

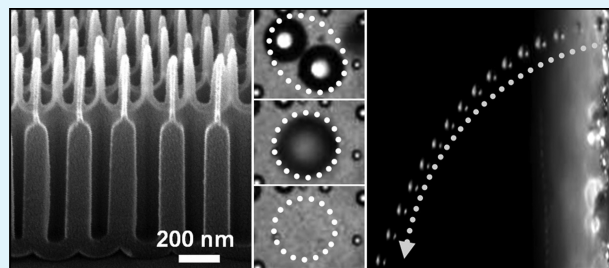
Condensate Microdrop Self-Propelling Aluminum Surfaces Based on Controllable Fabrication of Alumina Rod-Capped Nanopores

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ABSTRACT: Here, we report a type of aluminum-based condensate microdrop self-propelling (CMDSP) functional films based on the controllable fabrication of anodic alumina rod-capped nanopores, which can be realized by a three-step method based on the skillful combinations of well-established hard anodization, mild anodization and chemical etching techniques. Such a surface nanoengineering strategy is verified to be feasible via our exemplified experiments and scanning electronic microscopy characterizations. After fluorosilane modification, the surface nanostructure can induce the efficient self-jumping of small-scale condensate microdrops, especially below 50 μm . This work offers an avenue for developing CMDSP aluminum surfaces with self-cleaning, antifrosting, and antidewng functions.

KEYWORDS: superhydrophobic, condensate microdrop self-propelling, alumina rod-capped nanopores, anodization, etching



Condensate microdrop self-propelling (CMDSP) surfaces^{1–18} have attracted great interest because of their significant values in basic researches and technological innovations, e.g., moisture self-cleaning,¹⁰ antifrosting,^{11,12} electrostatic energy harvesting,¹³ enhancing condensation heat transfer,^{14–16} and designing planar drop-jumping thermal diodes.¹⁷ Differing from the macroscopic water drops shedding off usual superhydrophobic surfaces under gravity, the condensate microdrops can self-depart the CMDSP surfaces via their coalescence-released excess surface energy, without requiring such external force as gravity or steam shear force.² However, it is still a great challenge to develop aluminum-based CMDSP functional films, which are studied rarely to date despite their significant commercial values, e.g., used for developing novel energy-saving airplane wings and air-conditioner fins. Recently, He et al. have reported a type of CMDSP porous nanostructures by immersing the flat⁷ or micropatterned⁸ aluminum foils into hot water bath followed by silane modification. However, the formed porous nanostructure, made of poorly crystallized aluminum hydroxide, is intrinsically unstable from either chemical or mechanical perspectives¹⁹ and thus is difficult to be used in practical applications. On the other hand, electrochemical anodization is a type of well-known engineering technologies that have been widely used for improving the surface properties of aluminum materials such as hardening and anticorrosion.²⁰ However, usual anodic alumina nanopores cannot induce desired CMDSP function due to their high solid–liquid interface adhesion. Thus, we wonder if such industry-compatible technique can be innovated for qualifying the processing of CMDSP aluminum surfaces.

To achieve the CMDSP function, we must minimize the dissipation of coalescence-released weak excess surface energy

caused by solid–liquid interface adhesion.^{7,18,21} According to our previous report,¹⁸ it can be reasonably predicted that, compared with the usual anodic alumina nanopores, the rod-capped nanopores can not only greatly reduce the solid–liquid contact area and van der Waals attraction but also avoid the formation of capillary adhesion, which makes the total solid–liquid interface adhesion extremely low. In principle, the departure of condensate microdrops on the low-adhesion nanostructured surfaces can be powered by the coalescence-released excess surface energy while gravity effects can be considered negligible due to droplet sizes being much smaller than the capillary length (~ 2.7 mm for water).¹⁸ However, such a driving surface energy is very weak.¹⁸ Accordingly, different from the previous strategies of anodizing aluminum surfaces to construct microscopic rough structures so as to achieve the gravity-driven macroscopic droplet superhydrophobicity,^{23–27} the geometries of rod-capped nanopores should be rigidly controlled to minimize the dissipation of weak surface energy: (1) to minimize the apparent solid–liquid contact area and interface adhesion, the top sizes of rods should be as small as possible; (2) to avoid the sidewall and base adhesion caused by the penetration of condensates, the rod-to-rod spacing should be on the submicrometer length scale; (3) to avoid the higher sidewall adhesion caused by the clustering of building blocks, self-standing rods should be highly desired. Clearly, there is no report about the tailoring of such self-standing rod-capped nanopore structure with submicrometer-scale interspace, to the best of our knowledge. The next issue is how to achieve the

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anodized aluminum surface with self-standing rod-capped nanopores and verify its utility.

Here, we demonstrate a type of novel aluminum-based CMDSP films based on the controllable fabrication of anodic alumina rod-capped nanopores. A skillful surface nano-engineering strategy has been proposed: first patterning electropolished aluminum foils with hexagonally packed nanopits via one-step hard anodization and etching peeling (OS-HA-EP), then forming self-standing alumina nanorods at the triple cross junctions of nanopits via one-step mild anodization and etching widening (OS-MA-EW) and finally creating nanopores via OS-MA. This strategy is verified to be feasible via our experiments and scanning electronic microscopy characterizations. After low-surface-energy fluorosilane modification, the as-prepared nanostructure can induce the efficient self-jumping of small-scale condensate microdrops and always keep their sizes at micrometer scale, especially below 50 μm . This work offers an avenue for developing aluminum-based CMDSP surfaces with moisture self-cleaning, antifrosting, and antiwetting functions, for example, used for designing novel energy-saving and eco-friendly air-conditioner heat exchangers.

On the basis of our recent works of utilizing simple anodizing and etching technologies to fabricate unconventionally shaped alumina nanopores,^{28,29} we propose that such self-standing rod-capped nanopore can be in situ grown on the aluminum surfaces by a three-step processing procedure of skillfully combining hard anodization, mild anodization, and chemical etching techniques. The surface nanoengineering schematic is shown in Figure 1. First, the surface of aluminum foils can be

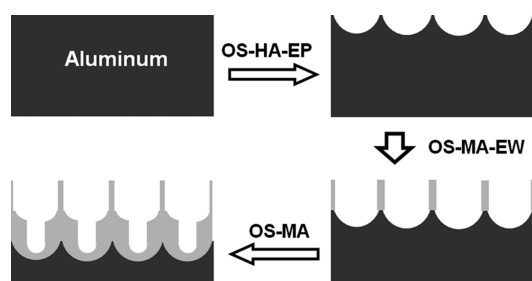


Figure 1. Schematic showing the tailoring of self-standing rod-capped nanopores on aluminum surface by a three-step processing procedure of skillfully combining the hard anodization, mild anodization, and chemical etching techniques. OS-HA-EP, OS-MA-EW, and OS-MA are the abbreviations of the one-step hard anodization and etching peeling, the one-step mild anodization and etching widening, and the one-step mild anodization, respectively.²⁸

patterned with self-ordered hexagonally packed nanopits via OS-HA-EP.²⁸ Their periods can be governed by electrochemical parameters (anodizing voltages and electrolyte ingredients). Subsequently, self-standing nanorods can be grown at the triple cross junctions of patterned nanopits via OS-MA-EW. The heights and top sizes of the formed nanorods can be determined by the MA and EW duration, respectively. Finally, nanopores can be further created at the sites of nanopits via OS-MA and their depth can be controlled by the MA duration. It should be pointed out that the HA is preferentially used here for surface patterning because its advantages in creating long-range ordering alumina nanopores at far higher growth rate as compared to the MA. In contrast, the very violent HA reaction is unsuitable for the tailoring of high-quality self-standing nanorods. Accordingly, to realize the

in situ growth of self-standing nanorods at the triple cross junctions of nanopits via the MA reaction, the anodization voltage U_{MA} at the OS-MA-EW stage should obey the equation: $U_{\text{MA}} = P/X_{\text{MA}}$ where P is the nanopore period and X_{MA} is the constant of MA in specific electrolyte.²⁸

Our studies have verified that such self-standing rod-capped alumina nanopores indeed can be finely tailored by the skillful combination of anodization and etching technologies. In this case, we only provide an exemplified rod-capped nanopore structure with the average top diameters of 40 nm, rod heights of 330 nm, pore periods of 200 nm and pore depths of 620 nm and its fabrication conditions as a demonstration. As shown in Figure 2a, hexagonally packed nanopits with the periods of 200

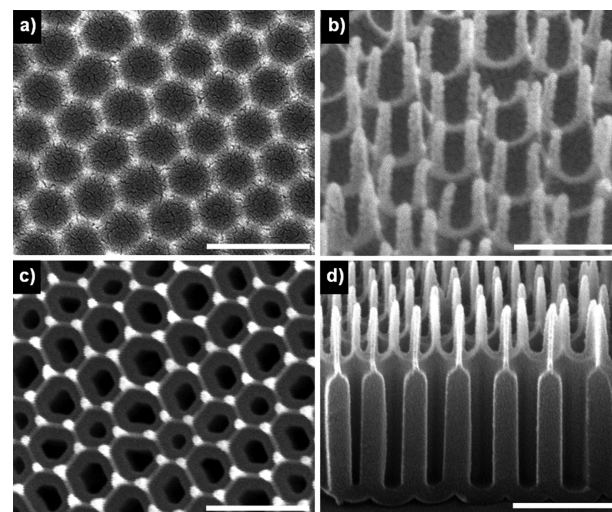


Figure 2. (a) SEM top-view of the as-patterned hexagonally packed nanopits. (b) SEM tilted-view of the self-standing nanorods grown at the triple cross junctions of patterned nanopits. (c, d) SEM (c) top-view and (d) side-view of the as-prepared self-standing rod-capped nanopores, respectively. Scale bars denote 500 nm.

nm can be first patterned on the surfaces of electropolished aluminum foils by HA in the mixed electrolyte of 0.3 M oxalic acid and 0.012 M sulfuric acid at $-5\text{ }^{\circ}\text{C}$ for 1.5 h, which anodization voltage is first fixed at 35 V for 10 min and then linearly increases at the rate of 0.5 V s^{-1} until reaching 110 V, followed by immersing into a mixed etchant of 0.03 M CrO_3 and 0.1 M H_3PO_4 at $65\text{ }^{\circ}\text{C}$ for 3 h to remove the formed oxide layer.²⁸ Subsequently, free-standing nanorods with average top diameters of 60 nm and heights of 330 nm (Figure 2b) can be in situ grown at the triple cross junctions of nanopits by first MA in 0.035 M H_3PO_4 at $10\text{ }^{\circ}\text{C}$ under 80 V for 1000 s and then etching in 0.09 M H_3PO_4 at $30\text{ }^{\circ}\text{C}$ for 90 min. The formation of self-standing nanorods can be ascribed to the different etching rate between the wall inner and outer, where the thicker anion-containing outer corrodes relatively easy, whereas the thinner anion-free inner at the cell border is hard to resolve.²⁹ After further MA reaction in 0.035 M H_3PO_4 at $10\text{ }^{\circ}\text{C}$ under 80 V for 2000 s, alumina nanopores with depths of 620 nm can be in situ grown at the sites of patterned nanopits. As a result, a typical self-standing rod-capped nanopore structure can be created on aluminum surfaces, which scanning electronic microscopic top view and side view are shown in Figure 2c, d, respectively. Evidently, the slight etching of alumina nanorod sidewalls in phosphoric acid is unavoidable during the last MA stage, but these slimed nanorods can still

self-stand on the nanopore film. Note that morphologies of all samples are characterized by the scanning electronic microscopy (FEI Quanta250 FEG, USA) after sputtering a layer of Au with thickness of ~ 15 nm.

After low-surface-energy fluorosilane modification, such rod-capped nanopore film presents the desired CMDSP function. Here, the samples were placed, together with a beaker containing 10 μL of heptadecafluorodecyltrimethoxysilane liquid, into a sealed glass container and then heated for 2 h at 120 $^{\circ}\text{C}$.⁶ The self-propelling details of condensate on the surface of nanosamples with the fixed substrate temperature of ~ 2 $^{\circ}\text{C}$, ambient temperature of ~ 25 $^{\circ}\text{C}$, and relative humidity of $\sim 90\%$ can be characterized by a high-speed high-resolution 3D microscope imaging equipment (Keyence VW-9000, Japan). Figure 3a shows typical optical top-views of self-

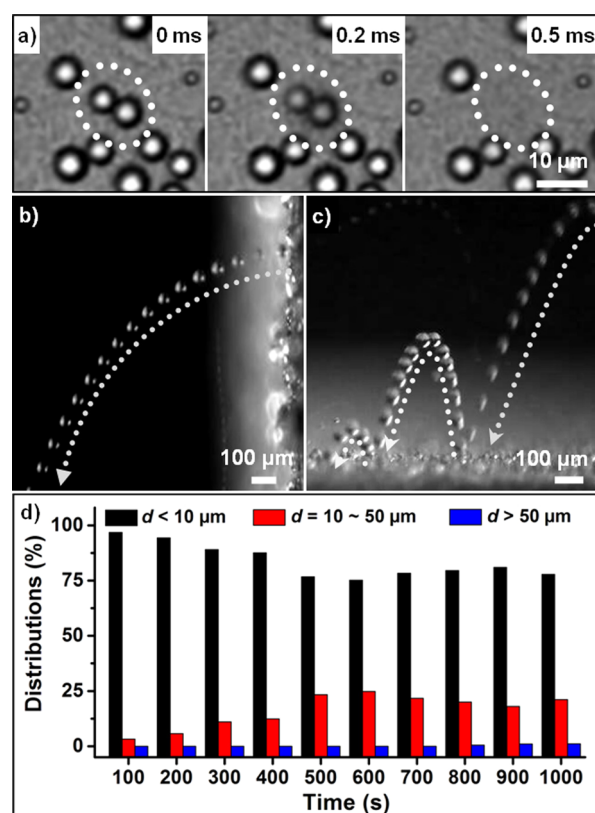


Figure 3. (a) Optical top views showing the coalescence-induced condensate microdrop self-departure on the vertical nanosample surface. (b) An overlapped optical side-view showing the trajectory of a merged microdrop ejecting from the vertical nanosample surface. (c) Typical overlapped optical image showing the continuous coalescence-induced jumping process of condensate microdrops on the horizontal nanosample surface, accompanied by its size scaling up. (d) Drop number distributions of residence condensate microdrops with diameter (d) of <10 , $10-50$, and >50 μm varied with time.

departure instant of several condensate microdrops on the vertical nanosample surface. The self-departure events are realized by the in-plane coalescence of adjacent microdrops, which is implemented by their respective growth due to preferential condensation of ambient vapor on the surface of microdrops. As shown in Figure 3b, the merged microdrop can eject from the nanosample surface and then fall along a parabolic trajectory. For horizontal nanosamples, the ejected condensate microdrops can fall back to the surface and trigger

new dynamically impact-induced coalescence events, resulting in continuous coalescence-induced jumping events (Figure 3c). To quantify and highlight the self-jumping capability of condensate microdrops on the nanosample surfaces, we analyze the drop number distribution of residence microdrops with diameters (d) of <10 , $10-50$, and >50 μm . First, we can count the numbers of microdrops with different sizes by analyzing the optical images captured under the magnification 400 \times . Then, their number distributions can be calculated through dividing each component by the total number. As shown in Figure 3d, the condensate microdrops with $d < 10$ μm occupy $\sim 80\%$, which fluctuates slightly with the condensation time extending; those with $d = 10-50$ μm occupy $\sim 20\%$; the condensate microdrops with $d > 50$ μm may be almost negligible. Evidently, such nanostructure possesses remarkable condensate microdrop self-propelling ability and can effectively control the sizes of condensate microdrops below 50 μm .

In conclusion, we have demonstrated that aluminum surfaces can be endowed with the desired CMDSP function by surface engineering of self-standing rod-capped alumina nanopores, which can be realized via skillfully combined hard anodization, mild anodization, and chemical etching technologies. This should be the first report of creating CMDSP films based on the controllable fabrication of rod-capped nanopore structures, to our knowledge. In principle, our used method is industry-compatible and very promising to be developed into practical aluminum-based surface nanoengineering technologies. Our work offers an avenue for developing the aluminum-based CMDSP films with self-cleaning, antifrosting, and antidew function, e.g., used for designing novel energy-saving and eco-friendly air-conditioner heat exchangers. We suppose that much efforts would be made in optimizing the surface nanostructure, especially controlling proper top sizes and heights of nanorods, to balance its CMDSP efficiency, heat transfer ability,³⁰ and mechanical stability, which are equally important to applications of such novel functional film.

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Author Contributions

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Notes

The authors declare no competing financial interest.

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