SUPPORTING INFORMATION

Novel green synthesis of Gd-doped TiO_2 nanoparticles for environmental remediation: Statistical modeling and process optimization

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S1 - Experimental method for photoelectrochemical measurement

The photocurrent measurement was conducted on a CHI604E electrochemical analyzer in a three-electrode system with a 0.5 M Na_2SO_4 electrolyte solution, using platinum wire as a counter electrode, Ag/AgCl as a reference electrode, and spin-coated prepared sample on glassy carbon electrode as a working electrode. Before starting the measurement, the electrolyte was purified with argon for 30 min. The working electrode was prepared by following steps: 5 mg of the photocatalyst was dispersed in 2 ml isopropyl alcohol and then 4 µl Naflon solution (5 wt%, Sigma Aldrich) was added to the solution, and the mixture was sonicated for 30 min. After that, the solution was spin-coated on the working electrode dried in air, and then sintered at 350 °C for 40 min to enhance adhesion. During light off-on cycling, the working electrode was exposed to 100 $mWcm^{-2}$ from a 300 W xenon lamp, and the photocurrent was measured at 0 V.

For the electrochemical study, the working electrode was prepared by Dr. Blade method following the standard procedure: The working electrode of Gd-doped TiO_2 was deposited on FTO using prepared nanoparticles, polyvinylidene fluoride (binder material), and carbon black with a mass ratio of 80:10:10 respectively. The above components were ground for an hour to form a homogenous mixture and then it was mixed with N-methyl-2-pyrrolidone (NMP) until it formed the slurry with the desired viscosity. Then prepared slurry was deposited on the well-cleaned FTO substrate and dried in an oven at 60 °C for 16 hr. The electrochemical impedance measurement (EIS) of the prepared sample was performed on Gamry Interface-1010 E electrochemical workstation system at room temperature with formed material deposited on FTO as working electrode (WE), Ag/AgCl as reference electrode (RE), and platinum wire as

counter electrode (CE) in three electrodes configurations in 0.5 M Na_2SO_4 aqueous electrolyte solution.

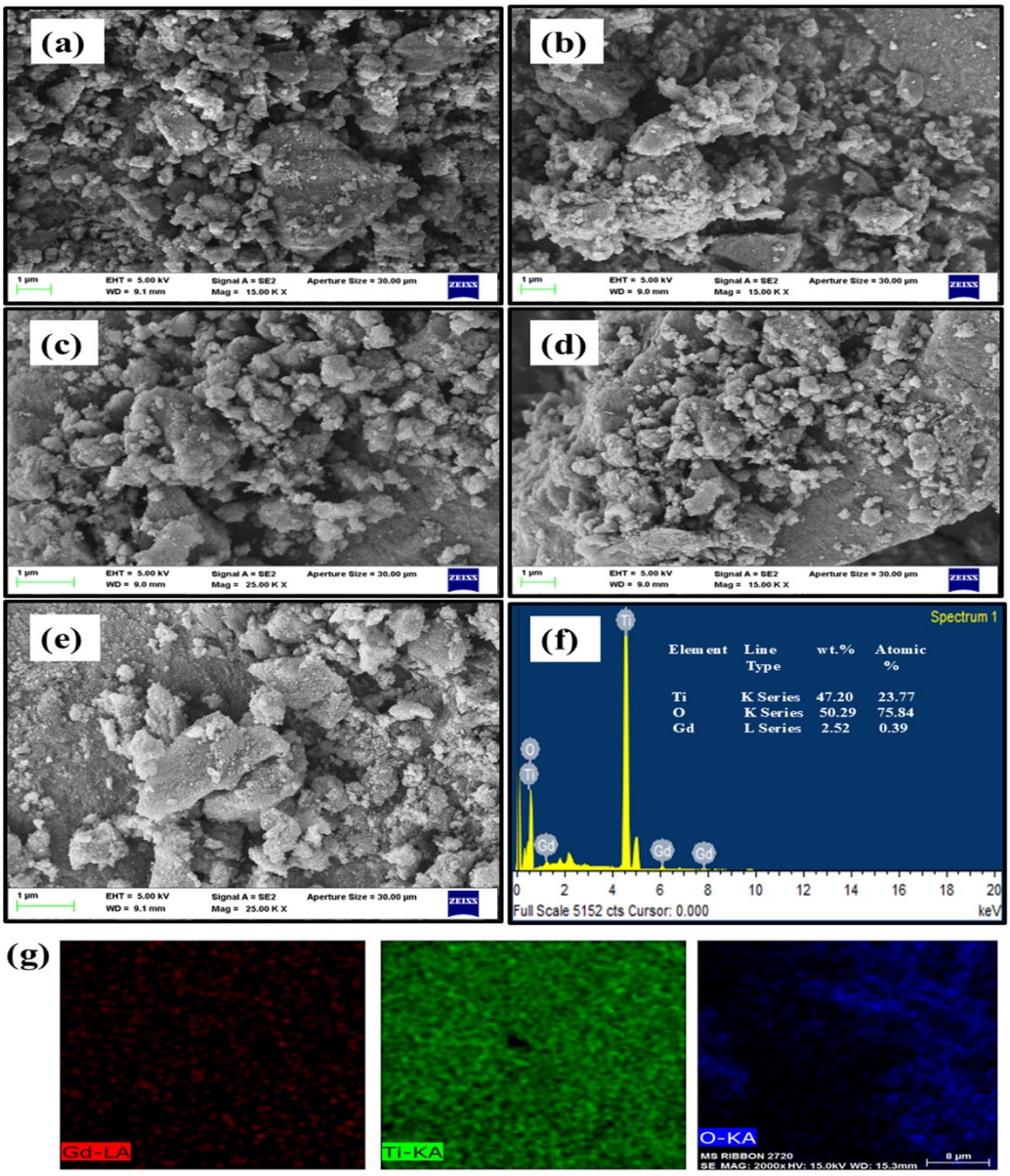


Fig. S1 SEM micrograph of: (a) GdT_0, (b) GdT_0.2, (c) GdT_0.4, (d) GdT_0.6, (e) GdT_0.8, and (f-g) EDS and elemental mapping of GdT_0.8 photocatalyst.

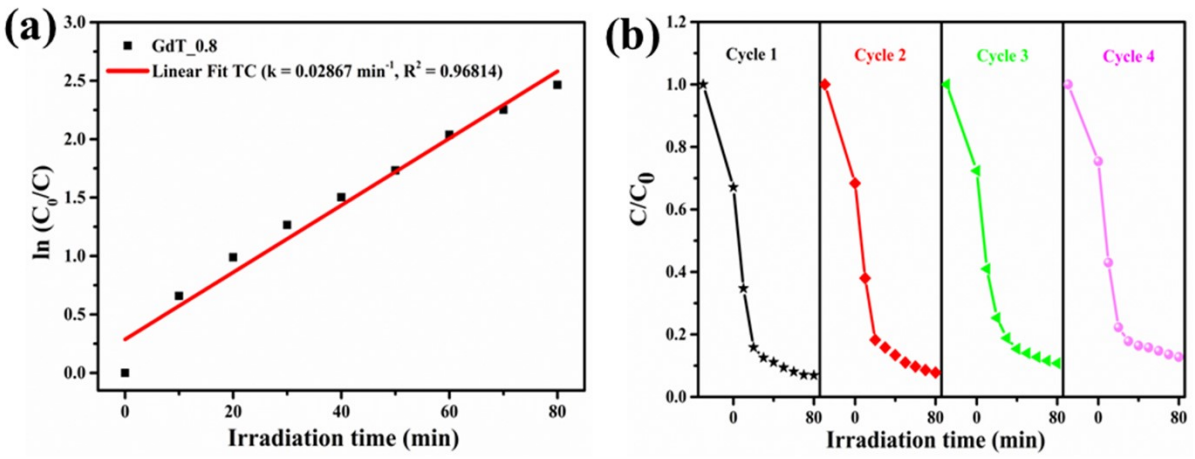


Fig. S2 (a) Kinetic plot for TC removal as a function of irradiation time under optimal conditions and (b) reusability test of 0.8%Gd-TiO_2 photocatalyst.

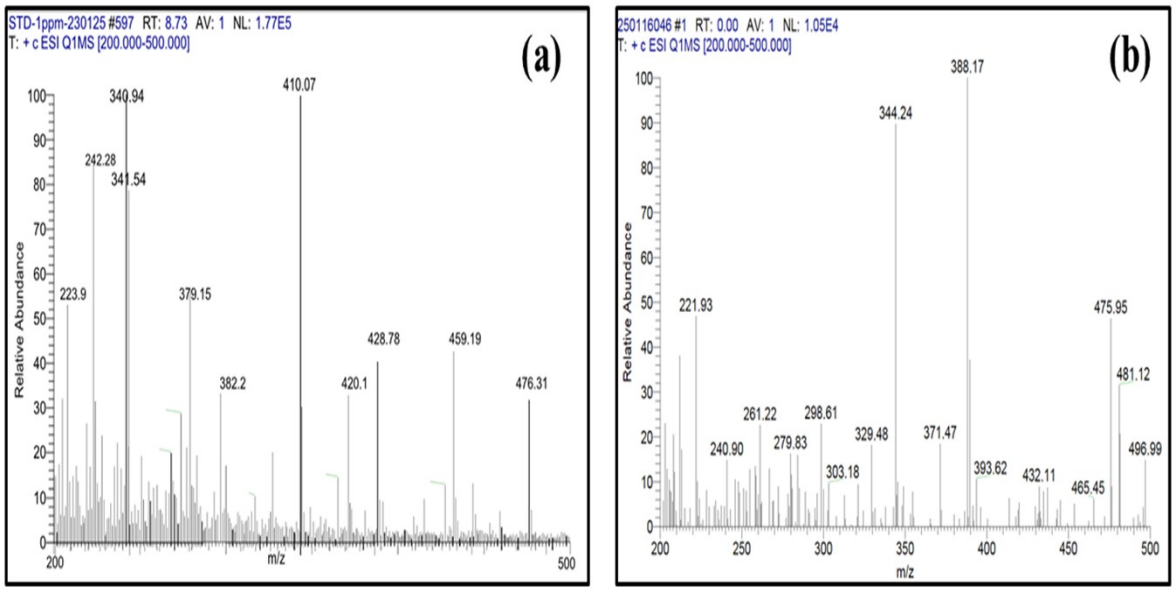


Fig. S3 LC-MS spectra of TC using Gd_0.8 photocatalyst: (a) before light irradiation and (b) after 80 min of light irradiation.

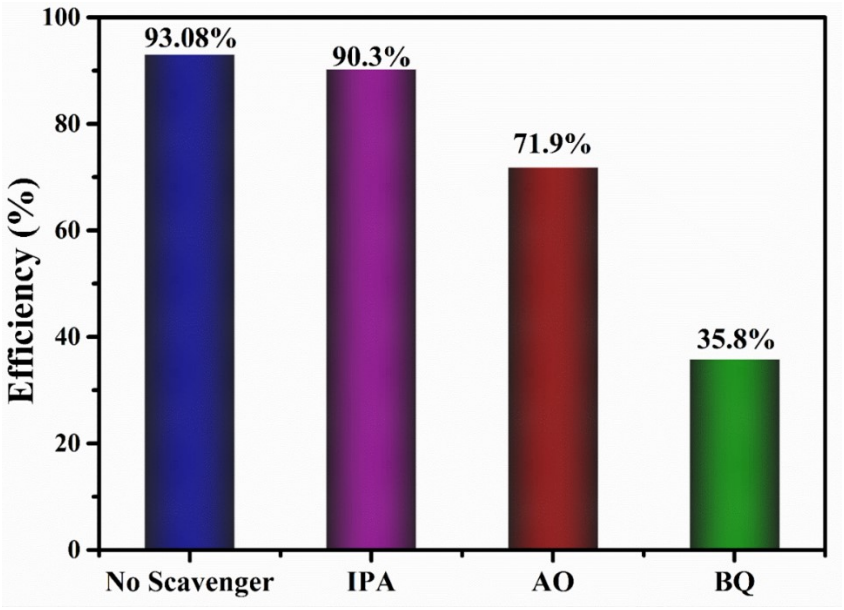


Fig. S4 Photocatalytic performance with the addition of different scavengers based on optimum conditions.

Table S1 Physicochemical properties of tetracycline

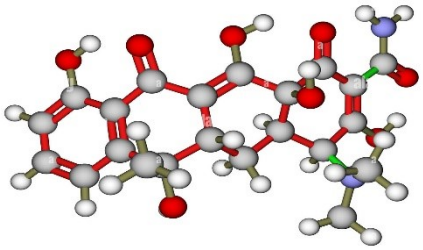
Antibiotic	Chemical structure	Chemical Formula	Molecular weight (g/mol)	λ_{max} (nm)
Tetracycline (TC)		$C_{22}H_{24}N_2O_8$	444.4	359

Table S2 Calculated structural parameters and energy band gap of prepared samples

Photocatalyst code	Crystallite size (nm)	Unit cell parameter		Dislocation density (δ) (nm^{-2}) (δ × 10^{-3})	Lattice strain (ε) (ε × 10^{-3})	Band gap (eV)
		a=b (Å)	c (Å)			
GdT_0	8.70	3.7835	9.4946	13.21	3.98	2.92
GdT_0.2	7.31	3.7833	9.4974	18.71	4.73	2.89
GdT_0.4	6.68	3.7857	9.4928	22.41	4.93	2.84
GdT_0.6	6.66	3.7863	9.4924	22.54	4.94	2.80

GdT_0.8	6.47	3.7866	9.4889	23.88	5.35	2.75

Table S3 BET surface area, pore volume, and mean pore diameter of 0% Gd-TiO_2 and 0.8% Gd-TiO_2

Photocatalyst Code	S_{BET} (m^2/g)	Pore volume (cm^3/g)	Mean Pore diameter (nm)
GdT_0	134.069	0.2161	3.8633
GdT_0.8	173.118	0.2833	3.8538

Table S4 Experimental and predicted values for TC removal were obtained through the RSM-based CCD method

Run No.	Catalyst dose (mg/100 ml)	TC concentration (mg/L)	pH value	Experimental Degradation efficiency	Predicted Degradation efficiency	Residual
1	10	10	4	79.75	79.28	0.47
2	20	10	4	90.88	92.87	-1.99
3	10	30	4	59.43	58.05	1.38
4	20	30	4	87.06	85.47	1.59
5	10	10	10	69.74	71.10	-1.36
6	20	10	10	62.63	63.77	-1.14
7	10	30	10	66.08	63.86	2.22
8	20	30	10	70.12	70.36	-0.24
9	7.5	20	7	68.86	70.56	-1.71
10	22.5	20	7	86.93	85.64	1.29
11	15	5	7	85.74	82.96	2.78
12	15	35	7	68.79	71.98	-3.19
13	15	20	2.5	79.82	80.68	-0.86
14	15	20	11.5	63.67	63.22	0.45
15	15	20	7	83.90	84.08	-0.18
16	15	20	7	85.35	84.08	1.27
17	15	20	7	83.30	84.08	-0.78

Table S5 ANOVA results for coefficients of quadratic model for TC degradation

Source	Sum of Squares	df	Mean Square	F-value	p-value	Status
Model	1627.91	9	180.88	29.8	< 0.0001	significant
A-Catalyst dose	315.56	1	315.56	51.99	0.0002	
B-TC con.	167.39	1	167.39	27.58	0.0012	
C-pH	423.7	1	423.7	69.81	< 0.0001	
AB	95.58	1	95.58	15.75	0.0054	
AC	218.7	1	218.7	36.03	0.0005	
BC	97.82	1	97.82	16.12	0.0051	
A^2	60.47	1	60.47	9.96	0.016	
B^2	73.86	1	73.86	12.17	0.0101	
C^2	248.84	1	248.84	41	0.0004	
Residual	42.49	7	6.07			
Lack of Fit	40.27	5	8.05	7.27	0.1254	not significant
Pure Error	2.22	2	1.11			
Cor Total	1670.4	16				

Table S6 ANOVA for the fitted quadratic polynomial model

Std. Dev.	2.46	R^2	0.9746
Mean	76	Adj. R^2	0.9419
C.V.% (Coefficient of variations)	3.24	Pred. R^2	0.8044
		Adeq. precision	18.427

Table S7 Comparison of prepared photocatalyst for degradation of pollutant with other reported work

Photocatalyst	Synthesis method	Experimental condition	Light source	Pollutant	Degradation efficiency (%)	References
α-Fe2O3/TiO_2	Wet impregnation and sonochemical method	[catalyst]: 0.614 g/L, [C_0]: 30 mg/L, [pH]: 5, [time]: 161 min	500W Halogen	Tetracycline	99.89%	[1]
g-C3N4 membrane reactor	-	[catalyst]: 0.56 g/L, [C_0]: 22.16 mg/L, [pH]: 9.78, [time]: 113.77	300W Xenon	Tetracycline	94.8%	[2]

		min	lamp			
CFs/g-C_3N_4/BiOBr	Chemical bath deposition method	[catalyst]: 0.15 g, [C_0]: 20 mg/L, [pH]: 4.6, [time]: 120 min	Visible light	Tetracycline hydrochloride	86.1%	[3]
Ce-MOF	Different methods	[catalyst]: 1 g/L, [C_0]: 120 mg/L, [pH]: 7, [time]: 120 min	UV light	Tetracycline	81.75%	[4]
$NiMoO_4$/g-C_3N_4	Ultrasound-assisted route	[catalyst]: 20 mg, [C_0]: 20 mg/L, [time]: 180 min	500W Xenon lamp	Tetracycline	89%	[5]
Graphene oxide/magnetite/cerium-doped titania	Sol-gel and Hummers method	[catalyst]: 50 mg, [C_0]: 25 mg/L, [time]: 60 min	300W Xe lamp	Tetracycline	82.92%	[6]
CdS-TNs/rGO nanocomposite	one-pot hydrothermal and impregnation-calcination method	[catalyst]: 75 mg, [C_0]: 30 mg/L, [time]: 90 min	UV light	Tetracycline	84%	[7]
Gd-doped TiO_2 nanoparticles	Sol-gel method	[catalyst]: 25 mg, [C_0]: 25 mg/L, [pH]: 7, [time]: 300 min	Visible light	Methylene blue dye	46.5%	[8]
Gd-doped $BiFeO_3$ nanoparticles	Sol-gel method	[catalyst]: 500 mg, [C_0]: 5 mg/L, [time]: 270 min	Visible light	Rhodamine dye	42.1	[9]
TiO_2 nanoparticles	Green synthesis using *Basil* leaves	[catalyst]: 25 mg, [C_0]: 10 mg/L, [pH]: 5, [time]: 150 min,	Solar light	Amoxicillin	91.63%	[10]
Boron and cerium-doped TiO_2 nanoparticles	EDTA-citrate method	[catalyst]: 1 g/L, [C_0]: 10 mg/L, [time]: 180 min, 90 min,	Solar light	ciprofloxacin and norfloxacin	93.16%, 93% and 93.22%, 93.6%	[11]
Gd, Fe and N co-doped TiO2 nanomaterials	Sol-gel method	[catalyst]: 0.1 g, [C_0]: 10 mg/L, [time]: 180 min, 90 min,	500W Xenon lamp	Methylene blue dye	97.4%	[12]
AgBreTiO2-Palygorskite	-	[catalyst]: 0.5 g/L,[C0]: 10 mg/L, [pH]: 9, [time]: 90 min	Visible light	Tetracycline hydrochloride	90%	[13]
Gd-doped TiO_2	Green synthesis via hydrothermal method	[catalyst]: 22.50 mg, [C_0]: 18.25 mg/L, [pH]: 5.02, [time]: 80 min	Visible light	Tetracycline	93.08%	**Present work**

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