

Electronic Supplementary Information

Black TiO₂ Inverse Opals for Visible-Light Photocatalysis

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1 Synthesis

1.1 Preparation of polystyrene (PS) nanospheres template

The monodispersed PS nanospheres (diameter of 360 nm) were prepared by a method of soap free emulsion polymerization,¹ and then a thickness of about 10.4 μm PS opal on the surface of the monocrystalline silicon wafer was obtained by evaporation induced self-assembly vertically.

1.2 Fabrication of white TiO_2 inverse-opals

Firstly, titanium isopropoxide (50 μL) was dropped to the 1 cm \times 4 cm PS opal template, and then was putted into a Petri dish at 70 $^\circ\text{C}$ in vacuum for 20 h. Secondly, the above-prepared sample was calcined in a tubular furnace at 500 $^\circ\text{C}$ for 5 h under O_2 atmosphere with a heating rate of 1 $^\circ\text{C}/\text{min}$.

1.3 Hydrogenation

The as-prepared WTIOs were hydrogenated at 500 $^\circ\text{C}$ (the heating rate is 5 $^\circ\text{C}/\text{min}$) for 2 h under H_2 atmosphere. At the end of the heating period, the sample was cooled to room temperature naturally under H_2 atmosphere, named black TiO_2 inverse opals (BTIOs).

1.4 Preparation of black TiO_2 inverse-opals fragments

The black TiO_2 inverse-opals fragments (BT Fs) can be obtained when BTIOs scraped from the silicon wafer surface.

1.5 Photocatalytic activity test

The photocatalytic degradations of methylene blue (MB, 100mL, 1.0×10^{-5}

⁵mol/L) were carried out in jacket beakers at room temperature. The jacket of beakers was filled with 1.0 mol/L NaNO₂ aqueous solution to filter off ultraviolet light² (Fig. S7). A 300 W Xe arc lamp with a cold trap was used as the light source. Prior to irradiation, the solution was stirred for 1 h in the dark room to reach the absorption-desorption equilibrium between the catalysts and MB. The concentration of the MB was analyzed by monitoring the absorbance at 664 nm by a TU-1900 UV-Vis spectrophotometer.

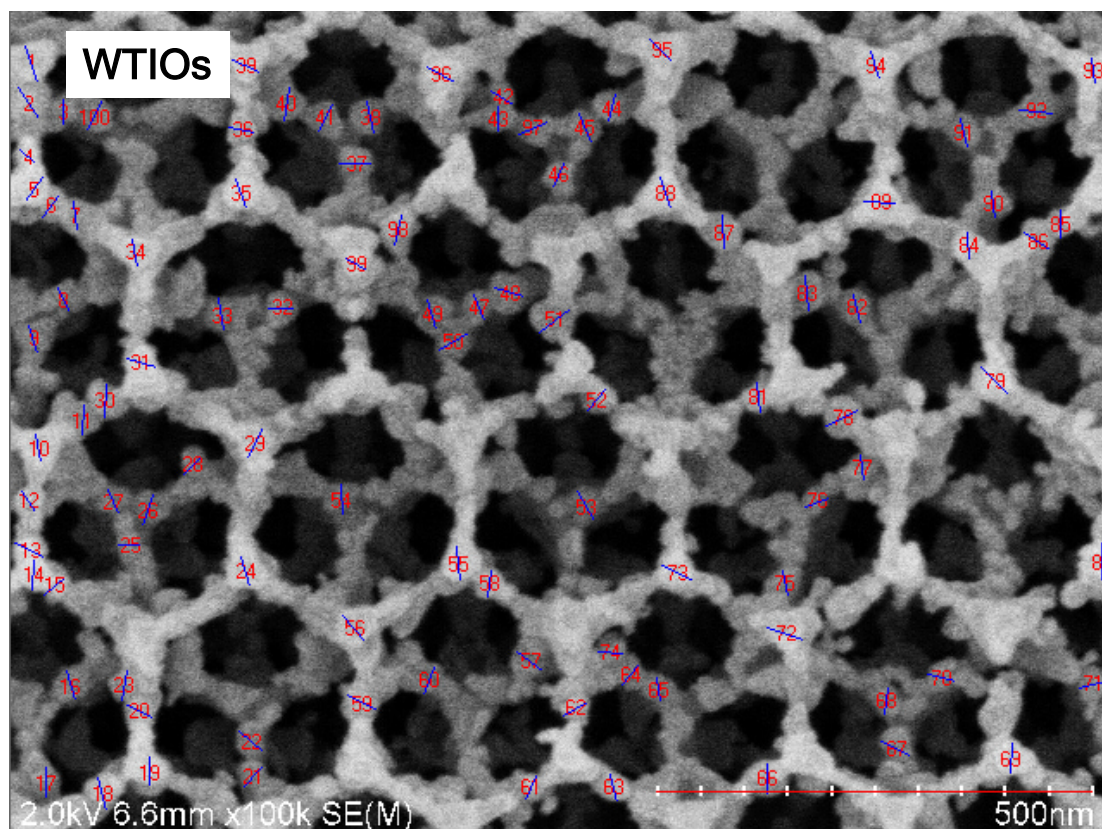
2 Characterization of TiO₂

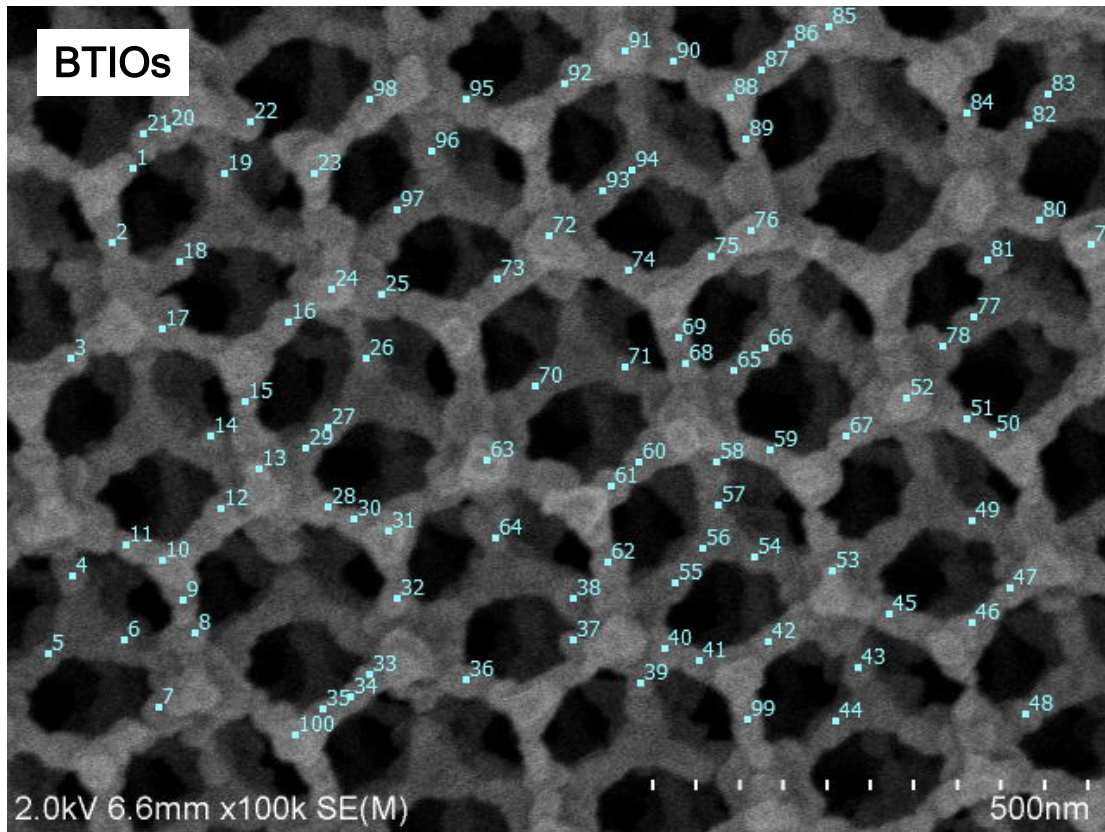
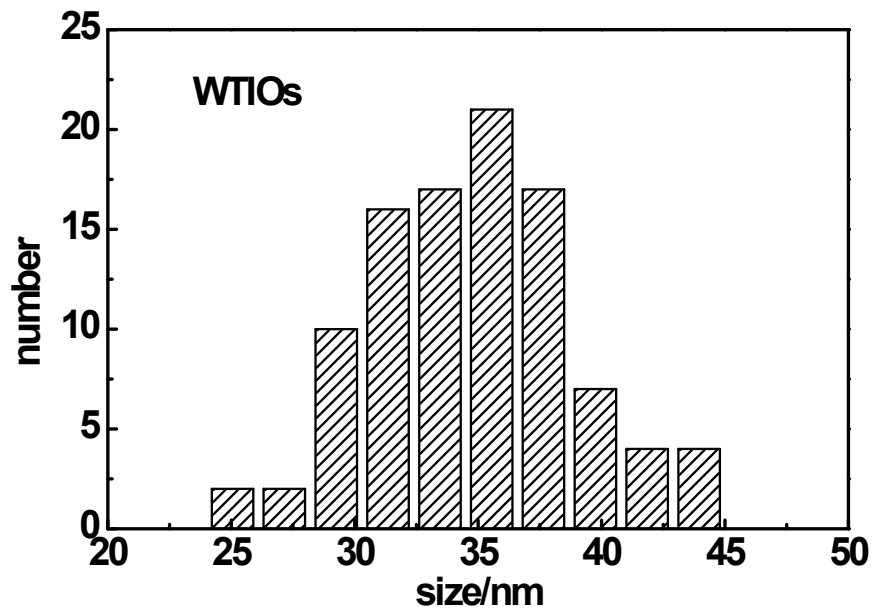
The morphologies of PS nanospheres, PS opals, WTIOs and BTIOs were observed by field-emission scanning electron microscopy (FE-SEM, Hitachi S-4800, operated at an accelerating voltage of 2 kV) and transmission electron microscopy (TEM, JEM-2100, operated at an accelerating voltage of 200 kV). The crystallinity of WTIOs and BTIOs was assessed by X-ray powder diffraction (XRD, Bruker D8, Cu K α 1 radiation, 40 kV, 40 mA). The bandgap of the samples was characterized with UV-Vis diffuse reflectance adsorption spectroscopy (UV-Vis, TU-1900) equipped with an integrating sphere, and BaSO₄ was used as a reflectance standard. Micro-Raman (Raman, Invia, 532 nm) analysis was used to study the vibrational modes of the samples. Brunauer-Emmett-Teller (BET, ASAP2020 MP) method was utilized to calculate the specific surface area.

2 Figures



Fig. S1 Digital photos of BTIOs and WTIOs





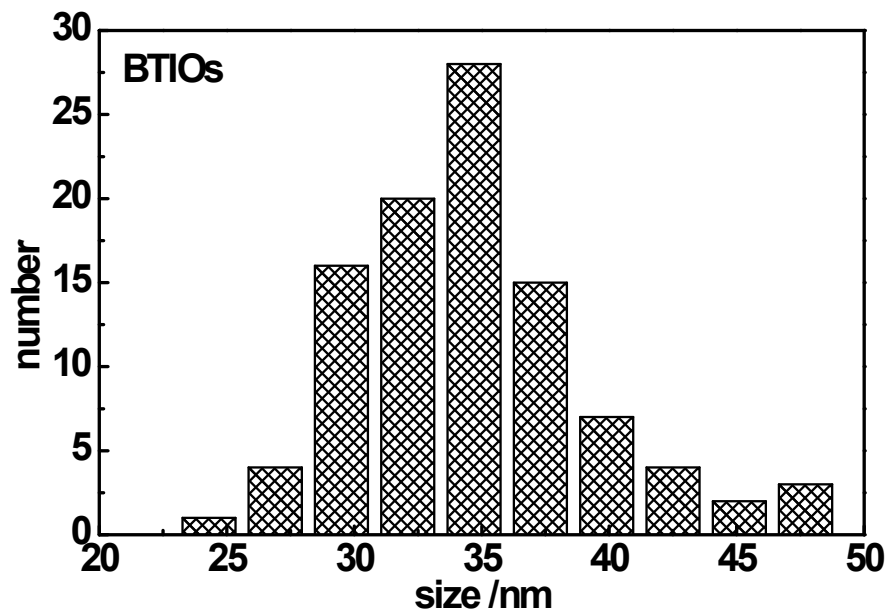


Fig.S2 the statistical data of TiO_2 grain size of WTIOs and BTIOs obtained from 100 particles in SEM images of WTIOs and BTIOs, respectively

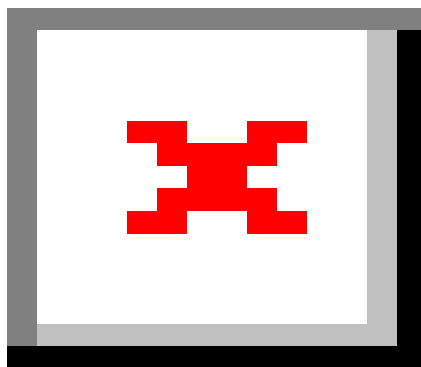


Fig. S3 SEM image of BT Fs

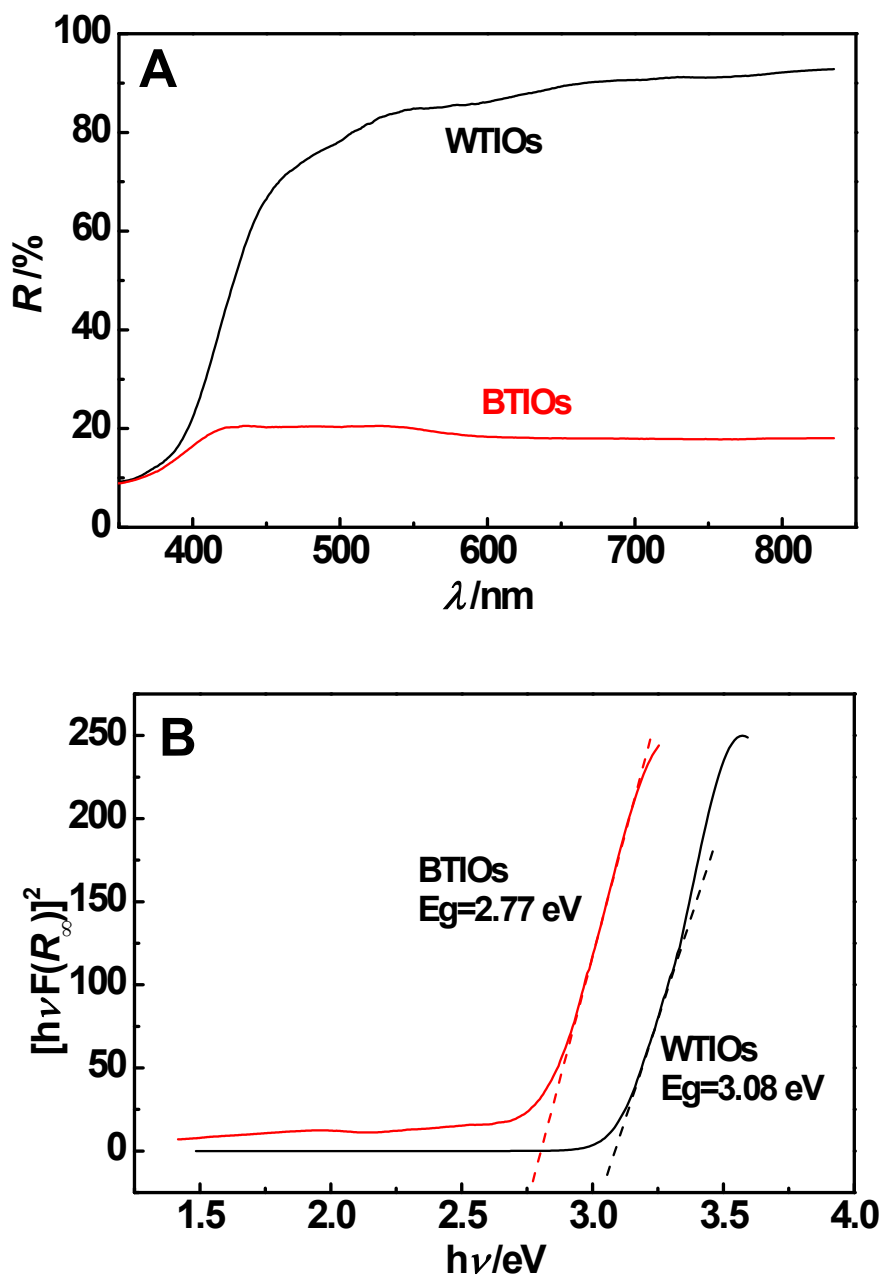


Fig. S4 UV-vis diffuse reflectance spectra (A) and the corresponding $\text{h}\nu - [\text{h}\nu F(R_\infty)]^2$ curves (B) of BTIOs and WTIOs

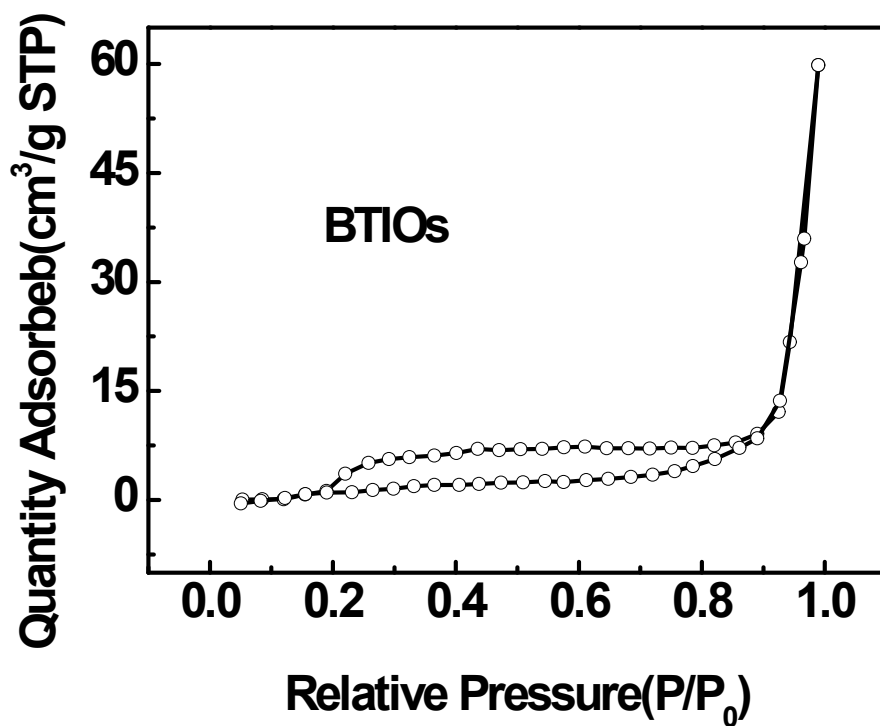
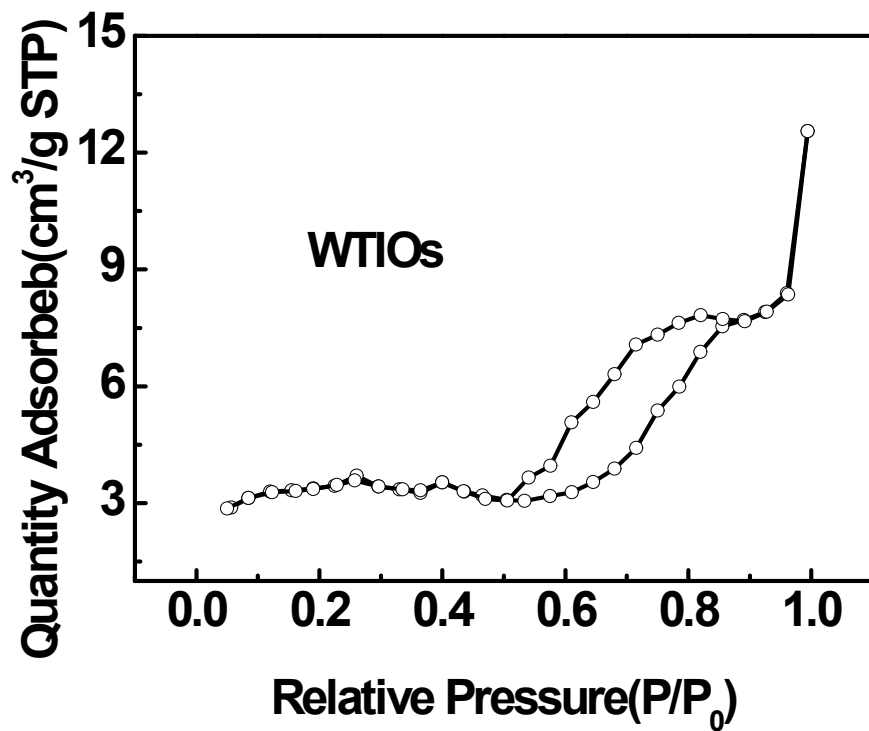


Fig. S5 Nitrogen isotherm adsorption-desorption curves of WTIOs and BTIOs

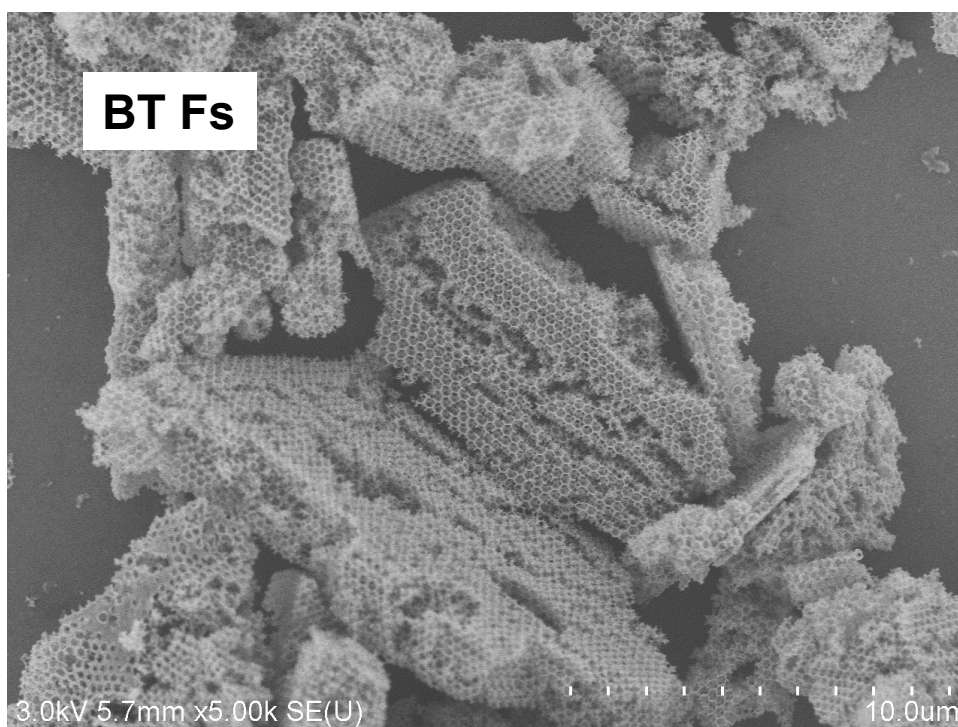
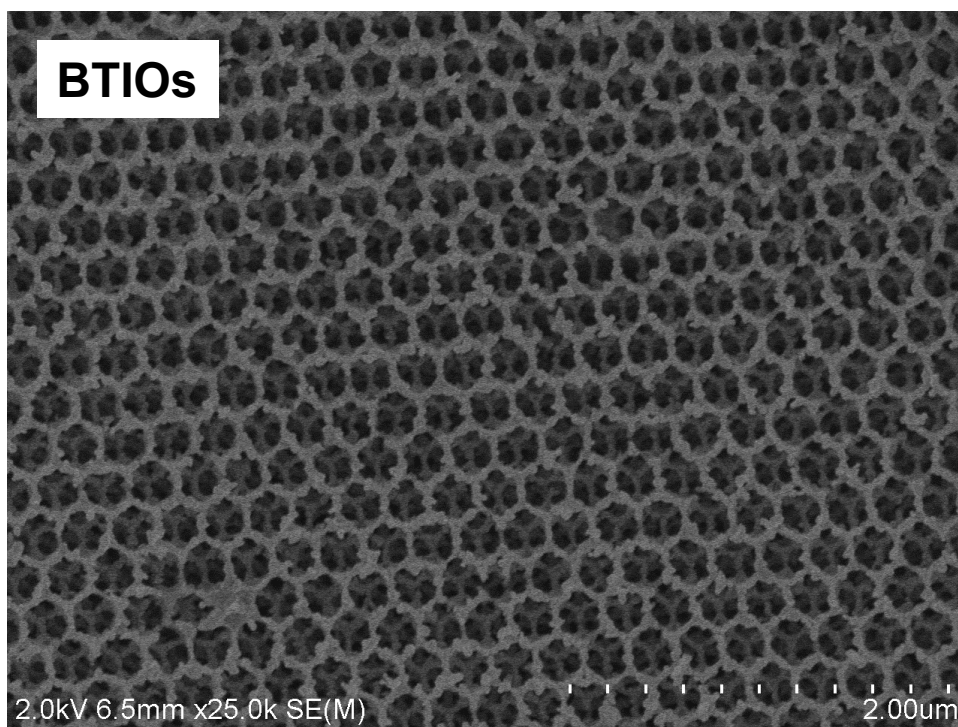


Fig. S6 SEM images of BTIOs and BT Fs after ten times recycling

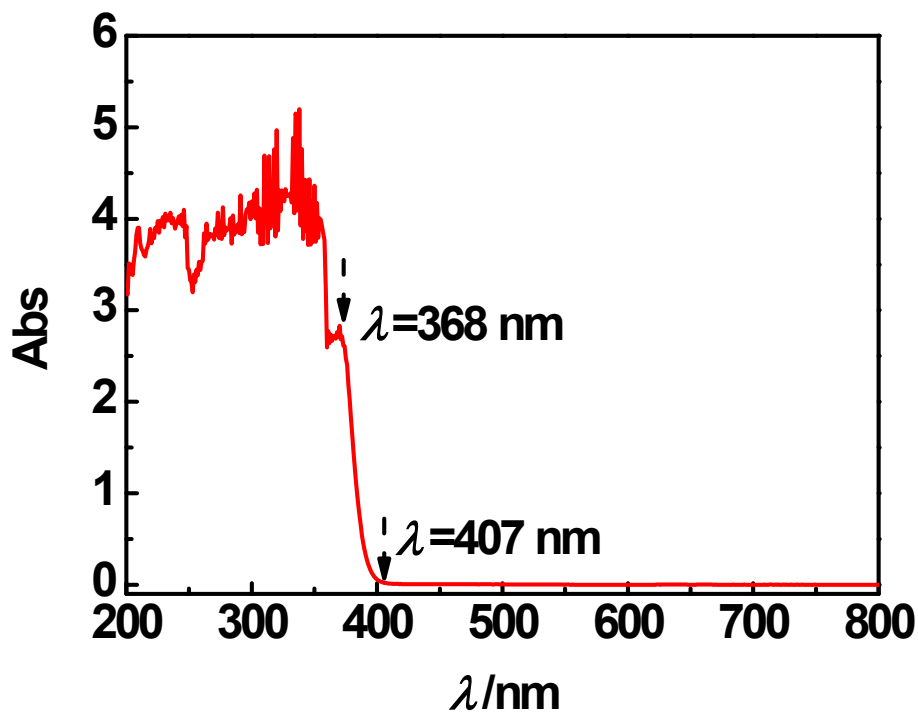


Fig. S7 The UV-vis adsorption spectrum of 1 mol/L NaNO₂ aqueous solution

4 References

- (1) Chen, X.; Li, Z.; Ye, J.; Zou, Z. Forced Impregnation Approach to Fabrication of Large-Area, Three-Dimensionally Ordered Macroporous Metal Oxides. *Chem. Mater.* **2010**, 22, 3583–3585.
- (2) Cheng P.; Li W.; Zhou T.; Jin Y.; Gu M. Physical and Photocatalytic Properties of Zinc Ferrite Doped Titania under Visible Light Irradiation. *J. Photochem. Photobiol. A* **2004**, 168(1): 97–101.