

Supplementary Information

Duplex nanoporous alumina and polyelectrolyte adsorption: more insights from a combined neutron reflectivity and electron microscopy study

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I- Synthesis details

n-type silicon wafers with an aluminum layer of 0.985 μm sputtered on the top surface and the edges were purchased from ACM and are shown in Fig. S1 (top image). The silicon wafers were left coated with their native oxide. Prior to anodization the silicon back surface should be masked with insulating material, for example nail polish because, under high electric field, it can be oxidized. Electrical contact was achieved by gluing with silver-paste an aluminum foil. The electric contact was also insulated up to a certain height. The samples showed a milky diffusive reflectance prior to anodization due to the large aluminum grains created during the sputtering process. As described in the main text, duplex nAAO are synthesized as follows. A first anodization is carried out during 488 s in 0.3 M oxalic acid under a constant voltage of 40 V. The current density is shown in Fig. S1 as a function of time. Then, the pores are chemically etched by immersing the wafer in a phosphochromic solution during 2h46 at 20°C. Finally a second anodization is performed under the same conditions as the first one during 288 s. It was noticed that after anodization the samples presented an interference pattern in the form of a colour gradient near the edges of the film (see Fig. S1, bottom image). The sample exhibits transparency and colored stripes, more prominent at the edges. The transparency is a result of the transformation of all the aluminum film while the colors implicate different thickness of the formed oxide. The different thicknesses can be caused either by non-homogeneous electric field during the anodization or due to the sputtering process.

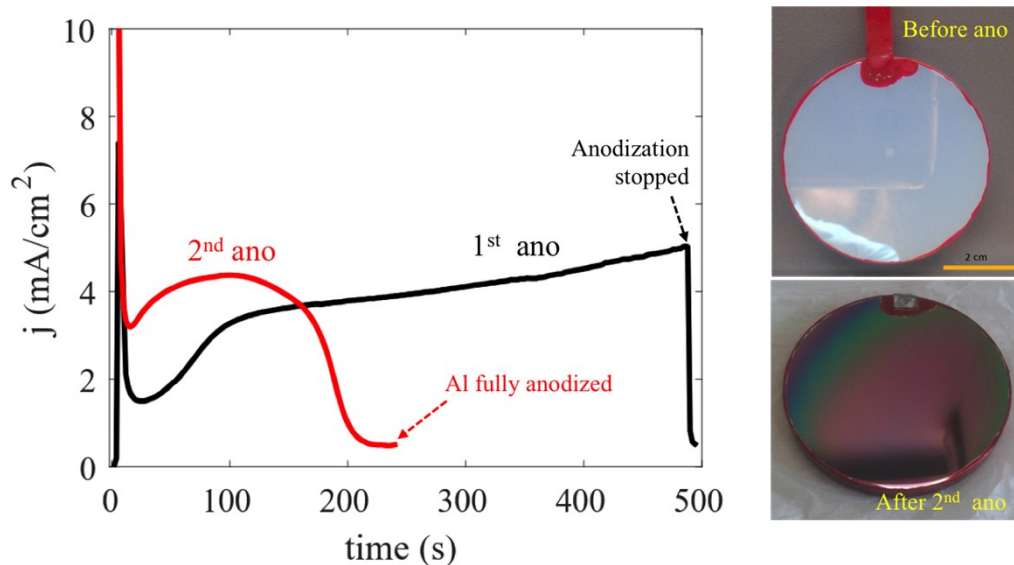


Fig. S1. Left: current density j versus time of the first (black) and second (red) anodization. Right: photos of bare wafer with Al coating (top) and after the second anodization (bottom).

The pores size and organization are accessed by Scanning Electron Microscopy (SEM) imaging. SEM was performed on a field effect gun scanning electron microscope (FEGSEM) SU-70 Hitachi semfeg using an accelerating voltage of 3 kV. The pores are disordered and grains expand on the whole sample surface (see Fig. S2a). By analyzing the SEM images the structural parameters such as the pore diameter, the pore size distribution (shown in Fig. S2b), porosity and pore density can be derived (see main text). Furthermore, to quantify the pore arrangement, the 2D Fast Fourier Transform (FFT) of the pore positions from SEM images was performed to compute the structure factor $S(q)$ (see Fig. S2c). Depending on the degree of pore ordering the $S(q)$ can be either reproduced by a hard sphere model for less ordered AAO or hexagonal model for clearly ordered AAO. For duplex nAAO the $S(q)$ is fitted with a hard sphere model because of the large deviation from the hexagonal lattice. The fitting parameters are the interpore distance D_{int} and the packing ordering η . One finds $D_{\text{int}} = 88$ nm and $\eta = 0.27$.

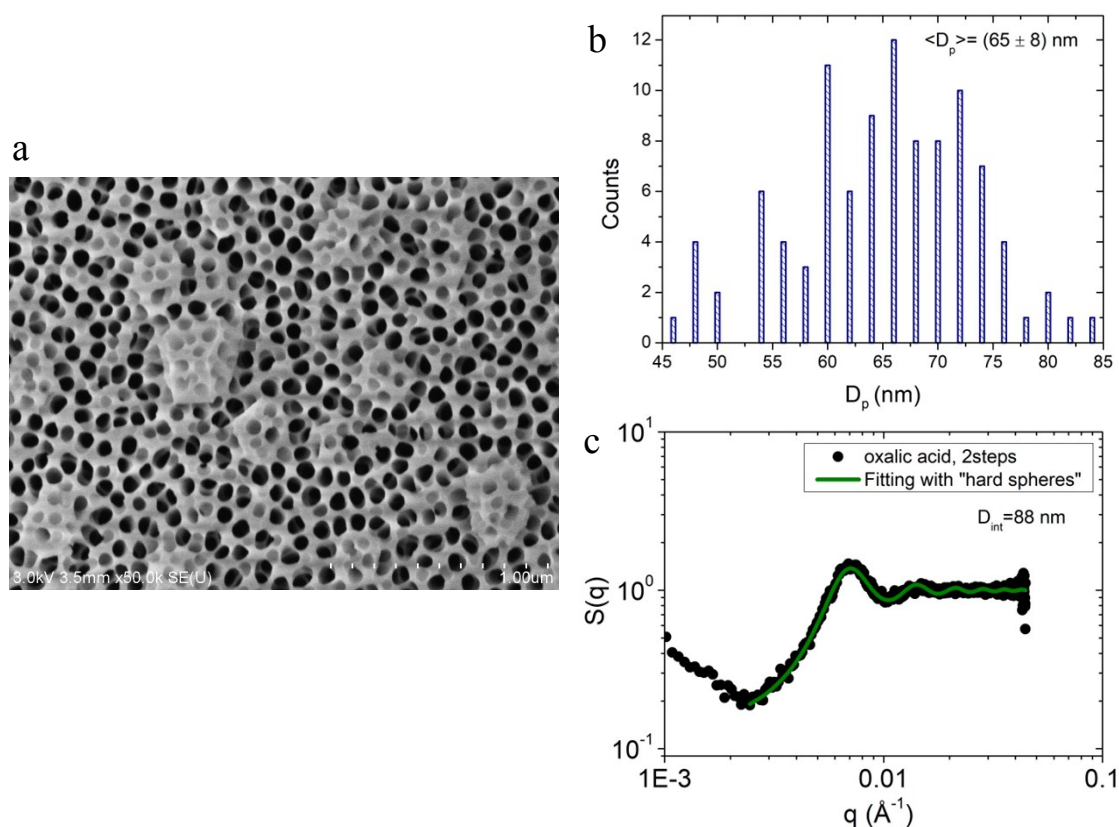


Fig. S2. (a) SEM top surface of duplex nAAO. (b) Top surface pore size distribution. (c) Structure factor $S(q)$ derived from SEM analysis with the best fit using a hard sphere model.

II- Post-H₂O NR measurement in D₂O

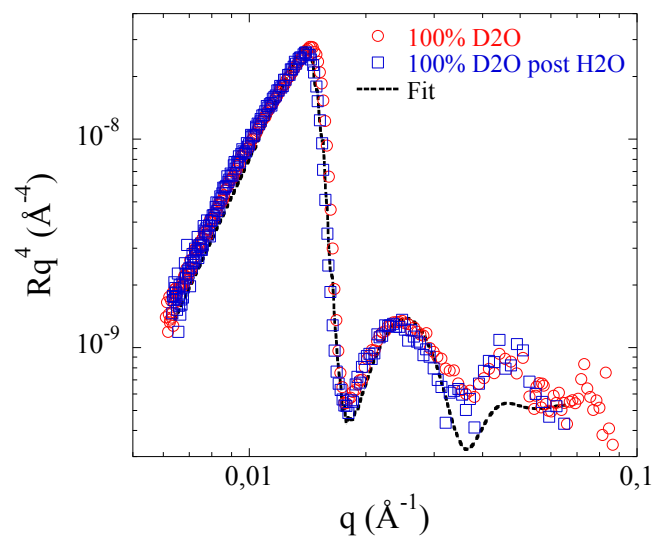


Fig. S3. Post H₂O NR measurement in 100% D₂O was performed to investigate possible nAAO transformation in water. The data is compared with the first 100% D₂O measurement and the results are similar.