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SUPPORTING INFORMATION

Stable Blue TiO_{2-x} Nanoparticles for Efficient Visible Light Photocatalyst

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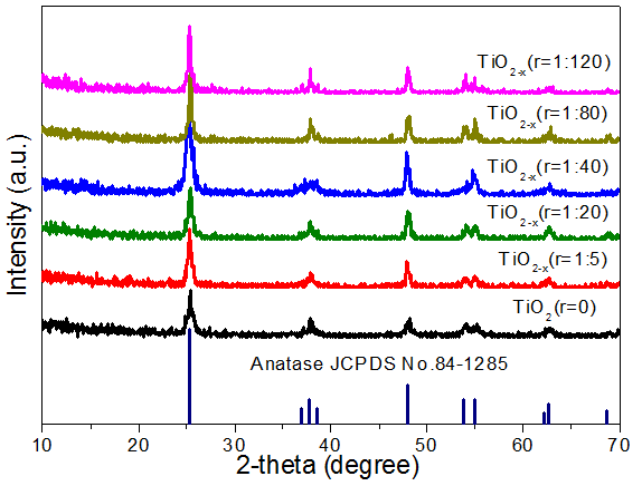

Figure S1. Evolution of XRD patterns prepared at different molar ratio of Ti^{4+}/Ti^{3+} under under the same conditions. The change of the value ranging from 0 to 1:120 has little effect on the crystal phase of Ti^{3+} self-doped TiO_{2-x}. All samples were crystallized into anatase phase by solvothermal treatment. Standard PDF card of anatase TiO_2 was given as reference.

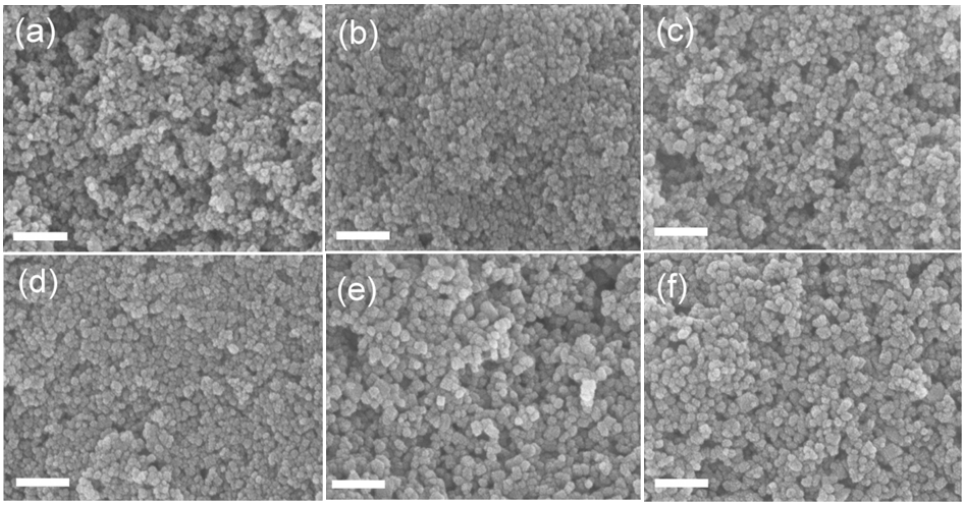

Figure S2. SEM images of self-doped TiO_{2-x} samples obtained with different ratios of $TiCl_3$ and TiF_4 reactants: (a) r = 0, (b) r = 1:5, (c) r = 1:20, (d) r = 1:40, (e) r = 1:80, (f) r = 1:120. The scale bars are 200 nm.

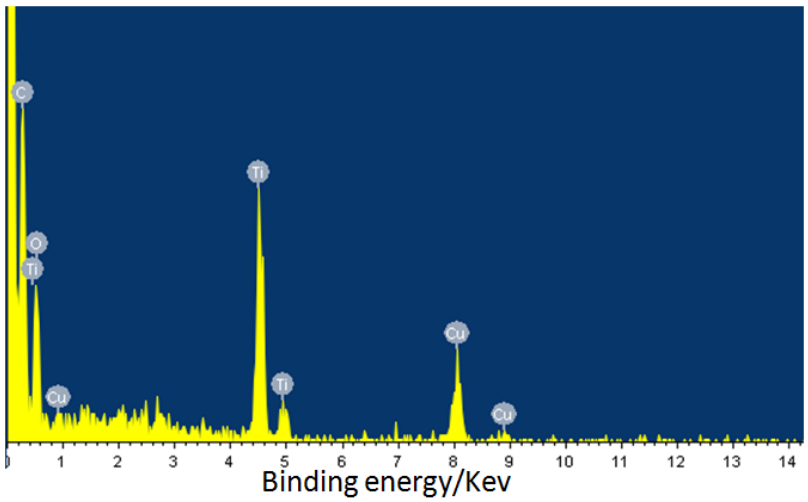

Figure S3. EDS spectrum of the obtained Ti^{3+} self-doped TiO_{2-x} (r = 1:40) sample.

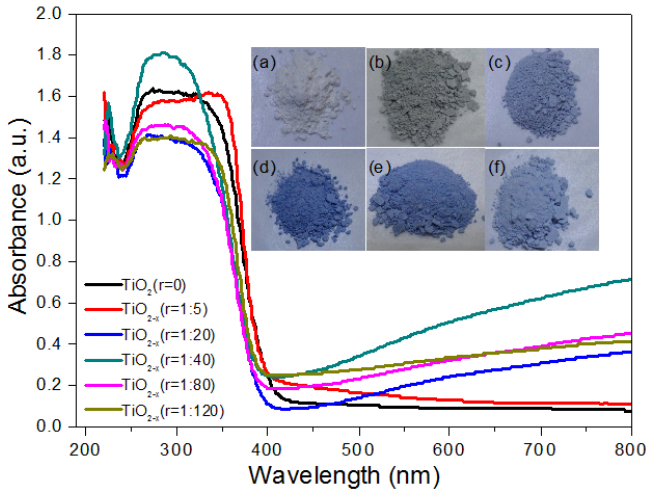

Figure S4. The UV−visible absorption spectra of samples prepared using different ratios of $TiCl_3$ and TiF_4. The inset is the photographs of corresponding samples by using (a) r = 0, (b) r = 1:5, (c) r = 1:20, (d) r = 1:40, (e) r = 1:80, (f) r = 1:120.

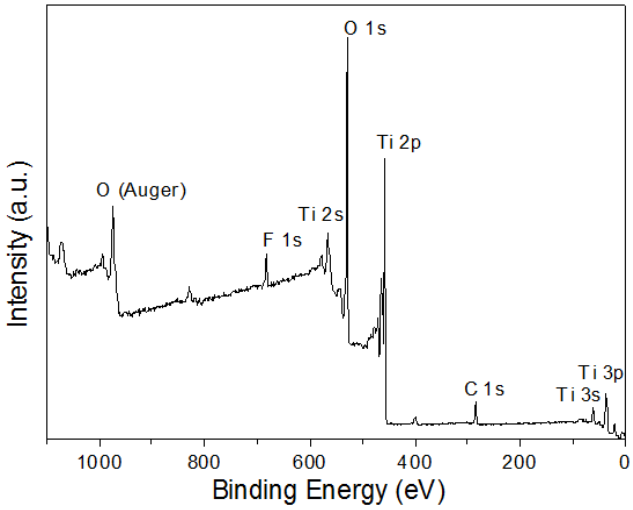

Figure S5. The survey XPS spectrum of Ti^{3+} self-doped TiO_{2-x} sample (r = 1:40).

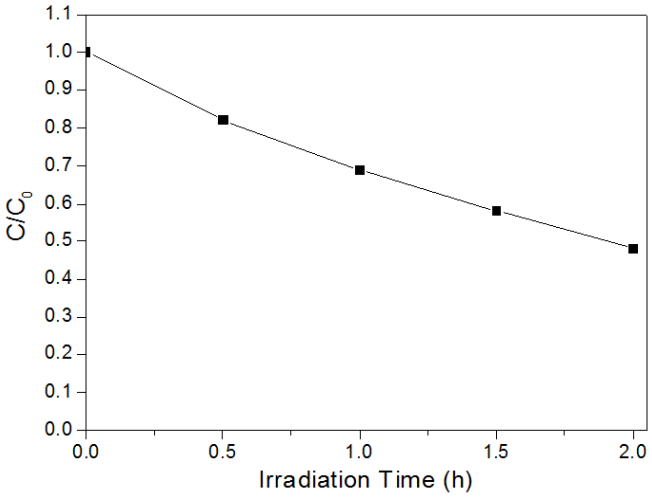

Figure S6. Photodecomposition of MB with TiO_2 synthesized using TiF_4 as a second reference under visible light irradiation ($\lambda \geq 400$ nm).

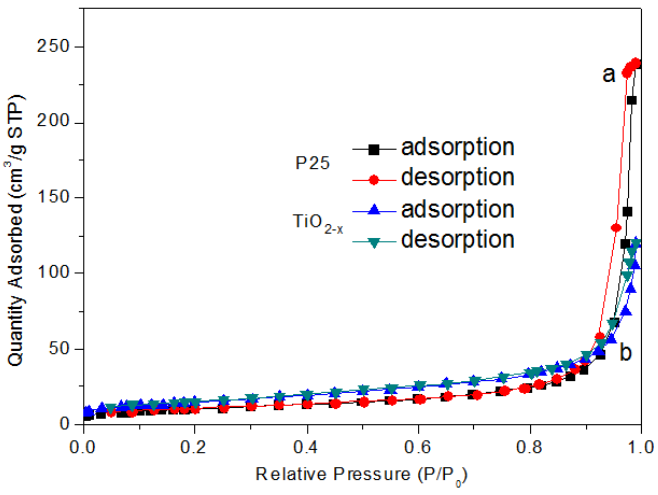

Figure S7. Nitrogen adsorption-desorption isotherms of (a) commercial Degussa P25 and (b) Ti^{3+} self-doped TiO_2 nanocrystals.

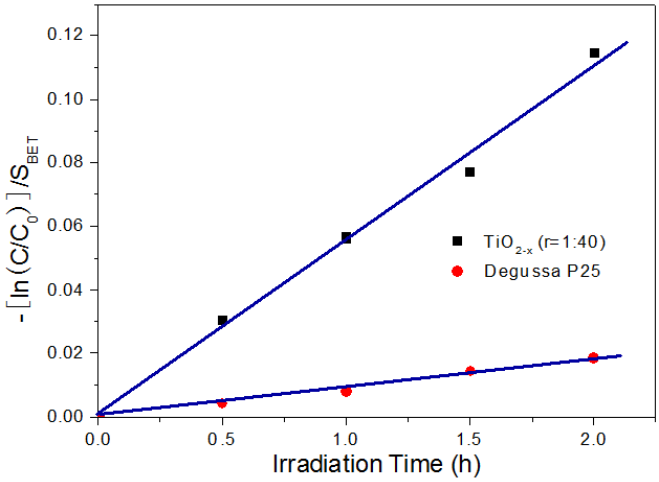

Figure S8. The Plot of $-[\ln(C/C_0)]/S_{BET}$ vs. time curves of photodegradation of MB with respect to irradiation time. The apparent rate constant k'_{MB} of MB photodegradation for Ti^{3+} self-doped TiO_{2-x} (0.114 h^{-1} m^{-2} g) is more than 6.2 times higher than that for Degussa P25 TiO_2 (0.0184 h^{-1} m^{-2} g).

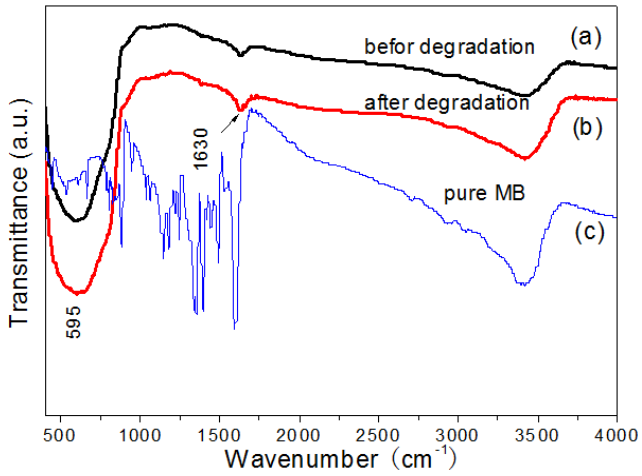

Figure S9. FTIR spectra of (a) the as-synthesized Ti^{3+} self-doped TiO_{2-x}, (b) recovered sample after photocatalytic reaction, and (c) pure methylene blue.

S10. The relevant reactions occurring on the blue titania surface and transfer of photogenerated carriers involved in the MB degradation process under visible-light irradiation.

$$TiO_{2-x} + h\nu \rightarrow e^- + h^+ \quad (1)$$

$$O_2 + e^- \rightarrow \bullet O_2^- \quad (2)$$

$$\bullet O_2^- + H^+ \rightarrow HO_2\bullet \quad (3)$$

$$2e^- + HO_2\bullet + H^+ \rightarrow \bullet OH + OH^- \quad (4)$$

$$\bullet HO_2 + H^+ + e^- \rightarrow H_2O_2 \quad (5)$$

$$H_2O_2 + e^- \rightarrow OH^- + \bullet OH \quad (6)$$

$$h^+ + H_2O \rightarrow H^+ + \bullet OH \quad (7)$$

$$h^+ + OH^- \rightarrow \bullet OH \quad (8)$$

$$\bullet OH, \bullet O_2^-, HO_2\bullet, h^+ + MB \rightarrow CO_2 + H_2O \text{ (MB = methyl blue)} \quad (9)$$