Electronic Supplementary Material (ESI) for Nanoscale Advances.
This journal is © The Royal Society of Chemistry 2021

Electronic supplementary information

Flexible fabrication of new-type porous anodic alumina membranes with tunable geometric feature by low-cost nanoimprint lithography

Xianzhong Lang,*[ab] Xudong Wang,[b] Ji Ma[b] and Teng Qiu[a]

[a]School of Physics, Southeast University, Nanjing 211189, P. R. China

[b]School of Microelectronics and Control Engineering, Changzhou University, Changzhou 213164, P.R. China

Email: xzlang@cczu.edu.cn

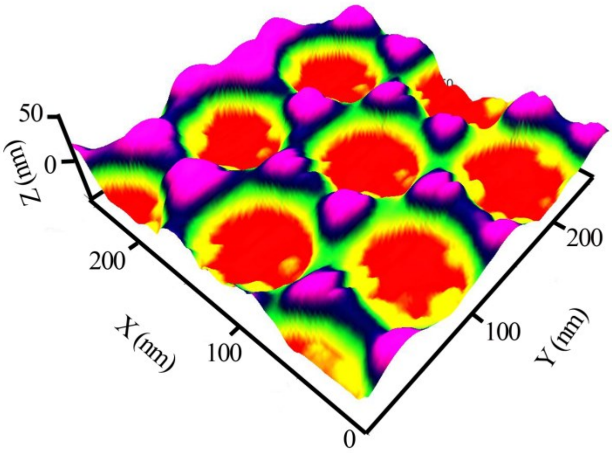

Figure S1. The 3D pseudo-color AFM image of a PAA stamp.

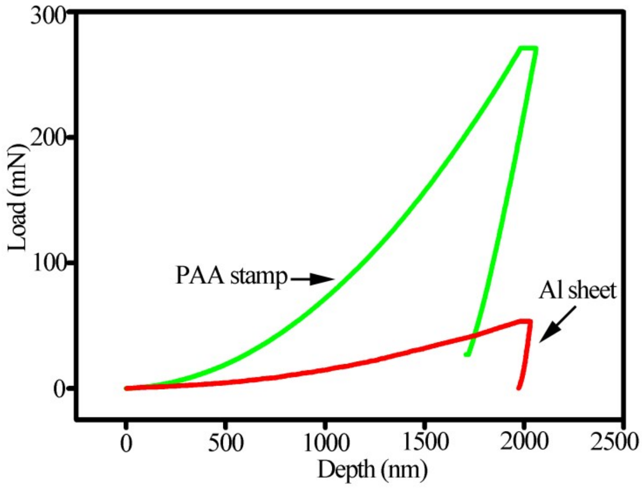

Figure S2. Typical load–displacement curve of PAA stamps and Al sheets. The calculation show that the hardness value of PAA stamps and Al sheets 5.1 GPa and 0.5 GPa, respectively. The load–displacement curve in figure S2 indicates that in the initial stage a smaller load leads to a greater depth, due to the sharp tip and small contact area.

Discussion on Appropriate Anode Voltages

Compared with conventional hexagonal with a pit spacing [Adv. Mater. Interfaces, 2017, 4, 1601116-1-1601116-7], there are three different pit spacings: 1/2 S_{pi}, √3/2 S_{pi}, and S_{pi} (Figure S3). It means that three spatial positions of pits and the corresponding anode voltages should be considered when the induced pores grow at the periodic graphite lattice pits (For example, V_{stamp} = 40 V and S_{pi} = 100 nm) (see Table S1 and Figure S4a).

According to the equifield strength controlled oxide layer growth model and field-enhanced oxide dissolution [Electrochim. Acta, 2005, 50, 2591-2595; J. Mater. Chem., 2008, 18, 5787-5795], protective oxide boundaries are able to prevent the creation of pores inside the boundary. This is caused by the suppression of the field-enhanced oxide dissolution on the areas of nanopits with negative cruvature. When anode voltage is 20 V, induced nanopore arrangement cannot maintain the pre-defined graphite lattice pattern because pores-suppressed area is so small that a large area in the center (C in Figure S4a) is not covered. When anode voltage is 34.6 V or 40 V, pore growth of ortho-pit (such as P_1 and P_2 in Figure S4a) is stunted by pores-suppressed area of P_0. Therefore, the appropriate anode voltage is determined to be values in the middle of the optimal voltages corresponding to 1/2 S_{pi} and S_{pi} (or, to be accurate√3/2 S_{pi}). Our results show that 28 V is appropriate to maintain the ordered graphite lattice arrangement because of modest pores-suppressed area and volume expansion rate [Appl. Surf. Sci., 227 2004 282–292]. In the same way, different appropriate V_{PAA} were chosen to fabricate new-type PAAs with different para-pore spacing (see Table S2).

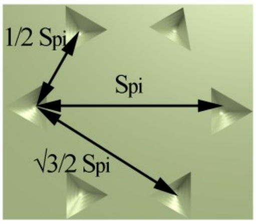

Figure S3. A schematic representation of nanopatterns with three different pit spacings 1/2 S_{pi}, √3/2 S_{pi}, and S_{pi}. 1/2 S_{pi}, √3/2 S_{pi}, and S_{pi} are the ortho-, meta-, and para-pit spacing, respectively.

Table S1. The functional relationship between the values of pit spacing (V_{stamp} = 40 V and S_{pi} = 100 nm) and possible appropriate anode voltages. The anode voltages are derived based on the nearly linear proportional relationship of S_{po} : anode voltage = 2.5 nm/V.

Pit spacing	**1/2 S_{pi}**	**$\sqrt{3}/2$ S_{pi}**	**S_{pi}**
Pit spacing (nm)	50	86.8	100
Anode voltage (V)	20	34.6	40

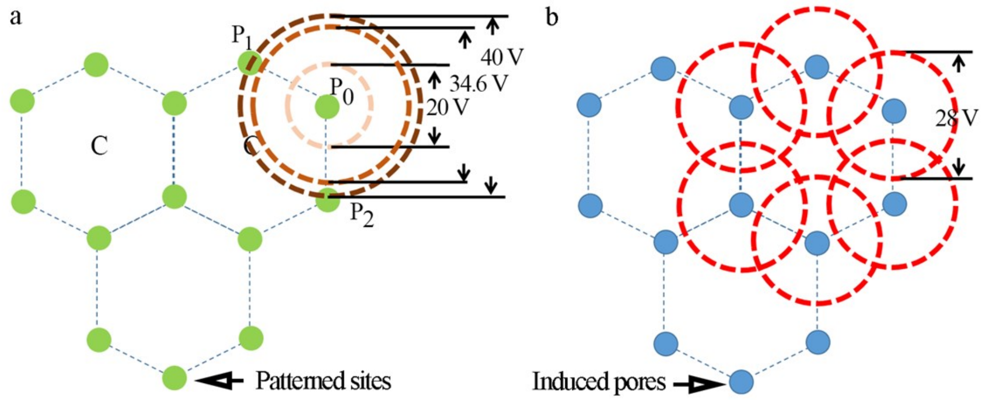

Figure S4. (a) A schematic representation of 2D nanopatterns (V_{stamp} = 40 V and S_{pi} = 100 nm) and the boundaries of pores-suppressed area of different anode voltages in Table S1**.** Green dots denote patterned sites and different orange dashed circles denote the boundaries of pores-suppressed area of different anode voltages during the anodization. (b) A schematic representation of induced pore array with ordered graphite lattice arrangement (V_{stamp} = 40 V and V_{PAA} = 28 V). Blue dots denote induced pores and red dashed circles denote the boundaries of pores-suppressed area of 28 V.

Table S2. The one-to-one correspondence between the values of V_{stamp} and V_{PAA}.

V_{stamp} (V)	30	40	50	60
V_{PAA} (V)	21	28	35	42

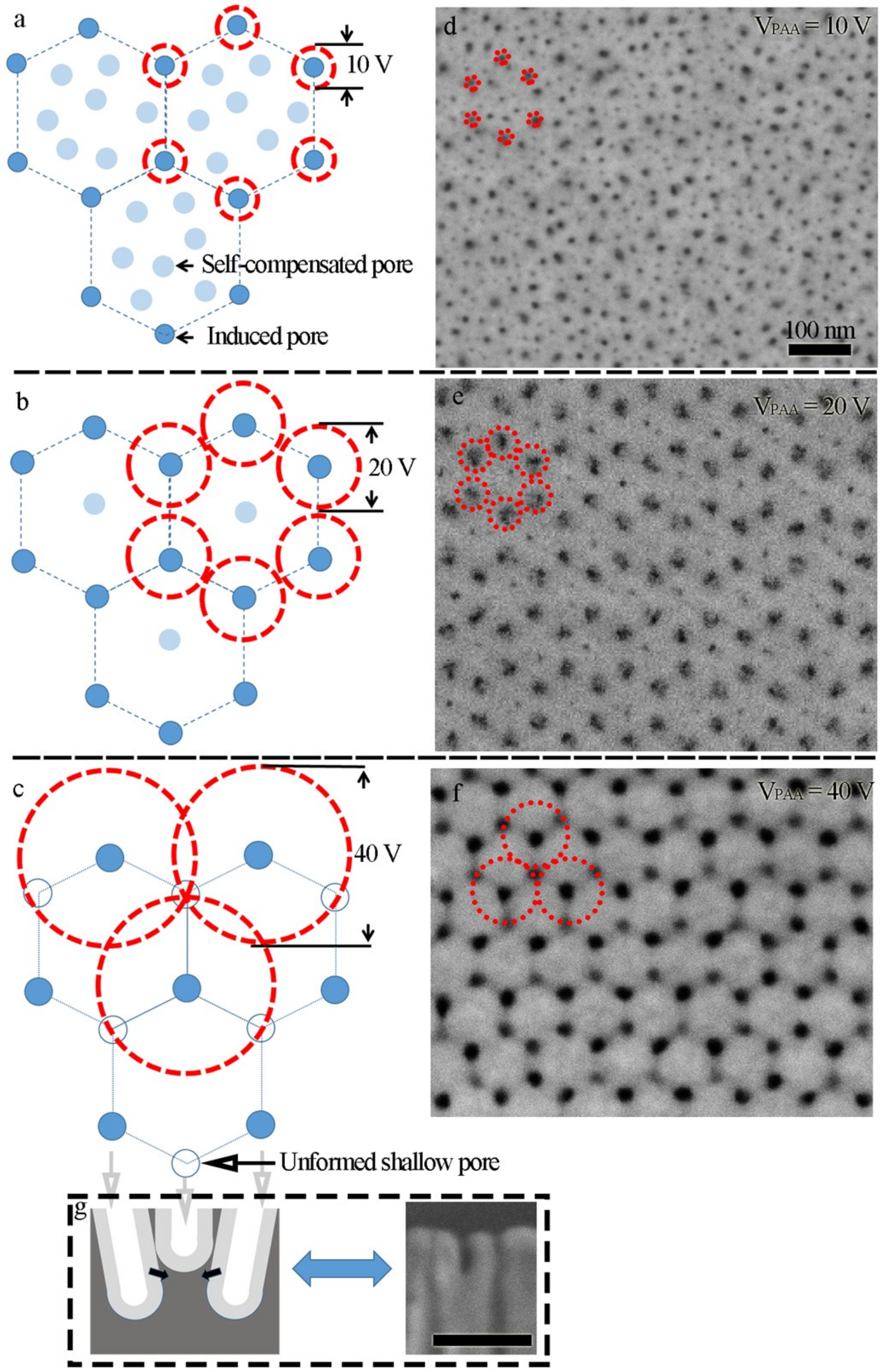

Figure S5. (a)-(c) The schematic diagram of new-type PAA with 2D surface topography. (a) V_{PAA} = 10 V. (b) V_{PAA} = 20 V and (c) V_{PAA} = 40 V. Red dashed circles denote the boundaries of pores-suppressed area, blue dots denote induced pores, light-blue dots denote self-compensated pores, and hollow blue circles denote unformed shallow pore. (d)-(f) Typical SEM images of new-type PAA with V_{PAA} of (a) 10 V, (c) 20 V and (e) 40 V, respectively. Red dashed circles in the insets also denote the boundaries of pores-suppressed area during the anodization. (g) The Schematic drawing (left) of a pore in the middle sandwiched and restricted by adjacent preferentially growing pores, and corresponding SEM image (right) showing the disappearance of pores at the early stage of anodization.

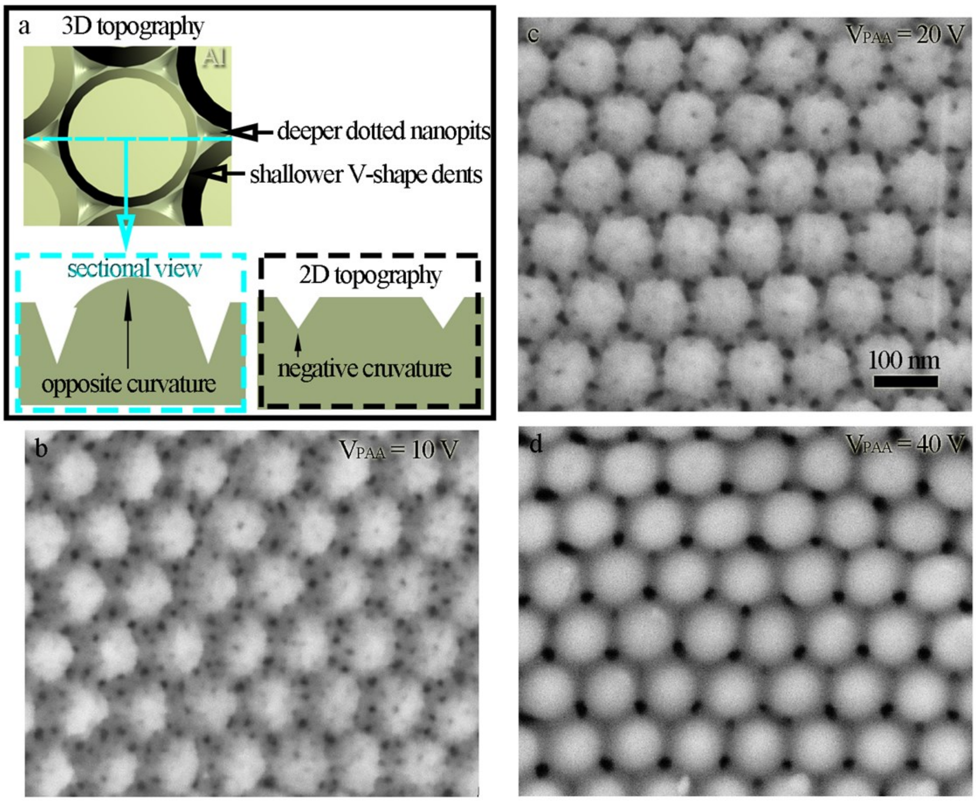

Figure S6. (a) shows that, compare with 2D Al pre-patterns, 3D Al pre-patterns have convex nanoislands with opposite curvature and shallower V-shape dents with negative curvature. (b)-(d) Typical SEM images of new-type PAA with V_{PAA} of (b) 10 V, (c) 20 V and (d) 40 V, respectively.