Supplementary Information

Photocatalytic Degradation of Ibuprofen on Titanium Oxide Nanoparticles: Insights into Degradation Kinetics, Mechanisms, Thermodynamics, Pathways, and Toxicity

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1. Characterizations of TiO_2 nanoparticle used as photocatalyst in this study

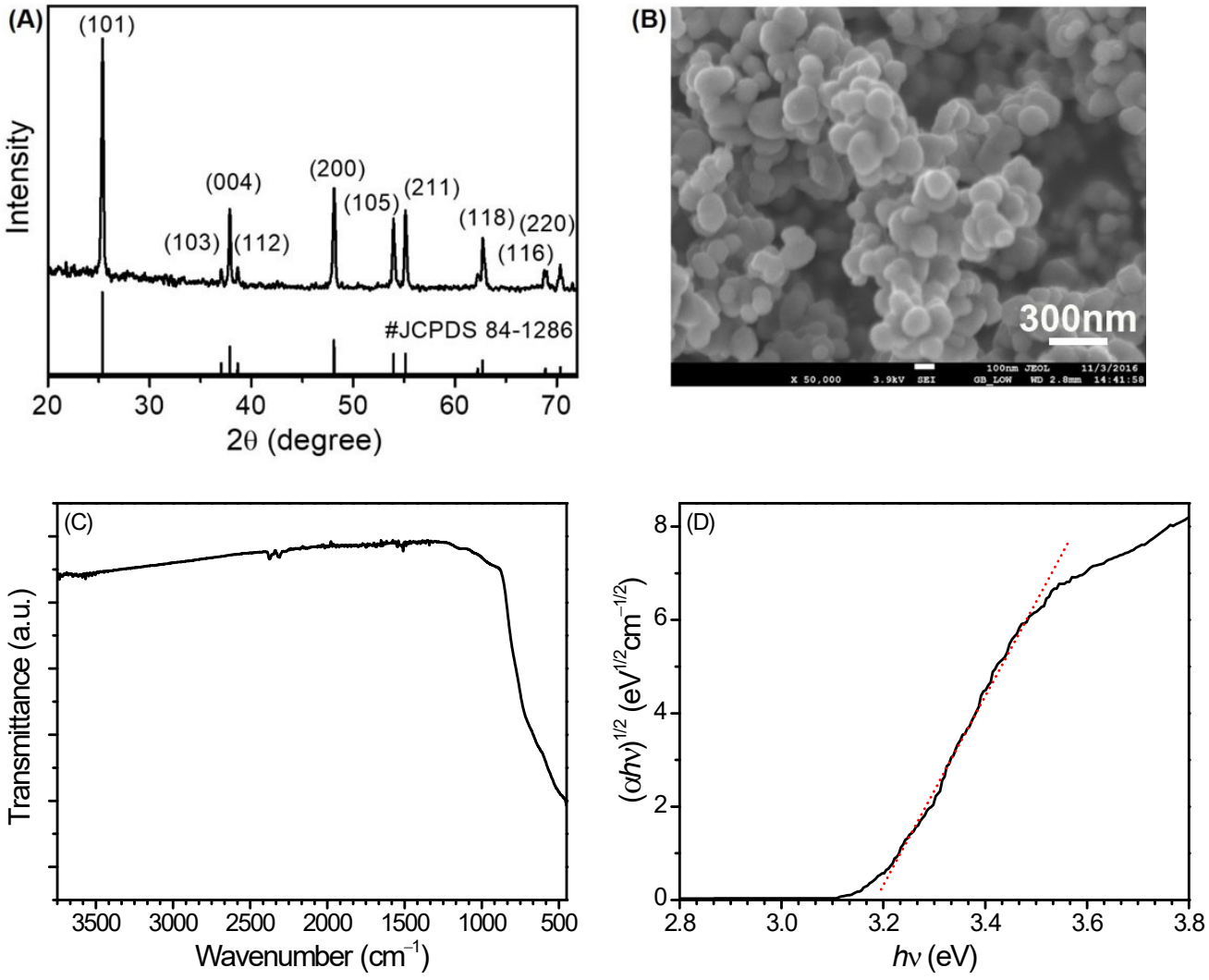


Figure S1. **(A)** TiO_2 NPs XRD data, with comparison to standard data #JCPDS 84-1286 for anatase, **(B)** SEM image of agglomerated TiO_2 NPs, **(C)** FTIR spectrum, and **(D)** the Tauc plot of TiO_2 NPs used in this study.

2. Absorption spectra of ibuprofen before and after adsorption on TiO_2 nanoparticle

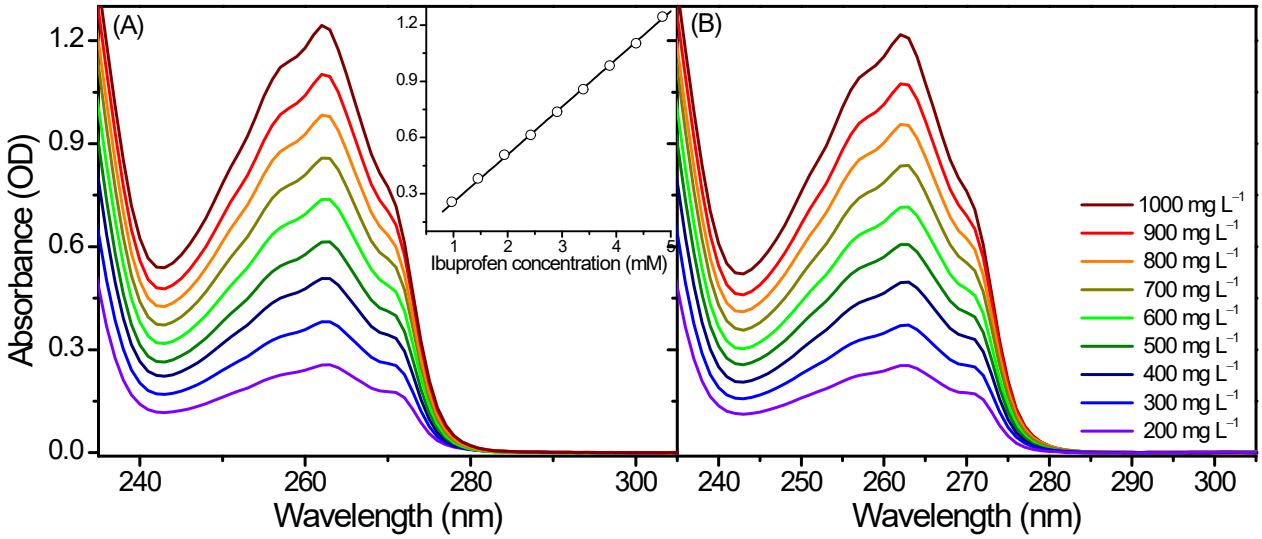


Figure S2. UV-Vis absorption spectra of IBU at concentrations in the range from 200 mg L^{-1} to 1000 mg L^{-1}; (a) before and (b) after being kept in petri dish in the presence of 10 mg TiO_2 NPs. Inset: linear plot of absorbance versus IBU concentration, form which the molar extinction coefficient of IBU was determined to be 254.74 ± 2.79 L mol^{-1} cm^{-1}.

3. Adsorption Isotherm

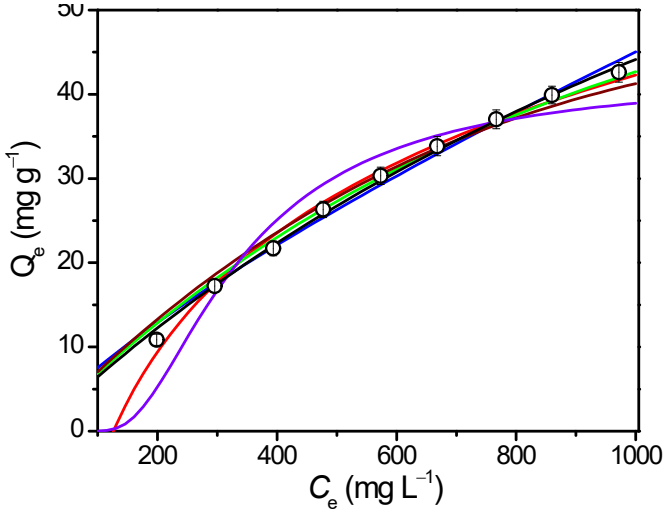


Figure S3. Plots of Q_e as a function of C_e for IBU adsorption on TiO_2 NPs, fitted with the Dubinin–Radushkevich (—), Elovich (—), Freundlich (—), Jovanović (—), Langmuir (—), and Temkin (—) isotherm models.

Table S1. Parameters of the Dubinin-Raduskevich, Elovich, Freundlich, Jovanović, Langmuir, and Temkin isotherm models for the IBU adsorption on TiO_2 NPs.

Isotherm model	Nonlinear Equation	Parameters	RK
Dubinin–Radushkevich	$Q_e = Q_m e^{-\beta\varepsilon^2}$	Q_m (mg g^{-1})	42.34 ± 2.32
		β (k mol J^{-1})^2	13.66 ± 2.38
		R^2	0.914
		χ^2	11.22
Elovich	$Q_e/Q_m = K_E C_e \, exp(-Q_e/Q_m)$	Q_m (mg g^{-1})	167.3 ± 12.5
		K_E (L mmol^{-1})	0.075 ± 0.013
		R^2	0.967
		χ^2	0.755
Freundlich	$Q_e = K_F C_e^{1/n}$	K_F	
		n	1.289 ± 0.231
		R^2	0.990
		χ^2	1.328
Jovanović	$Q_e = Q_m (1 - e^{-K_J C_e})$	Q_m (mg g^{-1})	62.79 ± 3.13
		K_J (L mmol^{-1})	1.14 ± 0.21 ×10^{-3}
		R^2	0.992
		χ^2	0.827
Langmuir	$Q_e = {Q_m K_L C_e}/{(1 + K_L C_e)}$	Q_m (mg g^{-1})	126 ± 4
		K_L (L mmol^{-1})	5.40 ± 0.7 ×10^{-4}
		R^2	0.997
		χ^2	0.275
Temkin	$Q_e = {RT}/{b_T}(\ln K_T + \ln C_e)$	K_T	126.2 ± 4.7
		b_T (kJ mol^{-1})	122.2 ± 3.5
		R^2	0.943
		χ^2	1.039

Note: Q_m represents the maximum adsorption capacity, β is a constant related to the mean free energy of adsorption, $\varepsilon = RT\ln\left(1 + {}^{1}/_{C_e}\right)$ is the Polanyi potential, K_E is the Elovich constant, where K_F is the Freundlich isotherm constant, n is an empirical the exponent signifying adsorption intensity, K_J is the Jovanović isotherm constant, K_L is the Langmuir isotherm constant related to the affinity of binding sites, R represents the gas constant, T is the temperature, b_T is the Temkin constant related to heat of adsorption, and K_T is the Temkin isotherm constant.

4. Direct photolysis of ibuprofen under 365-nm light irradiation

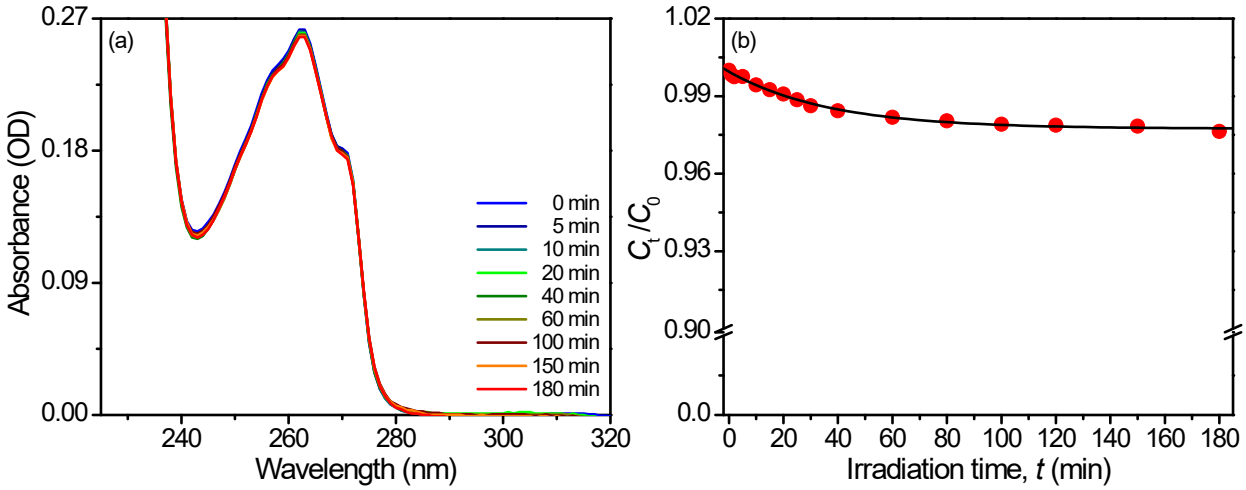


Figure S4. (a) UV-Vis absorption spectra of 200 mg L^{-1} IBU after 365-nm UV light irradiation for different exposure times, as indicated, and (b) plot of C_t/C_0 versus irradiation time, demonstrating that IBU exhibits negligible direct photolytic degradation.

5. Spectral deconvolution

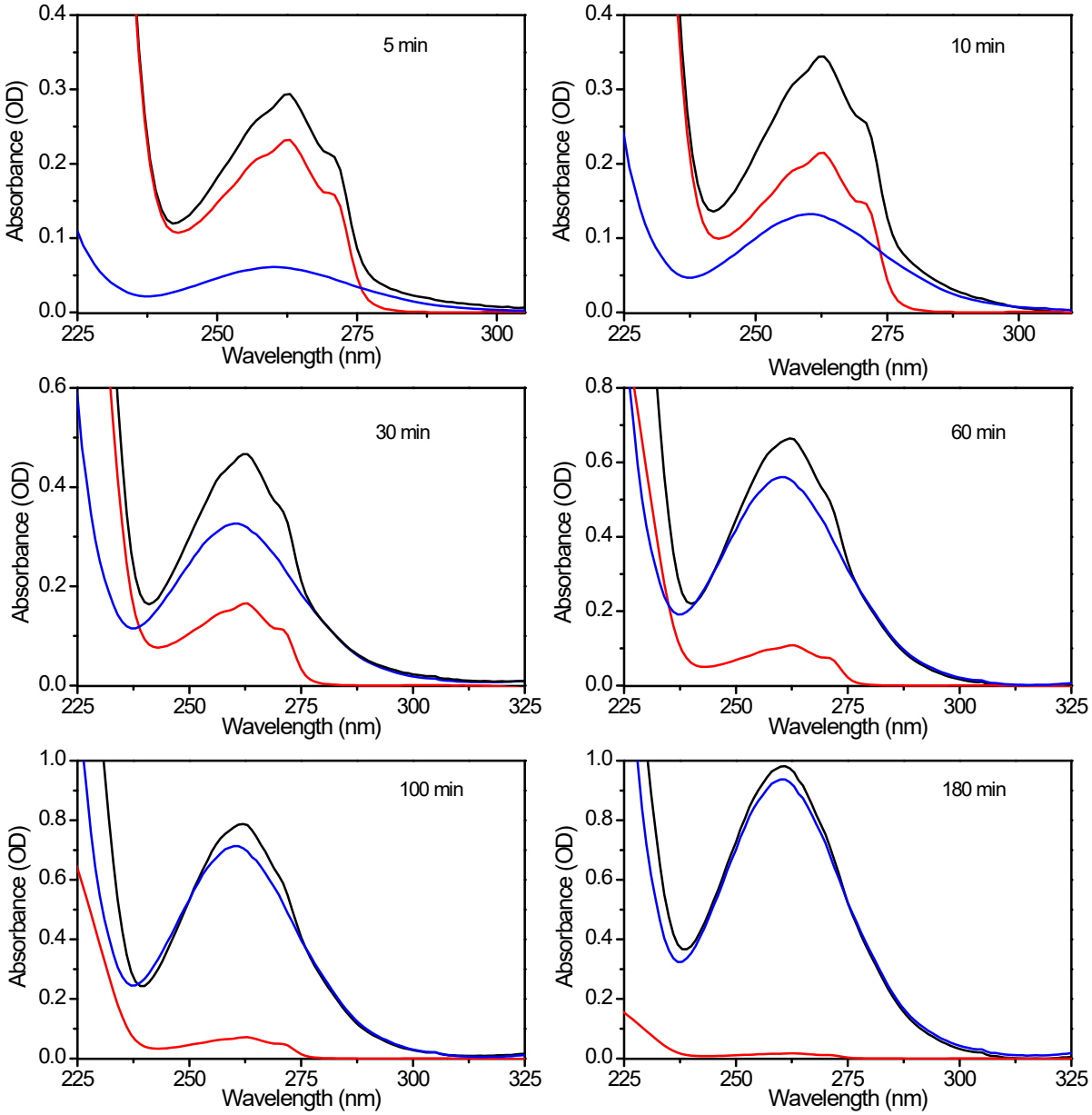


Figure S5. UV-Vis absorption spectra of 200 mg L^{-1} IBU (—) after photocatalytic degradation using 2.5 mg (or 0.125 g L^{-1}) TiO_2 NPs at different irradiation times, as indicated, together with spectra of IBU (—) and its photocatalytic products (—) obtained by deconvolution.

6. The effect of photocatalyst dosage

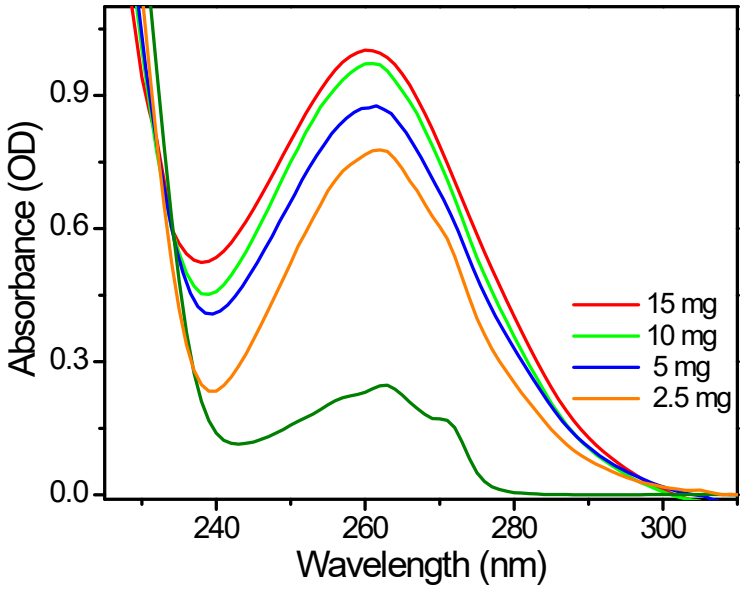


Figure S6. UV-Vis absorption spectra of 200 mg L^{-1} IBU before and after photocatalytic degradation using various amounts of TiO_2 NPs, in the range from 2.5 mg to 15 mg, after 100 minutes of 365-nm UV light irradiation.

7. The effects of scavengers

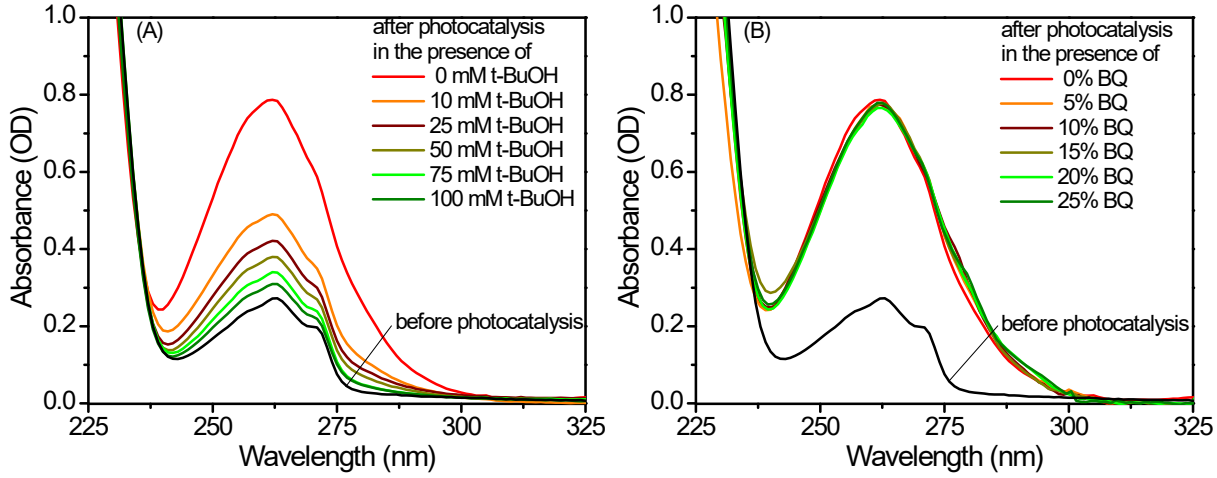


Figure S7. UV-Vis absorption spectra of 200 mg L^{-1} IBU with various added amounts of (a) tert-butylacohol (*t*-BuOH) and (b) para-benzoquinone (*p*-BQ) before and after photocatalytic degradation using 2.5 mg TiO_2 NPs upon irradiation for100 minutes.

Table S2. Comparison of observed degradation constant (k_{obs}) along with the activation energy (E_a) for the photocatalytic degradation of ibuprofen (IBU), rifampicin (RIF), and cephalexin (CEP) on TiO_2 NPs or $SrTiO_3$ NPs at room temperature under the same experimental conditions.

Pharmaceutical	*Photocatalyst*	ROS	k_{obs} (min^{-1})	E_a (kJ mol^{-1})	REF
IBU	TiO_2 NPs	$OH^{\bullet}$	0.013 ± 0.002	18.84 ± 0.56	This work
CEP	TiO_2 NPs	$O_2^{\bullet-}$, $OH^{\bullet}$	0.023 ± 0.003	3.949 ± 0.257	29
RIF	TiO_2 NPs	$O_2^{\bullet-}$, $OH^{\bullet}$	0.016 ± 0.002	1.585 ± 0.079	28
CEP	$SrTiO_3$ NPs	$O_2^{\bullet-}$, $OH^{\bullet}$	0.049 ± 0.005	15.75 ± 0.98	35
RIF	$SrTiO_3$ NPs	$O_2^{\bullet-}$, $OH^{\bullet}$	0.301 ± 0.015	2.415 ± 0.164	35

8. The effect of H_2O_2

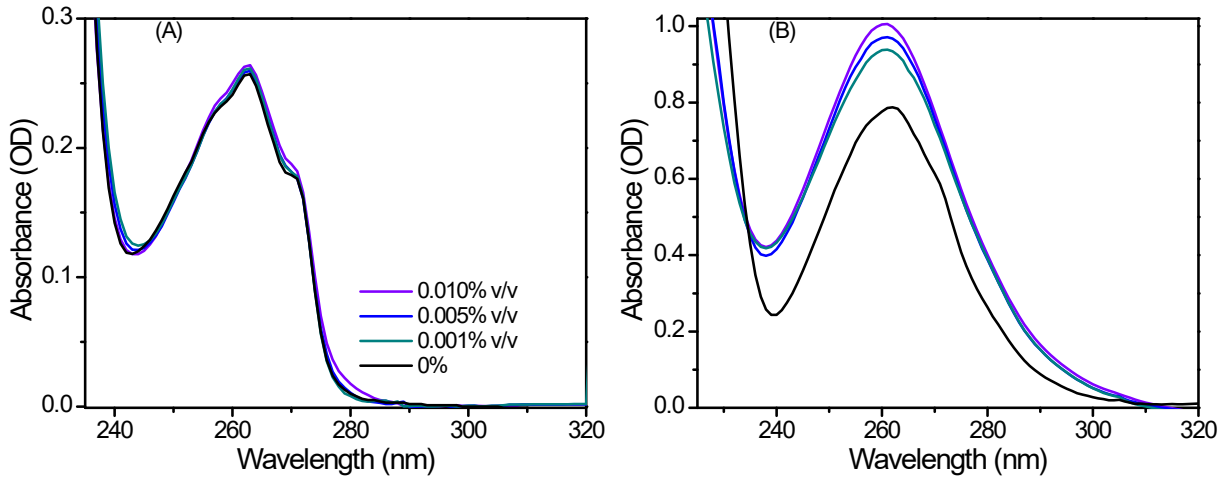


Figure S8. UV-Vis absorption spectra of 200 mg L^{-1} IBU with various added amounts of H_2O_2, as indicated; (a) before and (b) after photocatalytic degradation using 2.5 mg TiO_2 NPs upon irradiation for100 minutes.

9. The effect of pH

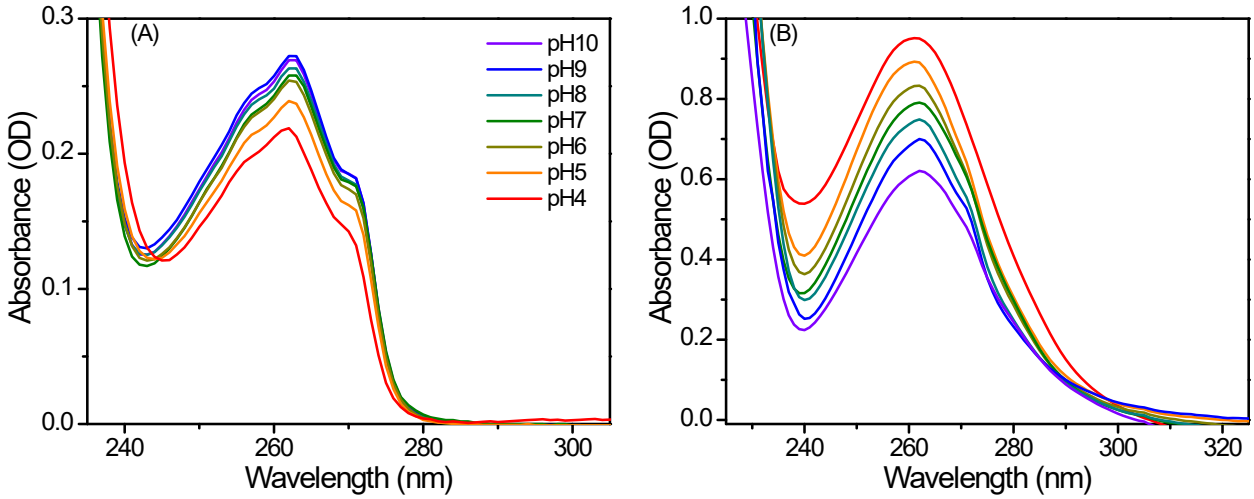


Figure S9. UV-Vis absorption spectra of 200 mg L^{-1} IBU at different pH levels, as indicated; (a) before and (b) after photocatalytic degradation using 2.5 mg TiO_2 NPs upon irradiation for100 minutes.

10. The effect of temperature

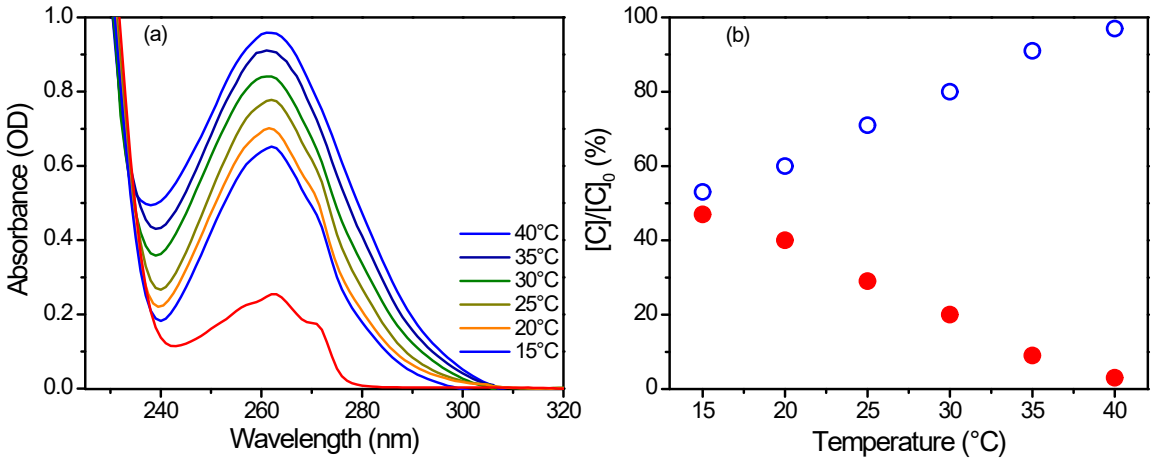
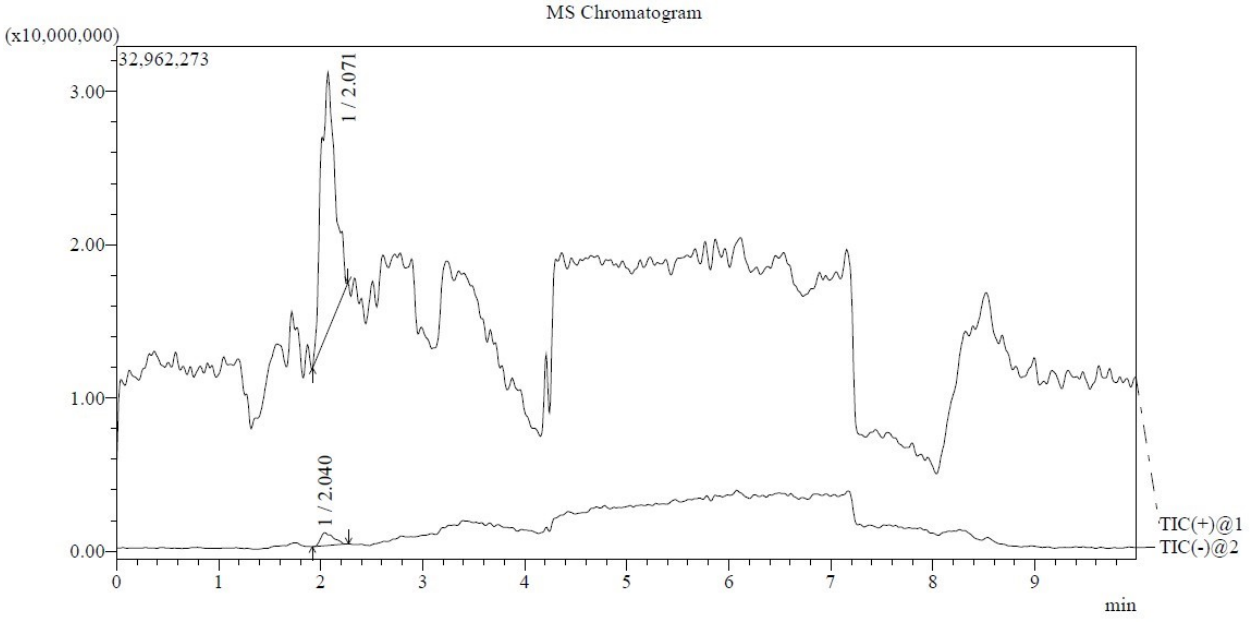


Figure S10. (a) UV-Vis absorption spectra of 200 mg L^{-1} IBU before and after photocatalytic degradation in the presence of 0.125 g L^{-1} TiO_2 NPs at different temperatures, as indicated, and (b) concentrations of IBU (●) and its photocatalytic degradation products (○) after 100 minutes of irradiation, highlighting that photocatalytic degradation is favorable at higher temperatures.

Table S3. Temperature-dependent k_{obs} and the thermodynamic parameters for the photocatalytic degradation of IBU on TiO_2 NPs.

	T (K)	k_{obs} (min^{-1})	ln k_{obs}	E_a (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})	ΔG (kJ mol^{-1})
IBU	313	0.0180	-4.018				-0.034 ± 0.002
	308	0.0169	-4.082				-0.033 ± 0.002
	303	0.0148	-4.210	18.84 ± 0.56	0.016 ± 0.001	0.161 ± 0.003	-0.032 ± 0.002
	298	0.0132	-4.330				-0.032 ± 0.002
	293	0.0111	-4.498				-0.031 ± 0.002
	288	0.0098	-4.622				-0.030 ± 0.002

11. The MS Chromatogram



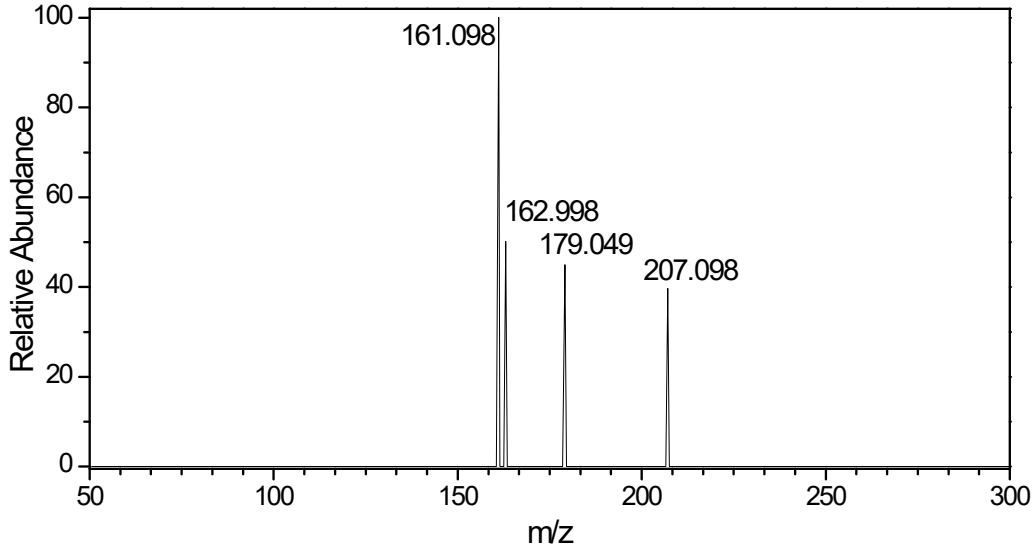


Figure S11. LC–MS/MS chromatograms of 200 mg L^{-1} IBU after photocatalytic degradation in the presence of 2.5 g L^{-1} TiO_2 NPs at 100 minutes of irradiation.