Supplementary information for Stabilizing TiS₂ nanosheets against oxidation via solvent exfoliation for energy storage.

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SEM and Raman of as purchased TiS2 powder





Figure S1 A) Raman of as purchased TiS2 Powder. B) SEM image that shows the expected layered structure of the starting material.

Raman spectrum of highly degraded TiS2 in aqueous surfactant dispersion



Figure S2 Raman spectra of highly degraded TiS2 in aqueous surfactant dispersion.

Absorption of fresh, size selected dispersions exfoliated in water + SC.



Figure S3 A)Absorption spectra of size selected dispersions in water+SC. The spectra have been normalized at 1.4 eV. B) Zoom in the absorption edge region of A spectra. There is a blue shift between the first and the second sample that saturates for samples with $\langle L \rangle \langle 248$ nm. Legend in A affects to spectra in B.

Absorption of fresh, size selected dispersions exfoliated in CHP.



Figure S4 A)Absorption spectra of size selected dispersions in water+SC. The spectra have been normalized at 1.4 eV. B) Zoom in the absorption edge region of A spectra. Note that in the samples exfoliated in CHP we have a continuous blue shift of the absorption edge with flakes <L> that saturates only at the two smallest samples. Legend in A affects to spectra in B.

Extinction of fresh/old sample in water.



Figure S5 Extinction spectra of fresh size selected samples (black) vs the 20 days old same dispersions. Top-right: largest, bottom left, smallest nanosheets.

SEM imaging of the TiS2-CNT composite used in the energy storage study:



Figure S6 SEM images of the TiS₂-CNT composite. From A to D the scale bar represents 10, 3, 1 and 0.2 μ m. The presence of CNT is more visible in the higher magnification images.

Electron diffraction spectroscopy:



Figure S7 Electron diffraction spectroscopy on fresh (A), one-month old (B) and 2-years old CHP-exfoliated TiS2 dispersions with an average lateral size of 452 nm. EDX spectra of fresh (D), one-month old (E) CHP-exfoliated TiS2 dispersions with an average lateral size of 100 nm. F) EDX on H2O-exfoliated 2-days old dispersion.

The oxidation mechanism in TiS_2 takes place when oxygen atoms replace sulphur atoms in the TiS_2 nanosheets. The ratio of S to Ti atoms is lower in those flakes with higher degree of oxidation. Figure S8 shows the Ti/S ratio for the samples measured in Fig S7.

S/Ti ratio in CHP-exfoliated nanosheets remain constant at a value of ~2.2 for the two chosen values. This support the lack of oxide peaks in the raman in aged CHP-exfoliated samples and the extremely low A_{re} obtained from the time dependent extinction measurements. On the other hand, the S/Ti ratio in the fresh water-exfoliated TiS₂ is ~2 indicating a higher degree of oxidation.

EDX suggests that our material does not have the expected stoichiometry (TiS₂). There is a 10% sulphur surplus.

The residual presence of Silicon atoms (0.5%) has been identified. The presence of this impurity most likely comes from the exfoliation process than in this particular set of sample was carried on using glass vials.



Figure S8 S to Ti ratio as a function of time for CHP-exfoliated large (black) and small flakes (red). The open square represents the Ti/S ratio of a 2 day old sample of water-exfoliated TiS2 nanosheets.

Modelling Aunre



Figure S9 From left to right: Pristine TiS2 flake, Flake oxidizing from the edges and flake oxidizing from defects.

The portion of unreacted material can be fitted using a simple model. As proposed in previous studies, TiS2 degradation star in both, edges and defects.^{1, 2} Accoring with Fig S1:

$$Area_{total} = \frac{L^2}{2} \tag{0.1}$$

When oxidizing from edges

$$Area_{TiS_2} = (L - 2A)(L/2 - 2A) \tag{0.2}$$

Where *A* is the oxigen penetration depth.

$$Area_{Ti_{x}O_{y}} = \frac{L^{2}}{2} - (L - 2A) \left(\frac{L}{2} - 2A\right)$$
(0.3)

When oxidizing from defects

$$Area_{TiS_{2}} = \frac{L^{2}}{2}(1 - \sigma \pi A^{2})$$
(0.4)

Where σ is the density of defects present in the flake.

$$Area_{Ti_xO_y} = \sigma \frac{L^2}{2} \pi A^2 \tag{0.5}$$

Considering both contributions (edge and defect oxidation) and normalizing respecting the total area:

$$A_{unre} = 2\left(1 - \frac{2A}{L}\right)\left(\frac{1}{2} - \frac{2A}{L}\right) - \sigma\pi A^2 \tag{0.6}$$

If we assume a non-constant σ that depends on flake's size:

$$\sigma(L) = \sigma_0 + \sigma_1 L + \sigma_2 L^2 \tag{0.7}$$

$$A_{unre} = 2(1 - \frac{2A}{L})(\frac{1}{2} - \frac{2A}{L}) - (\sigma_0 + \sigma_1 L + \sigma_2 L^2)\pi A^2$$
(0.8)

The value obtained for σ are in agreement with reported values for other TMDCs³⁻⁵ and fits nicely with the experimental A_{unre} values:



Figure S10 A) Experimental data (black dots) and model (dashed red line) of Aunre. B) σ value obtained from fitting the experimental data with our model.

Number of resonances in TiS2 spectrum

The second derivative of TiS2 extinction spectrum can be fitted using 4 Gaussians. Nevertheless, this model is neglecting the kink at ~1 eV because, due to the lower signal to noise ratio it is not observable in the 2^{nd} derivative extinction spectrum. There might be some minor contributions not taken in consideration at 2.8eV.



Figure S11 2nd derivative of TiS2 spectrum (black dots) and its fitting using 4 Gaussians (red line)



Resonances Shift as flake size's reduces

Figure S12 Position of main spectral resonances as a function of nanosheets' lateral size in water and CHP (A and C, respectively) "2eV" resonance shift with <L> for samples exfoliated in water and CHP (B and D, respectively).

Table S1 Literature comparison of the performance for TiS2 based anode electrode.

Fabrication method	Cut-off potential	Cyclability	Rate capability	Ref.
TiS2 nanoflakes/CNT composite by filtration	0.05-3 V	Cycles at 1 A/g, 826 mAh/g for 1 st cycle, and 843 mAh/g after 100 cycles	1055 mAh/g at 0.1 A/g, 912 mAh/g at 0.2 A/g, 890 mAh/g at 0.5 A/g, 849 mAh/g at 1 A/g, 752 mAh/g at 2 A/g, 592 mAh/g at 4 A/g	Our work
Grinded TiS ₂ with PVDF and carbon black	0.05-3 V 1.4-3 V	Cycles at 0.2 A/g, 761.1 mAh/g for 1st cycle, and 325.9 mAh/g after 100 cycles Cycles at 0.2 A/g, 190.2 mAh/g for 1st cycle, and 182.6 mAh/g after 100 cycles	-	6
Grinded TiS ₂ synthesized at high temperature from porous Ti and S powder	0.0-3 V	Cycles at 0.1 mA/cm2, 692 mAh/g for 1st cycle, and 669 mAh/g after 40 cycles (Charge)	-	7
TiS ₂ –MWCNT (1:1) hybrid as anode	0.01-3 V	450 mAh/g at 0.05 A/g for 1st cycle, and 340 mAh/g at 0.1 A/g after 50 cycles	-	8

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