

Electronic Supplementary Information (ESI):

Investigation of modified Nanopore Arrays by FIB/SEM Tomography

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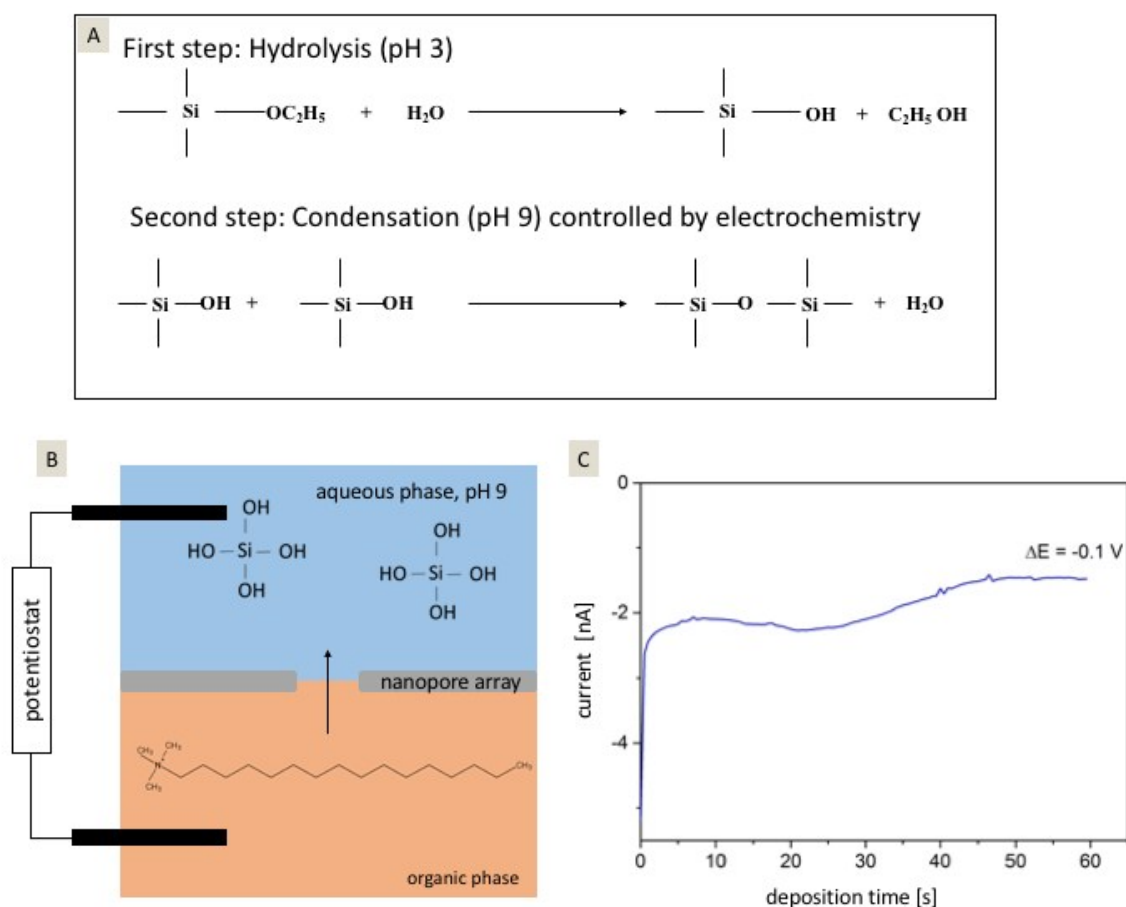


Fig. S1: Electrogeneration of the silica at the ITIES supported by a nanopore array. Chemical reactions of the silica formation at the ITIES (A), a schematic representation of the experimental set-up used for the silica electrodeposition (B) and a typical chronoamperogram recorded for the modification of a nanoporous array (C).

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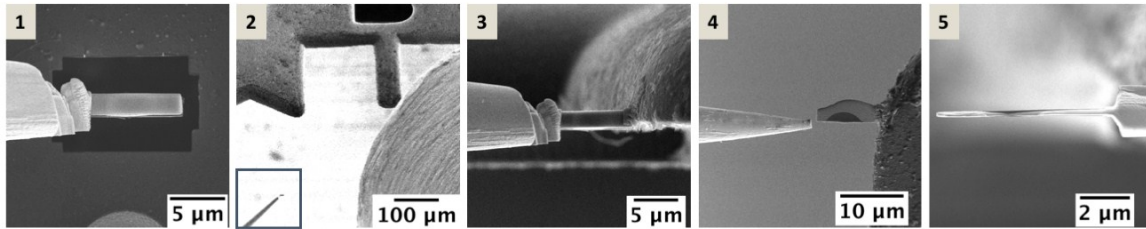


Fig. S2: Fabrication of a TEM foil as described in detail elsewhere¹

1. SE image of the released sample area of the SiN membrane (TEM lamella) attached by beam induced deposition of Pt/C to the micromanipulator needle.
2. Removing the lamella (marked area) from the sample and bringing the lamella in close proximity to the Cu grid. The FIB image shows also the GIS needle for Pt/C deposition.
3. SE image of the mounting of the lamella by Pt/C deposition to the Cu grid.
4. Removing the micromanipulator needle by FIB-milling.
5. In a last step, the TEM lamella is thinned by FIB-milling to a thickness of 150 – 200 nm.

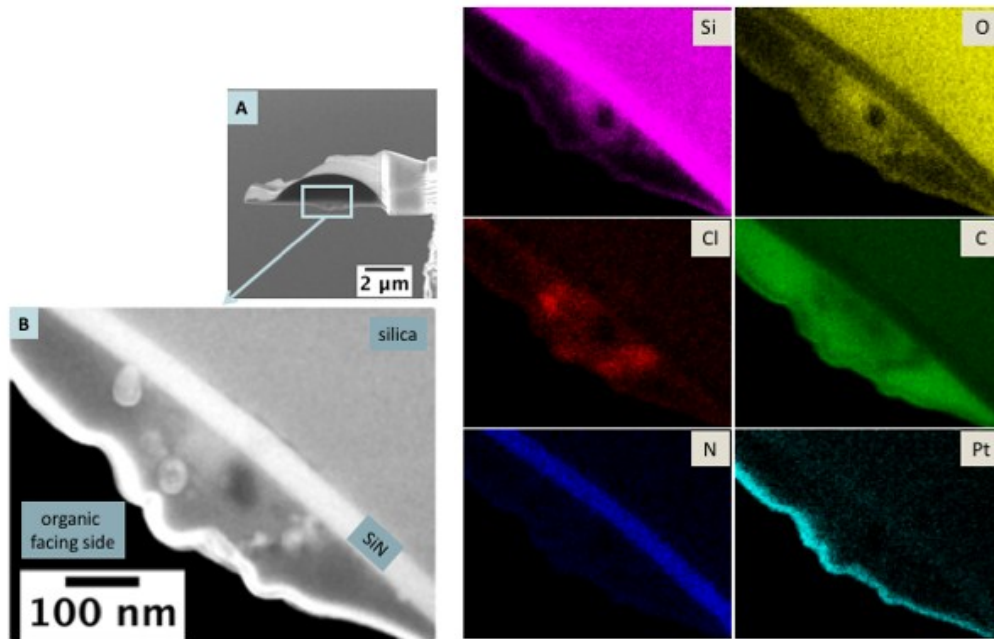


Fig. S3: SEM of a TEM lamella located at a TEM Cu grid (A), and SEM of the sample section characterized by EDX mapping (B). Signals according to the elemental composition are depicted in (C). Acceleration voltage: 10 kV.

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Mov. 1

STEM tomography of a nanopore array prior to electrochemical experiments. The membrane was tilted from -60° to 58.5° with 1.5° increment using an FEI Titan field emission microscope (FEI, ThermoFisher Scientific) at 300 kV acceleration voltage in parallel STEM mode, recording in the high angle annular dark field (HAADF) mode.

Mov. 2

The movie represents the 3D FIB/SEM stack of the residue structure located towards the organic electrolyte facing side of the membrane shown in Fig. 5 in the manuscript. FIB slicing was performed at 30 kV and 48 pA; SEM images were recorded at 5 kV and 86 pA using the TLD detector. Tilt correction was applied. 80 slices with a frequency of 10 nm/slice were recorded.

Mov. 3

3D FIB/SEM stack of the residue structure located towards the organic facing side of the membrane, according to Fig. 7 in the manuscript. . FIB slicing was performed at 30 kV and 48 pA; SEM images were recorded at 5 kV and 86 pA using the TLD detector. Cross-sections are recorded after tilt correction (38°). 300 slices with a frequency of 5 nm/slice were recorded and 116 slices are depicted.

References

- 1 M. H. F. Overwijk, F. C. van den Heuvel and C. W. T. Bulle-Lieuwma, *J. Vac. Sci. Technol. B Microelectron. Nanom. Struct.*, 1993, **11**, 2021–2024.