Electronic Supplementary Information (ESI) for

Colloidal BiF_3 nanocrystals: a bottom-up approach to conversion-type Li-ion cathodes

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Materials and Methods.

Chemicals. Toluene (99.9%, Sigma-Aldrich), ethanol (≥99.8%, Fluka), hexane (≥97%, Sigma-Aldrich), chloroform (≥99.8%, Sigma-Aldrich), bismuth(III) oxide (99.9%, ABCR), trifluoroacetic acid (TFA, ≥99.9%, Sigma-Aldrich), trifluoroacetic anhydride (TFAA, 99.5%, ABCR), trimethyloxonium tetrafluoroborate (Me_3OBF_4, >95%, TCI), acetonitrile (>99.9%, Sigma-Aldrich), oleic acid (90%, Sigma-Aldrich), N-Methyl-2-pyrrolidone (NMP, 99.8%, Fisher) were used as received. Oleylamine (OLA, Acros Organics, 80%) was distilled under reduced pressure to obtain a colorless liquid, dried under vacuum overnight at 105°C and kept in a nitrogen-filled glovebox.

Battery components. A 1 M solution of $LiPF_6$ (battery grade, Novolyte) was blended in dimethyl carbonate (DMC, Novolyte). The electrolyte was 1 M $LiPF_6$ in DMC + 3vol% 4-fluoro-1,3-dioxolan-2-one (FEC, battery grade, Solvionic). Carbon black (Super C65, TIMCAL), poly(vinylidene fluoride) (PVDF, MW ~534000, Sigma-Aldrich), Celgard separator (Celgard 2400, 25 μm microporous monolayer propylene membrane, Celgard Inc. USA), glass microfiber separator (GF/D, Whatman), Al foil (25 μm thick, 99.45% - metals basis, Alfa-Aesar), Li foil (99.9% - metals basis, Alfa-Aesar).

Synthesis of $Bi(TFA)_3$. The synthesis was carried out as reported elsewhere,[1] with slight modifications. Bi_2O_3 (~21 mmol, 10 g) was mixed with TFA (139 mmol, 10 ml) and TFAA (139 mmol, 20 ml) in a three-neck flask, connected to a Schlenk line, and stirred under N_2 atmosphere at 60°C for 24 h. The oxide fully dissolved forming viscous, brownish solution. The solvents were evaporated under vacuum, resulting in a white powder (yield: 96%).

Synthesis of 15 BiF_3 NCs. The NCs were synthetized via the hot injection method. $Bi(TFA)_3$ (1.85 mmol, 1 g) was solubilized in OLA (10 ml) by gentle heating at 50°C and stirring for 2-3 h, and kept under N_2 as a stock precursor solution. OLA (10 ml) was loaded into a three-neck flask and dried under vacuum for 1 h at 105 °C. Then the temperature was raised to 230 °C under nitrogen, followed by injection of 1 ml of the $Bi(TFA)_3$ stock solution with intense stirring (glass magnetic stirrers were used, since the TFA decomposition products reacted with Teflon-coated stirrers). After 2 min, TFA (0.5 ml) was injected into the mixture and 1 min later the reaction was quenched by cooling the flask. Toluene (20 ml) was injected at ~80°C. After cooling to room temperature, BiF_3 NCs were precipitated by adding ethanol (50 ml), followed by centrifugation at 8000 rpm for 7 min. The NCs were then redispersed in toluene (15 ml), along with oleic acid (~0.25 ml), precipitated with ethanol (20 ml) and centrifuged at 8000 rpm for 4 min. The redispersion/precipitation steps were repeated 2-3 times. Synthesis conditions for 6 and 25-50 nm NCs are specified in Table S1.

BiF_3 ligand stripping. The ligand stripping procedure was adapted from methods reported elsewhere.[2] Briefly, purified BiF_3 NCs were redispersed in hexane (10 ml). Me_3OBF_4 (300 mg, 2 mmol) was dissolved in acetonitrile (10 ml) and mixed with the hexane/NC solution. After vortexing or shaking for a few minutes, the NCs were precipitated from the solution. Chloroform (5 ml) was added and the mixture was centrifuged at 8000 rpm for 4 min. The ligand-free NCs were washed twice with an acetonitrile:chloroform 1:1 mixture and centrifuged at 10 krpm for 10 min. The NCs were dried under vacuum overnight and kept in a nitrogen-filled glovebox.

Preparation and testing of Li-ion half-cells. BiF_3 NCs (55.5 wt%) were first milled in an agate vessel in a planetary ball mill (Fritsch Pulverisette 7) with carbon black (45.5 wt%) at 200 rpm for 1 h. Then PVDF and NMP were added, followed by a second milling at 500 rpm for 1 h to homogeneously mix the components. The resulting homogenous slurry was cast onto Al foil and cut into 15 mm disks. The electrodes were then dried for 48 h at 80°C in a vacuum oven. The final electrode was composed of BiF_3 NCs (50 wt%), carbon black (40 wt%) and PVDF (10 wt%) and the mass-loading was typically between 0.20-0.30 mg per current collector. The Swagelok-type titanium cells were assembled in an argon-filled glovebox (O_2 < 1 ppm, H_2O < 1 ppm). Li foil served as both a quasi-reference and counter electrode and it was separated from the working electrode by a layer of Celgard and glass separators. A 1 M solution of $LiPF_6$ in DMC + 3vol% FEC was used as the electrolyte. The cyclic voltammetry and galvanostatic discharge/charge measurements were conducted using a MPG2 multi-channel workstation (Bio-Logic). Cells were cycled between 2-4 V vs. Li/Li^+ at 25 °C. The obtained capacities were normalized to the mass of the NCs.

Characterization. Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) images were obtained with a Phillips CM30 microscope at a voltage of 300 kV, with carbon coated Ted-Pella TEM grids used as substrates. High resolution TEM images were obtained with a JEOL 2200FS instrument. Wide-angle powder X-ray diffraction (XRD) spectra were measured using a STOE STADI P diffractometer operating in transmission mode, equipped with a germanium monochromator, Cu $K\alpha_1$ irradiation and a Dectris Mythen Silicon Strip Detector. Thermal analysis was conducted with a NETZSCH STA 409 C (Netzsch Geratebau, Selb/Bavaria) instrument combined with a custom-made coupling system with a BALZERS QMG 422 mass spectrometer (with a QMA 400 analyzer, off axis SEV, cross-beam ion source, mass range 1 – 511 m/e, chamber vacuum 10^{-7} mbar). The sample was heated to 500°C @ 1 °C min^{-1} in high vacuum (~10^{-6} mbar) in an alumina crucible, covered with a pinhole lid. Attenuated total reflectance (ATR) Fourier-transform infrared spectra were recorded using a Thermo Scientific Nicolet iS5 spectrometer.

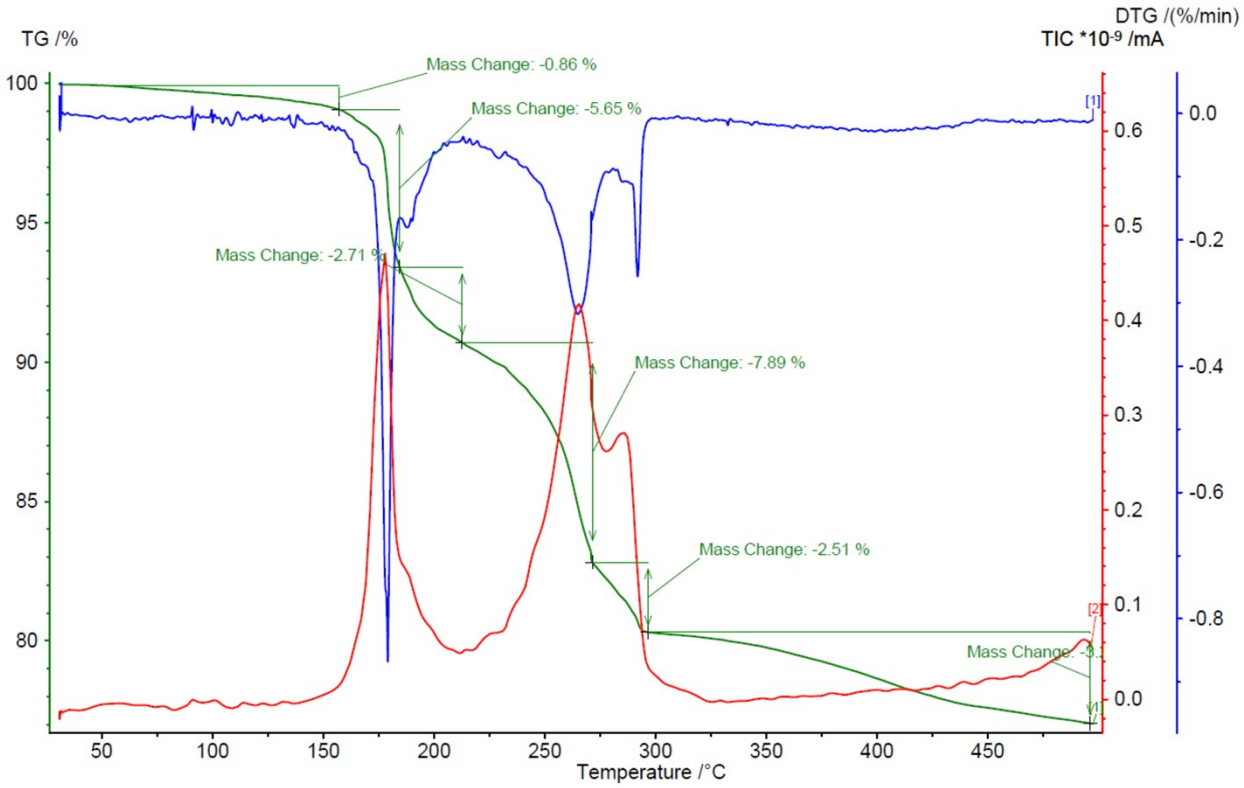

Figure S1. Thermogravimetric analysis of the $Bi(TFA)_3$ precursor.

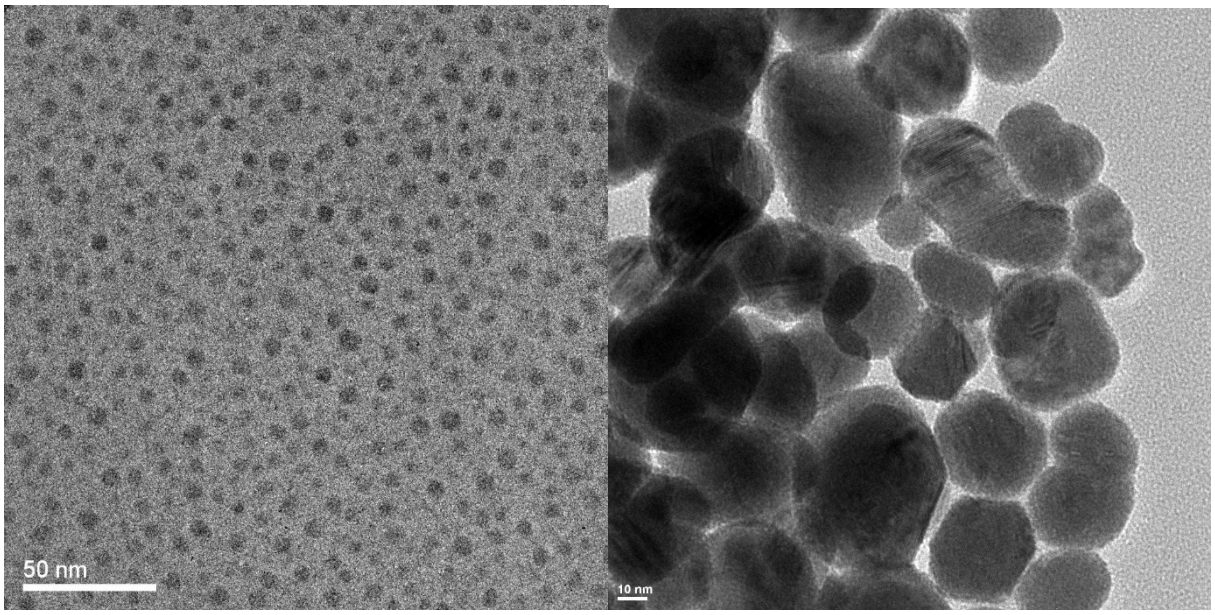

Figure S2. TEM images of 6 and 25-50nm BiF_3 NCs sizes obtained at the reaction conditions specified in Table S1.

Table S1. Synthetic parameters for obtaining BiF3 NCs with different sizes

Temperature (ºC)	$Bi(TFA)_3$ precursor amount (mmol)	Reation time (min)	NC size (nm)
230	0.75	2	6
230	0.185	2	15
230	0.185	3	25-50

Supporting references:

1. G. J. Reiss, W. Frank and J. Schneider, *Main Group Met. Chem.*, 1995, **18**, 287-294.
2. E. L. Rosen, R. Buonsanti, A. Llordes, A. M. Sawvel, D. J. Milliron and B. A. Helms, *Angew. Chem. Int. Ed.*, 2012, **51**, 684-689.