Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information for

Monodisperse CoSb Nanocrystals as High Performance Anode Material for Li-Ion Batteries

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Materials and Methods

I. Materials

Chemicals and solvents. Cobalt (II) chloride (99.99%, Aldrich), antimony (III) chloride ($SbCl_3$, 99.999%, ABCR), lithium diisopropylamide ($LiN(iPr)_2$, 97%, Sigma-Aldrich), 1-methyl-2-pyrrolidinone (Fisher BioReagents, anhydrous, 99.5%), sodium borohydride (ABCR-Chemicals, 98%), oleylamine (OLA, 90%, ACROS), oleic acid (OA, 90%, Aldrich), toluene (99.9%, Sigma-Aldrich), ethanol (≥ 99.9%, Scharlau), Hydrazine (Gerling Holz+Co) were used as received. Hydrazine (Gerling Holz+Co) and acetonitrile (ACN, Sigma-Aldrich) were used as received. OLA was dried prior to use at 100 °C under vacuum overnight.

Battery materials/components. Carboxymethyl cellulose (CMC, Daicel Fine Chem Ltd.), carbon black (Super C65, TIMCAL), 4-fluoro-1, 3-dioxolan-2-one (FEC, >98.0%, TCI), 1 M solution of $LiPF_6$ in ethylene carbonate/dimethyl carbonate (EC/DMC, Novolyte), a glass microfiber separator (GF/D, Cat No.1823-257, Whatman), coin-type cells (Hohsen Corp., Japan).

II. Methods

Synthesis of CoSb NCs. In a typical synthesis of 10 nm CoSb NCs, dried OLA (12 mL) was mixed with $CoCl_2$ (0.065 g, 0.5 mmol) in a 50-mL three-neck flask, additionally dried under vacuum for 45 minutes at 120ºC and then heated to 270ºC under nitrogen atmosphere. Afterward, $LiN(iPr)_2$ solution (3.6mmol, *i.e.* ~0.38 g, in 2 mL of OLA) was injected in the reaction mixture, followed by the injection of 0.5 mmol of $SbCl_3$ solution (~ 0.114 g, in 0.2 mL of toluene and 0.8 mL of ODE) in 30 seconds. The reaction mixture was kept for 15 h at 270ºC and then quenched quickly by cooling with an ice-water bath, followed by the injection of anhydrous toluene (12 mL) at *ca.* 150°C. Upon cooling, ~ 0.4 mL of oleic acid was added to the flask at *ca.* 50°C. Afterward, CoSb NCs were precipitated by adding ethanol (~ 60 mL), followed by centrifugation at 8500 rpm for 4 min. Then, CoSb NCs were redispersed in toluene (12 mL) comprising oleic acid (~0.25 mL), and subsequently precipitated by ethanol (12 mL) and centrifuged at 8000 rpm for 1 min. Finally, CoSb NCs were dispersed in common nonpolar solvents such as toluene or chloroform.

Synthesis of $CoSb_2$ NCs. $CoSb_2$ NCs were synthesized and purified according to the procedure developed for CoSb NCs, by doubling the molar amount of $SbCl_3$ to $CoCl_2$ (see **Table S2** for detailed experimental conditions).

Ligand Removal. NCs were precipitated with ethanaol, centrifuged at 8000 rpm for 4 min and redispersed in a acetonitrile/hydrazine solution (31.25:1 vol. ratio). Afterward, NCs/acetonitrile/hydrazine suspension was stirred for 2h at room temperature. Then, NCs were centrifuged at 8000 rpm for 4 min and washed three times with acetonitrile (~20 mL) to remove residual hydrazine. Lastly, NCs were separated from the solution by centrifugation (8000 rpm, 4 min) and dried under vacuum for 12h at room temperature.

Assembly of Li-ion batteries and their electrochemical testing. Electrodes composed of CoSb, $CoSb_2$ or Sb NCs were prepared as follows: the respective NCs after ligand removal were mixed with carbon black and CMC binder in the weight ratio of 64:21:15 for 1h by ball-milling using deionized water as a solvent. Obtained slurry was brush-painted on the Cu foil. The prepared electrodes were dried for 12h at room temperature in the ambient atmosphere and then for 2h under vacuum at 80°C. Electrode active material loadings were in the range of 0.5–0.6 mg cm^{-2} that corresponds to the areal capacity of *ca*. 0.3 mAh cm^{-2}. The thickness of prepared electrodes was *ca*. 20-25 μm. Coin-type cells (Hohsen Corp.) were assembled in an argon-filled glove box ($O_2 < 0.1$ ppm, $H_2O < 0.1$ ppm) using one layer of glass fiber separator. Li disc was used as the counter and reference electrode. 1 M $LiPF_6$ solution in EC/DMC (1:1 in volume) + 3 wt. % of FEC was used as an electrolyte (200 μL per cell). The galvanostatic cycling measurements were performed by a Lanhe (Wuhan, China) battery test system using voltage window of 0.02-1.5V *vs*. Li^+/Li. The obtained charge storage capacities of were normalized to their mass of NCs. Cyclic voltammetry was carried out using a MPG2 multi-channel workstation (Bio Logic).

III. Characterization

Material characterization. Transmission Electron Microscopy (TEM) images were collected using a Philips CM30 TEM microscope at 300 kV. Carbon-coated TEM grids (Ted-Pella) were used as substrates. Powder X-ray diffraction (XRD) was performed on a STOE STADI P powder X-ray diffractometer.

Table S1. Experimental conditions for CoSb NCs synthesis.

#	OLA, mL	$CoCl_2$, mmol	T(inj), ℃	$LiN(iPr)_2$, mmol	$SbCl_3$, mmol	Reaction time,	Mean size, nm	S, %
1	10	0.5	210	3.6	0.5	12 h	4.44	12.16
2	12	0.5	270	3.6	0.5	15 h	9.73	21.27
3	36	1.5	270	10.8	1.5	16 h	16.85	19.28
4	60	5	270	18	5	20 h	44.47	20.73

Table S2. Experimental conditions for $CoSb_2$ NCs synthesis.

#	OLA, mL	$CoCl_2$, mmol	T(inj), ℃	$LiN(iPr)_2$, mmol	$SbCl_3$, mmol	Reaction time,	Mean size, nm	S, %
1	12	0.25	240	3.6	0.5	40 min	4.63	20.1
2	12	0.25	300	3.6	0.5	1 h	9.4	19.1
3	50	1	270	14.4	2	20 h	15.02	15.3

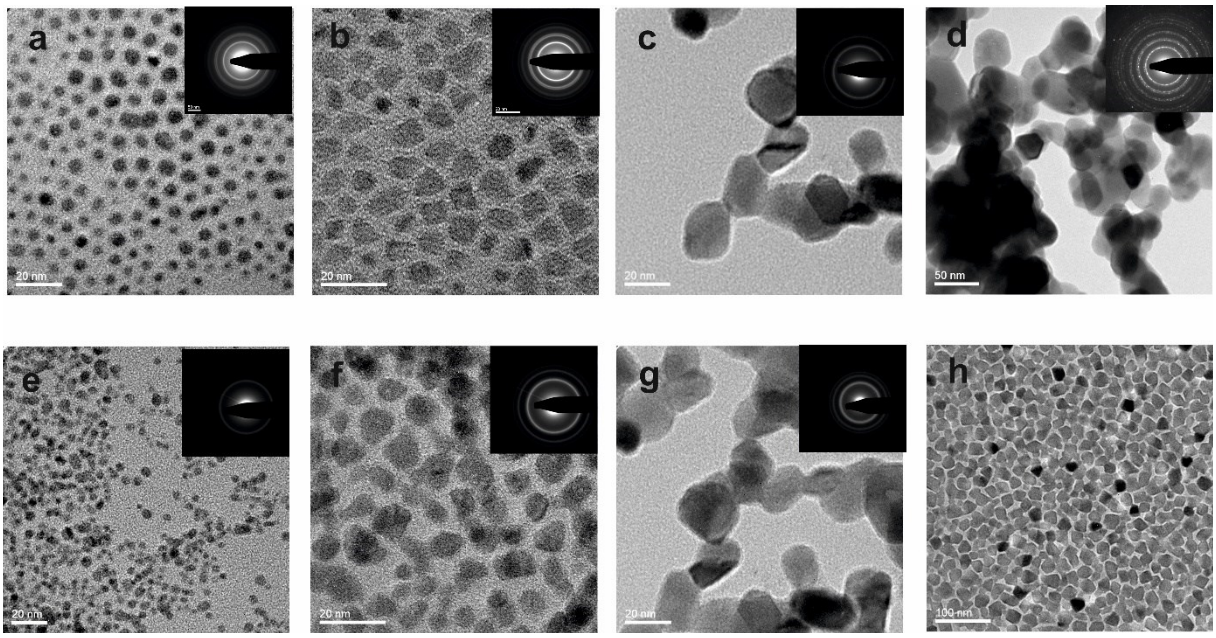

Figure S1. TEM images and corresponding selected area electron diffraction patterns of (a) *ca*. 5 nm CoSb NCs, (b) *ca.* 10 nm CoSb NCs, (c) *ca*. 20 nm CoSb NCs, (d) *ca*. 40 nm CoSb NCs, (e) *ca*. 5 nm $CoSb_2$ NCs, (f) *ca*. 10 nm $CoSb_2$ NCs and (g) *ca*. 20 nm $CoSb_2$ NCs. (h) TEM image of *ca*. 20 nm Sb NCs.

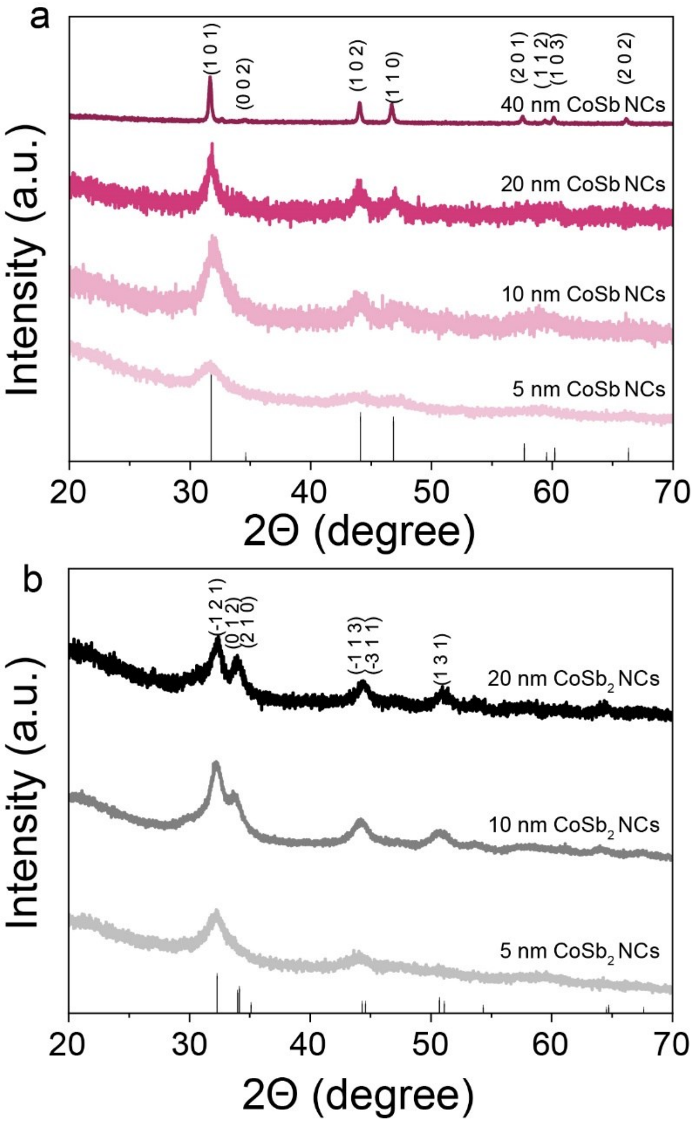

Figure S2. XRD patterns of (a) CoSb NCs and (b) CoSb$_2$ NCs.

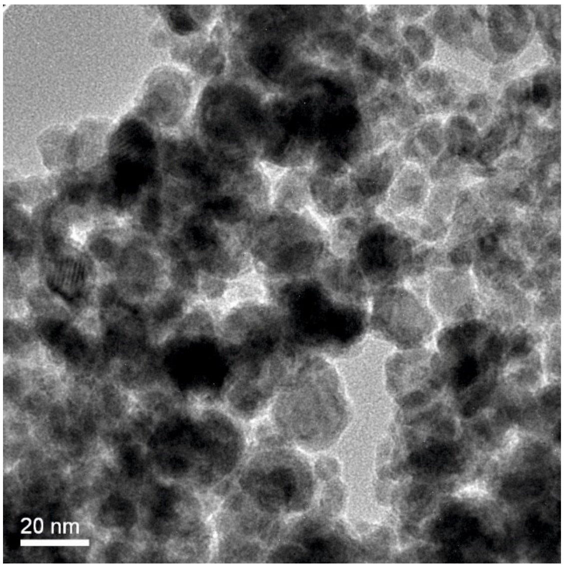

Figure S3. TEM image of *ca*. 20 nm CoSb NCs after ligand removal.

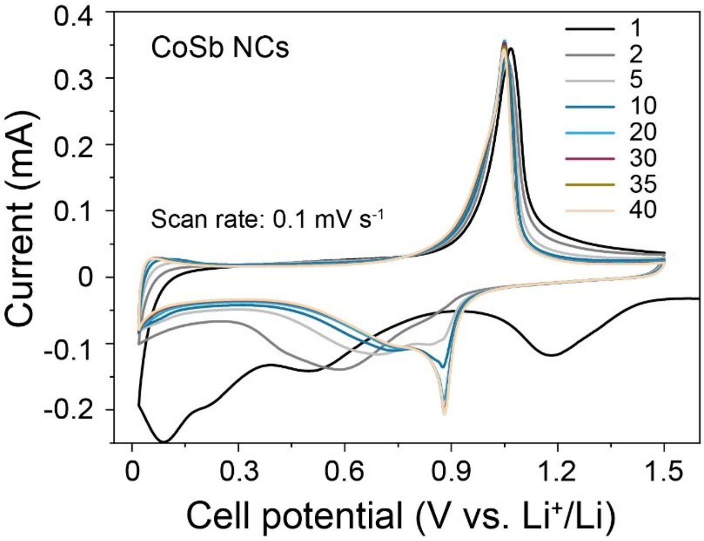

Figure S4. Cycling voltammetry curves of *ca*. 20 nm CoSb NCs for 1st, 2nd, 5th, 10th, 20th, 30th, 35th, and 40th cycles measured at a scan rate of 0.1 mV s^{-1}.

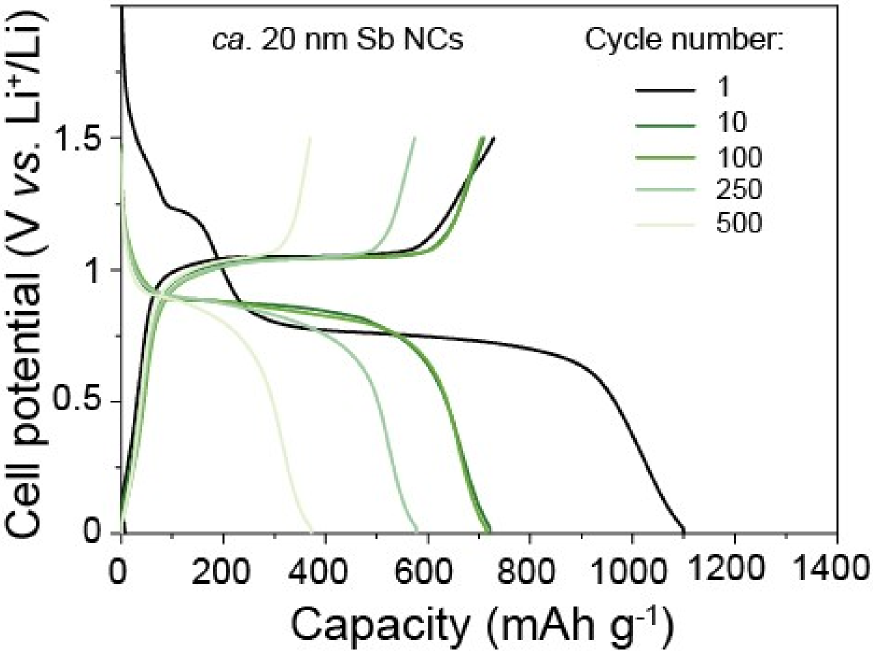

Figure S5. Galvanostatic charge-discharge curves of *ca*. 20 nm Sb NCs measured at current density of 660 mA g^{-1}. The initially higher capacity of Sb NCs as compared to their theoretical value of 660 mAh g^{-1} is attributed to the additional contribution of CB to the measured charge storage capacity.

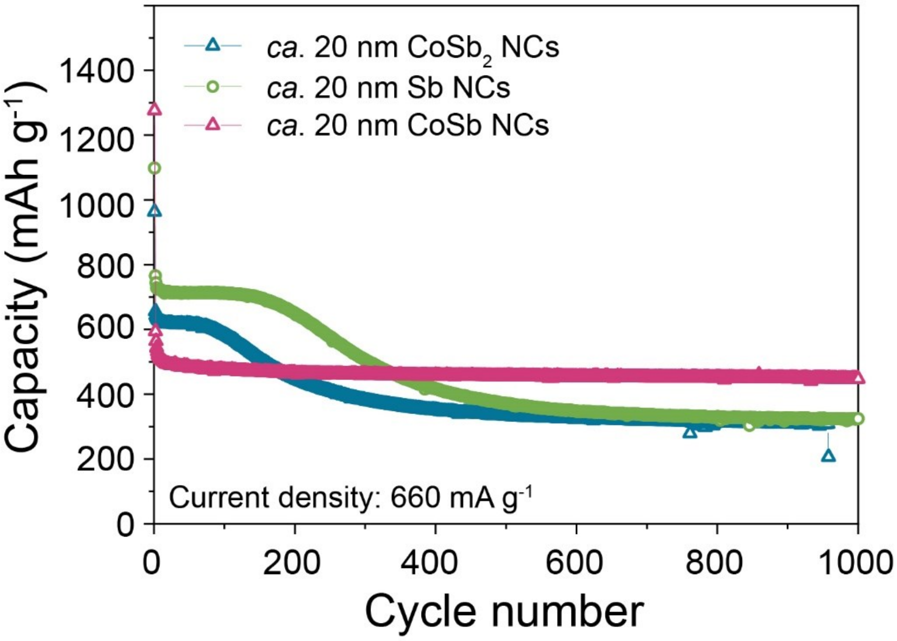

Figure S6. Comparison of cycling stability of electrodes composed of *ca*. 20 nm $CoSb_2$ NCs, *ca*. 20 nm CoSb NCs, and *ca*. 20 nm Sb NCs. Electrochemical measurements were performed using a half-cell configuration employing Li metal as a reference and counter electrode at a current density of 660 mA g^{-1}. The initially higher capacity of $CoSb_2$ NCs as compared to their theoretical value of 531 mAh g^{-1} is attributed to the additional contribution of CB to the measured charge storage capacity.

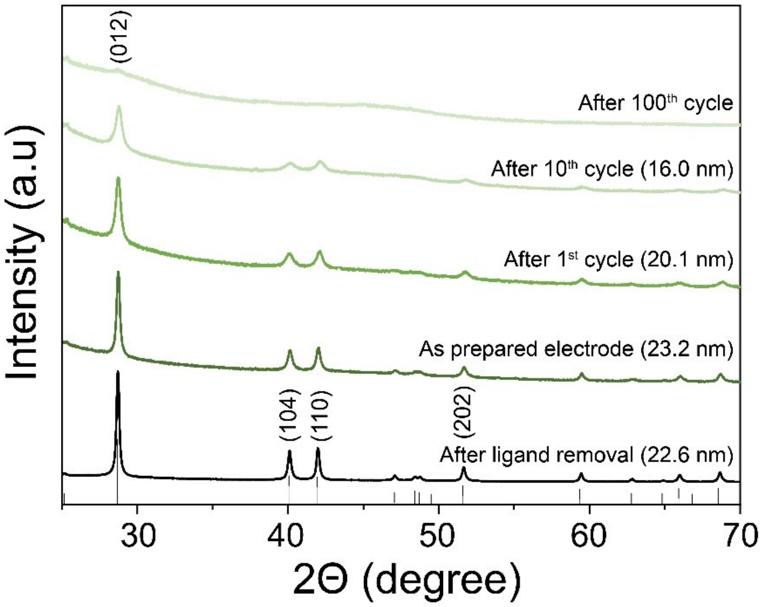

Figure S7. XRD patterns of Sb NCs after ligand removal, after electrode preparation, and after 1st, 10th, and 100th cycles.