Supporting Information

Fabrication of BN membranes containing thousands of cylindrical pores using an elegant approach

C. Marichy,[a†] V. Salles,[a] X. Jaurand,[b] A. Etiemble,[c] T. Douillard,[c] J. Faugier Tovar,[a] F. Cauwet[a] and A. Brioude[a]

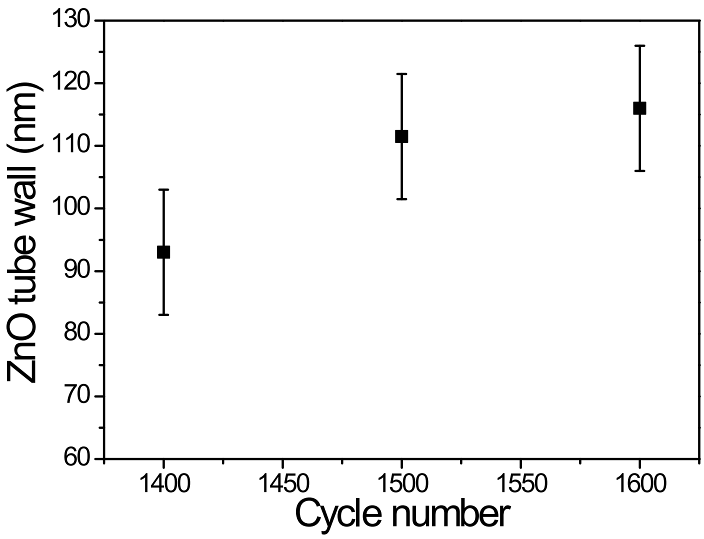
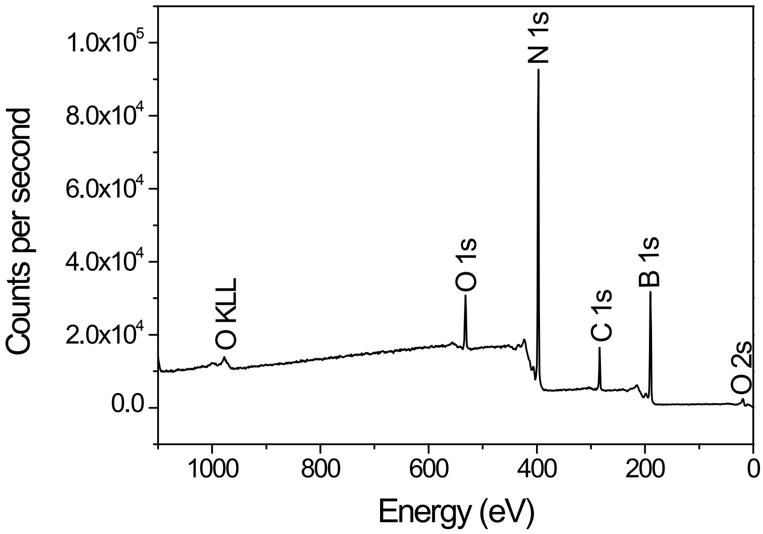


Figure S1. Thickness of tube walls, measured from SEM images, as a function of the ALD cycle number.

The thicknesses of the tube walls which are reported into the graph are an average of more than 20 values measured on at least five SEM images. Considering the measurement error in the image that can extend to 1-2 nm as a function of the magnification, and the error induced by the sample tilt toward the detector, the global measurement accuracy is estimated to be +/- 10 nm.

Table S1. XPS elemental quantification of the final BN membrane.

% at.	B	N	C	O	Zn
	41.1	41.0	11.7	6.2	-



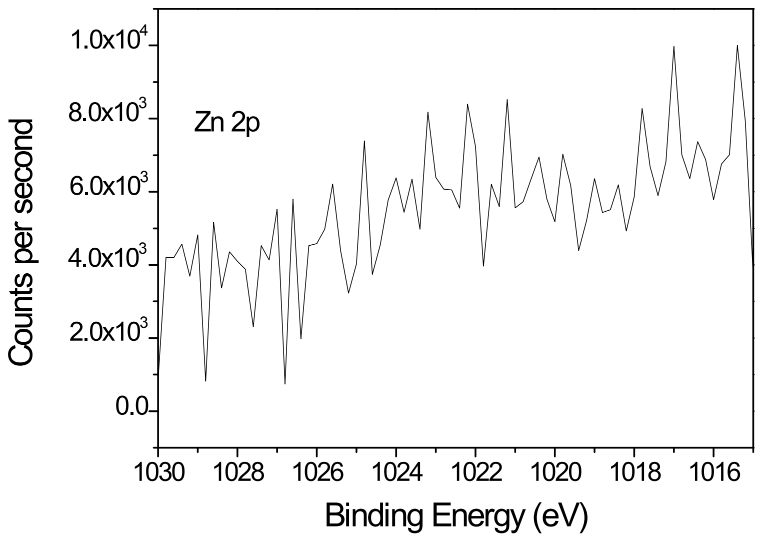


Figure S2. top: XPS survey spectrum, and bottom: XPS narrow scan of Zn 2p recorded from the BN membrane after annealing.

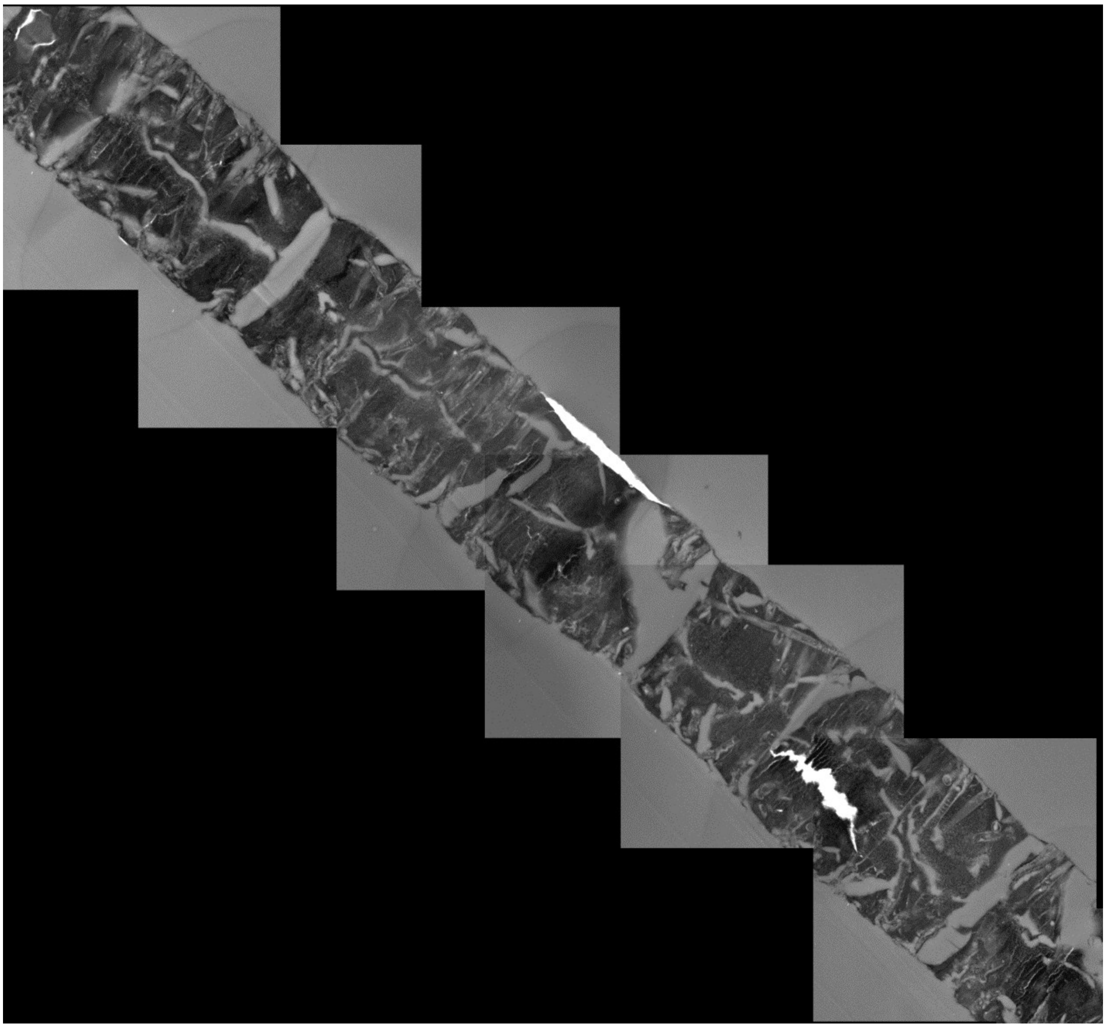


Figure S3. Stitching of bright field TEM images recorded from the cross section of BN membrane infiltrated with resin.

Table S2. Morphological parameters determined from FIB/SEM tomography analysis of BN membrane after treatment at 1000 °C of pbn/1500 cycles ZnO structure.

Porosity	Median diameter	connectivity	SSA	Tortuosity x	Tortuosity y	Tortuosity z
31.5 %	120 nm	97.8 %	> 10 $m^2.g^{-1}$	1.40	1.42	1.23

SSA: Specific surface area. SSA of > 24 μm^{-1} was determined and converted into $m^2.g^{-1}$ using a theoretical BN density of 2.3.

Measurement of specific surface area of the BN membrane

Half of a membrane, corresponding to a weight of 1 mg, was introduced inside a glass tube and degassed under vacuum at 200°C for 2h. Even if the results given in Figure S3 show a difference between adsorption and desorption curves, it is possible to plot the corresponding BET signal and to evaluate the specific surface area (SSA) with BET method. The measured SSA is thus ranging from 100 to 400 m²/g according to the slope used in Figure S1b. Taking into account that the sample weight is of about 1mg, the surface values corresponding to the range above mentioned SSA are between 0.1 and 0.4 m². The BET apparatus normally gives more accuracy when the surface of the sample is at least of 1 m², but in this case it should need a measurement with 10 membranes which is not really convenient at a lab scale.

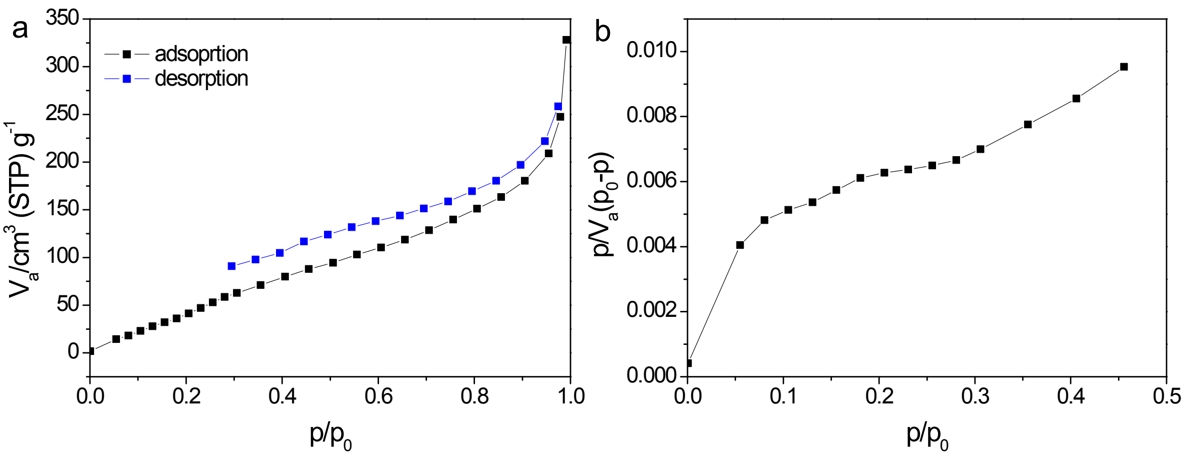


Figure S4. a) adsorption/desorption isotherm at 77 K using N_2 and b) the corresponding BET plot of the BN membrane presented in Figure 2k-o.

Calculation of specific surface area of PC and dense BN membranes

One side exterior surface for a PC membrane of 25 mm diameter and ~10 µm thick and total volume are:

$$S_{ext} = \pi r^2 = \pi \times 12.5^2 = 491\ mm^2$$

$$V_T = \pi r^2 l = \pi \times 12.5^2 \times 0.01 = 4.9\ mm^3$$

According to SEM imaging, one can consider a pore density of 1 pore/µm², the number of pores in one membrane is approximately:

$$N_{pore} = \frac{S_{membrane}}{pore\ density} = \frac{491}{(10^{-3})^2} = 4.9 \times 10^8\ pores$$

The pores having a diameter of 0.4 µm, the total pore surface and volume are:

$$S_{T_{pore}} = N_{pore} \times S_{pore} = N_{pore} \times 2\pi r l = 4.9 \times 10^8 \times 2\pi \times 0.2 \times 10^{-3} \times 10^{-2}$$

$S_{T_{pore}} = 6170\ mm^2$

$V_{T_{pore}} = N_{pore} \times V_{pore} = N_{pore} \times \pi r^2 l = 4.9 \times 10^8 \times \pi \times (0.2 \times 10^{-3})^2 \times 0.01$

$V_{T_{pore}} = 0.616\ mm^3$

And the total surface area of a PC membrane:

$S_{T_{PC}} = S_{T_{pore}} + 2S_{ext} - 2 \times N_{pore} \times S_{ext_{pore}}$

$S_T = 6170 + 2 \times 491 - 4.9\ \times 10^8 \times \pi \times (0.2 \times 10^{-3})^2 = 7029\ mm^2 = 7.03 \times 10^{-3}\ m^2$

One membrane weighting 4.4 mg, the specific surface area of PC membrane and porous percentage are **1.6 m^2/g and 12.6 %**, respectively.

Now, a dense BN membrane with 0.2 µm wide rod inside each pore is considered. The surface area of such membrane and the BN volume are:

$S_{T_{BN}} = S_{T_{PC}} + S_{T_{rods}} = S_{T_{PC}} + N_{pore} \times 2\pi r_{rod} l = 7090 + 4.9 \times 10^8 \times 2\pi \times 0.1 \times 10^{-3} \times 10^{-2}$

$S_{T_{BN}} = 10169\ mm^2 = 1.02 \times 10^{-2}\ m^2$

$V_{BN} = V_T - V_{pore} + V_{rods} = V_T - V_{pore} + N_{pore} \times \pi r_{rod}^2 l$

$V_{BN} = 4.9 - 0.616 + 4.9 \times 10^8 \times \pi \times (0.1 \times 10^{-3})^2 \times 0.01 = 4.44\ mm^3$

Considering a density of h-BN of 2.3 g/cm^3, the corresponding weight of the considered BN membrane is:

$m_{BN} = V_{BN} \times d_{BN} = 4.44 \times 10^{-3} \times 2.3 = 1.02 \times 10^{-2} g$

Therefore the theoretical specific surface area of the BN membrane containing 0.2 µm wide rod is **1 m^2/g.** According to the BET analysis, half membrane weighs approximately 1 mg. The specific surface area should be in this case around **5 m^2/g** which is at least one order of magnitude lower than the measured SSA. The result means that a secondary porosity appears during the sample pyrolysis.

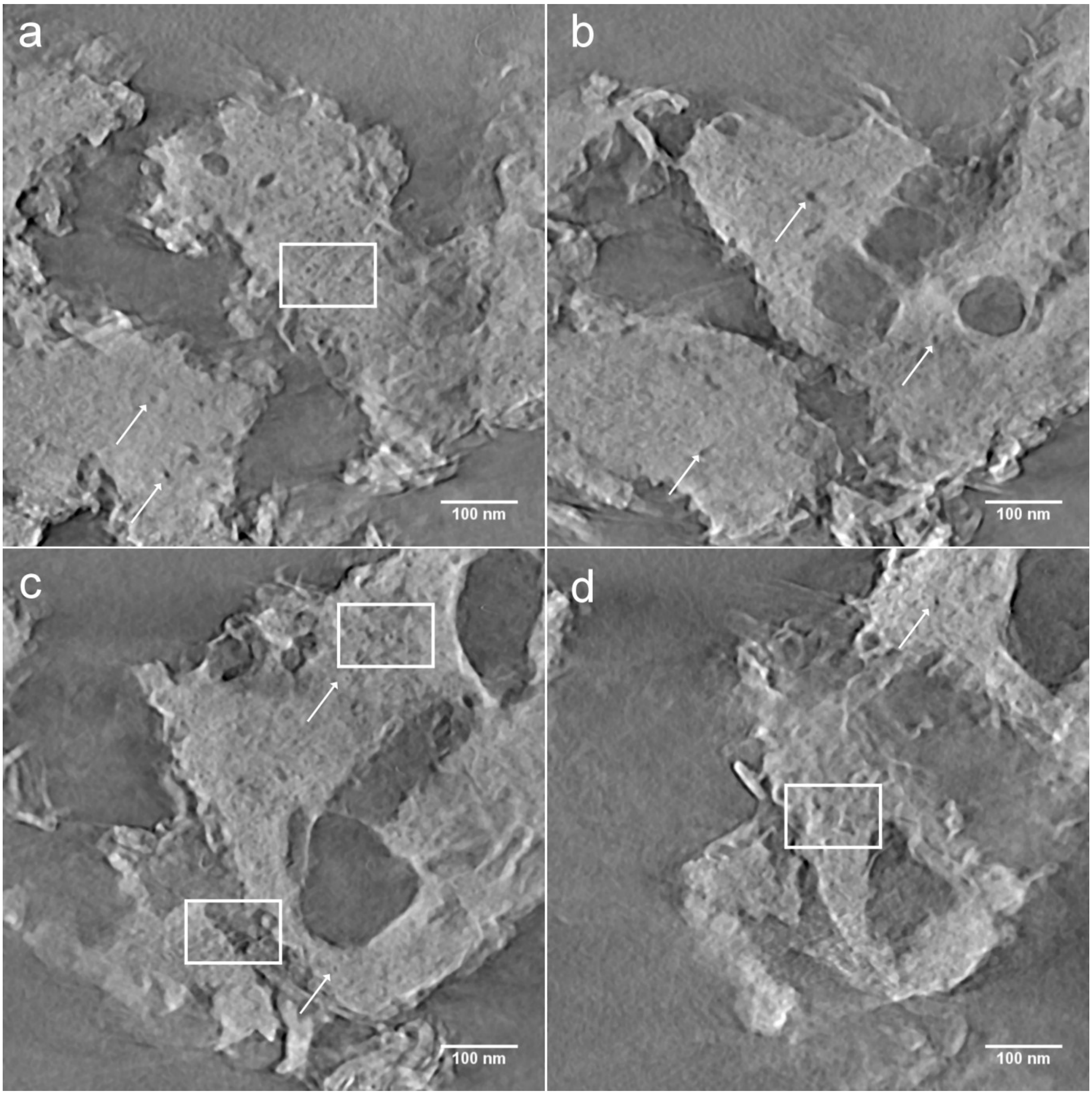


Figure S5. TEM images extracted from the image stack of tomography characterization. Pieces of BN membrane, dispersed onto a TEM grid, reveal a second order of porosity in the range of few ten nanometers. White squares and arrows point at the tiny pores visible in dark contrast.