Supporting Information

Black and Yellow Anatase Titania Formed by (H,N)-doping: Strong Visible-light Absorption and Enhanced Visible-light photocatalysis

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Experimental section

A. Synthesis. Tetrabutyl titanate (14 mL), urea (1 g) and ethanol absolute (20 mL) were mixed. Hydrochloric acid A.R. (1 mL), deionized water (5 mL) and ethanol absolute (10 mL) were also mixed. The second solution was gradually added dropwise to the first, and then a glass rod was used to stir the mixture until a white colloid formed. The mixture was placed in a water bath at 35 °C for 30 min. In room temperature, the mixture was gently stirred magnetically for about 2 min, left to sit overnight, and then gently stirred magnetically for about 2 min. The mixture was then heated in a water bath at 80 °C (keep water temperature not less than 75 °C when adding water into water bath during the process) until a pale yellow material formed after about 9 h (the material was uniformly dispersed by operation when it go on about 7 hours). The resulting material was calcined at 550 °C for 3 h and then cooled. The samples are named according to the calcination atmosphere; that calcined in air is designated Y(air), that calcined in Ar is designated B(Ar) and that calcined in N₂ is designated B(N₂).

B. Visible-light photocatalytic degradation. The photocatalytic activities of the TiO₂ samples were evaluated by degradation of methylene blue (MB) under visible-light irradiation. After ultrasound agitation (replace the water in ultrasonic apparatus once every ten minutes to maintain the temperature constant) for 30 min in the dark to reach the adsorption-desorption equilibrium between the MB and the photocatalyst (Fig. 5S). A 350-W Xe lamp with a cutoff filter (k ≥420 nm) to remove UV light was used for visible light irradiation. TiO₂ (30 mg) was then added to aqueous MB solution (10 mg/L, 30 mL). About 4 mL of the stirred, irradiated suspension was taken out every 30 minutes. After centrifugation, the degradation of MB was monitored by measuring the absorbance of the solution at 664 nm using a UV-vis spectrophotometer (Hitachi U-3900H).

C. Characterization. The phase composition of the synthesized black and yellow
TiO$_2$ powders were analyzed by powder X-ray diffraction (XRD, Bruker D8 Advance, Germany). The morphology of samples was characterized by transmission electron microscopy (TEM, Tecnai G2 F20). UV–visible diffuse reflectance spectra of the powders were acquired by a spectrophotometer (Hitachi U-3010). Surface electronic states of the powders were measured by X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250XI) with monochromatized Al Kα radiation using C 1s (284.8 eV) as the reference. Infrared spectra of the powders were obtained by an FTIR spectrometer (Bruker VERTEX70). Raman spectra were obtained on a Raman spectrometer (Bruker, SENTERRA). Photoluminescence (PL) spectra were measured on a fluorescence spectrophotometer (Hitachi F-4500) using an excitation wavelength of 300 nm, scanning rate of 240 nm/min, and photomultiplier tube voltage of 700 V. Electron paramagnetic resonance (EPR) spectra were acquired using a JES FA200 spectrometer at room temperature. Nitrogen adsorption and desorption measurements were acquired using JW-BK.

Fig.1S Comparison of Ti 2p XPS spectrum of B(N$_2$), B(Ar) and Y(air)
Fig. 2S EPR spectra of B(N₂), B(Ar) and Y(air)
Fig. 3S Comparison of N 1s XPS spectrum of (a) B(N₂), (b) B(Ar) and (c) Y(air)
Fig. 4S ToF-SIMS of B(N₂) (top) and B(Ar) (bottom)

Fig. 5S Adsorption-desorption equilibrium between the MB and the photocatalyst
Table 1S Physical and Structural Properties of samples

<table>
<thead>
<tr>
<th>Sample name</th>
<th>$S_{\text{BET}}$ (m$^2$.g$^{-1}$)</th>
<th>Pore volume (cm$^3$.g$^{-1}$)</th>
<th>Average pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B(N$_2$)</td>
<td>116.868</td>
<td>0.142</td>
<td>3.022</td>
</tr>
<tr>
<td>B(Ar)</td>
<td>71.262</td>
<td>0.108</td>
<td>2.137</td>
</tr>
<tr>
<td>Y(air)</td>
<td>66.558</td>
<td>0.114</td>
<td>4.018</td>
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