Electronic Supplementary Information

Colorful titanium oxides: new class of photonic materials

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EXPERIMENTAL SECTION

Materials. A 0.1 mm thick titanium foil (99.6%, Jinjia Metal, China) was cut into pieces of 40 × 10 mm^2. Ethylene glycol (EG), ammonia fluoride (NH_4F) were purchased from Macklin Chemical and used as received. All aqueous solutions were prepared using deionized (DI) water with a resistivity of 18.2 MΩ cm.

Preparation of 2D-TOPCs. The 2D-TOPCs were prepared by an electrochemical anodization method on titanium thin foil. Prior to anodization, the titanium foils were first degreased by sonicating in ethanol and room-temperature DI water, followed by drying in pure nitrogen stream. The anodization was carried out using a conventional two-electrode system with the titanium foil as an anode and a platinum foil (Aldrich) as a cathode respectively. All electrolytes consisted of 0.5 wt% NH_4F in ethylene glycol solution with 2 vol% water. All the anodization experiments were carried out at room temperature. The titanium foil was anodized at 60 V for 30 min, and then the as-grown nanotube layer was ultrasonically removed in DI water. Then, the pre-patterned titanium foils were cleaned with DI water and dried off with N_2 gas, and annealed in air at different temperatures for 1 h with a heating rate of 5 °C/min.

Characterization of 2D-TOPCs. The morphology of the TiO_2 nanotubes and 2D-TOPCs were determined by filed-emission scanning electron microscope (FESEM, FEI

Quanta 600). The diffuse reflectance UV-vis adsorption spectra were recorded on spectrophotometer (Shimadazu, UV 3600), with fine $BaSO_4$ powder as reference. The crystalline structure was analyzed by X-ray diffraction (XRD, Bruker D8 Discover diffractometer, using Cu Kα radiation, λ = 1.540598 Å). Photoelectron Spectroscopy (XPS) data were collected by an Axis Ultra instrument (Kratos Analytical) under ultrahigh vacuum ($<10^{-8}$ torr) and using a monochromatic Al Kα X-ray source operating at 150 W. The survey and high-resolution spectra were collected at fixed analyzer pass energies of 160 and 20 eV, respectively. Samples were mounted in floating mode in order to avoid differential charging. Charge neutralization was required for all samples. Binding energies were referenced to the C 1s binding energy of adventitious carbon contamination which was set at 285 eV.

Electromagnetic Simulations. The optical absorption spectra of 2D-TOPCs were simulated using FDTD method with Lumerical FDTD Solutions software. The simulation domain sizes were determined from the SEM image of the samples. All the dimensions were set to match the actual geometry of the 2D-TOPCs. The wavelength scanning range of 200−800 nm was performed using incident plane wave for illumination.

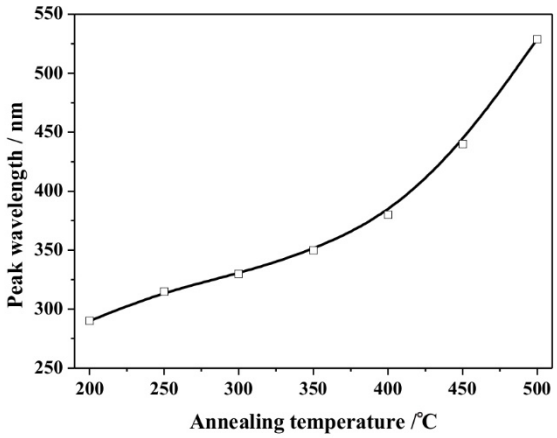

Fig. S1 Relationship of peak wavelengths of 2D-TOPCs and annealing temperatures.

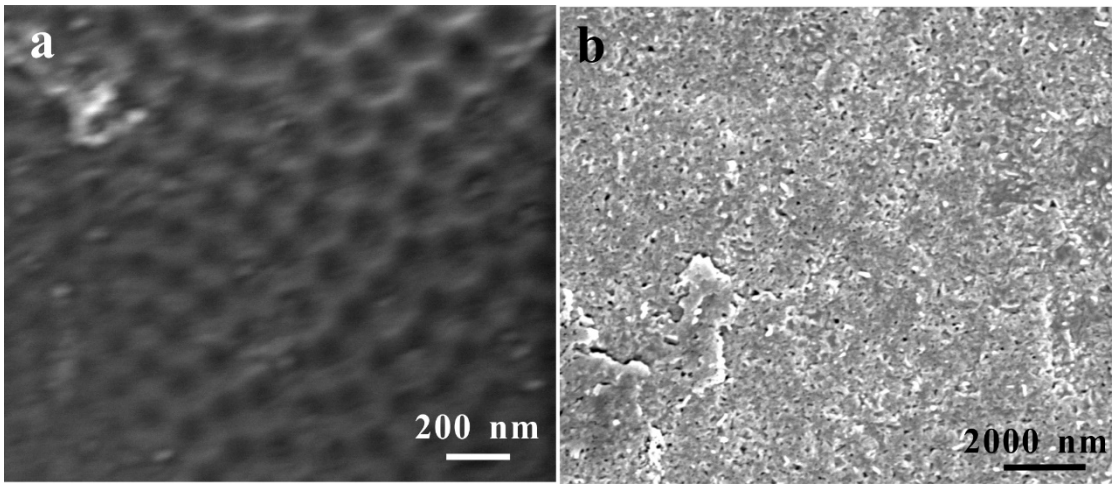

Fig. S2 SEM image of patterned titanium foil annealed at (a) 600 °C and (b) 700 °C.

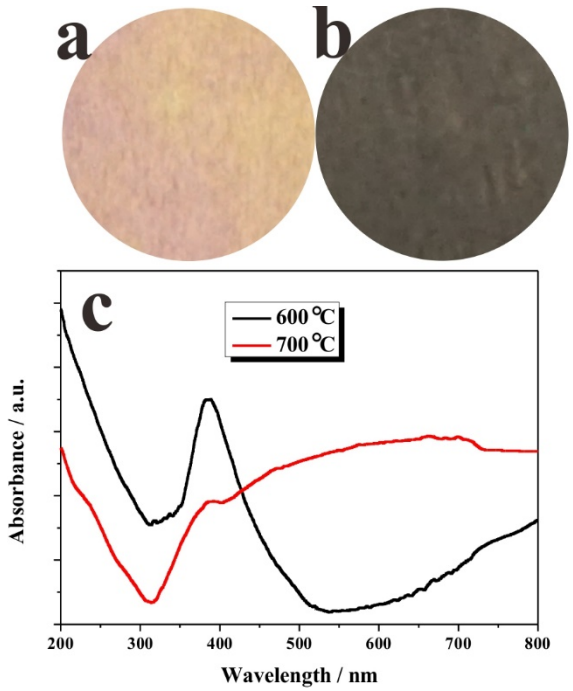

Fig. S3 Digital photos of patterned titanium foils annealed at (a) 600 °C and (b) 700 °C and (c) UV-vis diffuse reflectance absorption spectra.

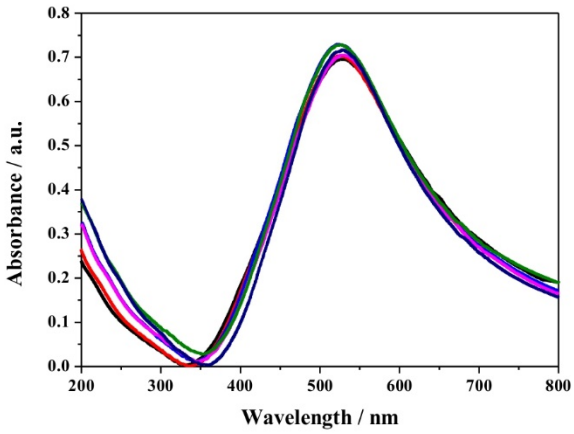

Fig. S4 UV-vis diffuse reflectance absorption spectra of six 2D-TOPC-500 samples.

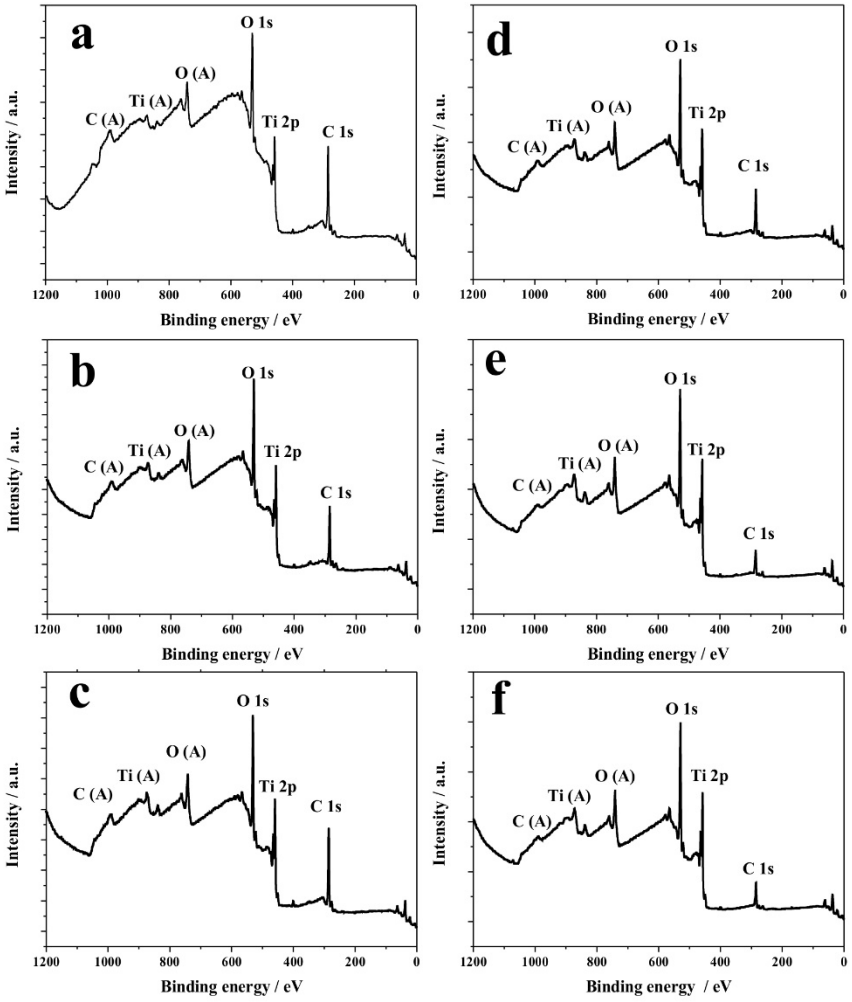

Fig. S5 XPS survey of TOPCs after annealing at different temperatures: (a) no annealing, (b) 200 °C, (c) 300 °C, (d) 400 °C, (e) 500 °C, (f) 600 °C.

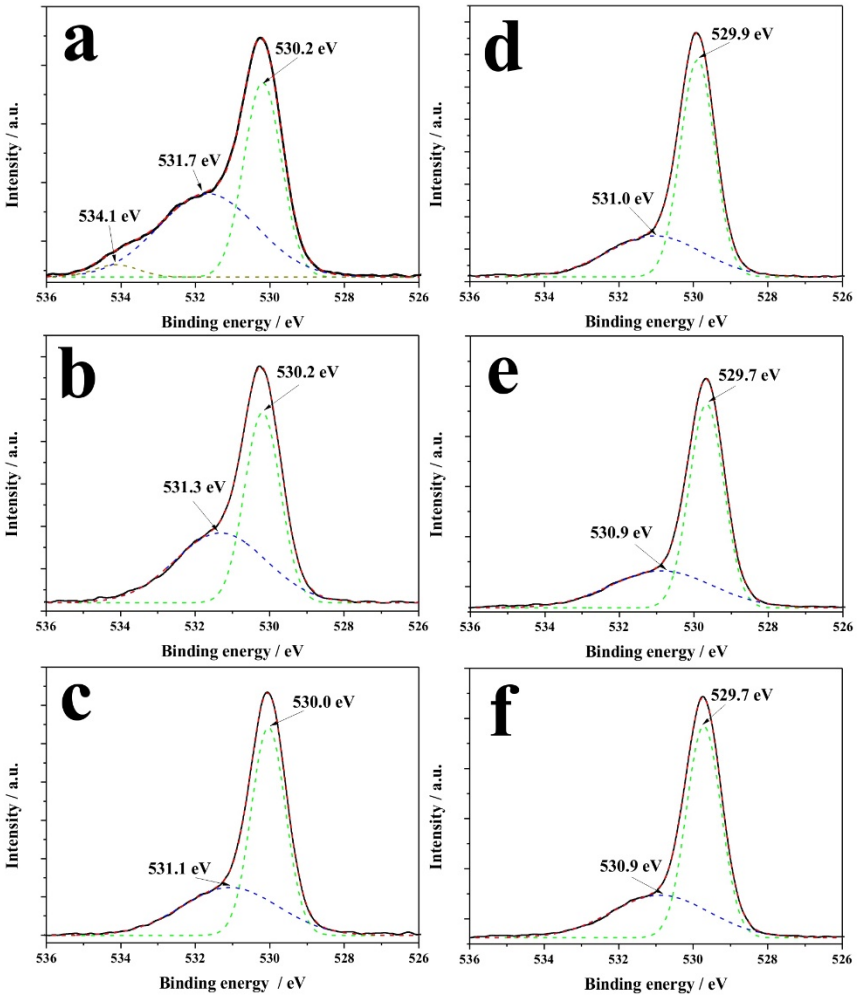

Fig. S6 XPS core level of O 1s after annealing at different temperatures: (a) no annealing, (b) 200 °C, (c) 300 °C, (d) 400 °C, (e) 500 °C, (f) 600 °C.