

Electronic Supplementary Information

For

**Ultrathin open-ended porous TiO₂ membranes for surface
nanopatterning in fabricating nanodot arrays**

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1. Experimental section

Fabrication of the UOP-TM on Si substrate

In this work, the anodizations were performed in a conventional two-electrode system with Ti foil as the working electrode and a graphite sheet as counter electrode. The electrolytes used in the anodizations were the ethylene glycol solutions containing 0.3 wt% NH_4F and different amounts of water. Before anodization, Ti foils were degreased by sonication in acetone, ethanol and deionized water sequentially, and then dried in air. The fabrication process of the UOP-TM mainly involved four steps: twice pre-anodizations, main anodization, pore-opening anodization and water-assisted transfer. Firstly, the twice pre-anodizations of the Ti foil were carried out in the same electrolyte with water addition of 2 vol% at a constant voltage of 60 V at 15 °C in a processing sequence: (i) 2 h pre-anodization and removal of the formed TiO_2 layer, (ii) 10 min pre-anodization and removal of the formed TiO_2 layer. Then, the main anodization of the remaining Ti foil was carried out at the same condition as that of pre-anodizations but the anodization time reduced to a few dozens of seconds. Afterwards, the following pore-opening anodization was carried out in the electrolyte without water addition at a high voltage of 120 V for 40 s. Finally, by inserting the Ti foil in water, the ultrathin open-ended porous TiO_2 membrane (UOP-TM) floating on water could be obtained, and then it could be picked up using Si slice or other substrates.

Fabrication of Bi nanodot arrays

With the fabricated UOP-TM as mask on Si substrate, Bi was deposited on Si substrate through the pores of UOP-TM by electron-beam vacuum evaporation apparatus. The vacuum was 2×10^{-4} Pa, the nominal evaporation thickness was 30 nm. After removal of the UOP-TM by adhesive tape, Bi nanodot arrays on Si substrate can be obtained.

Characterization

The morphologies of the samples were observed using a field-emission scanning electron microscope (FE-SEM, Hitachi S4800).

2. Discussion about the twice pre-anodizations

The twice pre-anodizations, including a long-time pre-anodization for 2 h and a short-time pre-anodization for 10 min, are necessary for fabrication of UOP-TM with good ordering and straight pores. The long-time pre-anodization can wipe out the surface scratches as well as create ordered concaves on the Ti foil (Fig. S1a). However, new anodization upon these concaves at the same conditions always results in the branched pores for the reason that the size of the concaves is too large to guide a new pore initiation (Fig. S1b). Actually, the concaves gradually become larger during the anodization, the longer the anodization lasts, the larger the concave pits will be. To create concaves with appropriate size for guiding new pore initiation, a second short-time pre-anodization is carried out. After removal of the thin TiO_2 layer formed at the

second pre-anodization, the concaves on Ti substrate (Fig. S1c) possess smaller size compared to that shown in Fig. S1a. Moreover, the porous TiO₂ membrane grown upon these concaves would have straight through pores (Fig. 2b).

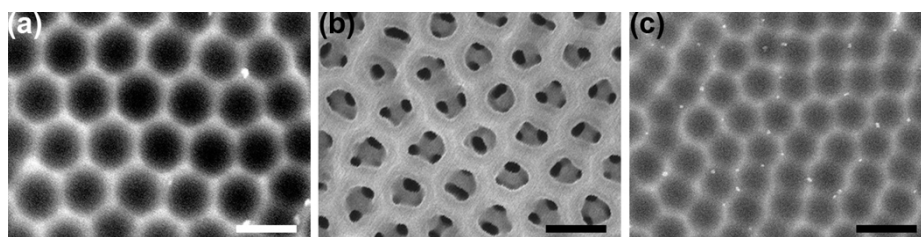


Fig. S1. (a) Top view SEM image of the ordered concaves created by the first long-time pre-anodization for 2 h. (b) Top view SEM image of the TiO₂ membrane grown upon the concaves created by the first long-time pre-anodization. (c) Top view SEM image of the ordered concaves created by the second short-time pre-anodization for 10 min. The bars in all the images correspond to 200 nm.

3. Additional supporting Figures and table

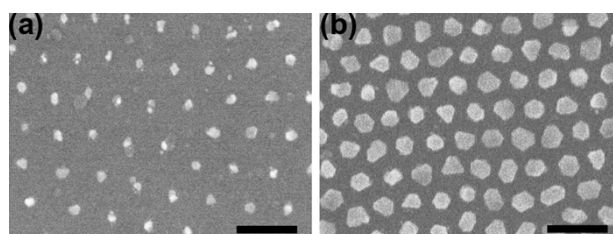


Fig. S2. The SEM images of the Bi nanodot arrays with different dot diameter (D) and dot interval (d): (a) $D \approx 30$ nm and $d \approx 130$ nm, (b) $D \approx 65$ nm and $d \approx 100$ nm. The bars in all the images correspond to 200 nm.

Fabrication processes	First pre-anodization	Second pre-anodization	Main anodization	Pore-opening anodization	Etching in HF solution
Parameters	40 V-3 h	40 V-30 min	40 V-90 s	120 V-40 s	3 min

Table S1. Detailed fabrication parameters of the UOP-TM with smaller pore interval. The first pre-anodization, second pre-anodization and main anodization were carried out in electrolyte with water addition of 1 vol%.