

Molecular Precursor Mediated Selective Synthesis of Phase Pure Cubic InSe and Hexagonal In₂Se₃ Nanostructures: New Anode Materials for Li-ion Batteries

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Experimental

Materials and method

InCl₃, oleylamine (OAm), 1-octadecene (ODE) and analytical grade solvents were procured from commercial sources. bis(4-methyl-2-pyridyl)diselenide; [Sepy(Me-4)]₂ [¹H NMR (CDCl₃) δ: 2.20 (s, 6H, Me), 6.89 (d, 2H, 4.1 Hz), 7.62 (s, 2H), 8.31 (d, 2H, 4.9 Hz). ¹³C{¹H} NMR (CDCl₃) δ: 21.0 (Me), 123.4, 123.9, 148.8, 149.0, 154.0 (ring carbons); ⁷⁷Se{¹H} NMR (CDCl₃) δ: 476 ppm] was prepared according to the literature method with slight modification.¹ Elemental analyses were carried out on a Thermo Fischer Flash EA-1112 CHNS analyser. The ¹H, ¹³C{¹H} and ⁷⁷Se{¹H} NMR spectra were recorded on a Bruker Advance-II NMR spectrometer operating at 300, 75.47 and 57.24 MHz, respectively. Chemical shifts are relative to internal chloroform peak for ¹H and ¹³C{¹H} NMR spectra and external Ph₂Se₂ (δ: 463 ppm relative to Me₂Se) in CDCl₃ for ⁷⁷Se{¹H} NMR spectra.

Thermogravimetric analyses (TGA) were carried out on a Nitzsch STA 409 PC-Luxx TG-DTA instrument, which was calibrated with CaC₂O₄·H₂O. The TG curves were recorded at a heating rate of 10°C min⁻¹ under a flow of argon. X-ray powder diffraction patterns were obtained on a Philips PW-1820 diffractometer using Cu-Kα radiation. B.E.T. measurement was carried out for studying the adsorption–desorption characteristics on a SORPTOMATIC 1990 at liquid nitrogen temperature (77 K). Prior to the experiment, ~100 mg of the sample was degassed at 10–2 mbar at 100 °C to remove any absorbed gas molecules or moisture. Optical diffuse reflectance measurements in the range 200-1100 nm (1.12 eV to 6.2 eV) were performed on a JASCO V-670 two-beam spectrometer with a diffuse reflectance (DR) attachment consisting of an integration sphere coated with BaSO₄ which was used as a

reference material. Measured reflectance data were converted to absorption (A) using Kubelka-Munk remission function.² The band gaps of the samples were estimated by extrapolating the linear portion of the plot to X (energy) axis. SEM and EDS measurements were carried out on ULTRA 55 FESEM of Zeiss and Oxford Inca instruments, respectively. A Zeiss Libra 200 FE Transmission electron microscope (TEM) operating at accelerating voltage of 200 kV was used for TEM studies. The samples for TEM and SAED were prepared by placing a drop of sample dispersed in acetone/toluene on a carbon coated copper grid.

Intensity data for $\text{In}[\text{Sepy}(\text{Me-4})]_3$ (**1**) was collected from a single crystal at 298(2) K on a XtaLAB Synergy, Dualflex, HyPix four-circle diffractometer with a micro-focus sealed X-ray tube using a mirror as a monochromator and a HyPix detector. The diffractometer was equipped with a low-temperature device and used Mo-K_α radiation ($\lambda = 0.71073 \text{ \AA}$). The unit cell parameters (Table 1) were determined from 25 reflections measured by a random search routine. All data were integrated with CrysAlis PRO and a multi-scan absorption correction using SCALE3 ABSPACK was applied.³ The structures were solved by iterative methods using OLEX 1.2 and refined by full-matrix least-squares methods against F^2 using SHELXL-2017/1.^{4,5} All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their U_{iso} values constrained to 1.5 times the U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms. Disordered moieties were refined using bond length restraints and displacement parameter restraints. Molecular structures were drawn using ORTEP.^{6,7}

Synthesis of $\text{In}[\text{Sepy}(\text{Me-4})]_3$ (**1**)

To a freshly prepared methanolic solution of $\text{NaSepy}(\text{Me-4})$ [in situ obtained by reducing $\{\text{Sepy}(\text{Me-4})\}_2$ (400 mg, 1.16 mmol) with NaBH_4 (87.7 mg, 2.32 mmol) in methanol], solid InCl_3 (172.4 mg, 0.78 mmol) was added and the reaction mixture was stirred at room temperature for 2 h. The solvents were evaporated under vacuum and the residue was washed thoroughly with diethyl ether followed by water to remove any unreacted ligand and sodium chloride. The final product was dried under reduced pressure and recrystallized from toluene to afford colorless crystals (yield: 692 mg, 94%), m.p. 224°C (dec.). Anal. Calcd. for $\text{C}_{18}\text{H}_{18}\text{InN}_3\text{Se}_3$: C, 34.42; H, 2.88; N, 6.69%. Observed: C, 32.46; H, 2.71; N, 5.97%. ^1H NMR (CDCl_3) δ : 2.0 (s, 3H, 4-Me); 6.8 (d, 5.1Hz, 1H, H-5), 7.4 (s, 1H, H-3), 7.5 (d, 5.4Hz, 1H, H-6) (ring

proton). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ : 21.1 (4-Me), 119.9, 128.9, 145.2, 150.0, 164.4 (ring carbons). $^{77}\text{Se}\{^1\text{H}\}$ NMR (CDCl_3) δ : 332.3 ppm.

Preparation of Indium Selenide nanostructures

The indium selenide nanostructures were prepared using $\text{In}[\text{Sepy}(\text{Me-4})]_3$ (**1**) as single source molecular precursor by hot injection method utilizing high boiling solvents like OAm and ODE. In a typical hot injection method, 9 mL of high boiling solvent (OAm or ODE) was taken in a three-necked round bottom flask and degassed at 120°C under argon flow for 30 min. Subsequently, the temperature was raised to 250°C . In the pre-heated solvent, required amount of the precursor **1** (300 mg, 0.47 mmol), dispersed in OAm (1 mL) was swiftly injected. The reaction temperature dropped by around $15\text{--}20^\circ\text{C}$ upon injection; however, the set temperature was attained in no time. The temperature was maintained for 5 minutes after which the heat source was removed and the reaction mixture was allowed to cool to 60°C and methanol (5 mL) was injected to ensure complete precipitation of the nanostructures. The synthesized material was collected after repeated washing with methanol and toluene mixture followed by centrifugation at 8000 rpm for 10 min to remove excess capping agent. The final product was obtained as brown residue.

Electrochemical characterization

To evaluate the electrochemical performance of cubic InSe and hexagonal In_2Se_3 , electrodes was fabricated by mixing 70% of active material, 20% of Super P and 10% of carboxymethyl cellulose (CMC) binder in water. After 30 min of mixing, the slurry was uniformly coated on Cu foil and dried at 50°C for 12 h in a hot air oven. The mass loading of InSe and In_2Se_3 on 1×1 cm Cu foil was $2.5\text{--}3.0$ mg cm^{-2} . For CR2032 coin cell assembly, Li metal was used as the counter electrode, Whatman Glass Microfiber as the separator, and 1M LiPF_6 in ethylene carbonate (EC) and dimethylcarbonate (DMC) (1:1, v/v) as electrolytes in an Ar-filled glove box (MBRAUN, UNIlab plus). The performance of the Li-ion half-cell battery was measured using a NEWARE battery charging unit (NEWARE Technology, Ltd, Shenzhen, China) at different current densities within the voltage range of 0.01–3 V (vs. Li/Li⁺). Cyclic voltammetry (CV) was carried out on an Origaflex OGF 500 potentiostat/galvanostat (Origalys, France) within a voltage range of 0.1–3 V at different scan rate. The electrochemical impedance spectroscopy (EIS) was performed using Novocontrol Alpha-A High Frequency

Analyzer with 10 mV AC voltage in the frequency range of 1 Hz to 1 MHz. The specific capacity of the InSe and In₂Se₃ anodes were calculated based on the weight of the same.

Figure captions:

Figure S1. ¹H NMR spectra of In[Sepy(Me-4)]₃ (**1**) in CDCl₃

Figure S2. ¹³C{¹H} NMR spectra of In[Sepy(Me-4)]₃ (**1**) in CDCl₃

Figure S3. ⁷⁷Se{¹H} NMR spectra of In[Sepy(Me-4)]₃ (**1**) in CDCl₃

Figure S4. Packing diagram featuring intermolecular C4–H4···Se1 interactions of In[Sepy(Me-4)]₃ (**1**)

Figure S5. Thermogravimetric analysis of In[Sepy(Me-4)]₃ (**1**)

Figure S6. EDS spectra of (a) hexagonal In₂Se₃ and (b) cubic InSe synthesized by thermolysis of **1** at 250°C for 5 minutes in ODE and OAm respectively.

Figure S7. 2D elemental mapping of (a) hexagonal In₂Se₃ and (b) cubic InSe synthesized by thermolysis of **1** at 250°C for 5 minutes in ODE and OAm respectively.

Figure S8. (a) Typical N₂ adsorption/desorption isotherm and (b) BJH plot for the as synthesized In₂Se₃ nanomaterials.

Figure S9. (a) Typical N₂ adsorption/desorption isotherm and (b) BJH plot for the as synthesized InSe nanomaterials.

Figure S10. SEM micrographs of the electrodes consists of (a) hexagonal In₂Se₃ and (b) cubic InSe after 200 cycle run.

Figure S11. EDS spectra of the electrodes consists of (a) hexagonal In₂Se₃ and (b) cubic InSe after 200 cycle run.

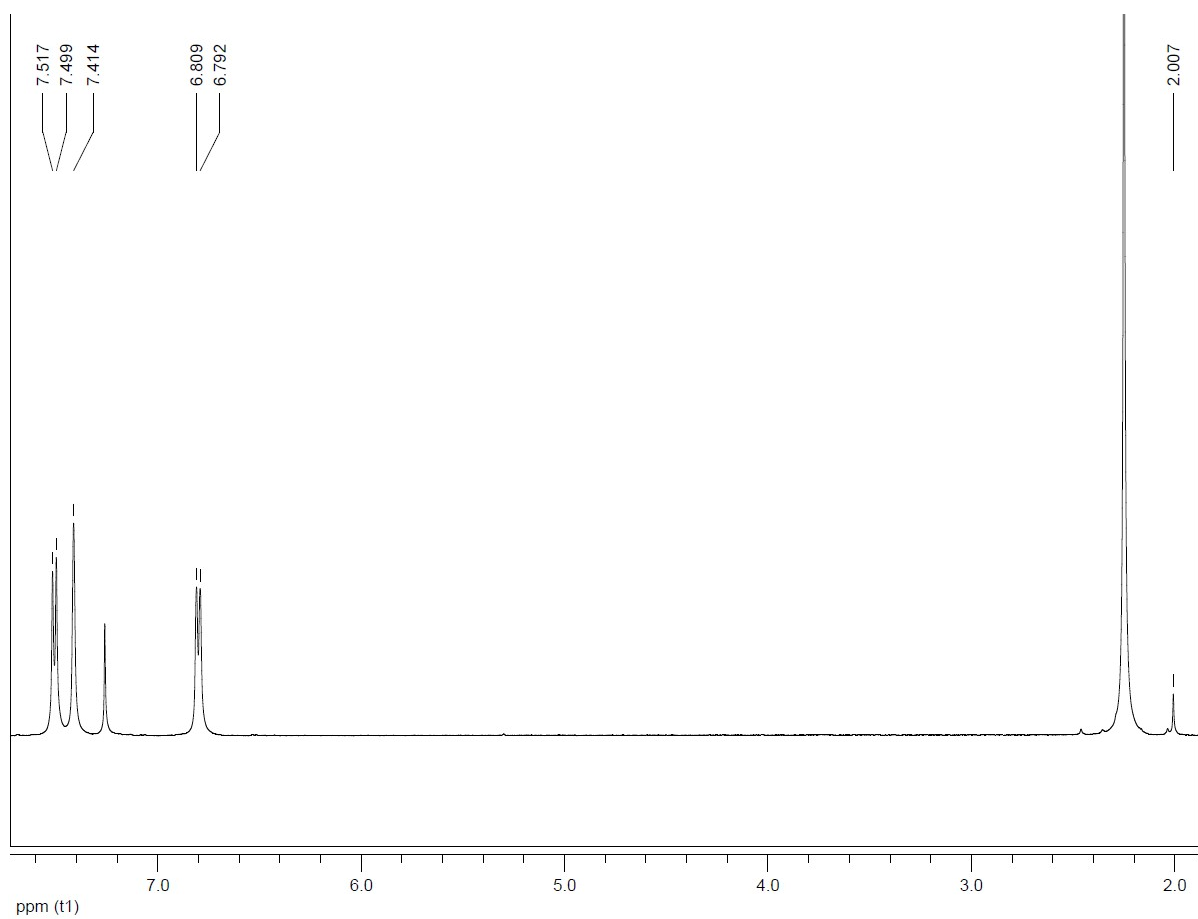


Figure S1. ^1H NMR spectra of $\text{In}[\text{Sepy}(\text{Me-4})]_3$ (**1**) in CDCl_3

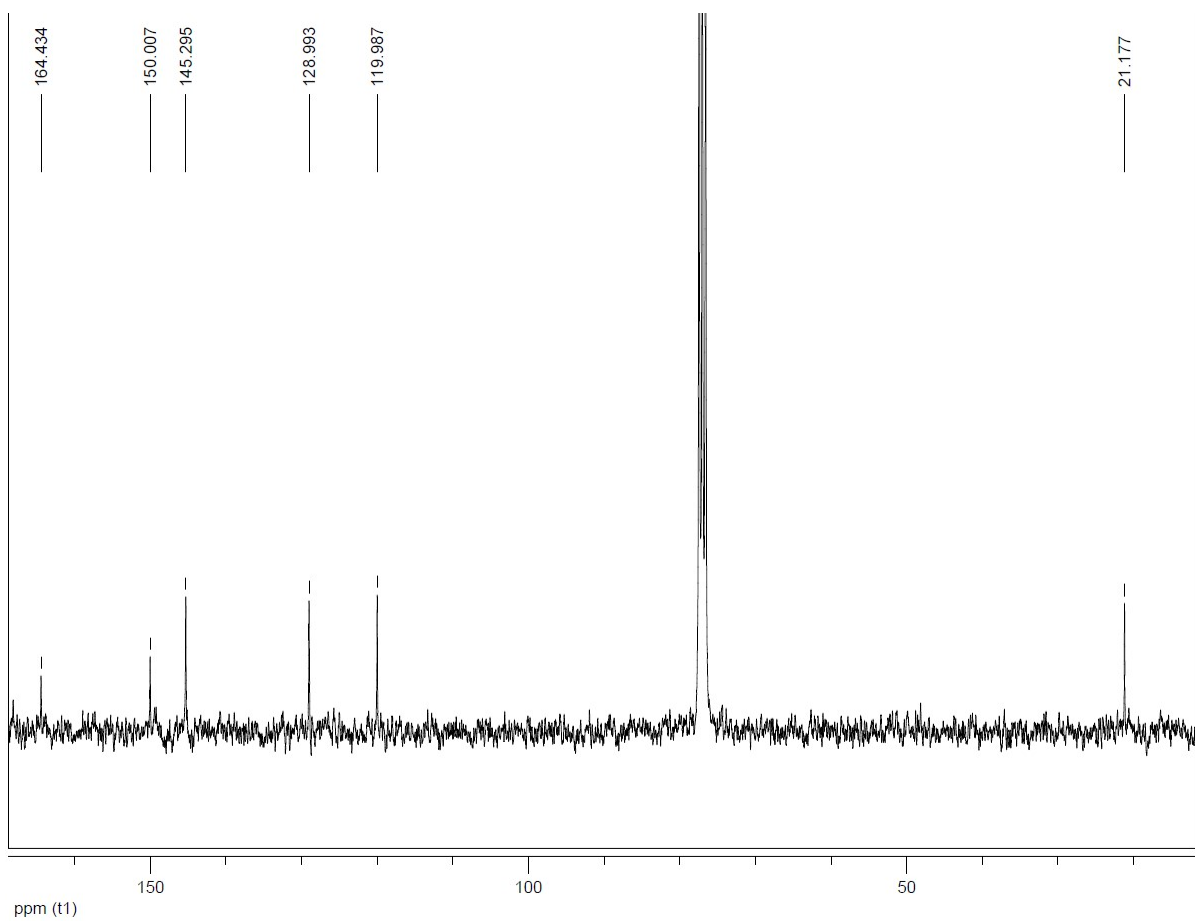


Figure S2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of $\text{In}[\text{Sepy}(\text{Me-4})]_3$ (1) in CDCl_3

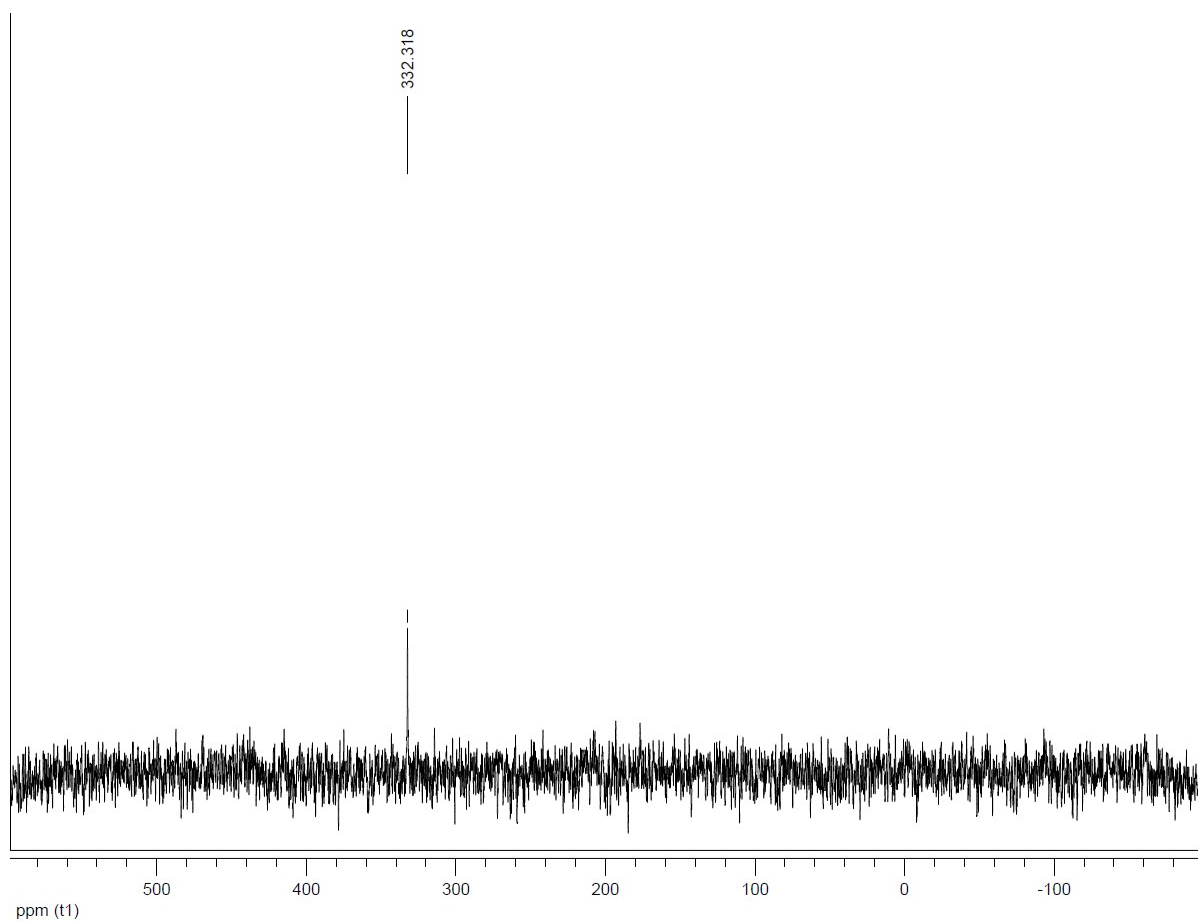


Figure S3. $^{77}\text{Se}\{^1\text{H}\}$ NMR spectra of $\text{In}[\text{Sepy}(\text{Me-4})]_3$ (**1**) in CDCl_3

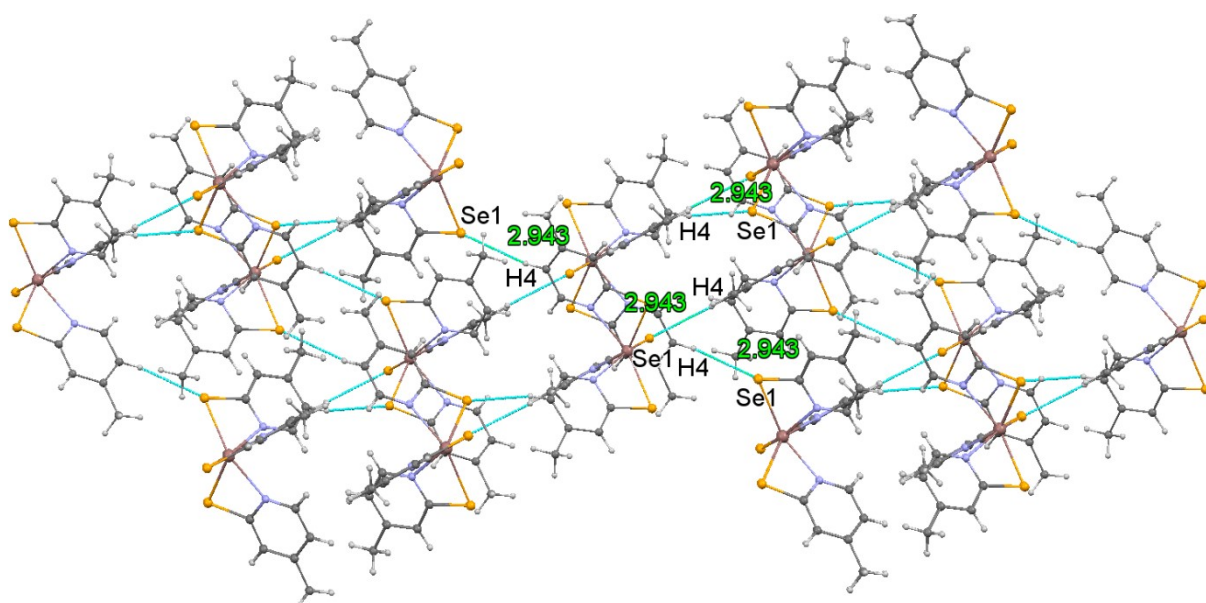


Figure S4. Packing diagram featuring intermolecular $\text{C4-H4}\cdots\text{Se1}$ interactions of $\text{In}[\text{Sepy}(\text{Me-4})]_3$ (**1**)

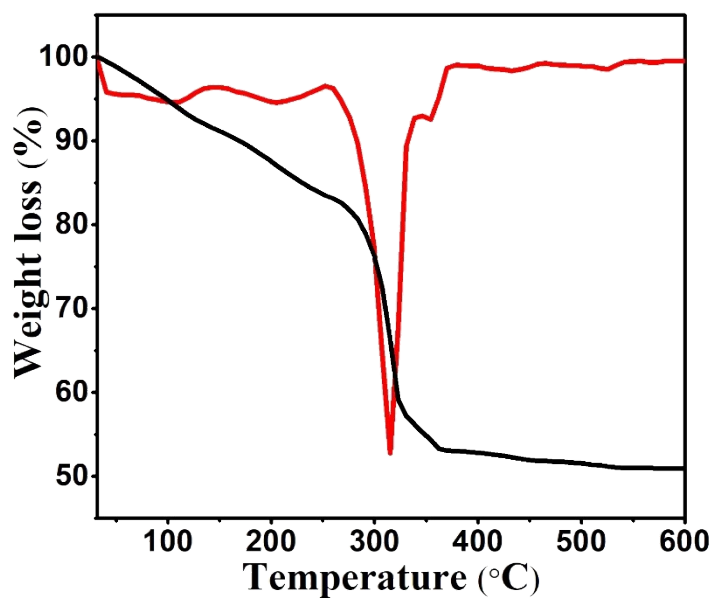


Figure S5. Thermogravimetric analysis of $\text{In}[\text{Sepy}(\text{Me-4})]_3$ (**1**)

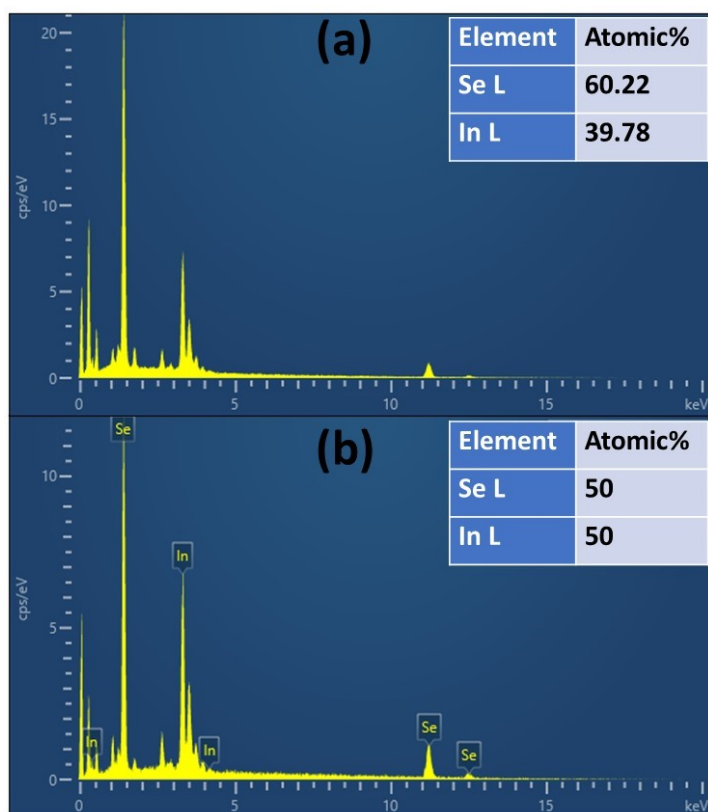


Figure S6. EDS spectra of (a) hexagonal In_2Se_3 and (b) cubic InSe synthesized by thermolysis of **1** at 250°C for 5 minutes in ODE and OAm respectively.

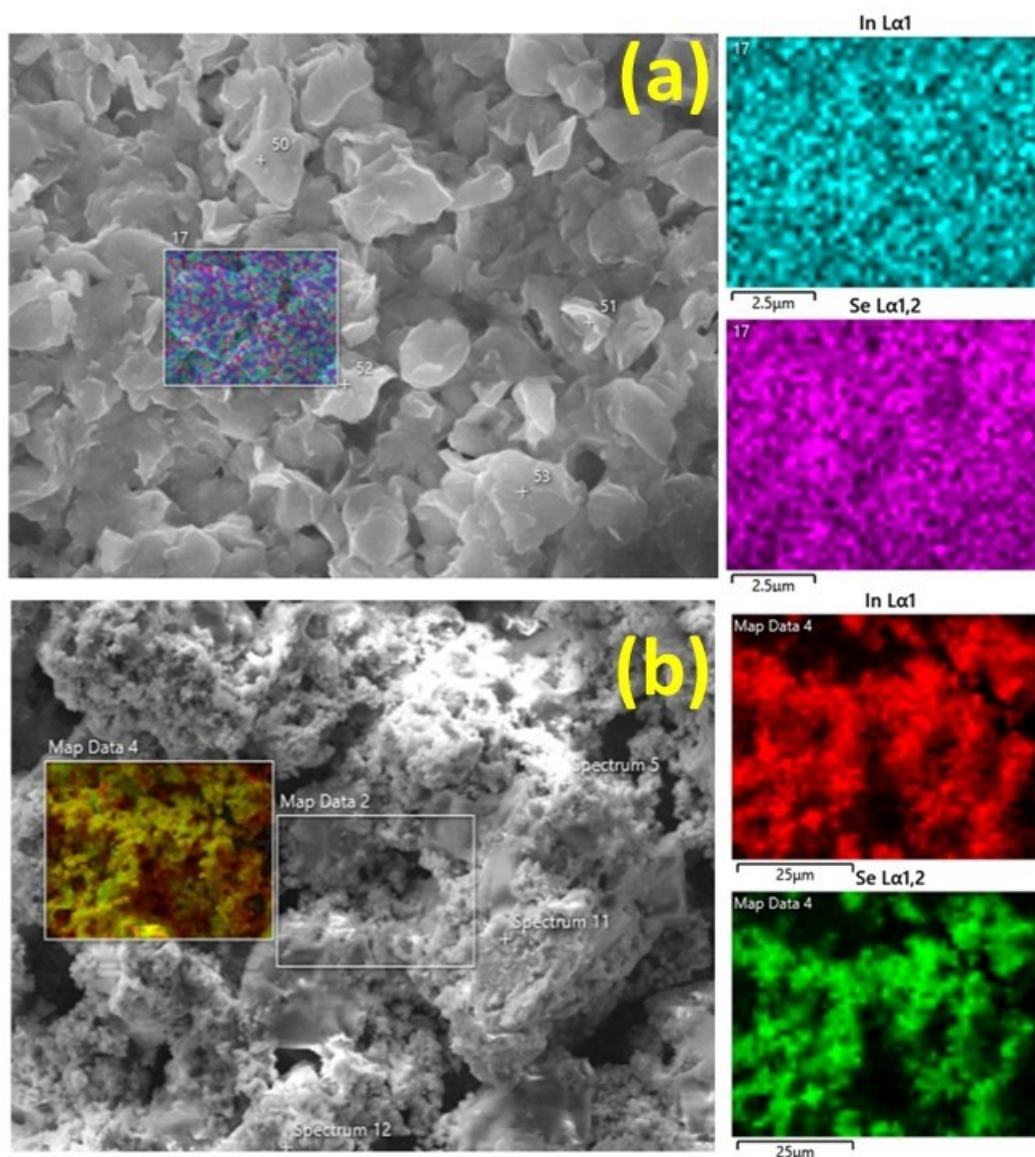


Figure S7. 2D elemental mapping of (a) hexagonal In_2Se_3 and (b) cubic InSe synthesized by thermolysis of **1** at 250°C for 5 minutes in ODE and OAm respectively.

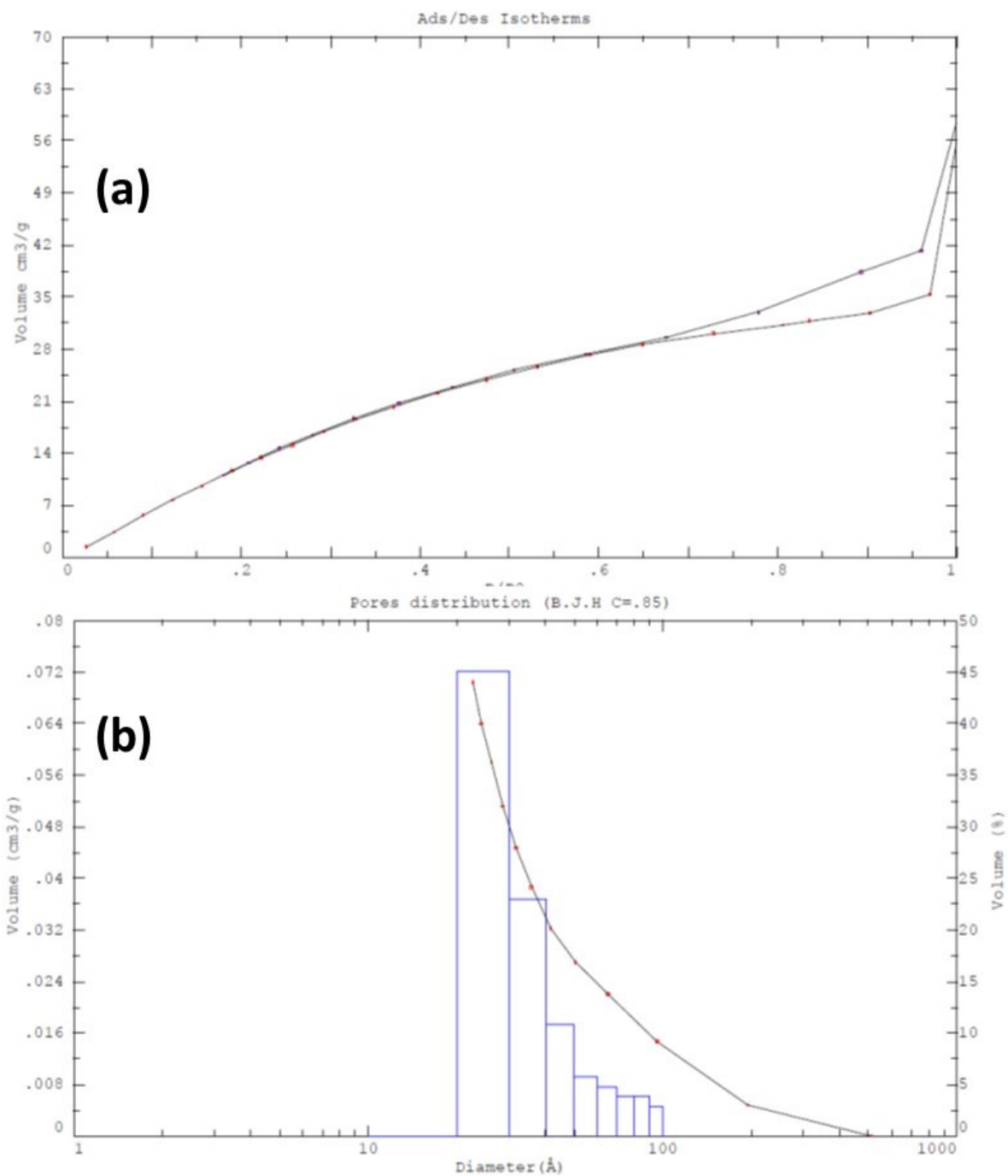


Figure S8. (a) Typical N_2 adsorption/desorption isotherm and (b) BJH plot for the as synthesized In_2Se_3 nanomaterials.

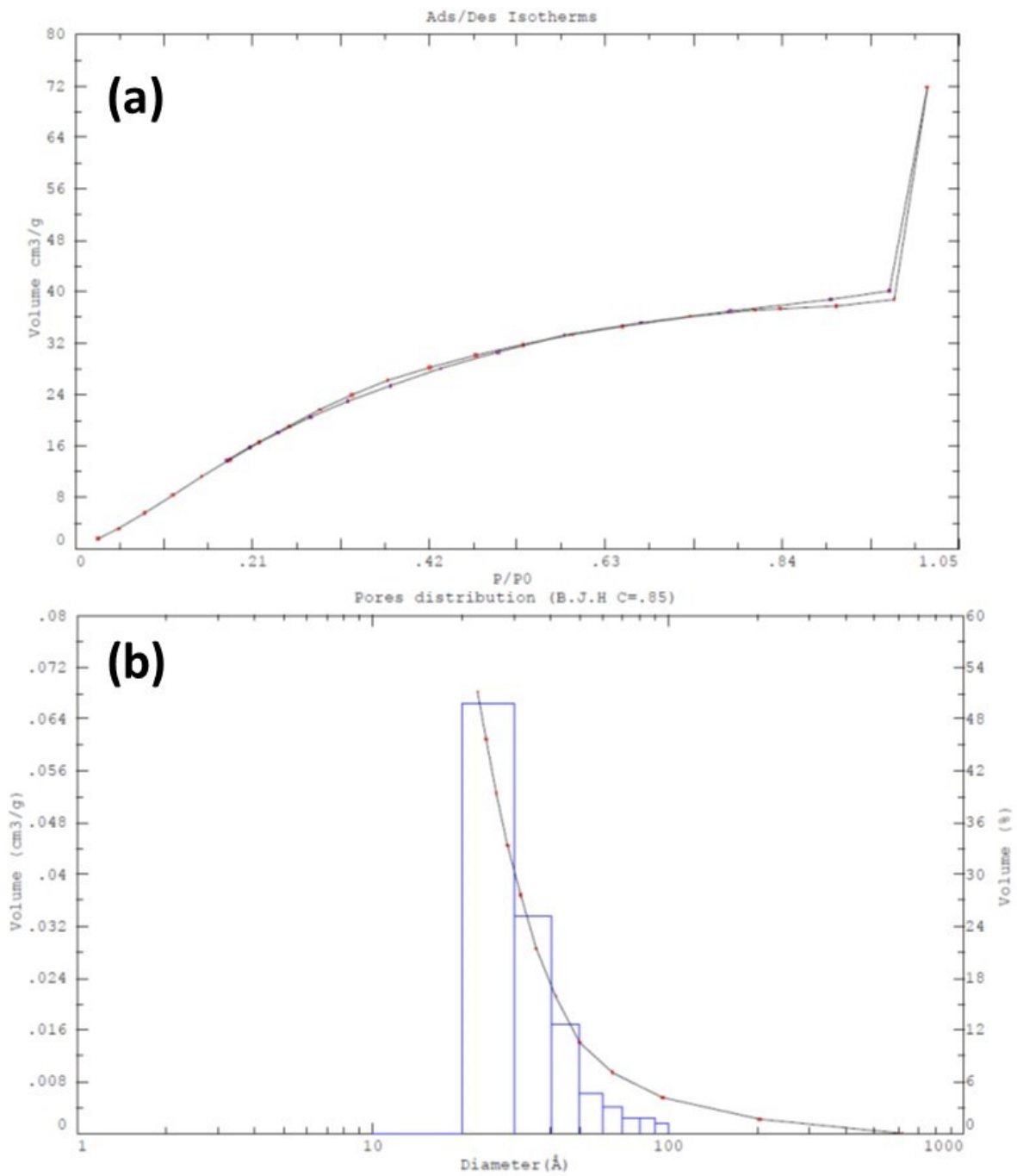


Figure S9. (a) Typical N_2 adsorption/desorption isotherm and (b) BJH plot for the synthesized InSe nanomaterials.

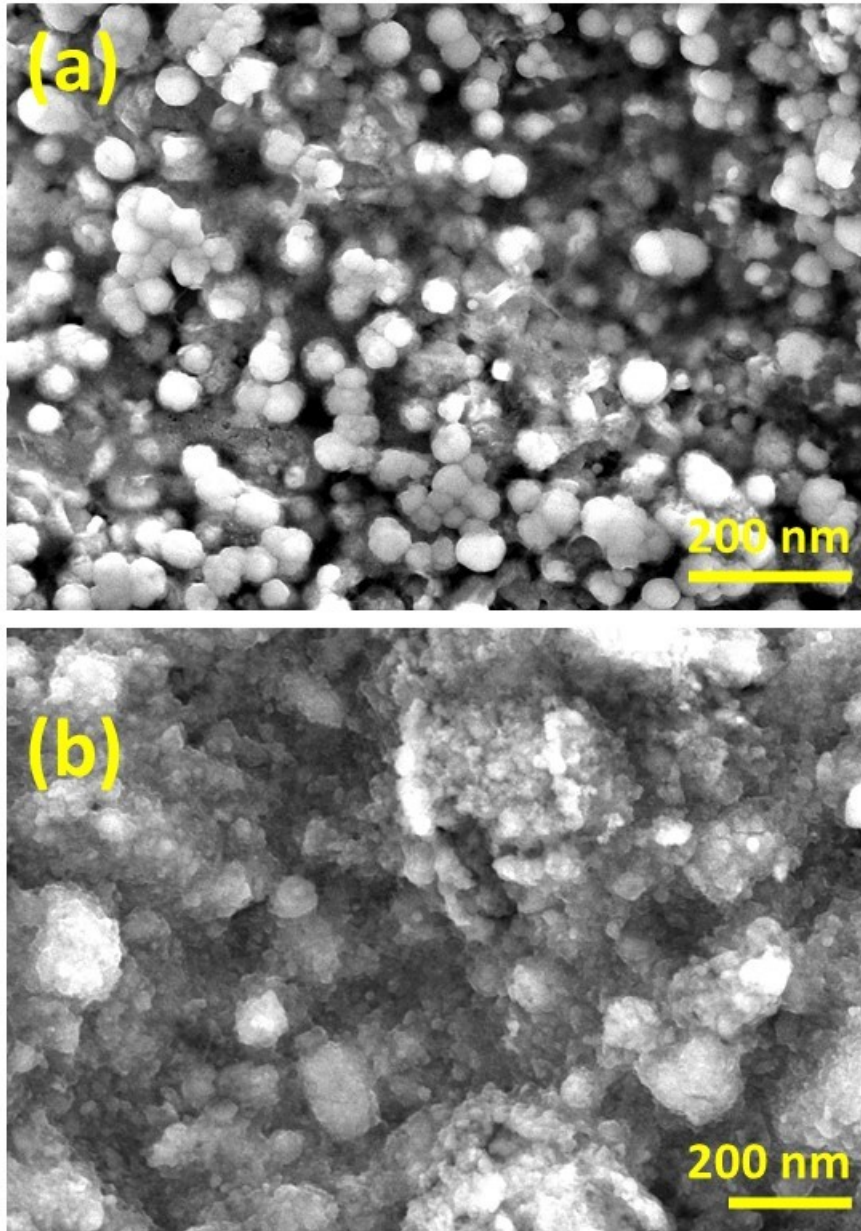


Figure S10. SEM micrographs of the electrodes consists of (a) hexagonal In_2Se_3 and (b) cubic InSe after 200 cycle run.

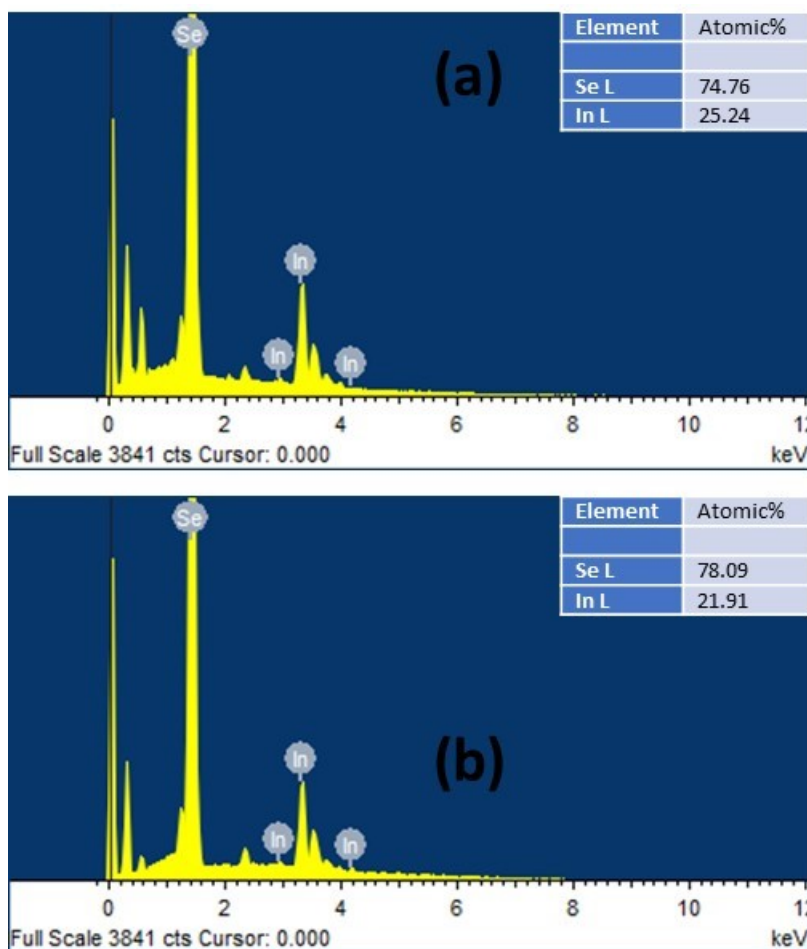


Figure S11. EDS spectra of the electrodes consists of (a) hexagonal In_2Se_3 and (b) cubic InSe after 200 cycle run.

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