Supporting Information

Novel bismuth-selone molecular precursor based selective synthesis of Bi_2Se_3 nanoplates and nanosheets: A promising electrocatalyst for hydrogen evolution in neutral medium.

Atharva Yeshwant Kulkarni,[a#] Dwaipayan Majumder,[b#] Sandeep Nigam,[c,d] Vaidehi S. Tripathi,[b,d] Amey P. Wadawale,[c] Jitendra Bahadur,[e] Ankita Pathak,[f] Gourab Karmakar,[c,d]* Rohit Singh Chauhan,[a]* Adish Tyagi[c,d]*

[a]*Department of Chemistry, K. J. Somaiya College of Science and Commerce, Vidyavihar, Mumbai 400077, India.*

[b]*Radiation and Photochemistry Division, Bhabha Atomic Research Centre, Mumbai-400085.*

[c]*Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400085, Homi Bhabha National Institute, Mumbai 400094, India*

[d]*Homi Bhabha National Institute, Anushaktinagar, Mumbai- 400094, India*

[e]*Materials Science Division, Bhabha Atomic Research Centre, Mumbai – 400 085, India*

[f]*Technical Physics Division, Bhabha Atomic Research Centre, Mumbai – 400 085, India*

[#]*These authors contributed equally.*

Email: tyagia@barc.gov.in, gourabk@barc.gov.in, rohit.chauhan@somaiya.edu.

1. Experimental

1.1 Chemicals

All the experiments were carried out under an inert atmosphere. The solvents were purchased from commercial sources and used without any purification. Bismuth trichloride ($BiCl_3$) was purchased from Sigma Aldrich. The ligand 3-benzyl-1-methyl-(1H)-imidazole-2(3H)-selone (**L**) was prepared as per the reported procedure [1]. ^1H NMR (DMSO-d_6) δ: 3.59 (s, 3H, NCH_3), 5.30 (s, 2H, CH_2), 7.15-7.17 (1H, d, Im), 7.21-7.24(1H, d, Im) 7.32-7.39 (m, 5H, Ph); ^{13}C NMR (DMSO-d_6) *δ*: 36.85, 51.80, 119.61, 121.32, 128.06, 128.82, 136.83, 155.21 (C═Se). $^{77}Se\{^1H\}$ (DMSO-d_6) δ: 18.70 ppm.

1.2 Instrumentation

The ^1H and $^{13}C\{^1H\}$ and $^{77}Se\{^1H\}$ 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 DMSO-d_6 peak for ^1H and $^{13}C\{^1H\}$ NMR spectra and external Ph_2Se_2 (δ: 463

ppm relative to Me_2Se) in $CDCl_3$ for $^{77}Se\{^1H\}$ NMR spectra. Elemental analyses were carried out on a Thermo Fischer Flash EA1112 CHNS analyzer.

Single crystal crystals were performed using Rigaku XtaLAB Synergy S four-circle equipped with a micro-focus sealed X-ray tube, a mirror monochromated hybrid Pixel Array Detector and CuKα radiation (λ=1.5418 Å). Intensity data for **1** were collected at room temperature 298K. The obtained data were processed using CrysAlisPro 1.171.40.57a (2019). Empirical absorption correction was done using spherical harmonics implemented in SCALE3 ABSPACK scaling algorithm. The crystal structure was solved by utilizing Olex2 with the help of SHELXLT 2018 [2]. Reflections were merged by SHELXL according to the crystal class for the calculation of statistics and refinement. All non-hydrogen atoms were refined with anisotropic displacement parameters and all hydrogen atoms were placed in calculated positions. Molecular structures of complex **1** were generated using Mercury 2023.2.0 [3]. The crystallographic and structural determination data are given in Table.1.

Thermogravimetric analysis (TGA) was carried out on a Netzsch STA 409 PC-Luxx TG–DTA instrument, which was calibrated with $CaC_2O_4.H_2O$. The TG curve was recorded at a heating rate of 10°C min^{-1} under flowing argon. IR was studied using Fourier-transformed infrared spectroscopy (FT-IR) in the range of 400–4000 cm^{-1} in ATR mode at room temperature using a Bruker instrument (model Alpha-2).

The X-ray powder diffraction patterns were obtained using a Philips PW-1820 diffractometer using Cu-Kα radiation. Optical diffuse reflectance measurements in the range 200–1100 nm (1.12 eV to 6.2 eV) was performed using a JASCO V-670 two-beam spectrometer with a diffuse reflectance (DR) attachment consisting of an integration sphere coated with $BaSO_4$ which was used as the reference material. The measured reflectance data were converted to absorption (A) using the Kubelka–Munk remission function [4]. The band gaps of the samples were estimated by extrapolating the linear portion of the plot to X (energy) axis.

All electrochemical experiments were performed using autolab PGSTAT 302N potentiostat. A three-electrode cell was employed for electrochemical studies. The cell contained nickel foam coated catalysts as working electrode, platinum disk as auxiliary and saturated calomel electrodes as reference. All data were reported with respect to reversible hydrogen electrode (RHE) which is converted by the following equation:

$$E\ (RHE) = E(SCE) + 0.244 + 0.059 \times pH$$

20 ml aliquot of 1 M phosphate buffer solution (PBS) at pH 7 deaerated by argon purging was used for the electrochemical studies. The linear sweep voltammoogramms were measured at a sweep rate of 5 mV/s. The Tafel slope was evaluated by performing LSV at very slow sweep rate of 0.5 mV/s. Impedance spectra has been obtained in the frequency range of 1 MHz to 10 mHz and is fitted to suitable equivalent circuit to obtain the values of the circuit elements.

1.3 Synthesis of $[(\mathbf{L})_2\mathbf{BiCl_2(\mu\text{-}Cl)}]_2$ (**1**)

3-benzyl-1-methyl-(1H)-imidazole-2(3H)-selone (**L**) (80 mg, 0.32mmol) and $BiCl_3$ (100 mg, 0.32 mmol) was added to a toluene (10ml) under nitrogen atmosphere and was allowed to stir for 5 hours at room temperature. The resultant orange precipitate was filtered using whatman filter paper. The residue obtained was washed thoroughly with hexane and diethyl ether to remove the impurities. The product was dried and recrystallized in methanol and acetonitrile mixture (1:1) to give orange crystals of **1**. (Yield: 148 mg, 55 %); m.p.: 155°C (dec)). Anal. Calcd. for $C_{44}H_{48}Bi_2Cl_6N_8Se_4$; C, 32.31; H, 2.96; N, 6.85 %; Found: C, 32.61; H, 2.99; N, 6.91 %. IR (ATR, cm^{-1}): 3158(w), 3124(w), 3098(w), 2948(w), 1606(w), 1560(s), 1471(s), 1459(s), 1452(s), 1408(s), 1396(s), 1358(m), 1331(m), 1297(w), 1181(w), 1124(w), 1078(w), 1029(w), 777(w), 734(s), 696(m), 568(w), 460(m). ^{1}H NMR (DMSO-d_6) δ: 3.61 (12H, s, N-CH_3), 5.32 (8H, s, N-CH_2), 7.14-7.16 (8H, d, Im), 7.20-7.23 (8H, d, Im), 7.27-7.39 (20H, m, Ph); ^{13}C{^{1}H} NMR (DMSO-d_6) δ: 36.96, 52.05, 120.24, 121.89, 128.12, 128.86, 129.18, 136.64, 152.57; ^{77}Se{^{1}H} NMR (DMSO-d_6) δ: 118.01 ppm.

1.4 Preparation of Bismuth selenide nanostructure

The Bi_2Se_3 nanostructures were prepared both by thermolysis and pyrolysis methods using $[(L)_2BiCl_2(\mu\text{-}Cl)]_2$ (**1**) as a molecular precursor. In a typical experiment $[(L)_2BiCl_2(\mu\text{-}Cl)]_2$ (**1**) was dispersed in 10 ml of OAm in a three-necked round-bottomed flask and degassed at 110 °C under nitrogen flow for 15 min. The reaction mixture was heated to a required temperature 220 °C and kept for 30 mins. The resulting nanocrystals were separated by centrifugation and purified by washing several times with a mixture of methanol and chloroform and dried. In case of pyrolysis $[(L)_2BiCl_2(\mu\text{-}Cl)]_2$ (**1**), the title complex 150 mg was placed in a quartz boat inside a tube furnace and annealed at 350 °C for 2h under flowing argon. The black residue obtained was cooled at room temperature and collected for characterization.

1.5 Electrode preparations

Ni foam (NF) sheet was cleaned with 1 M HCl, washed with distilled water and acetone repeatedly and subsequently dried in vacuum oven at 60° C for 6 hours. The catalyst materials have been coated on the cleaned Ni foam sheets. 80 (wt.%) catalyst, 10 (wt. %) super P carbon and 10 (wt. %) polyvinylidene fluoride as binder were grinded and mixed in N-Methyl-2-pyrrolidone solvent. This mixture was coated on Ni foam sheet and dried under IR lamp. The catalyst loading was maintained at 1.156 mg/cm^2. Each experiment was performed by taking 0.5 cm × 0.5 cm Ni-foam sheet as working electrode.

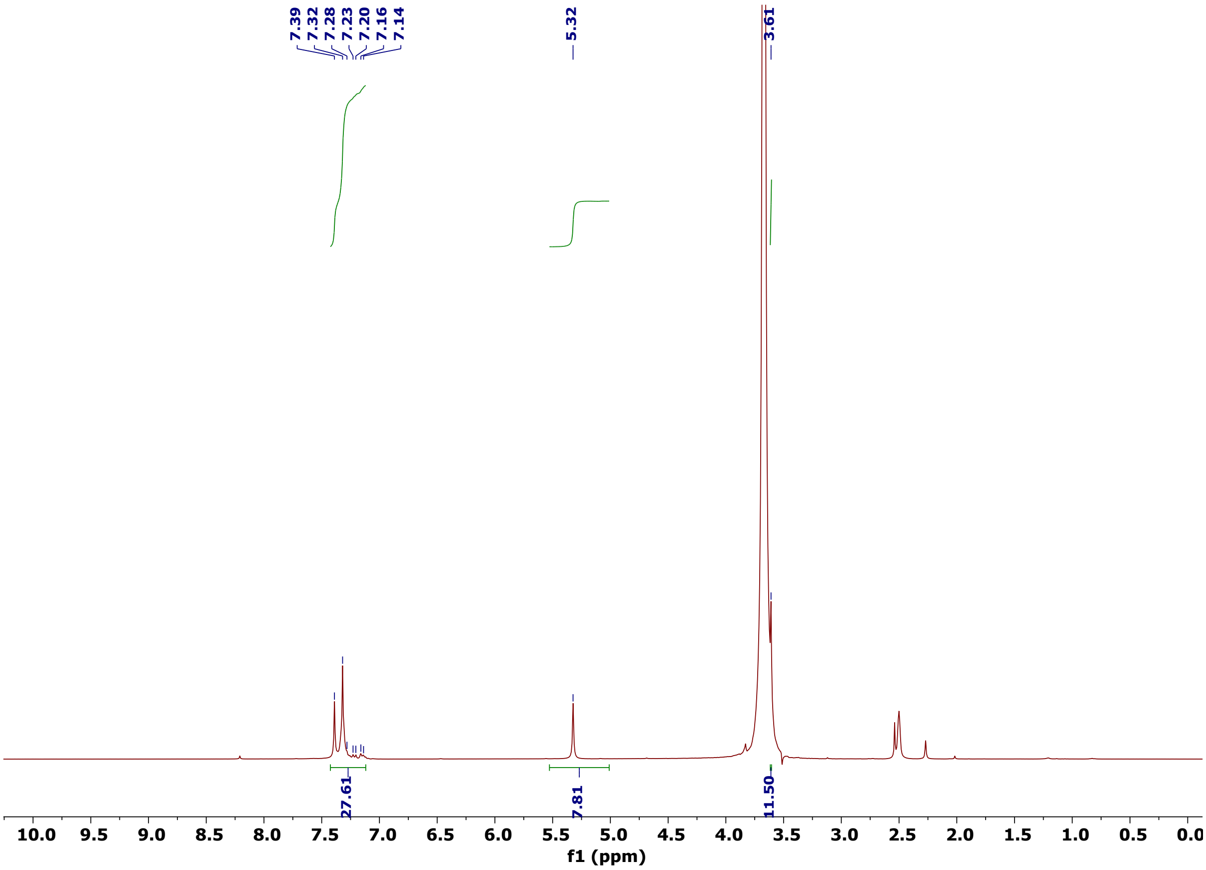


Figure S1. ^{1}H NMR spectrum of $[(\mathbf{L})_2BiCl_2(\mu\text{-}Cl)]_2$ DMSO-d_6 at R.T.

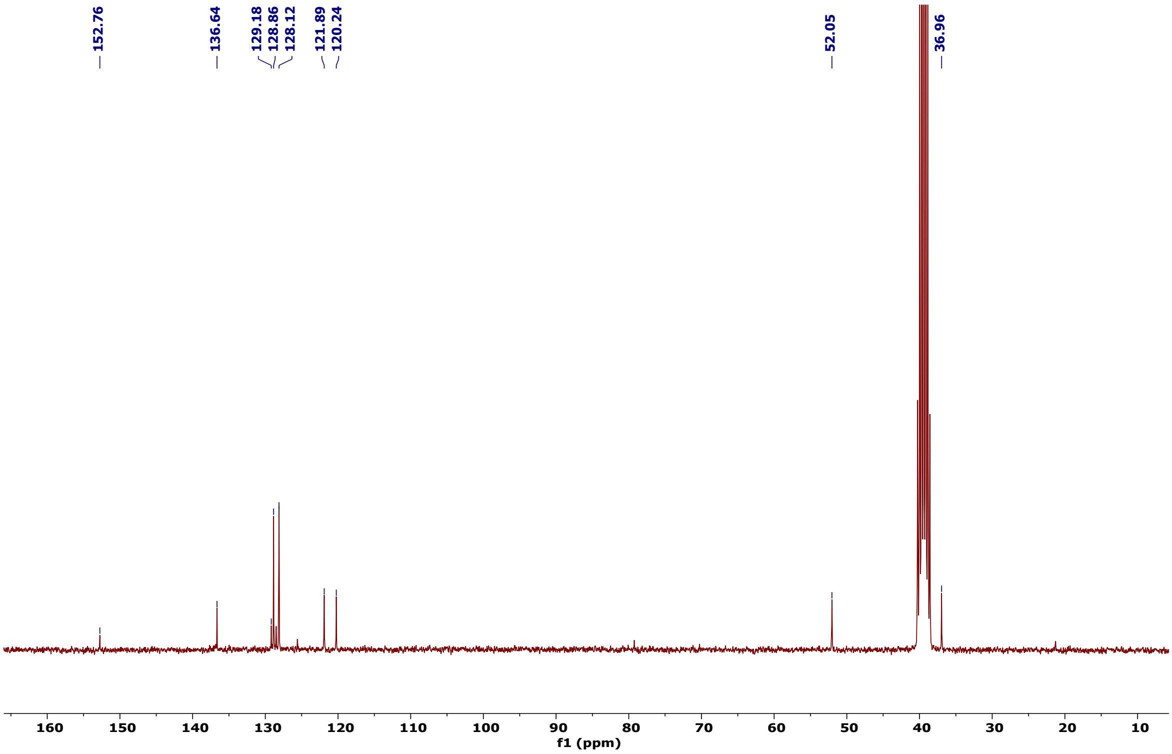


Figure S2: ^{13}C NMR spectrum of [(**L**)$_2$BiCl$_2$(μ-Cl)]$_2$ in DMSO-d$_6$ at R.T.

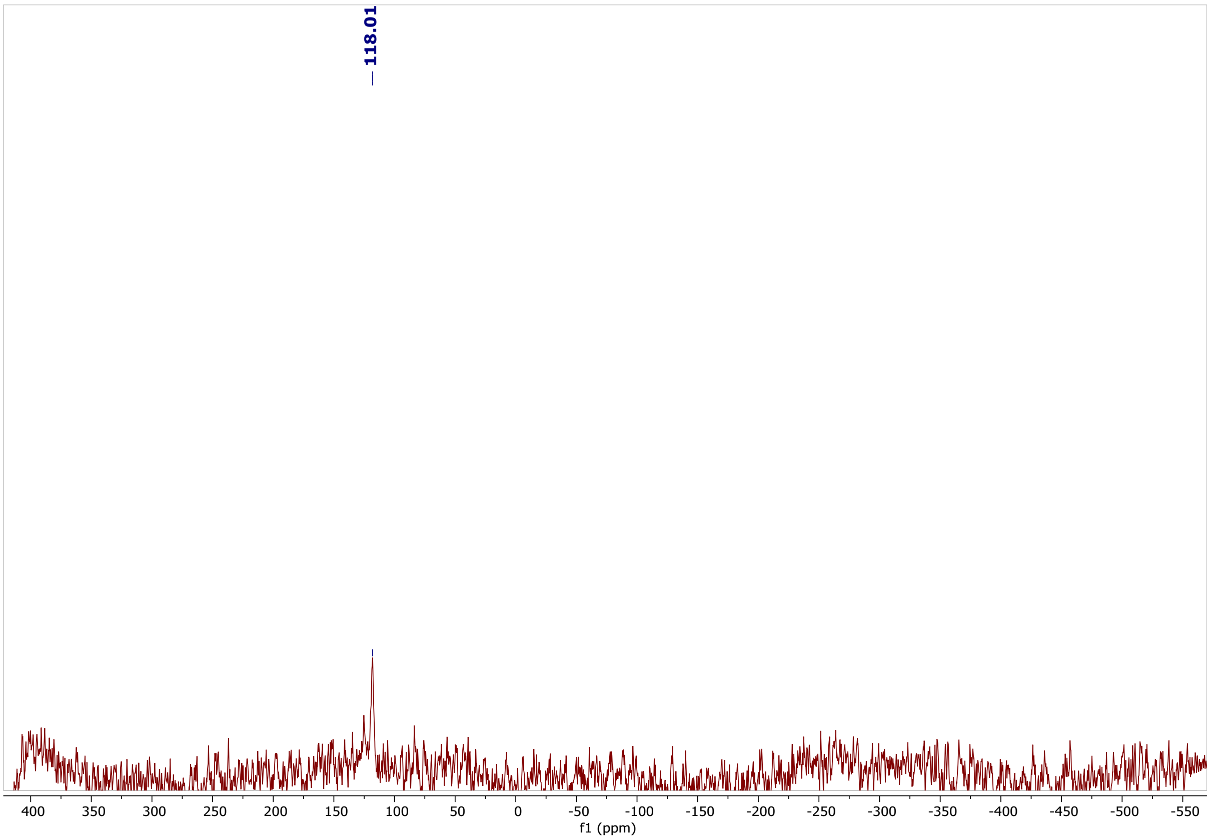


Figure S3: ^{77}Se{^{1}H} NMR spectra of [(**L**)$_2$BiCl$_2$(μ-Cl)]$_2$ CDCl$_3$ at R.T.

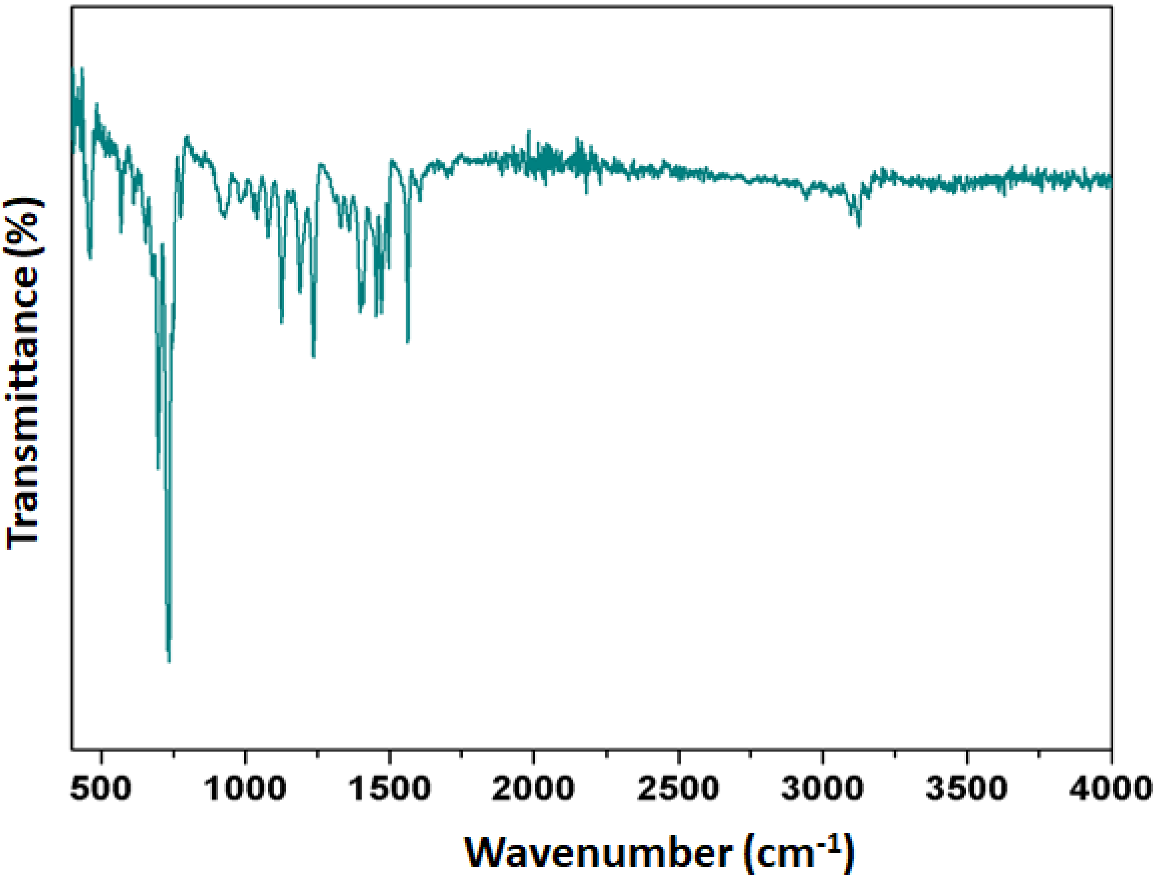


Figure S4: IR Spectrum of $[(\mathbf{L})_2BiCl_2(\mu\text{-}Cl)]_2$ in $CDCl_3$ at R.T.

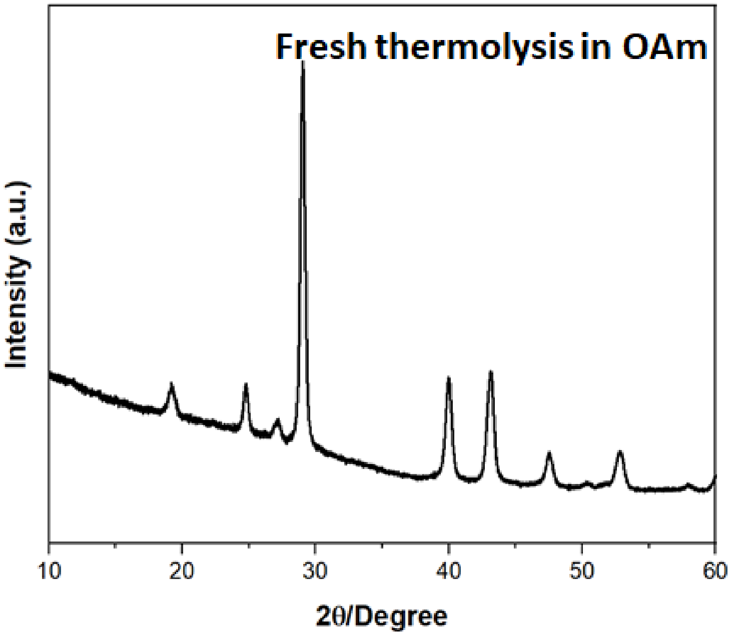


Figure S5: PXRD of crude product obtained from the solvent assisted thermolysis of complex 1

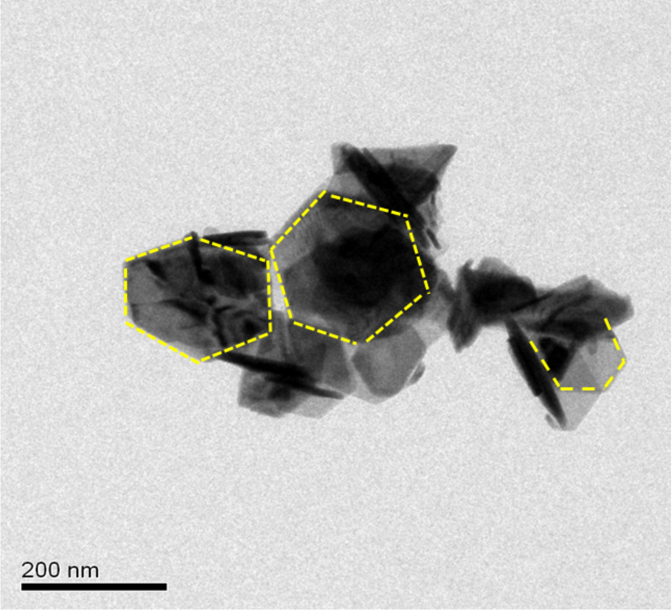


Figure S6: TEM images of the Bi_2Se_3 hexagonal nanosheets obtained in OAm at 200°C for 30 minutes using heat-up method.

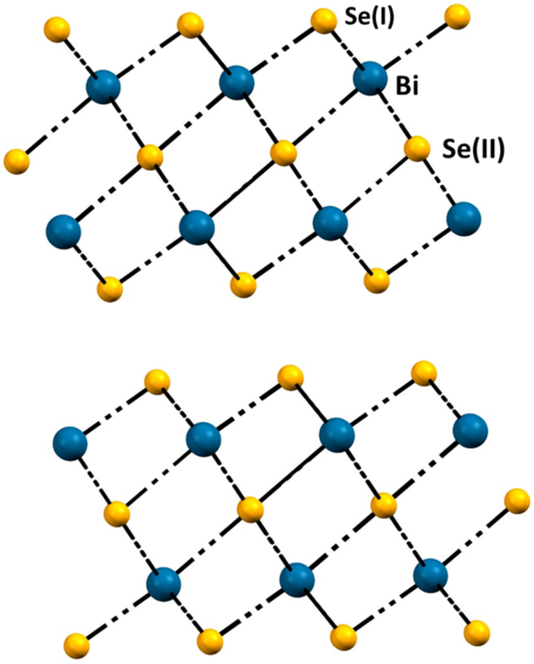
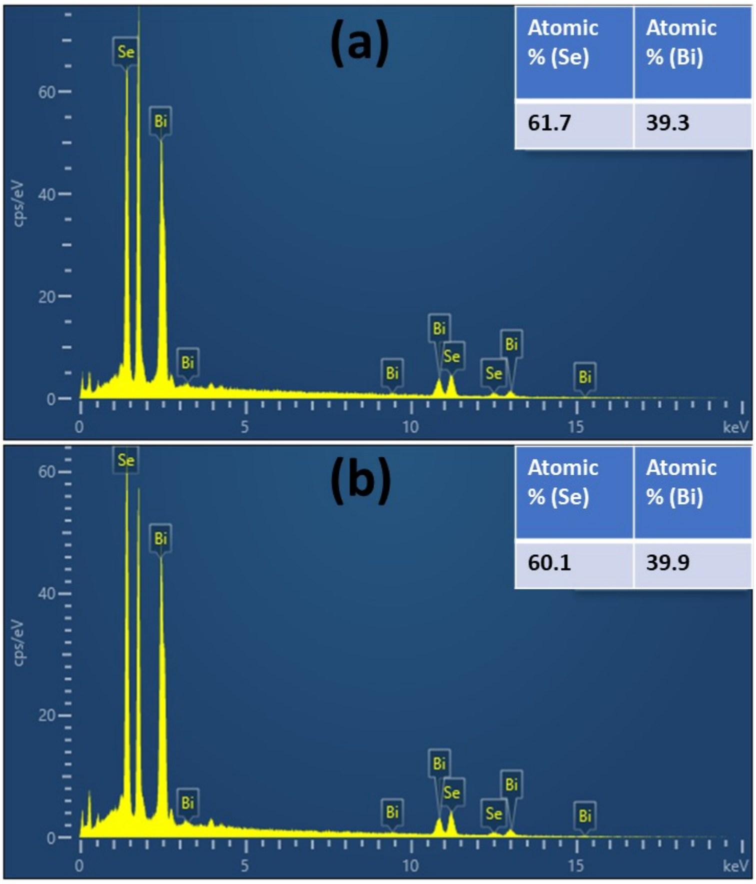


Figure S7: Crystal Structure of rhombohedral Bi_2Se_3 along a-axis (ICSD collection code 165226).



(a)

Atomic % (Se)	Atomic % (Bi)
61.7	39.3

(b)

Atomic % (Se)	Atomic % (Bi)
60.1	39.9

Figure S8: EDS spectra of (a and b) Bi2Se3 nanoplatelets and nanosheets prepared in pyrolysis and OAm, respectively.

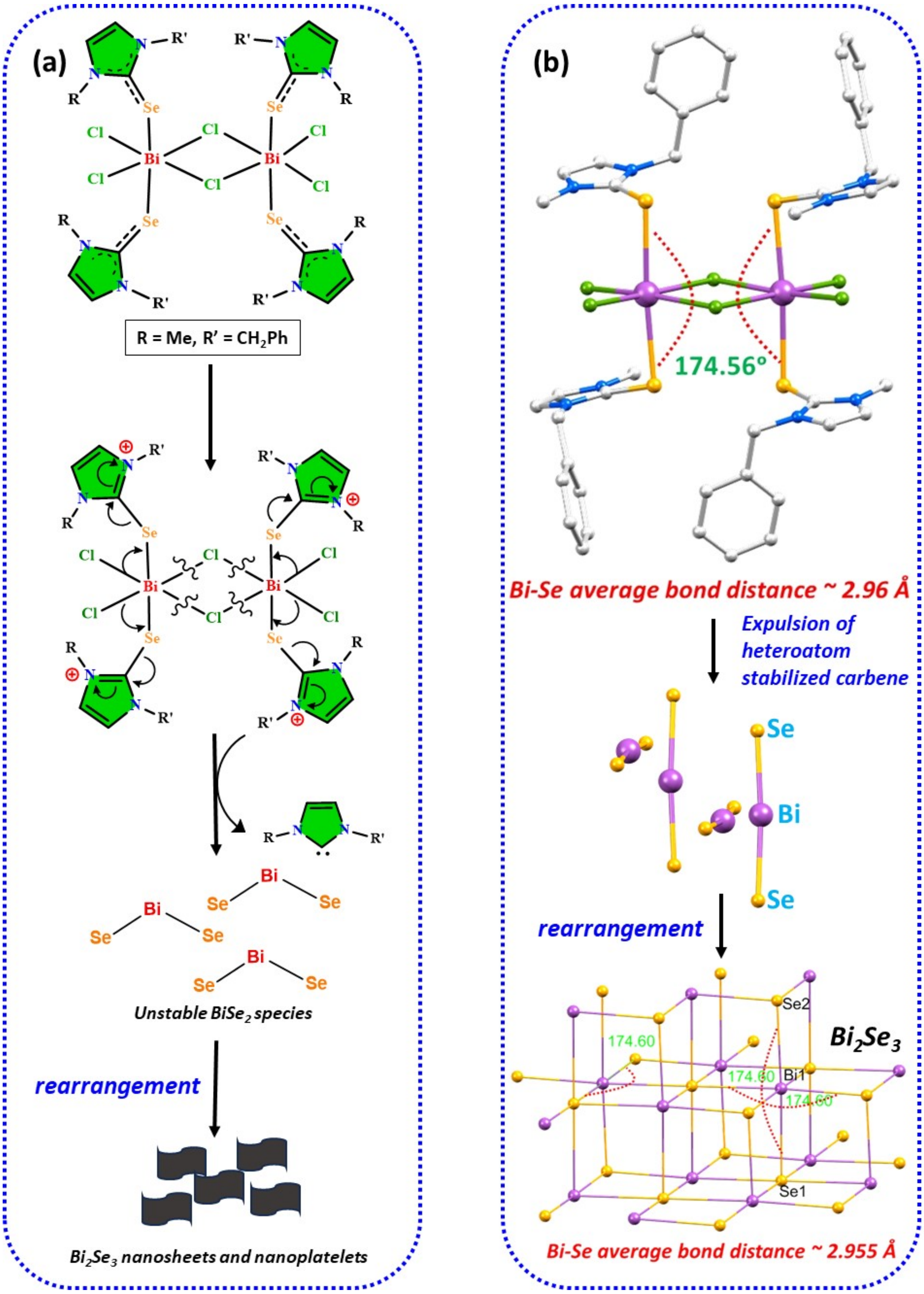


Figure S9. (a) Plausible mechanism for breakdown of the imidazole-selone precursor resulting in the formation of Bi_2Se_3. (b) resemblance of the physical parameters in the complex with that of rhombohedral Bi_2Se_3 crystal supporting the decomposition mechanism.

Table S1: Comparison of recently reported HER catalysts with Bi_2Se_3 nanosheets.

Sr. No.	Catalyst	Overpotential (η_{10} in mV)	Medium	Ref.

1	Au@Bi_2Se_3	380	0.5M H_2SO_4	5
2	Bi_2Se_3	508	0.5M H_2SO_4	5
3	FeP NPs@NPC	386	1M PBS	6
4	Ni_2P NPs@NPC	433	1M PBS	6
5	CuS	375	3M NaCl	7
6	Bi_2Se_3 nanosheets	372	1 M PBS	**This work**

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