

Electronic Supplementary Information

Contribution of Lamellar Morphology on Photocatalytic Activity of Alkaline-Hydrothermally Treated Titania in Rhodamine B Photodegradation.

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S1. Particle Size Distribution

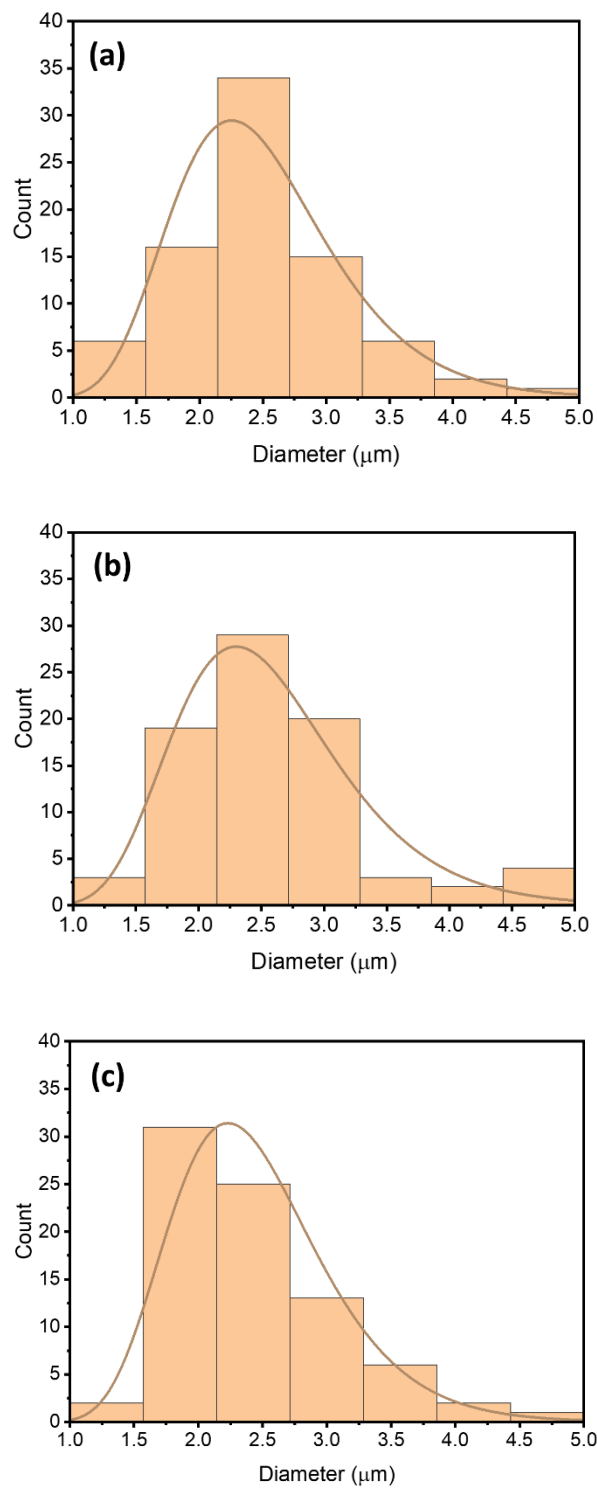


Figure S1. Particles Size Distribution of (a) S-AS, (b) S-HT, and (c) S-HT-500.

S2. Particle Size Distribution

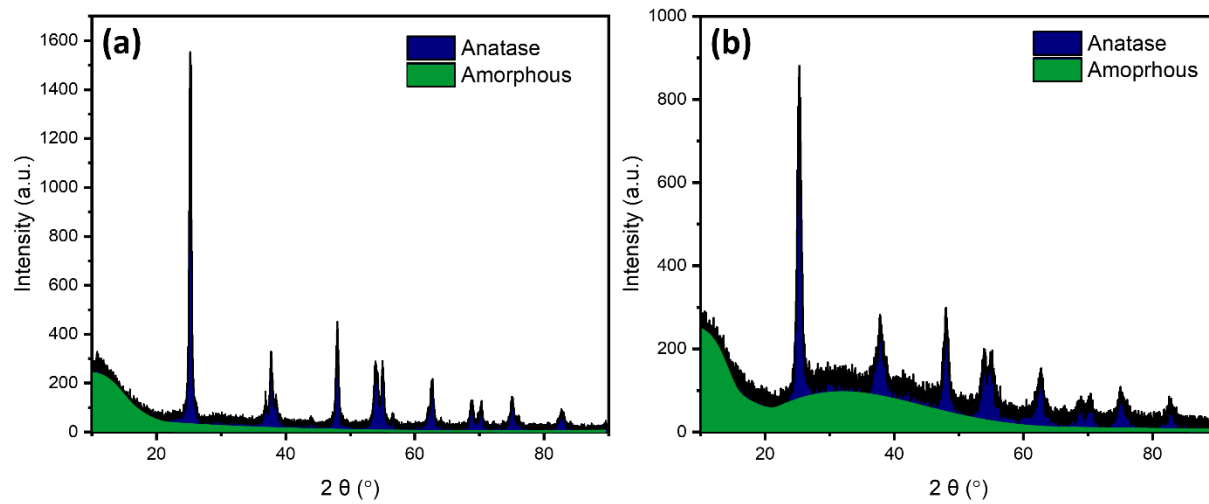


Figure S2. XRD pattern of (a) S-500 and (b) S-500-HT. The Blue area represents the anatase phase, while the green area represents the amorphous phase.

S.3 Determining of {001} facet percentage

The interplanar spacing or d -spacing of the anatase crystal can be determined using Bragg's equation:

$$2d_{hkl} \sin \theta = n\lambda \quad (\text{S1})$$

$$\sin \theta = \frac{n\lambda}{2d_{hkl}} \quad (\text{S2})$$

The first-order reflection from (100) planes occurs at an angle given by:

$$\sin \theta (1^{st} \text{ order } 001) = \frac{1\lambda}{2d_{001}} \quad (\text{S3})$$

The second-order reflection from the same set of planes then occurs at an angle:

$$\sin \theta (2^{nd} \text{ order } 001) = \frac{2\lambda}{2d_{001}} \quad (\text{S4})$$

It is always referred to as the first-order reflection from (200) planes, i.e.

$$\sin \theta (1^{st} \text{ order } 002) = \frac{1\lambda}{2d_{002}} \quad (\text{S5})$$

Similarly, the third and fourth-order reflection from (001) planes is at an angle:

$$\sin \theta (3^{rd} \text{ order } 001) = \frac{3\lambda}{2d_{001}} \equiv \sin \theta (1^{st} \text{ order } 003) = \frac{1\lambda}{2d_{003}} \quad (\text{S6})$$

$$\sin \theta (4^{rd} \text{ order } 001) = \frac{4\lambda}{2d_{001}} \equiv \sin \theta (1^{st} \text{ order } 004) = \frac{1\lambda}{2d_{004}} \quad (\text{S7})$$

Note that the $d_{001} = 2d_{002} = 3d_{003} = 4d_{004}$, thus we can obtain the d_{001} value by knowing the d_{004} value. We have tabulated the calculation result of d_{hkl} spacing of anatase based on the XRD pattern in Table S3-1.

Table S3-1. The unit cell parameters of samples calculated using Bragg's equation

Samples	d_{004}	d_{200}	d_{001}	d_{100}	θ
S-HT-500	2.3783	1.8921	9.5132	3.7842	68.3°
S-500-HT	2.3764	1.8919	9.5056	3.7838	68.3°
A-HT-500	2.3758	1.8934	9.5032	3.7868	68.3°
A-500-HT	2.3799	1.8899	9.5196	3.7798	68.3°
P25 Degussa	2.3810	1.8950	9.5240	3.7900	68.3°

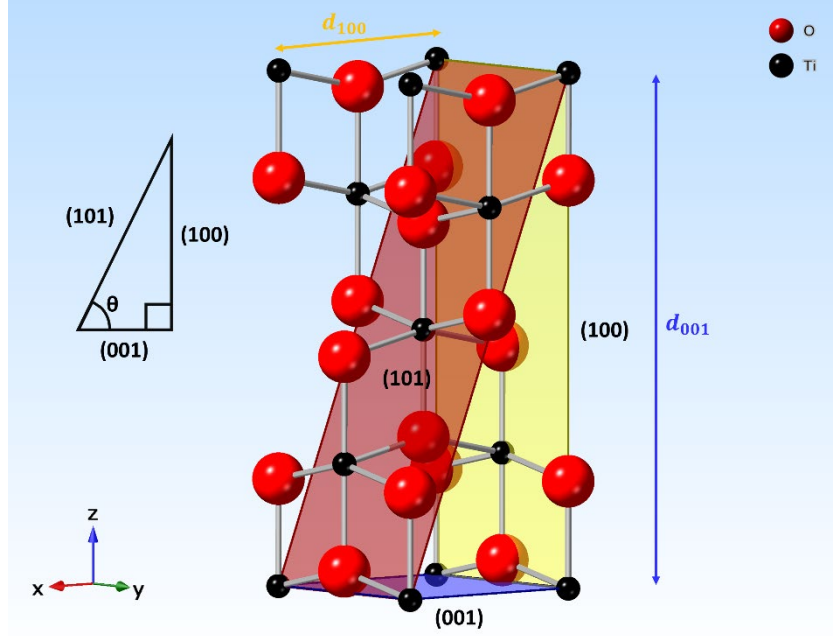


Figure S3-1. The schematic of the anatase unit cell.

The crystal system of anatase is tetragonal ($I4_1/amd$) with unit cell $a = b \neq c$; $\alpha = \beta = \gamma = 90^\circ$, where $a = b = d_{100}$ and $c = d_{001}$. We know θ is the angle between the (101) and (001) planes, as shown in Figure S3-1, where:

$$\theta = \tan^{-1} \frac{d_{001}}{d_{100}} \quad (\text{S8})$$

thus, using equation S8, we can calculate θ for each sample as tabulated in Table S3-1.

Since the crystallite consists of several unit cells, thus the ratio of d_{100} to d_{001} is equal to the ratio of the average crystallite size along [100] direction (D_{100}) to the average crystallite size along [001] direction (D_{001}), which can be written as:

$$\theta = \tan^{-1} \frac{d_{001}}{d_{100}} = \tan^{-1} \frac{D_{001}}{D_{100}} \cong 68.3^\circ \quad (\text{S9})$$

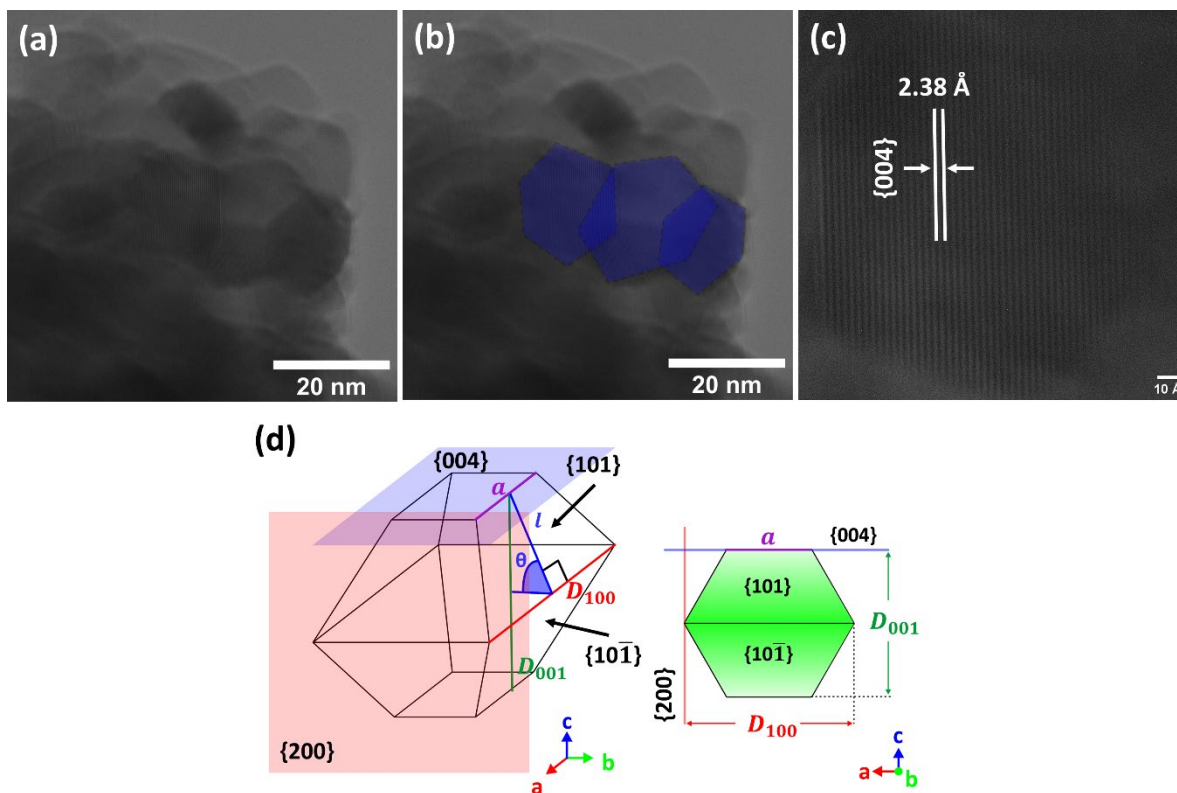


Figure S3-2. (a) HRTEM images of the calcined sample show the square–bipyramidal shape of crystallites. (b) Projected crystallites to {010} plane are depicted as blue hexagons and at higher magnification, (c) a hexagonal shaped crystallite shows vertical lattice fringes representing the {004} interplanar distance. (d) The geometric scheme of a truncated square–bipyramidal shaped anatase crystallite.

The percentage of {001} facet can be calculated by knowing the crystallite truncated length (a). We use the geometry approach to calculate the a value since it has a relation with D_{100} and D_{001} . The average crystallite size (D_{hkl}) calculated using the Scherrer equation:

$$D_{hkl} = \frac{K \times \lambda}{B_{hkl} \times \cos \theta_{hkl}} \quad (\text{S10})$$

Where D_{hkl} is the mean crystallite size in $[hkl]$ direction, K is a dimensionless shape factor (in this case, we use $K = 0.94$), λ is the source X-ray wavelength (in this case, we use $\text{Cu } K_{\alpha} = 1.540 \text{ \AA}$), B_{hkl} is the line broadening at half the maximum intensity (FWHM) of (hkl) peak, θ_{hkl} is the Bragg angle.

As shown in Figure S3-2, we can calculate the values of a and l using the following equations:

$$a = D_{100} - \frac{D_{001}}{\tan \theta} \quad (\text{S11})$$

$$l = \frac{D_{001}}{2 \sin \theta} \quad (\text{S12})$$

The percentage of {001} facet can be calculated by dividing the area of (001) plane to the crystallite total surface area:

$$A_{\{001\}} = a \times a = \left(D_{100} - \frac{D_{001}}{\tan \theta} \right)^2 \quad (\text{S13})$$

$$A_{\{101\}} = \left(\frac{D_{100} + a}{2} \right) \times l = \left(2D_{100} - \frac{D_{001}}{\tan \theta} \right) \times \frac{D_{001}}{2 \sin \theta} \quad (\text{S14})$$

$$\% \{001\} \text{ facet} = \frac{\left(D_{100} - \frac{D_{001}}{\tan \theta} \right)^2}{\left(D_{100} - \frac{D_{001}}{\tan \theta} \right)^2 + \frac{2D_{001}}{\sin \theta} \left(2D_{100} - \frac{D_{001}}{\tan \theta} \right)} \times 100 \% \quad (\text{S15})$$

S4. The Rietveld refinement and the corresponding Williamson-Hall plot

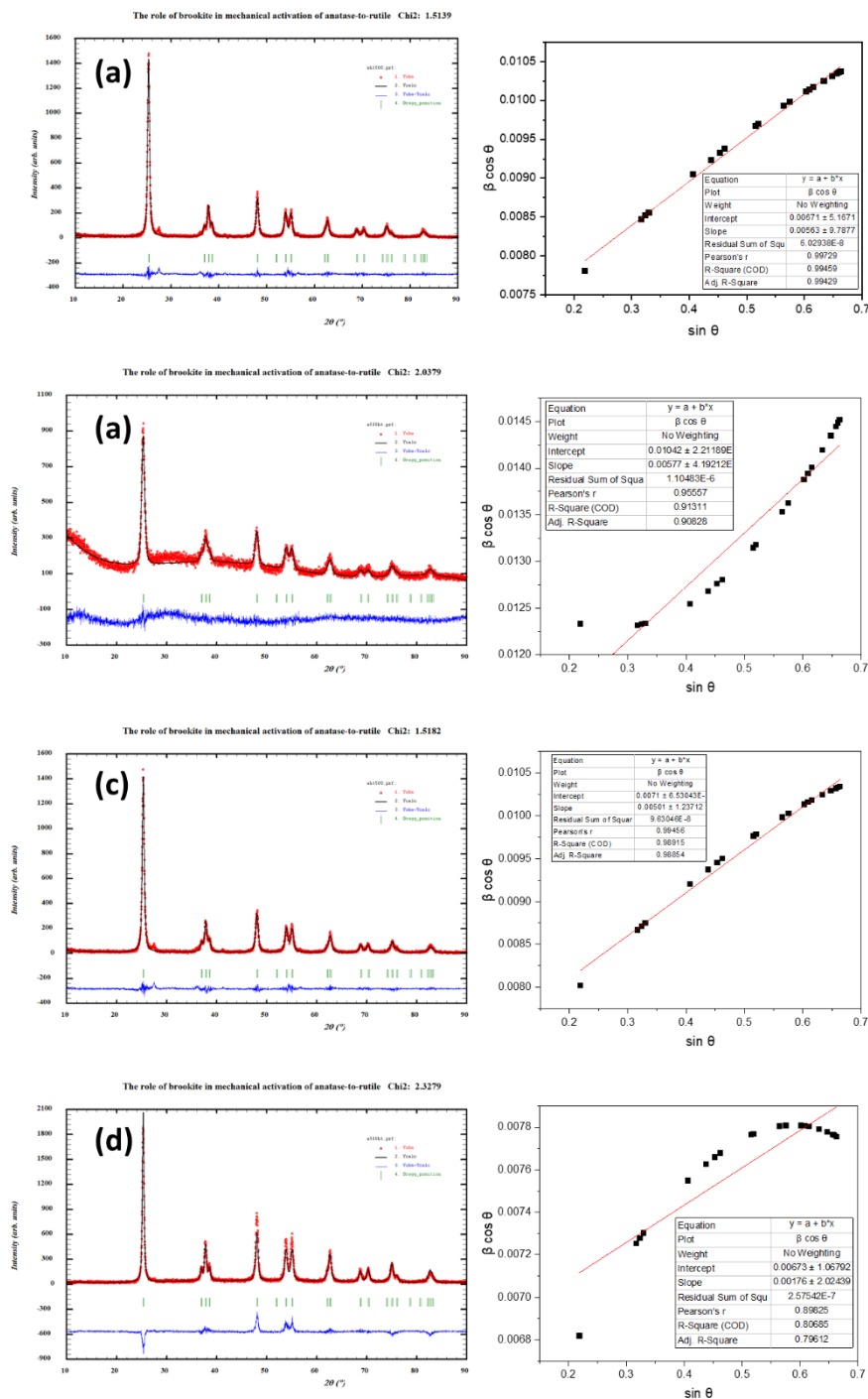


Figure S4. The Rietveld refinement results and the corresponding Williamson-Hall plot of (a) S-HT-500, (b) S-500-HT, (c) A-HT-500, and (d) A-500-HT.

S5. N₂ physisorption results

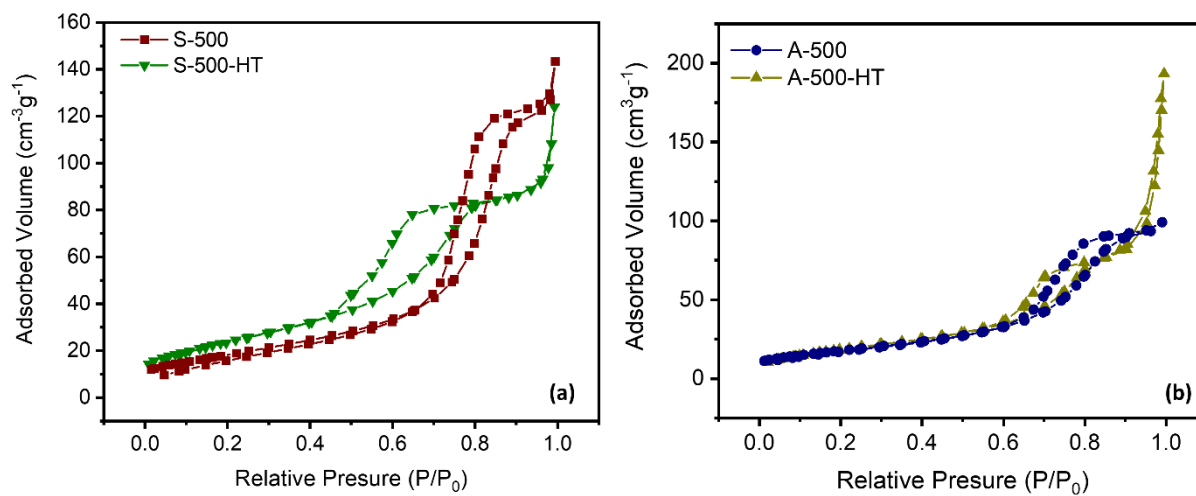


Figure S5. N₂ physisorption isotherm of (a) S-500 vs. S-500-HT and (b) A-500 vs. A-500-HT.

S6. HRTEM images of each synthesized step

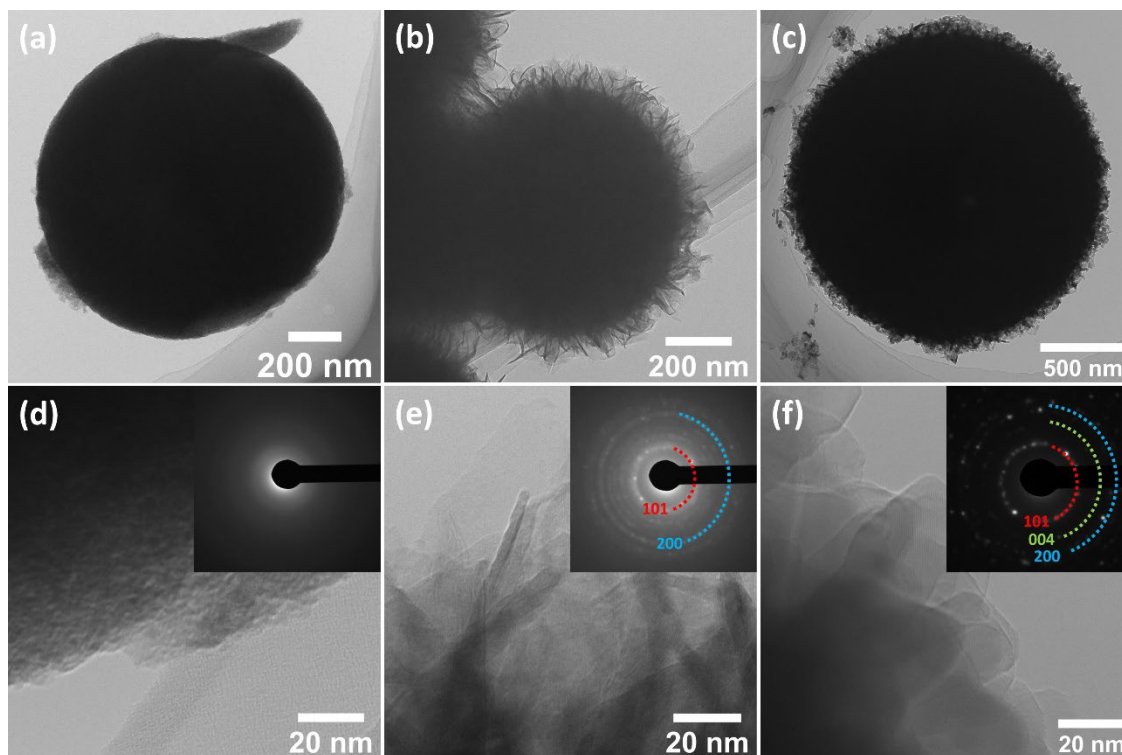


Figure S6. (a-c) TEM and (d-f) HRTEM images of samples: (a,d) as-synthesized, (b,e) hydrothermally-treated, and (c,f) calcined samples. The inset of (d-f) is the corresponding SAED pattern.

S7. Photodegradation of Rhodamine B

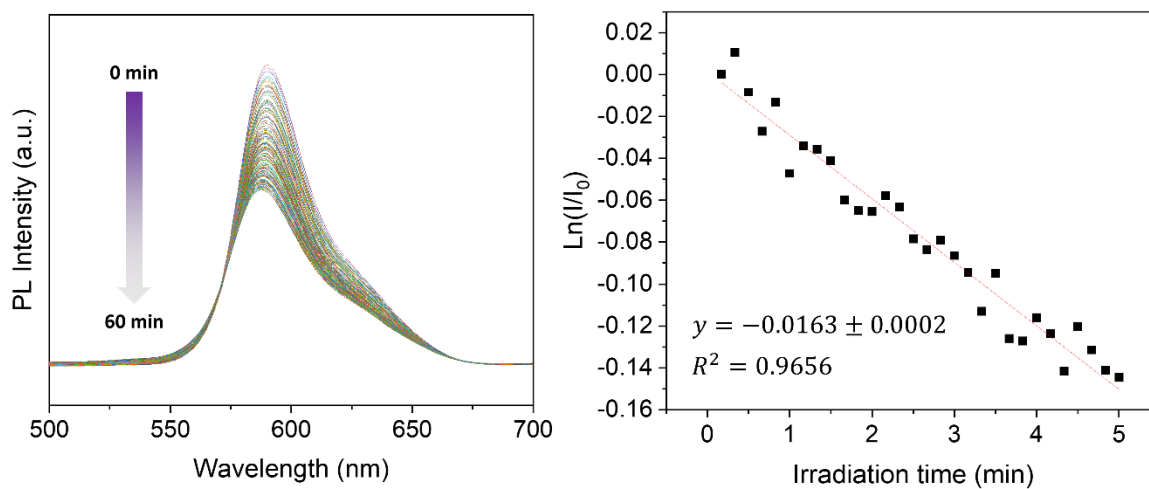


Figure S7. Evolution of PL spectra of rhodamine B with respect to the irradiation time and the corresponding first-order kinetic plots.