Supporting Information

Antimony Chalcogenides van der Waals Nanostructures for Energy Conversion and Storage

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Sb2SaSb2SaSb2SaSb2SaSb2SaSb2SaSb2SaSb2SaSb2SaSb2Ta</t

B) Shear force exfoliation

A) Starting Sb₂X₃

Figure S1. Photographs of the workflow. Left column (A): initial aspect of the bulk Sb_2X_3 -start crystals showing centimeter(s) size fragments. Middle column (B): exfoliation of Sb_2X_3 by shear force exfoliation in aqueous surfactant, sodium cholate. Suspension of sulfosalts in ice bath along and immediately after top shear mixing using a 750 W Bosch hand blender for 1 hour of processing. Right column (C): Photographs of final aspects of the obtained suspensions of exfoliated materials Sb_2X_3 -exf; Fine powder of the shear exfoliated Sb_2S_3 -exf obtained from centrifugation and washing of the top 75% materials in suspensions. Example of colloidal suspensions in DMF for Sb_2Te_3 -start (left) and Sb_2Te_3 -exf (right) before sonication, showing immediate dispersion of the exfoliated materials.

C) Exfoliated Sb₂X₃



Figure S2. Sb₂X₃ characterization. SEM micrographs of the bulk Sb₂S₃ (top A) and Sb₂Se₃ (middle B) and Sb₂Te₃ (C) crystals, scale bars represent 10 and 1 μ m.



10µm

10µm

10µm

Figure S3. SEM micrograph of the pnictogen chalcogenide Sb₂X₃ starting materials with the respective mapping of elements, scale bars represents 10 μ m. A) Sb₂S₃-start, B) Sb₂Se₃-start and C) Sb₂Te₃-start.



Figure S4. EDX spectra of Sb₂X₃-start. A) Sb₂S₃-start; B) Sb₂Se₃-start; C) Sb₂Te₃-start.

	Sb ₂ S ₃ –start	Sb ₂ Se ₃ –start	Sb ₂ Te ₃ –start
Sb	28.7	19.2	23.7
Х	39.8	29.5	32.3
Ο	2.4	1.4	5.6
С	29.1	49.9	38.4
X/Sb	1.4	1.5	1.4

Table S1. EDS quantification of elements of starting Sb_2X_3 (% at.), with X=S, Se or Te.



Figure S5. DLS showing lateral size distribution of the Sb₂X₃-exf (A). TEM micrographs of the shear exfoliated Sb₂S₃ (B) Sb₂Se₃ (C) and Sb₂Te₃ (D) sheets with the respective mapping of elements, scale bars represent 1 μ m.



Figure S6. Thickness measurements of Sb₂X₃-exf: A) Sb₂S₃-exf; B) Sb₂Se₃-exf; C) Sb₂Te₃-exf. Left: Topographical image of the nanosheets drop cast onto ITO glass, scale bar represents 10 μ m. Right: Examples of height profiles curves distribution sampled from the surface.



Figure S7. Wide XPS survey spectra of Sb₂X₃-start (A1-C1) and Sb₂X₃-exf (A2-C2), referenced to the carbon C 1s peak at 284.5 eV.

			% at.	
Name	Position	Sb_2S_3 -start	Sb ₂ Se ₃ -start	Sb ₂ Te ₃ -start
S 2p	161.3	26.9	-	-
Se 3p	160.4	-	22.2	-
Te 3d	568.5	-	-	18.5
Sb 3d + O 1s	528.4	24.3	19.1	23.6
C 1s	284.5	48.7	58.7	57.8

Table S2. Quantification of individual elements of Sb₂X₃-start obtained from the XPS survey spectra.

Table S3. Data of heterogeneous electron transfer (HET) rate constant, k^{0}_{obs} , for Sb₂X₃.

	ΔE (mV)	k ⁰ obs (cm s ⁻¹)
Sb ₂ S ₃ -start	103	4.72x10 ⁻³
Sb ₂ S ₃ -exf	118	2.83 x10 ⁻³
Sb ₂ Se ₃ -start	232	0.56 x10 ⁻³
Sb ₂ Se ₃ -exf	460	0.08 x10 ⁻³
Sb ₂ Te ₃ -start	76	9.91 x10 ⁻³
Sb ₂ Te ₃ -exf	80	8.50 x10 ⁻³





Figure S8. LSV polarization curves of Sb₂X₃ for OER in 1.0 M KOH (A) and the average overpotential required for current density of 10 mA /cm² (B). LSV of ORR in 1.0 M KOH (C) and the average half-peak potential (D). All error bars correspond to standard deviations based on triplicate measurements. Scan rate: 5 mV/s.



Figure S9. Stability tests of Sb₂X₃-start HER performance by LSV polarization curves before and after 100 CVs in 0.5 M H₂SO₄ (A), 3.5 wt.% NaCl (B), 0.1 M PBS (C) and 1.0 M KOH (D) with a ν of 5 mV/s.

Table S4. HER data summarized for Sb_2X_3 -start and Sb_2X_3 -exf in the different media.

	кон			PBS		3.5 wt.% NaCl			H ₂ SO ₄			
Sb ₂ X ₃	η (V) @10 mA/cm²	Tafel slope (mV/dec)	<i>j</i> 0 (mA/cm²)	η (V) @10 mA/cm²	Tafel slope (mV/dec)	j₀ (mA/cm²)	η (V) @10 mA/cm²	Tafel slope (mV/dec)	j₀ (mA/cm²)	η (V) @10 mA/cm²	Tafel slope (mV/dec)	j₀ (mA/cm²)
Sb ₂ S ₃ -start	1.49	93	4.9x10 ⁻⁵	1.18	163	2.8 x10 ⁻⁵	1.30	439	2.1 x10 ⁻³	1.38	81	1.5 x10 ⁻⁸
Sb_2S_3 -exf	1.03	60	1.1 x10 ⁻⁴	1.05	118	3.0Ex10 ⁻⁵	1.10	311	3.8 x10 ⁻³	0.91	90	1.2 x10 ⁻⁵
Sb_2Se_3 -start	1.52	150	3.8 x10 ⁻⁴	*	*	*	1.24	379	3.5 x10 ⁻³	1.27	221	7.3 x10 ⁻³
Sb_2Se_3 -exf	1.08	108	5.8 x10 ⁻⁴	1.22	115	3.6 x10 ⁻⁷	1.13	183	2.8 x10 ⁻⁴	1.20	179	1.9 x10 ⁻⁴
Sb_2Te_3 -start	1.41	117	3.3 x10 ⁻³	1.63	103	1.5 x10 ⁻⁷	1.60	397	9.1 x10 ⁻³	1.26	154	3.3 x10 ⁻⁷
Sb_2Te_3 -exf	1.43	208	1.1 x10 ⁻⁴	1.28	95	1.2 x10 ⁻⁴	1.13	294	6.1 x10 ⁻⁴	1.07	199	3.4 x10 ⁻⁶



Figure S10. CVs of GC electrode modified with Sb_2X_3 -bulk (A, C, E) and Sb_2X_3 -exf (B, D, F) at scan rates (v) from 10-500 mV/s. All CVs done in aqueous electrolyte 0.1 M KCl, reference Ag/AgCl.

Electrochemical measurements

Studies of the inherent electrochemistry of modified electrodes were made in 0.1 M phosphatebuffered solution (PBS, pH 7.2) using cyclic voltammetry at 0.1 V/s scan rate, in a potential window of -1.5 to 1.5 V. Solutions were purged with nitrogen gas before measurements. The heterogeneous electron transfer (HET) rates measurements were done at a scan rate of 0.1 V/s, for 2.0 mM of the ferro/ferricyanide redox probe in a 0.1 M KCl solution. The k^0_{obs} values were determined using the method developed by Nicholson which relates ΔE_p to a dimensionless parameter, ψ , and consequently to k^0_{obs} . The roughness factor was not considered in this case. The diffusion coefficient of $D = 7.26 \times 10^{-6}$ cm² s⁻¹ for Fe(CN)₆^{3-/4-} was used.

The hydrogen evolution reaction (HER), oxygen reaction reduction (ORR) and oxygen evolution reaction (OER) were performed by linear sweep voltammetry (LSV) at a scan rate of 0.005 V/s. The HER was performed in 0.5 M H₂SO₄ (acidic media), 3.5 wt. % NaCl, 0.1 M PBS (neutral) and 1.0 M KOH (alkaline media), while ORR and OER were done exclusively in alkaline media. For HER, LSV measurements were performed *vs* Ag/AgCl and the potentials were converted to the reversible hydrogen electrode (RHE) according to the Nernst equation E_{RHE} (V) = $E_{Ag/AgCl}$ + 0.059pH + $E^{0}_{Ag/AgCl}$. For OER, the overpotential is given by η (V) = $E_{RHE} - E^{0}_{a}$, with E^{0}_{a} =1.23 V.

The HER mechanism has been thoroughly studied, and there are two widely accepted mechanisms. Both are two-step mechanisms that begin with the adsorption of a proton onto the electrode surface through an electrochemical reduction process (Volmer step): Volmer adsorption step:

$$H_3 O^+ + e^- \rightarrow H^{\bullet}_{ads} + H_2 O \qquad b \approx 120 mV/dec \quad (1)$$

This step is followed either by the recombination of two hydrogen atoms adsorbed on the surface (Tafel desorption step):

$$H^{\bullet}_{ads} + H^{\bullet}_{ads} \rightarrow \uparrow H_2 \qquad b \approx 30 mV/dec \qquad (2)$$

or by the direct bonding of a hydrated proton with the adsorbed hydrogen atom which includes an electron transfer from the electrode surface (Heyrovsky step).

$$H_{ads} + H_3 O^+ + e^- \rightarrow \uparrow H_2 + H_2 O \quad b \approx 40 mV/dec \quad (3)$$

It is important to highlight the fact that HER is a two-step reaction involving adsorption of hydrogen ion and desorption of hydrogen molecule. Depending on the electrode surface, either the first or the second step can be rate determining.

The CV and galvanostatic charge/discharge curves for capacitance studies were performed in purged 5 M KOH solution. The amount of active material was taken as 5 μ g, since 1 μ L of DMF

colloidal suspensions containing 5 mg/mL Sb_2X_3 was drop-cast onto the GC working electrode surface and allowed to dry at room temperature.

To obtain capacitance from CV measurements, the relationship of scan rate and capacitive current can be used

$$C = \frac{dQ}{dE} = \frac{I}{dE/dt}$$
(Eq. S1)

where C is capacitance (F), I is current at a chosen potential and dE/dt corresponds to the scan rate of CV experiment (v). The weight specific capacitance density can be obtained by dividing C by the mass of the material drop cast onto the electrode surface (F/g).

The specific capacitance was calculated from the galvanotactic charge-discharge curves based on the same equation. Where in this case, I (A) refers to the discharge current; dE (V) represents the potential change within the discharge time dt (s).

Experimental Procedures

Synthesis. Antimony chalcogenides were prepared by direct reaction of element and chalcogenide in quartz glass ampoule under high vacuum. The quartz glass ampoule (25x100mm) was filled with stoichiometric amount of metal and chalcogenide corresponding to 10 g of antimony chalcogenide with accuracy better than 0.5 mg. The ampoule was evacuated on the base pressure of $1x10^{-3}$ Pa and melt sealed by oxygen-hydrogen welding torch. The ampoule was placed horizontally in muffle furnace and heated on 700 °C using heating rate of 5 °C/min. The ampoule was held on temperature for 5 hours and cooled on room temperature using cooling rate 1 °C/min. Finally, the formed crystals of antimony chalcogenide were mechanically removed from the ampoule and shortly grinded in agate mortar to obtain powder used as a starting material for further exfoliation.

Materials processing. Approximately 500 mg of the starting material was initially grinded and then submitted to shear force mixing in fresh aqueous surfactant SC for 1 h using an immersion 750 W hand blender at full speed, from Bosch (MSM 67190GB), as shown in **Figure S1**. The top 75% of the resulting dispersions were decanted and the bottom 25% was not processed, as it contains wider fragments or non-exfoliated material. For removal of surfactant excess, aqueous washing and successive centrifugations at different rotation speeds were employed. The production yields of recovered exfoliated material from the top 75% of the suspensions was ca. 10 %.

Structural and morphological characterization. To obtain SEM micrographs, scanning electron microscopy (JEOL 7600F, Japan) was used, at an acceleration voltage of 5 kV (otherwise specified). EDS measurements were conducted at a higher acceleration voltage

of 20 kV. The XPS spectra were obtained using X-ray photoelectron Phoibos 100 MCD-5 spectrometer (SPECS, Germany) with a monochromatic Mg K α radiation (SPECS XR50, $h\nu$ = 1253 eV, 200 W) as the X-ray source, the spectra were calibrated to the C 1s peak at 284.5 eV. In both cases, the materials investigated using an AI sample stub with conductive carbon tape on top of which the powders were fixated.

Transmission electron microscopy images were obtained using EFTEM Joel 2200 FS microscope. Sample was prepared by drop casting of sample suspension (1 mg/mL) on 200 mesh TEM grid. Elemental maps and EDS spectra were enquired with SDD detector X-MaxN 80 T S from Oxford Instruments (England). The dynamic light scattering (DLS) was performed using Zetasizer Nano ZS (Malvern, England). The measurement was performed at room temperature (20 °C) using glass cuvette. X-ray powder diffraction data were collected at room temperature on Bruker D8 Discoverer (Bruker, Germany) powder diffractometer with parafocusing Bragg–Brentano geometry using CuK α radiation ($\lambda = 0.15418$ nm, U = 40 kV, I = 40 mA). Data were scanned over the angular range 10–80° (20) with a step size of 0.019° (20). Data evaluation was performed in the software package EVA. The heights determinations of Sb₂X₃-exf sheets were done by optical profilometer measurements. A suspension of the respective Sb₂X₃-exf (0.1 mg/ mL) was drop cast onto an ITO glass. Images and profiles were obtained with an optical profilometer (Sensofar, Spain). Data treatment was done with MountainsMap[®] 7.4 version (Digital Surf, France), taken by considering six to ten different zones within the surface.