Electronic Supplementary Information

Black TiO$_2$ Inverse Opals for Visible-Light Photocatalysis

Linlin Xin$^a$ and Xuefeng Liu$^b$

$^a$ School of Chemical and Material Engineering, Jiangnan University, Wuxi, 214122, PR China.

$^b$ The Key Laboratory of Food Colloids and Biotechnology, Ministry of Education, Jiangnan University, Wuxi, 214122, PR China.

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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 \(\mu\)m 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 \(\mu\)L) was dropped to the 1 cm\(\times\)4 cm PS opal template, and then was putted into a Petri dish at 70 °C in vacuum for 20 h. Secondly, the above-prepared sample was calcined in a tubular furnace at 500 °C for 5 h under O\(_2\) atmosphere with a heating rate of 1 °C/min.

1.3 Hydrogenation

The as-prepared WTIOs were hydrogenated at 500 °C (the heating rate is 5 °C/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, \(1.0\times10^{-3}\) mol/L)
were carried out in jacket beakers at room temperature. The jacket of beakers was filled with 1.0 mol/L NaNO\textsubscript{2} aqueous solution to filter off ultraviolet light\textsuperscript{2} (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 TiO\textsubscript{2}

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\textsubscript{α1} 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 BaSO\textsubscript{4} 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.
Figures

Fig. S1 Digital photos of BTIOs and WTIOs
Fig. S2 the statistical data of TiO₂ 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 $\nu - [h\nu F(R_{\infty})]^2$ 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
