cells were assembled in an argon-filled glove box ($O_2 < 0.1$ ppm, $H_2O < 0.1$ ppm) using one layer of Celgard separator. For assembling Li-ion batteries, a Li foil was used as the counter and reference electrode. A solution of 1 M $LiPF_6$ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 in volume) was used as electrolyte. To improve cycling stability 3% of FEC were added to electrolyte. The charge/discharge cycling measurements were performed by a Lanhe (Wuhan, China) battery tester with the potential range 0.005-2.0V vs. Li^+/Li. The loading of active materials was ~ 0.5 mg cm^{-2}. The obtained capacities were normalized to the mass of NCs.

III. Characterization

Material characterization. Transmission Electron Microscopy (TEM) images were obtained using a Philips CM30 TEM microscope at 300 kV. High resolution TEM images were measured on a JEOL 2200FS at 200 kV. Carbon-coated TEM grids (Ted-Pella) were used as substrates. Average size and size distribution (%, FWHM of the Gaussian fit to size-histogram) are obtained from TEM images by counting at least 100 NCs using Nano Measurer software (http://nano-measurer.software.informer.com). Powder X-ray diffraction (XRD) was measured on a STOE STADI P powder X-ray diffractometer. EDX elemental analysis was performed using Hitachi S-4800 SEM microscope.

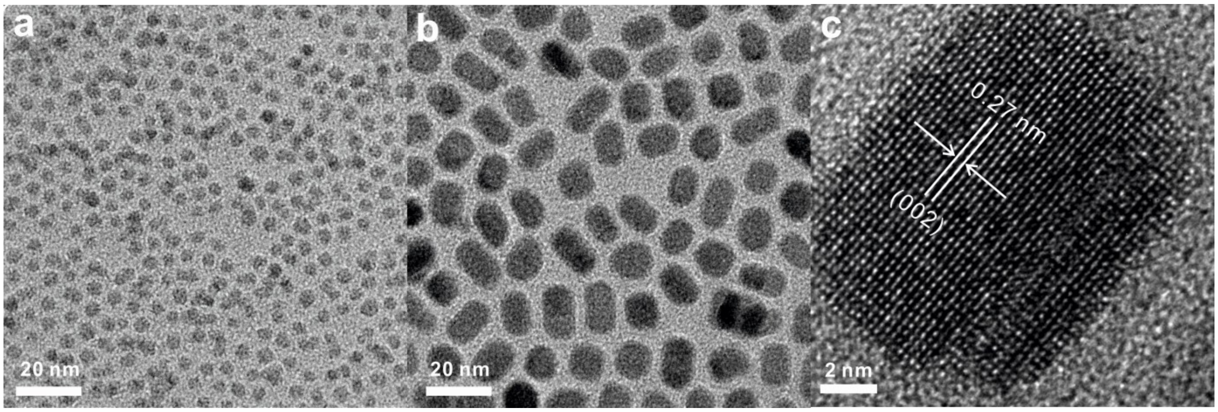

Figure S1. TEM images (a) 5 nm and (b) 13 nm $CoSn_2$ NCs. HR-TEM image of 13 nm $CoSn_2$ NCs.

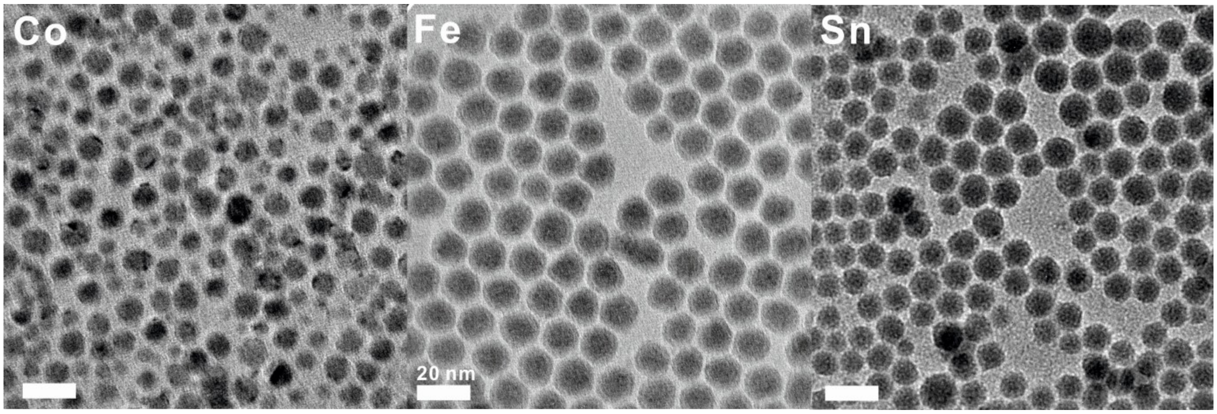

Figure S2. TEM images of Co, Fe and Sn NCs.

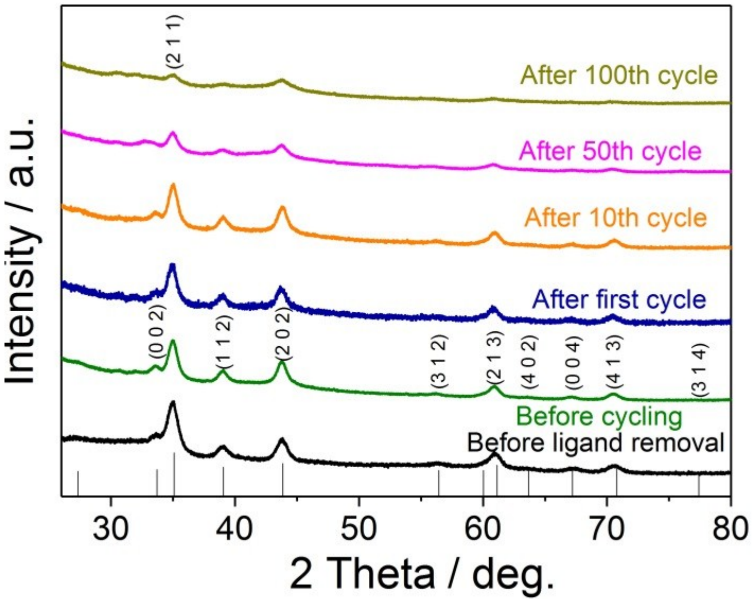

Figure S3. Ex-*situ* XRD patterns of $FeSn_2$ NCs before and after (charged $FeSn_2$ NCs) electrochemical cycling.

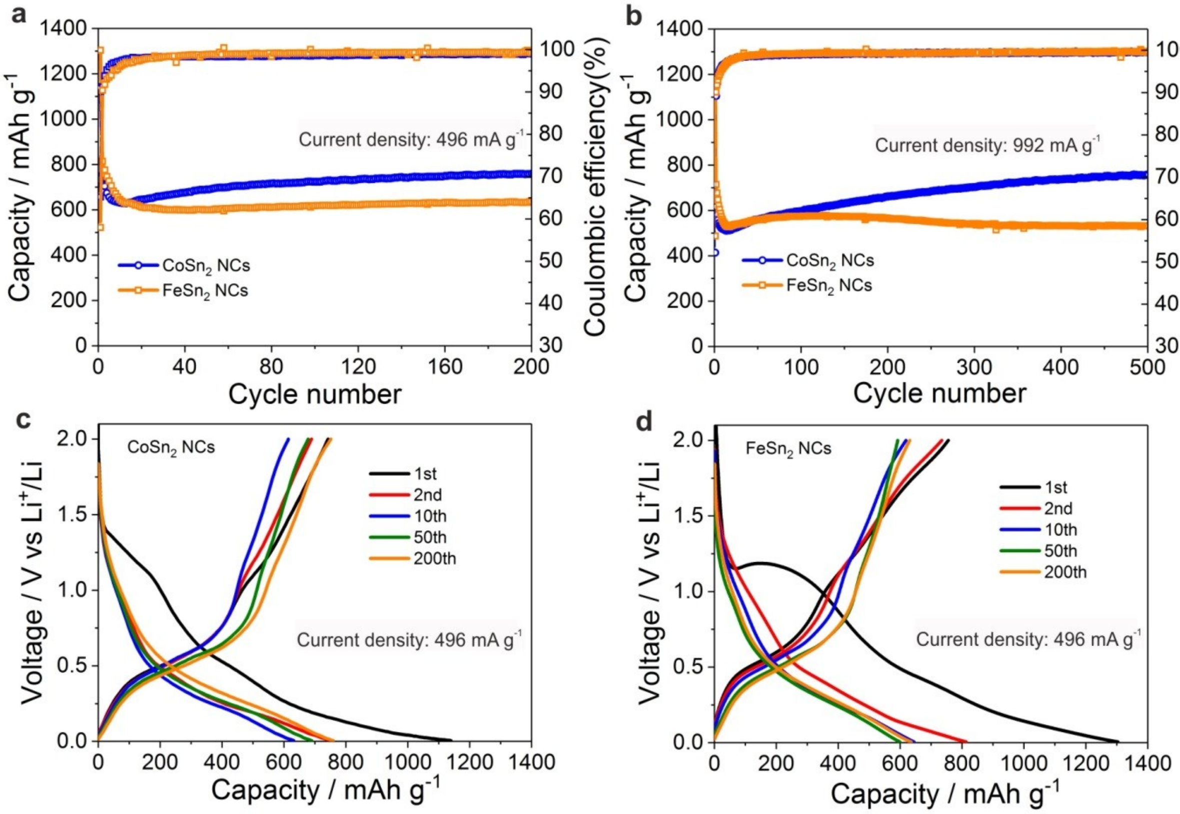

Figure S4. (a, b) Comparison of the cycling stability of Li-ion anodes composed of $CoSn_2$ and $FeSn_2$ NCs in Li-ion half-cells at current densities of 496 mA g^{-1} and 992 mA g^{-1}. (c, d) Galvanostatic discharge/charge voltage curves of $CoSn_2$ and $FeSn_2$ NCs measured at current density of 496 mA g^{-1}. All cells were cycled at room temperature in the potential range 0.005–2.0 V *vs*. Li$^+$/Li.

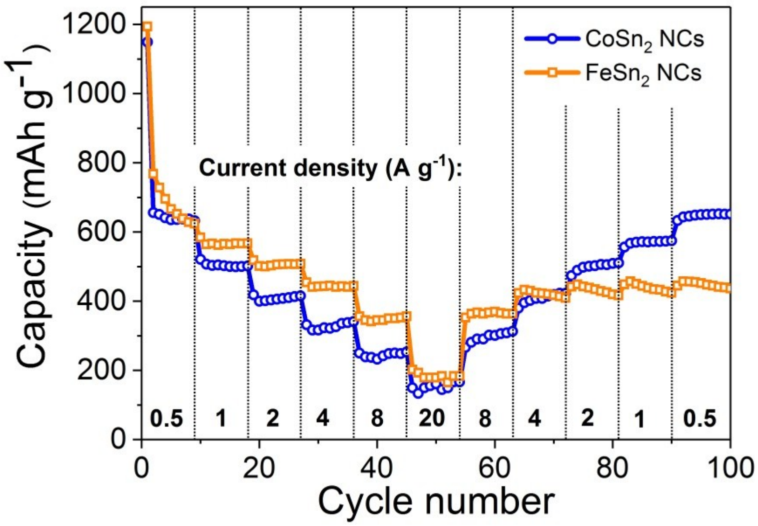

Figure S5. Rate capability tests of Li-ion anodes composed of CoSn$_2$ and FeSn$_2$ NCs at current density of 0.5-20 A g^{-1}.