Supporting Information

Template-free synthesis of mesoporous anatase yttrium-doped TiO$_2$
nanosheet-array films from waste tricolor fluorescent powder with high photocatalytic activity

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Part I. Experimental

Materials: Waste tricolor fluorescent powders used in this work were purchased from Huake, Jiangxi Rare Earth New Materials Co., Ltd. All chemicals were purchased from Chemical Reagent Company of Beijing in analytical grade.

Liquid-liquid extraction experiments: The liquid-liquid extraction experiments were conducted according to a previous literature.$^1$ In a typical liquid-liquid extraction, 1.5 g of
Potassium sodium tartrate (PST, KNaC$_4$H$_4$O$_6$·4H$_2$O) was dissolved in 300 mL of distilled water (pH = 7), the pH of the aqueous phase was adjusted by using NaOH. 15 g of WTFP were mixed with 200 mL of the chloroform phase containing 1-pentanol (1-pentanol/ chloroform ratio was 1/4), and shaken for 1 to 2 min. After that, the mixed organic phase and aqueous phase, at an organic/aqueous (O/A) volume ratio of 2:3, were shaken at room temperature for 5 min. RFP was extracted into the upper phase (aqueous), washed with de-ionized water and absolute ethanol, and then dried at 60 °C. Three times of extraction were necessary to separate the RFP with good recovery and grade. The detail process flow sheet is shown in Fig. S1.

**Fig. S1.** Flow sheet for separation of the Waste Tricolor Fluorescent Powder (WTfp).

**Fabrication of mesoporous anatase Y-TiO$_2$ nanosheets film:** The mesoporous Y-TiO$_2$ nanosheets was fabricated by solvothermal method. Firstly, a layer of TiO$_2$ nanoparticles was deposited on the quartz substrate via sol-gel method according to our previous publication.$^2$ Subsequently, the seeded slide was put into an autoclave containing a solution with 1 mL tetrabutyl titanate, 40 mL glacial acetic acid and 1 wt % - 10 wt % the above RFP (with respect to the solution). We have adopted the following terminology for the different materials synthesized: X % Y-TiO$_2$, where X corresponds to the amount of RFP added into the solution. Finally, the
solvothermal reaction was carried out at 160 °C from 1 h to 10 h. After the solvothermal treatment, the as-synthesized products was washed with de-ionized water for 6 times and then dried at 60 °C. At last, the obtained films were calcined at different temperature for 2 h.

**Characterization:** The crystal structure was examined by X-ray diffraction (XRD) analysis with a Bruker axs D8 Advance using Cu Kα radiation (Bruker, Germany). The percentage of anatase (XA) in the film can be calculated using the equation as below:\(^3\)

\[
X_A(\%) = \frac{100}{1+1.265(I_R/I_A)}
\]

where \(I_A\) and \(I_R\) are the intensity of the anatase peak at \(2\theta = 25.3°\) and the intensity of rutile peak at \(2\theta = 27.4°\). The morphology of the nanocrystals was examined by S-4300 field-emission scanning electron microscopy (SEM) (Hitachi, Japan) and JEM-2100F high-resolution transmission electron microscopy (TEM) (JEOL, Japan). Fourier transform infra red spectra (FTIR) were carried out using diffused reflectance model on a Varian FTS-7000 Fourier Transform Infrared Spectrometers. X-ray fluorescence spectrometry (XRF, PANalytical PW2403) was used to analyze the chemical compositions of Y-TiO₂ films. The pore size distribution was calculated from the adsorption branch of the sorption isotherms using the Barret-Joyner-Halenda (BJH) method. X-ray photoelectron spectroscopy (XPS) data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W Al Kα radiation (E = 1486.6 eV) in a base pressure of 3×10⁻⁹ m bar. The binding energies were referenced to the C1s line at 284.8 eV from adventitious carbon.

**Photocatalytic activity measurements:** The photocatalytic activity of the films attached on the same-sized quartz was evaluated on the basis of the degradation rate of Methyl Orange (MO)
aqueous solutions. A 300W Xenon lamp (PLS-SXE300, Beijing TrustTech) was used as the simulated solar light source. In the typical photocatalytic experiment, all the films (2.0 × 1.5 cm²) were immersed in 20 mL of an aqueous MO solution (10 ppm) in a quartz cell. Prior to irradiation, all the films were soaked in dark for 1.0 hour to ensure the absorption-desorption equilibrium of the dye on the surface of catalysts. After illumination for given period of 0 min, 30 min, 60 min, 90 min and 120 min, the concentration of MO was analyzed by a Perkin-Elmer Lamda 750S UV-visible spectrophotometer. Lambert-Beer rule was applied at the characteristic absorbance bands of dyes, MO 464 nm, to determine their concentration changes. The degradation efficiency of MO was calculated according to the following equation.

\[
MO \text{ degradation} \left( \% \right) = \frac{C_0 - C_t}{C_0} \times 100\% \quad (2)
\]

Where \( C_0 \) is the initial concentration of MO and \( C_t \) is the MO concentration after illumination time \( t \).
Part II. Discussion

Fig. S2. SEM image of TiO$_2$ nanoparticles synthesized by the same solvothermal process without added RFP, which exhibited a uniform rod shape.
**Fig. S3.** EDX image obtained from the 2.5 wt% Y-TiO₂ film. The EDX image clearly indicates that Yttrium doping in TiO₂.

**Table S1** Composition of 2.5 wt% Y-TiO₂ films determined by EDX.

<table>
<thead>
<tr>
<th>element</th>
<th>Amount of element in 2.5 wt% Y-TiO₂ film</th>
</tr>
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<tbody>
<tr>
<td>O K</td>
<td>31.98 wt%</td>
</tr>
<tr>
<td>Ti K</td>
<td>67.95 wt%</td>
</tr>
<tr>
<td>Y K</td>
<td>0.07 wt%</td>
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</tbody>
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Fig. S4. SEM images of the Y-TiO$_2$ nanosheet arrays obtained at different solvothermal reactions temperature for 6 h: a) 100 °C; b) 120 °C; c) 140 °C; and d) 180 °C.
Fig. S5. SEM images of a) 1wt % Y-TiO₂ film; b) 5 wt % Y-TiO₂ film.
Fig. S6. Lifetime of photo-degradation MO over 2.5 wt% Y-TiO₂ film under the simulated solar light irradiation.

The photodegradation of MO was cycled 5 times under the same condition to use to investigate the stability of the 2.5 wt% Y-TiO₂ film. As shown in Fig. S6, 2.5 wt% Y-TiO₂ film exhibited very similar photocatalysis activity in 5 times of repeated tests, revealing it is a highly stable photocatalyst.

References