

Supplementary Information

Materials and Methods

Gram scale synthesis of Bi₂S₃ necklace nanowires

The synthesis followed closely the protocol outlined in *L. Cademartiri et al., Angew. Chem.-Int. Edit. Engl.* **47**, 3814 (2008). (Ref 5.)

All reagents were obtained from Aldrich unless otherwise stated and were used as received.

6.34 mmol of bismuth citrate (III) was dispersed in 8.4 ml of oleylamine (70% tech. – 100g bottle – Aldrich) in a 50 ml three-necked flask equipped with a condenser and thermocouple. The third neck was sealed with a septum. The system was rinsed with N₂ three times and then maintained under a N₂ positive pressure. The solution was stirred and heated to 130°C over the course of 30 min and then kept at that temperature for 30 min. A solution of 31.16 mmol of sulfur dissolved in 20.8 ml of oleylamine (70% tech. – 100g bottle – Aldrich) was then quickly injected into the flask using simultaneously two plastic syringes without needle. The reaction can be scaled up easily to multigram scale provided that the addition of the sulfur solution is performed via the top neck of the flask, by pouring the solution through a funnel. The temperature controller is quickly set to 100°C – the temperature should stabilize after 5-10 minutes of growth. During growth N₂ was allowed to flow through the flask. The solution turned dark brown a few minutes after injection and the nanocrystals were allowed to grow for 1 to 120 min. The reaction was then quenched with ~140 ml of cold toluene (dichloromethane and THF are excellent solvents as well – hexane is a poor solvent). Insolubilized/unreacted materials were removed by centrifugation. A 2:1 volume of acetone was added quickly to the supernatant making it become turbid. The mixture was centrifuged, the supernatant discarded and the precipitated nanowires redispersed in toluene, THF or dichloromethane. The purification cycle needs to be performed as rapidly as possible to avoid a prolonged exposure of the wires to acetone, which can reduce their colloidal stability. The purification cycle can be repeated for a second time (longer centrifugation might become necessary – the nanowires won't form a pellet when precipitating in presence of acetone but will form a compact gel at the bottom of the test tube – the gel can be redispersed in a good solvent).

To avoid the nanowire solution from gelling (especially after two cycles of purification) the non-solvent must be carefully and promptly eliminated. After purification the solution of nanowires was diluted with toluene and placed in a rotary evaporator to preferentially remove acetone. This procedure must be continued till acetone isn't distilled out of the solution anymore – eventually toluene can be added to prevent the solution to become too concentrated. The materials prepared in this way are colloiddally stable for > 2 years if kept in the dark at relatively high concentrations (between 0.01 and 1wt%) .

Bulk chemospinning.

Bulk chemospinning of Bi₂S₃ ultrathin nanowires was performed by using the following protocol. A dilute solution (10⁻⁶ M) of ethylene diamine (EA) in toluene or THF and a

Bi₂S₃ ultrathin nanowire dispersion (0.1wt% in Toluene or THF) were prepared. To inject the nanowire dispersion in the EA solution, 1ml and 3ml syringes with stainless steel needles having different nozzle size (160 to 400 μm inner diameter) were used. The needle tip was immersed in the EA solution and the nanowire dispersion was injected with a flow of ~3 ml per minute. The flow of the solution through the needle induced the orientation of the nanowires.

Interfacial chemospinning

A dilute solution (10^{-7} M) of ethylene diamine (EA) in toluene or THF and a Bi₂S₃ ultrathin nanowire dispersion (0.1 to 0.5wt% in Toluene or THF) were prepared. 3ml syringes with 160 μm inner diameter stainless steel needles were used. The nanowire dispersion was injected keeping the needle tip at the EA solution/air interface with a flow 1-2 ml per minute. Both bulk and interfacial chemospinning were performed at room temperature in ambient atmosphere.

IR characterization

IR spectra were obtained on a Spektrum One 2000 (Bruker) FTIR spectrometer in transmission geometry with the nanowires and fibres deposited on undoped Si wafers supplied by Wafer World. To generate thick enough films, multiple depositions were done and residual solvent was evaporated at 60°C for several hours in an oven before taking the measurements.

Conductivity and Profile measurements

In order to measure their conductivity bismuth sulphide microfibers were sparsely placed on highly resistive glass slides (corning 1737). Two rectangular co-planar aluminum contacts (0.25cm x 0.5cm), spaced apart by 400μm were deposited onto individual microfibers by physical vapor deposition. The aluminum contacts were deposited such that the microfibers ran perpendicular to and traversed the 400μm gap separating the pair of aluminum contacts. A Keithley 6517 electrometer was used to measure the current through these microfibers as different biases were applied across the pair of aluminum contacts. A Tencor Instruments Alpha-Step 200 profilometer was used to measure the cross sectional area (Fig. S4) at multiple positions along the length of the microfibers and the minimal area was used in calculating the conductivity of the bismuth sulphide microfibers.

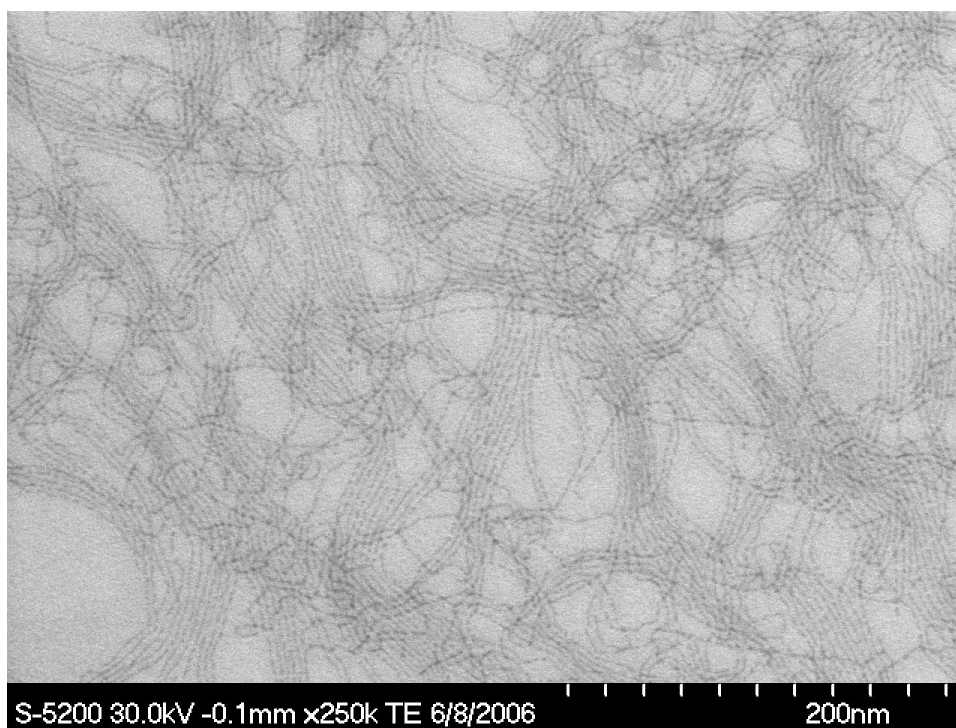


Figure S1. Representative TEM micrograph of Bi_2S_3 ultrathin nanowires.

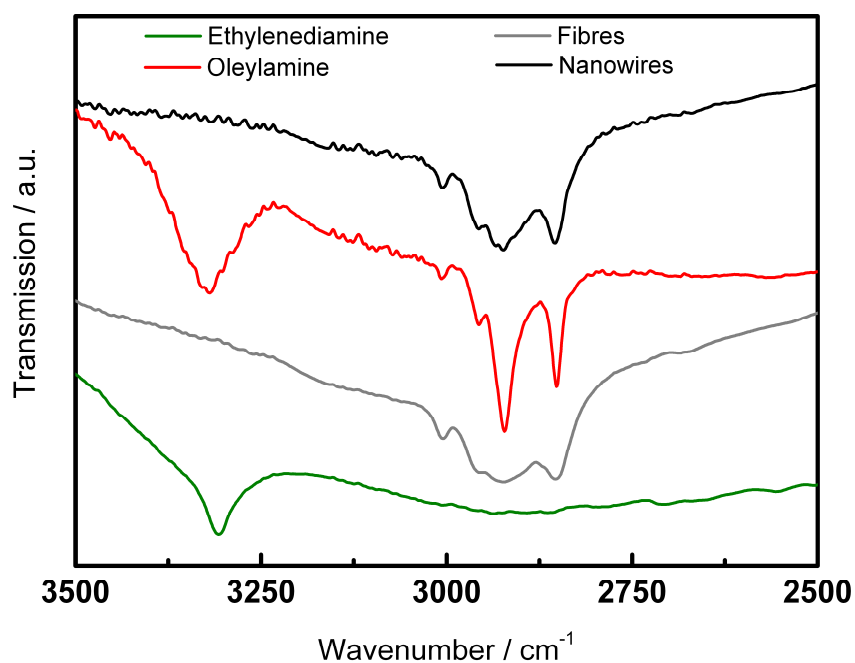


Figure S2. FTIR spectra of the $\nu(\text{X-H})$ region showing the C-H and N-H stretch of oleylamine capped Bi_2S_3 nanowires (black line) and fibres crosslinked by ethylene diamine (grey line), as well as oleylamine (technical purity, 80 %) and ethylene diamine (red and green lines, respectively). The $\nu(\text{N-H})$ bands visible in the organic ligands around 3300 cm^{-1} are not observed in the fibres and wires at the same wavenumber,

presumably due to a substantial lowering and broadening of the N-H stretching frequency by coordination to the Bi_2S_3 surface.

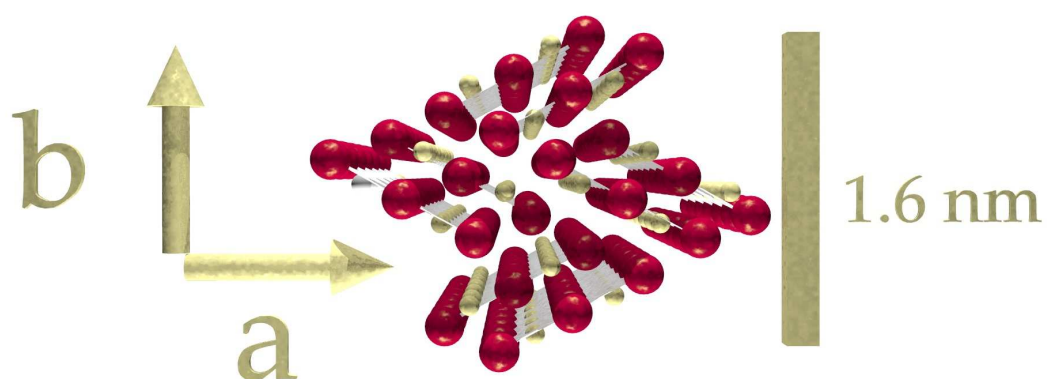


Figure S3. Proposed atomic structure for the Bi_2S_3 nanowires. In yellow are the Bi atoms, while in red are the S atoms. Notice how half of the bismuths reside at the surface.

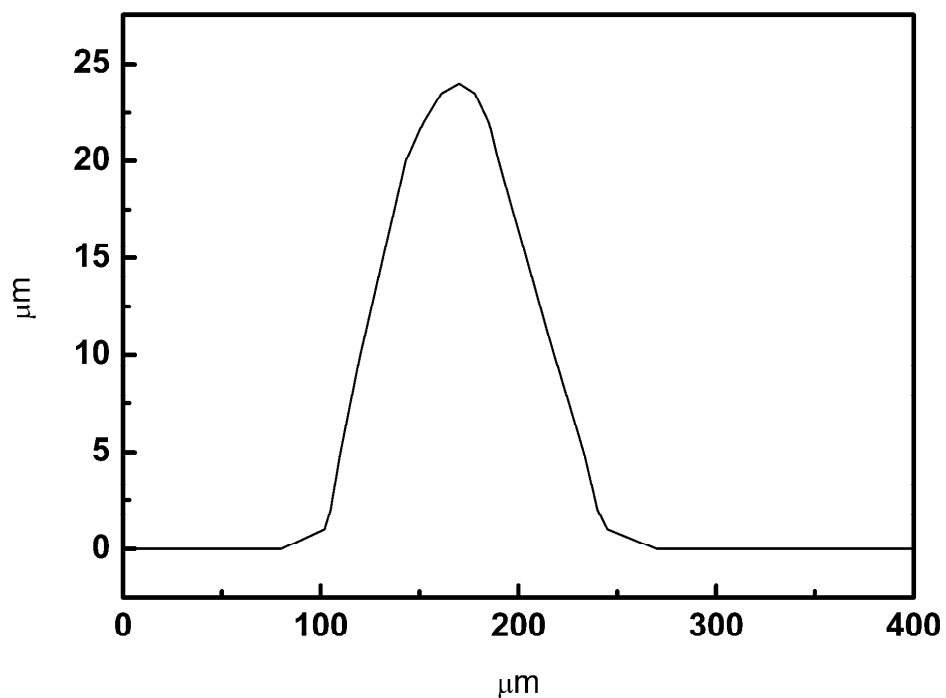


Figure S4. Profile of a nanowire microfiber produced by chemospinning. The methodology used to obtain this data is outlined in the Materials and Methods in this document.

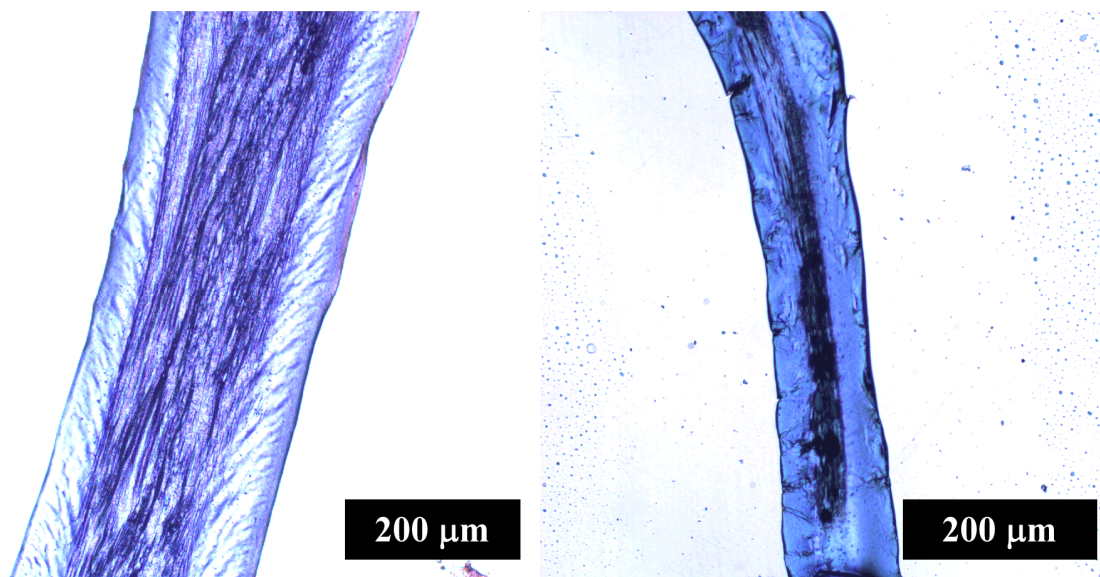


Figure S5. Optical microscope (reflectance) image of 250 and 100 μm fibers.

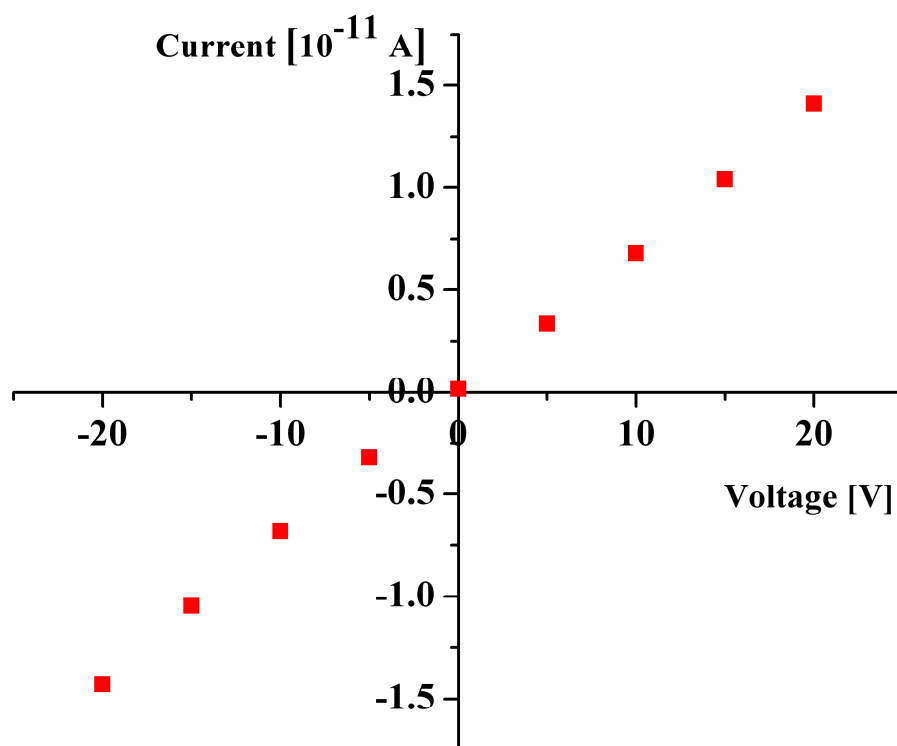


Figure S6. VI plot of a Bi_2S_3 nanowire microfiber giving a conductivity of $8.5 \times 10^{-7} \text{ S/m}$

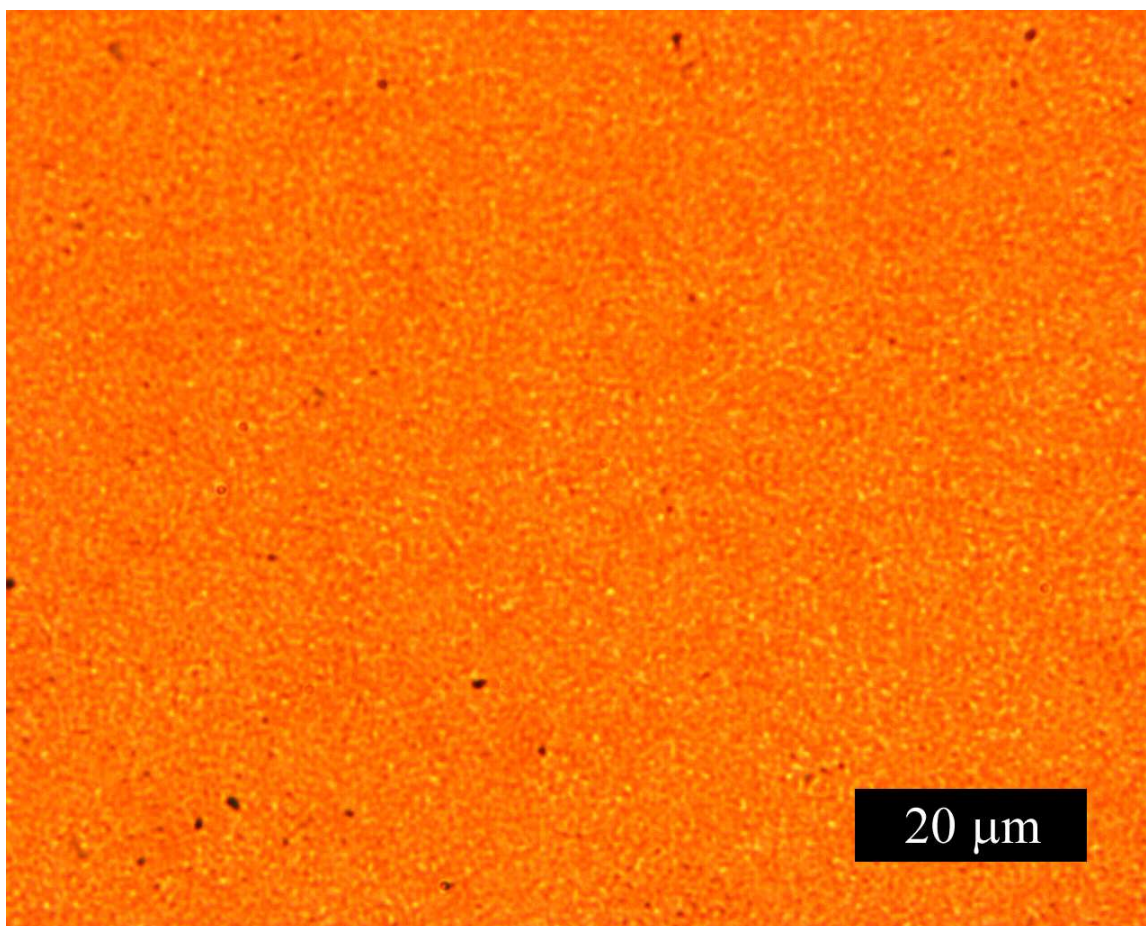


Figure S7. Optical microscope (transmission dark field) of a membrane obtained by interfacial chemospinning.

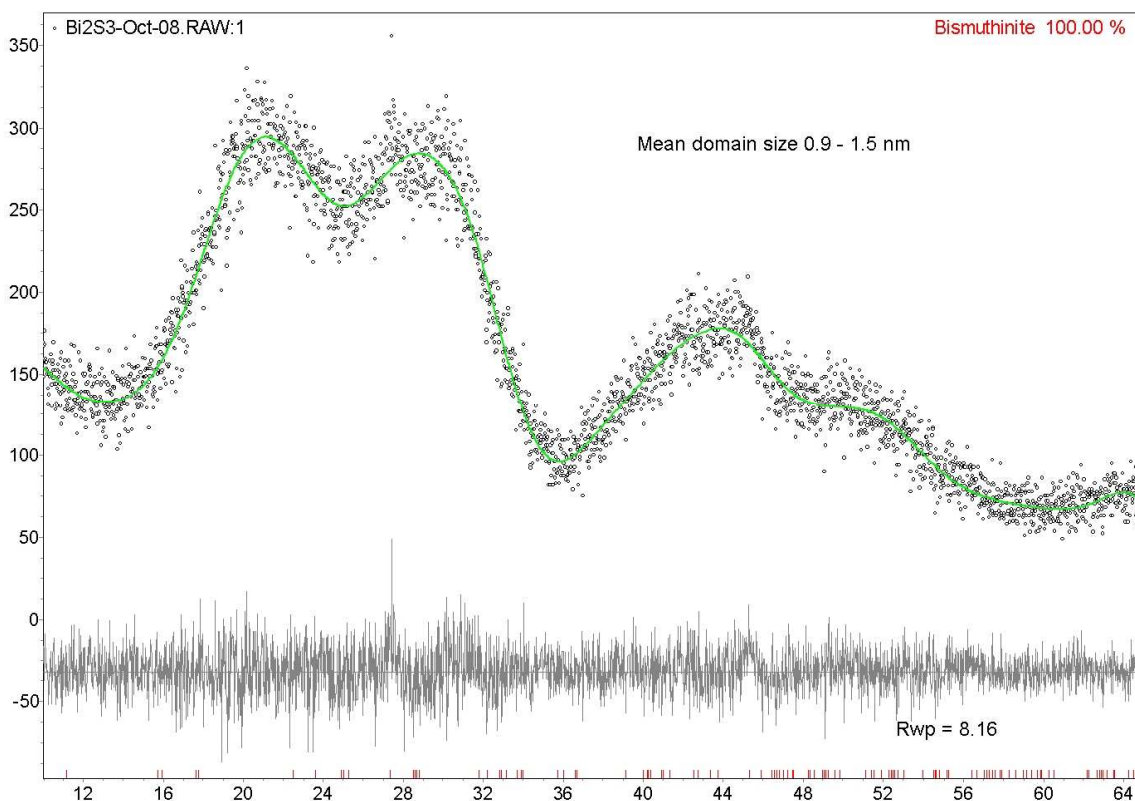


Figure S8. XRD pattern obtained from a thick film of Bi₂S₃ (bismuthinite) nanowires. The Rietveld refinement (green line) confirms that the data are attributable to the bismuthinite lattice. The black solid line represents the difference between the experimental data (black scatter) and the Rietveld refinement (green solid line). The Rietveld refinement further shows that the nanowires are comprised of approximately spherical crystallites between 0.9 and 1.5 nm in size, consistent with what shown in *L. Cademartiri et al., Angew. Chem.-Int. Edit. Engl.* **47**, 3814 (2008). (Ref 5.) and with the microscopy data. According to the model presented in that manuscript, these nanowires are consisting of spherical crystalline domains along the nanowire, in a pearls-on-a-necklace fashion.