# Supporting Information

# Controlled Nanoscale Diffusion-Limited Chemical Etching for Releasing Polystyrene Nanocones from Recyclable Alumina Templates

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## Experiment details

**Preparation of the conical PAA templates:** The electro-polished highly pure Al foil (99.999 %) was firstly anodized in a mixture solution of $H_3PO_4$, $CH_3OH$ and $H_2O$ ($V_{H_3PO_4}$:$V_{CH_3OH}$:$V_{H_2O}$ = 1: 10: 89) at -5 °C under a constant voltage of 195 V for 12 h. Self-ordered nanopits pattern was left on the sample surface after the removal of porous alumina layer via immersing the sample into a mixed solution of 1.8 wt% $CrO_3$ and 6 wt% $H_3PO_4$ at 65 °C for 3 h. The pre-patterned sample was then anodized under the same conditions above for 300 s, followed by a etching step performed in phosphoric acid solution (5 wt%) at 30 °C for 20 min. The conical PAA templates could be obtained after such anodization and etching repeated for 5 times. Besides, the cyclical PAA templates with the same depths, diameters and pore distances have also been prepared as the contrast sample. The pre-patterned sample was anodized under the same conditions for 1500 s, followed by one-step etching in phosphoric acid solution (5 wt%) at 30 °C for 80 min.

**Preparation of polystyrene nanocones:** The as-purchased polystyrene film was firstly placed on the PAA templates. Then, the polystyrene and template module was sandwiched between two glass slides, which was impressed at 140 °C under 6.7 $\times 10^5$ Pa for 30 min. After the module cooled down to room temperature, it was taken out and then dipped into a 5 wt% phosphoric acid solution at 30 °C for 15 min to realize the nanoscale etching of surface layer of alumina internal walls adjacent to the polymer fillers. Finally, the as-prepared polystyrene nanocone or nanorod arrays were detached manually from the PAA templates. In contrast, the conical PAA templates were modified by fluorinated silane ($CF_3(CF_2)_7CH_2CH_2Si(OCH_3)_3$, Shin-Etsu Chemical Co., Japan) using vapour phase method. The PAA templates were placed in a glass container with 0.2 $cm^3$ FAS, and then heated in an oven maintained at a temperature of 150 °C for 1 h.

**Characterization:** The microscopic morphologies of the PAA templates and polystyrene nanocones were observed under a field-emission scanning electron microscope (FE-SEM: S-4800 Hitachi) after the samples were coated with a 15 nm Au. We generally observed five batches of samples and at least twenty pores per sample under high-resolution scanning electronic microscope. Considering that the alumina walls are thinned only several to tens of nanometers in a so short etching time, we must record high-magnification SEM images ever time to reduce the measurement errors of the width (WH) of the conical nanopores at half depth as soon as possible. It was found that so small sample area (0.9 $cm^2$) is insufficient to produce the gradient structures during the etching process due to no apparent diffusion limitation. Accordingly, the data points are collected randomly, then analyzed and recorded in Fig. 2D while the SEM side-views shown in Fig. 2A-C are given uniformly from the centre of the samples. For the larger area of samples, the centre and edge are observed to determine the difference of thinning of pore walls under different etching conditions.

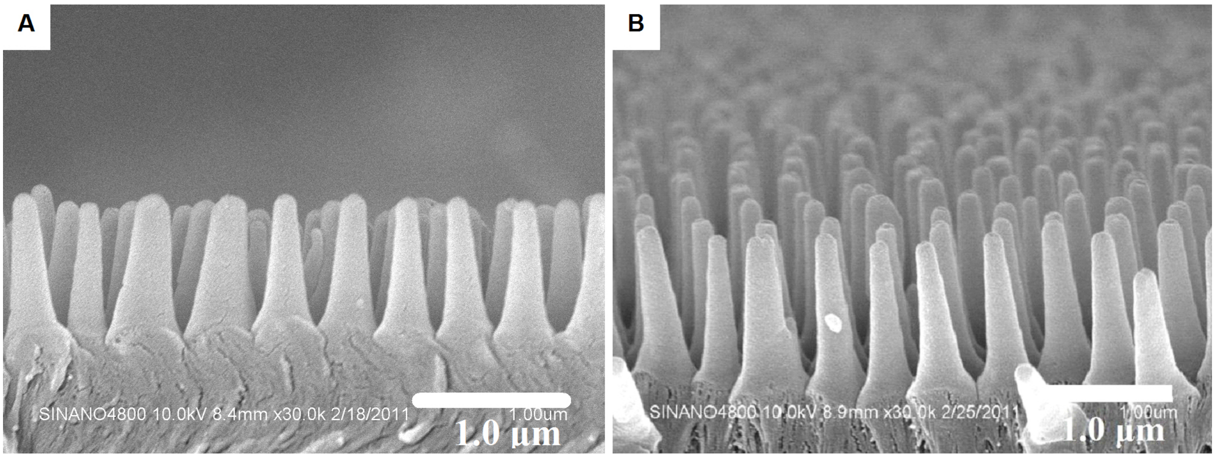


**Figure S1.** Side-views of the as-prepared polystyrene nanocones from the 1$^{nd}$-recycled PAA templates (A) and the 2$^{nd}$-recycled (B). The SEM side-view of the polystyrene nanocones replicated from the initial PAA template (Fig. 1D) has been shown in Fig. 1C. Clearly, these data further indirectly demonstrate the feasibility of the controlled nanoscale etching for the detaching and recycling of the PAA templates from the replicated polystyrene nanocones.

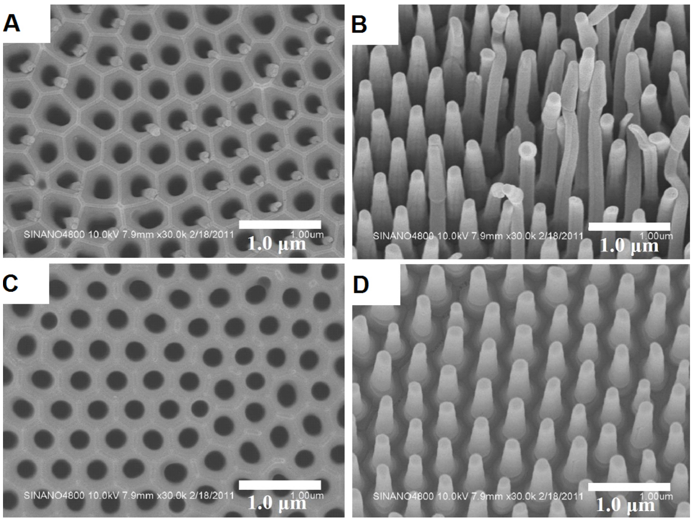


**Figure S2.** SEM top-views of the PAA templates after the replication-etching-detaching process with varied etching time: A) 5 min and C) 30 min. The SEM oblique views of the as-prepared polystyrene nanocone arrays after the detaching action are corresponding to the panel B) and D), respectively. It is evident that a part of polystyrene nanocones was elongated and even ruptured during the detaching as the etching time is too short. On the other hand, as the etching time is too long, the surface texture of the PAA templates was apparently destroyed, accompanied with the widening of the nanopores, which are detrimental to their recycling.

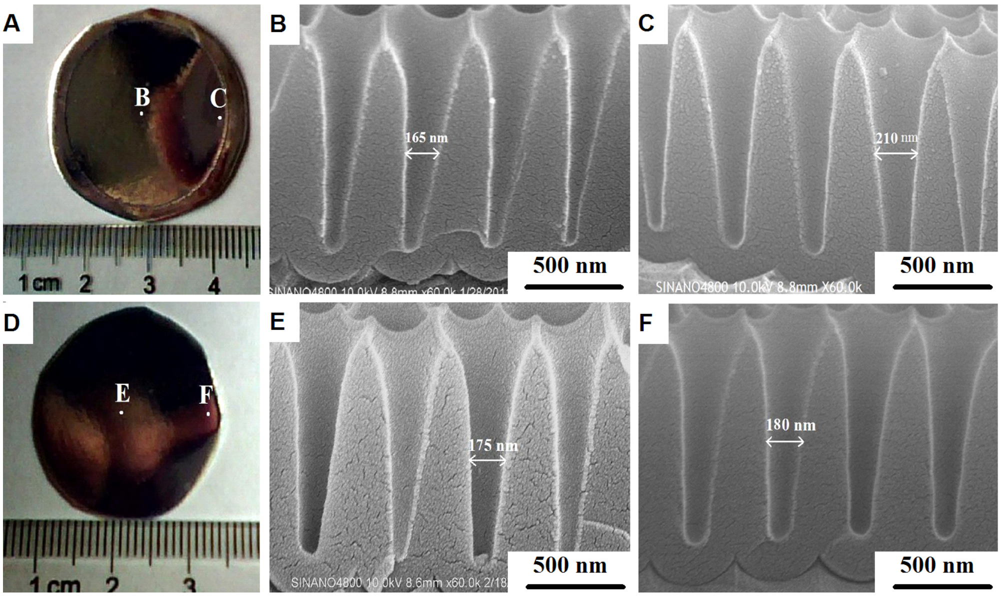


**Figure S3.** A photograph of a detached PAA template where the etching time required for the effective detaching of the replicated polystyrene nanocones is 40 min at the etchant temperature of 30 °C; B, C) SEM Side-views of nanopores at the centre and edge place of the template corresponding to the panel A, respectively. D) A photograph of a PAA template that was detached only needing the etching time of 13 min as the etchant temperature was set to be 50 °C. E, F) SEM Side-views of nanopores at the centre and edge place of the template corresponding to the panel D, respectively. It is evident that the longer etching aggravates the difference of the wall thinning at the centre and edge due to the restricted diffusion. Remarkably, such difference can be effectively solved by raising the etchant temperature.

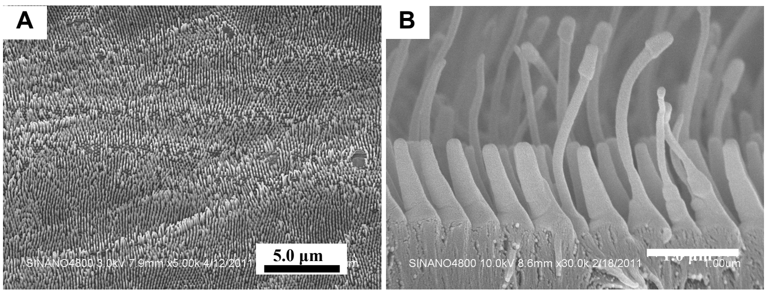


**Figure. S4** SEM oblique view (A) and side-view (B) of polystyrene nanocones detached from the silanized conical PAA templates.

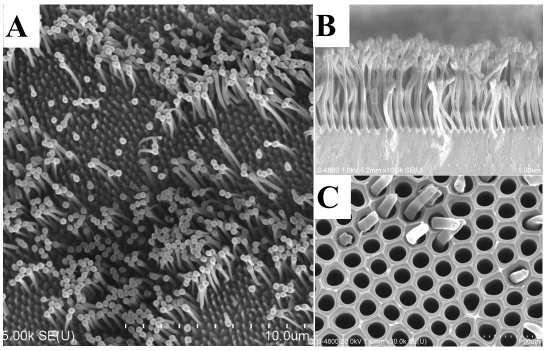


**Figure S5.** SEM oblique view (A) and side view (B) of the replicated polystyrene nanocones detached from the cylindrical PAA template after the replication-etching-detaching. The adopted etching time is 15 min. C) The locally magnified SEM top-views of the cylindrical PAA template after the detaching, which is corresponding to the panel A). The depth of the nanopores is ca. 950 nm