Supporting Information

Deterministic Synthesis of Cu_9S_5 Flakes Assisted by Single-layer Graphene Array

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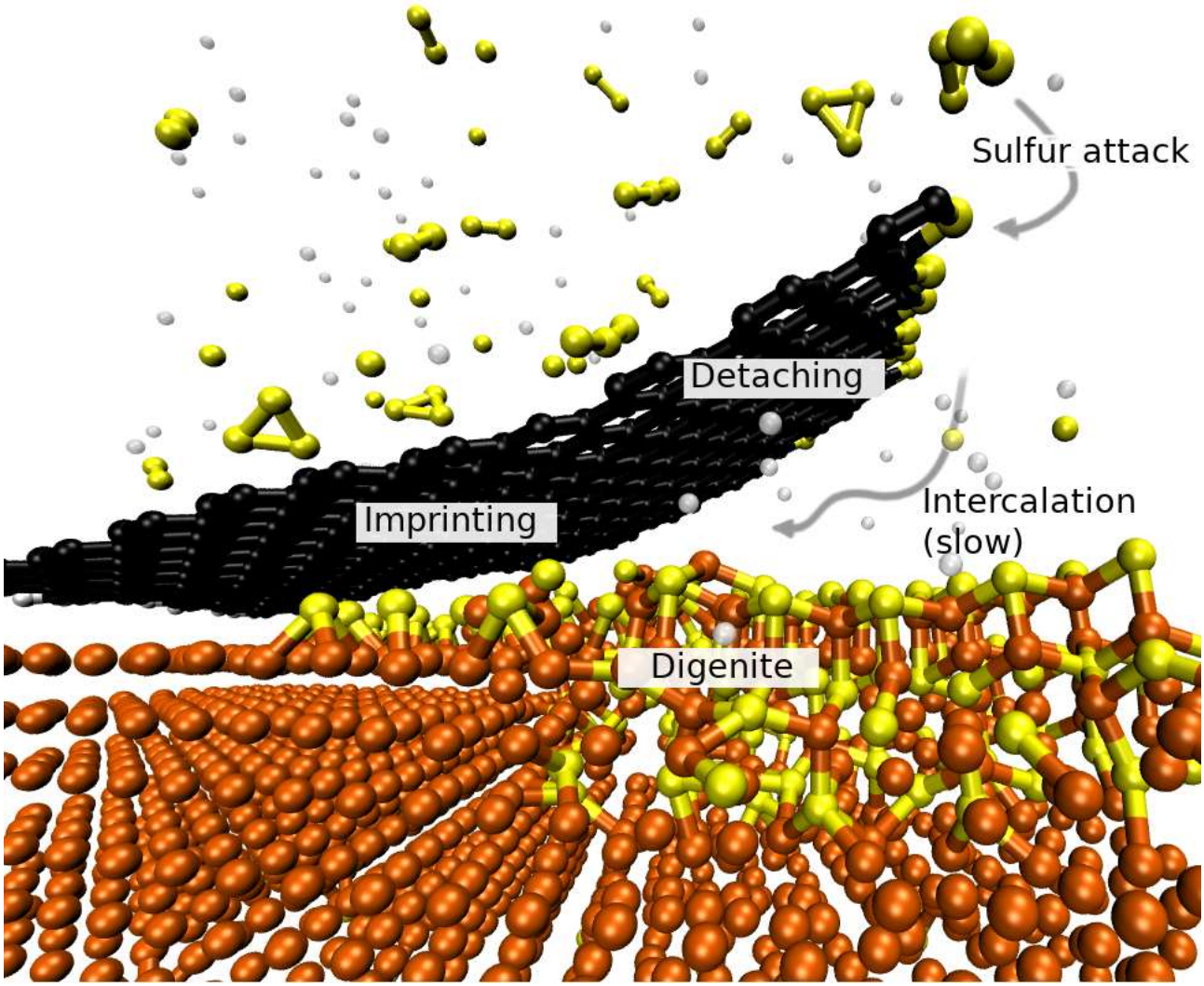

Figure S1. Schematic for the mechanical detachment of graphene during the sulfurization process.

Schematic representation of the process steps. At the beginning (left) graphene adheres to Cu (111). The sulphur atoms begin to intercalate passing from the edges or flaws of the flakes. The sulphur begins to attack Cu. The intercalation of S is slowed down by the presence of graphene and the attack occurs in the deficiency of sulphur atoms, thus favouring the formation of digenite. During the formation of digenite, the increase in volume and the interaction between graphene decreases, favouring mechanical detachment. Finally, the graphene detaches and, in the case, is chemically attacked by S.

In case of the graphene etching, we can hypothesize the following two-step process. The graphene is carbonized at high temperature. Then, the carbon disulphide is formed at high temperature (750 °C), following the chemical reaction (1):

C (solid) + 2S (gaseous) → CS_2 (gaseous)

Then, carbon disulphide, is oxidized due to residual oxygen in the growth reactor.

CS_2 (gaseous) + 3 O_2 (gaseous) → CO_2 (gaseous) + 2 SO_2 (gaseous)

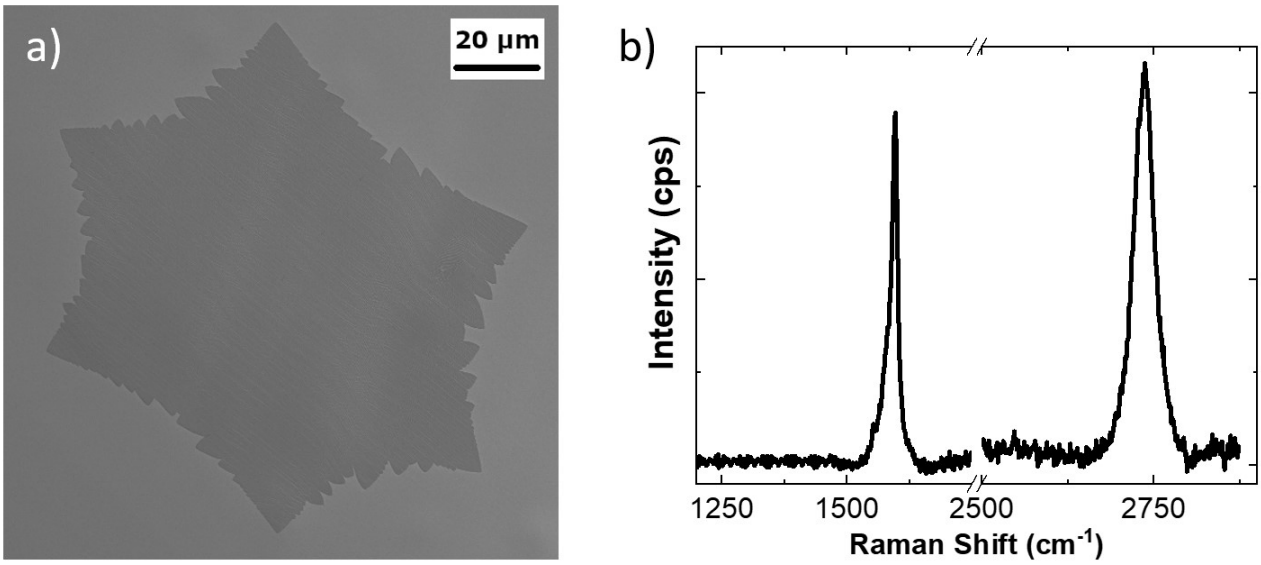

Figure S2. Characterization of CVD grown graphene on copper. Figure S1a) shows a representative SEM image of a graphene crystal on copper foil, before the sulfurization process. Figure S1b) shows the Raman spectrum of graphene on copper.[1] The graphene spectrum on Cu has a 2D peak with a single Lorentzian shape and with a full width at half-maximum FWHM(2D) ~31.2 cm^{-1}, a signature of single layer.[2]

The G peak position, Pos(G), is ~1595 cm^{-1}, with FWHM(G) ~17cm^{-1}. The 2D peak position, Pos(2D) is ~2736 cm^{-1}, The G and 2D peak positions are in agreement with 473 nm laser excited Raman spectrum for graphene on copper. The 2D to G peak intensity and area ratios, I(2D)/I(G) and A(2D)/A(G), are ~1.23 and ~2.2, respectively. No D peak is observed, indicating negligible defects.[3]

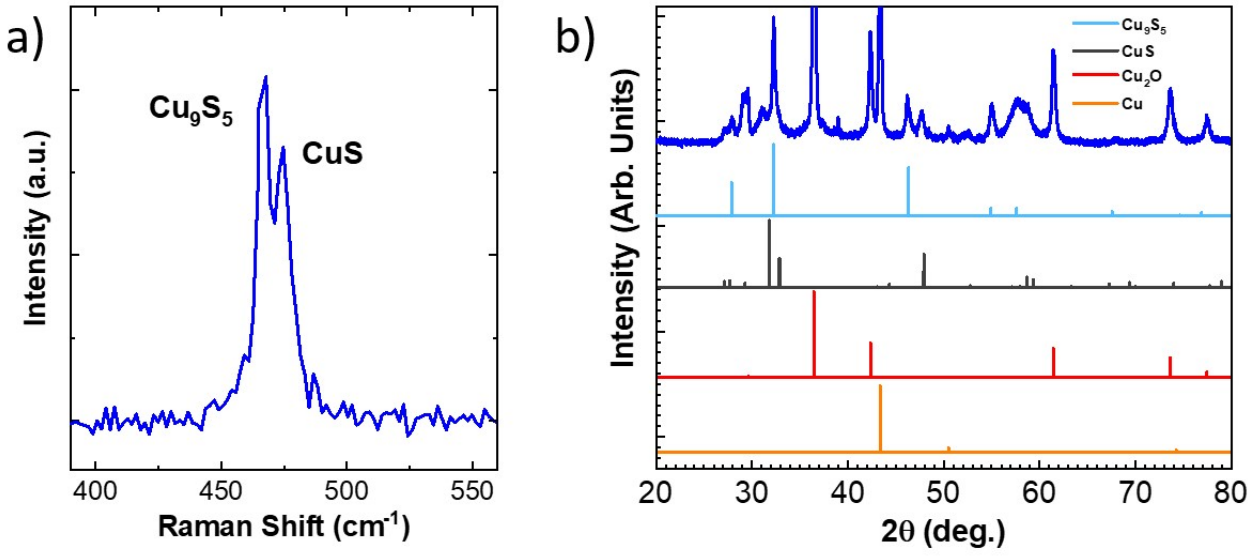

Figure S3. Structural characterization of the residual material. The material outside the flake has been gently scratched from the PDMS thick film with a scalpel. The obtained powder is analysed by means of Raman spectroscopy and X-ray diffraction (XRD). Figure S2a) presents the Raman spectrum, showing a double peak structure. The peaks are set at 467.8 cm^{-1} and 474.6 cm^{-1}, related to the digenite and covelite phases, respectively. This analysis reveals the coexistence of Cu_9S_5 and CuS phases in the material outside

the flakes. The XRD (Figure S2b)) analysis confirms the coexistence of two phases, characterized by partial preferential orientation as expected for a 2D epitaxial growth process. In addition, it reveals that the transfer method presents still some issues, in fact the XRD pattern (Figure S2(b)) presents different peaks related to copper and copper oxide (Cu_2O), revealing that in the first step of the transfer process some copper residuals are transferred. In both cases strong [111] orientation of the cubic structures is detected. All the reference patterns are computed based on the single crystal structure, in particular Cu_9S_5 and CuS were taken from references [4,5].

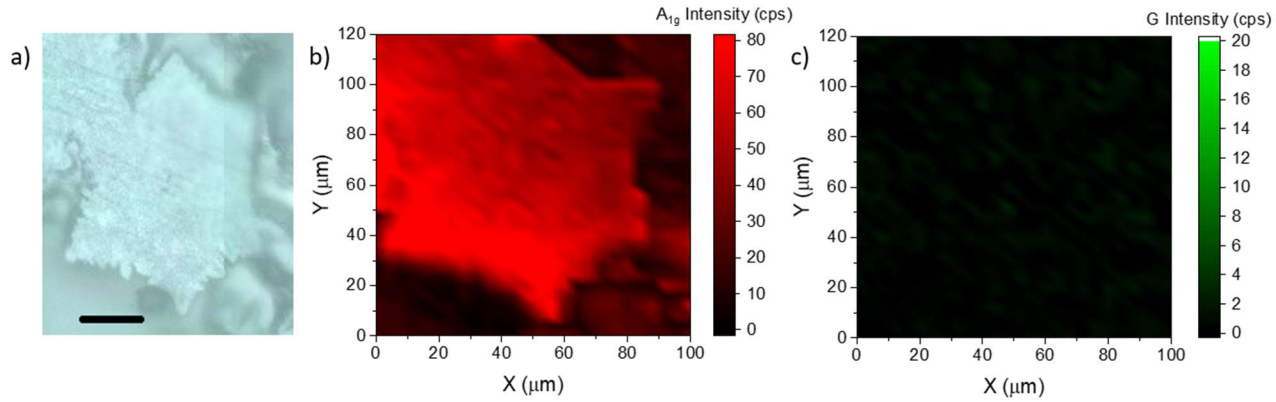

Figure S4. Raman mapping of the Cu_9S_5 flake. Figure S4 a) shows the optical image of the Cu_9S_5 flake in analysis. Figure S4 b) presents the intensity map of the A_{1g} peak, while Figure S4 c) presents the intensity map of the graphene G mode obtained at 1597 cm^{-1}, considering the Raman spectrum presented in Figure S2. The G intensity map confirms the complete removal of graphene from the Cu_9S_5 area, due to the absence of any graphene related Raman signal.

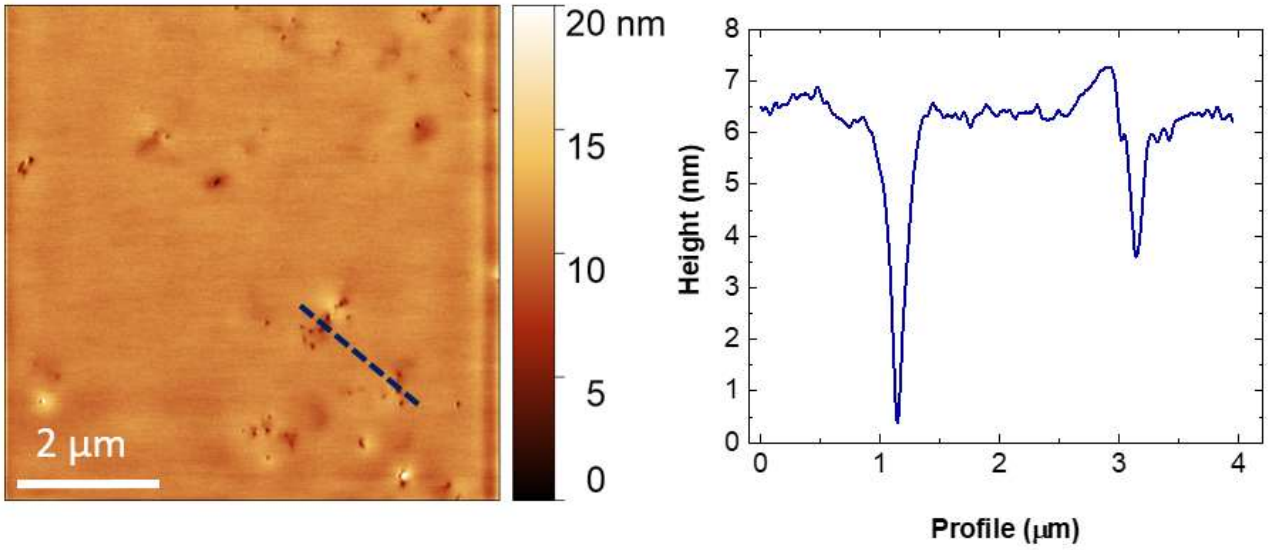

Figure S5. Line profile of the pits found by AFM analysis.

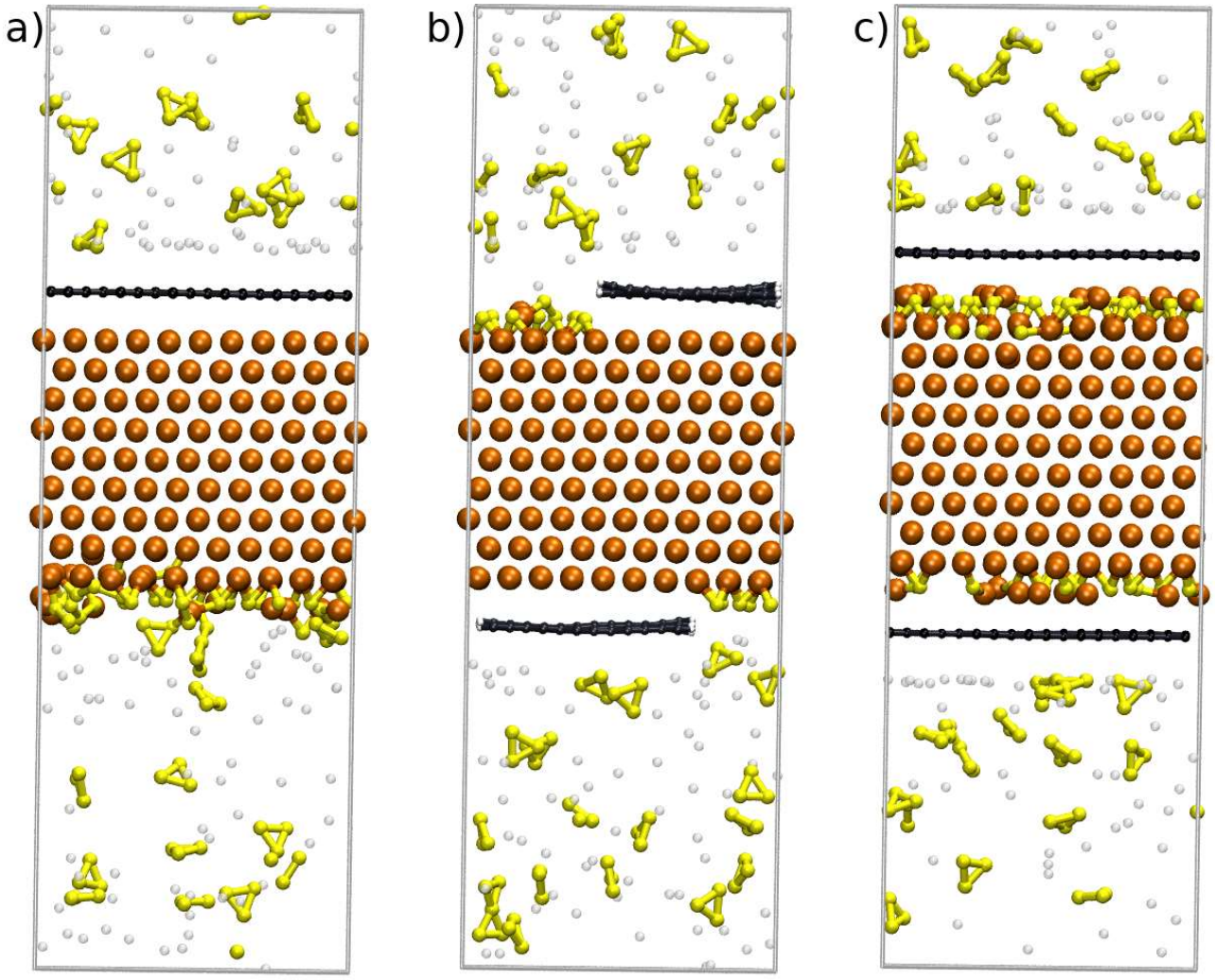

Figure S6. Representation of the three atomistic models used to perform the MD simulations. Cu: orange. Carbon/graphene: black. Sulphur; yellow. Argon: white. The copper plate consists of 9 thick single-layer Cu(111) surfaces arranged in a hexagonal closed package configuration (hcp). For each system, two Cu(111) surfaces of approximately 2.5x2.2 nm^2 were available. a) Top: Cu(111) covered by graphene layer. The graphene layer was placed 3 Å from the surface and rotated by 30° with respect to its standard unit cell to limit the stretching of the carbonaceous structure to no more than 4%. a) Bottom: bare Cu(111) surface directly exposed to the S/Ar mixture. The simulation box was filled with 113 argon atoms and 112 sulphur atoms. b) The second system was built by placing a 13 Å wide graphene ribbon on one of the two Cu(111) surfaces (top) and a second wider graphene ribbon (i.e. 16 Å wide) on the other Cu(111) surface (bottom). The carbon atoms of the edges were saturated with hydrogen. The simulation box was filled with 113 argon atoms and 112 sulphur atoms. c) The third system was modelled by placing 36 sulphur atoms on one of the Cu(111) surfaces (top) and 18 sulphur atoms on the other surface (bottom). Sulphur atoms were placed at about 2/3 Å from the Cu atoms. Each decorated Cu(111) surfaces were then covered with a graphene layer

placed at 5 Å from the metal surface. System counts a total of 86 argon atoms and 142 sulphur atoms.

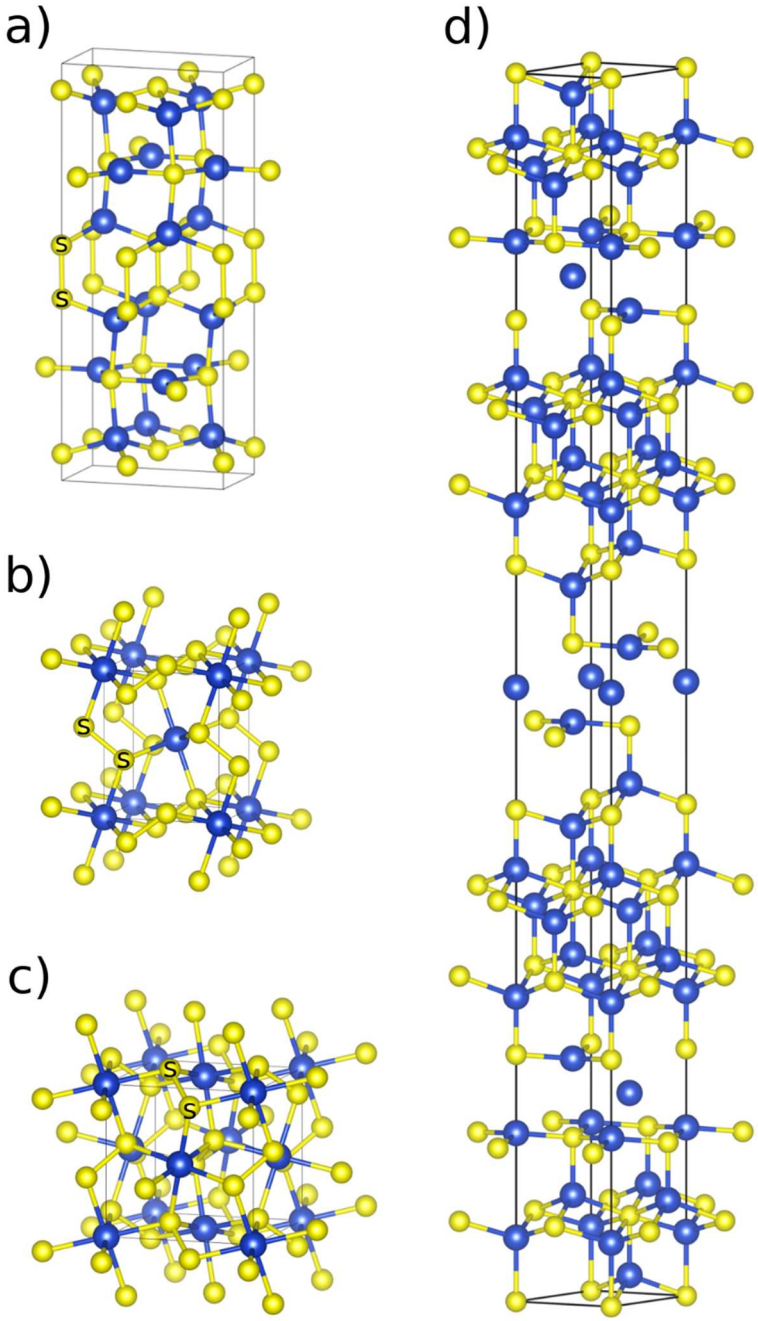

Figure S7. Example of crystal models for copper monosulphide CuS (a), two different forms of copper disulphide CuS_2 (b, c) and digenite Cu_9S_5 (d). Yellow sulfur, blue copper. CuS (a) and CuS2 (b,c) lattices contain both single sulphur atoms as well disulphide chemical groups (S-S motif). To the contrary digenite (d) contains only monosulphide atoms. The structures were taken from www.materialsproject.org[6] and refer to these

Digital Object Identifiers (DOI):

a) CuS DOI: 10.17188 / 1268899

b) CuS_2 DOI: 10.17188 / 1308143

c) CuS_2 DOI: 10.17188 / 1187284

d) Cu_9S_5 DOI: 10.17188 / 1266502

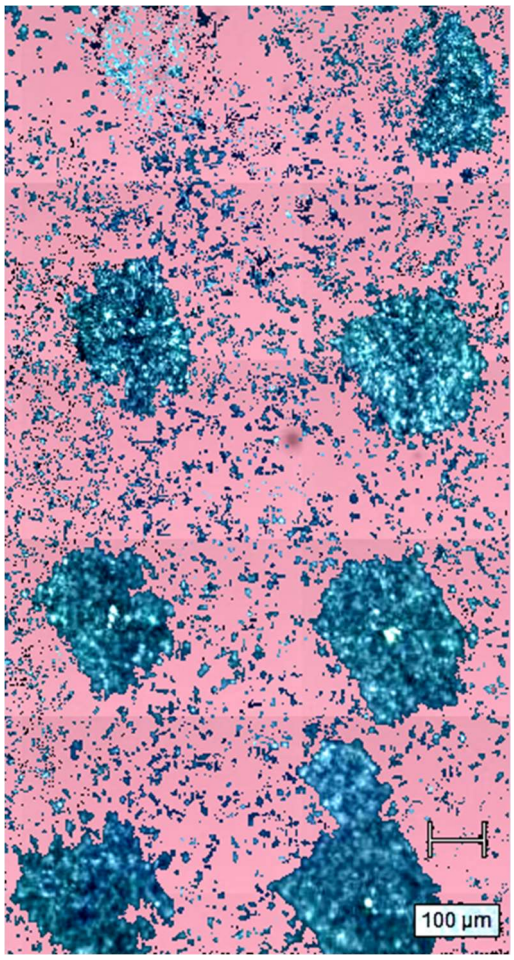

Figure S8. Optical image of the transferred flakes on the PDMS thick film. The transfer process has an efficiency of the 50%, half of the flakes are damaged in transfer process. Some residual material is transferred.

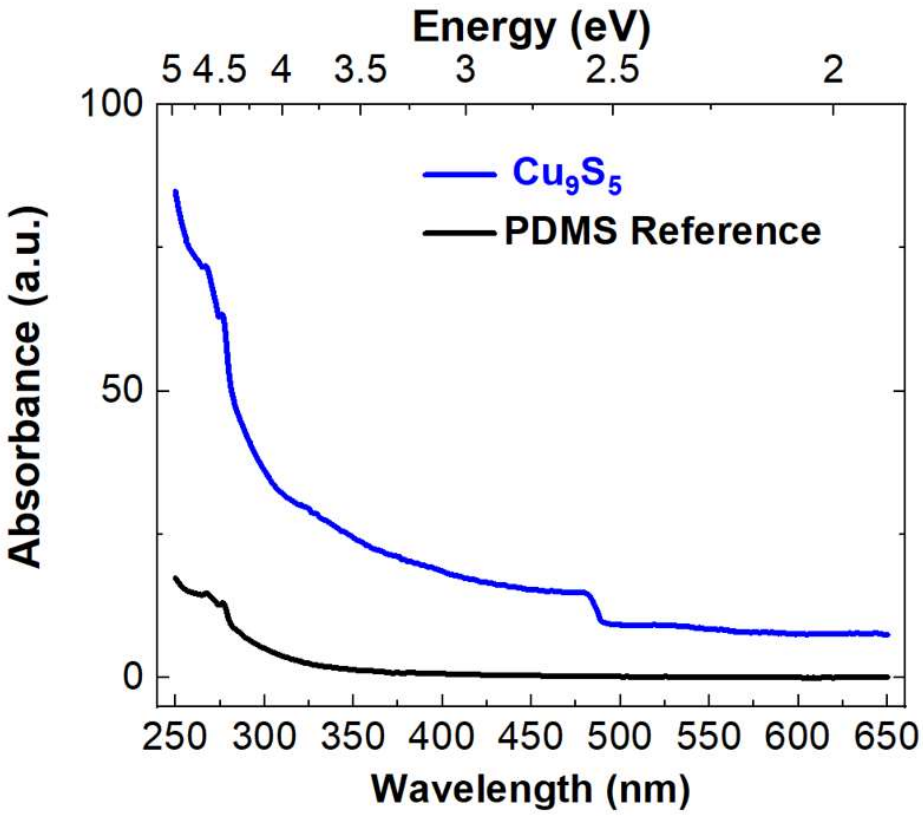

Figure S9. Absorbance spectra for the PDMS thick film (black line) and the α-Cu_2S flakes on PDMS. The absorbance of the Cu_9S_5 flakes on top of the PDMS thick film is strongly increased probably due to scattering effect of the residual material, see Fig. S3.

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