# Supporting information

## Experimental section

### Materials

Poly(Ethylene Terephthalate) (PET) film (thickness 13 µm, biaxial orientation) was purchased from Goodfellow (ES301061). Diethyl Zinc (DEZ) ($Zn(CH_2CH_3)_2$, 95% purity, CAS: 557-20-0), Trimethyl aluminum (TMA) ($Al(CH_3)_3$, 97% purity, CAS:75-24-1), were purchased from Sterm Chemical. α-hemolysin from Staphylococcus aureus (H9395), Sodium chloride (S9888), Hexamethyldisilazane (HMDS) (reagent grade, ≥99%), Polyadenylic acid potassium salt noted poly(A) (P9403), Polyuridylic acid potassium salt noted Poly(U) (P9528), Polyinosinic acid potassium salt noted poly(I) (P4154) and Polycytidylic acid potassium salt noted poly(C) (P4903) (polydispersity from 600 to 4000 bases) were obtained from Sigma Aldrich. Demineralized water was obtained by milliQ system (Millipore).

### Fabrication of biomimetic single nanopore

Single nanopore on (PET) film has been built using a single track. PET film (thickness 13 µm, length 24 cm, width 4 cm) is positioned on the trajectory of a diffracted $^{78}$Krypton ion (9.5MeV) beam in GANIL (Caen France). A detector is positioned behind the film in order to count the number of ions crossing the film. When the detector counts one, the beam is stopped. The PET film is kept in an inert Helium atmosphere to preserve the tracks. The chemical etching has been obtained as follows. The tracked film is exposed 24 h per side to an ultraviolet light (Fisher bioblock; VL215.MC, 312 nm) and immersed during 5 minutes in NaOH solution (3 M) at 50°C.[1] Then the film is rinsed with demineralized water.
$Al_2O_3$/ZnO films thin films have been designed using a custom made ALD setup.[2] $Al_2O_3$ ALD ultrathin films has been synthesized using alternating exposures of TMA and $H_2O$ at 60 °C with the following cycle times: 0.1 s pulse (TMA), 20 s exposure, and 40 s purge with dry Argon with a flow rate of 100 sccm; A 2 s pulse ($H_2O$), 30 s exposure and 60 s purge. Alternating exposures of DEZ and $H_2O$ with the following cycle times: 0.2 s pulse (DEZ), 20 s exposure, and 40 s purge with dry Argon; a 2 s pulse ($H_2O$), 30 s exposure and 60 s purge were used to deposit the ZnO ALD ultrathin films. The growth per cycle was about 2 Å/cycle and 2.1 Å/cycle for $Al_2O_3$ and ZnO respectively.
Different sequences of 5 cycles of $Al_2O_3$ followed by 5 cycles of ZnO, were used to reduce the pore diameter to sub-10 nanometric range. After ALD deposition, samples were functionalized by a 24 hours Hexamethyldisilazane (HMDS) vapor exposure at room temperature in order to perform hydrophobic surfaces. The expected result from the HMDS treatment was the replacement of the -OH bond on the surface of the ALD layer by a hydrophobic ($(CH_3)_3Si$–) bond. The final diameter single nanopore has been estimated to 5.4 nm after HMDS grafting.
The bilayer thickness and chemical composition was analyzed by SAXS (Xenocs GenX equipped with a molybdenum anode and a MAR2300 2D imaging plate detector) and EDX (Hitachi 4500 coupled with a Thermofisher EDX detector). The HMDS single nanopore modification has been confirmed by XPS measurement (ESCALAB 250 Thermo Electron) and the determination of the contact angle. (supporting information).

### Ion current recordings

Single nanopore is mounted between two chambers of conductivity Teflon tubs containing buffer solution (KCl 1M, Tris 10mM, EDTA 1mM, pH=8 and $\sigma$=95mS.cm$^{-1}$). The current is measured by one AgCl electrode (XM410, Tacussel, France) plugged to the positive end of the amplifier and a platinum electrode (XM140, Tacussel, France) connected to the ground. Ion current is recorded by patch-clamp post amplifier (EPC800, HEKA electronics, Germany) using voltage clamp mode (200mV) and a sampling frequency 10KHz. Acquisition data have been performed by Instrutech LIH 8+8 acquisition card using patchmaster software (HEKA electronics, Germany). A lab-made analyze software (Matlab, Matworks, USA) is used to data analysis of the duration ($\Delta t$), the depth ($\Delta I$), the relative depth ($\Delta I/I_0$). Minimal value of $\Delta I/I_0$ (0.03) is imposed by the signal/noise ratio.

**Design of biomimetic single nanopore**

The nanolaminates were synthesized by alternating 5 ALD cycles of $Al_2O_3$ and 5 ALD cycles of ZnO. The number of bilayers depends of the initial diameter of the pore and it can be tuned between 1 and 14 bilayers. In order to determine the growth rate per cycle, the chemical structure, and the roughness and to confirm the nanolaminate structure of our samples, ALD layers deposited with the same parameters mentioned above were performed with different types of support such as silicon substrates, PET films and PC membrane.. After deposition, samples were characterized using scanning electron microscopy (SEM, S-4800, Hitachi), Energy-dispersive X-ray spectroscopy (SEM, S-4500, coupled with a Thermofisher EDX detector), SAXS (Xenocs GenX equipped with a molybdenum anode and a MAR2300 2D imaging plate detector), XPS (ESCALAB 250 Thermo Electron), AFM (NANOMAN 5 from Veeco instrument controlled with a Nanoscope V software), and the determination of a contact angle (GBX - Digidrop, Romans, France).

**a. Chemical and structural characterizations**

*SEM measurement.* Growth rate per cycle for both materials has been determined using SEM (Figure S1) on monolayers and multilayers of ZnO and $Al_2O_3$. The growth per cycle is about 2.1 Å/cycle for ZnO and 2 Å/cycle for $Al_2O_3$ at 60°C. [3]

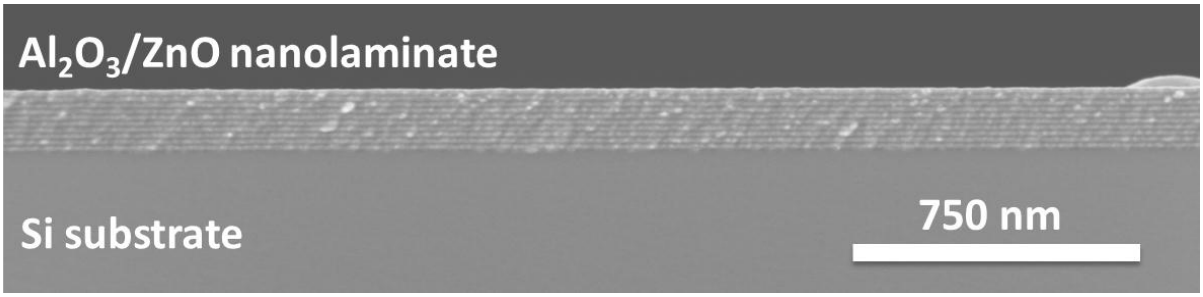


**Figure S1.** SEM images of nanolaminate cross-sections with bilayer thicknesses of 24.8 nm.

*EDX measurement.* Chemical composition of the deposit nanolaminates was examined using EDX on PET film. Figure S2 shows that Zn, Al, O and C have been detected.

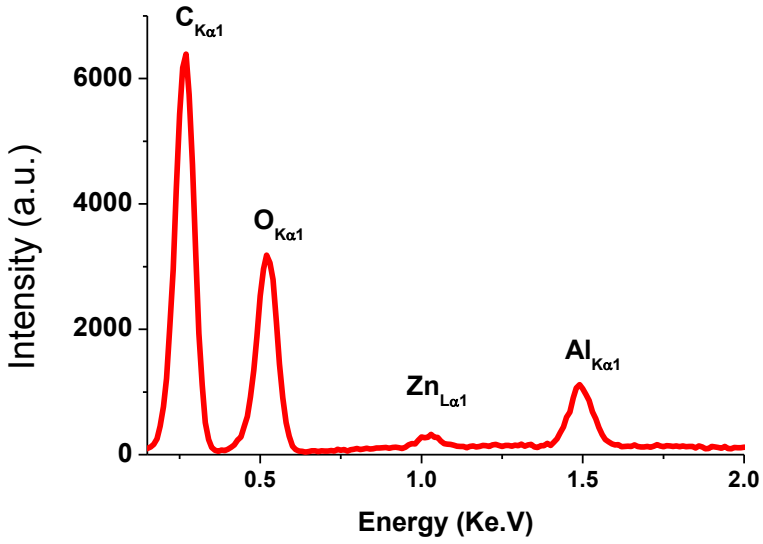


Figure S2. EDX measurement of ZnO/$Al_2O_3$ nanolaminates deposited on PET membrane

*AFM Characterization.* AFM measurement has been performed on 3 samples, the first is 20 cycles $Al_2O_3$ the second is 20 cycles ZnO and the third is 2 repetitions of 5 cycles $Al_2O_3$/ 5 cycles ZnO. All films were prepared on Si substrate in order to evaluate the roughness of the surface. AFM measurements (reported in Table 1) show that nanolaminate ultrathin films are smoother than $Al_2O_3$ and ZnO monolayers.

**Table S1**. AFM measurement on ZnO, $Al_2O_3$ and nanolaminates thin films

| Ultrathin film | Roughness |
|---|---|
| 20 cycles ZnO | 0.34 |
| 20 cycles $Al_2O_3$ | 0.32 |
| 2 repetitions of 5 cycles $Al_2O_3$ / 5 cycles ZnO | 0.25 |

*SAXS Characterization*. SAXS measurement have been performed on nanolaminates prepared by 35 sequences of 5 cycles $Al_2O_3$ / 5 cycles ZnO on PC track etched membrane with a pore diameter of 200 nm in order to determine the growth per bilayer $Al_2O_3$ / ZnO nanolaminates (Figure 3). The SAXS profile presents 2 main features: (i) a structure peak at q = 2.53 $nm^{-1}$, corresponding to a characteristic distance of 2.48 nm in the real space. This distance corresponds to the width of a double-layer deposited by ALD, (ii) A $q^{-4}$ slope in the low q region, characteristic of a sharp interface between the air in pores and the layers deposited by ALD. This is a proof of the quality of the deposition in terms of width control and homogeneity.

We note here that XPS has been used as an indirect way to measure the nanolaminate double-layer thickness and then estimate the diameter of the single nanopore based on this value. The diameter and the homogeneity of the nanolaminate deposited inside the the single nanopore could not be determined directly by other techniques such as transmission electron microscopy due to its high aspect ratio (L = 13µm).

The homogeneity of the diameter of the single nanopore has been checked by NaCl conductance measurement. As show in figure S4, At high salt concentration the slope of linear fit of conductance/concentration curve are similar for biomimeticnano pore and theoretical bulk conductance model (diameter 5mn lengh 13 µm). At low concentration the conductance is constant due to Debye exclusion effect.

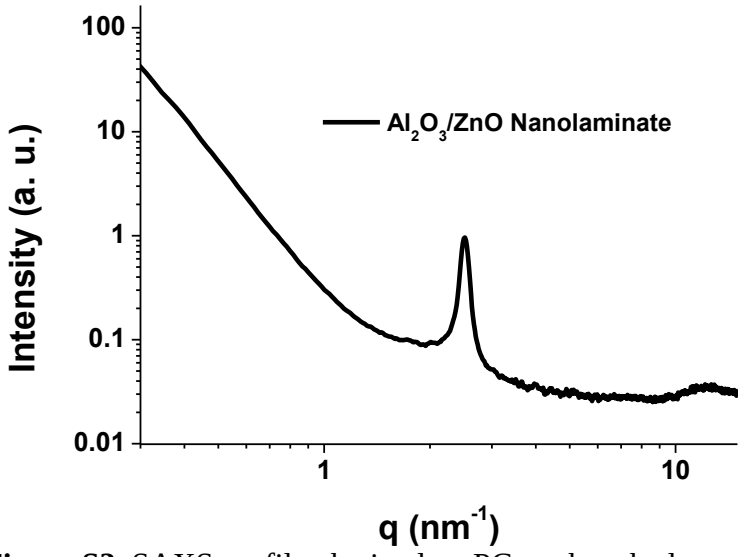


**Figure S3.** SAXS profile obtained on PC track etched membrane (Whatman-Nucleopore, diameter 200 nm, density $7.10^8$ pore $cm^{-2}$) after 35 sequences of 5 cycles $Al_2O_3$ / 5 cycles ZnO

*XPS Measurement.* XPS measurement was performed on PET membrane with 3 bilayers of 5 cycles $Al_2O_3$ / 5 cycles ZnO before and after (Table 2) HMDS treatment in order to evaluate the effect of the HMDS grafting on the surface. The success of the grafting has been attested by the observation of Silicon in low content (Si 2p binding energies 100.38 eV) that corresponds to Si-$CH_3$ bond.

**Table S2.** XPS measurement on PET membrane covered with 3 bilayers of 5 cycles $Al_2O_3$/5 cycles ZnO before and after HMDS grafting

| *PET/$Al_2O_3$/ZnO* | *Peak BE (eV)* | *At. %* | *PET/$Al_2O_3$/ZnO/HMDS* | *Peak BE (eV)* | *At. %* |
|---|---|---|---|---|---|
| Al2p | 73.83 | 11.96 | Al2p | 74.01 | 11.46 |
| C1s | 284.82 | 21.40 | C1s | 284.78 | 25.82 |
| O1s | 531.32 | 46.76 | O1s | 531.50 | 43.48 |
| Zn2p3 | 1021.56 | 19.88 | Zn2p3 | 1021.66 | 17.89 |
| Si2p | - | - | Si2p | 100.39 | 1.34 |

*Contact angle*. Contact angles with water were measured by applying a water droplet of 2.3 µL to the surface. The hydrophobicity was confirmed by the determination of a contact angle of 92°C on the treated HMDS surface.

## References

1 S. Sirijarukul; E. Balanzat; E. N. Vasina; P. Dejardin, *J Membrane Sci*, 2007, **296**, 185-194.
2 J. Bachmann; R. Zierold; Y. T. Chong; R. Hauert; C. Sturm; R. Schmidt-Grund; B. Rheinlander; M. Grundmann; U. Gosele; K. Nielsch, *Angew Chem Int Edit*, 2008, **47**, 6177-6179.
3 R. Raghavan; M. Bechelany; M. Parlinska; D. Frey; W. M. Mook; A. Beyer; J. Michler; I. Utke, *Appl Phys Lett*, 2012, **100**.