

Supporting Information for

Colloidal Synthesis of the Mixed Ionic-Electronic Conducting NaSbS₂ Nanocrystals

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1. Experimental Section:

1.1. Chemicals: Sodium hydroxide (**NaOH**), Triphenyl antimony (**Ph₃Sb**), Sulphur powder, oleic acid (**OA**), Oleylamine (**OLA**), Lauric acid (**LAc**), octanoic acid (**OctAc**) and butanoic acid (**ButAc**), dodecyl amine (**DDAm**), octyl amine (**OctAm**), butyl amine (**ButAm**), anhydrous hexane, acetone and methanol were purchased from sigma Aldrich and used without further purification treatment.

1.2. Preparation of Oleylamine-Sulfur complex (OLA-S). S source was made by stirring 0.3 mmol of sulphur powder in 2 mL of OLA under Ar atmosphere until a red solution formed.

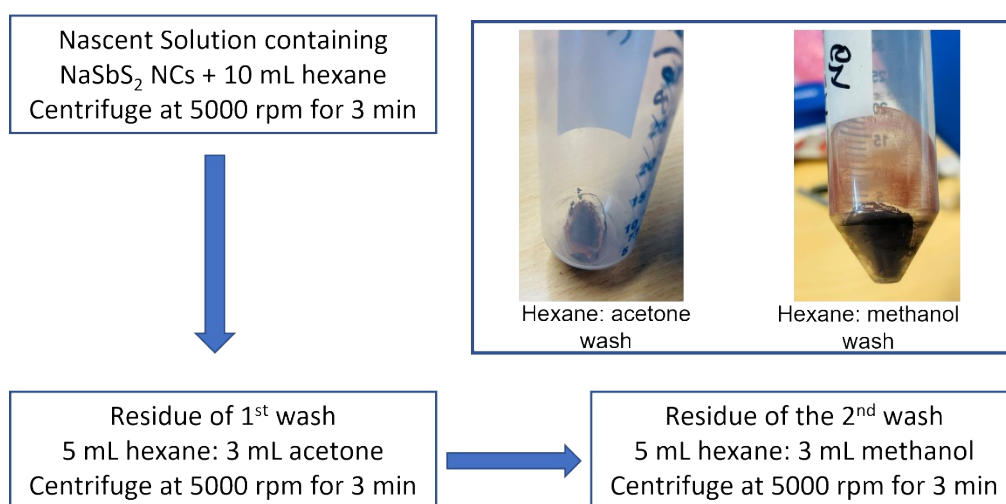
1.3. Synthesis of NaSbS₂. For the synthesis of NaSbS₂ NCs, a total of 0.4 mmol of a 3:1 molar mixture of NaOH (0.3 mmol/11.7mg) and Ph₃Sb (0.1 mmol/35mg) powder was stirred with 8 mL (0.024 moles) of OLA and 2 mL (0.006 moles) of OA. For 30 minutes, the reaction solution was evacuated at 120 °C. During the evacuation, the pressure of the vacuum pump was maintained below 200 mTorr. The reaction mixture was then heated to 250 °C in an argon atmosphere. After heating the solution to 250 °C, 2 mL of OLA-S precursor was rapidly injected. The reaction solution was kept at this temperature for 30 minutes after injection. The flask was then cooled to 90 °C by disconnecting the heating mantle. The final NaSbS₂ NCs were precipitated by adding 8 mL of hexane followed by centrifugation as described below.

1.4. Synthesis of NaSbS₂ at different temperatures. In a three-neck flask containing 8 mL of OLA and 2 mL of OA, NaOH (0.3 mmol/11.7mg) and Ph₃Sb (0.1 mmol/35mg) powder were introduced to synthesize NaSbS₂ at different reaction temperatures. For 40 minutes, the mixture was evacuated at 120 °C. After heating the solution to 280 and 310 °C in an argon atmosphere, 2 mL of OLA-S precursor was rapidly injected. After injection, the reaction solution was held at this temperature for 30 minutes. By removing the heating mantle, the flask was cooled to 90 °C. To precipitate the NaSbS₂ NCs, 8 mL of hexane was added.

1.5. Synthesis of NaSbS₂ with different chain length ligands. We conducted two studies using systematic ligand composition change keeping the molar ratio of amine: acid (4:1 moles) constant to explain the effect of ligands. Oleic acid (OA) or oleylamine (OLA) was used as the starting materials for each reaction, while the counterpart was changed with acid or amines of different chain length. In one series of experiment the reaction was carried out using a combination of oleylamine and different chain length carboxylic acids including lauric acid (**LAc**), octanoic acid (**OctAc**) and butanoic acid (**ButAc**) while in another series the reaction was carried out using oleic acid and different amine like dodecyl amine (**DDAm**), octyl amine (**OctAm**) and butyl amine (**ButAm**).

1.6. Purification of the NCs. The synthesized NCs quenched with 10 mL of hexane were transferred in 50 mL centrifuge tubes and vortex properly, then centrifuged for 3 minutes at 5000 rpm. The supernatant was discarded and the residue was

collected. At this stage in the residue, two different products (reddish NCs with some white gel-like by-products) could be distinguished by color. We used a mixture of nonpolar and aprotic polar solvents to remove by-products. The residue was dispersed in a mixture of hexane (5 mL) and acetone (3 mL). The solution was then centrifuged at 5000 rpm for 5 minutes. We were able to reduce gel-like by-product but it was still present with the NCs in the residue. The residue was then further purified with a methanol/hexane (3 mL:5 mL) solution at 5000 rpm for 5 minutes. We noticed the complete removal of the by-product (white gel) after methanol/hexane wash. The NCs were then characterized with different techniques as mentioned below.



Scheme S1: Schematic description of washing procedure for purification of NCs.

2. Characterization Methods.

Transmission electron microscopy (TEM) and angular dark-field scanning transmission electron microscopy (DFSTEM) of synthesized NCs was carried out using a 200 kV JEOL JEM-2011F microscope equipped with a Gatan camera. Washed samples were drop casted on a glass slide for XRD analysis. The XRD patterns of samples reported were acquired on an Empyrean X-ray diffractometer equipped with a Cu K α radiation and a Lynxeye one dimensional detector. The XPS analysis of samples were carried out on Kratos Axis Ultra spectrometer. Binding energies (BE) were determined using C 1s at 284.8 eV as a charge reference. The samples were drop-cast on glass slides and dried under Ar before measurements. FTIR measurements were performed on a PerkinElmer FTIR instrument. The previously washed and dried sample was used for FTIR measurements.

3. Transport properties measurements.

Approximately 0.1 g of NC was synthesized for transport property measurements. The NCs were carefully washed via a series of washing cycles to remove the surface ligands until they were unable to disperse well in the solvent. Before measuring the

transport properties, the washed NCs were vacuum-dried overnight in an oven at 80 °C. The dried powder was then cold pressed into a 60 μm thick pellet at a pressure of 5 MPa for 60 seconds using 100 mg of NaSbS_2 powder.

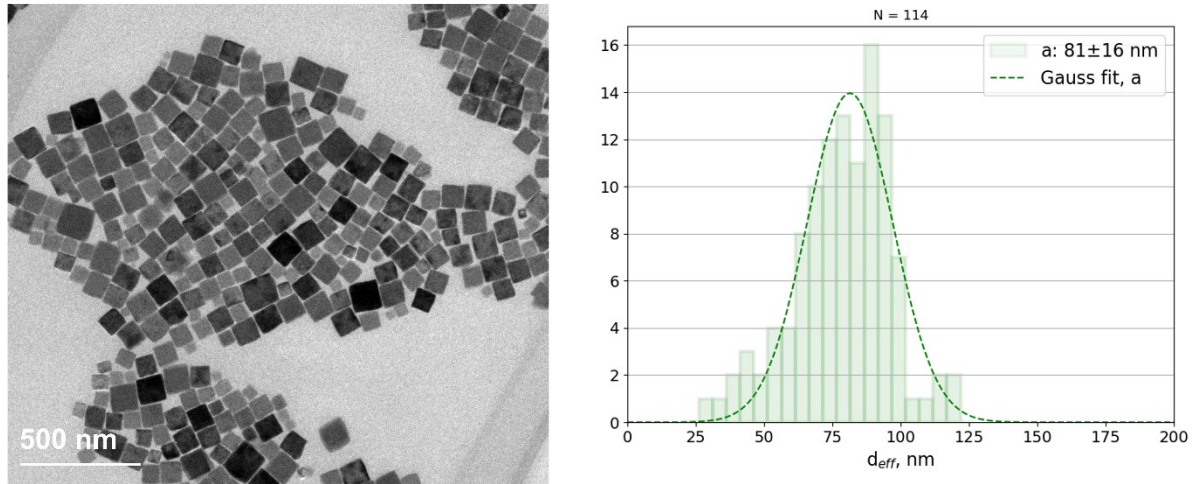


Figure S1. Size distribution histogram for NaSbS_2 synthesized at 250 °C.

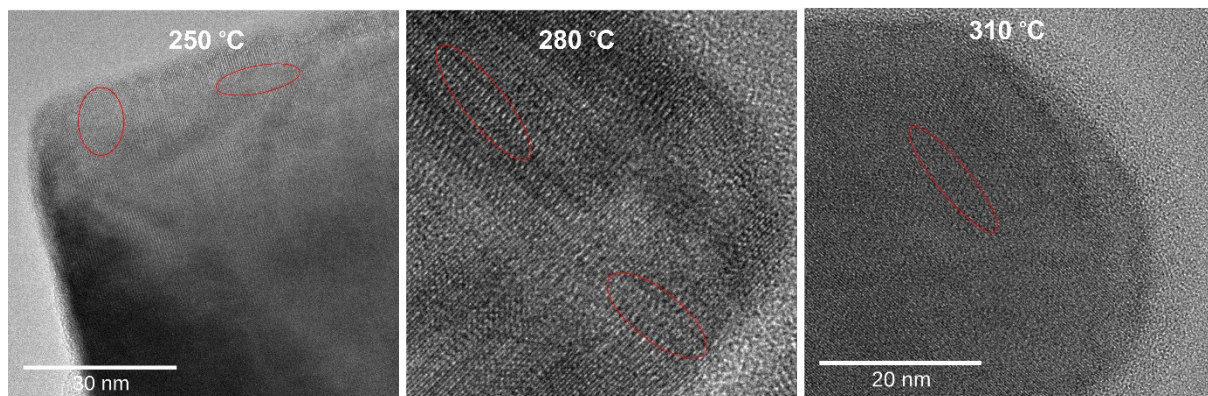


Figure S2. HRTEM of NaSbS_2 NCs synthesized at different reaction temperatures (250, 280 and 310 °C) respectively.

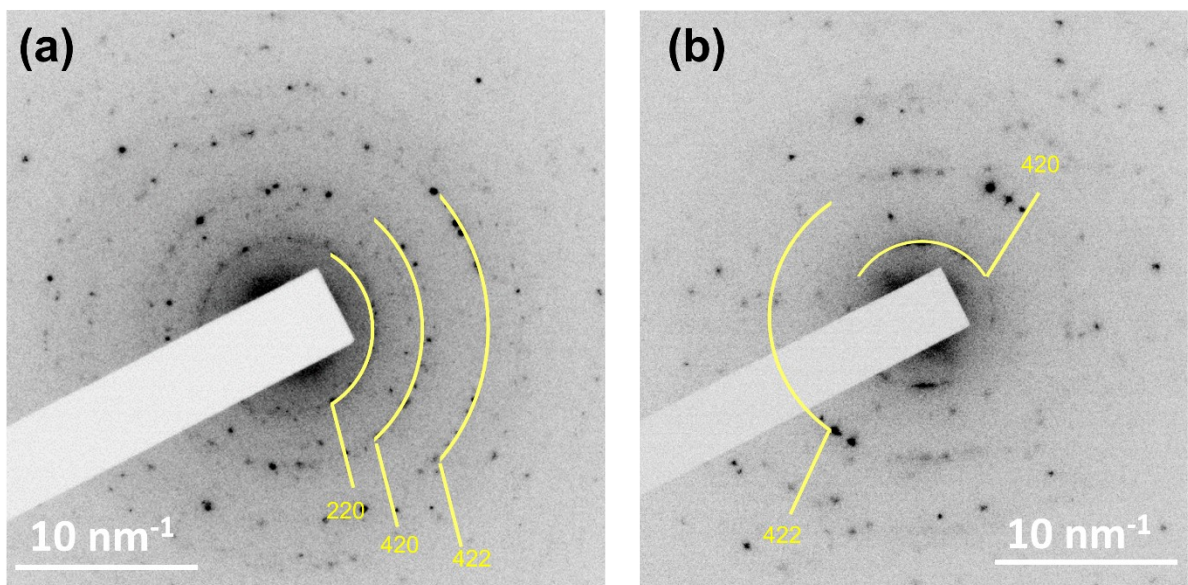


Figure S3. (a, b) Selected area electron diffraction pattern for NaSbS₂ NCs obtained at different temperatures (280 and 310 °C) respectively.

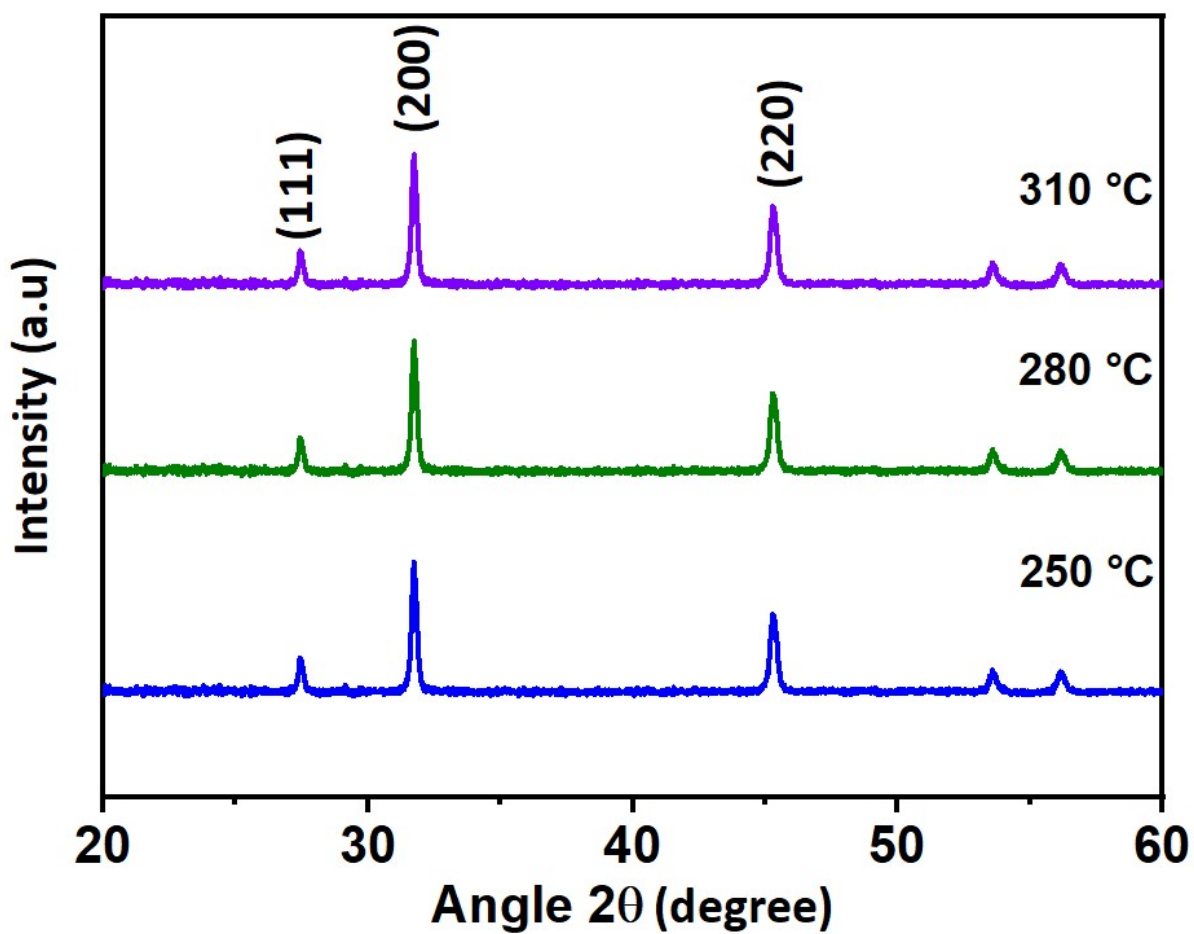


Figure S4. XRD spectra of NaSbS₂ NCs synthesized at 250, 280 and 310 °C

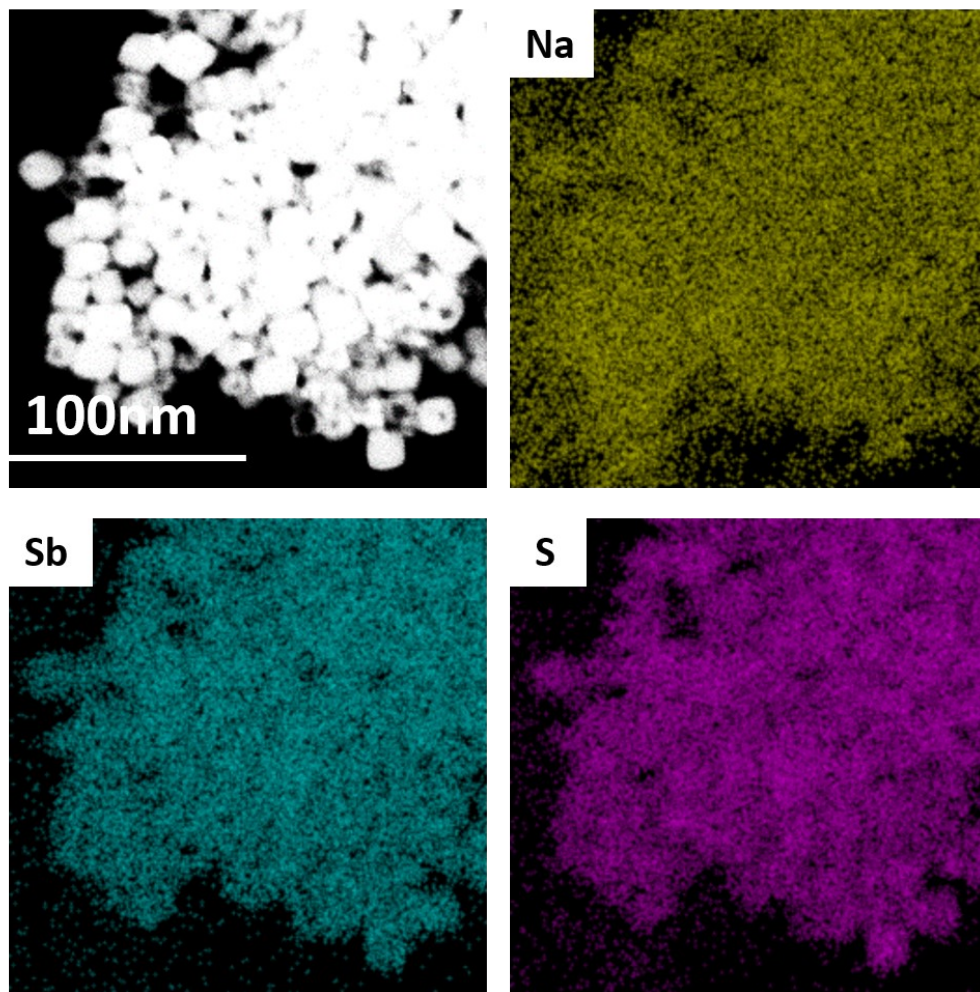


Figure S5. EDX elemental mapping for NaSbS₂ nanocubes for 280 °C sample.

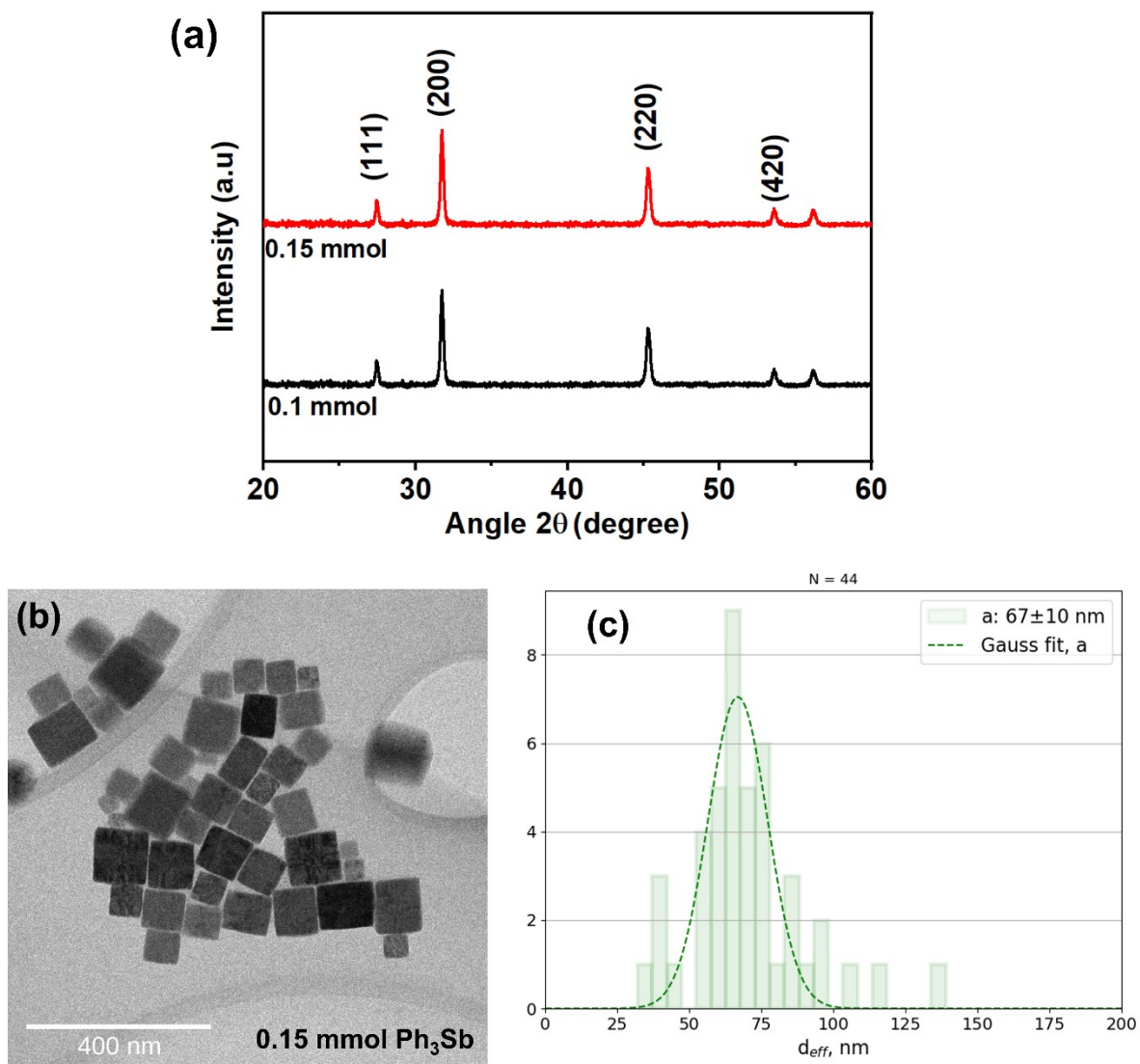


Figure S6: (a) TEM images of NaSb_2 NCs grown from 0.15 mmol Sb precursor, (b) XRD pattern of NaSb_2 NCs prepared using 0.1 and 0.15 mmol of Sb precursor.

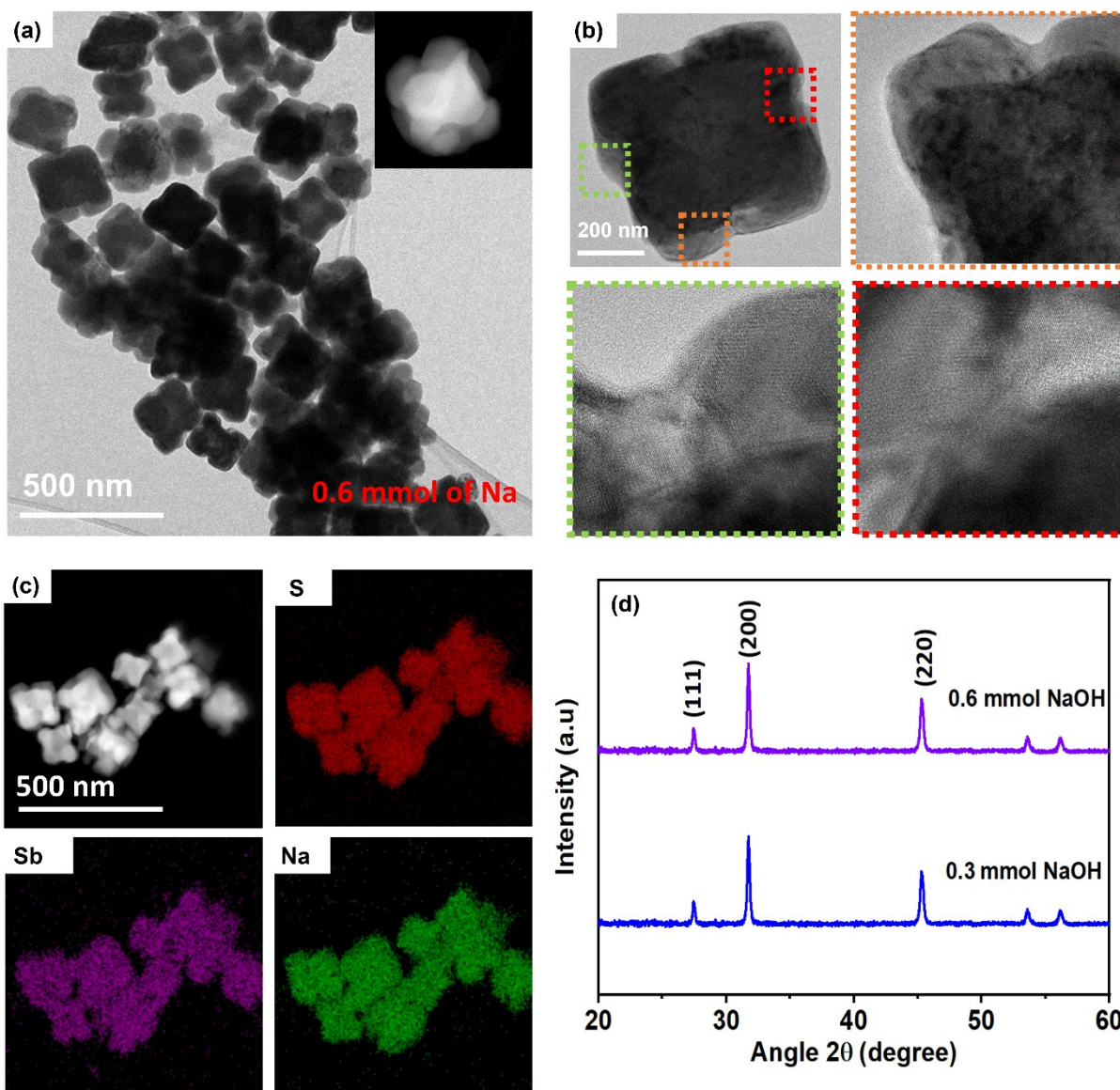


Figure S7: (a, b) TEM images and magnified TEM images of selected areas of NaSbS₂ NCs grown from 0.6 mmol Na precursor, (c) EDX elemental mapping of the NaSbS₂ NCs for the sample prepared with 0.6 mmol of Na precursor, and (d) XRD pattern of NaSbS₂ NCs prepared using 0.3 and 0.6 mmol of Na precursor.

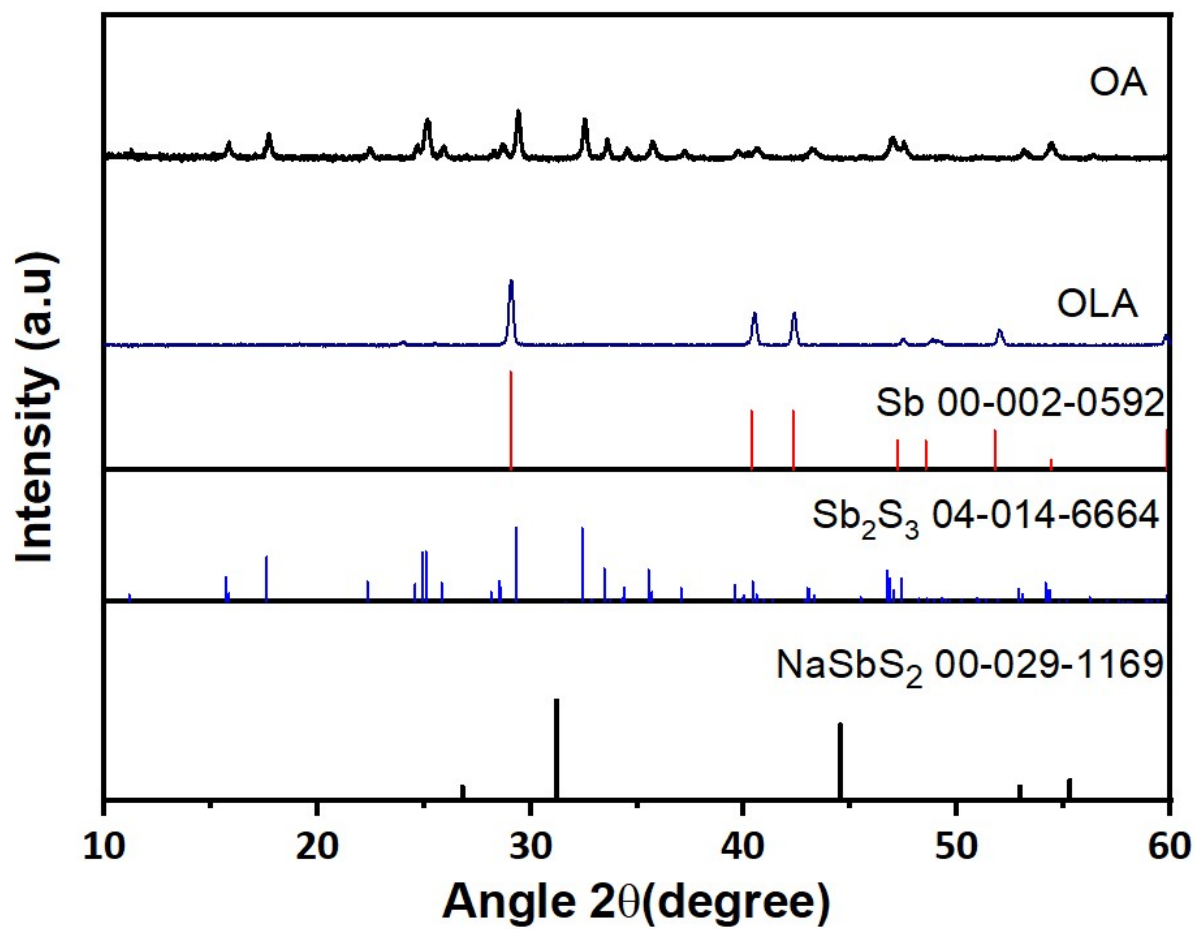


Figure S8. XRD pattern of ligand-controlled reactions for NaSbS₂.

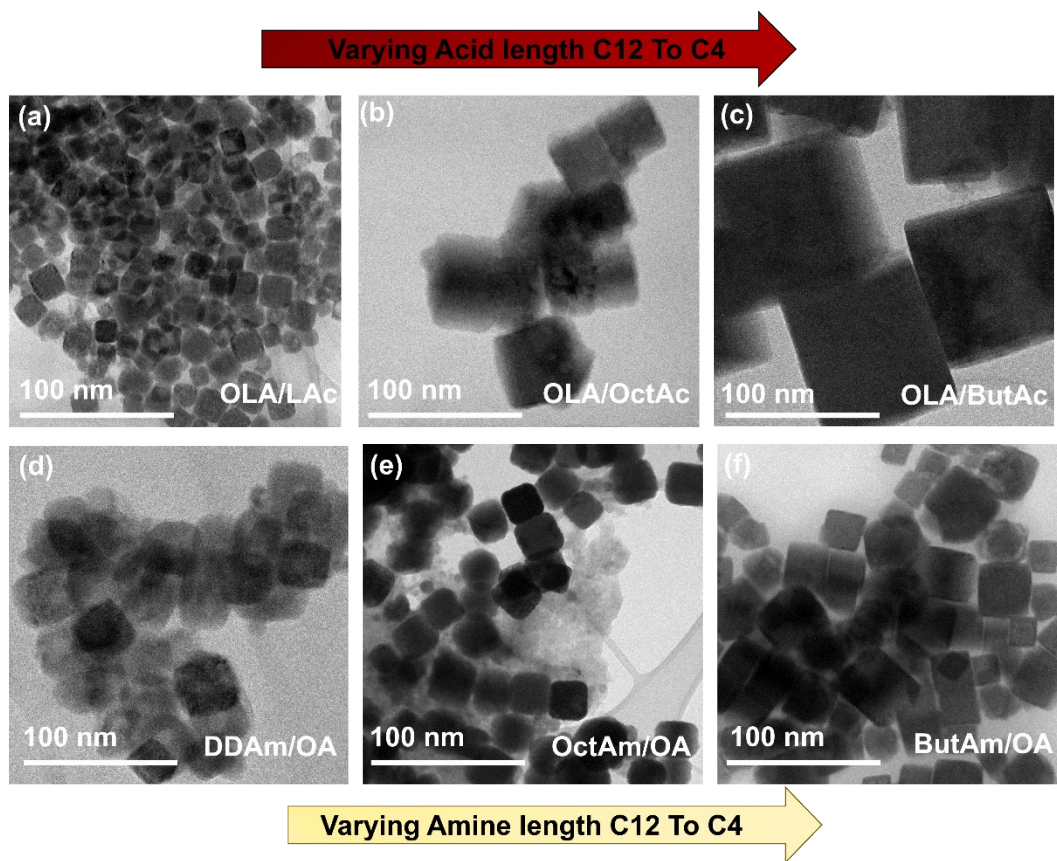


Figure S9: Low resolution TEM images of NaSbS_2 NCs from 250 °C using acid and amines of different chain lengths. Panel (a-c) shows TEM images for variation of acid from C12 to C4 . Panel (d-f) shows TEM images of amines from C12 to C4.

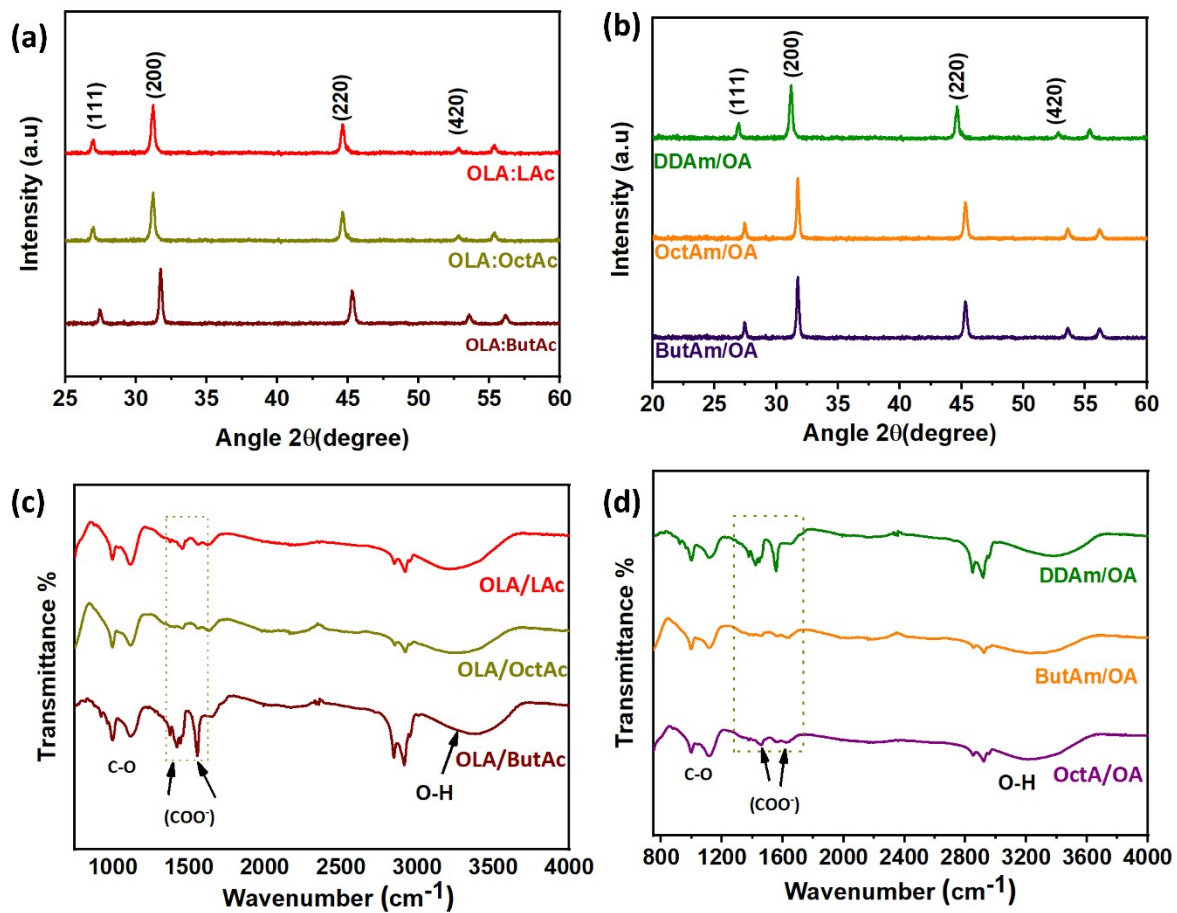


Figure S10. XRD pattern of NaSbS₂ NCs synthesized with different chain length of (a) carboxylic acid (b) amines and FTIR spectra (c and d respectively).

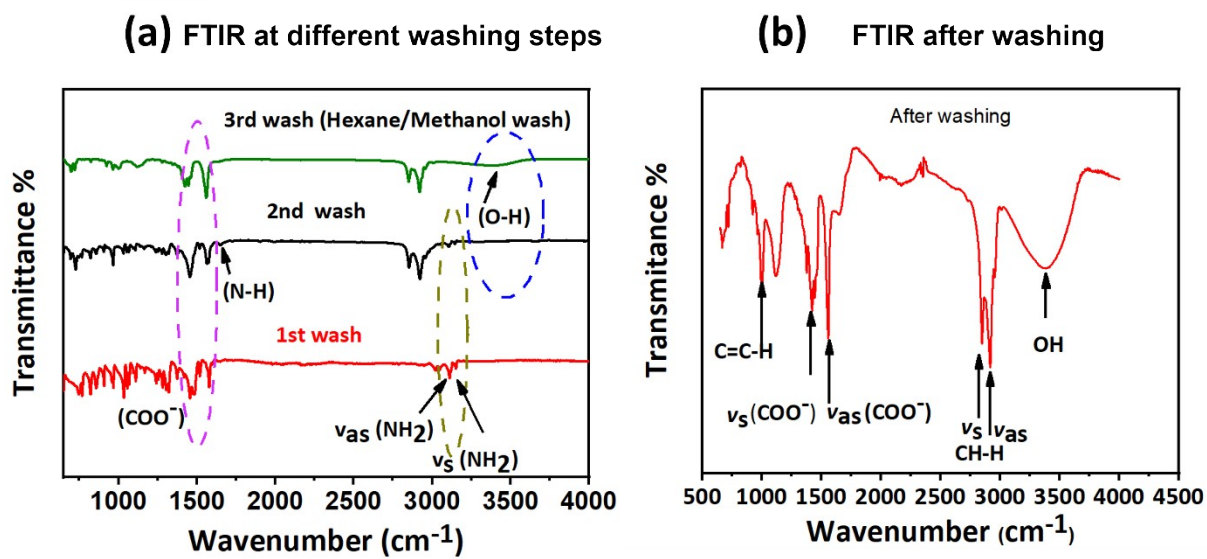


Figure S11. (a) shows FTIR spectra of the NaSbS₂ sample at different washing steps and (b) shows FTIR spectra of the NaSbS₂ sample after purification.

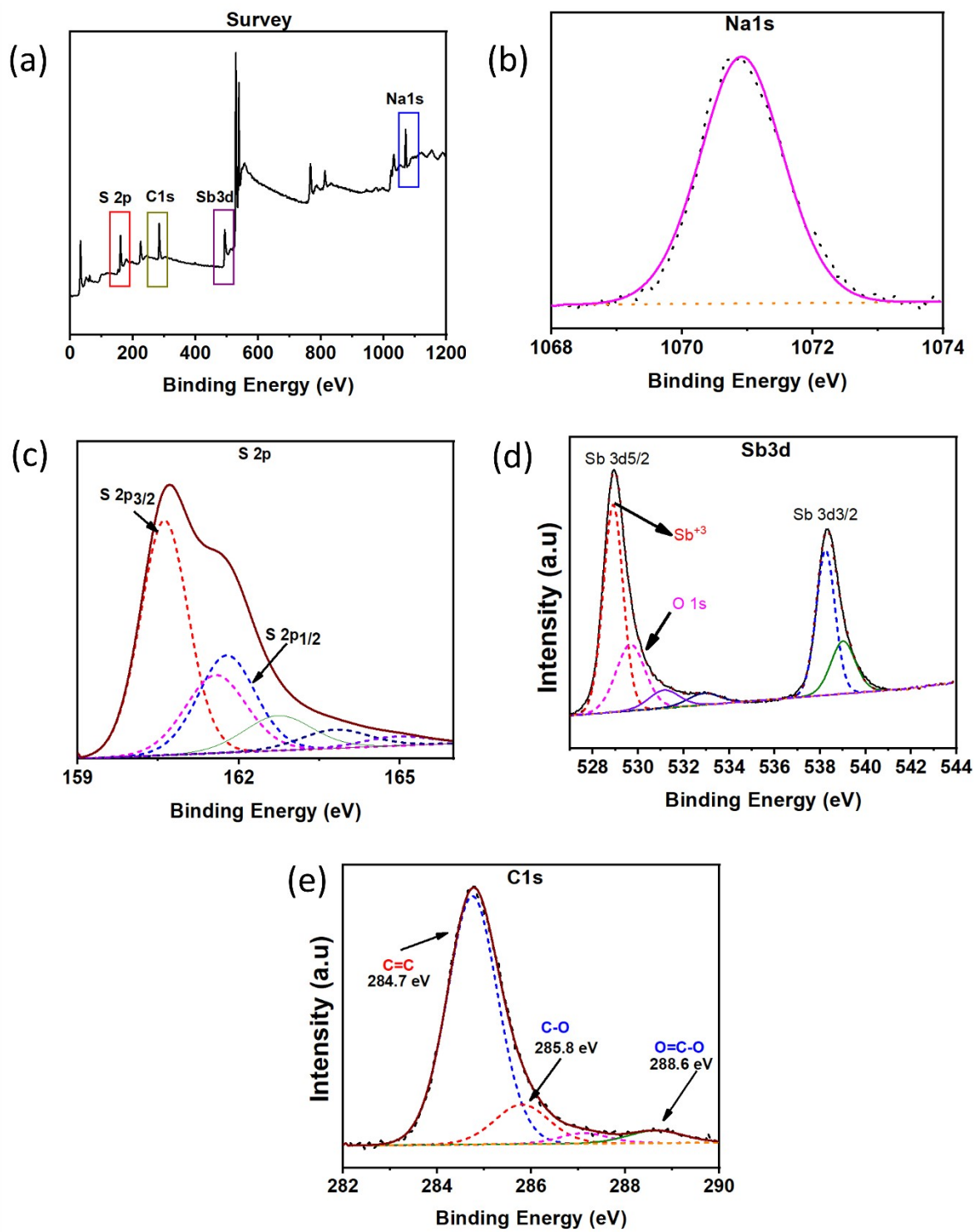


Figure S12. XPS analysis of cubic NaSbS_2 (a) survey (b) Na 1s (c) S 2p (d) Sb 3d (e) C 1s.

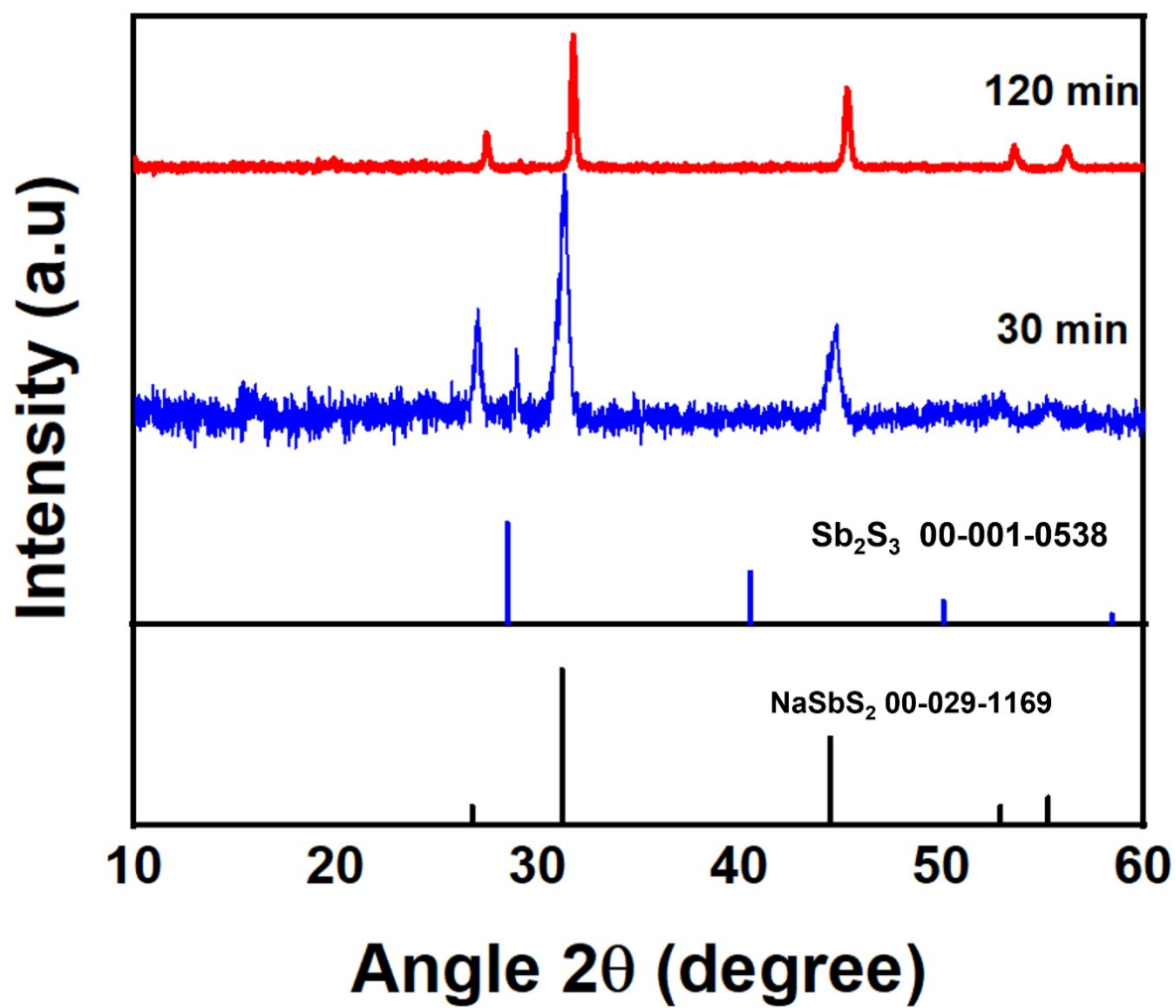


Figure S13: Xrd of NaSbS₂ NCs prepared using Na oleate and Sb oleate at 250 °C.

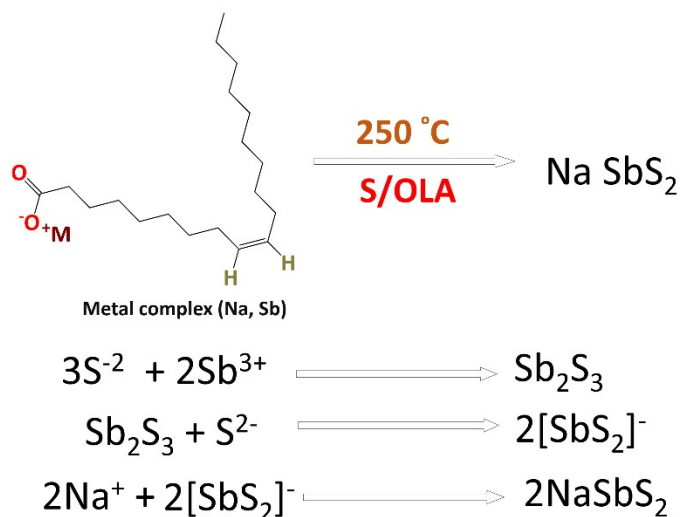


Figure S14. Schematic for the proposed reaction mechanism for the synthesis of NaSbS₂.

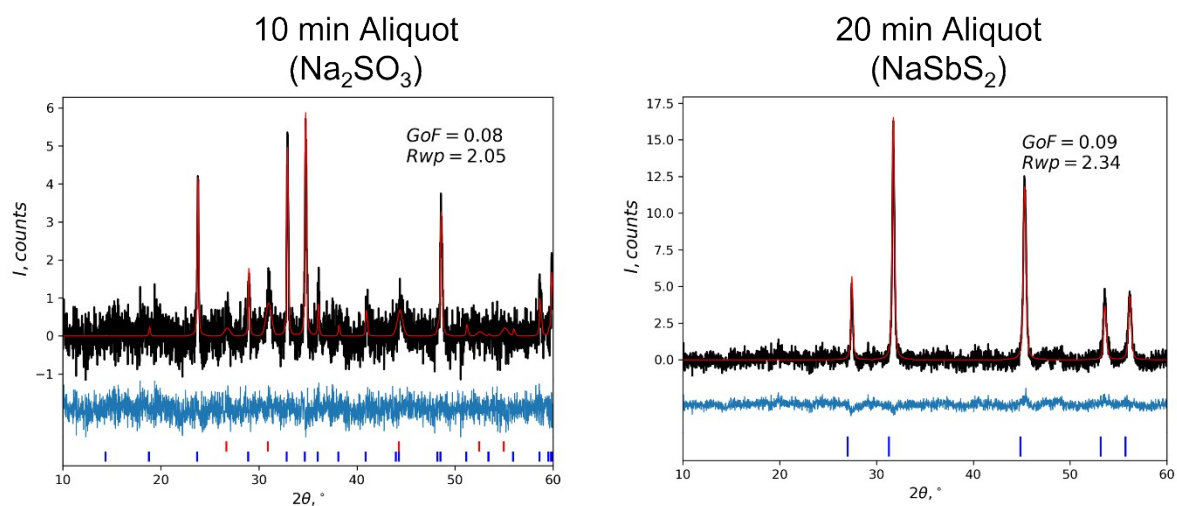


Figure S15: Rietveld refinement graphs of the XRD pattern of 10 min and 20 min aliquots. The lattice parameters fit with the CIF file 00-005-0653 (Na₂SO₃) and 00-029-1169 (NaSbS₂).

Table S1: Table collated different reaction conditions for the synthesis of NaSbS₂.

Sr#	Reaction precursors	Reaction time	Product	Reaction temperature	Solvent	Injection
1	Sb ₂ S ₃ + S + Na ₂ S.9H ₂ O	2 hr	Sb ₂ S ₃	250 °C	OLA/ODE	
2	Sb(III) acetate + Na ₂ S + 1-ddt	30min	Sb ₂ S ₃	250 °C	OLA/ODE	
3	Sb (III) Cl + Na ₂ S + S	1hr	Sb ₂ S ₃ +NaCl	250 °C	OLA/ODE	
4	Sb (III) Cl + NaOH + S		Sb ₂ S ₃ +NaCl	250 °C	OLA/ODE	
5	Ph ₃ Sb + NaOH + S	3 hr	NaSbS ₂ + Sb ₂ S ₃	250 °C	OLA/OA/ODE	
6	Ph ₃ Sb + NaOH + S	30min to 5hr	NaSbS ₂	250 °C	OLA/OA	
7	Ph ₃ Sb + NaOH + S	30	NaSbS ₂	150 to 350 °C	OLA/OA	
8	Ph ₃ Sb + NaOH + S	30	NaSbS ₂	250 °C	OLA/OA	Double injection
9	Ph ₃ Sb + Na ₂ S + S + NaOH	30	NaSbS ₂	250 °C		Excess of sulphur
10	Sb ₂ S ₃ + S + NaOH + 1-ddt	12hr	Sb ₂ S ₃	250 °C	OLA/OA	

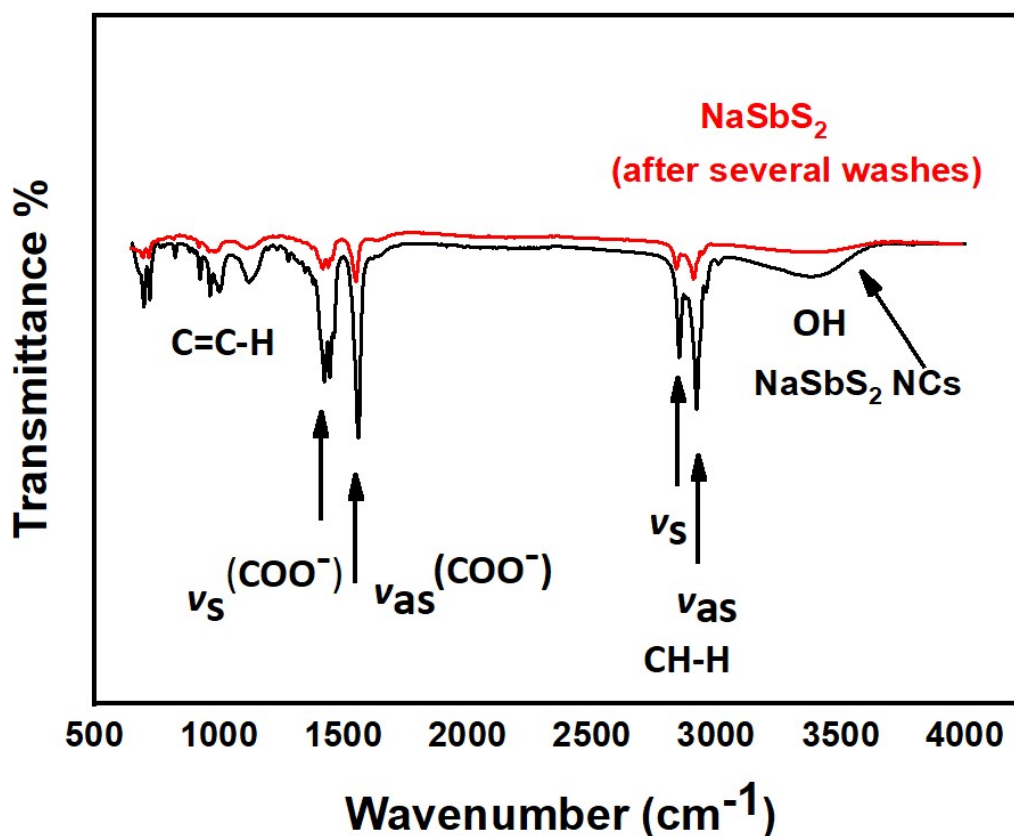


Figure S16. shows FTIR spectra of the NaSbS₂ NCs after washing and NaSbS₂ NCs after several washes for transport properties measurements.