Supplementary Information

Electrospray Deposition-Induced Ambient Phase Transition in Copper Sulphide Nanostructures

Arijit Jana, Sourav Kanti Jana, Depanjan Sarkar, Tripti Ahuja, Pallab Basuri, Biswajit Mondal, Sandeep Bose, Jyotirmoy Ghosh, Thalappil Pradeep*

DST Unit of Nanoscience (DST UNS) and Thematic Unit of Excellence (TUE), Department of Chemistry, Indian Institute of Technology, Madras, Chennai – 600036, India.

*Email: pradeep@iitm.ac.in

Table of Contents

Experimental Section

1) Electrospray deposition:

Electrospray deposition experiments were carried out using a home-made nanospray emitter. For all the ESD experiments, a glass capillary emitter was tailored by pulling borosilicate glass capillary of proper dimension (0.86 mm inner diameter, 1.5 mm outer diameter and 1.5 cm length) using a micropipette puller instrument (P-97) purchased from Sutter instruments, USA. A platinum filament was used to cut the glass capillary into two parts. Prior to making ultrafine capillary tip (20 to 25µm), operating conditions of the micropipette puller were set as heating temperature of 565 ^{o}C, initial and final pull velocities of 11 µm/sec and 9 µm/sec, respectively. Optical microscopic images of the as prepared capillary tips are shown in the Fig. S1. Sulphur solution in toluene: methanol mixture (8:2, v/v) was filled in the capillary tip, by using a capillary injector. Finally, a platinum wire connected with the positive terminal of the high voltage DC power supply was inserted inside the capillary and while the negative terminal was connected to the copper plate to generate the spray plume. Formation of spherical sulphur was observed during ESD. Fig. S2 shows the TEM images of the sulphur particles with diameters of 100 to 150 nm, after 1 min sulphur spray over the TEM grid. A 532 ±10 nm (≤ 10 mW) green laser pointer was used for confirming the generation of the spray plume. This laser pointer was purchased from UKTECHLAB, UK. During ESD, spray current was measured by using a Keithley Picoammeter. All the spray current data are summarized in Table S1. To confirm the chemical nature of the spray plume, mass spectrum was collected using an ion trap LTQ XL (Thermo Scientific) mass spectrometer.

2) Solution phase photoconductivity measurements of Cu_2S nanopyramids:

For the photoelectrochemical measurements of the Cu_2S nanopyramids, a CHI600A potentiostat was used, while impedance spectroscopic measurements were carried out by using a Bio-Logic SP-200 instrument. Both the electrochemical measurements were performed in 0.01 (M) Na_2SO_4 solution, used as an electrolyte. A 195 W white light source from Newport, India was used as a source for solar energy irradiation. The formation of the gas bubbles during photo-electrochemical process was analyzed by a Thermostar Balzer MS instrument. Quadstar 32 Bit software was used to record the data.

3) Solid state conductivity measurements of $Cu_{1.8}S$ platelets assembled film:

For studying the electrical property of the $Cu_{1.8}S$ platelets, we peeled off the platelets by using a Scotch tape. Basic schematic representation of the peeled off methods was shown in Fig. S8. After etching the platelets from the copper plate, a black thin film was formed on the Scotch-tape. Continuous

arrangements of the platelets was confirmed by using optical and SEM images, shown in Fig. S9 and S10, respectively. This film was used to measure the electrical conductivity. Afterwards, we made four probe contacts on the film by using silver paste and ultrafine copper wires. Among four contacts, two contacts were connected to the positive terminal and while the other two contacts were connected to the negative terminal of the potentiostat. A CHI600A instrument was used to study the current-voltage (I-V) response of the film in a wide potential range (-1.5V to +1.5V).

Instrumentation

1) Microscopic characterization:

All the SEM measurements were performed using a FEI Quanta environmental scanning electron microscope (ESEM) in the high vacuum mode. EDAX spectra were recorded using the same instrument. TEM measurements were performed using a JEOL 3010 high resolution transmission electron microscope (HRTEM) operated at 200 kV. A Gatan 794 multiscan CCD camera was used for image collection. All the optical microscopic images were collected using a LEICA optical microscope with LAS V4.8 software.

2) Spectroscopic characterization:

Raman spectroscopic measurements were carried out by using a confocal Raman microscope, CRM Alpha 300 S, WITec GmbH, Germany by using 532 nm frequency doubled Nd: YAG laser with 40 mW output power (sample power was used ≤ 5 mW). X Ray photoelectron spectroscopy (XPS) measurements were carried out using an ESCA probe TPD equipped with polychromatic Mg Kα X ray light source (hγ =1253.6 eV). Powder XRD measurements were conducted using a D8 Advance Bruker, using Cu Kα as the X Ray source (hγ = 8047.8 eV).

Optical absorption spectroscopic measurements were carried out in the solid state, by using a Perkin Elmer LAMBDA 950 UV-VIS-NIR spectrophotometer. Spectrum was collected in the diffuse reflectance mode (% R) using 60 mm integrating sphere. Perkin Elmer UV Win-lab 6.4.0.973 software was used to collect the spectrum in reflectance mode and the spectrum was converted to Kubelka Munk (K-M) absorption spectrum. Solid state photoluminescence spectral measurements were carried out using the same Raman microscope.

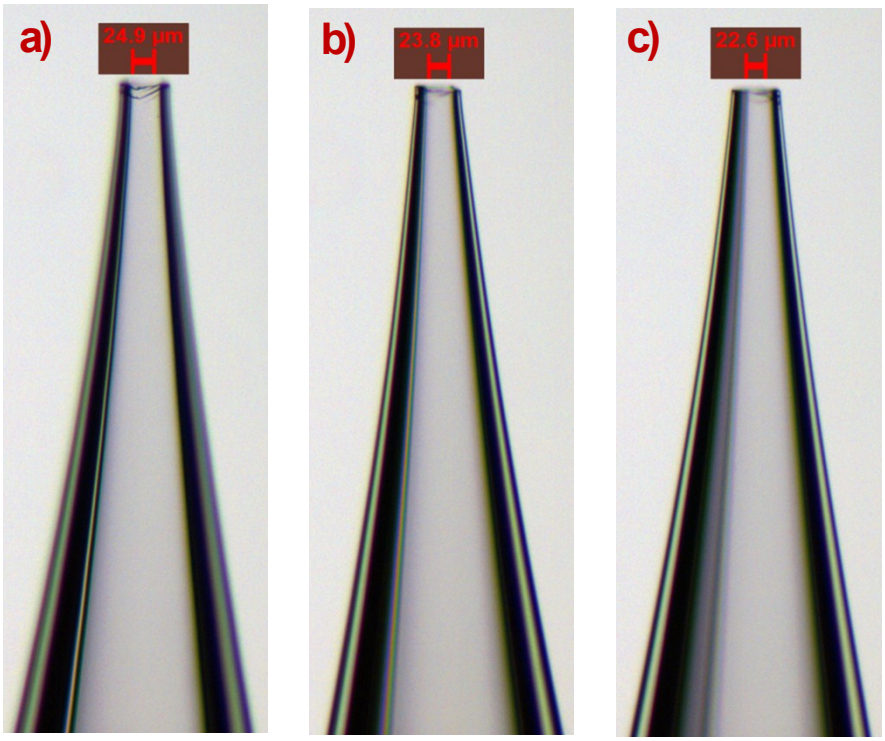

Fig. S1 Optical microscopic images of three different capillary tips, made separately with tip diameters of a) 24.9, b) 23.8 and c) 22.6 µm.

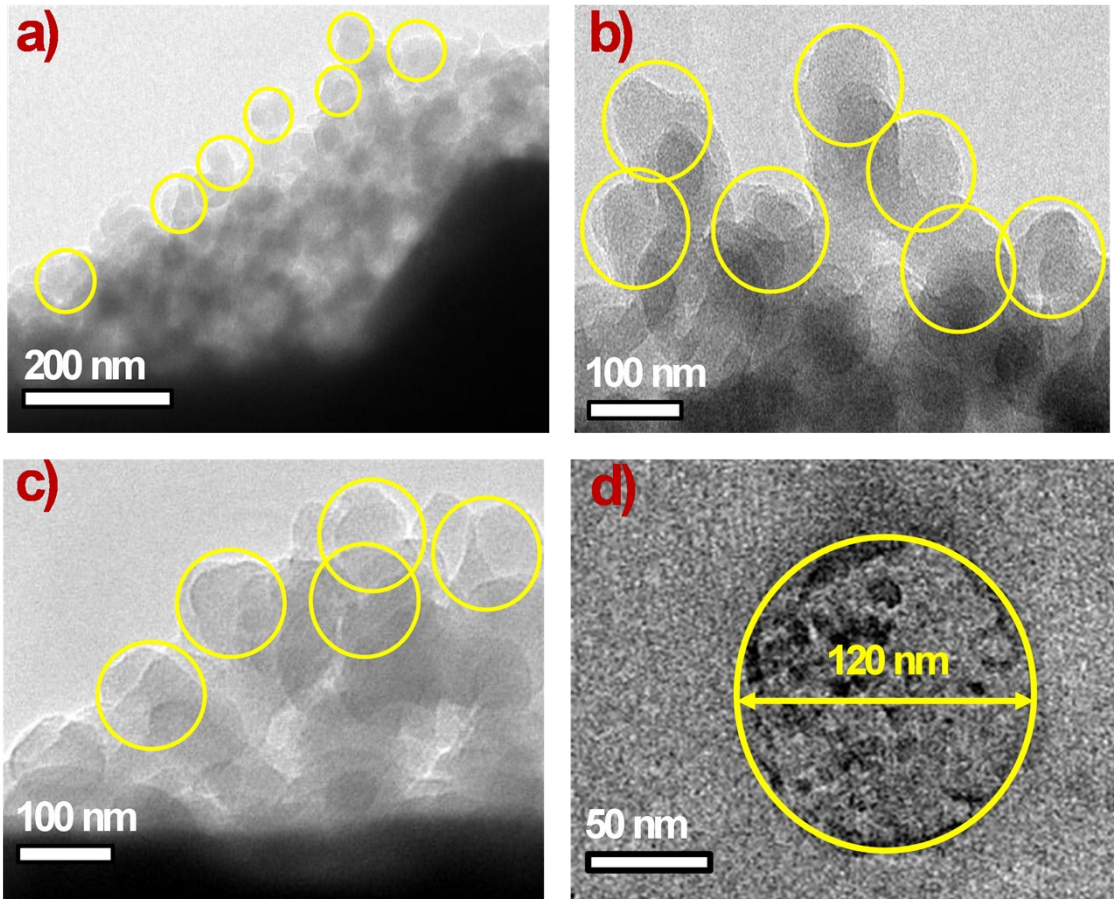

Fig. S2 TEM images of the sulphur particles forms during ESD over a TEM grid after 1 min of deposition, a) image at lower magnification, b, c) images at higher magnification at two different regions, d) Single particle of amorphous sulphur.

Table S1 Spray current measurements at varying applied voltages and tip to collector distances.

Tip to collector distance	Applied voltage	Spray current	Remarks
6 mm	1.3 kV	0.01440 nA	no spray
	1.4 kV	0.03084 nA	no spray
	1.5 kV	9.93265 nA	spray plume
	1.6 kV	11.6066 nA	spray plume
	1.7 kV	12.0823 nA	spray plume
	1.8 kV	14.5945 nA	spray plume
	1.9 kV	23.3021 nA	liquid Jet spray
	2.0 kV	28.9206 nA	liquid Jet spray
	2.1 kV	37.837 nA	liquid Jet spray
	2.2 kV	49.499 nA	liquid Jet spray
2 mm	1.65 kV	36.205 nA	liquid jet spray
4 mm		20.2080 nA	liquid jet spray
6 mm		10.3652 nA	spray plume
8 mm		9.5611 nA	spray plume
10 mm		0. 2356 nA	no spray
12 mm		0.01249 nA	no spray

- Spray current in the range of 10 to 15 nA is suitable for gentle spray emission. Spray currents more than 20 nA is due to liquid get formation and it is inappropriate for the experiments.

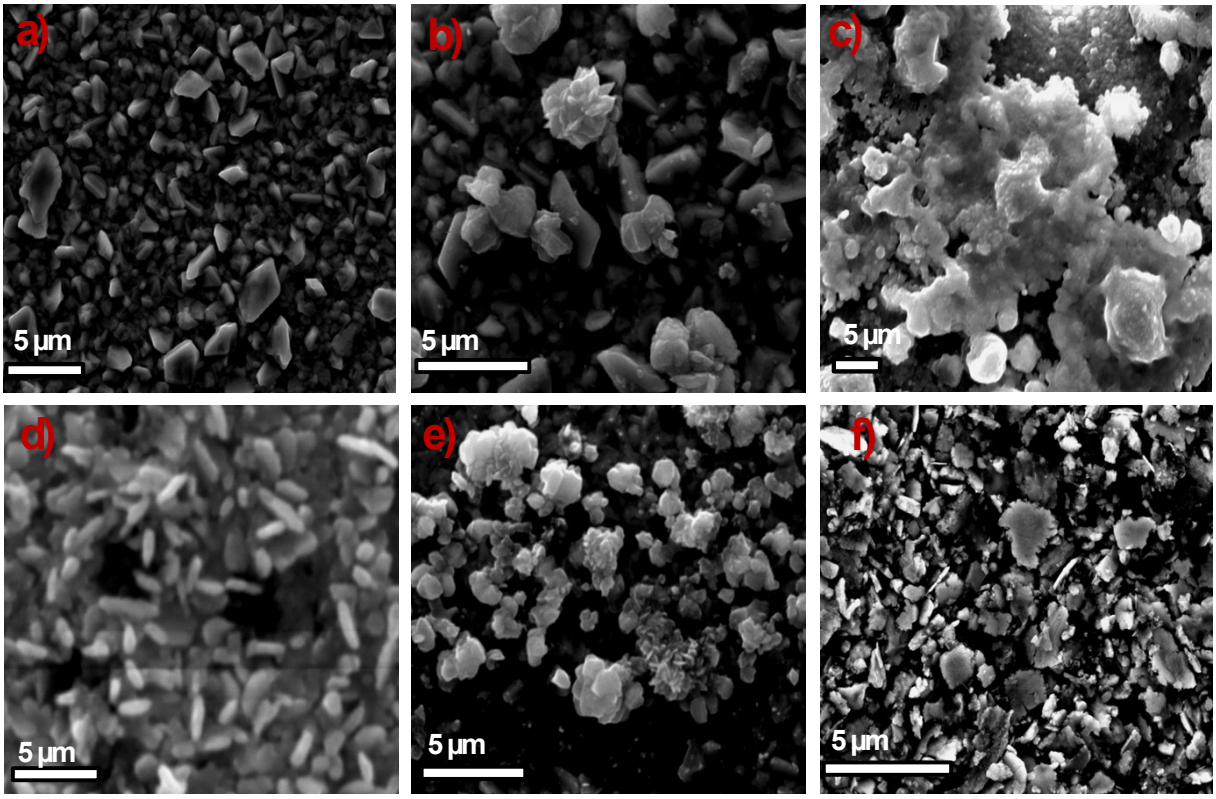

Fig. S3 a, b, c) SEM images of the TEM grid after different times of sulphur spray (a) 3 min, (b) 7 min, (c) 30 min. d, e, f) SEM images of the copper plate after different time of spray, (d) 7 min, (e) 15 min and (f) toluene extracted platelets after 15 mins of spray.

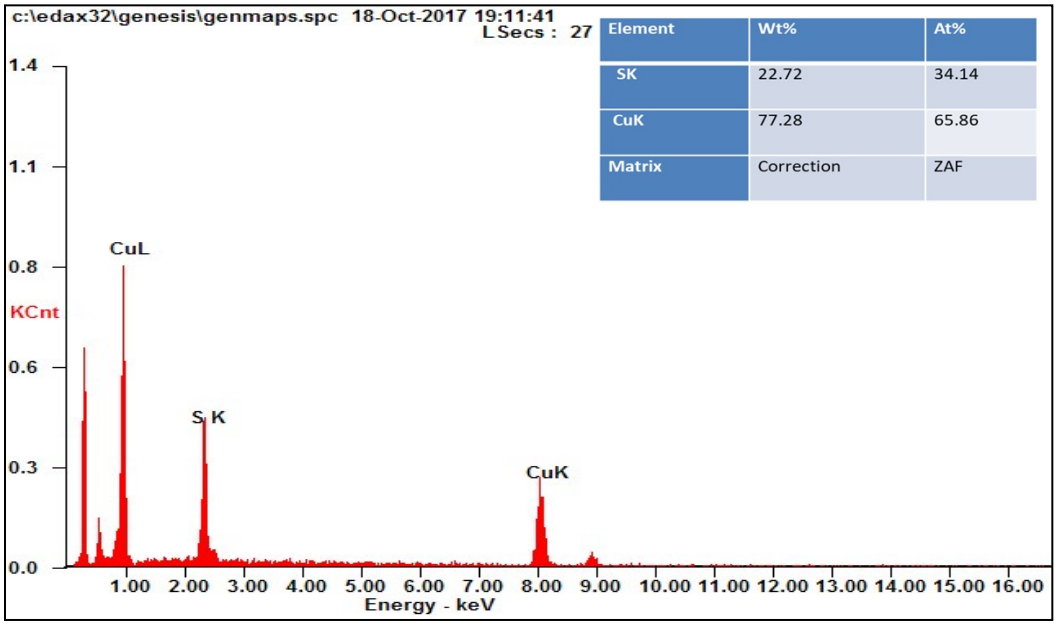

Fig. S4 EDAX spectrum of the Cu_2S nanopyramids (inset shows the elemental distribution of the Cu_2S nanopyramids).

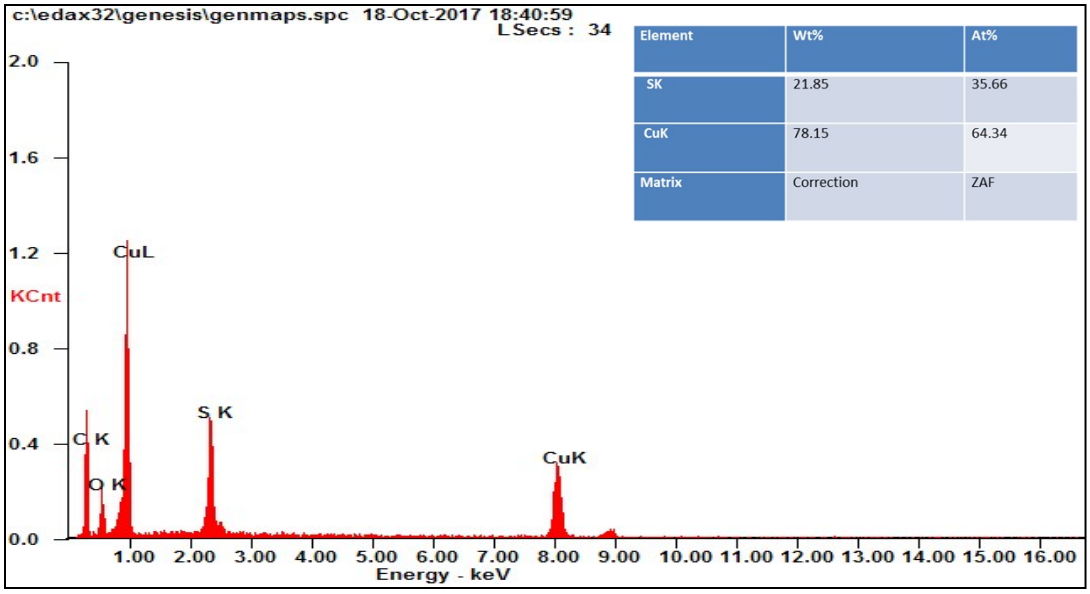

Fig. S5 EDAX spectrum of the $Cu_{1.8}S$ platelets (inset shows the elemental distribution for the $Cu_{1.8}S$ platelets).

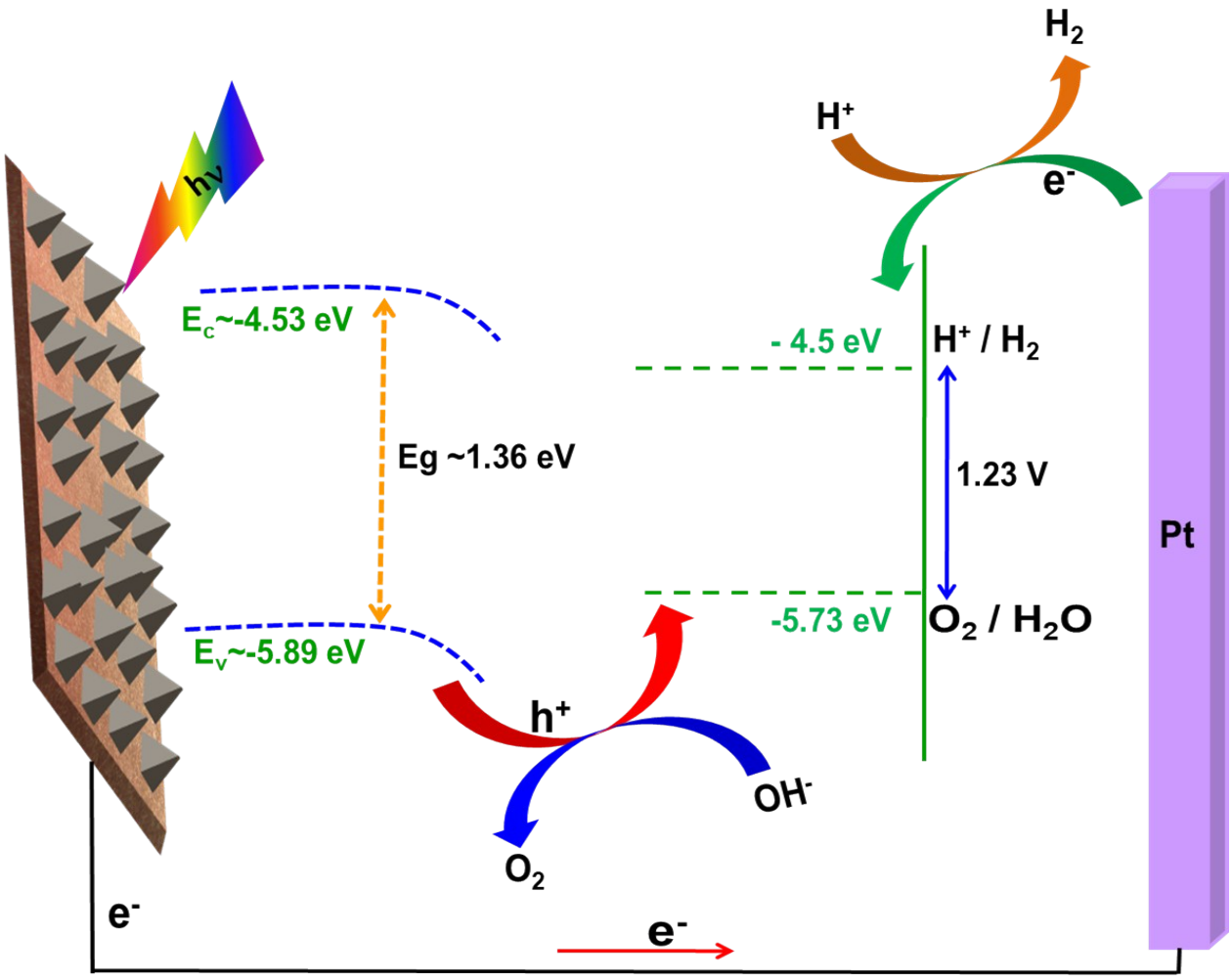

Fig. S6 Schematic representation of the photoelectrochemical process at Cu_2S nanopyramids.

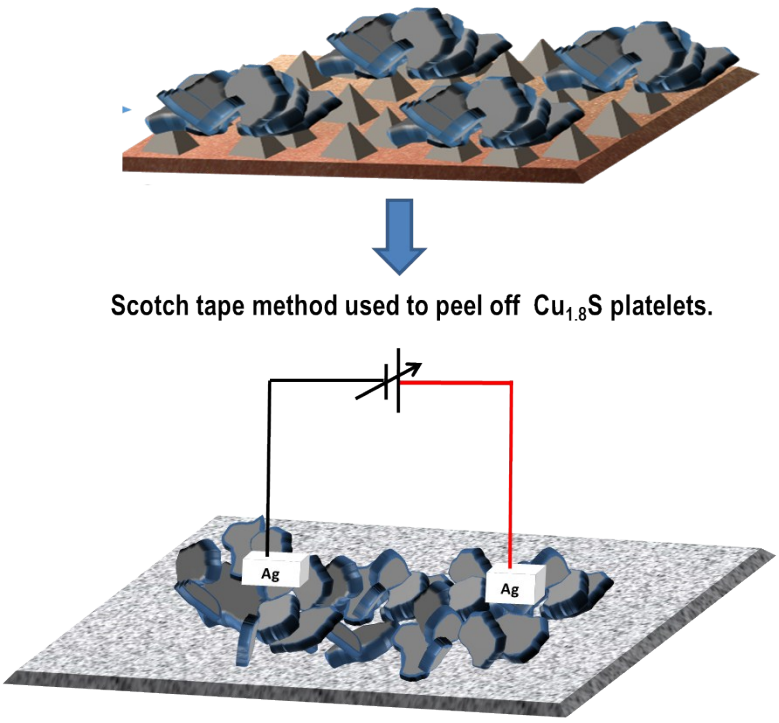

Fig. S7 Schematic representation of the scotch tape peeled off method of $Cu_{1.8}S$ platelets and electrical circuit preparation for solid state conductivity measurements.

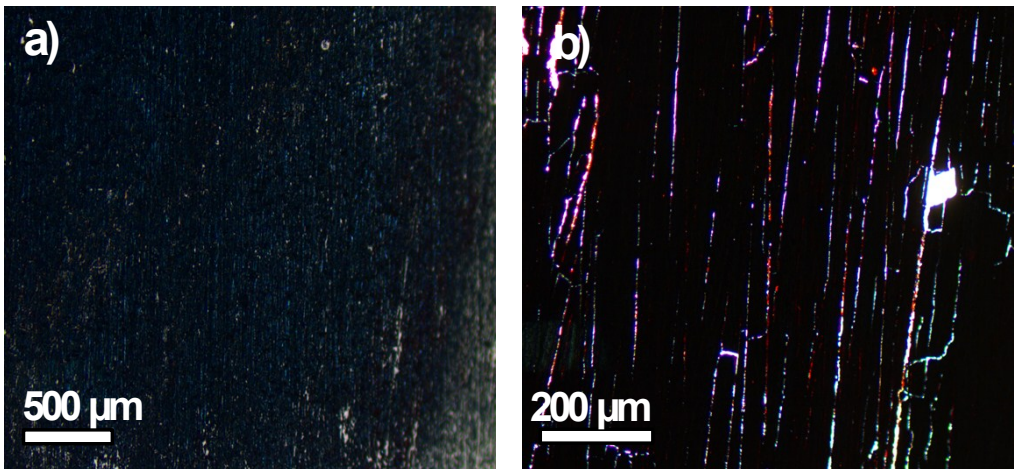

Fig. S8 Optical microscopic images of the film made by $Cu_{1.8}S$ platelets at different a) 10X and b) 40X magnification.

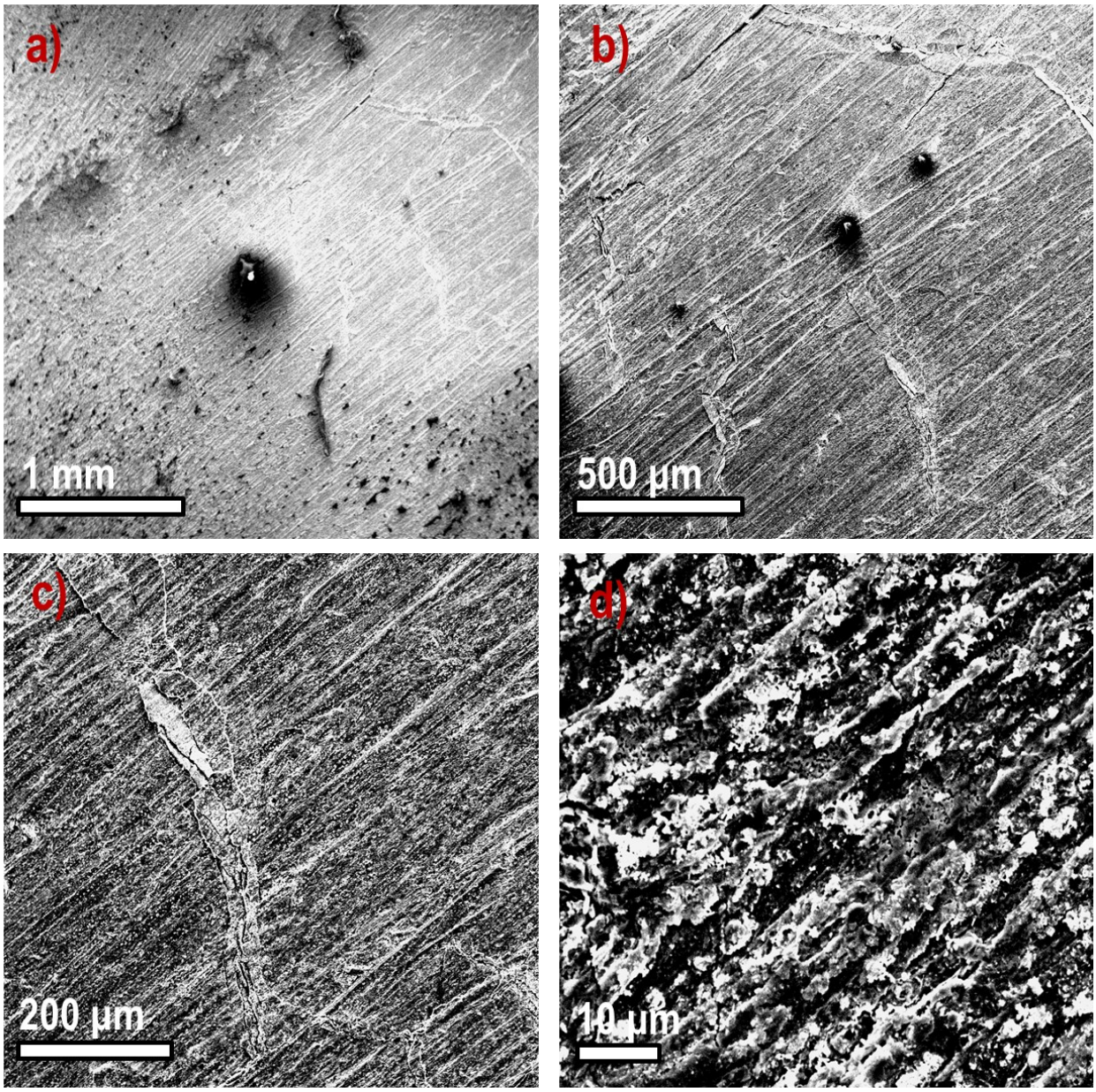

Fig. S9 SEM images of the film under different magnification, a, b) lower magnification and c, d) higher magnification.