Electronic Supplementary Information (ESI)

Multilevel self-organization on anodized aluminium: discovering hierarchical honeycombs from nanometre to sub-millimetre scale

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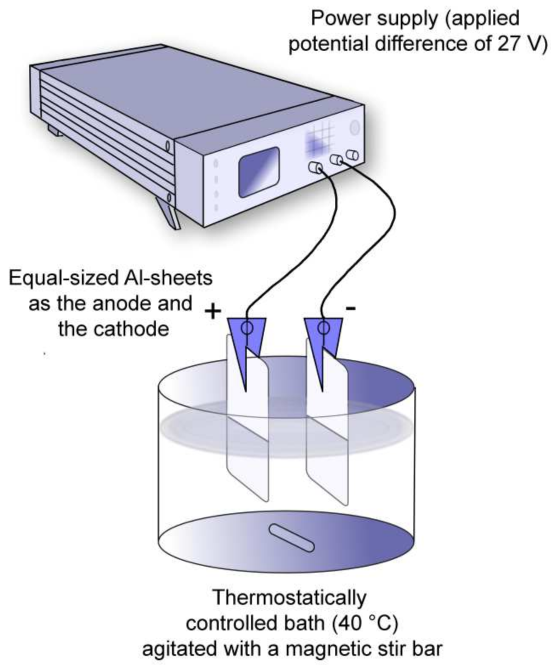

Fig. S1 Schematic representation of a conventional two-electrode anodizing setup adapted for the manufacturing of the hierarchical macro-/nanotextured aluminium monoliths. The cell is filled with 0.3 M H_2SO_4 aqueous electrolyte solution. Thus, the experiment is conducted under the conditions similar in all respects to previously described by Masuda and Hasegwa apart from the anodizing temperature.[1] For the encapsulation of the sponge-like hierarchical metallic monolith into nanoporous alumina shell, the experiment was suspended, the bath was cooled down from 40 °C to 0 °C, and the experiment was resumed at this low temperature and the same applied voltage of 27 V for another 15 minutes.

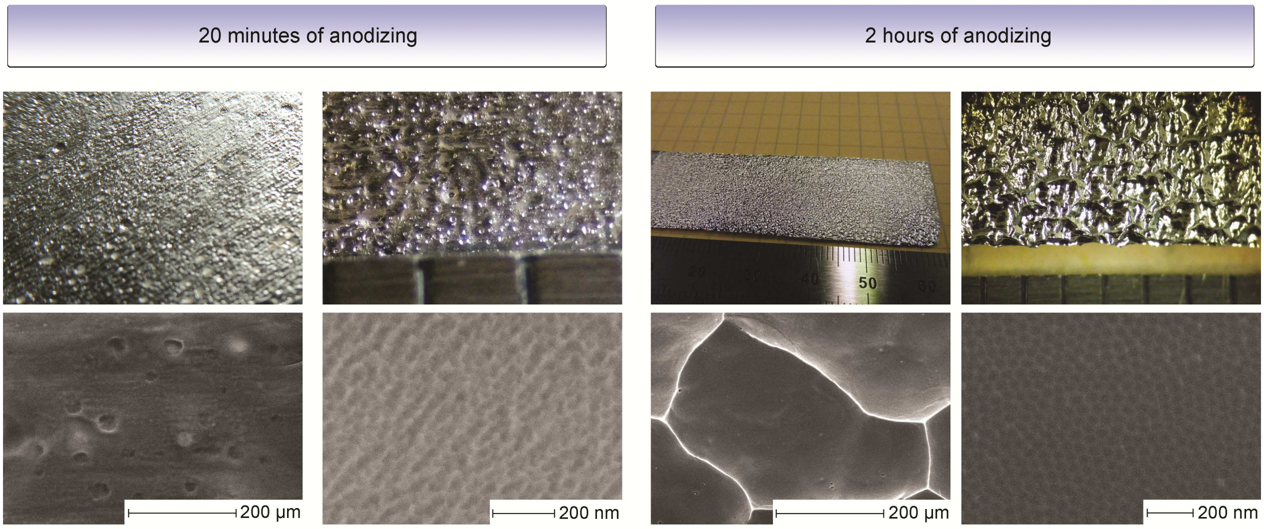

Fig. S2 Macroscopic photographs and scanning electron microscopy (SEM) images demonstrating the intermediate stages of aluminium surface evolution towards the hierarchical sponge-like morphology upon anodizing in 0.3 M H_2SO_4 electrolyte at 27 V and 40 °C. The images are taken after 20 min and 2 h of the electrochemical etching (regular-shaped polygonal pores on the upper level of hierarchy were achieved after 4 h of oxidation). After the first 20 minutes (left), the macropore nucleation sites appear on the etched aluminium surface as small craters, but the first 'trumpet-shaped' pores can be already also observed. At the nanoscale level of hierarchy, a steady-state has not been achieved yet, and therefore SEM reveals no hexagonal cell arrangement. After 2 h (right), a system of macropores separated by well-defined ridges can be observed, and the tendency of nanoscale cells towards hexagonal self-ordering also becomes evident.

Table S1 Pore and cell size variation ranges and corresponding aluminium anodizing conditions from selected references.

Electrolyte	Voltage (V)	Temperature (°C)	Pore diameter (nm)	Cell size (nm)	Reference
0.3 M Sulphuric acid (H_2SO_4)	27	0	15-40	63	Masuda *et al.*,[1] Asoh *et al.*[2]
0.3 M Oxalic acid ($H_2C_2O_4$)	40	0	67 ± 6 (pores are widened by etching in 5% H_3PO_4 at 30 °C for 90 min.)	99 ± 8	Masuda and Fukuda[3]
0.1-3.0 M Selenic acid (H_2SeO_4)	37-51	0	≈ 40	95-110	Kikuchi *et al.*[4]
10 wt% Phosphoric acid (H_3PO_4)	160	3	267	420	Li *et al.*[5]
0.5-2.0 M Phosphonic acid (H_3PO_3)	150-180	0-20	132 (under optimized conditions: 1.0 M, 150 V and 20 °C)	370-440	Akiya *et al.*[6]
2-5 M Malonic acid ($CH_2(COOH)_2$)	120	5	—	300	Ono *et al.*[7]
3-5 M Tartaric acid ($HOOC(CHOH)_2COOH$)	195	5	—	500	Ono *et al.*[7]
0.3 M Tartronic acid (HOOC(CHOH)COOH)	110	0	48 ± 13	222 ± 24	Pashchanka and Schneider[8]
0.125 M Citric acid ($C_3H_5O(COOH)_3$)	260-450	10-30	230	1100	Mozalev *et al.*[9]
0.3 M Sulphuric acid (H_2SO_4)	27	40	—	450 000 – 900 000; 50-60 (two superimposed hierarchical textures)	This work

References

1. H. Masuda, F. Hasegwa and S. Ono, *J. Electrochem. Soc.*, 1997, **144**, L127-L130.
2. H. Asoh, K. Nishio, M. Nakao, A. Yokoo, T. Tamamura and H. Masuda, *J. Vac. Sci. Technol. B*, 2001, **19**, 569-572.
3. H. Masuda and K. Fukuda, *Science*, 1995, **268**, 1466-1468.
4. T. Kikuchi, O. Nishinaga, S. Natsui and R. O. Suzuki, *Electrochim. Acta*, 2014, **137**, 728-735.
5. A. P. Li, F. Müller, A. Birner, K. Nielsch and U. Gösele, *J. Appl. Phys.*, 1998, **84**, 6023-6026.
6. S. Akiya, T. Kikuchi, S. Natsui, N. Sakaguchi and R. O. Suzuki, *Electrochim. Acta*, 2016, **190**, 471-479.
7. S. Ono, M. Saito and H. Asoh, *Electrochim. Acta*, 2005, **51**, 827-833.
8. M. Pashchanka and J. J. Schneider, *J. Phys. Chem. C*, 2017, **121**, 23683-23692.
9. A. Mozalev, I. Mozaleva, M. Sakairi and H. Takahashi, *Electrochim. Acta*, 2005, **50**, 5065-5075.