

Controlled Synthesis of Photoresponsive Bismuthinite (Bi₂S₃) Nanostructures Mediated Through a New 1D Bismuth-pyrimidylthiolate Coordination Polymer as Molecular Precursor

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Experimental

Bismuth nitrate pentahydrate (Bi(NO₃)₃·5H₂O), oleylamine (OAm) and analytical grade solvents were obtained from commercial sources. The ligand; 4,6-dimethyl-2-mercaptopyrimidine: (2-HSpymMe₂) (¹H NMR (D₂O) δ: 2.49 (s, Me); 6.94 (s, CH-5). ¹³C{¹H} NMR (D₂O) δ: 19.6 (Me); 111.5 (CH-5); 168.0 (C-2); 173.3 (C-4,6)) was prepared according to a literature method.¹ Elemental analyses were carried out on a Thermo Fischer Flash EA1112 CHNS analyzer. The ¹H, ¹³C{¹H} and ³¹P{¹H} NMR spectra were recorded on a Bruker Advance-II NMR spectrometer operating at 300, 75.47 and 121.49 MHz, respectively. Chemical shifts are relative to internal chloroform peak for ¹H NMR spectra.

Thermogravimetric analyses (TGA) were carried out using a Nitzsch STA 409 PC-Luxx TG-DTA instrument that was calibrated with CaC₂O₄·H₂O. The TG curves were recorded at a heating rate of 10°C min⁻¹ under a flow of argon. The X-ray powder diffraction patterns were obtained using a Philips PW-1820 diffractometer using Cu-K_α radiation. Raman spectral studies were carried out on Seki's STR300 Raman spectrometer using an excitation wavelength of 532 nm. The spectrograph was calibrated using the 520.5 cm⁻¹ line from a

silicon wafer. 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 BaSO₄ which was used as the reference material. The measured reflectance data were converted to absorption (A) using the 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 using an ULTRA 55 FESEM of Zeiss and Oxford Inca instruments, respectively. A Zeiss Libra 200 FE Transmission electron microscope (TEM) operating at an accelerating voltage of 200 kV was used for TEM studies. The samples for TEM were prepared by placing a drop of sample dispersed in acetone/toluene on a carbon coated copper grid.

Single crystal X-ray data for [Bi(4,6-Me₂pymS)₃] (**1**) was collected at 100K using a Bruker APEX-II CCD, using synchrotron ($\lambda = 0.41328 \text{ \AA}$) diffraction source. Intensity data were collected using ω steps CCD area detector images spanning at least a hemisphere of reciprocal space. The crystal structure was refined by full-matrix least square methods against F^2 using SHELXL-2018/3.³ All non-hydrogen atoms were refined with anisotropically displacement parameters, and all hydrogen atoms were placed in calculated positions. Molecular structure of complex **1** was generated using Mercury 3.8.

Synthesis of [Bi(4,6-Me₂pymS)₃]_n (1**)**

To a methanolic solution of (4,6-Me₂pymSH.HCl) (87 mg, 0.62 mmol) and NEt₃ (125 mg, 1.24 mmol), solid Bi(NO₃)₃·5H₂O (100 mg, 0.21 mmol) was added. The reaction mixture was stirred for 4 hrs at room temperature. The resulting turbid solution was dried under reduced pressure. A pale-yellow solid was washed thoroughly with methanol and extracted in hot toluene-methanol mixture. The ensuing solution was kept at -5°C to afford pale yellow crystals of the title complex (yield 156 mg, 84% yield), m.p. 240°C. Anal. Calcd. for C₁₈H₂₁N₆S₃Bi: C, 34.5; H, 3.35; N, 13.41; S, 15.3 %, Observed: C, 34.4; H, 3.29; N, 13.33; S, 15.1 %.

Synthesis of bismuth sulfide nanomaterials

Bismuth sulfide nanomaterials were synthesized by thermolysis of [Bi(4,6-Me₂pymS)₃] in OAm as high boiling solvents employing heat-up method. Three sets of experiments were

carried out to investigate the effect of the reaction conditions (temperature and duration) on the phase purity and morphology of the nanostructures. In a typical heat-up method, 10 mL of OAm was taken in a three-necked round bottom flask along with 100 mg of **1** and degassed at 120°C under nitrogen flow for 30 min. Subsequently, the temperature was elevated to a predetermined value and the reaction was continued for a particular duration while maintaining the temperature, after which the reaction mixture was allowed to cool to 60°C followed by addition of 5 mL methanol to ensure complete precipitation of the nanostructures. The reaction conditions were 130°C for 10 minutes, 130°C for 30 mins and 150°C for 10 minutes. The synthesized material was collected after repeated washing with methanol and toluene mixture followed by centrifugation at 8000 rpm for 10 minutes to remove excess capping agent. The final product was collected as shiny black residue

Photo electrochemical cell experiment

Photo-responsivity of the nanostructures was measured in a photo electrochemical cell prepared by using silicon/copper selenide geometry as the working electrode, Pt wire as counter and pseudo reference electrodes, respectively and aqueous Na₂S (0.6 M): aqueous Na₂SO₃ (0.8 M) (1:2) as the electrolyte. The working electrode (silicon/Bi₂S₃) was prepared by spin coating a colloidal solution of the bismuth sulfide nanostructures in toluene on the rough surface of n-type Si wafer of (100) orientation having thickness of 200 μm and resistivity of 1-10 Ωcm. The spin coated film was dried at 150°C for 2 h under air. The process was repeated many times till a uniform coating was obtained on the silicon surface. Fluorescent white lamp (36 W, UV content < 3%) was used as radiation source with light intensity at the cell being 200 μWcm⁻².

Theoretical calculations

All calculations have been carried out using Vienna Ab-initio Simulation Package (VASP)⁴⁻⁶ software. The electron-ion interactions were described by the projector augmented wave (PAW) method.⁷ The the exchange-correlation energy has been calculated under spin polarized generalized gradient approximation⁸ using the Perdew-Burke-Ernzerhof (PBE) functional. The cut off energy for the plane wave basis set was fixed at 400 eV. Conjugate gradient minimization was used for ionic relaxation. The geometries are considered to be converged when the force on each ion becomes 0.01 eV/Å° or less. Three-dimensional

periodic boundary conditions were applied to approximate a bulk orthorhombic Bi₂S₃ (bismuthinite) (Space group: Pbnm). Conventional unit cell containing 20 atoms (8 Bi, 12S) were used for calculations. Structural optimization was performed with respect to unit cell parameters and atomic coordinates. A Monkhorst–Pack k-point grid of 5x5x5 was used to map the first Brillouin zone. The optimized lattice parameters are a = 11.276 Å, b = 11:321 Å and c = 4:073 Å, which is in good agreement with experimental lattice parameters a = 11:150 Å, b = 11:322 Å and c = 3:988 Å. Within the 3.4 Å, Bi atom surrounded by seven S atoms.

Table 1. Selected bond lengths (Å) and bond angles (°) of [Bi(4,6-Me₂pymS)₃]_n (**1**)

Bi-S(1A)	2.5837(5)	Bi-S(1B)	2.6141(4)
Bi-S(1C)	2.6546(5)	Bi-N(2A)	2.7526(17)
S(1A)-C(1A)	1.7492(17)	S(1B)-C(1B)	1.7545(18)
S(1C)-C(1C)	1.7520(16)		
S(1A)-Bi-S(1B)	79.046(15)	S(1B)-Bi-S(1C)	87.758(15)
S(1C)-Bi-S(1A)	87.168(16)	N(2A)-Bi-S(1A)	58.98(3)
N(2A)-Bi-S(1B)	137.57(3)	N(2A)-Bi-S(1C)	84.49(4)
C(1A)-S(1A)-Bi	91.24(6)	C(1B)-S(1B)-Bi	94.81(6)
C(1C)-S(1C)-Bi	94.76(6)		

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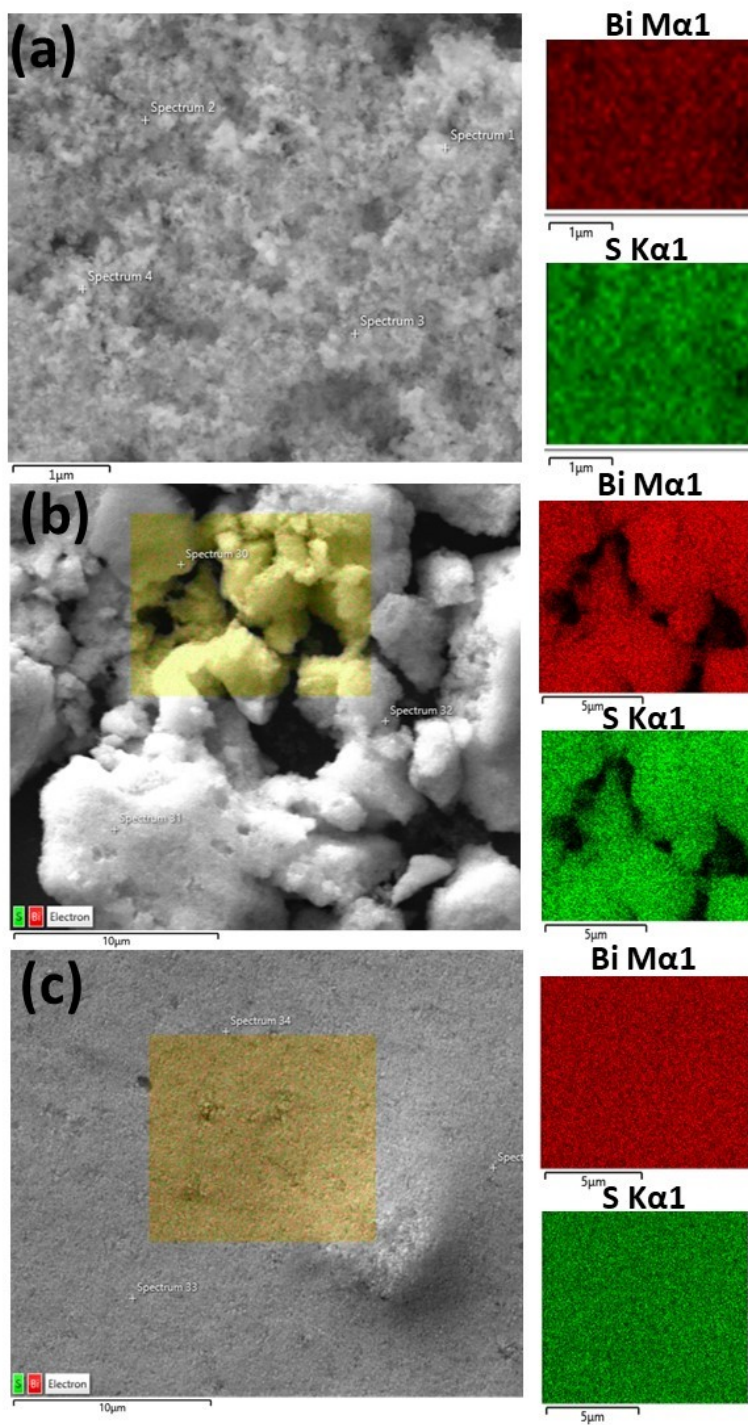


Fig. S1. 2D elemental mapping of Bi_2S_3 synthesized at (a) 110°C, 10 min (**BS1**), (b) 110°C, 30 min (**BS2**) and (c) 150°C, 10 min (**BS3**).

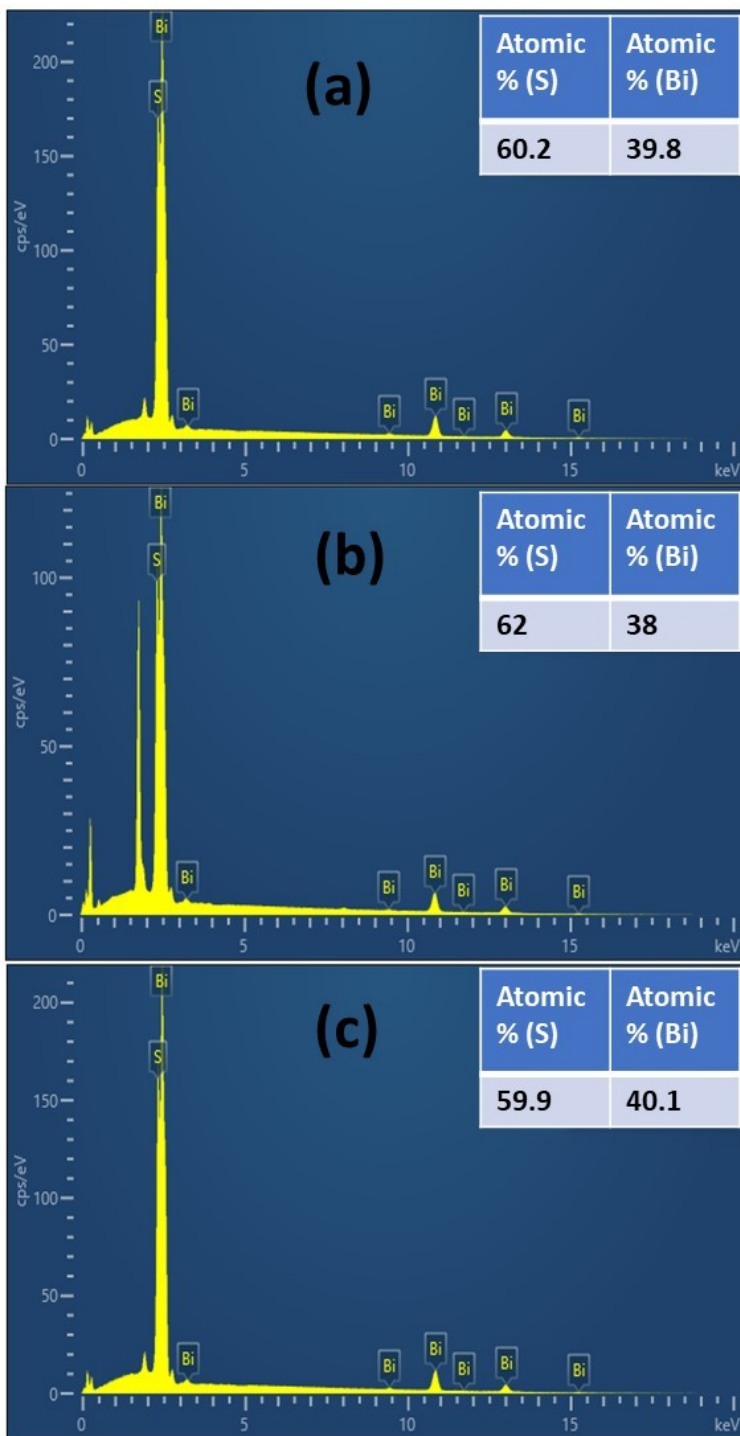


Fig. S2. EDS spectra of Bi_2S_3 synthesized at (a) 110°C , 10 min (**BS1**), (b) 110°C , 30 min (**BS2**) and (c) 150°C , 10 min (**BS3**).

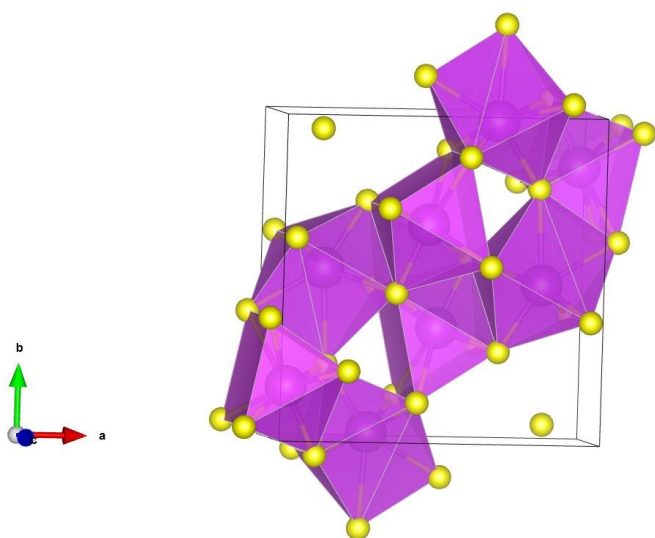


Fig. S3. Bi_2S_3 structure with each Bi atom surrounded by seven S atoms within 3.4 Å interatomic distance.