Supplementary Information

Preparation of layered TiO_2 nanotube arrays

The anodization of Ti foils (99.6+% purity) was carried out in a two-electrode electrochemical cell with Pt foil as counter electrode around room temperature. The electrolytes are prepared from NH_4F (99.5% purity), DI H_2O, ethylene glycol (99.8% purity) and/or formamide (99.5% purity), with contents described in text. After anodization, the samples were treated with ultrasonic cleaning in methanol to remove the debris, and kept in methanol before characterization. For SEM characterization, nanotube arrays were peeled from Ti by bending Ti foil mechanically.

Separation of TiO_2 nanotube segments

Layered TiO_2 nanotube arrays were peeled from Ti by soaking in a 0.5 wt% oxalic acid solution, and then kept at 40 ^{o}C for 12 hrs, treated with sonication to disperse the segments, precipitated by centrifuge and washed with water.

Samples for Photocatalytic H_2 production

Samples for photocatalytic H_2 production test were prepared from anodization under periodic 35 V (120 min) and 0 V (5 min) for 3 cycles in the electrolyte containing 3:1 (v/v) formamide-ethylene glycol as solvent, 0.5 wt% NH_4F and 5 vol% H_2O, using Ti foils as working and counter electrodes. The arrays were peeled from Ti by soaking in a 0.5 wt% oxalic acid solution for about 10 minutes. For unseparated sample, the arrays were washed with water and methanol successively, and then crystallized by calcination at 650 °C in air for 3 hrs, with heating rate of 2 °C /min. For separated sample, the arrays were kept in the 0.5 wt% oxalic acid solution at 40 ^{o}C for about 12 hrs, and then treated with sonication to disperse the segments. After that, the separated nanotube segments were washed and calcined in the same way as unseparated sample.

Photocatalytic H_2 production

2.6 mg of each crystallized sample was photodeposited with 0.3 wt% Pt as cocatalyst from solution containing 80 mL H_2O, 20 mL methanol and a calculated amount of H_2PtCl_6. A 300 W Xenon lamp was used to irradiate the vacuum solution for 0.5 hr. After that, the system was evacuated again, and then photocatalytic H_2 evolution was analyzed by gas chromatography.

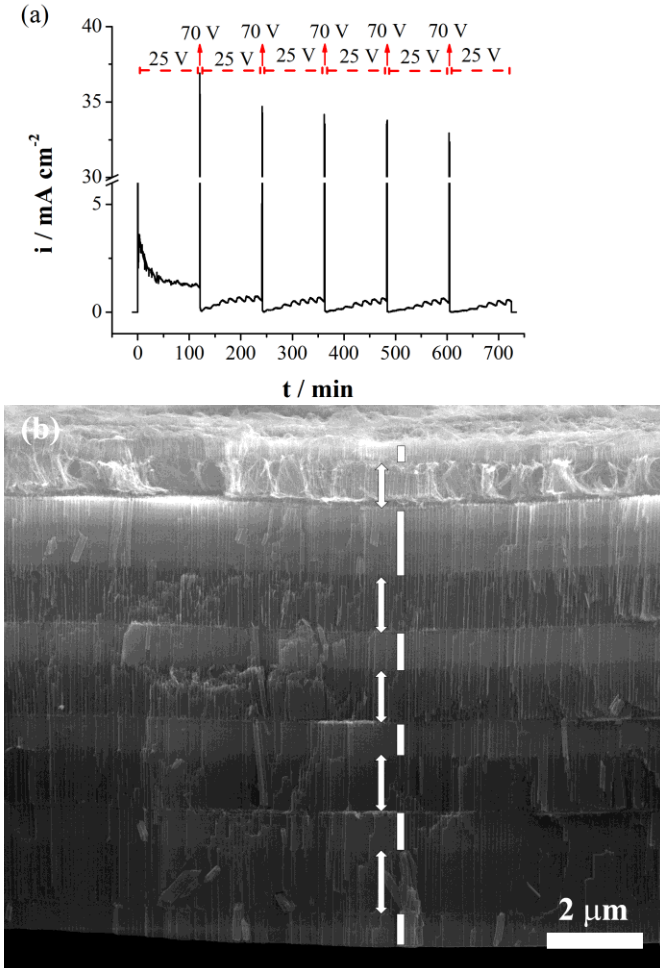


Fig. S1 (a) The current-time transient during anodization, (b) SEM image of the sample without ultrasonic cleaning to see the first layers. The TiO_2 nanotube array was prepared by anodization at periodic 25 V (120 min) and 70 V (1 min) in the ethylene glycol electrolyte containing 0.3 wt% NH_4F and 2 vol% H_2O. Layers grown at 25 V and 70V are marked with line segments and double-headed arrows, respectively. The number of layers matches well with the anodization procedure.

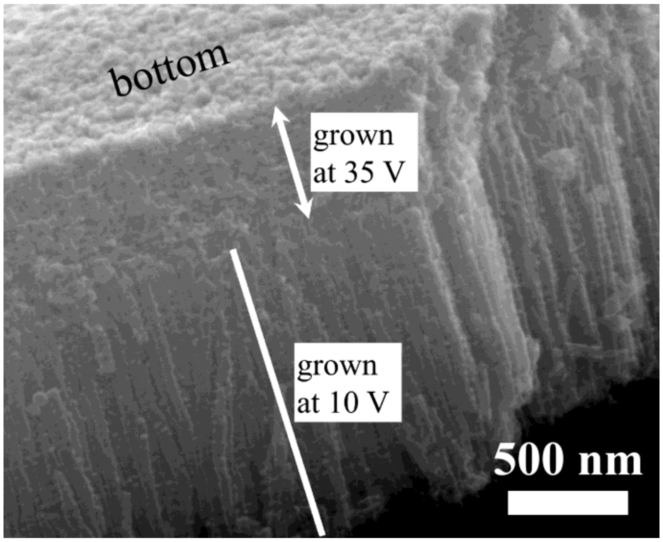


Fig. S2 A SEM image of a TiO_2 nanotube array on 3-D nanopores prepared by applying voltages of 10 V (410 min) and then 35 V (10 min) in the formamide electrolyte containing 0.5 wt% NH_4F and 5 vol% H_2O

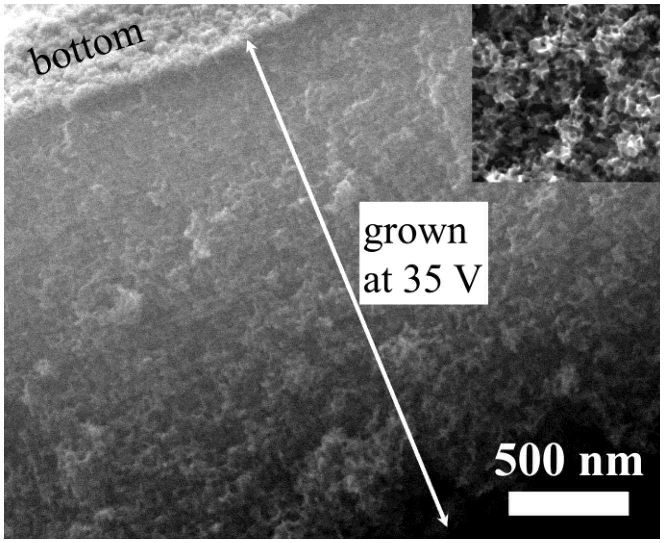


Fig. S3 A SEM image of a TiO_2 nanopores film prepared by applying voltages of 2.5 V (1200 min) and then 35 V (32 min) in the formamide electrolyte containing 0.5 wt% NH_4F and 5 vol% H_2O. The inset is a top image of the film.

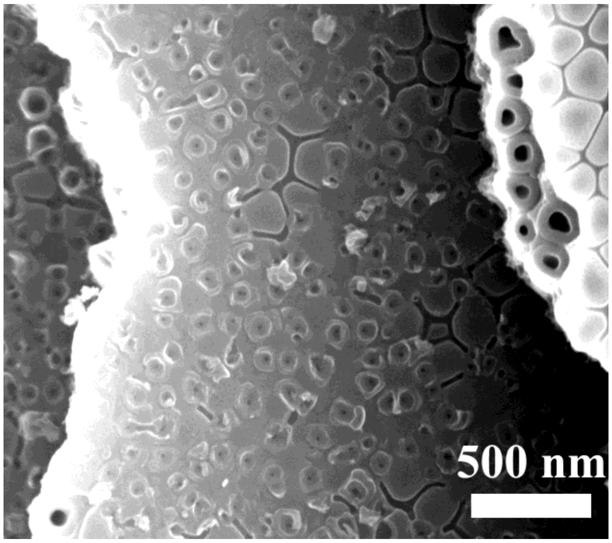
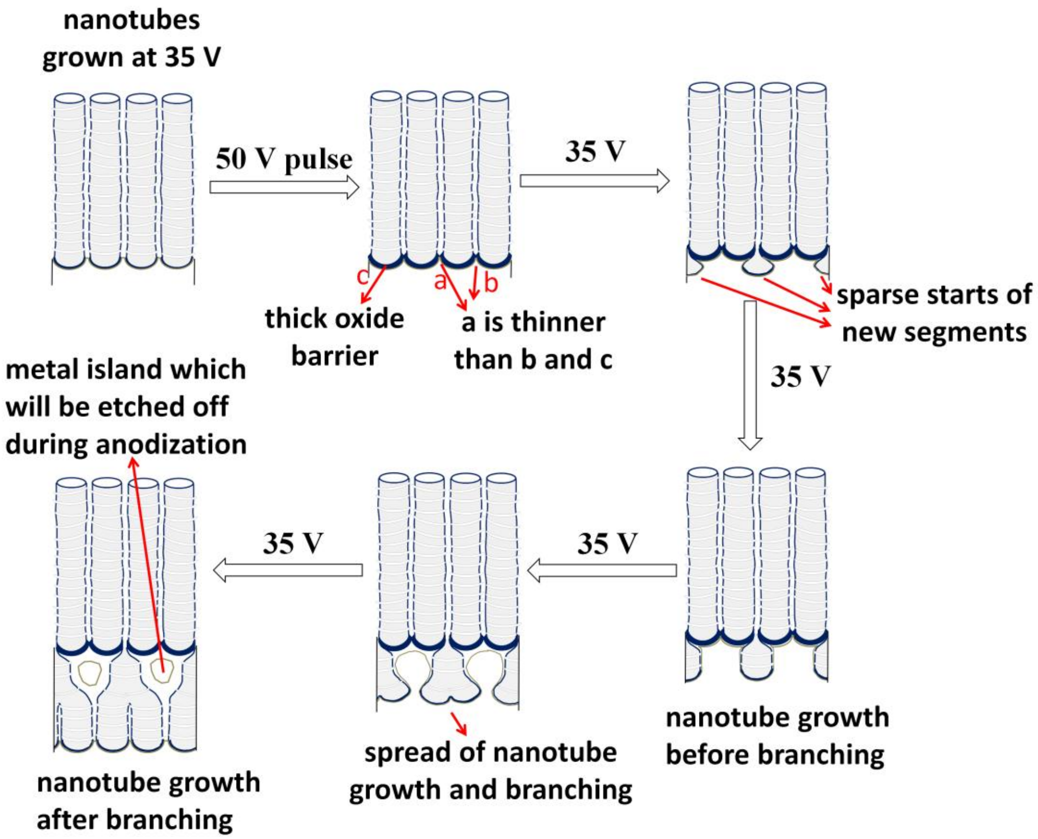


Fig. S4 A bottom SEM image of a cracked piece of layered TiO_2 nanotube array prepared by anodization at periodic 35 V (120 min) and 50 V (0.5 min) in the electrolyte containing 3:1 (v/v) formamide-ethylene glycol as solvent. The pinpricks are remnant joints to the succeeding segments, which show the position of the starting points of subsequent growth of nanotubes.



Scheme S1 A diagram of the formation of branched nanotube segments from two-voltage anodization in formamide electrolytes

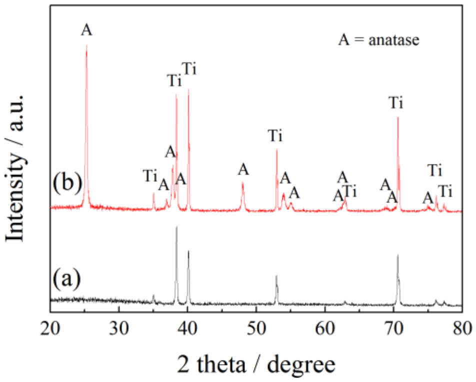


Fig. S5 Typical XRD patterns of (a) as-prepared layered TiO_2 nanotube array on Ti substrate, and (b) the sample subjected to calcination at 450 °C for 3 hrs. The array was prepared in the ethylene glycol electrolyte by applying alternating voltages of 25 V (120 min) and 70 V (1 min), the same as Fig. S1.

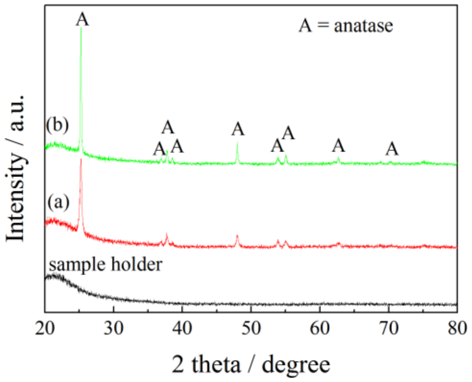


Fig. S6 XRD patterns of samples from calcination of (a) separated TiO_2 nanotube segments, and (b) unseparated TiO_2 nanotube arrays at 650 °C for 3 hrs

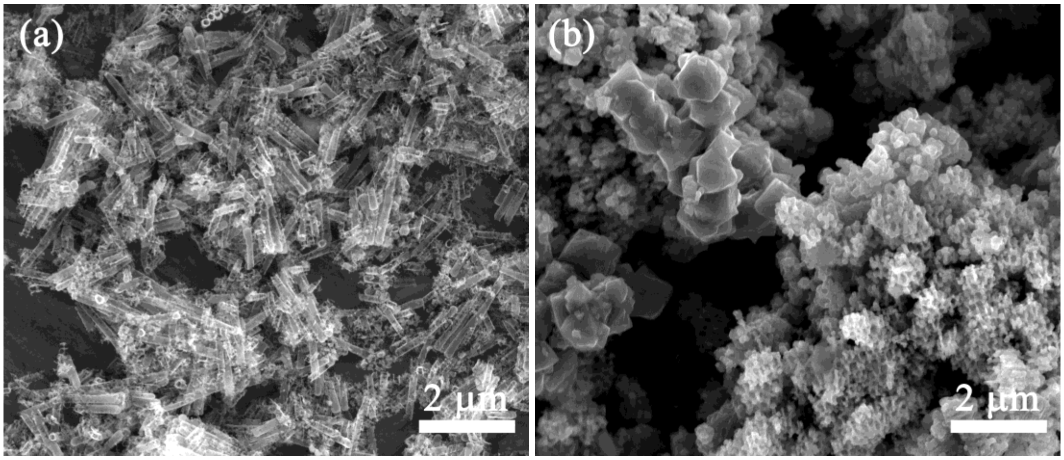


Fig. S7 SEM images of samples from calcination of (a) separated TiO_2 nanotube segments, and (b) unseparated TiO_2 nanotube arrays at 650 °C for 3 hrs