Supporting information:
Sn₃O₄ exfoliation process investigated by density
functional theory and modern scotch-tape experiment

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1. Extra results

1.1. Experimental setup - Sn₃O₄ nanobelts synthesis

The Sn₃O₄ NBs were synthesized through a carbothermal reduction method, which start from a carbon source mixed to the starting oxide, allowing the synthesis temperature to decreases as a result of an increase in the vapor pressure of the precursor materials [1]. Based on this, 1.0 g of the precursor was prepared by mixing up SnO₂ (Sigma-Aldrich, 99.9 % purity) and carbon black (Union Carbide, > 99 % purity) in a 1.5:1 molar ratio. The sample was placed on an alumina (Al₂O₃) boat and inserted in the middle of a horizontal tubular furnace. The temperature in the middle of the furnace reached 1135 °C by a heating rate of 10 °C min⁻¹ and was kept at this temperature for 75 min [1].

A constant flux of N₂ (160 sccm) was upheld during the entire synthesis and, in order to obtain Sn₃O₄ NBs, an oxygen counter flow of 0.6 sccm was inserted when the temperature reached 900 °C, ensuring a mixed atmosphere

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until the end of the process [1]. White and yellow wool-like materials were formed at different tube temperatures and retrieved from the alumina tube walls. From our knowledge, the white and yellow materials are SnO_2 and Sn_3O_4 NBs, respectively[1], in which the latter is our subject of study.

1.2. Theoretical exfoliation energy

Fig. S1: Exfoliation energy convergence obtained by density functional calculations within vdW pairwise corrections, PBE+D3. The exfoliation energy was obtained by placing the Sn_3O_4 layers far apart, increasing the layer-layer distance, $d_{\text{Sn-Sn}}$, from 4 Å to 30 Å and computed according to the Eq. 2 presented in the main text.

1.3. SnO and SnO_2 NB FIB-SEM manipulation

From Fig. S2, one can see the thickness of the removed lamella from two different Sn_3O_4 NBs. In Fig. S2a, we show the same NB presented in Fig. 2a from the main text but taken with the sample holder at 52°. In this sample, the lamella thickness was estimated by the depth of the gap left in the original NB, giving a rough value of 13 nm. This thickness is slightly higher than the expected value, nevertheless can be explained by the difficult to find the edges of the gap during the measurement, and on the other hand by the thin layer of platinum

Fig. S2: (a) FIB-SEM image of the same Sn_3O_4 NB presented in Fig. 2a of the main text, but with the sample holder at 52° . The measured depth of the gap left on the NB was about 13 nm; (b) Different approach to measure the thickness of a different lamella. This FIB-SEM image shows a value of about 10 nm, matching with the theoretical calculations.

Fig. S3: (a) SnO NB raised from the substrate after trying to perform the exfoliation process in the FIB-SEM; (b) Sn_3O_4 lamella removed from a Sn_3O_4 NB; (c) SnO_2 nanobelt also lifted-out from the Si^0 as occurred with the SnO NB.

covering the sample after the platinum electron beam induced deposition (Pt-EBID) used to attach the manipulator to the top layer of the NB, increasing the height by a few nanometers, as can be easily seen on the position indicated by the white arrow on Fig. S2a.

Another approach to measure the lamella thickness is shown in Fig. S2b. In this attempt, the Easy-Lift[®] manipulator tip containing the removed lamella was warped by pushing the tip against the substrate. After bending the manipulator, it was possible to measure the thickness of this Sn_3O_4 lamella. The obtained value was about 10 nm, as expected from theoretical calculations.

In Fig. S3, we show FIB-SEM images regarding how each nanobelt of the Sn_xO_y system behaves when the same exfoliation procedure described in the main text was used. In Fig. S3a, one can see a SnO NB after we attempt to

remove a lamella, similar as we did with the Sn_3O_4 NB (Fig. S3b), nonetheless the SnO NB was completely lifted-out, instead of staying on the substrate without a thin lamella. Thus, this FIB-SEM experiment endorses the idea that interactions between two Sn_3O_4 layers at the stacking direction is larger for the SnO than Sn_3O_4 . Even though knowing that this exfoliation process was not likely to occur on the SnO_2 NB, once it is not a layered material, we tried the same, but as expected, no lamella was removed, i.e., the NB was entirely pulled out from the Si^0 substrate, as can be seen in Fig. S3c.

1.4. Electronic structure properties

Fig. S4: In upper panel, we show the total density of states (TDOS) for the deeper states of distinct Sn_3O_4 structures using PBE+D3. In bottom panel, we present the local density of states (LDOS) for deeper states of the monoclinic structure using PBE+D3.

Fig. S5: The local density of states separated by effective coordination number for selected Sn_3O_4 bulk structures. The triclinic, monoclinic, MH-1 and MH-2 structures, obtained by PBE+D3, are showed for comparison. The two latter structures represent higher energy isomers.

- [1] P. H. Suman, E. Longo, J. A. Varela, M. O. Orlandi, Controlled synthesis of layered Sn_3O_4 nanobelts by carbothermal reduction method and their gas sensor properties, *J. Nanosci. Nanotechnol.* **14** (9), 2014, 6662–6668. <https://doi.org/10.1166/jnn.2014.9356>.