

## Supplementary Information

### Free-standing membranes from the chemical exfoliation of mesoporous amorphous titania thin film

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#### Experimental Methods

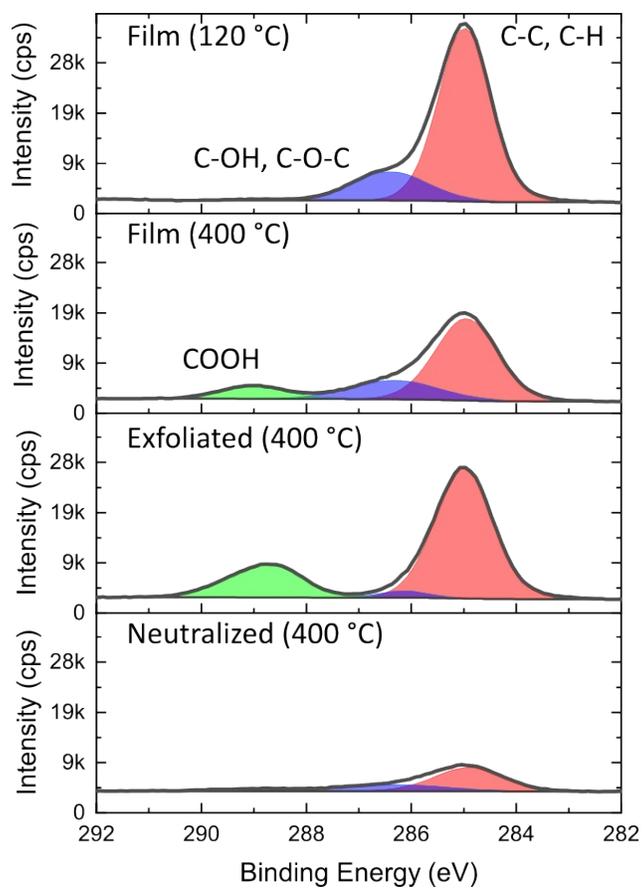
*Initial film preparation:* Fabrication of the film was previously reported elsewhere.<sup>S1</sup> Briefly, a precursor solution of HCl, TiCl<sub>4</sub> and water was mixed with a PS-*b*-PEO was dissolved in a mixture of deionized water, THF, ethanol, HCl, TiCl<sub>4</sub> (in a 36.4:13.5:6.3:3.5:1 molar ratio). This solution was spin-coated on an Si substrate (1.3 × 1.3 cm<sup>2</sup>) at 3000 rpm for 30 s and aged for 2 h under controlled temperature and humidity (23 °C, 30–40%RH).

*Chemical exfoliation:* The as-prepared films were first heated on a hot plate at 120 °C for 10 h, although various temperatures between 60 and 200 °C were also applied to determine the optimal conditions. Thereafter, the samples were immersed in an alkaline solution of NaOH (0.02–1 M) or Na<sub>2</sub>CO<sub>3</sub> (0.1–3 M) until the films were completely peeled off from the surface. Data in this work are presented using NaOH 0.05M. Although any substrate can be used to deposit the free-standing films, we collected the samples on Si chips for subsequent characterization. To facilitate the collection, the whole process can be carried out in a

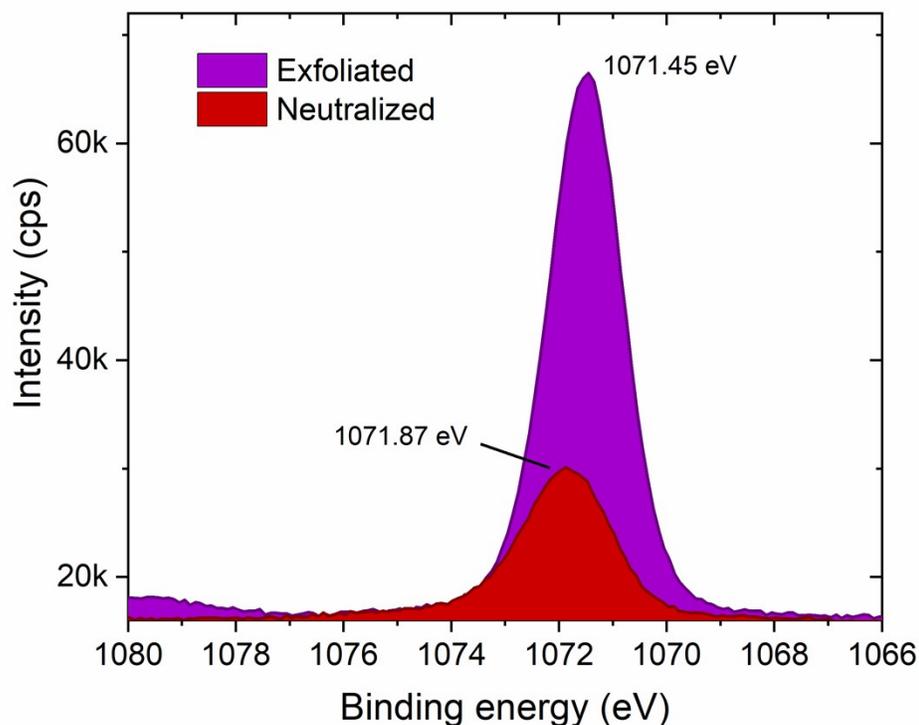
separation funnel hosting the alkaline solution, where the film-on-Si can be flipped upside down at the liquid surface and held as such by capillary forces.

*Neutralization:* Immediately after the film detached from the parent Si chip, a 0.1 M HCl solution was added to the strongly alkaline exfoliation solution until pH of  $7 \pm 0.5$  was reached. The acid was injected using a syringe mounted on a syringe pump and delivered at a flow of 0.5 ml/min. Essentially, the inflow should not disturb the free-standing membrane, as it can be easily displaced from the receiving surface.

*Characterization:* Field-effect scanning electron microscopy (FESEM) images were obtained using a Hitachi SU8230 with acceleration and deceleration voltages of 2.5 and 1.5 kV, respectively and a working distance of 3 mm. Atomic force microscopic (AFM) images were acquired on a Nanoscope5 (Bruker Japan) in the tapping mode. Transmission electron microscopy (TEM) analysis was carried out with a JEOL JSM-2100. 2D GISAXS profiles were measured using a Rigaku NANO-Viewer (microfocus rotating anode; Cu K $\alpha$  radiation; 40 kV, 30 mA) using a camera length of 680 mm. X-ray diffraction (XRD) patterns were obtained with a RIGAKU Smart Lab 9kW with a monochromated Cu K $\alpha$ 1 X-ray source (45 kV, 200 mA). X-ray photoelectron spectroscopy (XPS) analysis was achieved using a PHI Quantera SXM (ULVAC-PHI), with a monochromated Al K $\alpha$  X-ray source (100 W, 20 kV); the energies were calibrated using the C 1s peak (285 eV). XPS data have not been normalized, and therefore, comparative intensities between the samples are meaningful, reflecting differences in thicknesses, crystal densities, or elemental scarcity.



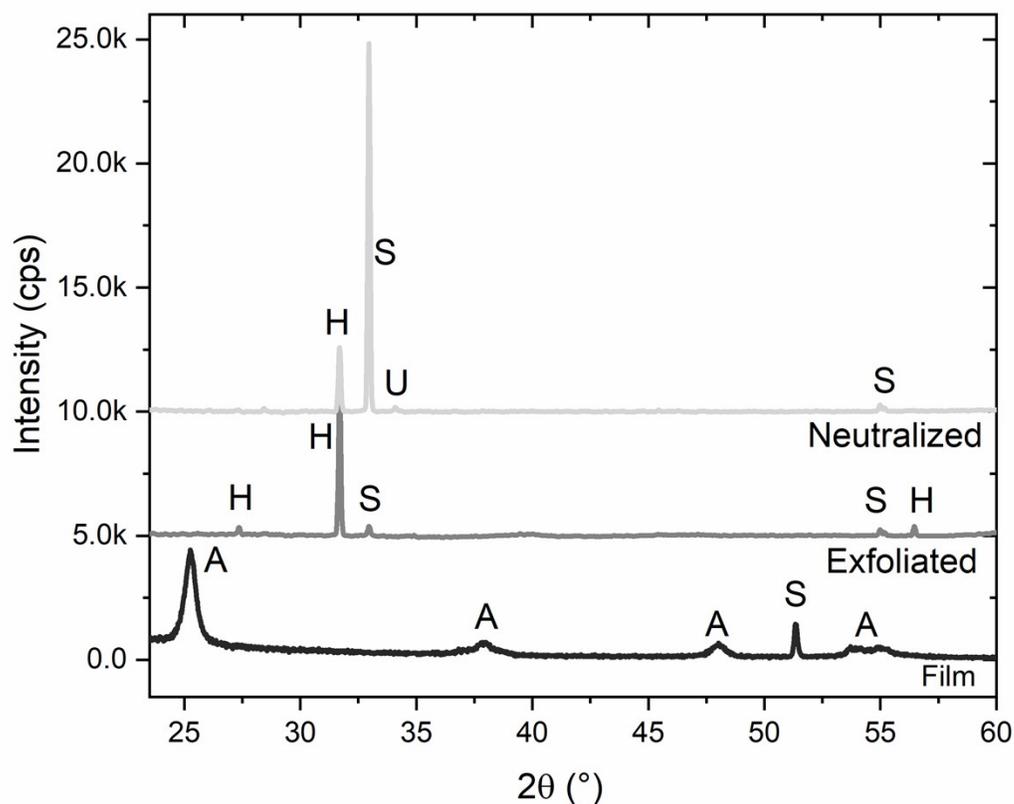
**Fig. S1** XPS study emphasizing spectra resolved around C 1s, O 1s, and Ti 2p. Four samples were considered: films annealed at 120 and 400 °C, as well as exfoliated film without and with neutralization step, followed by 400 °C thermal treatment.



**Fig. S2** XPS spectra resolved on Na 1s for the exfoliated and neutralized samples.

**Note related to Na 1s on *exfoliated* sample:** Na<sup>+</sup> ions are known to find a strong affinity with the ether oxygens present in the PEO chains,<sup>S2</sup> therefore the presence of Na<sub>2</sub>CO<sub>3</sub> is also possible.

**Note related to Na 1s on *neutralized* sample:** The slight shift in the binding energy of Na 1s can be attributed to a lesser contribution from the Na<sup>+</sup> species found in TiONa terminals, likely converted into TiOH terminals during the neutralization step, undergoing further homocondensation, under the assumption that a considerable amount of TiONa was formed. The available reports on the behaviour of Na binding energy within sodium titanate compounds remains scarce and little certitudes can be drawn from these results.



**Fig. S3** XRD of the film, exfoliated and neutralized samples (all annealed at 400 °C). Annotated peaks refer to TiO<sub>2</sub> anatase (A), silicon substrate (S), NaCl halite (H) as well as unknown assignment (U). N.B. Although the peak at 34.0° (U) matches TiO<sub>2</sub> cotunnite (ICSD 182578), standard synthetic procedures generally require high temperatures and pressures.

## References

- S1 V. Malgras, Y. Shirai, T. Takei and Y. Yamauchi, *J. Am. Chem. Soc.*, 2020, **142**, 15815–15822.
- S2 V. Palomares, P. Serras, I. Villaluenga, K. B. Hueso, J. Carretero-González and T. Rojo, *Energy Environ. Sci.*, 2012, **5**, 5884.