## **Supporting Information**

## Modulation of pore sizes of titanium dioxide photocatalysts by a facile template free hydrothermal synthesis method: Implications for photocatalytic

## degradation of rhodamine B

Shivatharsiny Rasalingam, Chia-Ming Wu, and Ranjit T. Koodali\*

Department of Chemistry, University of South Dakota, Vermillion, SD 57069

Tel #: 605-677-6189

Fax #: 605-677-6397

E-mail: <u>Ranjit.Koodali@usd.edu</u>

\* Corresponding Author

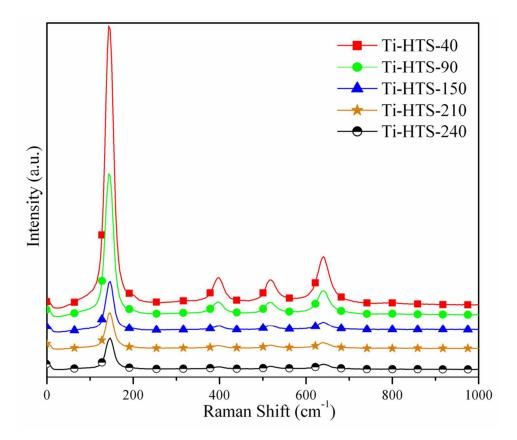
Table S1. Optimal instrumental conditions for ESI-MS studies.

Parameters	Optimal values/conditions	
Infusion rate	$10 \mu \text{Lmin}^{-1}$	
Spray Shield voltage	600 V	
Mode	Positive	
Mass range $(m/z)$	50-500	
Capillary voltage	80 V	
Drying gas temperature	400 °C	
Nebulizer pressure	10 psi	
Needle voltage	5000 V	
Detector	Dynode ion detector	
Electron multiplier voltage	1360 V	

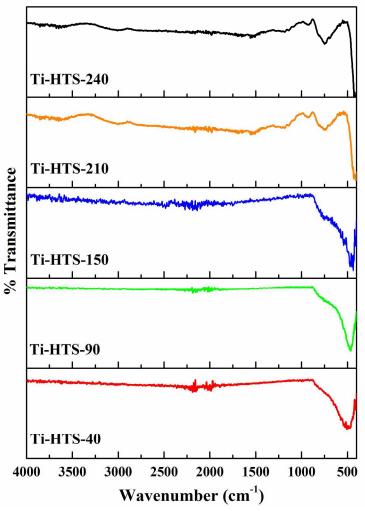
Sample	$k_{app} \times 10^{-5} [s^{-1}]$	$\mathbf{R}^2$
Ti-HTS-40	25.9	0.991
Ti-HTS-90	59.8	0.985
Ti-HTS-150	96.9	0.933
Ti-HTS-210	97.9	0.962
Ti-HTS-240	109.8	1.000

Table S2. Dye degradation rate constants of  $TiO_2$  materials.

Ti-HTS refers to TiO<sub>2</sub> hydrothermal synthesized materials and the following number denotes the hydrothermal treatment temperature in °C.  $k_{app}$  is the photocatalytic pseudo first-order degradation rate constant.



**Fig. S1.** Raman spectra of TiO<sub>2</sub> materials prepared at different hydrothermal temperatures of 40, 90, 150, 210, and 240  $^{\circ}$ C.



**Fig. S2.** FT-IR spectra of TiO<sub>2</sub> materials prepared at different hydrothermal temperatures 40, 90, 150, 210, and 240  $^{\circ}$ C.

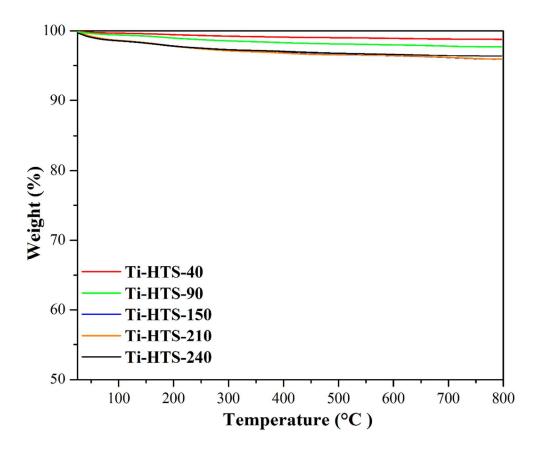


Fig. S3. TGA analysis of TiO<sub>2</sub> materials.

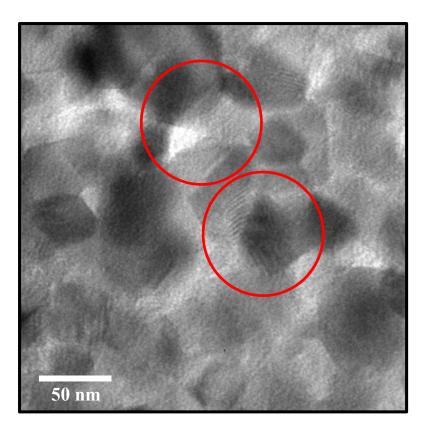


Fig. S4. TEM image of a representative  $TiO_2$  material (Ti-HTS-40) prepared at the hydrothermal temperature of 40 °C.

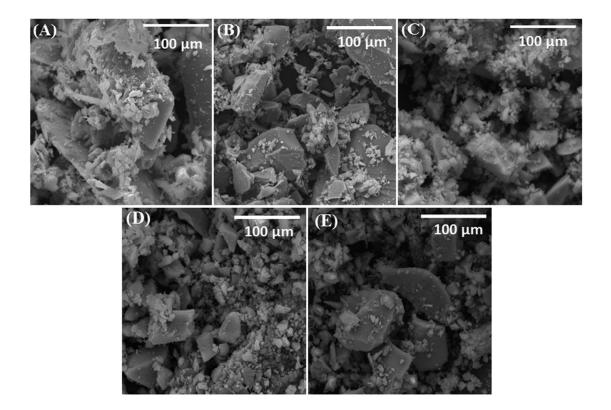
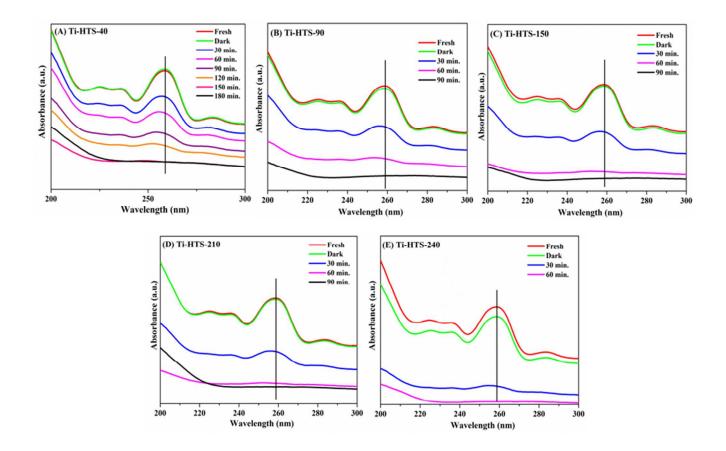
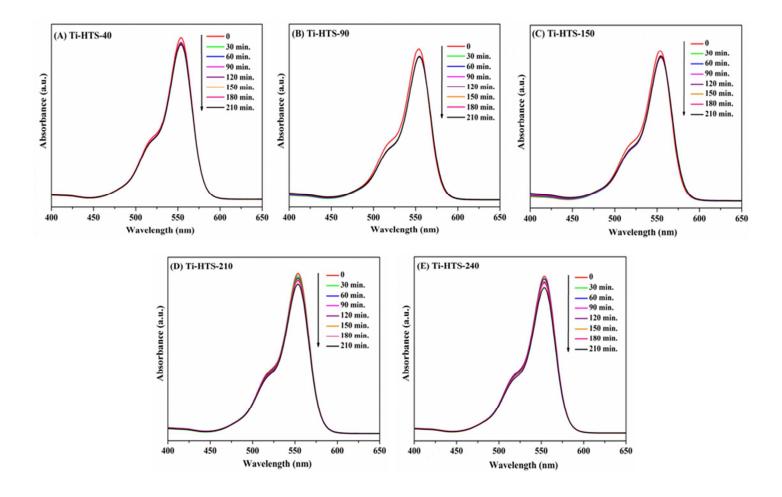


Fig. S5. SEM images of TiO<sub>2</sub> materials.



**Fig. S6.** Absorption spectra (aromatic region) of RhB dye degraded under visible light irradiation for 6 h using (A) Ti-HTS-40, (B) Ti-HTS-90, (C) Ti-HTS-150, (D) Ti-HTS-210, and (E) Ti-HTS-240 prepared at different hydrothermal temperatures of 40, 90, 150, 210, and 240 °C respectively



**Fig. S7.** Absorption spectra of RhB after dark adsorption with time for (A) Ti-HTS-40, (B) Ti-HTS-90, (C) Ti-HTS-150, (D) Ti-HTS-210, and (E) Ti-HTS-240

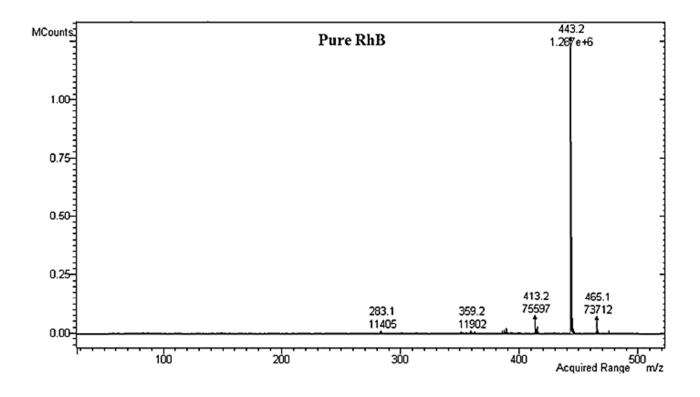


Fig. S8. ESI-MS of Pure RhB.

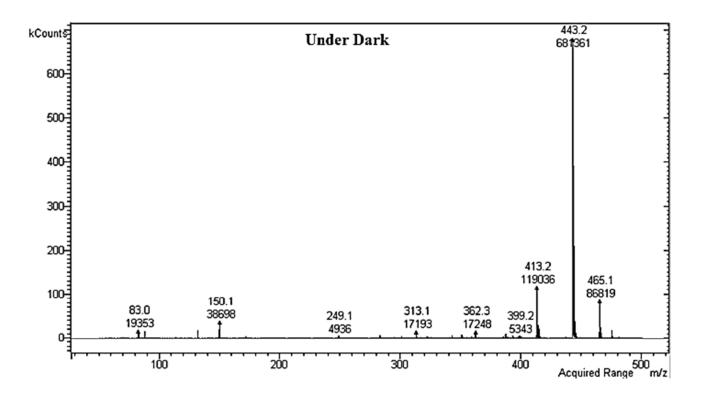


Fig. S9. ESI-MS of RhB solution after dark adsorption over Ti-HTS-40.

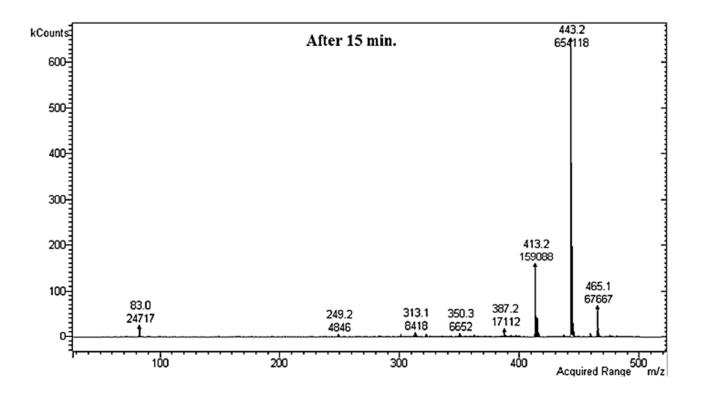


Fig. S10. ESI-MS of RhB solution after 15 min. of photocatalytic reaction with Ti-HTS-40.

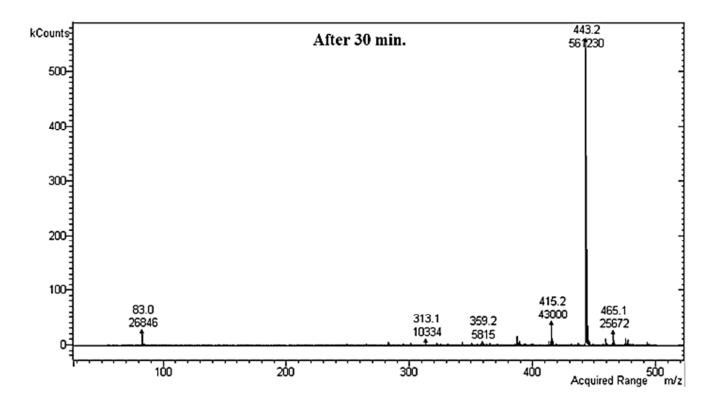


Fig. S11. ESI-MS of RhB solution after 30 min. of photocatalytic reaction with Ti-HTS-40.

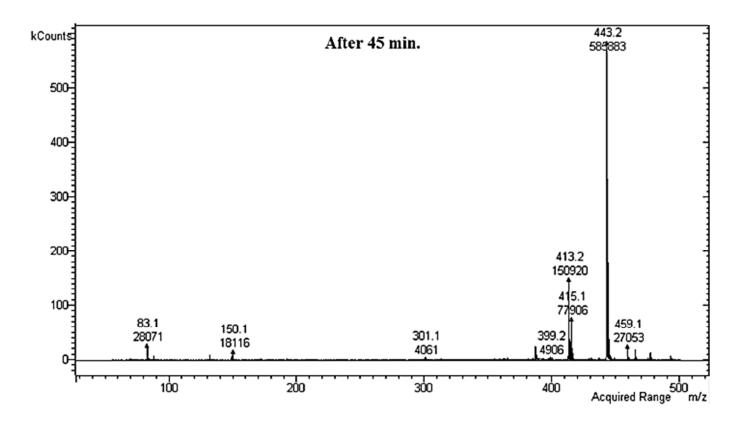


Fig. S12. ESI-MS of RhB solution after 45 min. of photocatalytic reaction with Ti-HTS-40.

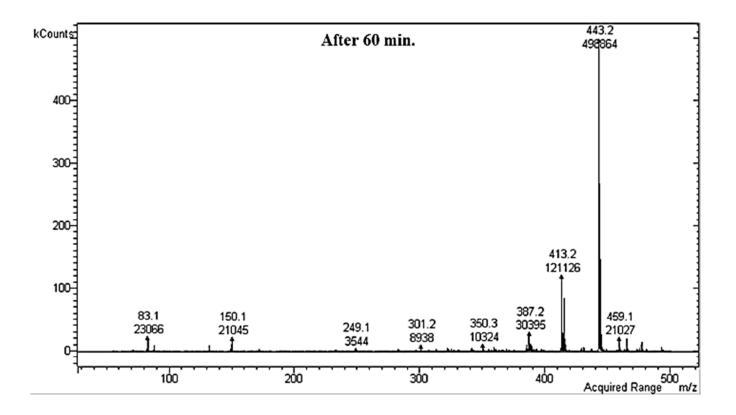


Fig. S13. ESI-MS of RhB solution after 60 min. of photocatalytic reaction with Ti-HTS-40.

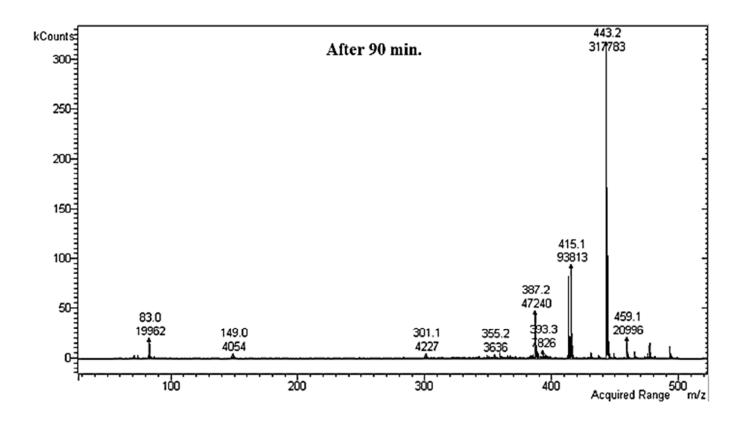


Fig. S14. ESI-MS of RhB solution after 90 min. of photocatalytic reaction with Ti-HTS-40.

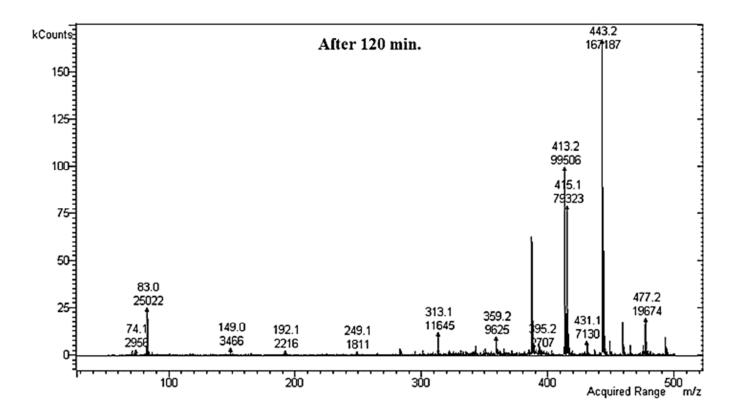


Fig. S15. ESI-MS of RhB solution after 120 min. of photocatalytic reaction with Ti-HTS-40.

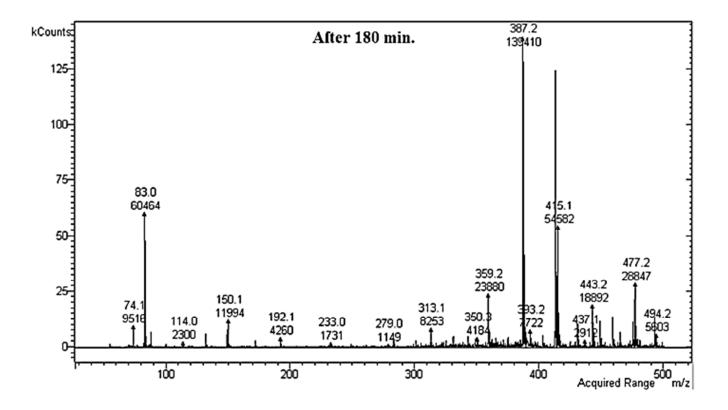


Fig. S16. ESI-MS of RhB solution after 180 min. of photocatalytic reaction with Ti-HTS-40.

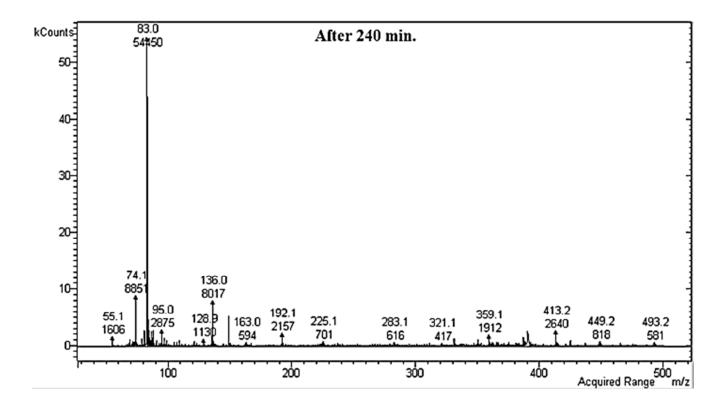


Fig. S17. ESI-MS of RhB solution after 240 min. of photocatalytic reaction with Ti-HTS-40.

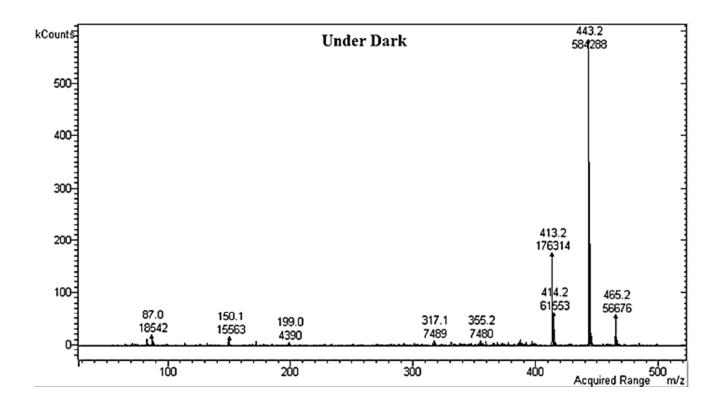


Fig. S18. ESI-MS of RhB solution after dark adsorption over Ti-HTS-240.

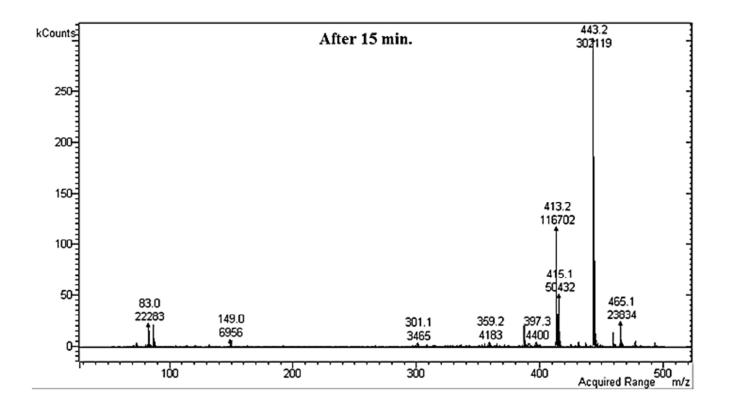


Fig. S19. ESI-MS of RhB solution after 15 min. of photocatalytic reaction with Ti-HTS-240.

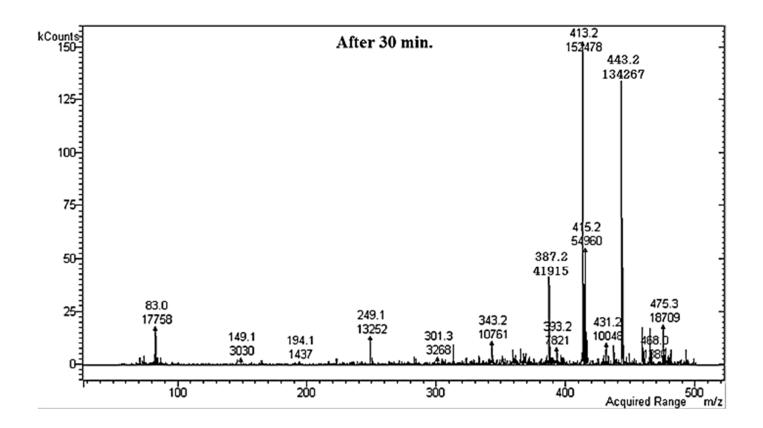


Fig. S20. ESI-MS of RhB solution after 30 min. of photocatalytic reaction with Ti-HTS-240.

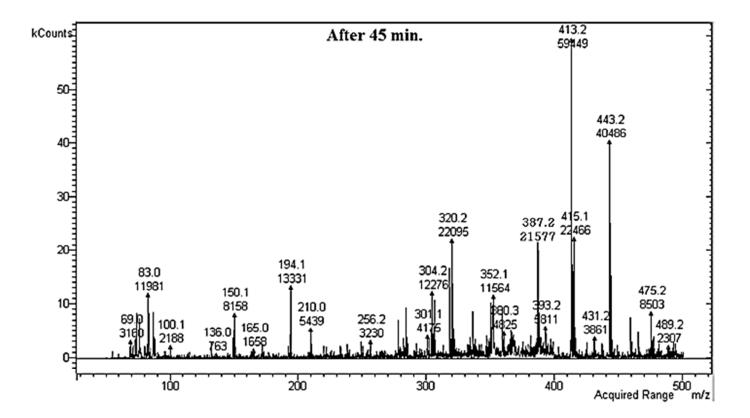


Fig. S21. ESI-MS of RhB solution after 45 min. of photocatalytic reaction with Ti-HTS-240.

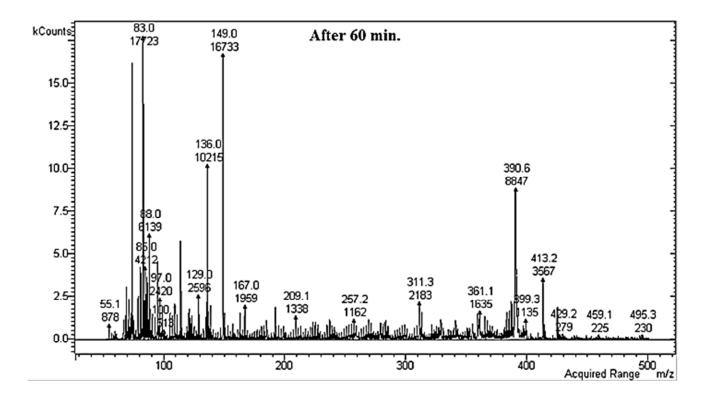
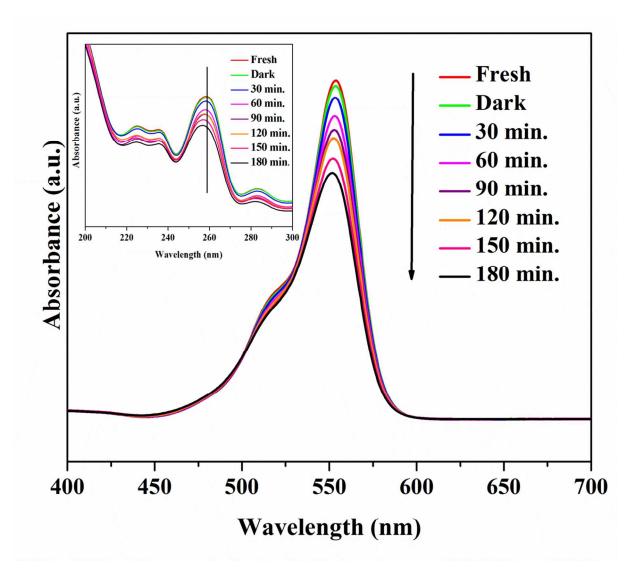
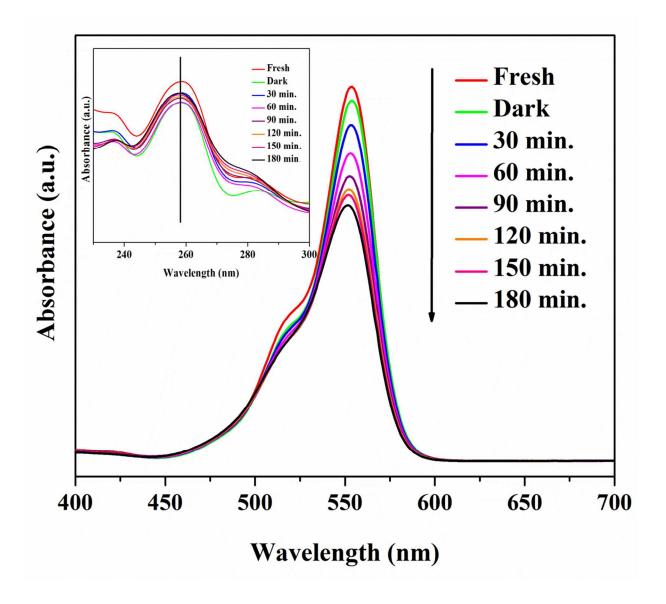


Fig. S22. ESI-MS of RhB solution after 60 min. of photocatalytic reaction with Ti-HTS-240.



**Fig. S23.** UV-Vis spectra of RhB filtrate after visible light irradiation under  $N_2$  flow for Ti-HTS-240. Inset shows the absorbance spectra for the aromatic region of RhB.



**Fig. S24.** UV-Vis spectra of RhB filtrate after visible light irradiation for Ti-HTS-240 in the presence of isopropyl alcohol (IPA). Inset shows the absorbance spectra for the aromatic region of RhB.