

Electronic Supplementary Information (ESI)

Evidence for electrohydrodynamic convection as a source of spontaneous self-ordering in porous anodic alumina films

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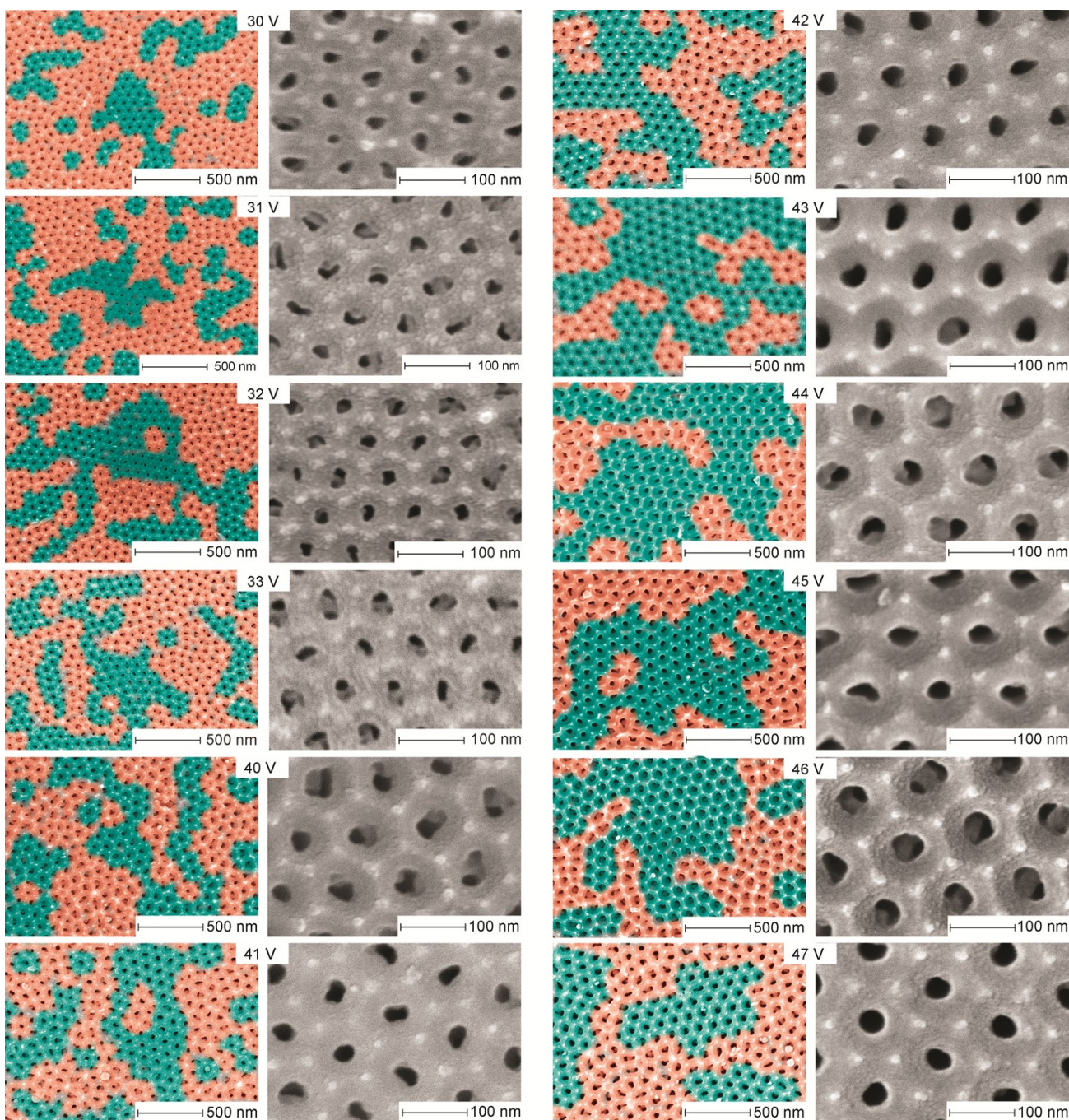


Fig. S1 SEM analysis of porous anodic alumina films obtained from 0.2 M oxalic acid electrolyte at different anodization voltages.

Morphological parameters of the porous alumina layers formed in 0.2 M oxalic acid electrolyte

After anodic oxidation of aluminium at 30 V (the mean voltage from the confidence interval predicted by the eqn. (1) in the article text, using $P = 0.057 \pm 0.024$), pore diameters d_p averaged 18 ± 2 nm and interpore distances D_{int} were in the range 75 ± 4 nm (see Fig. S1). The observed pore sizes d_p after anodization at 42 V and 43 V (where 43 V is the critical ΔU , optimized for the best hexagonal ordering of practically flawless individual cells) are close to each other and lie within the interval 27 ± 2 nm. At the applied voltage of 45 V (the upper limit of the optimized process window for the best hexagonal arrangement), d_p increases to 38 ± 3 nm. The interpore distances D_{int} obtained at 42 V, 43 V, and 45 V are 103 ± 2 nm, 106 ± 4 nm, and 119 ± 5 nm, respectively. Note that the pore and cell dimensions at 45 V are characterized by a larger spread in values and higher d_p/D_{int} ratio (only parameters within ordered domains were measured, the disordered areas are excluded from our statistical treatment).

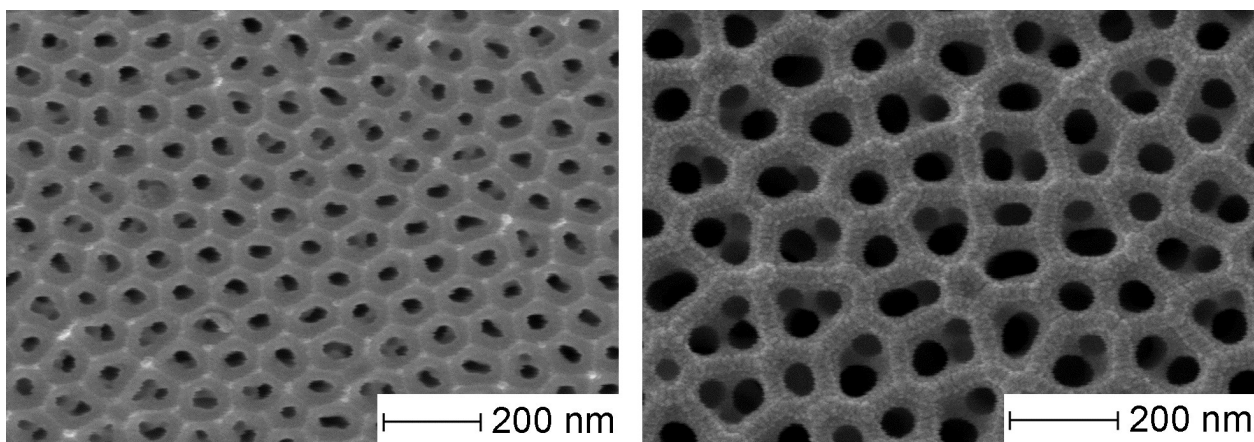


Fig. S2 SEM images of porous alumina films obtained from the classical 0.3 M oxalic acid electrolyte at 40 V (left) and 60 V (right) potential difference. When the voltage significantly exceeds optimal values, enlarged cells with double and triple pore openings are preferably formed. This feature was used in our work (in addition to other structural parameters) to determine the upper limit of the optimal process windows for smaller electrolyte concentrations (see the close-up images at 46 V in Fig. S1, at 45 V in Fig. S3, and at 48-50 V in Fig. S4).

Morphological parameters of the porous alumina layers formed in 0.1 M oxalic acid electrolyte

Oxidation at 14 V (the middle of the predicted process window 14 ± 6 V) resulted in 9 ± 1 nm pore sizes (see Fig. S3). The distance between the neighboring pores averaged 19 ± 2 nm. Although there was no regular hexagonal pattern, it is noteworthy that the spacing between adjacent holes was rather uniform. Interestingly, hexagonally ordered domains of the exceptionally large 0.7-1.1 μm size were sometimes observed on the sample formed at 40 V (see Fig. S3). However, this result could not be always reproducibly achieved, and thus, the voltage of 40 V cannot be regarded as the optimal one. The size of well-defined long range ordered domains at 44 V is up to 1.5 μm , the pore size $d_p = 24 \pm 2$ nm, and the interpore distance $D_{int} = 113 \pm 3$ nm (all parameters are measured within ordered areas).

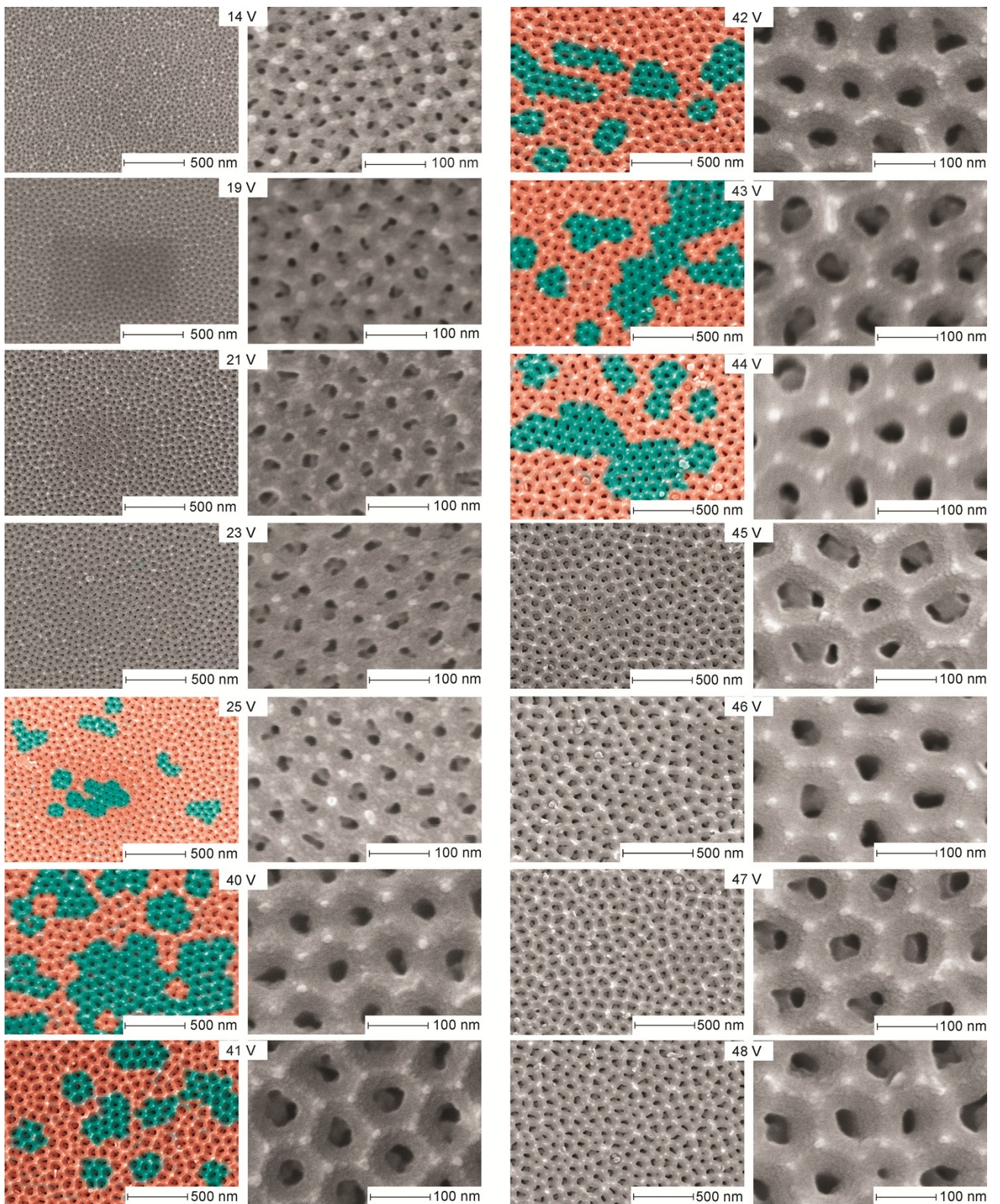


Fig. S3 Detailed SEM examination of porous alumina films formed in 0.1 M oxalic acid electrolyte at different tested voltages. The origin of the abnormal enlargement (out of the general trend) of the ordered domain size at 40 V is not entirely clear yet.

Morphological parameters of the porous alumina layers formed in 0.05 M oxalic acid electrolyte

The pore sizes d_p after oxidation at 5 V are within the confidence interval 6 ± 1 nm; the calculation of the interpore distance D_{int} was difficult due to the stochastic pore arrangement, but the spacing between the nearest neighbouring pores can be roughly estimated as 26 ± 3 nm (see Fig. S4). It should be noted that reasonably large domains (up to $\approx 0.7 \mu\text{m}$) composed of six-fold coordinated pores were formed at 40–42 V. This observation is consistent with the previous finding for PAOX films obtained from 0.1 M electrolyte at 40 V, where the long-range ordering could be also seen. However, both these cases are rather abnormal when compared to the self-ordering behavior of PAOX in more concentrated 0.3 M oxalic acid. For instance, extrapolation of this data suggests that the self-ordering in 0.3 M anodizing electrolyte should occur at a voltage below 40 V as well (more precisely at around 25 V, if we take into account 0.2–0.8 μm large domains formed in 0.2 M solution at 32 V, and plot a line using three experimental points for 0.05 M, 0.1 M, and 0.2 M concentrations), but this does not happen in practice. The pore size d_p at 45 V averaged 32 ± 2 nm, and the interpore distance D_{int} was 117 ± 5 nm.

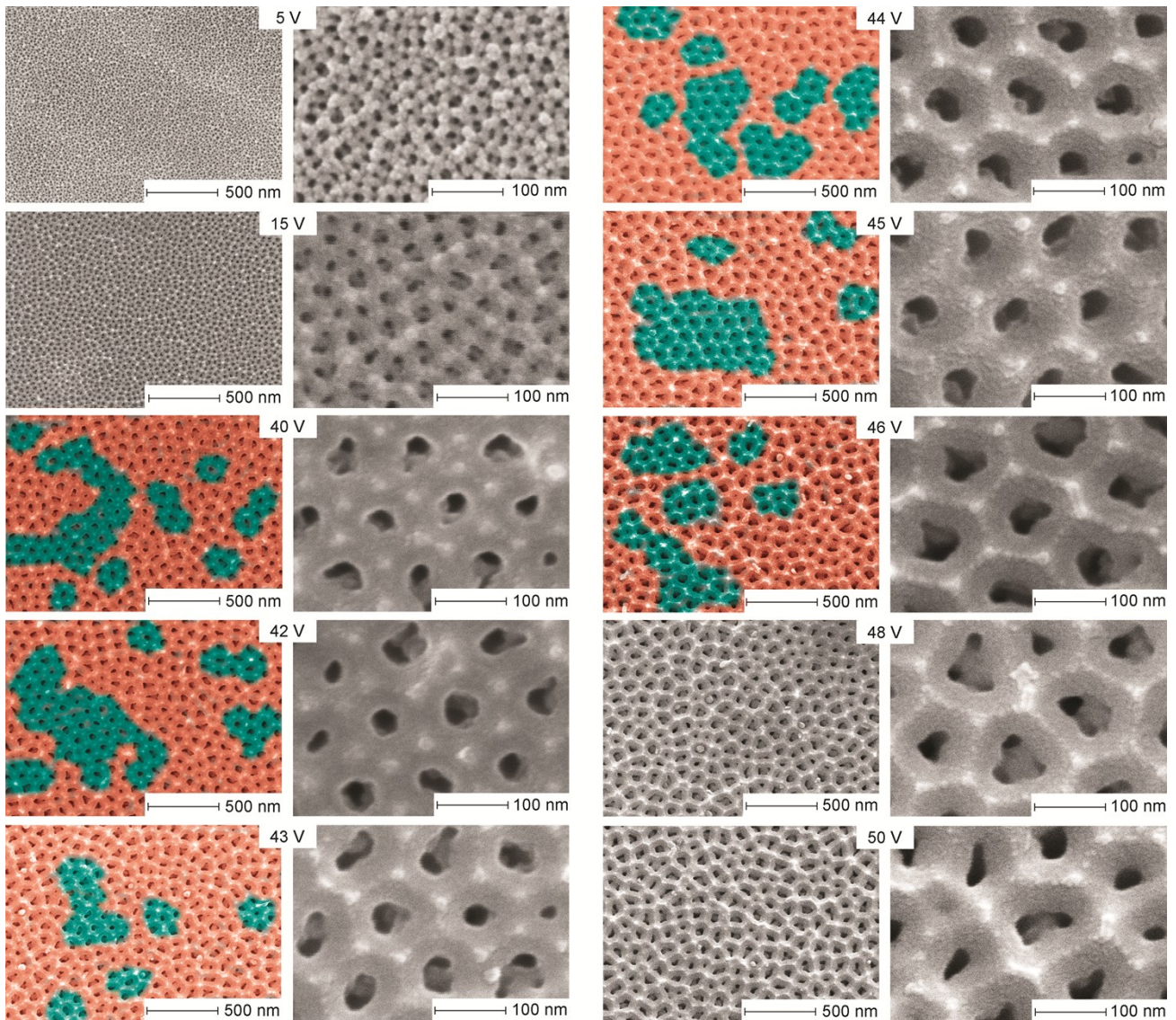


Fig. S4 Morphologies of porous alumina films obtained from 0.05 M oxalic acid electrolyte at different voltages.