

Supporting Information

Graphene oxide/core-shell structured $\text{TiO}_2@\text{TiO}_{2-x}$ nanocomposites with highly efficient visible-light photocatalytic performance

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Experimental section

Preparation of titania precursor. Titania precursor come from the preparation method of black titania we reported before (reference 9). Tetrabutyl titanate (14 mL), urea (1 g) and ethanol absolute (20 mL) were mixed. Hydrochloric acid A.R. (1 mL), distilled 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.

Preparation of graphene oxide/core-shell structured $\text{TiO}_2@\text{TiO}_{2-x}$ nanocomposites. Grapheme oxide (100 mg) (Nanjing XFNANO Materials Tech Co.) was added into the mixture and stirred magnetically for about 3 h. 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 GT(air) and that calcined in N_2 is designated GT(N_2).

Visible-light photocatalytic degradation. The photocatalytic activities of the samples were evaluated by monitoring the degradation of methylene blue (MB) in an aqueous solution under visible-light irradiation. After stirred for 90 min in the dark to reach the adsorption-desorption equilibrium between the MB and the photocatalyst. The solution was illuminated by a 350-W Xe lamp with a cutoff filter ($k \geq 420$ nm) to remove UV light. Photocatalyst (50 mg) was then added to aqueous MB solution (40 mg/L, 50 mL). Circulating water was used to cool the solution to prevent solvent evaporation. About 4 mL of the stirred, irradiated suspension was taken out every 20 minutes. After centrifugation, the degradation of MB was determined with a UV-Vis spectrophotometer by measuring the peak intensity at 664 nm.

Characterization. The phase composition of GT(N_2) and GT(air) were obtained with powder X-ray diffraction (XRD, Bruker D8 Advance, Germany). TEM was

characterized by Tecnai G2 F20. The optical absorption spectra of samples were obtained at room temperature by a spectrophotometer (Hitachi U-3010). XPS experiments were measured by Thermo ESCALAB 250XI with monochromatized Al K α radiation using C 1s (284.8 eV) as the reference. Infrared spectra of the samples were obtained with an FTIR spectrometer (Bruker VERTEX70). Raman spectra were collected on a Raman spectrometer (Bruker, SENTERRA). Photoluminescence (PL) spectra were measured on a F-4500 FL Spectrophotometer using an excitation wavelength of 240 nm, scanning rate of 1200 nm/min, and photomultiplier tube voltage of 700 V. Electron paramagnetic resonance (EPR) spectra were collected using a JES FA200 spectrometer at room temperature. Nitrogen adsorption and desorption measurements were obtained with JW-BK.

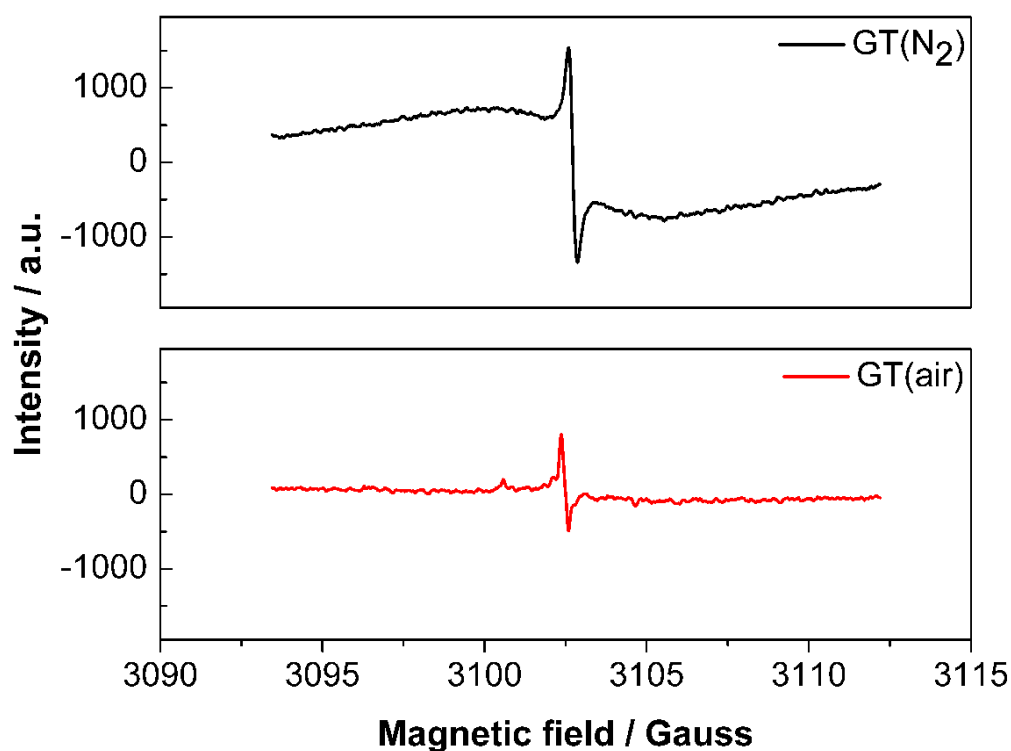


Fig.S1 EPR spectra of GT(N₂) and GT(air)

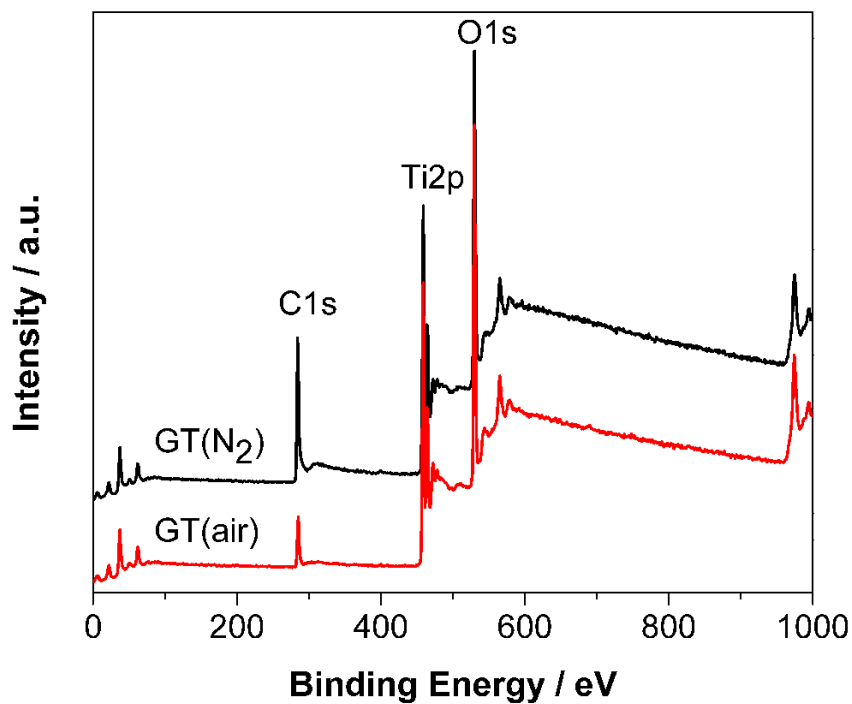


Fig.S2 XPS survey spectra of GT(N₂) and GT(air)

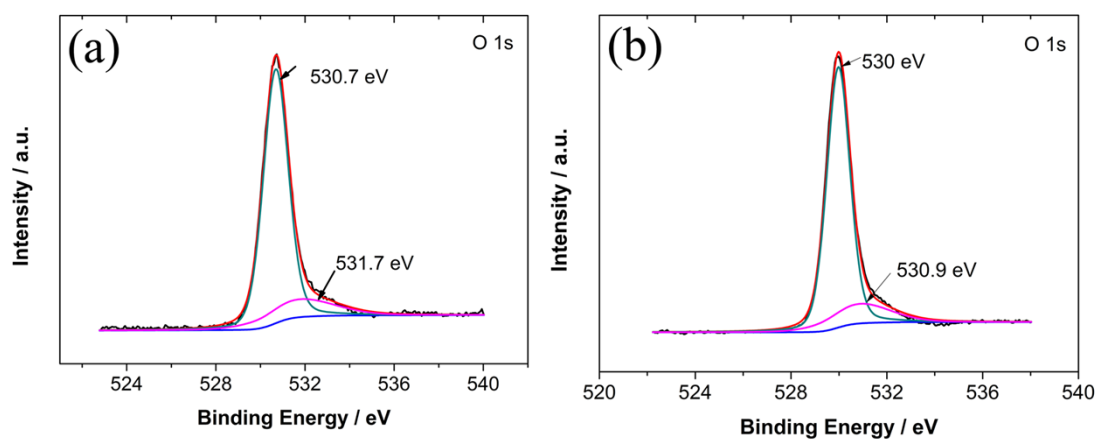


Fig.S3 XPS obtained for (a) O 1s of GT(N₂) and (b) O 1s of GT(air)

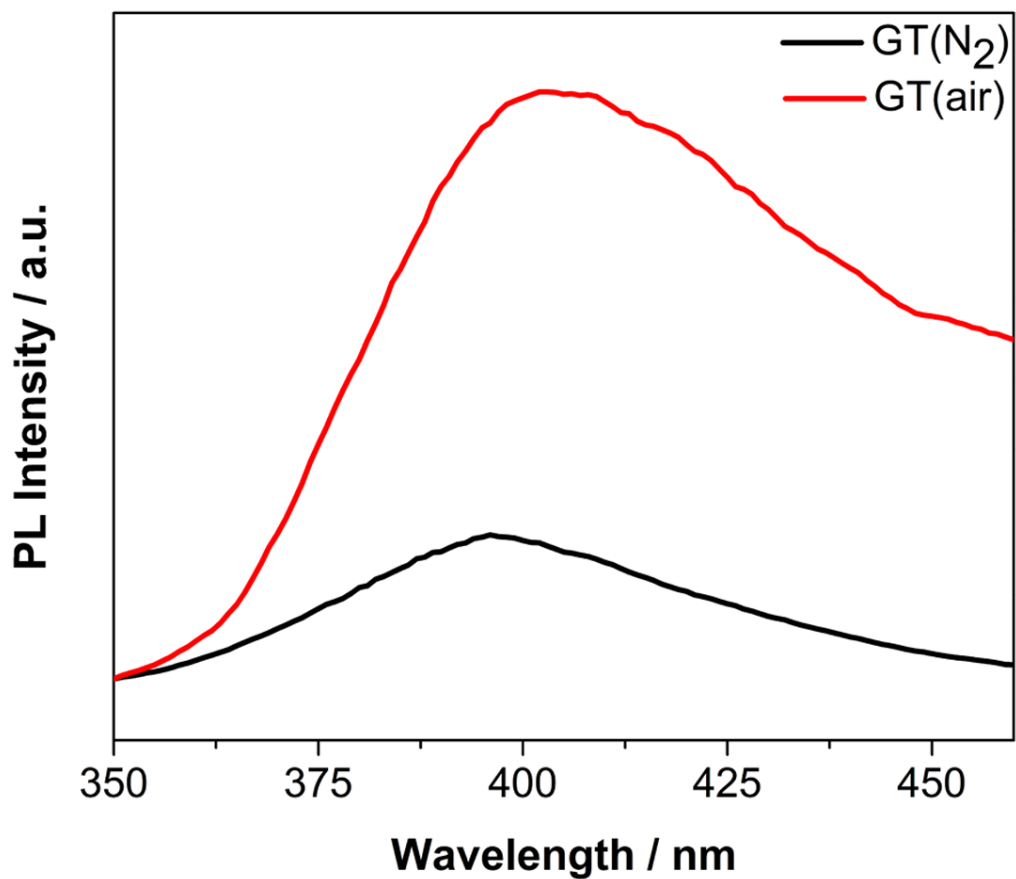


Fig.S4 PL emission spectra of samples

Table S1 Physical and Structural Properties of samples

Sample name	$S_{\text{BET}}(\text{m}^2 \cdot \text{g}^{-1})$	pore volume ($\text{cm}^3 \cdot \text{g}^{-1}$)	average pore size (nm)
GT(N ₂)	72.92	0.1048	7.282
GT(air)	68.33	0.1307	6.156