

Supporting information for

**Monodisperse and inorganically capped Sn and
Sn/SnO₂ nanocrystals for high performance Li-ion
battery anodes**

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Complete references 7, 10, 13 and 16 of the Main Text with full author list:

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Materials and Methods

I. Materials

Chemicals and solvents. Lithium bis(trimethylsilyl)amide ($\text{LiN}(\text{SiMe}_3)_2$, 97 %, Aldrich), Sodium bis(trimethylsilyl)amide ($\text{NaN}(\text{SiMe}_3)_2$, 95%, Aldrich), potassium bis(trimethylsilyl)amide ($\text{KN}(\text{SiMe}_3)_2$, 95%, Aldrich), lithium hydride (LiH , 95%, Aldrich), oleic acid (OA, 90%, Aldrich), Tin (II) chloride (SnCl_2 , anhydrous, 98%, ABCR), Tin (II) trifluoromethanesulfonate ($\text{Sn}(\text{CF}_3\text{SO}_3)_2$, 97%, Aldrich), Tin acetate ($\text{Sn}(\text{Ac})_2$, Aldrich), Bis[bis(trimethylsilyl)amino]tin(II) ($\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$, 95%, Aldrich), tetrachloroethylene (TCE, $\geq 99\%$, Aldrich), octadecene (ODE, 90%, Aldrich), lithium triethylborohydride (also known as superhydride, $\text{Li}(\text{Et}_3\text{BH})$, 1.0 M solution in THF, Aldrich), diisobutylaluminum hydride ($(i\text{-Bu}_2\text{AlH})_2$, 1.0 M solution in THF, Aldrich), boran-tert-butylamine complex ($(\text{CH}_3)_3\text{CNH}_2 \cdot \text{BH}_3$, 97%, Aldrich), formamide (FA, $\geq 99\%$, Aldrich), acetonitrile ($\geq 99\%$, Aldrich), oleylamine (OLA, techn., TCI), potassium sulfide (anhydrous, 95%, STREM) and potassium hydrosulfide (anhydrous, 94%, STREM) were used as received.

Battery components: Carbon black (Super C65, provided by TIMCAL), 1 M 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, 20 μm microporous trilayer membrane (PP/PE/PP), Celgard Inc. USA) and glass-fiber separator (EUJ-grade, Hollingsworth & Vose Company Ltd., United Kingdom), Carboxymethyl cellulose (CMC, Grade: 2200, Lot No. B1118282, Daicel Fine Chem Ltd).

II. Methods

Synthesis of Tin nanoparticles. In a typical synthesis of 16 nm Sn NCs, oleylamine (OLA, 20g) was loaded into the three-neck flask and dried under vacuum at 140°C for 1.5h under constant stirring. After cooling of oleylamine down to 50°C , the flask was briefly opened to add anhydrous SnCl_2 and again dried under vacuum at 140°C for 30min. In parallel, $\text{LiN}(\text{SiMe}_3)_2$ (3.6mmol, 0.601g) was solved in 2ml toluene in glovebox. Then the temperature of SnCl_2 /OLA mixture was increased to 180°C under argon, followed by the injection of $\text{LiN}(\text{SiMe}_3)_2$ /toluene solution, and, in 10s, 0.6 mL of 1M DIBAH solution in THF. The solution immediately turned dark brown upon injection of DIBAH. In 1 hour, the reaction solution was quickly cooled to room

temperature using ice-water bath. Upon cooling, at about 120-150°C, 10 ml of anhydrous toluene were injected into the reaction flask. After cooling, Sn NCs were precipitated by adding 40 ml of ethanol following by their centrifugation at 8000rpm for 4min. The Sn NCs were redispersed in tetrachloroethylene (TCE) solution of oleic acid (~6 mL, 1ml OA/50ml TCE) to replace the weakly bound OLA molecules. Finally, the Sn NCs were precipitated second time by 10 ml of ethanol, centrifuged and redispersed in common nonpolar solvents such as TCE, chloroform or toluene forming long-term stable solutions. The synthesis parameters for several NC sizes are summarized in Table S1.

Further remarks on the synthesis. (i) Sn NCs of similar quality can be obtained using superhydride or borane tert-butylamine complex as reducing agent (Figure S2). (ii) For $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ as a precursor, 0.5 mmol of this compound in 1ml ODE (dried) was injected into the reaction flask just prior to the addition of $\text{LiN}(\text{SiMe}_3)_2$. (iii) The optimal balance between the quality and reaction yield can be obtained in the temperature range of 180-210°C. For a given temperature, the optimal growth time may vary for various commercial batches of oleylamine and can be determined by taking aliquots (Figure S10).

Table S1. Experimental conditions in the synthesis of Sn NCs (corresponding to Figure 1 of the Main text).

#	Mean size, nm	σ , %	T(inj), °C	OLA, g	SnCl_2 , mmol	LiNTMS , mmol	DIBAH, mmol	Reaction time
1	9	8.3	180	20	0.5	3.6	0.6	10 sec
2	12	5.0	210	20	0.5	3.6	0.6	10 sec
3	16	7.7	180	20	0.5	3.6	0.6	1-4h
4	23	7.6	210	20	0.5	3.6	0.6	$\geq 6\text{h}$

Ligand exchange with K_2S or KHS. For a typical ligand exchange using S^{2-} or HS^- ions, 1mL of Sn NCs in TCE (~5 mg/mL) was mixed with 1mL of K_2S or KHS solution in FA (~5 mg/mL). The mixture was stirred for about 1h to allow complete phase transfer of Sn NCs from TCE to the FA phase. The FA phase was separated and triply washed with toluene. Then, Sn NCs were precipitated by adding ~1 mL of acetonitrile, followed by centrifuging. Finally, NCs were re-dispersed in DI water.

III. Characterization

Transmission Electron Microscopy (TEM) images data were obtained using Philips CM30 TEM microscope operated at 300 kV. Carbon-coated TEM grids from Ted-Pella were used as substrates. Mean size and size distribution of NCs was determined by PEBBLES free software (<http://pebbles.istm.cnr.it/>) in automatic mode for at least 100 NCs per each sample.¹ Size deviations of NCs were calculated via formula (1) using Gaussian fit of measured size histograms:

$$S = \frac{FWHM}{2d} * 100\% \quad (1)$$

where FWHM is fullwidth at half maximum of the Gaussian fit; d is diameter of NCs at maximum of the Gaussian fit.

Scanning transmission electron microscopy (STEM) investigations were performed on the aberration-corrected HD-2700CS (Hitachi; cold-field emitter), operated at an acceleration potential of 200 kV. A probe corrector (CEOS) is incorporated in the microscope column between the condenser lens and the probe-forming objective lens providing excellent high-resolution capability (beam diameter ca. 0.1 nm in ultra-high resolution mode). Different detectors can be chosen for imaging in bright field (BF) and high-angle annular dark field (HAADF) modes.

Powder X-ray diffraction patterns were collected with STOE STADI P powder diffractometer, operating in transmission mode. Germanium monochromator, Cu K α 1 irradiation, and silicon strip detector Dectris Mythen were used.

Solution phase ^{119}Sn NMR spectra were recorded at 186.5 MHz using Bruker 500 Spectrometer. Spectra were obtained at room temperature or 35° C without locking. The pulse width was set at 10 μs and the relaxation delay was 0.5 s. The number of scans was 60000. The NMR samples were prepared in 5 mm tube in glovebox using dried solvents (0.05M [Sn]). All spectra were referenced to $\text{Sn}(\text{CH}_3)_4$.

The Magic Angle Spinning (MAS) ^{119}Sn NMR experiments were performed on Bruker AMX400 Spectrometer at 300 K using a 2.5 mm zirconia rotors and a spinning speed of 20 kHz. The spectral frequency was set at 149.25 MHz, and a 90° pulse length of 0.3 μs was used. The relaxation delay was 2 s and the number of scans was 40000. All spectra were referenced to $\text{Sn}(\text{CH}_3)_4$.

Dynamic light scattering (DLS) and ζ -potential data were obtained using a Zetasizer Nano-ZS (Malvern Instruments, U.K.). ζ -potential was calculated from the electrophoretic mobility using Henry's equation in the Smoluchowski limit.

Attenuated total reflectance (ATR) FTIR spectra were recorded using Thermo Scientific Nicolet iS5 FTI-IR spectrometer. Samples were deposited onto Si substrates, turned upside down and pressed against diamond ATR crystal. Liquid samples were measured by placing a small droplet directly onto ATR crystal.

Preparation of Sn-based anodes and electrochemical testing. In a typical electrode preparation, Carbon black was stirred for 10 min with 0.2wt% aqueous solution of CMC. The resulting suspension was ball-milled for 1.5h and mixed with appropriate amount of the freshly prepared aqueous dispersion of Sn/SnO_2 NCs with known concentration. Obtained homogeneous suspension was drop-cast and dried on Ti current collector (13 mm diameter) to provide coverage of approximately 3mg/cm². All electrochemical measurements were conducted in homemade, reusable and air-tight coin-type cells. Test cells were assembled in an Argon-filled glovebox with water and oxygen content below 1 ppm. Lithium metal served as both reference and counter electrode. An active electrode was covered with Celgard separator membrane and a glass fiber separator of 1mm thickness was placed between working and reference electrode. As an electrolyte, mixture of ethylene carbonate and dimethyl carbonate 1: 1 (w/w), with 1M LiPF_6 was used. Optionally, 3% fluoroethylene carbonate (FEC) was added to improve cycling stability. All

charge-discharge galvanostatic tests and cyclic voltammetry scans were conducted on MPG2 multi-channel workstation (Bio Logic).

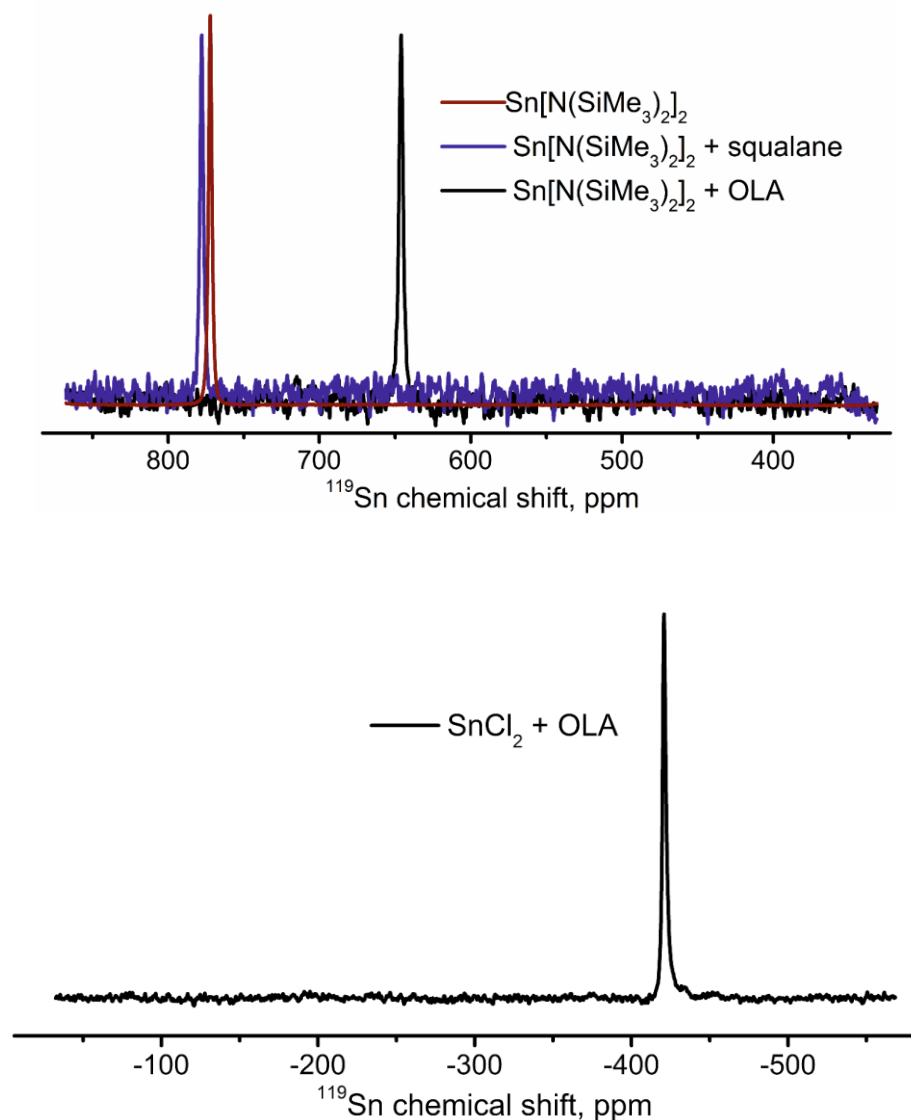


Figure S1. (top panel) In order to test whether $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ is an actual precursor, its ^{119}Sn NMR spectra were recorded at room temperature in a pure, liquid state ($\delta(^{119}\text{Sn})=772\text{ppm}$, red curve), in its solution in non-coordinating solvent such as squalane (blue curve), where it remains intact and only slight solvent effect is observed ($\delta(^{119}\text{Sn})=779\text{ppm}$), and in strongly-coordinating solvent oleylamine (OLA, black curve), where it is assumed to be additionally coordinated with neutral OLA molecules ($\delta(^{119}\text{Sn})=646\text{ppm}$). **(bottom panel)** ^{119}Sn NMR spectrum of SnCl_2 in OLA ($\delta(^{119}\text{Sn})= -420\text{ppm}$) is also different from that of $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2/\text{OLA}$ solutions. However, they both convert into same Tin-oleylamido species ($\delta(^{119}\text{Sn})= 62.5\text{ppm}$) upon the addition of Lithium silylamide or Lithium dimehtylamide. Note: spectra of all samples (Figures 2 and S1) exhibited only one type of species in their NMR spectra.

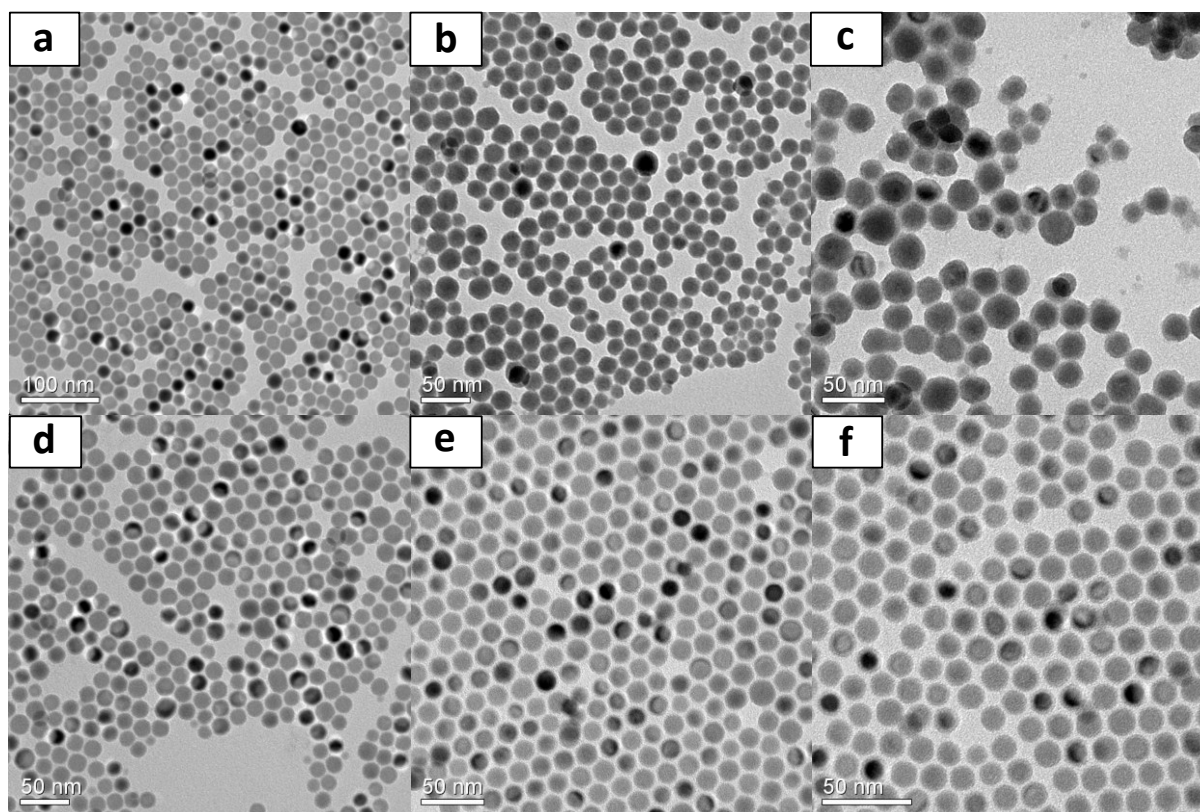


Figure S2. TEM images of Sn NCs synthesized from SnCl_2 and DIBAH in combination with various bases (A - LiNMe_2 , B - $\text{NaN}(\text{SiMe}_3)_2$, C - $\text{KN}(\text{SiMe}_3)_2$, D - LiH); and from SnCl_2 and $\text{LiN}(\text{SiMe}_3)_2$ by varying reducing agent: (E) superhydride (LiEt_3BH) and (F) boran-tert-butylamine complex ($((\text{CH}_3)_3\text{CNH}_2 \cdot \text{BH}_3)$).

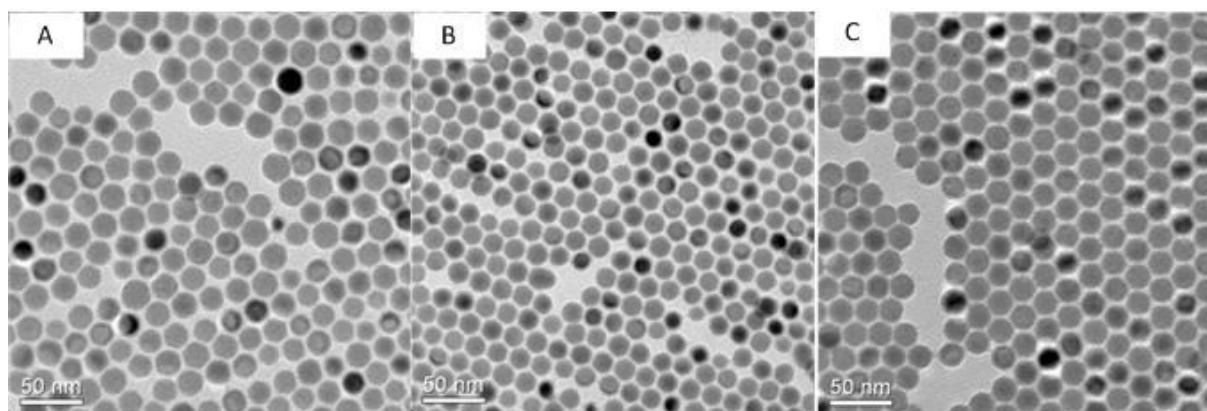


Figure S3. TEM images for Sn NCs synthesized from $\text{LiN}(\text{SiMe}_3)_2$ and DIBAH, combined with various Tin(II) precursors: (A) $\text{Sn}(\text{Ac})_2$, (B) $\text{Sn}(\text{CF}_3\text{SO}_3)_2$ and (C) $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$.

Synthesis without LiNTMS

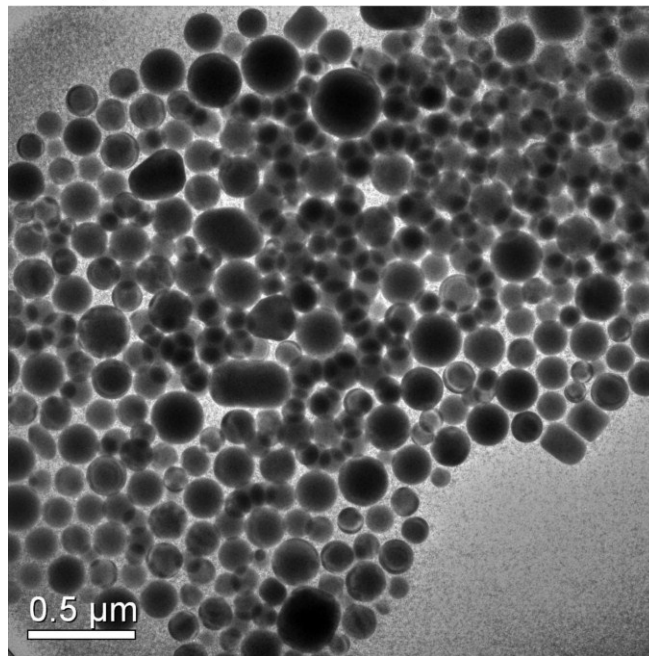


Figure S4. TEM image of Sn precipitate collected after direct injection of DIBAH into SnCl_2/OLA solution, without $\text{LiN}(\text{SiMe}_3)_2$.

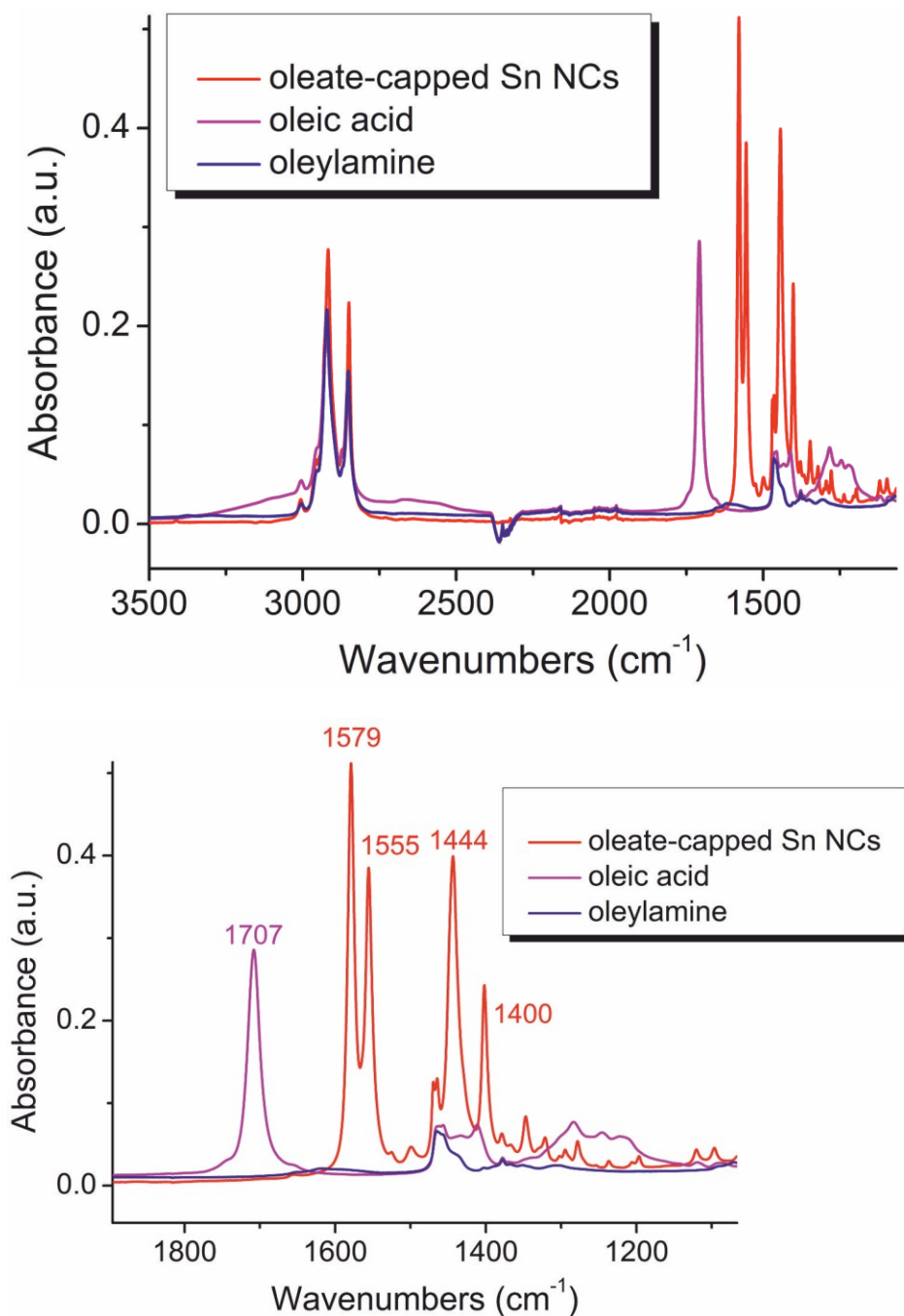


Figure S5. ATR-FTIR spectra of oleate-capped Sn NCs before ligand exchange (red curve) and reference oleic acid and oleylamine. The peak at 1707 cm^{-1} is attributed to C=O band of protonated oleic acid, and is absent in their surface-bound oleate. Peaks at 1579, 1555, 1444 and 1400 cm^{-1} originate from $\nu(\text{COO}^-)$ vibrations in anionic carboxylate.

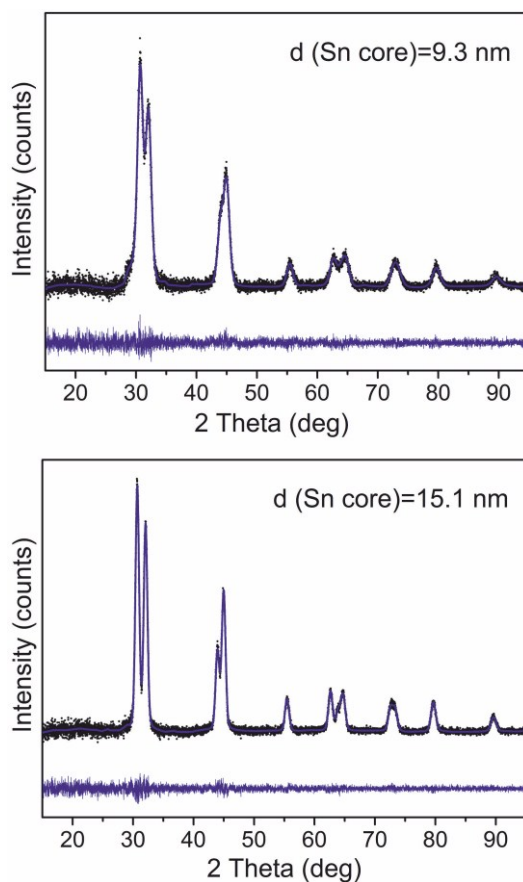


Figure S6. XRD spectra of Sn NCs showing finite size broadening. Crystallite size is calculated from the formula:

$$D(\text{\AA}) = \frac{180K\lambda(\text{\AA})}{\pi\sqrt{I_g}}$$

where I_g is refined parameter, which accounts for the isotropic peak broadening due to domain size and K is shape factor. Blue line is a fitted profile using Rietveld refinement along with difference plot (bottom blue line). Rietveld refinement was carried out using FullProf Suite (<http://www.ill.eu/sites/fullprof>).

Sample	Pattern				Phase	
	Chi2	Rp	Rwp	Rexp	Rbragg	RF
Sn (9.3 nm)	0.932	19.6	13.0	13.47	1.003	0.7828
Sn (15.1 nm)	0.917	22.6	16.0	16.66	0.7752	0.7444

The Chi2 factor was less than 1 in all cases, which shows that the correct model of a NC is selected, including all refined parameters. Pattern R-factors are somewhat high due to background from amorphous SnO₂, while R-factors for the Sn phase are low in agreement with its high crystallinity.

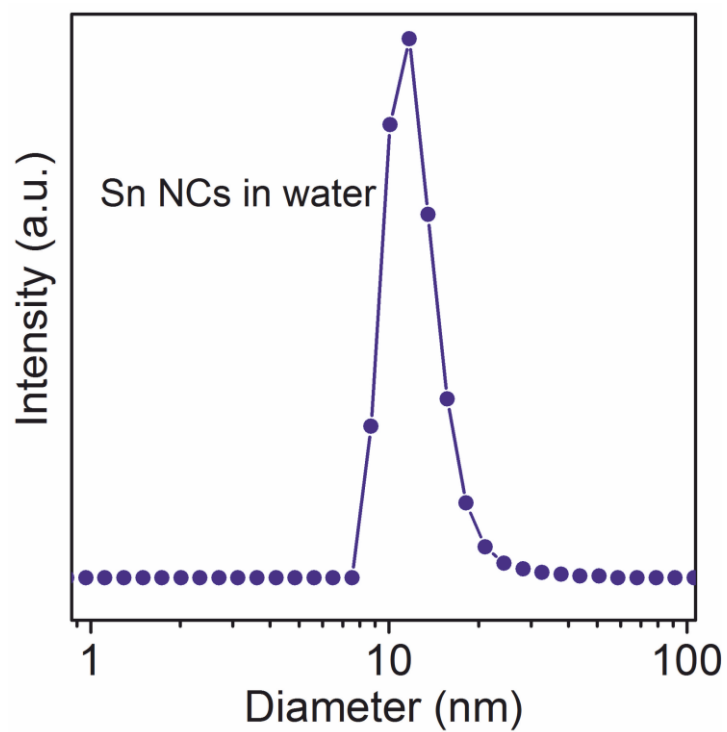


Figure S7. Distribution of scattering intensity vs. hydrodynamic diameter obtained by dynamic light scattering for inorganically-functionalized Sn/SnO₂ NCs in aqueous solution.

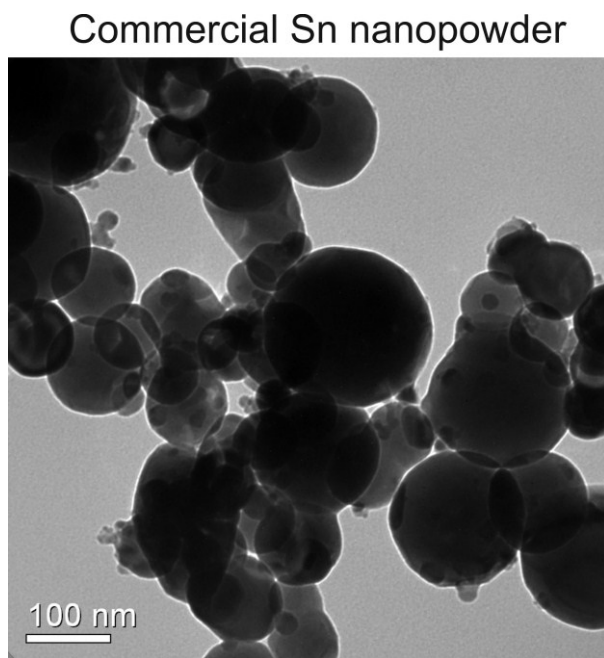


Figure S8. TEM image of commercial Sn nanopowder (Aldrich).

Commercial SnO₂ nanopowder

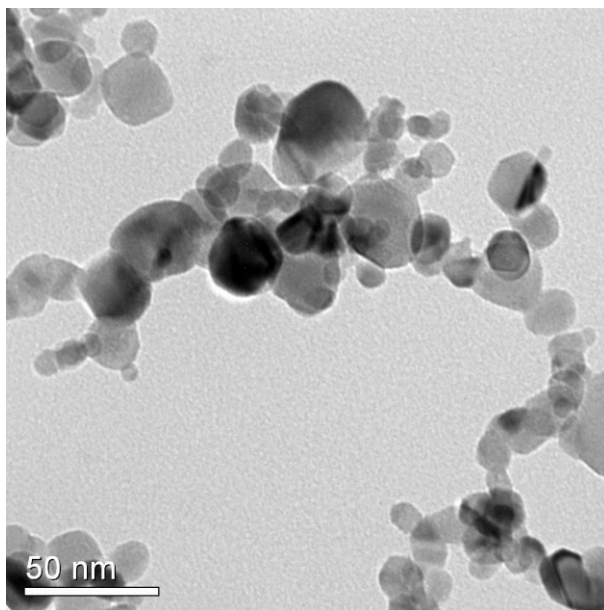


Figure S9. TEM image of commercial SnO₂ nanopowder (Aldrich).

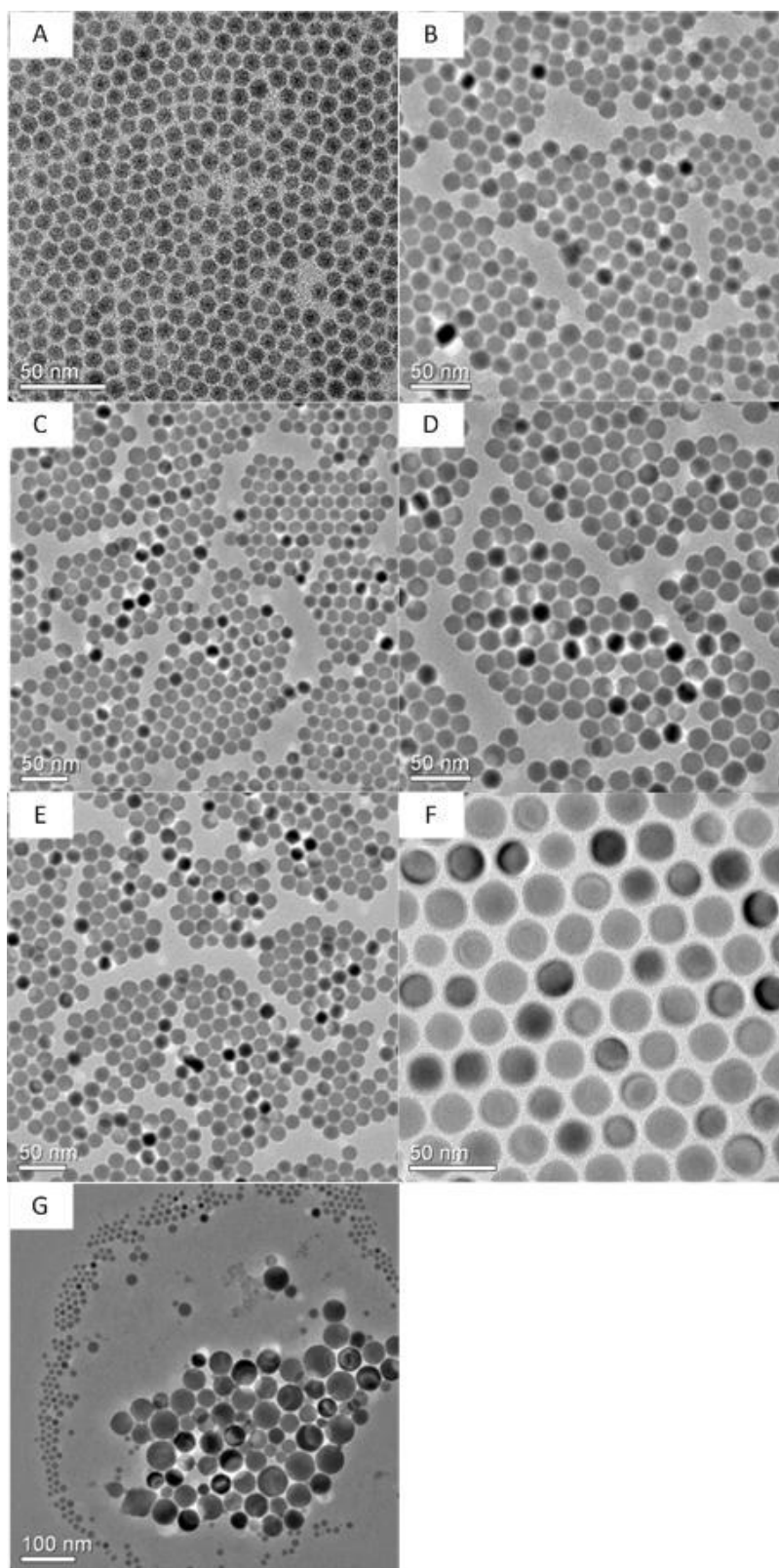


Figure S10. TEM images for Sn NCs synthesized at $T=180^{\circ}\text{C}$ at different reaction times: (A) 10 sec; (B) 1 min; (C) 5min; (D) 1h; (E) 6h; Images (F) and (G) correspond to the sample obtained at $T=210$ and $T=230^{\circ}\text{C}$ using reaction time of $\sim 6\text{h}$.

SUPPORTING REFERENCES

- (1) Mondini, S.; Ferretti, A. M.; Puglisi, A.; Ponti, A. *Nanoscale* **2012**, *4*, 5356.