

Electronic Supplementary Information

Thermal insulation with 2D materials: liquid phase exfoliated vermiculite functional nanosheets

Iwona Janica,^{a,b,c,†} Stefano Del Buffa,^{c,†} Agnieszka Mikołajczak,^{a,b} Matilde Eredia,^c Dawid Pakulski,^{a,b,c}
Artur Ciesielski,^{*b,c} Paolo Samorì^{*c}

^aFaculty of Chemistry, Adam Mickiewicz University in Poznań, Umultowska 89b, 61-614 Poznań, Poland; ^bCentre for Advanced Technologies, Adam Mickiewicz University, Umultowska 89c, 61-614 Poznań, Poland; ^cUniversité de Strasbourg, CNRS, ISIS, 8 allée Gaspard Monge, 67000 Strasbourg, France

[†]These authors contributed equally

Table of Contents:

1.	COLLOIDAL STABILITY OF VERMICULITE DISPERSIONS AFTER EXFOLIATION	S2
2.	PH OF VERMICULITE DISPERSIONS AFTER THE EXFOLIATION PROCESS	S3
3.	MORPHOLOGICAL CHARACTERIZATION OF VERMICULITE OBTAINED BY ULTRASOUND-ASSISTED EXFOLIATION.....	S4
4.	MORPHOLOGICAL CHARACTERIZATION OF VERMICULITE OBTAINED BY SHEAR-MIXING EXFOLIATION.....	S6
5.	N ₂ ADSORPTION/DESORPTION ISOTHERMS	S8
6.	REFERENCES.....	S9

1. Colloidal stability of vermiculite dispersions after exfoliation

The visual appearance of the dispersion after the exfoliation processes differs significantly with respect to the starting material. The amount of sediment is strongly reduced as to indicate an increased colloidal stability as a consequence of the decreased particle size; the brownish color of the dispersion is much more intense and the suspension becomes more turbid, representing a larger amount of dispersed material. A haze-looking particulate was also visible in backlight as to indicate the presence of aggregates with an ordered structure. Optical birefringence of exfoliated vermiculite dispersions is indeed documented in the literature and it is ascribed to a nematic liquid crystalline-like ordering of 2D nanosheets[1].

The colloidal stability of vermiculite dispersions was tested by measuring their Z-potential and by estimating the time required for a complete sedimentation by visual observations. Z-potential measurements were carried out by means of a 90Plus/BI-MAS system by Brookhaven Instruments (New York, NY, USA) working with a 15 mW solid state laser ($\lambda = 635 \text{ nm}$) as the light source. Z-Potential was determined from the electrophoretic mobility using the Helmholtz–Smoluchowski approximation. All measurements were performed on freshly prepared dispersions, after equilibration for 5 min at 25 °C. Despite the presence of large (likely non-exfoliated) particles that sediment quickly (within the first hour), the colloidal stability of aqueous dispersions of exfoliated vermiculite is satisfactory. The average Z-potential value results to be $-18 \pm 3 \text{ mV}$, indicating the presence of a poorly electrostatic-stabilized dispersion. However, the time before observing complete sedimentation is far longer than 24 hours, easily allowing for further processing of vermiculite nanosheets in the dispersed phase (*e.g.*, centrifugation, functionalization, mixing with other chemical species, etc.) or for their successful deposition onto solid surfaces (*e.g.*, by means of spray coating, solvent casting, inkjet printing, etc.).

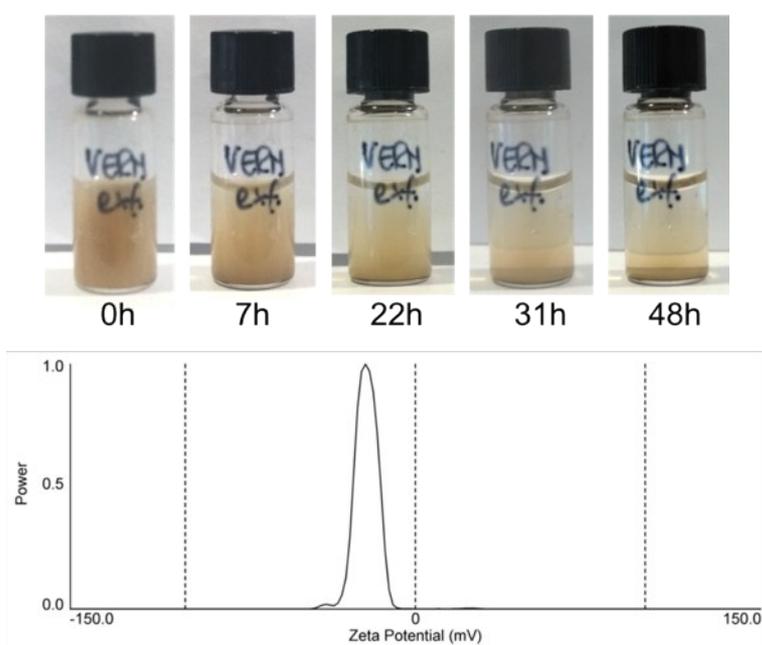


Figure S1. Photographs of aqueous dispersions of exfoliated vermiculite (with shear-mixing) at different times (native pH, T = 25 °C, approx. 0.05 %wt) and Z-potential measurement obtained on the same dispersion (after dilution to meet measurement criteria).

2. pH of vermiculite dispersions after the exfoliation process

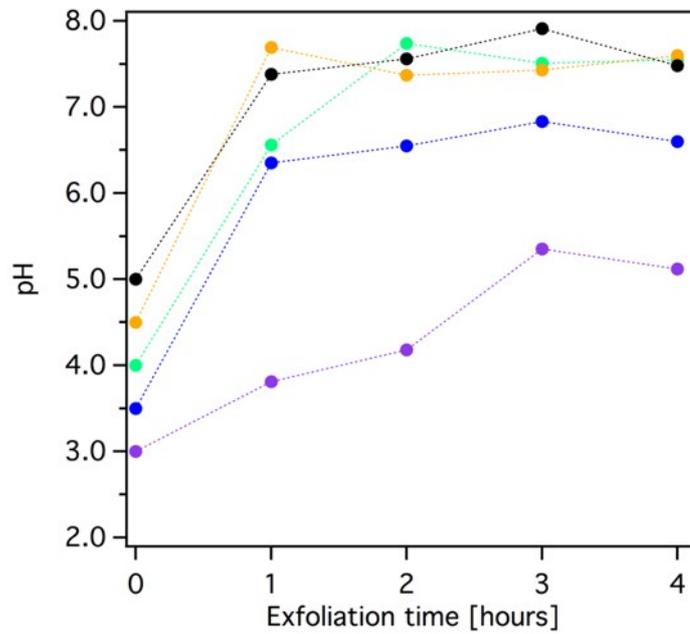


Figure S2. Final pH of vermiculite dispersion after ultrasound-assisted exfoliation at different times.

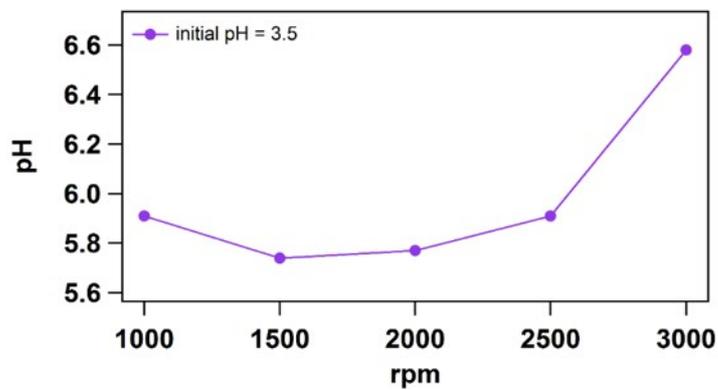


Figure S3. Final pH of vermiculite dispersion after exfoliation using shear forces for different mixing speed (exfoliation time=20min, initial pH = 3.5).

3. Morphological characterization of vermiculite obtained by ultrasound-assisted exfoliation

In order to conduct microscopic characterization, Si/SiO₂ substrates were cleaned with acetone and isopropyl alcohol (sonicated for 30 min in ultrasonic bath) for removing the protective photoresist layer, and then dried under nitrogen flow. The substrates were then treated with UV-O₃ (PSD Pro Series, Novascan) for 5 min followed by 25 min of exhaust. The samples for AFM and SEM characterization were prepared by spray coating/drop casting vermiculite dispersions on top of SiO₂/Si substrates. The samples were then heated on a hot plate (100°C) to remove all the remaining water. Morphological characterization was performed by scanning electron microscope (SEM, focused ion beam FEI Helios NanoLab 66), while atomic force microscopy (AFM) imaging was carried out using a Veeco Dimension 3100 operating on a Nanoscope IV control unit, under ambient conditions. Topographic and phase imaging was performed in tapping mode using antimony n-doped silicon tips (resonant frequency= 320 kHz, k=42 N/m; TESPA-V2, Bruker). The thickness and lateral size of the exfoliated vermiculite samples were determined by analysis of AFM images with Gwyddion software (version 2.50).

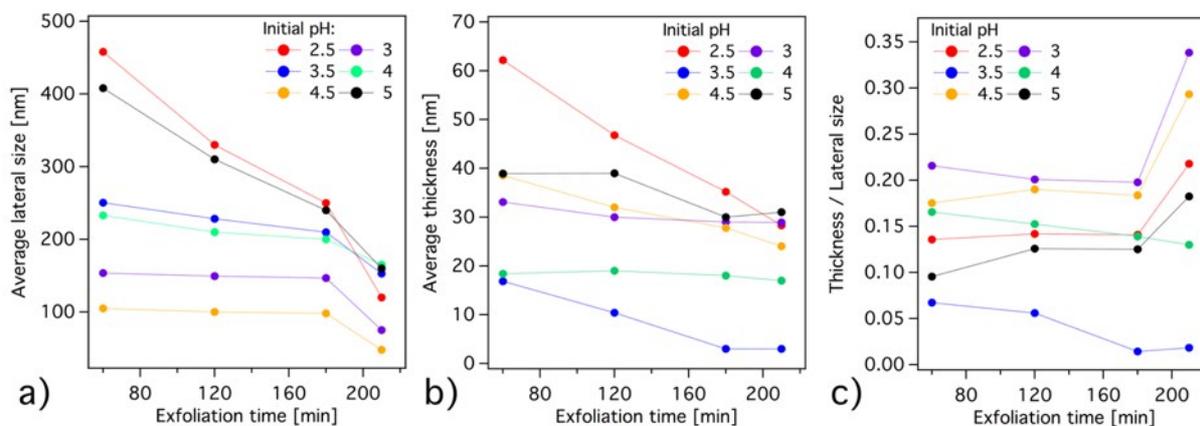


Figure S4. a) Average lateral size, b) thickness and c) lateral size-to-thickness ratio for vermiculite exfoliated with ultrasounds as a function of exfoliation time and pH, obtained by analysis of AFM images.

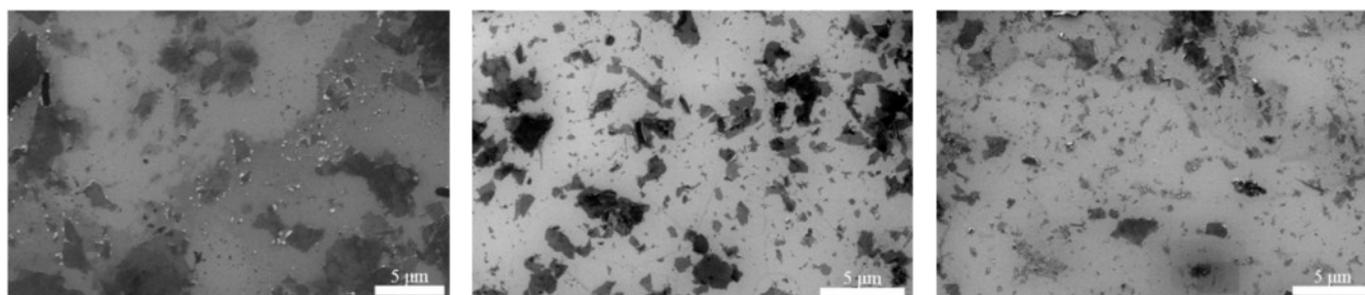


Figure S5. SEM images of vermiculite exfoliated using ultrasounds at pH = 3.5 (from left to right: 1h, 3h and 4h; scale bar= 5 μm). The imaged samples were prepared by spray-coating the vermiculite ink on the top of Si/SiO₂ substrates.

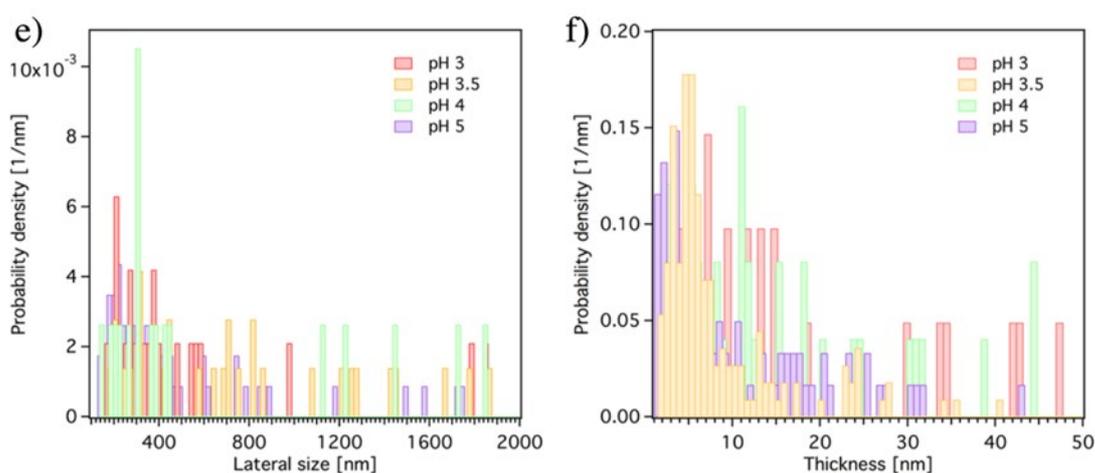
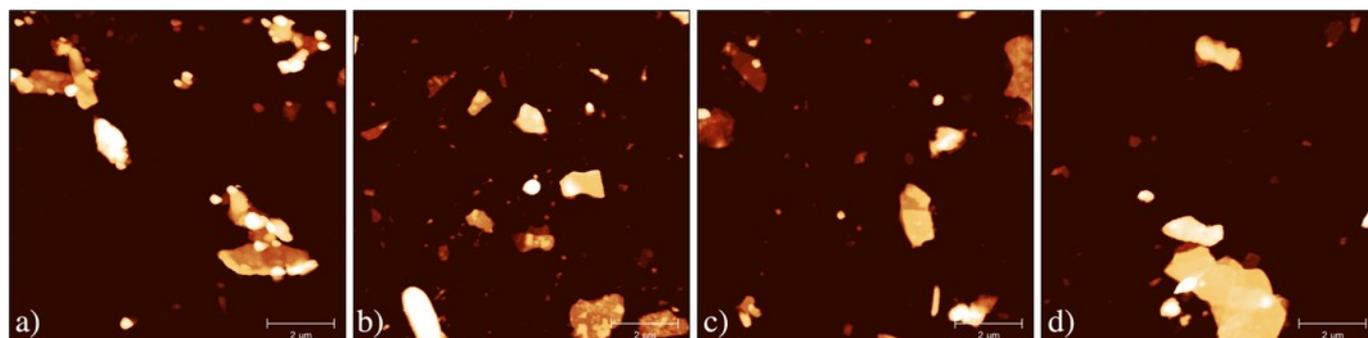


Figure S6. a-d) Representative AFM topographical images of vermiculite exfoliated with ultrasounds for 1 h at different pH (a) pH=3, Z-scale= 100 nm, lateral scale bar= 2 μm ; b) pH=3.5, Z-scale= 50 nm, lateral scale bar= 2 μm ; c) pH=4, Z-scale= 80 nm, lateral scale bar= 2 μm ; d) pH=5, Z-scale= 50 nm, lateral scale bar= 2 μm) and corresponding e) lateral size (analyzed flakes: 18-55) and f) thickness (analyzed flakes: 27-159) distributions normalized by the total number of analyzed flakes.

4. Morphological characterization of vermiculite obtained by shear-mixing exfoliation

The measurement of vermiculite flakes size in water dispersions were performed by means of diffraction analysis with Mastersizer 3000 laser analyzer, equipped with a HYDRO-SM wet dispersion unit (Malvern Instruments). Each distribution curve (volume density % vs size) represents the average of 10 measurements of 5 s each. A direct comparison of the flake size distribution of vermiculite dispersions after exfoliation with ultrasounds and shear forces at the same pH is shown in Figure S6.

While exfoliation by shear-mixing results in homogenous size distribution with a peak centered around 50 μm (some larger agglomerates are also present), ultrasound-assisted exfoliation produces nanosheets with a broader flake size distribution, but with a larger fraction of fine particles. In other words, the ultrasound-assisted exfoliation results to be a more vigorous process with smaller flakes being formed, while shear mixing is less effective but able to produce a more homogenous dispersion with larger particle size.

D-values corresponding to the distribution curves shown in Figure S6 results to be: $D_{10}=6.03 \mu\text{m}$, $D_{50}=61.90 \mu\text{m}$, $D_{90}=2440 \mu\text{m}$ for vermiculite exfoliated with ultrasounds, and $D_{10}=18.06 \mu\text{m}$, $D_{50}=57.20 \mu\text{m}$, $D_{90}=1150 \mu\text{m}$ for vermiculite exfoliated with shear forces. These values represent the intercepts for 10%, 50% (median of the distribution) and 90% of the total volume distribution of the sample, *e.g.* $D_{50}=61.90 \mu\text{m}$ means that half of the sample is composed of particles having a volume equivalent spherical diameter below 61.90 μm .

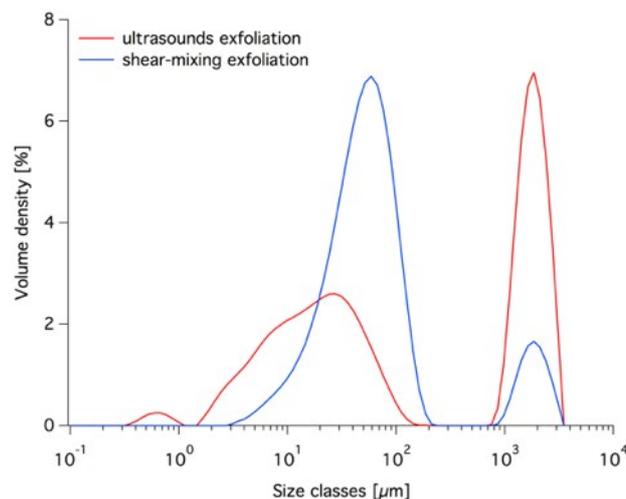


Figure S7. Distribution of flake size (volume-based) of vermiculite exfoliated with ultrasounds and shear forces at pH 3.5, obtained by laser diffraction.

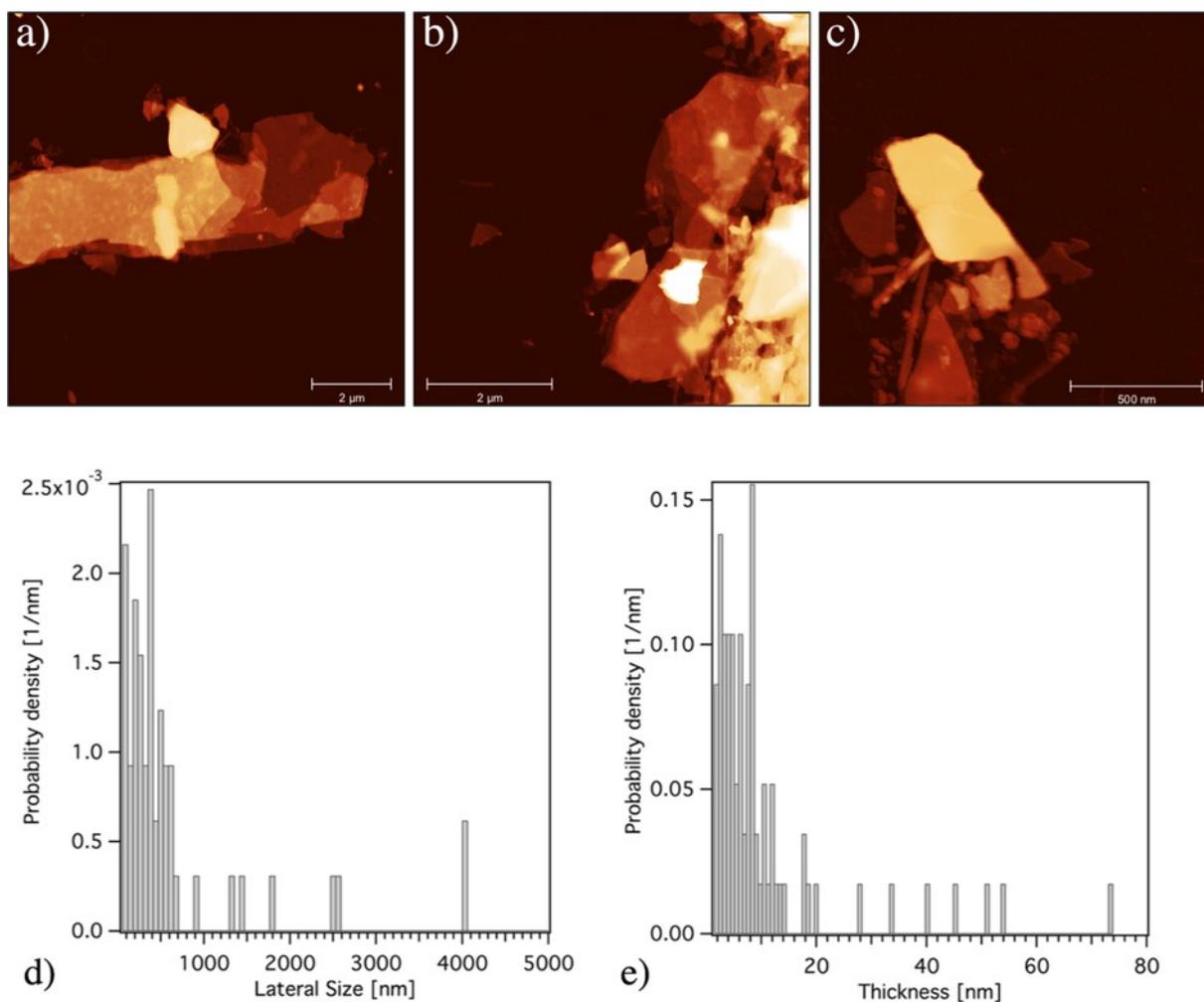


Figure S8. Representative topographical AFM images (a) Z-scale= 120 nm, lateral scale bar= 2 μm; b) Z-scale= 120 nm, lateral scale bar= 2 μm; c) Z-scale= 60 nm, lateral scale bar= 500 nm) of vermiculite exfoliated using shear forces (3000 rpm, 20 min, pH=3.5) and corresponding d) lateral size (analyzed flakes: 55) and e) thickness (analyzed flakes: 80) distributions normalized by the total number of analyzed flakes.

5. N₂ adsorption/desorption isotherms

N₂ adsorption/desorption isotherms were measured with a Quantachrome Autosorb iQ on degassed samples (100°C under vacuum for 12 h). All measurements have been performed at least twice on duplicate samples. Specific surface area and pore size distribution were determined using the BET and BJH (on desorption data) method, respectively.

The N₂ adsorption isotherms of raw and exfoliated (ultrasounds and shear-mixing) vermiculite are shown in Figure S8. All isotherms display a type IV shape typical of mesoporous adsorbents, in which, according to the IUPAC definition, there is an unrestricted monolayer-multilayer adsorption up to high p/p^0 followed by pore condensation inside non-rigid aggregates of plate-like particles, that is responsible for a type H3 hysteresis[2]. Specific surface area results to be 6 m²/g for the raw mineral, 22 m²/g and 108 m²/g for the samples exfoliated by shear mixing and ultrasounds (pH 3.5), respectively. The increase of specific surface area (4-fold and 18-fold increment) is a direct consequence of the occurred exfoliation process, while the difference observed with the two methods can be explained by considering the smaller particle size obtained with ultrasounds, as observed by means of AFM and granulometry. Exfoliated vermiculite samples also show a significant increase in the total pore volume and a shift of the pore size distribution peak (mostly ascribable to intra-particle voids) towards larger values, suggesting a direct role of the exfoliation process on the meso-scale organization of the clay structure. Total pore volume results to be 0.0018 cc/g for raw vermiculite, 0.038 cc/g and 0.157 cc/g for vermiculite exfoliated by shear mixing and ultrasounds, respectively. The absence of micro- and nano-porosity can be taken as a further evidence that the fine structure of the material is retained, *i.e.* no structural defects are introduced in the clay sheets upon exfoliation.

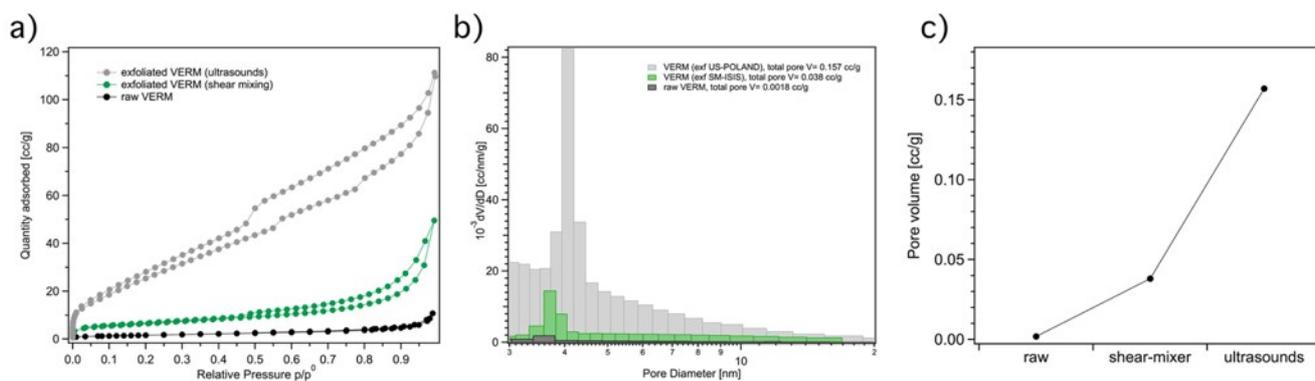


Figure S9. a) N₂ adsorption/desorption isotherms, b) corresponding pore size distribution and c) total pore volume of raw and exfoliated vermiculite (shear mixing and ultrasound-assisted exfoliation at pH 3.5).

6. References

- [1] Shao, J. J. *et al.* Self-assembled two-dimensional nanofluidic proton channels with high thermal stability. *Nat. Commun.* **2015**, *6*, 7
- [2] Thommes, M. *et al.* Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report) *Pure Appl. Chem.* **2015**, *87*, 1051-1069