

Supporting Information

Nanostructured $\text{Ti}_{1-x}\text{S}_x\text{O}_{2-y}\text{N}_y$ Heterojunctions for Efficient Visible-Light Induced Photocatalysis

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Additional Experimental Details

Pass energy of 50 eV and a step size of 0.2 eV were used for obtaining the N 1s and S 2p high-resolution XPS spectra of S, N co-doped heterojunctions. For recording the high resolution Ti 2p and O 1s spectra, pass energy of 20 eV and step size of 0.2 eV were used. Charge compensation of the samples during the XPS analysis was achieved using a low-energy electron flood gun. Quantitative surface chemical analysis was performed using the high-resolution core level spectra followed by the removal of a nonlinear Shirley background. The binding energies of various elements present in the heterojunctions were calculated by fixing the CC/CH component of the C 1s peak at 285 eV. For recording the UV-vis absorption spectra, the powder samples were thoroughly mixed with anhydrous KBr, and discs were prepared by using a 4 mm die. The Kubelka-Munk function $F(R_\infty)$ (which is equivalent to absorbance) was plotted against wavelength, and band gap values were calculated by extrapolating the lower wavelength cut-off region. Prior to the nitrogen adsorption-desorption studies, all samples were vacuum degassed at 300 °C for two hours. Specific surface area of the heterojunction samples were calculated from the linear portion ($P/P_0 = 0.05-0.2$) of the Brunauer-Emmett-Teller (BET) model. Barret-Joyner-Halenda (BJH) model of desorption branch was employed for the precise calculation of pore diameter and pore volumes. For analyzing the photoluminescence (PL) spectra, powder samples were dispersed in deionised water (0.01 g in 100 ml) with the help of an ultrasonicator

(for 30 min) and spectra were recorded using a Perkin-Elmer PL spectrometer (LS-55B) at an excitation wavelength of 260 nm. For TEM analysis, powder samples were suspended in water, sonicated for 30 minutes and dried on formvar-coated copper grids.

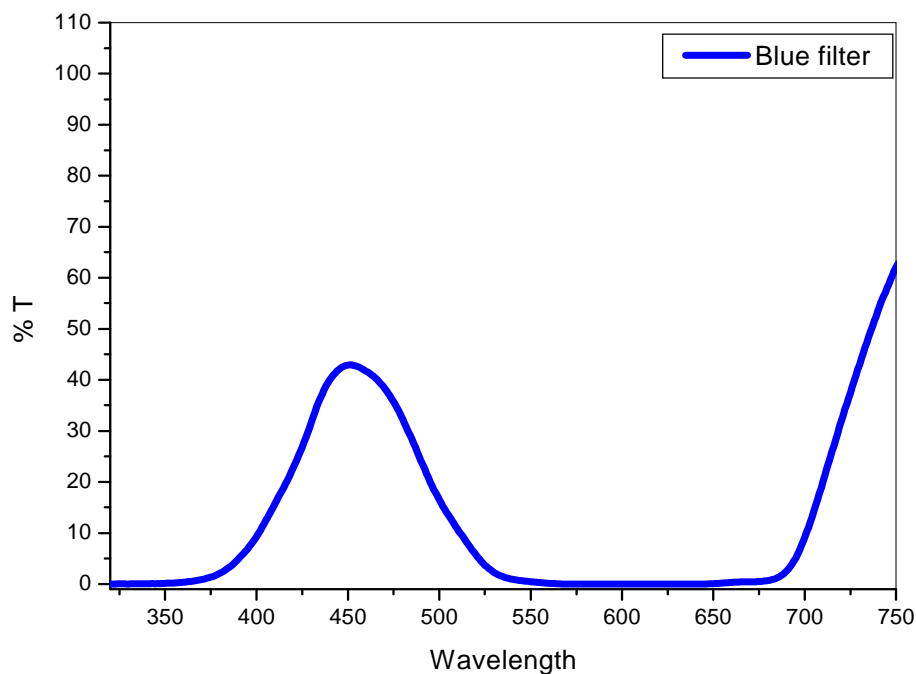


Figure S1. Transmission spectrum of primary blue filter used for visible-light induced photocatalytic studies

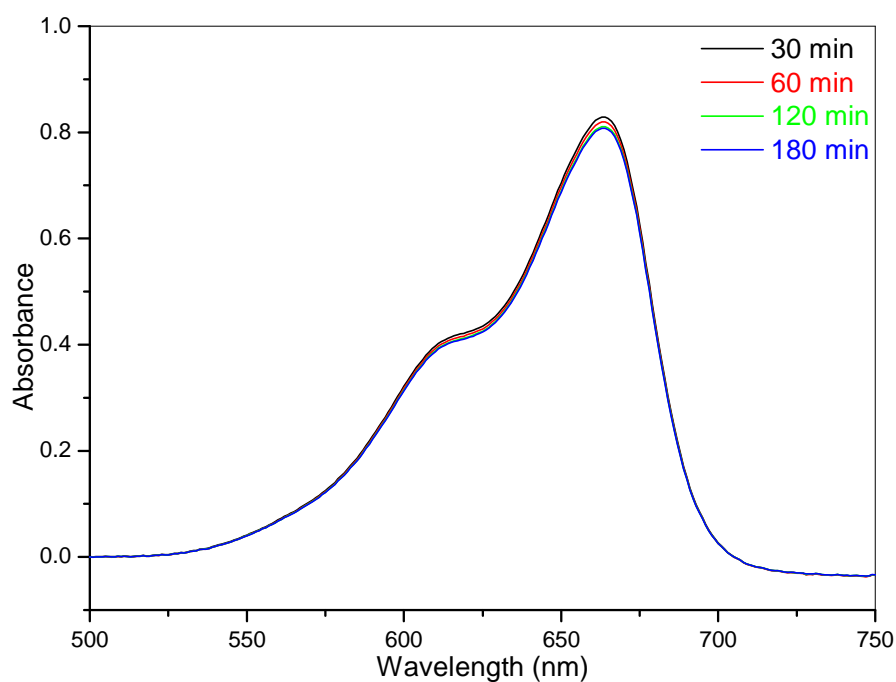


Figure S2. Absorption spectra of methylene blue at regular time intervals of visible-light irradiation in the absence of TiO_2

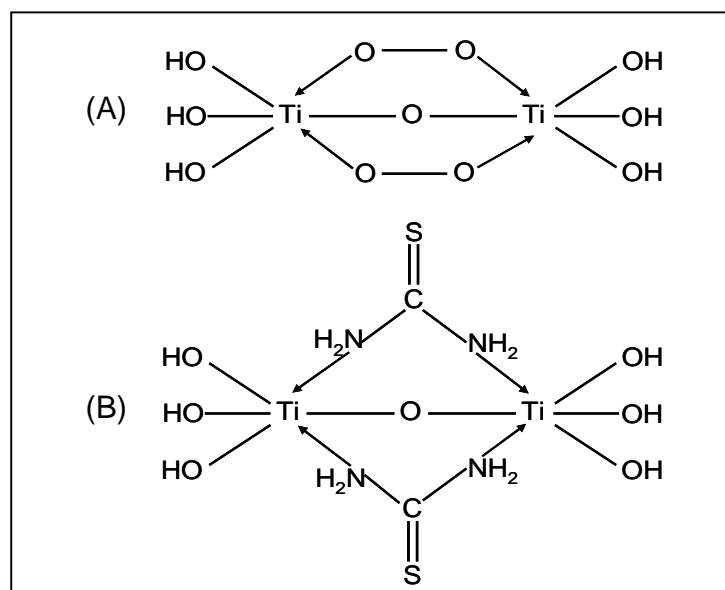


Figure S3. Structure of TiO_2 precursors (A) peroxo-titania complex and (B) proposed structure of thiourea modified peroxo-titania complex

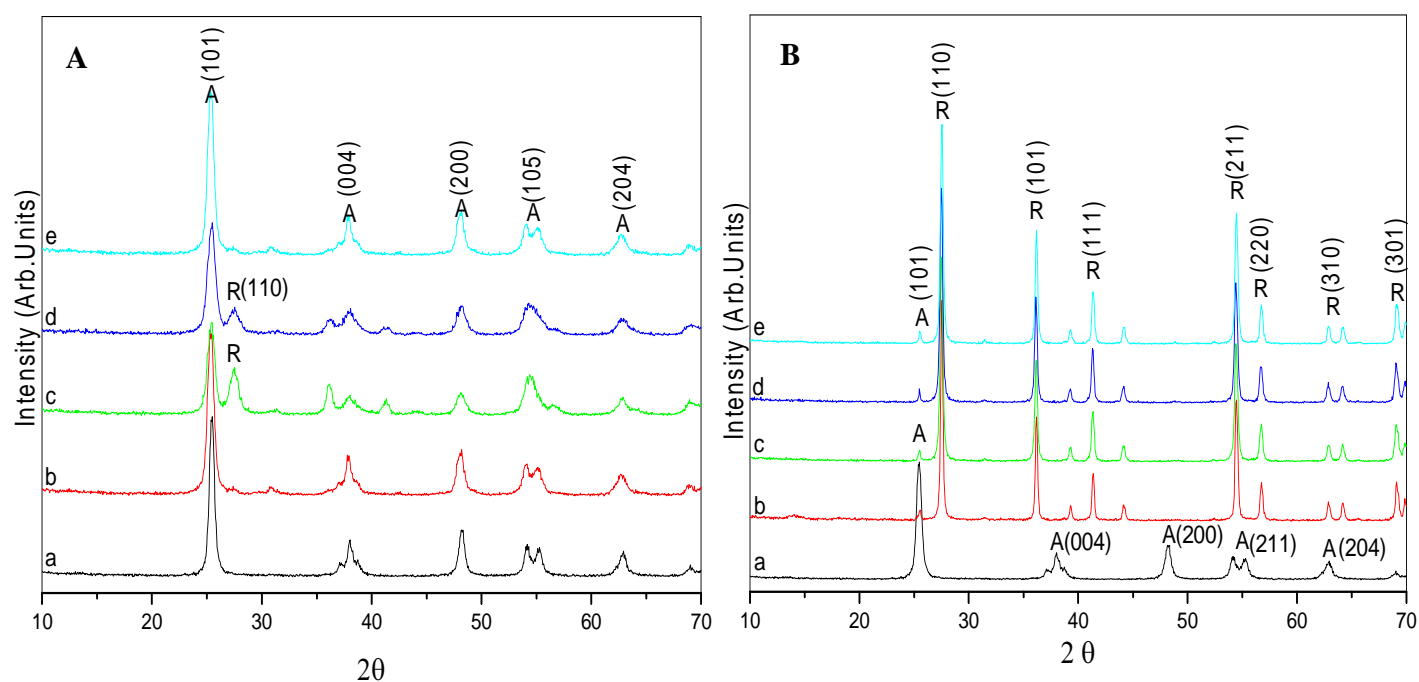


Figure S4. XRD patterns of titania calcined at (A) 600 °C and (B) 800 °C (a) control TiO_2 (b) 0.1 TU- TiO_2 (c) 0.2 TU- TiO_2 (d) 0.4 TU- TiO_2 and (e) 0.8 TU- TiO_2 (A = anatase; R= rutile)

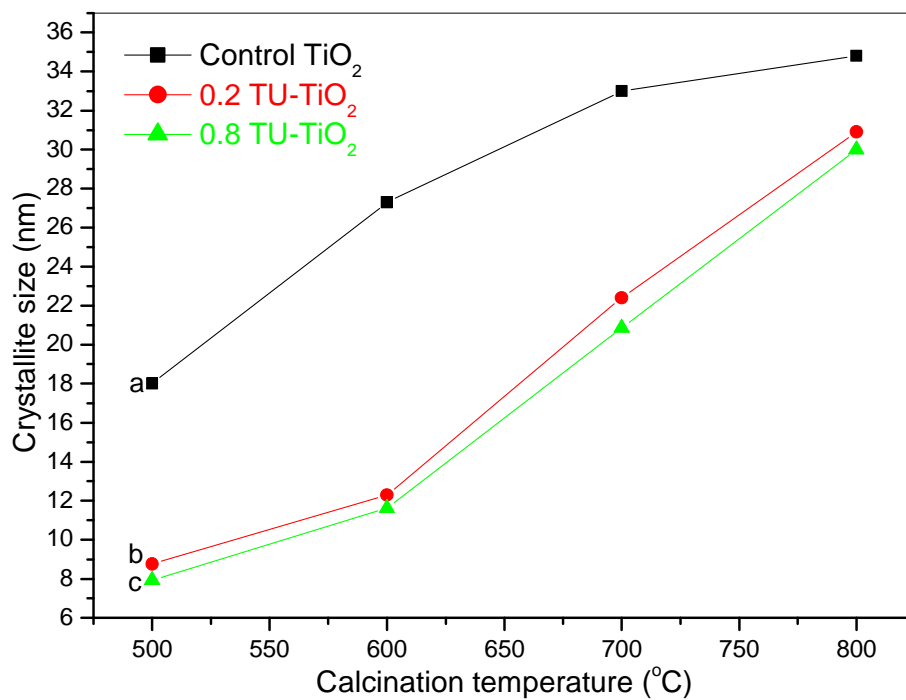


Figure S5. Effect of thiourea concentration on TiO₂ crystallite size (a) control TiO₂ (b) 0.2 TU-TiO₂ and (c) 0.8 TU-TiO₂

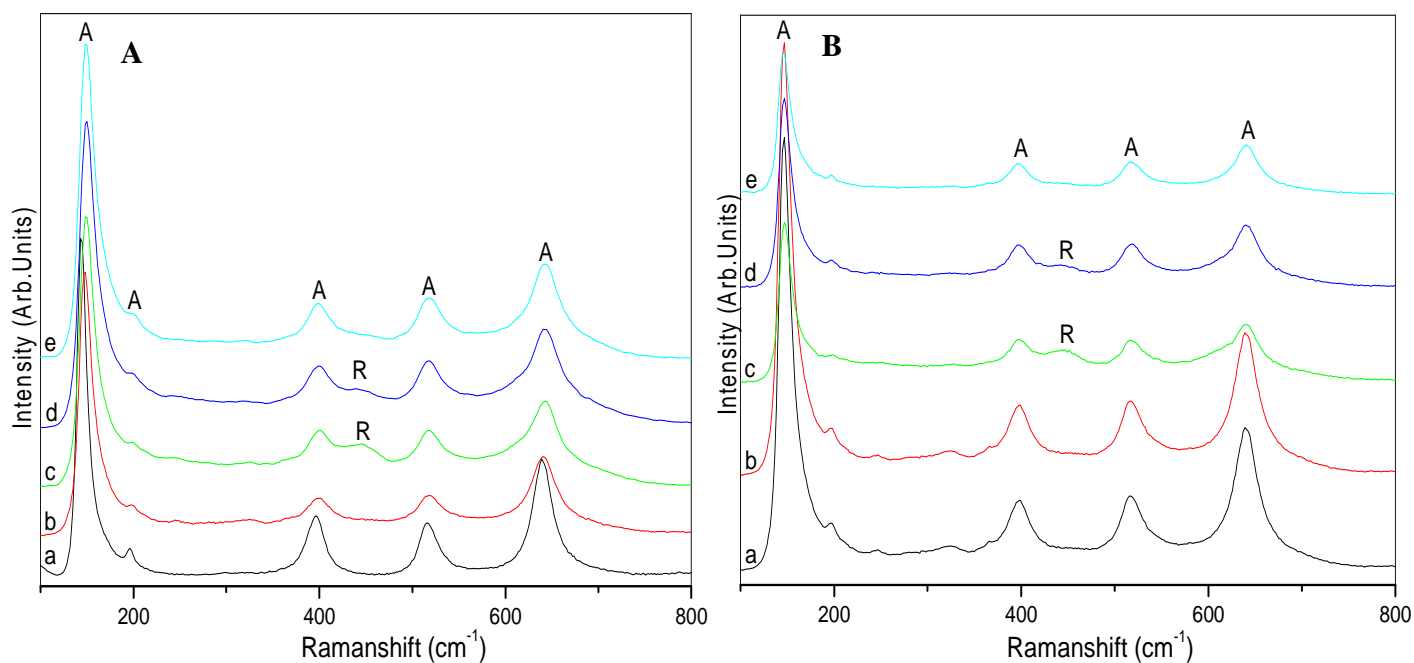


Figure S6. Raman spectra of titania calcined at (A) 500 °C and (B) 600 °C (a) control TiO₂ (b) 0.1 TU-TiO₂ (c) 0.2 TU-TiO₂ (d) 0.4 TU-TiO₂ and (e) 0.8 TU-TiO₂ (A = anatase; R= rutile)

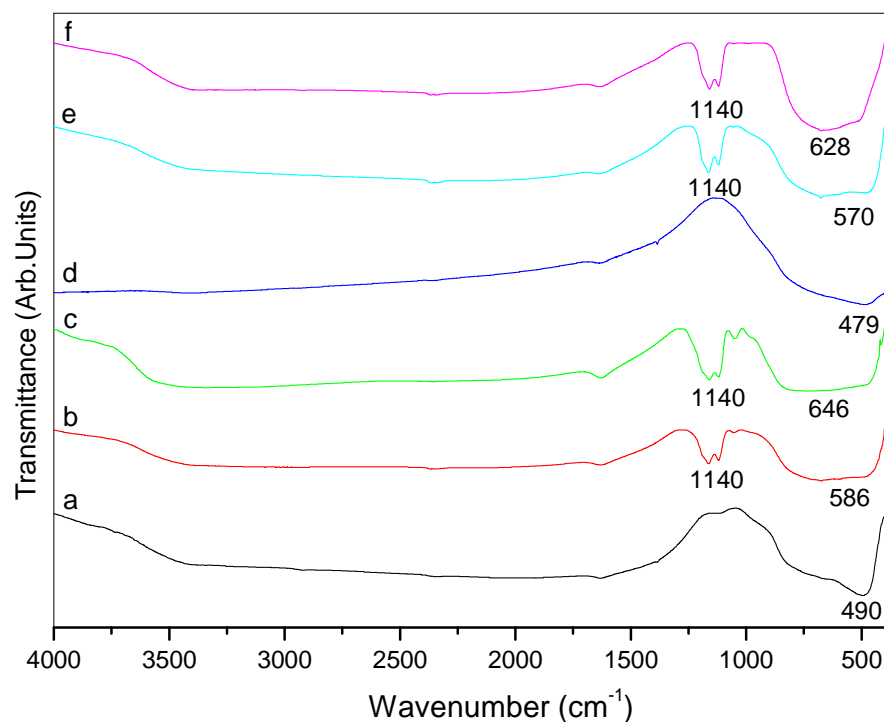


Figure S7. FT-IR spectra of calcined titania (a) control TiO_2 calcined at 600 °C (b) 0.1 TU- TiO_2 calcined at 600 °C (c) 0.8 TU- TiO_2 calcined at 600 °C (d) control TiO_2 calcined at 700 °C (e) 0.1 TU- TiO_2 calcined at 700 °C and (f) 0.8 TU- TiO_2 calcined at 700 °C

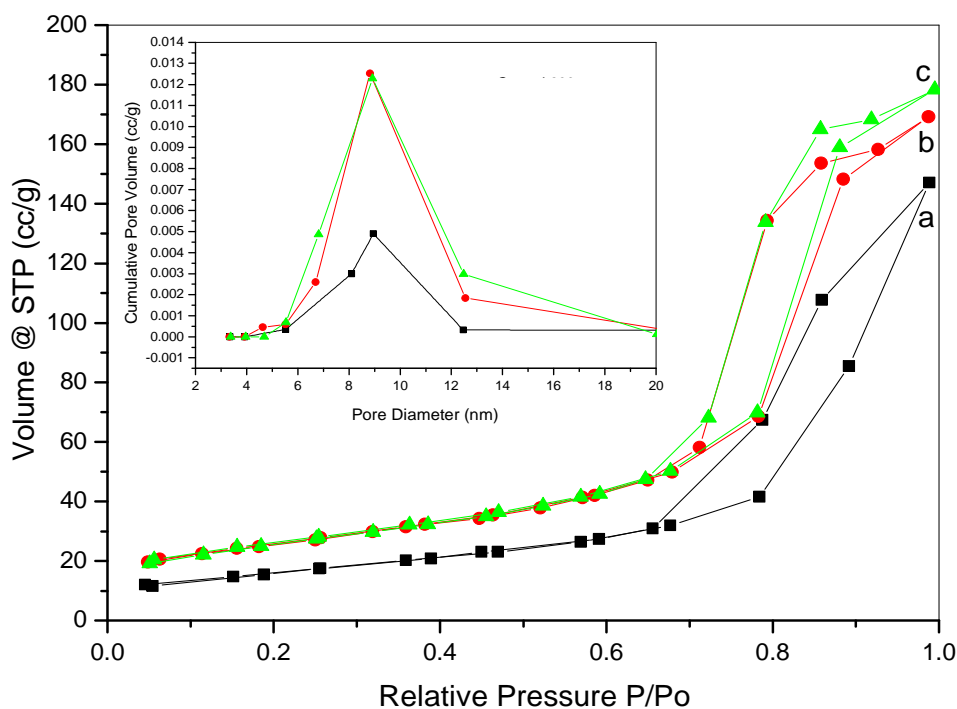


Figure S8. N_2 adsorption-desorption isotherm and the pore size distribution (inset) of samples calcined at 600 °C (a) control TiO_2 (b) 0.2 TU- TiO_2 and (c) 0.8 TU- TiO_2

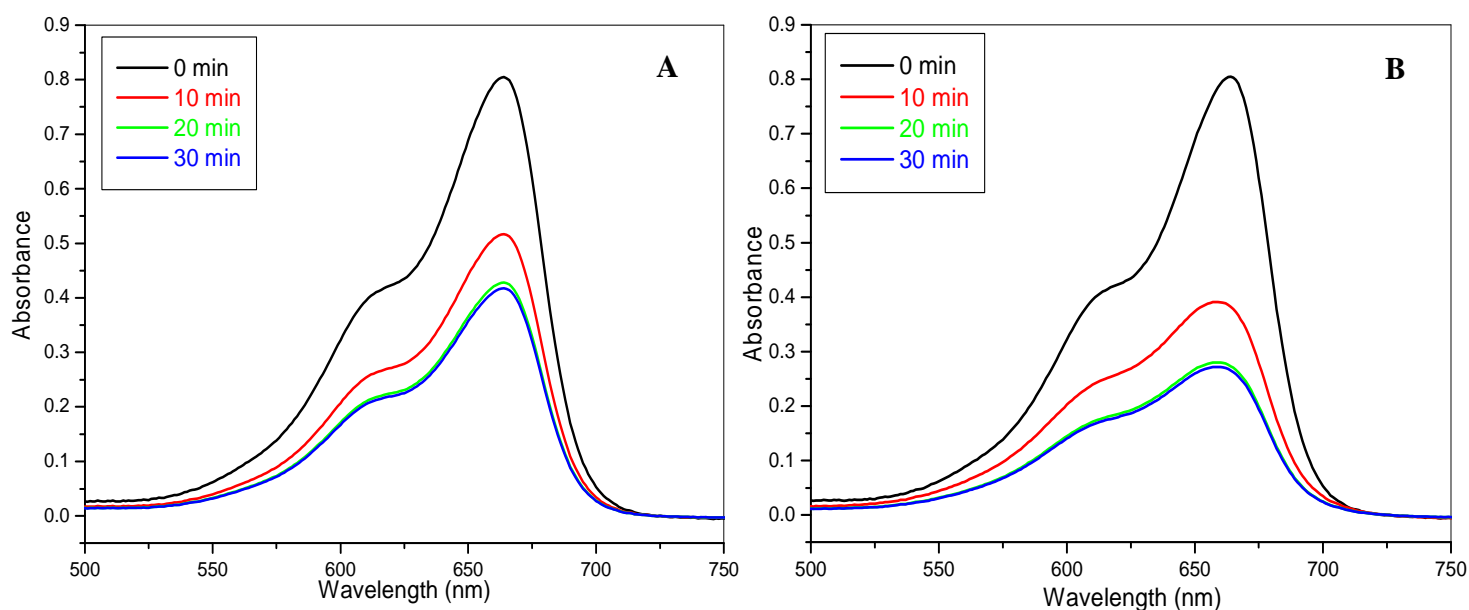


Figure S9. Absorption spectra of methylene blue at regular time intervals in the absence of visible-light using (A) Degussa P-25 and (B) 0.2 TU-TiO₂ calcined at 600 °C

Table S1. Amount of anatase and rutile phase present in S, N co-doped titania samples obtained at various calcination temperatures (A = anatase, R= rutile)

Calcination temperature (°C)	Control TiO ₂		0.1 TU-TiO ₂		0.2 TU-TiO ₂		0.4 TU-TiO ₂		0.8 TU-TiO ₂	
	A (%)	R (%)	A (%)	R (%)	A (%)	R (%)	A (%)	R (%)	A (%)	R (%)
500	100	0	100	0	71	29	81	19	100	0
600	100	0	100	0	62	38	78	22	90	10
700	100	0	90	10	12	88	21	80	54	46
800	100	0	5	95	4	96	5	95	4	96

Table S2. Photocatalytic rate constants (k) for visible-light induced methylene blue degradation using S, N co-doped titania obtained at various calcination temperatures.

Calcination temperature (°C)	Control TiO ₂	0.1 TU-TiO ₂	0.2 TU-TiO ₂	0.4 TU-TiO ₂	0.8 TU-TiO ₂
500	0.0151	0.0160	0.0231	0.0194	0.0179
600	0.0163	0.0184	0.0323	0.0212	0.0201
700	0.0159	0.01642	0.01701	0.0179	0.0193
800	0.0121	0.0131	0.0139	0.0145	0.0152