# Supporting information

## Size-selective separation of macromolecules by nano-channel titania membrane with self cleaning (de-clogging) ability

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*Membrane Synthesis*: Ti foils (10µm thickness, 99.6 % purity, Advent) were de-greased by sonicating in acetone, isopropanol, and methanol, rinsed with deionized (DI) water and dried in a nitrogen stream. The electrolyte was prepared by mixing glycerol and 10 %( w/v) $K_2HPO_4$ [1]. Before anodization, the electrolyte was preheated at 180°C for 3 hr to reduce the water content of the electrolyte. Electrochemical anodization was carried out in a two electrode system with the cleaned Ti foil (protected at the edges with a silicon polymer) and a platinum counter electrode. A high-voltage potentiostat system of Jaissle IMP 88 PC was used for anodization, applying 1 V for 90 min. The experiment was stopped at the moment of sudden current drop (Fig. S1), which indicated the complete anodization of Ti foil. Anodized samples were soaked in DI overnight to remove excess electrolyte, and finally dried in an oven at 50°C.

Structural characterization of the sample was done using a field-emission scanning electron microscope Hitachi FE-SEM S4800. Cross-section images were taken from membrane fragments. TEM was taken on plan-view samples prepared by mechanical grinding and polishing followed by $Ar^+$ ion beam milling. The conventional TEM investigations were carried out with a Philips CM 30 T/STEM instrument. For the HRTEM investigations a Philips CM 300 UT with a point resolution of 1.75Å was employed. X-ray diffraction analysis (XRD) for crystalline phase identification was performed with a X'pert Philips PMD with a Panalytical X'celerator detector using graphite monochromized Cu Ka radiation (Wavelength 1.54056 Å). The composition and the chemical state were characterized using X-ray photoelectron spectroscopy (XPS, PHI 5600, US).

For protein separation experiments, a two chamber permeable cell prepared from transparent polymer (and a quartz glass window) was used as schematically shown in Fig. S3. The membrane was mounted in between an O ring and a separating block. In all the experiment, 800 μg of proteins were dissolved in 1X PBS, this solution was filled into the reservoir. The proteins were cytochrome C (Sigma-Aldrich), BSA (Thermo Scientific) and β-galactosidase (Sigma-Aldrich). The outlet chamber was filled with PBS. The concentration of proteins in outlet chamber was quantified by collecting 50 μl of PBS at fixed time intervals. Protein quantification was done using a Micro BCA protein quantification kit (Pierce).

A complete clogging of membrane was achieved by long time exposure to protein solutions. UV induced self-cleaning was performed for 30 min using a He-

Cd laser. The membrane was exposed to UV/ LASER radiation directly through the quartz window on the reservoir side. The composition of clogged and cleaned membrane samples were characterized using X-ray photoelectron spectroscopy (XPS). As a control experiment, the influence of UV radiation on a protein rich surface of a smooth alumina foil was investigated by XPS (see Fig. S5).

[1] Kim, D.; Lee, K.; Roy, P.; Birajdar, B. I.; Spiecker, E.; Schmuki, P. Angew. Chem., Int. Ed. 2009, 48, 9326.

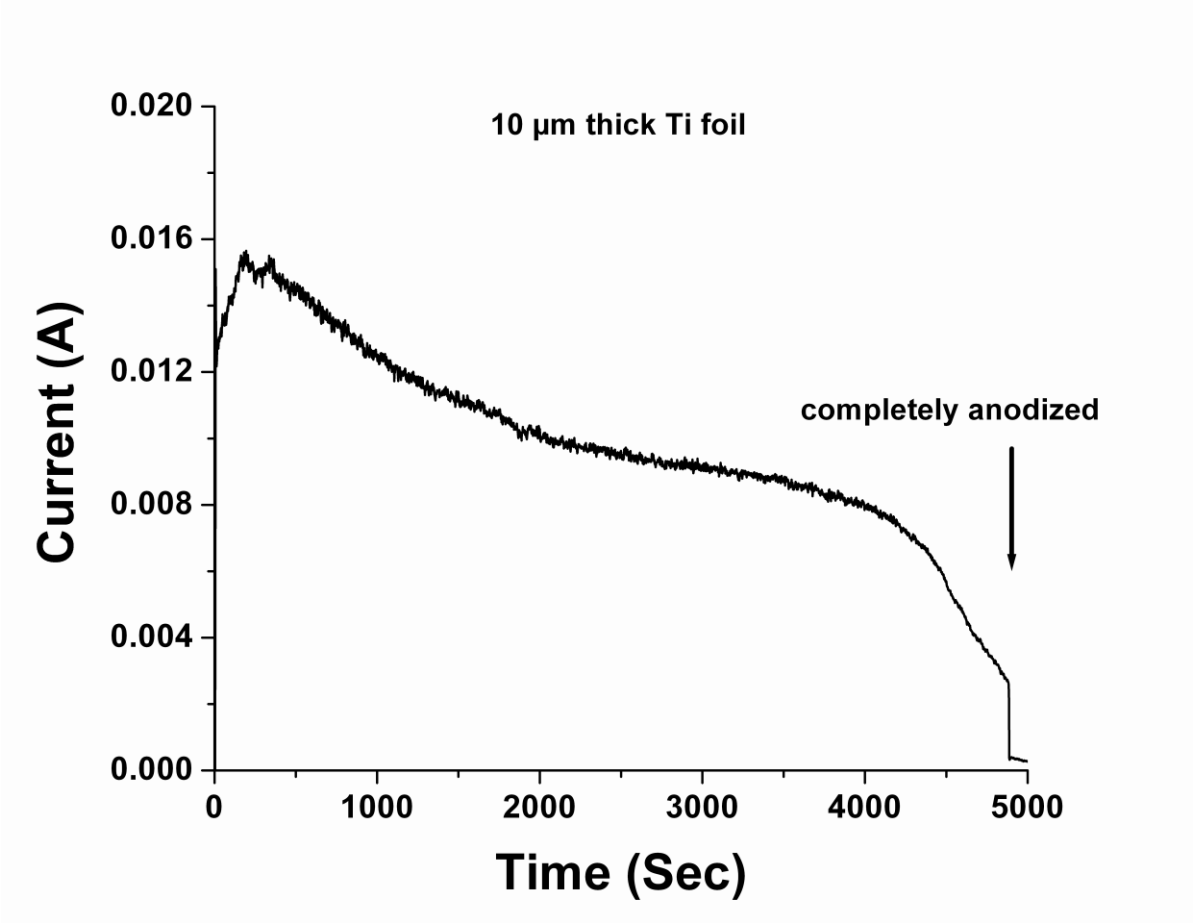
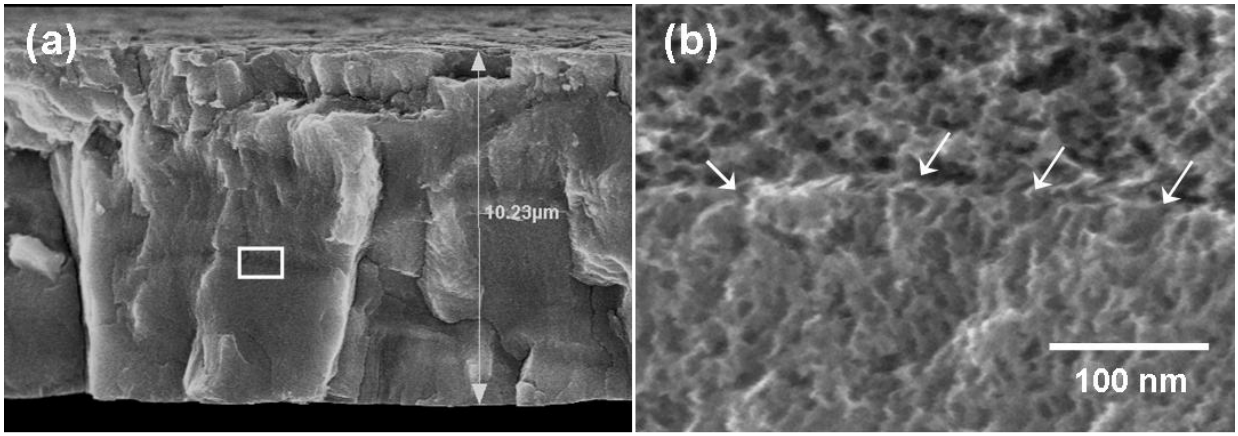
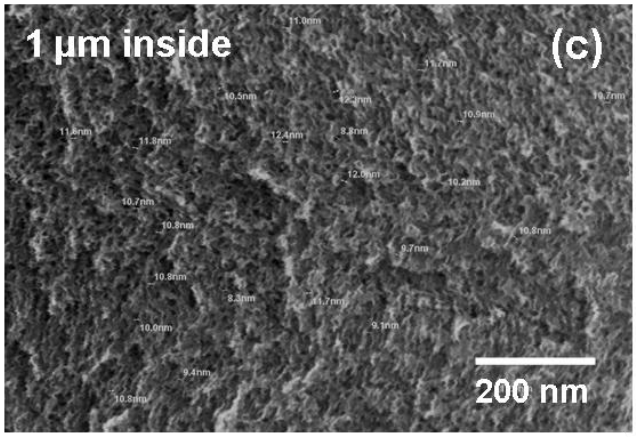
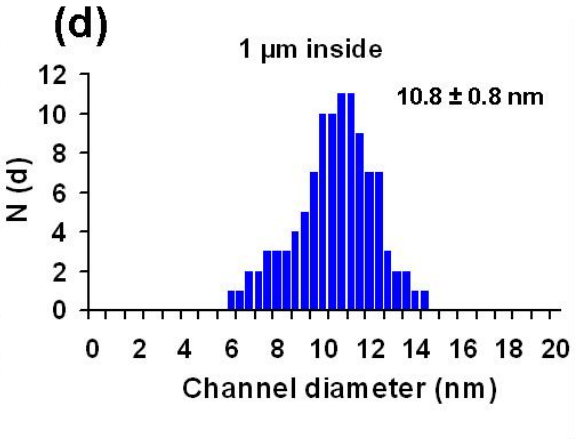
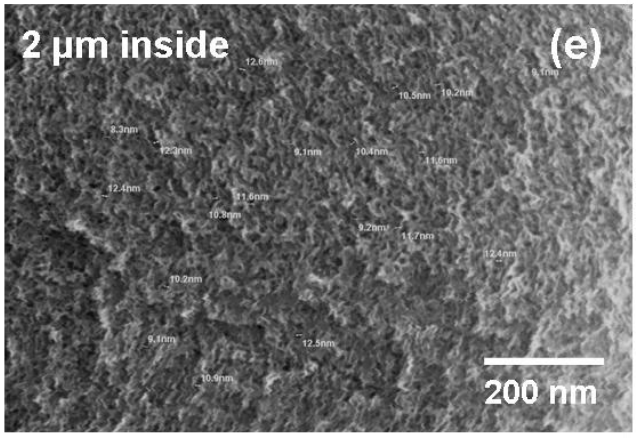


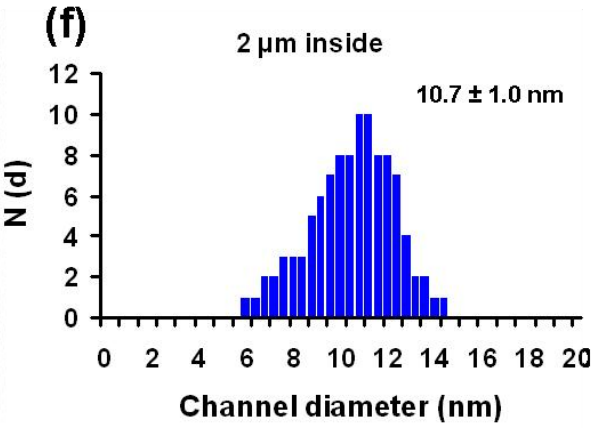

**Figure S1**: Current vs time (*I* - *t*) plot during membrane anodization in 10 % (w/v) $K_2HPO_4$ containing glycerol electrolyte at 180°C on a 10 µm thick Ti-foil.


(a)
10.23μm
(b)
100 nm


1 μm inside
(c)
200 nm


(d)
1 μm inside
10.8 ± 0.8 nm
N (d)
Channel diameter (nm)


2 μm inside
(e)
200 nm


(f)
2 μm inside
10.7 ± 1.0 nm
N (d)
Channel diameter (nm)

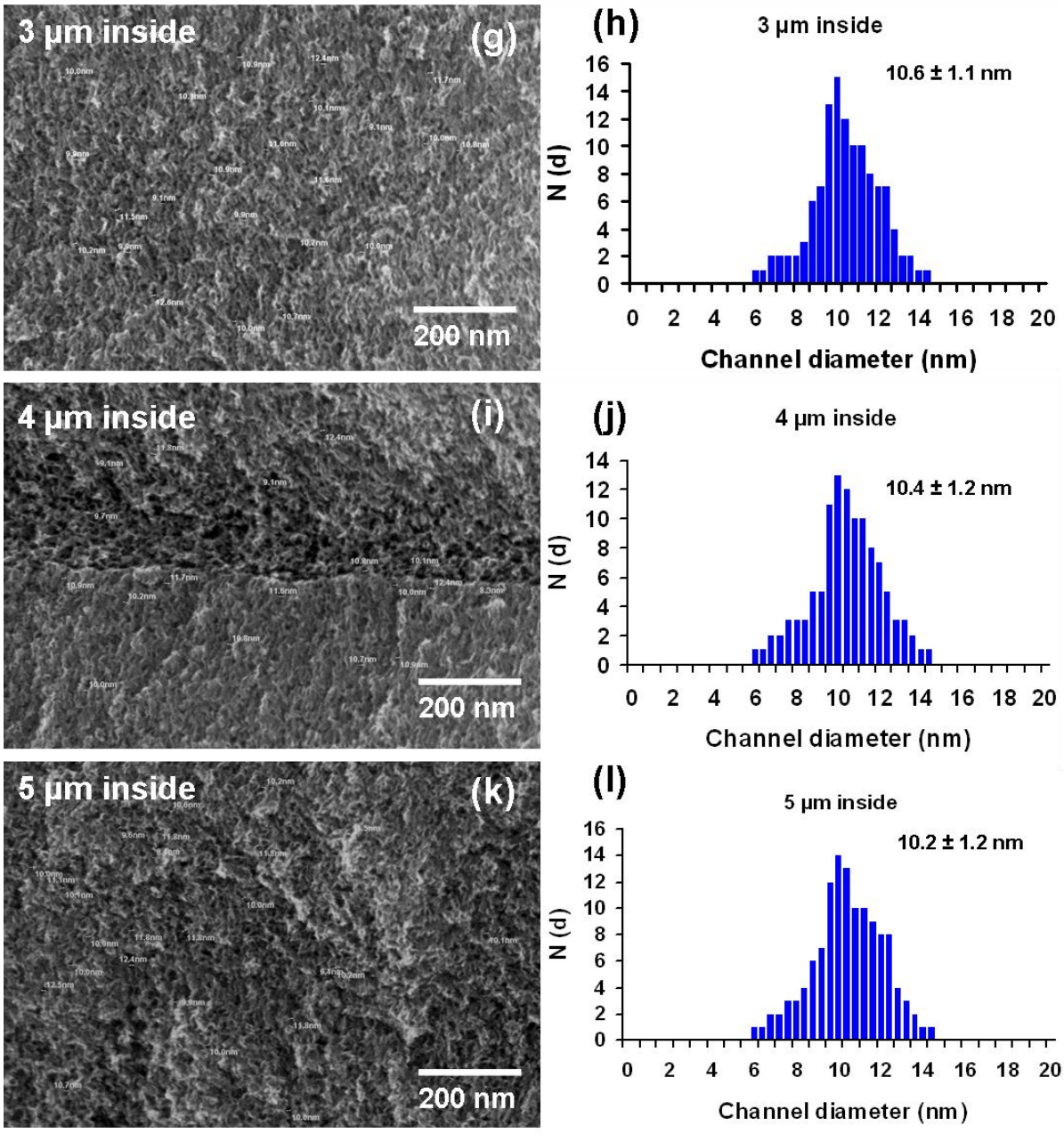



**Figure S2**: Cross-section SEM images of (a) 10 µm thick $TiO_2$ nanochannel membrane and (b) zone where the two growing oxide layers meet (center of the membrane) demonstrating the 'through hole' morphology (indicated by arrows). (c)-(l) SEM images and corresponding pore size distribution from membrane cross-section taken every micrometer from the outside to the center of the

membrane. This demonstrates the highly uniform channel width over the entire cross-section of the membrane.

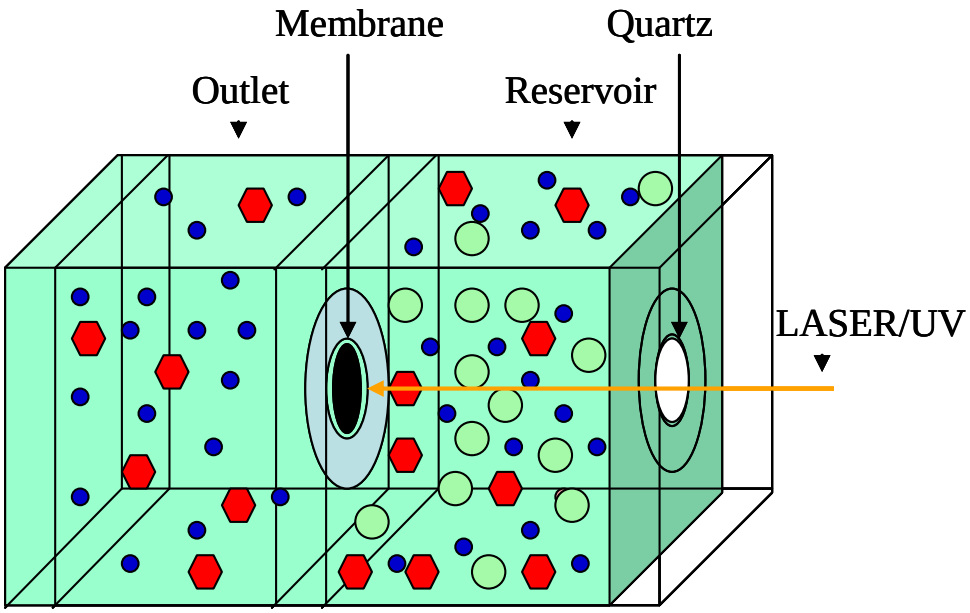



**Figure S3**: Schematic of the permeation cell.

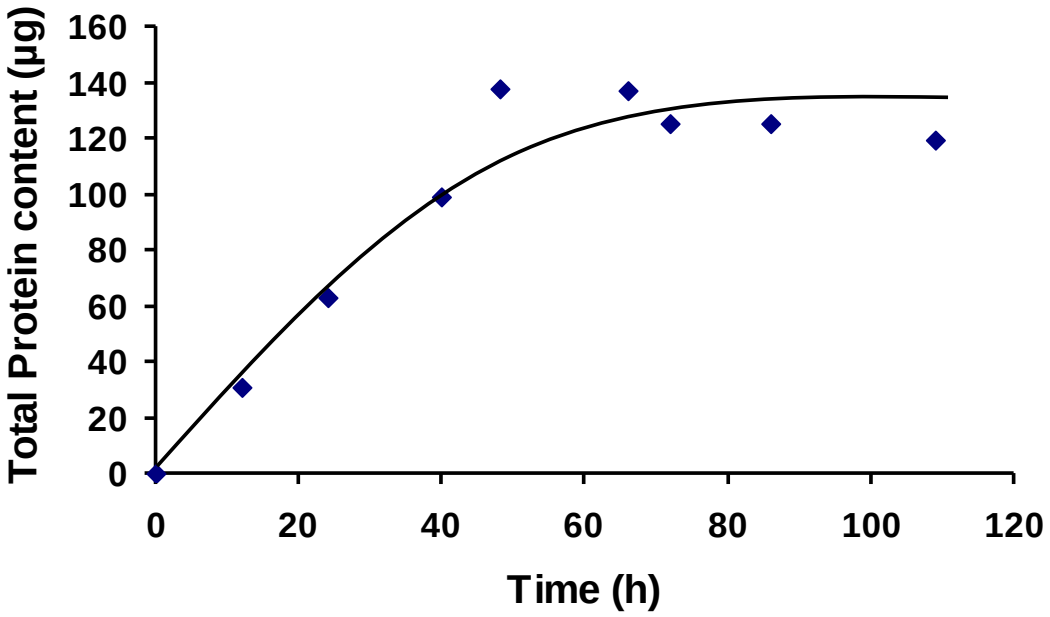



**Figure S4**: Permeability experiment (as in Fig. 2) but using a mixture of the three proteins (Cyt. C, BSA and β-Gal). The results show that in this case the total protein permeation is for mixed protein solutions identical to the sum of the individual fluxes of Cyt. C, BSA and β-Gal (compare Fig. 2). However, clogging occurs earlier compared to single protein solutions.

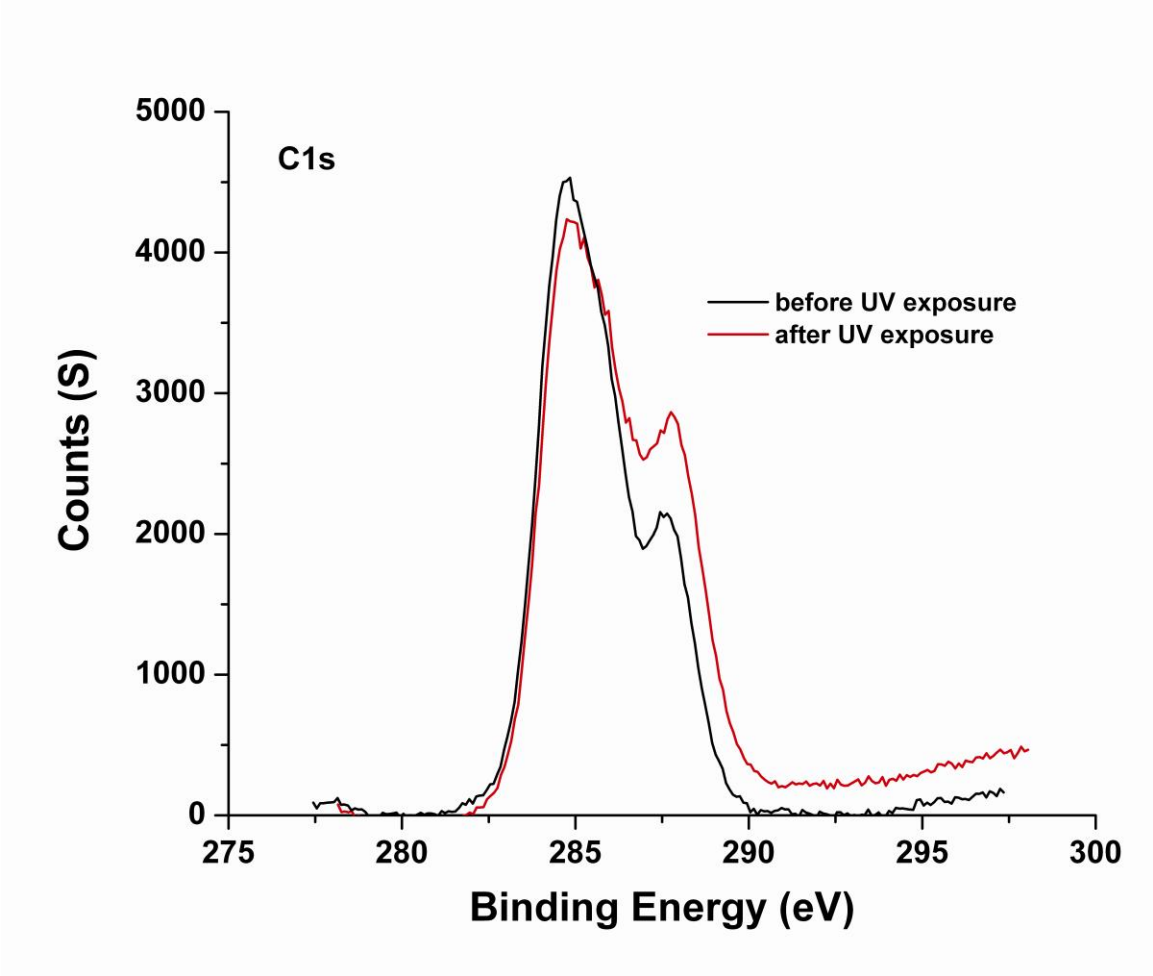



**Figure S5**: Reference XPS C1s peaks from protein coated $Al_2O_3$ before and after UV exposure.

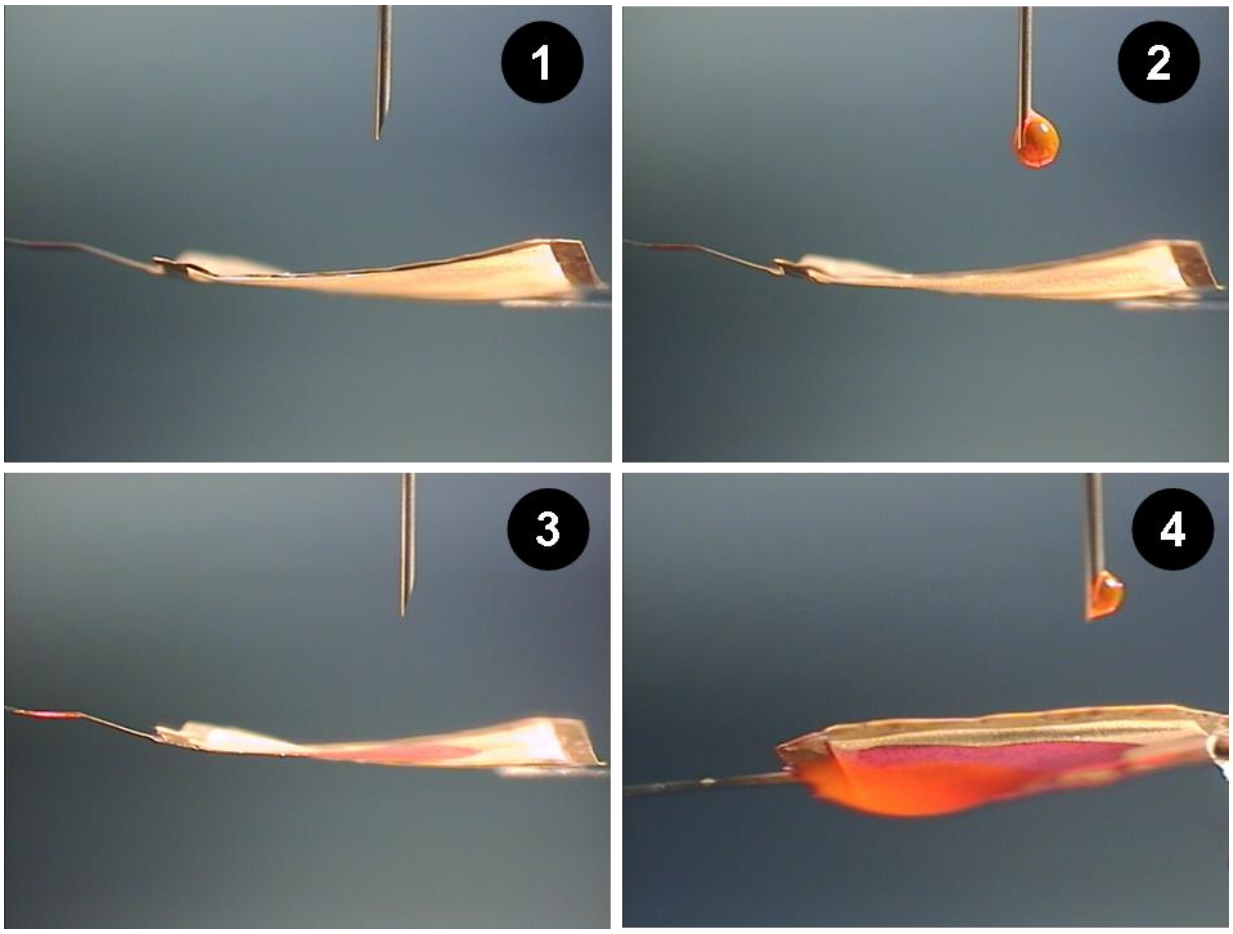



**Figure S6**: Sequence of optical images demonstrating water permeation through a 10 μm thick $TiO_2$ nano-channel membrane.

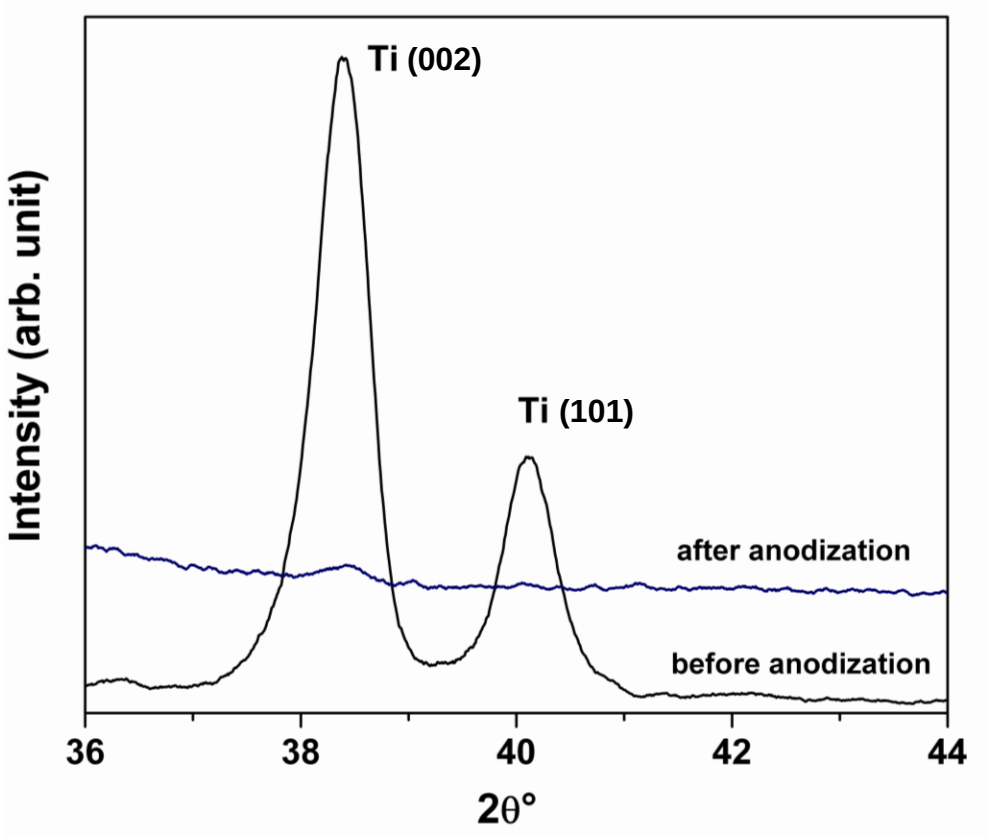



**Figure S7**: XRD pattern of Ti foil before and after anodization, indicating that no metallic Ti is left in the membrane.