Supporting Information

Few-Layer Antimonene by Liquid-Phase Exfoliation
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1. Materials and Methods

Commercially available antimony material (99.9999%, Smart Elements), deionized Millipore Milli-Q water (R > 18.2 MΩ) and 2-propanol (99.8 %, Panreac) were used.

Atomic Force Microscopy (AFM) imaging: AFM measurements were carried out using a Cervantes Fullmode AFM from Nanotec Electronica SL. WSxM software (www.wsxmsolutions.com) was employed both for data acquisition and image processing. All the topographical images shown in this work were acquired in contact mode to avoid possible artefacts in the flake thickness measurements. OMCL-RC800PSA cantilevers (probe.olympus-global.com) with a nominal spring constant of 0.39 N/m and tip radius of 15 nm were employed. Low forces of the order of 1 nN were used for imaging to ensure that the flakes would not be deformed by the tip.

Surface preparation: SiO₂ surfaces were sonicated for 15 min. in acetone and 15 min. in 2-propanol and then dried under an argon flow.

Atomic Absorption Spectrometry: Antimony determination was carried out by flame atomic absorption spectrometry using a ContrAA 700 high-resolution atomic absorption spectrometer (Analitik Jena, Germany). The main line for antimony at 217.5815 nm was employed for all the analysis. The atomization was performed using an air acetylene flame with an acetylene flow rate of 60 L h⁻¹ and at a 6.0 mm burner height. The aspiration rate was fixed at 5 mL min⁻¹. All measurements were carried out in triplicate.

Turbidimeter: Measurements were carried out using a HI-88713 Bench Top Turbidity Meter Hanna Instruments.

Optical absorption spectroscopy (OAS) was measured on suspensions using an Agilent 8452 diode array recorded over a 190–1100 nm range.

Transmission Electron Microscopy (TEM): Images were obtained in a JEOL JEM 2100 FX TEM system with an accelerating voltage of 200 kV. The microscope has a multiscan charge-coupled device (CCD) camera ORIUS SC1000 and an OXFORD INCA X-Ray Energy Dispersive Spectroscopy (XEDS) microanalysis system.

Scanning Transmission Electron Microscopy (STEM) combined with electron energy-loss spectroscopy (EELS): Obtained at 80 kV in a JEOL ARM200cF equipped with a spherical aberration corrector and a Gatan Quantum EEL spectrometer.

Field-Emission Scanning Electron Microscopy (FESEM): studies were performed on a Philips XL 30 S-FEG microscope operating at an accelerating voltage of 10 kV.

Raman spectroscopy: Scanning Raman Microscopy on individual flakes was performed using a Horiba Jobin Yvon LabRAM HR Evolution confocal Raman spectrometer equipped with a microscope and an automated XYZ–table (excitation wavelengths 785, 633, 532, 473, 457 and 405 nm) with a laser spot size of ~1 μm (Olympus LMPlanFl 100x, NA 0.80). The incident laser power was kept as low as possible to avoid structural sample damage and the grating was 1800 g·mm⁻¹. The spectra were recorded under
ambient conditions. Relocalization was achieved by using the optical contrast of nanomaterials deposited on opaque bilayered substrates.

**Standard exfoliation procedure:** 10 mg of powdered antimony were put on a 20 mL vial with 10 mL of an 4:1 2-propanol:water mixture. The mixture was sonicated for 40 min. at 400 W and 24 kHz delivering the ultrasound power in pulses 0.5 s long every 1 s. Then, the resulting black suspension was centrifuged at 3000 rpm (845 rcf) for 3 min. and the clear supernatant was recovered. 20 μL of the suspension were casted on a SiO₂ surface and allowed to dry.

**Sonicator device:** Sonication was performed using a Hielscher UP400S ultrasonic processor equipped with a 3 mm sonotrode.

**Centrifugation** was carried out in a MPW-350R centrifuge using 2 mL Eppendorfs.

1. Determination of Experimental Exfoliation Conditions

1.1 Solvent Selection

Several pure solvents were tested in order to get liquid exfoliation of crystals of antimony. The solvents were selected based on its surface energy in order to match with the layered crystals and minimize the energy cost of the exfoliation according to the enthalpy of mixing per unit volume as shown in eq. (1),

$$\frac{\Delta H_{\text{mix}}}{V_{\text{mix}}} \approx \frac{2}{T_{\text{layer}}} \left( \delta_{\text{layer}} - \delta_{\text{solvent}} \right)^2 \phi$$

eq. (1)

Where \( \delta_i = \sqrt{E_i^{\text{sur}}} \) is the square root of the component surface energy, \( T_{\text{layer}} \) is the thickness of an antimonene flake and \( \phi \) the volume fraction.\(^3\) The surface energy of the antimonene is still unknown. Therefore we just tried to test several solvents according to their surface tension (Table S1).

**Table S1.** Surface tension of the tested solvents.

| Solvents             | Surface tension (mN/m) |
|----------------------|------------------------|
| Ethanol              | 22.1                   |
| 2-Propanol           | 23.0                   |
| Acetone              | 25.2                   |
| Chloroform           | 27.5                   |
| N-methyl-2-pyrrolidone | 40.8                  |
| Water                | 72.8                   |
10 mg of powdered antimony in 10 mL of the solvent were sonicated for 40 min. at 400 W and 24 kHz but only sedimentation, or very little dispersion of material were observed immediately after sedimentation for 12 h (Table S2). Based in our previous results with the exfoliation of graphite we tested mixtures of organic solvents with water. Indeed, the best result was obtained with the mixture 4:1 2-propanol:water. Other tested experimental conditions are collected in Table S2 showing poor concentration of material in suspension. The concentration of antimony was estimated based on the turbidimetric measurements on the suspensions (Figure S1).

![Figure S1. Calibration of the turbididy (NTU units) versus concentration (g/L).](image)

**Table S2. Summary of the experimental conditions tested.**

| Pure solvent   | Turbidity (NTU) | Concentration (g/L) |
|----------------|-----------------|---------------------|
| 2-Propanol     | 29.2            | 0.074×10³           |
| NMP            | 32.9            | 0.085×10³           |
| 2-Propanol/H₂O |                 |                     |
| (4:1)          | 60.7            | 1.74×10³            |
| (2:1)          | 28.3            | 0.71×10³            |
| (1:1)          | 23.9            | 0.57×10³            |
| (1:2)          | 14.8            | 0.28×10³            |
| H₂O            | 6.3             | 0.01×10³            |

**1.2 Adjustment of the Exfoliation Experimental Setup**

Once the solvent is selected, several experimental factors may affect to the liquid phase exfoliation process of a layered material to form a stable dispersion. These include the sonication time, initial quantity of the material or the centrifugation time and speed, among others.

Figure S2 shows the effect of the sonication time on the concentration. The variation in the concentration from sonication times ranging between 20 to 90 min is not very
significant. However, we have observed that larger sonication times produce a dramatic decrease in the concentration probably due to degradation.

**Figure S2.** Study of few-layer antimonene flakes concentration (g/L) found in suspension *versus* sonication time (centrifugation after sonication was used to get a homogeneous suspension). This measure was determined by atomic absorption spectrometry.

The analysis of the effect in the final concentration of antimony in suspension based on the initial quantity of antimony in 10 mL of 2-propanol:water (4:1) is given in Table S3. It can be observed that an increase of the initial amount of antimony does not cause a significant effect on the concentration.

**Table S3.** Analysis of the amount of initial antimony powder dispersed in 10 mL of 2-propanol:water (4:1) and the final concentration of antimony obtained in suspension.

| Initial Quantity (g) | Turbidity (NTU) | Concentration (g/L) |
|----------------------|-----------------|---------------------|
| 0.001                | 51.2            | 1.43×10⁻³           |
| 0.01                 | 60.7            | 1.74×10⁻³           |
| 0.02                 | 55.3            | 1.56×10⁻³           |
| 0.05                 | 58.9            | 1.67×10⁻³           |

The optimization of the centrifugation time shows that the best results are obtained at short times (Table S4). The effect of the centrifugation process in concentration is noteworthy. Indeed further improving of centrifugation conditions is expected to lead to dispersions with controlled flake sizes in the future, but such optimization is beyond the scope of this work.
Table S4. Study of the effect of the centrifugation time on the final concentration.

| Centrifugation time (min) | Turbidity (NTU) | Concentration (g/L) |
|--------------------------|-----------------|---------------------|
| 3                        | 60.7            | 1.74×10⁻³           |
| 10                       | 10.1            | 0.13×10⁻³           |
| 30                       | 6.17            | 0.01×10⁻³           |

1.3 Stability of the Antimony Suspensions

The suspension of antimony obtained upon sonication for 40 min. at 400 W of 10 mg of powdered antimony with 10 mL of 2-propanol:water (4:1) shows good stability with the time. After 24 h only ca. 20 % of the initial material observed in suspension is deposited, and at long times, 72 h, an extra 10 % of the initial material is deposited.

Table S5. Stability of the antimony suspension with the time.

| Time (h) | Turbidity (NTU) | Concentration (g/L) |
|----------|-----------------|---------------------|
| 0        | 60.7            | 1.74×10⁻³           |
| 1        | 55.3            | 1.56×10⁻³           |
| 2        | 54.9            | 1.55×10⁻³           |
| 3        | 53.1            | 1.49×10⁻³           |
| 24       | 50.2            | 1.40×10⁻³           |
| 48       | 46.7            | 1.29×10⁻³           |
| 72       | 44.4            | 1.22×10⁻³           |
| 96       | 42.6            | 1.12×10⁻³           |
| 120      | 41.2            | 1.11×10⁻³           |
| 144      | 40.1            | 1.08×10⁻³           |
| 168      | 39.3            | 1.05×10⁻³           |
We also measured the UV-vis absorption spectra of the suspensions showing a continuous decrease of the intensity as a function of time, likely related with precipitation and/or reaggregation of the nanosheets, in good agreement with the turbidity experiments (Figure S3). All the samples exhibited a broad spectrum with no alteration of its shape, suggesting that no degradation is occurring.

**Figure S3.** Absorbance spectra of few-layers antimonene suspensions as a function of time, showing a decrease in the intensity, related to the sedimentation process.
1.2 Determination of the Morphological Features

**Figure S4.** Representation of the height (left panels) and lateral dimension (right panels) variation of few-layer antimonene flakes *versus* sonication time. The analysis was done measuring the dimensions of the antimony layers by atomic force microscopy. Area measured using WSxM 5.0 software.[1a]
2. Additional Characterization Data

2.1 Total reflection X-Ray Fluorescence Analysis

Figure S5. Total reflection X-Ray Fluorescence Spectra of a suspension of few-layer antimonene showing that it only contains antimony and some traces of arsenic (probably from impurities in the starting material). The signal of silicon comes from the sample holder, and argon from the atmosphere. The silicon peak is not completely displayed for clarity.
2.2 Atomic Force Microscopy

Figure S6. AFM topographic images showing different areas with few-layer antimonene flakes. Notice the angles observed in the edges of the flakes, mainly multiples of 60 °, as expected for a hexagonal structure.

Figure S7. AFM topographic images of different few-layer antimonene flakes. Solid lines correspond to the profiles along the dashed lines, showing step heights multiple of ~ 4 nm.
Figure S8. (a) AFM topographic image of a FL antimonene flake taken immediately after exfoliation. (b) Same as in (a) but two weeks later. (c) Profiles taken along the lines drawn in a-b. Please notice the similarity of the corrugation on the antimonene flakes confirming the absence of environmental degradation.

Figure S9. High resolution topographic AFM images corresponding to four consecutive scans on the same 5 x 5 nm² area taken after exposing the sample to atmospheric conditions during more than two weeks. Left and right panels were acquired with scanning angles of 0 and 90 ° respectively. Vertical and horizontal arrows show the direction of the slow and fast scan directions used to acquire each of the images. The observed periodicity is compatible with the antimonene hexagonal atomic lattice.
2.3 Electron Microscopy Studies

2.3.1 Aberration corrected scanning transmission electron microscopy (STEM) combined with electron energy-loss spectroscopy (EELS).

Figure S10. (a) Low magnification HAADF image of a flake (top left) along with an atomic resolution image (image taken along the [0 -1 2] direction). (b) Two dimensional EELS maps acquired near the edge of the flake, exhibiting the signal below the C K (blue), Ca L\textsubscript{2,3} (gray scale), O K (green) and Sb M\textsubscript{4,5} (red) absorption edges. Results in (a, b) obtained at 80 kV in a JEOL ARM200cF equipped with a spherical aberration corrector and a Gatan Quantum EEL spectrometer. The LPE method is carried out with 2-propanol that contains 0.2 ppm of Ca according to the information provided by Panreac.

2.3.2 Transmission Electron Microscopy (TEM).

Figure S11. (a) TEM image of a thin antimony flake. (b) Magnification of the green area in (a). (c) Digital magnification of the blue region in (b). (d) Electron diffraction pattern, showing the hexagonal symmetry.
Figure S12. X-Ray Energy Dispersive Spectroscopy (XEDS) microanalysis of few-layer antimonene flakes.

2.4 Raman Spectroscopy

Figure S13. Micromechanically exfoliated flake measured with different laser excitation wavelengths.
Figure S14. Influence of the laser excitation wavelength on the Raman spectra of bulk antimony.

Figure S15. Detection of thin flakes monitoring the Silicon intensity. (a) AFM image of a micrometric flake and its corresponding profile showing a thickness of ca. 15 nm. The inset corresponds to the optical micrograph of the same area. (b) Silicon intensity Raman map showing a decrease in the 521 cm\(^{-1}\) signal that clearly reveals the morphology of the flake.
2.5 Theoretical calculations

The phonon frequencies at the $\Gamma$-point and Raman cross sections were calculated in the frame of density functional perturbation theory on the level of the local-density approximation (LDA) to the exchange-correlation functional as implemented in the Quantum Espresso suite.\[^5\] We modeled the electron-ion interaction through norm conserving pseudopotentials generated with the ONCVPSP package,\[^6\] where we included the 4d, 5s, and 5p states in the set of valence electrons and applied a cutoff energy of 1200 eV. We used the primitive cells of studied systems, i.e. of hexagonal symmetry in case of the 2D materials and rhombohedral in case of the $\beta$-phase of bulk Sb, and fully optimized the atomic positions and the lattice vectors in the periodic directions until the residual forces between atoms were smaller than 0.01 eV/Å. Here, we used ABC stacking for all structures. Interactions of the few-layer systems with residual periodic images due to the 3D boundary conditions were minimized by maintaining a vacuum layer of at least 25 Å. Based on the geometries, we then calculated the $\Gamma$-point phonon frequencies and Raman tensors. We used 17x17x17 Monkhorst-Pack k-point samplings for ground state calculations, geometry optimizations and frequency calculations for the few-layer (bulk) materials. For the Raman calculations, we reduced the grid densities to 14x14x1 (14x14x14), as we were mainly interested in the relative intensities. For the bulk system, the Raman intensities were calculated in the approximation of fixed occupation of the electronic bands, \textit{i.e.} as a semiconductor. The Raman activities shown in Figure 4b of the main text were derived from the calculated Raman tensor under the assumption of backscattering configuration.\[^7\]

Due to the observed underestimation of the $\Gamma$-point calculated frequencies in bulk Sb compared to experiment, we took great care in choosing our method and tested our optimized geometries and phonon frequencies for bulk Sb against several exchange-correlation functionals (LDA, PBE, PBEsol), pseudopotentials and DFT codes employing different basis sets (GPAW, Elk). We thereby ensured consistency and ruled out errors from underconvergence of energies and forces or the pseudopotential approximation. We note that our obtained frequencies deviate from the ones reported recently by Wang \textit{et al.} in Ref. \[^8\]: Using the VASP code, they predict phonon frequencies for bulk Sb that are close to the experimental values of 110 cm$^{-1}$ and 150 cm$^{-1}$. On the other hand, the reported frequencies for the three Raman active modes of monolayer Sb are significantly lower than in our calculations. Second, the relative intensities of the $E_g$ and $A_{1g}$ peaks in the simulated Raman spectrum of bulk Sb are opposite to those in our calculations. Unfortunately, we were unable to identify the origin of the deviations based on their reported computational parameters. A contributing factor to the discrepancies might be freezing the semi-core 4d electrons in the employed pseudopotentials/PAWs, which in our experience can change the predicted phonon frequencies in antimony relative to smaller-core pseudopotentials. We believe this underlines the sensitivity of the predicted vibrational properties of Antimony structures to the employed pseudopotential and exchange-correlation approximations and motivates further theoretical studies of the vibrational properties of this material.
Table S1. Calculated phonon frequencies (in cm$^{-1}$) at the $\Gamma$ point in few-layer and bulk antimony. The irreducible representations of the symmetry group D$_{3d}$ corresponding to the vibrations is indicated. Rows of the table contain modes with identical displacement pattern for the different layer numbers.$^a$

|       | 1L       | 2L       | 3L       | Bulk                      |
|-------|----------|----------|----------|---------------------------|
|       | $a^\ast$ 4.01 Å | $a^\ast$ 4.15 Å | $a^\ast$ 4.19 Å | Hex: $a^\ast$ 4.3 Å, $c^\ast$ 11.0 Å |
| $E_g$ | 45.2     | 36.2     |          | Rhomb: $a^\ast$ 4.427 Å, $\phi^\ast$ 58.08$^\circ$ |
| $A_{1g}$ | 52.9     | 40.3     |          |                           |
| $E_u$ | 57.6     |          |          |                           |
| $A_{2u}$ | 66.8     |          |          |                           |
| $E_g$ | 166.5 (150$^b$) | 149.94   | 141.2    | 88.8 (100$^b$)             |
| $A_{1g}$ | 159.11   | 153.8    |          |                           |
| $E_u$ | 156.1    |          |          |                           |
| $A_{2u}$ | 208.3 (195$^b$) | 185.3    | 172.7    | 137.4 (148$^b$)           |
| $A_{1g}$ | 186.5    | 181.4    |          |                           |

$^a$ Sketches of the calculated displacement patterns of the optical phonon modes are shown for 3L Sb. Analogous to the bilayer structure, the qualitative shape and symmetry of these displacement patterns can be derived from those of the monolayer form (refer to Ref. [9] for a more detailed discussion). The six modes of the 3L structure with highest frequencies show an unintuitive behavior: a larger change in interlayer bond-lengths due to the lattice vibrations leads to a lower frequency. The optimized lattice constants are given for each system. The strong increase of the lattice constants for decreasing layer numbers can be traced back to the nature of the interlayer bonding in antimony, which has a significantly stronger covalent character than the noncovalent bonding in layered materials such as MoS$_2$ and graphite. The outmost layers thus undergo an atomic rearrangement and contraction due to a lack of bonding partners at the surface; the effect increases with decreasing film thickness. $^b$ values taken from Ref. [7].
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