

Molecular precursor mediated facile synthesis of photo-responsive stibnite Sb_2S_3 nanorods and tetrahedrite $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ nanocrystals

Agnes Thomas,^{#a} Gourab Karmakar,^{#b,c} Alpa Y. Shah,^b Sali Vikram Lokhande,^a Atharva Yeshwant Kulkarni,^a Adish Tyagi,^{b,c*} Rohit Singh Chauhan,^{a*} N. Naveen Kumar,^d Avadhesh Pratap Singh.^e

^aDepartment of Chemistry, K. J. Somaiya College of Science and Commerce, Vidyavihar, Mumbai 400077, India.

^bChemistry Division, Bhabha Atomic Research Centre, Mumbai 400085, Homi Bhabha National Institute, Mumbai 400094, India

^cHomi Bhabha National Institute, Anushaktinagar, Mumbai- 400094, India

^dMaterials Science Division, Bhabha Atomic Research Centre, Mumbai – 400 085, India

^eDepartment of Chemistry, Kamla Nehru Institute of Physical and Social Sciences, Sultanpur-228118, India

[#]These authors contributed equally.

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

Experimental

Materials and methods

All reactions were carried out under a nitrogen atmosphere in dry and distilled analytical grade solvents at room temperature by using Standard Schlenk techniques. SbCl_3 , copper(II) acetylacetonate ($\text{Cu}(\text{acac})_2$), triethylamine, oleylamine (OAm) and analytical grade solvents were procured from Aldrich chemicals and used without further purification. The ligand, 2-Mercapto-4,6-dimethylpyrimidine was prepared according to literature methods [1]. Elemental analyses were carried out on a ThermoScientific Flash EA1112 elemental analyzer. ^1H NMR spectra was recorded on a Bruker Avance-II-300 NMR spectrometer operating at 300 MHz respectively. Chemical shifts are relative to the internal chloroform peak at $\delta=7.26$ ppm for ^1H .

Thermogravimetric analyses (TGA) were carried out using a Nitzsch STA 409 PC-Luxx TG-DTA instrument that was calibrated with $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$. The TG curves were recorded at a heating rate of $10^\circ\text{C min}^{-1}$ under a flow of argon. The X-ray powder diffraction patterns were obtained using a Philips PW-1820 diffractometer using Cu-K_α radiation. 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 [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 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 crystals [Sb(4,6-Me₂pymS)₃] were measured at room temperature 298 K on Bruker D8 Venture X-ray diffractometer having a micro-focus sealed X-ray tube Mo-K α ($\lambda=0.71073\text{\AA}$) using ω scans. The crystal structure was solved using SHELXT [3] and refined using Olex2 [4] suite. All the hydrogen atoms were geometrically fixed and refined using the riding model. Multi-scan method was employed for the absorption correction. The molecular structure was drawn using ORTEP [5]. Crystallographic and structural determination data are listed in Table 1.

Synthesis of [Sb(4,6-Me₂pymS)₃] (1)

To a methanolic solution of (4,6-Me₂pymSH·HCl) (184.31 mg, 1.31 mmol) and NEt₃ (265.92 mg, 2.62 mmol) in nitrogen atmosphere, solid SbCl₃ (100 mg, 0.44 mmol) was added. The reaction mixture was stirred vigorously for 3 hrs at room temperature. The resulting turbid solution was filtered and kept at room temperature to give pale yellow crystals of the title complex (yield 381 mg, 86% yield), m.p. 190°C (decomp). Anal. Calcd. for C₁₈H₂₂N₆SbS₃: C, 39.97; H, 4.07; N, 15.55; S, 17.77 %. Found: C, 39.74; H, 4.02; N, 15.19; S, 17.70 %. ¹H NMR (DMSO-d₆) δ (ppm): 2.22 (s, 3H, CH₃), 7.08 (s, 1H, CH).

Preparation of Sb₂S₃ and Cu₁₂Sb₄S₁₃ nanostructures

The Sb₂S₃ nanostructures were prepared by thermolysis of [Sb(4,6-Me₂pymS)₃] in OAm employing heat-up technique, whereas Cu₁₂Sb₄S₁₃ nanostructures were prepared by the co-thermolysis of [Sb(4,6-Me₂pymS)₃] and Cu(acac)₂ employing the same method.

In a typical heat-up experiment, [Sb(4,6-Me₂pymS)₃] (300 mg, 0.55 mmol) was taken into a three-necked flask containing OAm (10 mL). The solution was slowly heated upto 180°C with vigorous stirring under flowing argon and the temperature was maintained. After the required growth time (10 minutes), the heat source was removed and the temperature was rapidly brought down to 70°C before adding methanol (5 mL) to ensure complete precipitation of the

Sb₂S₃ nanostructures. 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 obtained as shiny chocolate brown residue.

For the synthesis of Cu₁₂Sb₄S₁₃ nanostructures, Cu(acac)₂ (144 mg, 0.55 mmol) and [Sb(4,6-Me₂pymS)₃] (300 mg, 0.55 mmol) (1:1 molar ratio) were co-thermolyzed in 10 mL OAm employing the same procedure as adopted for the synthesis of Sb₂S₃. The final product was isolated as shiny black residue.

Photo electrochemical cell experiment

Photo responsiveness of the nanostructures was measured in a photo electrochemical cell prepared by using silicon/Sb₂S₃ and silicon/Cu₁₂Sb₄S₁₃ geometry as the working electrode, Pt wire as counter and pseudo reference electrodes, respectively and Na₂S (0.6 M):Na₂SO₃ (0.8 M) (1:2) as the electrolyte. Working electrode of silicon/Sb₂S₃ and silicon/Cu₁₂Sb₄S₁₃ were prepared by drop casting a colloidal solution of Sb₂S₃ and Cu₁₂Sb₄S₁₃ nanostructures in chloroform on the rough surface of n-type Si wafer of (100) orientation having thickness of 200 μm and resistivity of 1-10 Ω cm. The drop casted film was dried at 150°C for 2 h. 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.

References:

1. A. Tyagi, G. Karmakar, B. P. Mandal, D. D. Pathak, A. Wadawale, G. Kedarnath, A. P. Srivastava and V. K. Jain, *Dalton Trans.*, 2021, **50**, 13073-13085.
2. B. P. Invernizzi, D. Dupont and C. Caze, *Opt. Eng.*, 2001, 40, 1082-1092
3. G.M. Sheldrick, *Acta Cryst.*, 2015, A71, 3–8.
4. O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann, *J. Appl. Cryst.* 2009, 42, 339–341.
5. C. K. Johnson, ORTEP II, Report ORNI 5136, Oak Ridge National Laboratory, Oak Ridge, 1976.

Figure captions:

Fig. S1 Packing diagram of $[\text{Sb}(\text{4,6-Me}_2\text{pymS})_3]$ (**1**) featuring (a) $\text{Sb1}\cdots\text{N6}$ and $\text{C10-H10B}\cdots\text{S1}$ and (b) $\text{C3-H3}\cdots\text{S1}$ short contacts.

Fig. S2 pXRD pattern of the residue obtained after furnace heating of $[\text{Sb}(\text{4,6-Me}_2\text{pymS})_3]$ (**1**) at a rate $10^\circ\text{C min}^{-1}$ under flowing Ar at 300°C .

Fig. S3 (a) 2-D elemental mapping and (b) EDS spectra, of Sb_2S_3 nanostructures synthesized by thermolysis of **1** in OAm at 180°C for 10 min.

Fig. S4 Selective area electron diffraction pattern of Sb_2S_3 nanorods.

Fig. S5 (a) 2-D elemental mapping and (b) EDS spectra, of $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ nanostructures synthesized by co-thermolysis of **1** with $\text{Cu}(\text{acac})_2$ (in 1:1 molar ratio) in OAm at 180°C for 10 min.

Fig. S6 The Selective area electron diffraction pattern of $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ nanocrystals.

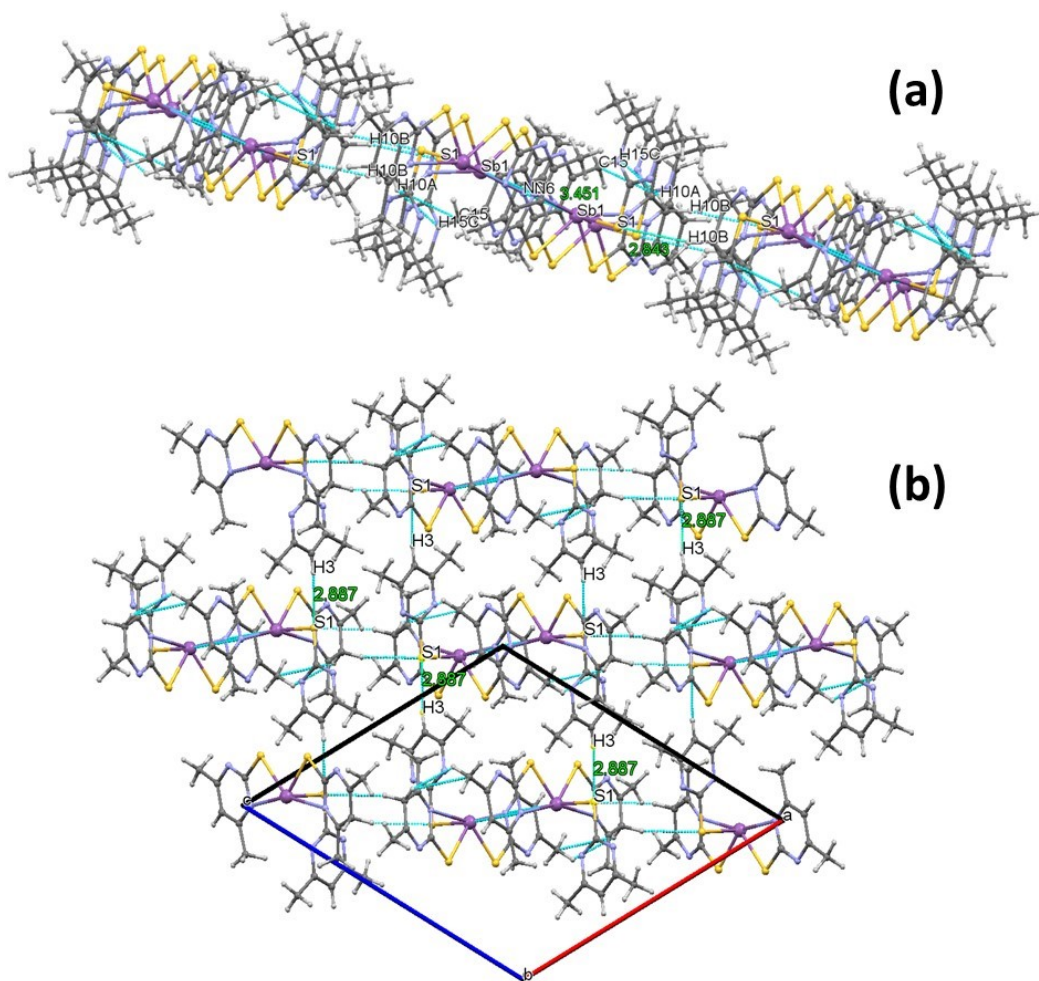


Fig. S.1. Packing diagram of [Sb(4,6-Me₂pymS)₃] (1) featuring (a) Sb1...N6 and C10-H10B...S1 and (b) C3-H3...S1 short contacts.

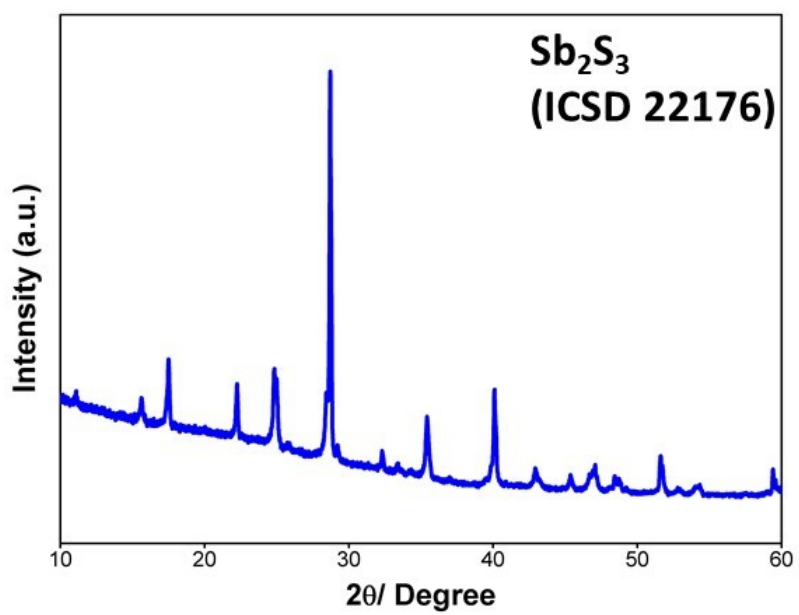


Fig. S.2. pXRD pattern of the residue obtained after furnace heating of [Sb(4,6-Me₂pymS)₃] (1) at a rate 10°C min⁻¹ under flowing Ar at 300°C.

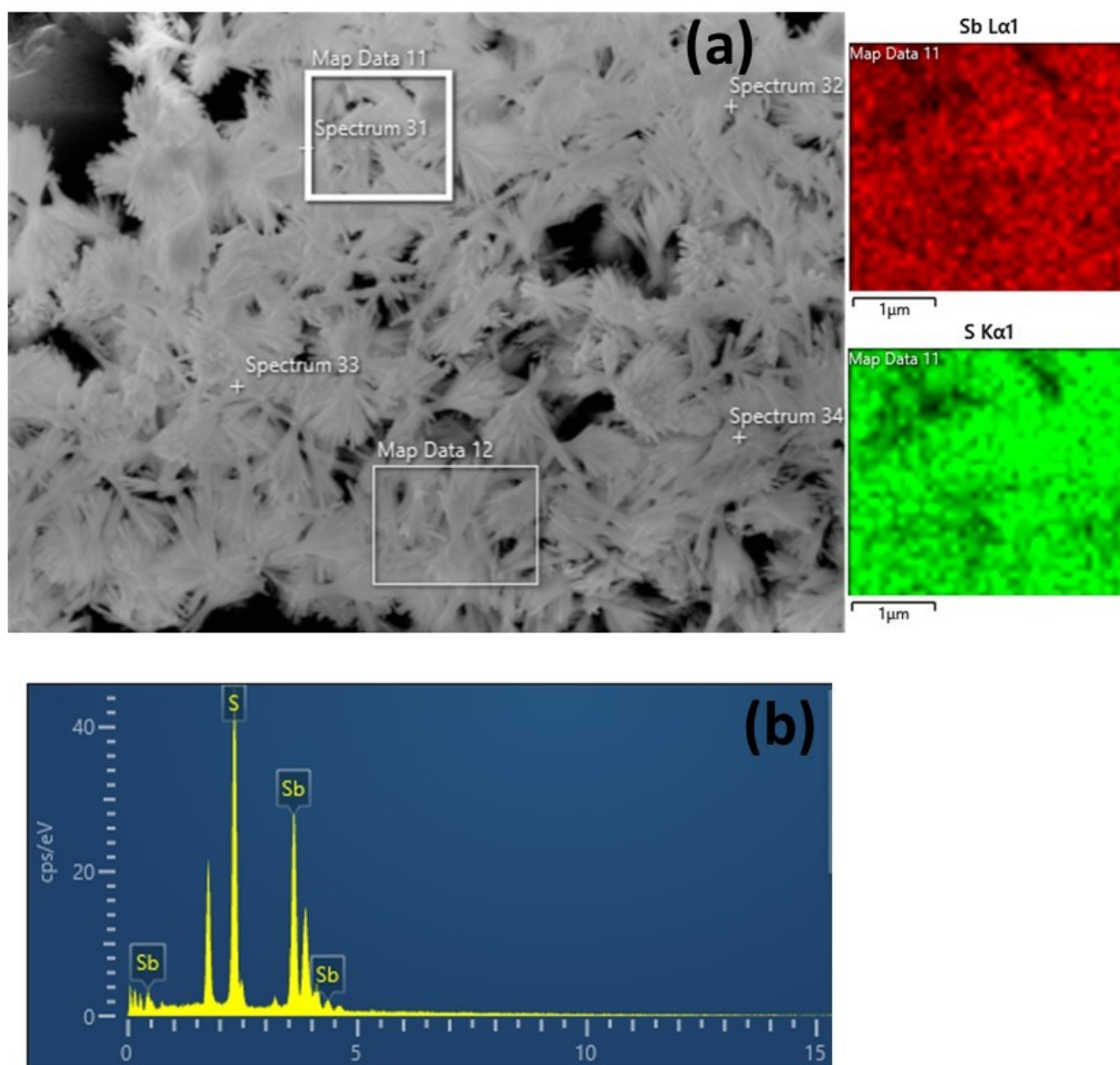


Fig. S3 (a) 2-D elemental mapping and (b) EDS spectra of Sb_2S_3 nanostructures synthesized by thermolysis of **1** in OAm at 180°C for 10 min.

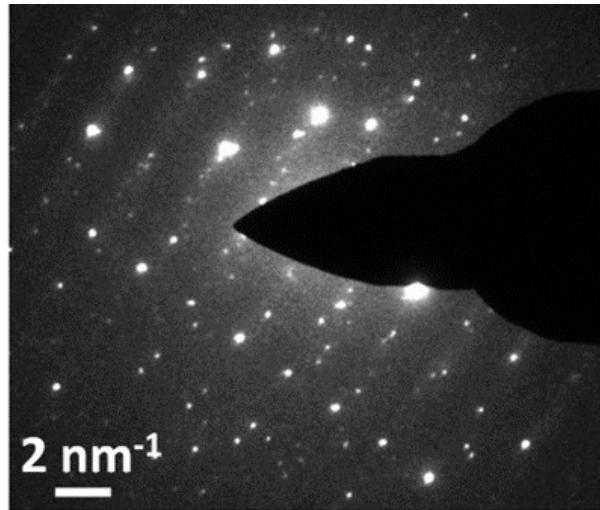


Fig. S4 Selective area electron diffraction pattern of Sb_2S_3 nanorods.

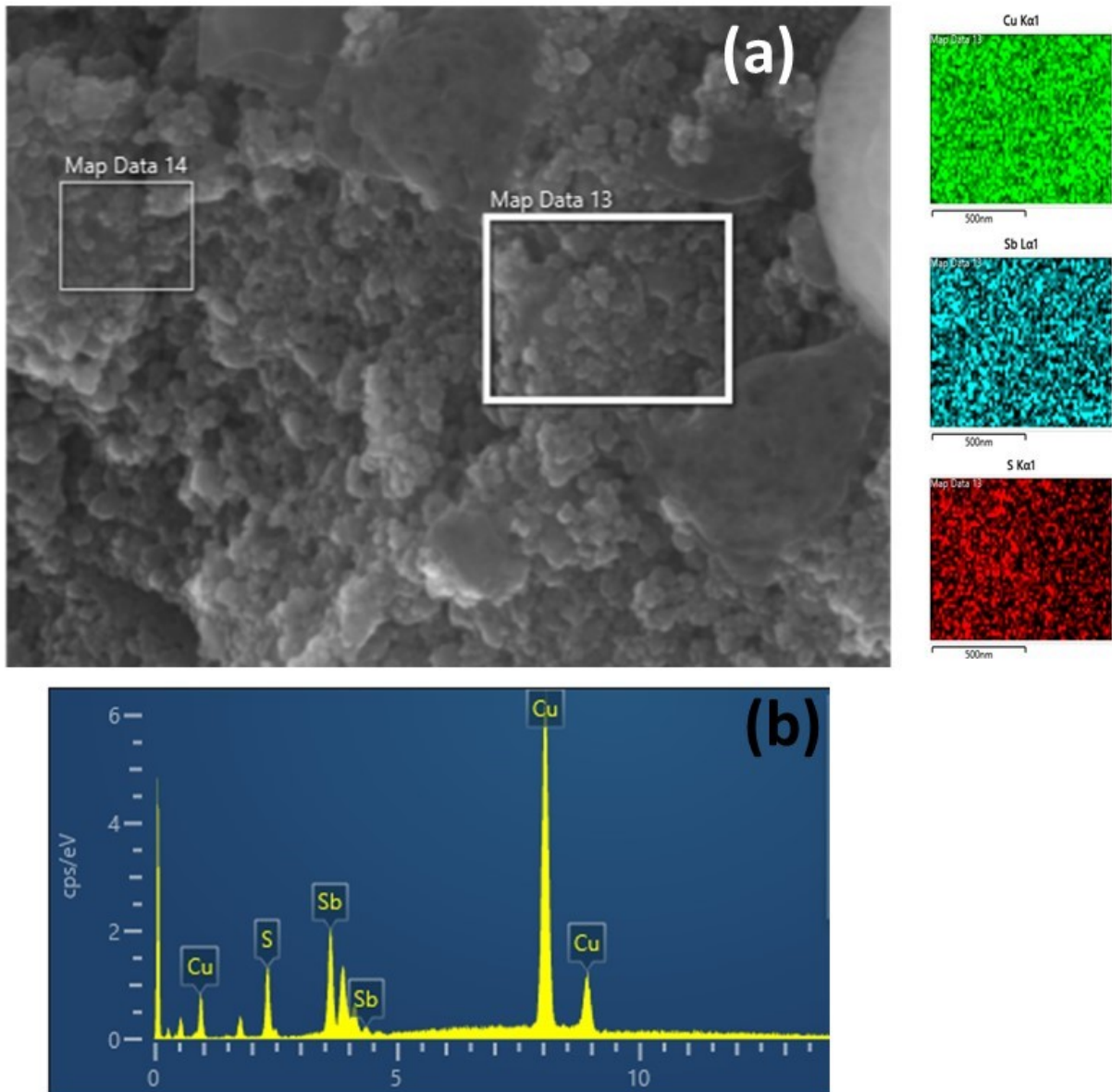


Fig. S5 (a) 2-D elemental mapping and (b) EDS spectra of $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ nanostructures synthesized by co-thermolysis of **1** with $\text{Cu}(\text{acac})_2$ (in 1:1 molar ratio) in OAm at 180°C for 10 min.

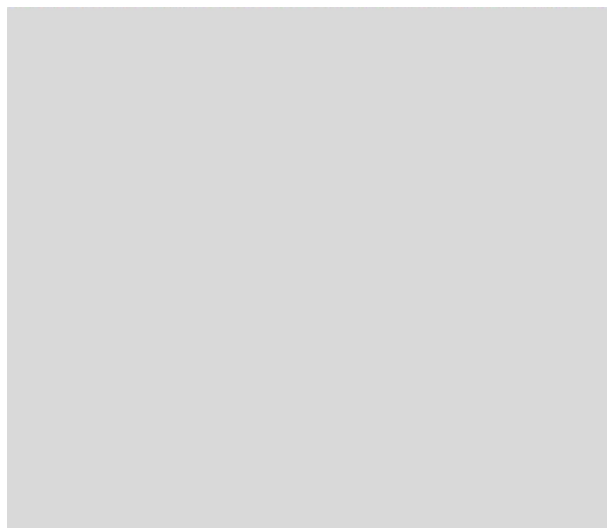


Fig. S6 Selective area electron diffraction pattern of $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ nanocrystals.