

## Supporting Information

### C/Si/core-shell structured $\text{TiO}_2@\text{TiO}_{2-x}$ nanocomposites with excellent visible-light photocatalytic performance

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#### Experimental section

##### 1. Preparation of titania precursor

Titania precursor come from the preparation method of black titania we reported before (reference 17). 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.

##### 2. Preparation of C/Si/core-shell structured $\text{TiO}_2@\text{TiO}_{2-x}$ nanocomposites.

Sucrose (2g) was grinded into powder. The accepted powder and silicon powder (0.6g) were 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 CST(air) and that calcined in  $\text{N}_2$  is designated CST( $\text{N}_2$ ).

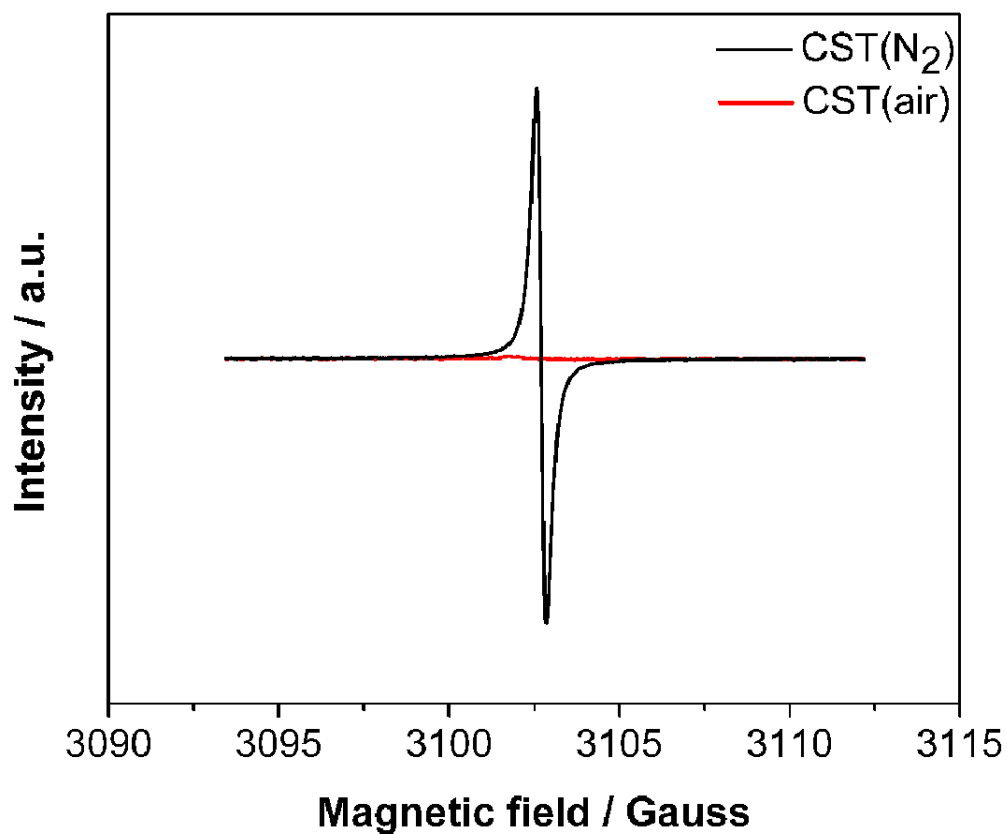
##### 3. Visible-light photocatalytic degradation

The photocatalytic activities of the samples were evaluated by photodegradation of 10 mg/L methylene blue (MB) dye solution under visible-light irradiation. 50 mg of photocatalyst was added to 50 ml of aqueous MB solution. Prior to irradiation, the powder suspension was stirred for 180 minutes in dark to attain 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. Circulating water was used to cool the solution to prevent solvent evaporation. Every 20 minutes, about 4 mL of the suspensions were collected and centrifuged, and then determined with a UV-Vis spectrophotometer by measuring the peak intensity at 664 nm.

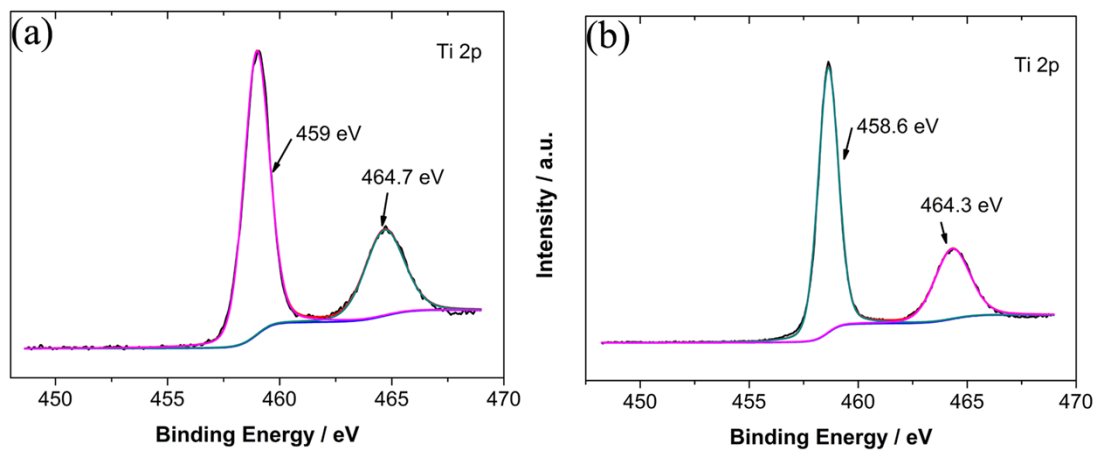
##### 4. Characterization

The structural characterization of the all samples was performed by X-ray diffraction (XRD, Bruker D8 Advance, Germany). TEM was obtained from Tecnai G2 F20. The optical absorption spectra of samples were obtained at room temperature by a spectrophotometer (Hitachi U-3010). The surface composition and chemical states of the samples were examined by XPS using a Thermo ESCALAB 250XI equipped with monochromatized Al  $K\alpha$  radiation using C 1s (284.8 eV) as the reference. Infrared spectra of the samples were determined by an FTIR spectrometer (Bruker

VERTEX70). Raman spectra were collected on a Raman spectrometer (Bruker, SENTERRA). Photoluminescence spectra (PL) were performed on a F-4500 FL Spectrophotometer with the excitation wavelength of 240 nm, scanning rate of 1200 nm/min. Nitrogen adsorption and desorption measurements were determined by JW-BK. Electron paramagnetic resonance (EPR) spectra were recorded on a JES FA200 spectrometer at room temperature.



**Fig. S1** EPR spectra for of CST(N<sub>2</sub>) and CST(air).



**Fig. S2** XPS spectra for (a) Ti 2p of CST(N<sub>2</sub>) and (b) Ti 2p of CST(air).

Table 1 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)
CST(N <sub>2</sub> )	81.1	0.0892	2.93
CST(air)	67.6	0.1128	2.09