Spent-Coffee Grounds-Derived Biochar-Supported Heterogeneous Photocatalyst: A Performance Evaluation and Mechanistic Approach for the Degradation of Pentachlorophenol

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Text S1

Measurement of pH of Point of Zero Charges (pH_{PZC})

The measurement of pH of point of zero charges (pH_{PZC}) of the CGBT composite was determined with the following procedure: (1) a 25 mL sodium chloride (NaCl, 0.01 M) solution was placed into 60 mL glass bottle. The initial solution pH was adjusted to successive initial values between 2.0 and 12.0, and 0.05 g of the sample was added to the glass bottle. (2) The glass bottle was filled with N_2 to eliminate the effect of carbon dioxide (CO_2) on the pH change, and then shaken at 40 ^{o}C. (3) The final solution pH was measured after a desired contact time of 48 h. The difference between the final pH and the initial pH, denoted as Δ pH, was plotted against the initial pH. The solution pH at which the curve crosses the line of Δ pH = 0 was taken as the pH_{PZC} of sample

Text S2

Description of quantum yield (QY), figure-of-merits (FOM), and space-time yield (STY)

Metrics based on the absorbed or incident irradiation and photon flux are crucial for evaluating catalytic systems for wastewater treatment. The literature has observed that a comparison has been made considering the conversion or degradation efficiencies under applied experimental conditions. However, a catalyst performing well under given experimental conditions may not necessarily provide optimal performance under variable conditions [1]. The comparative assessment of different systems based on conversion/degradation efficiency could not provide a meaningful comparison of actual performance. Consequently, there is an imperative need to perform the figure-of-merit based system performance that considers all the essential variables

in the catalytic processes. Besides, the performances of photocatalytic systems can be evaluated on a quantitative basis with the aid of diverse performance metrics such as the quantum yield (QY) and space-time yield (STY). Fundamentally, the QY of a reaction can be quantitively determined by calculating the number of absorbed photons by the surface of the photocatalyst in a reaction using the equation (1) [2].

$$QY = \frac{Decay\ rate\ of\ pollutant\ (molecules\ per\ second)}{Photon\ flux\ (photons\ per\ second)} \tag{1}$$

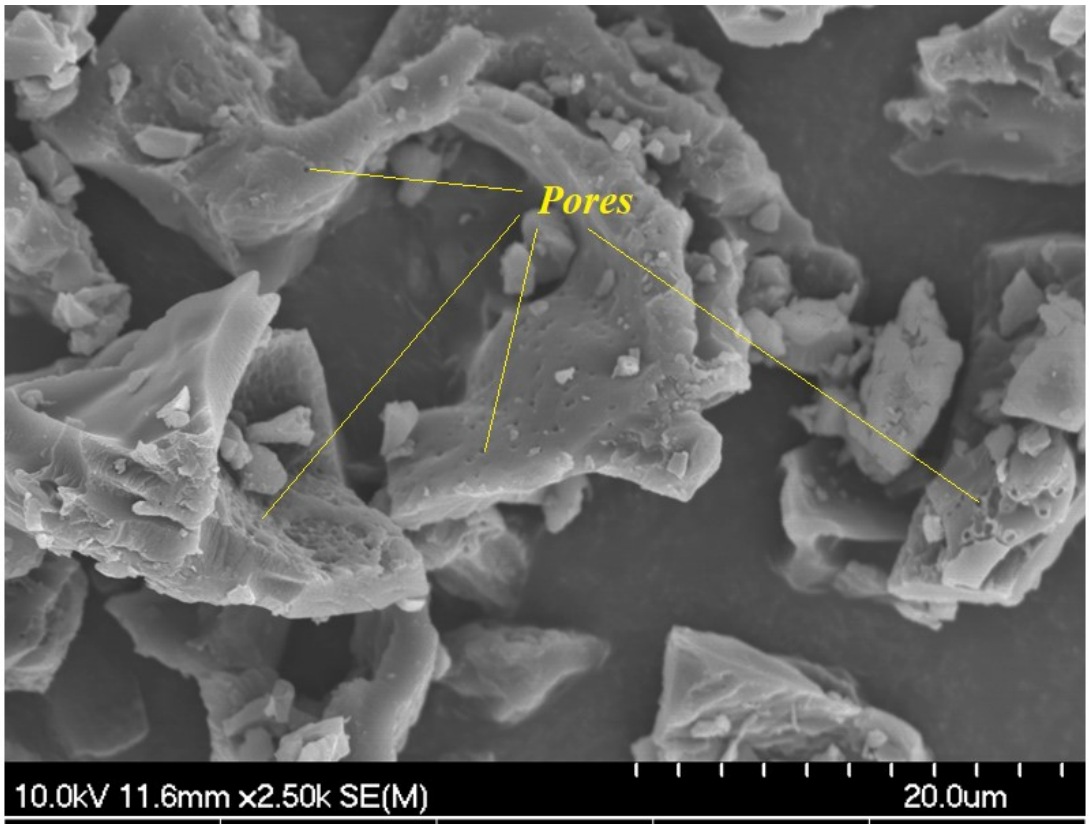
As the mass of photocatalyst is utilized in the reaction system, the process is different between different studies, space-time yield (STY) and figure-of-merit (FoM) are considered to normalize such effects, which are not considered in calculating QY [3]. STY and FoM are also computed to assess the performance of the system using equations 2 and 3, respectively.

$$STY = \frac{QY\ (molecules\ per\ photon)}{Mass\ of\ catalyst\ (g)} \tag{2}$$

$$FoM = \frac{Conversion\ efficiency\ (\%)}{Mass\ of\ catalyst\ (g) x\ Initial\ pollutant\ concentration (g\ L^{-1})\ x\ irradiation\ time (min) x\ Pow} \tag{3}$$

In the industrial sector, STY is defined as the net amount of product formation per unit time per packed volume of the catalyst bed [4]. In our study, the STY concept can be considered as the quantitative analysis of the amount of organic contaminant degraded per unit time by a unit mass of catalyst. Our comparison of STY and FoM in conjunction with QY values provides judicious comparative performance among the different reaction systems employed and considers all associated variables in the reaction system. Accordingly, we compared our reaction system for

wastewater treatment with the other reported studies based on parameters such as irradiation light intensity and wavelength, a mass of catalyst, degradation and irradiation time, volume of the reaction medium, initial concentration, and molecular weight of the organic contaminant. All these parameters were used to compute the QY, STY and FoM values, and the results are compiled in Table S3.



Element	C	O	Mg	K
Wt. %	92.34	3.66	0.38	3.63

Fig. S1. SEM image of biochar and weight percentage of elements.

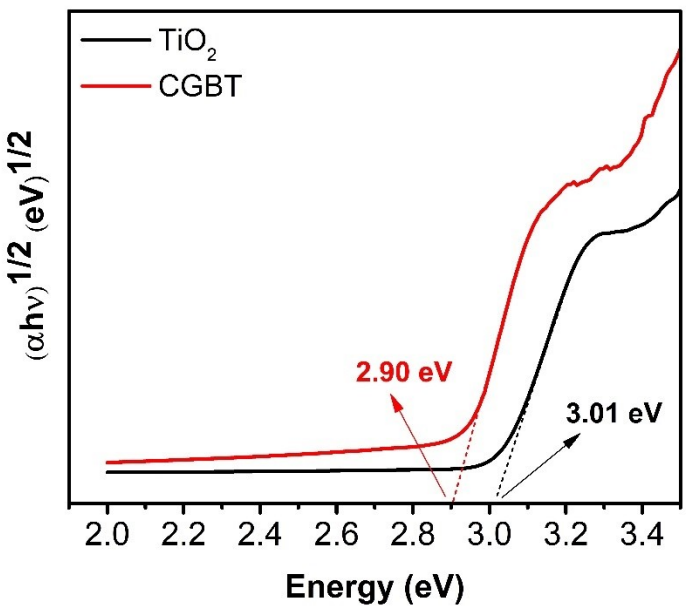


Fig. S2 Tauc plot of the synthesized photocatalysts

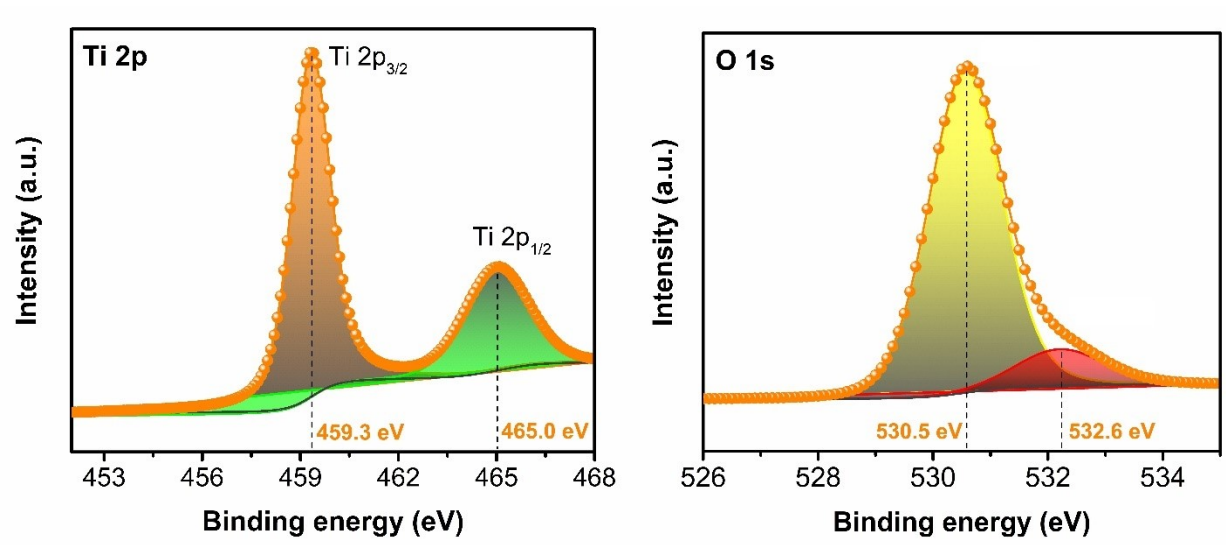


Fig. S3 High-resolution XPS Ti 2p and O 1s spectra of TiO_2 nanoparticles.

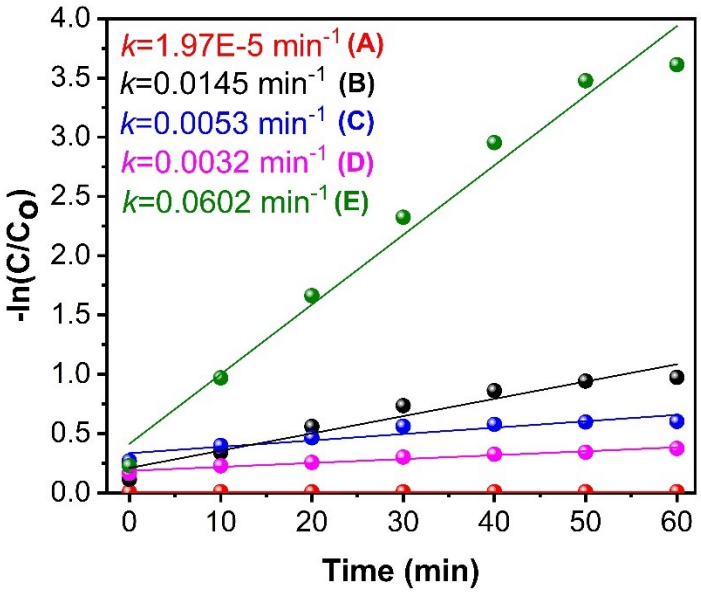


Fig. S4. Rate kinetics of photocatalytic degradation of PCP under photolysis (A) and in the presence of catalysts: TiO_2 (B), CGB (C), SCG (D), and CGBT (E) nanocomposite

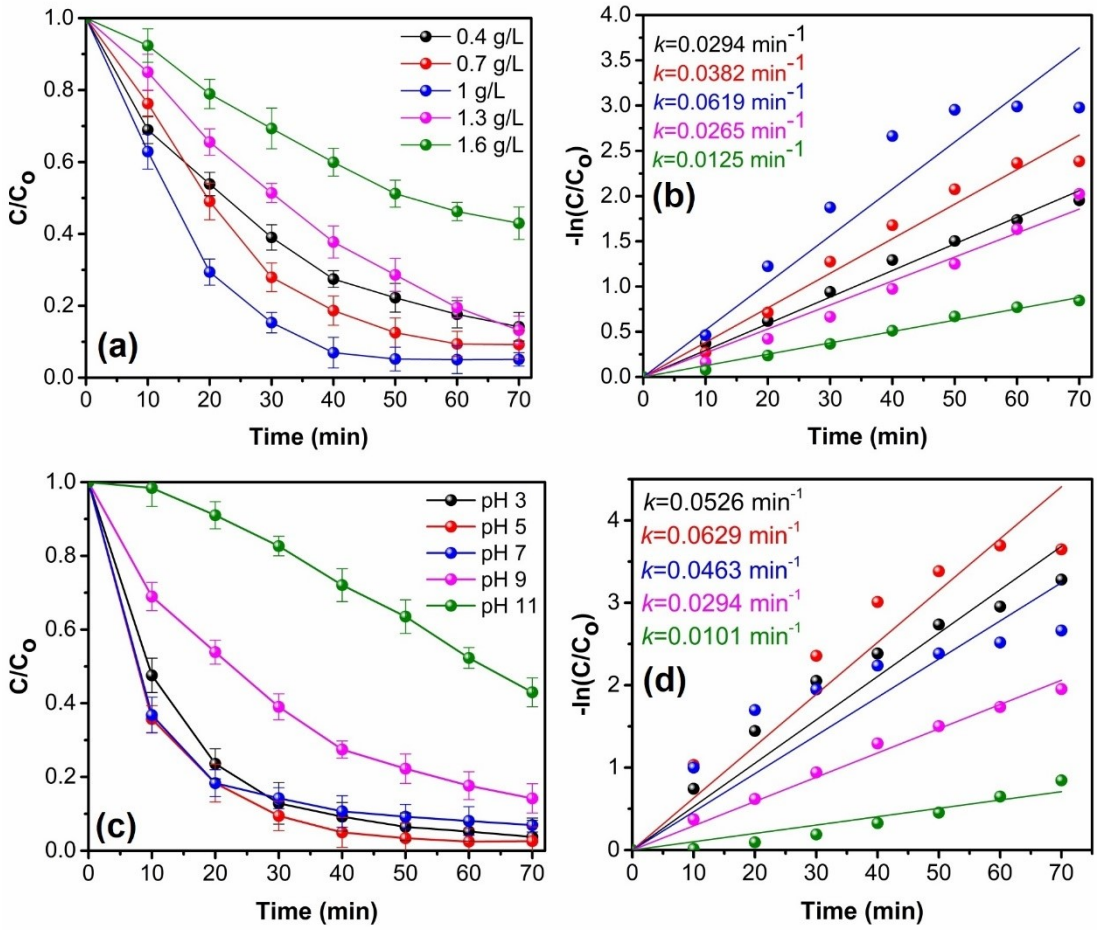


Fig. S5. (a) Effect of varying concentrations of CGBT nanocomposites on the photocatalytic degradation and (b) rate kinetics of PCP; (c) Effect of solution pH on the photocatalytic degradation and (d) rate kinetics of PCP (d) [$(PCP)_o$=10 mg L^{-1} and UV light irradiation)

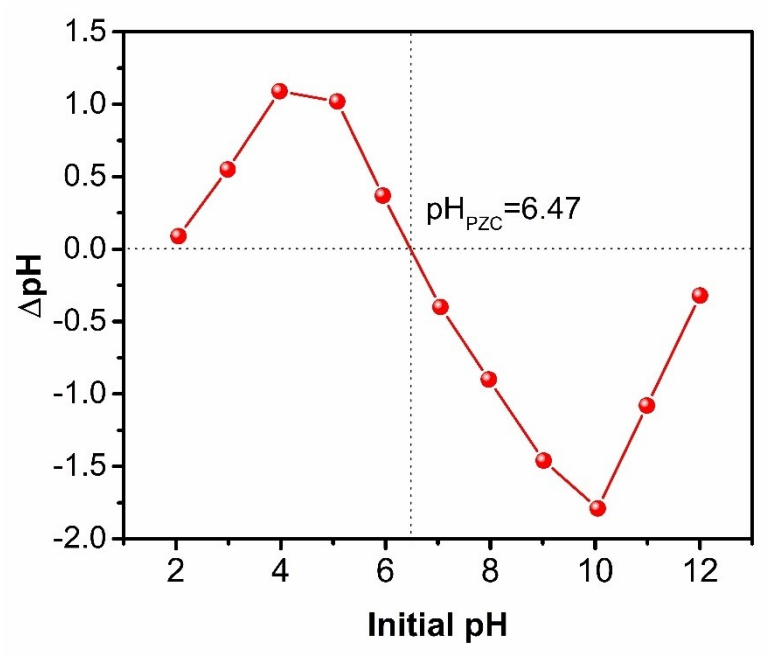


Fig. S6 Point of zero charge (pH_{PZC}) of CGBT nanocomposites.

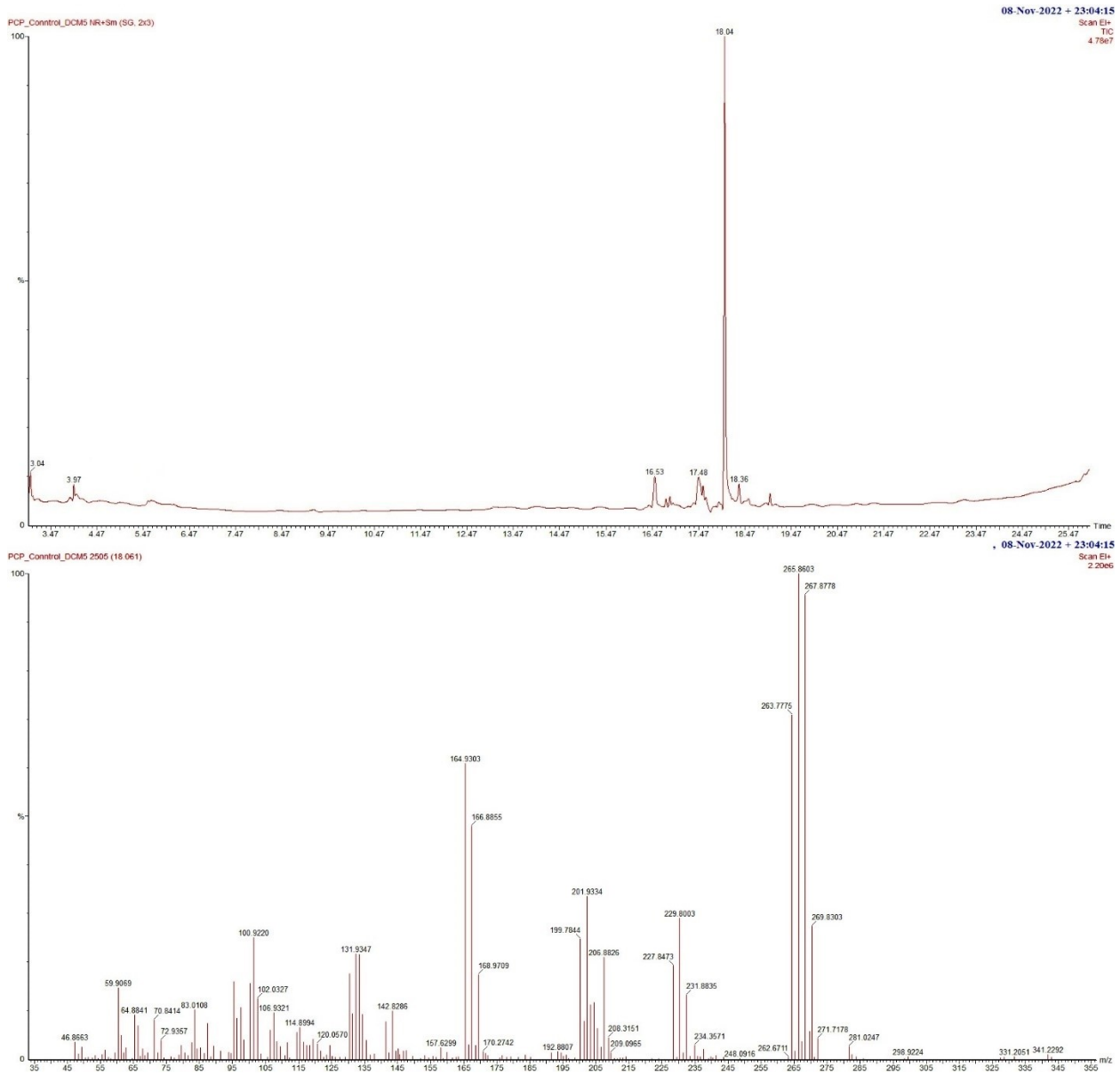


Fig. S7. GC chromatogram for PCP and mass spectra of PCP at t_R=18.04

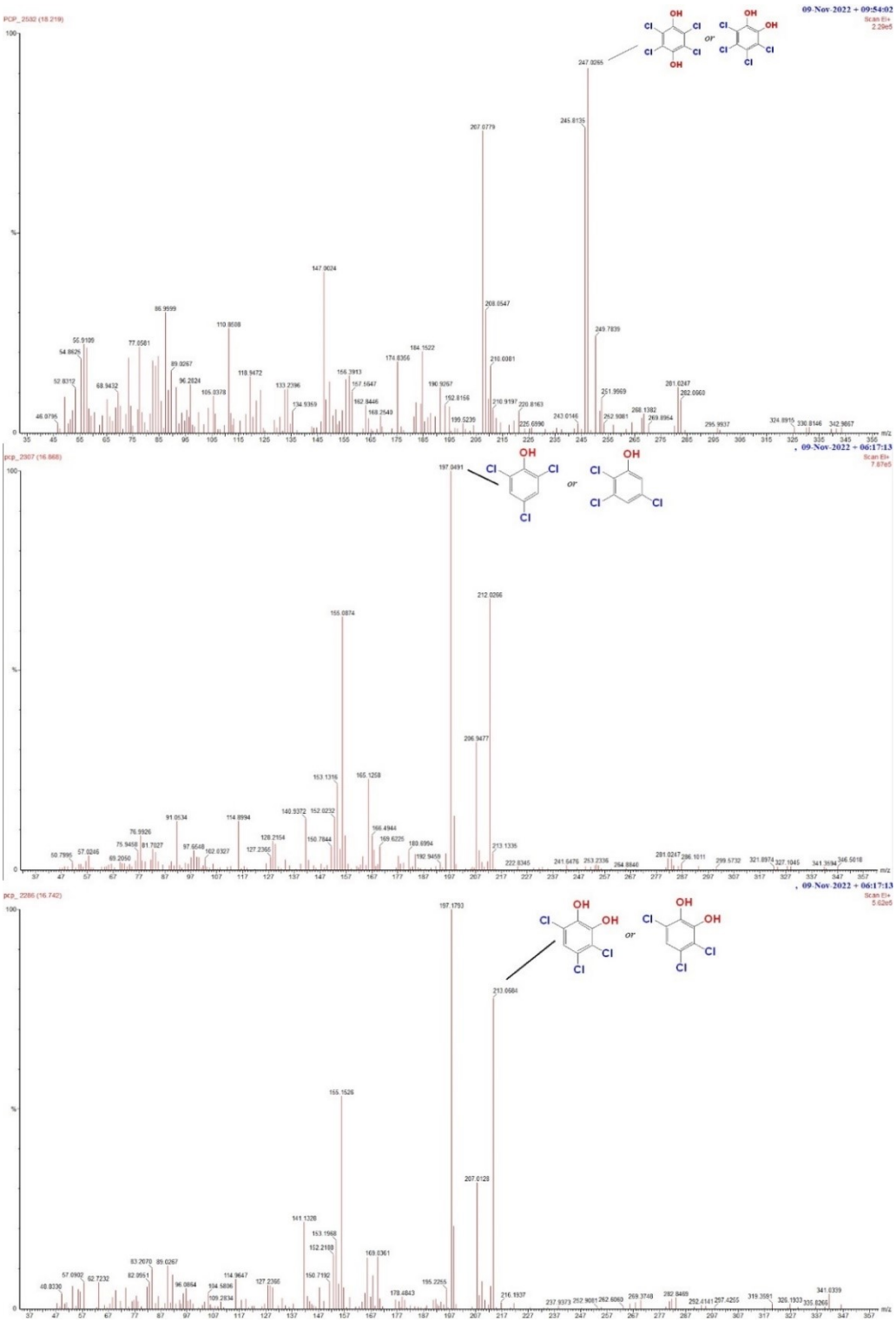


Fig. S8. Mass spectra of transformed products of PCP under photocatalytic degradation using CGBT nanocomposites.

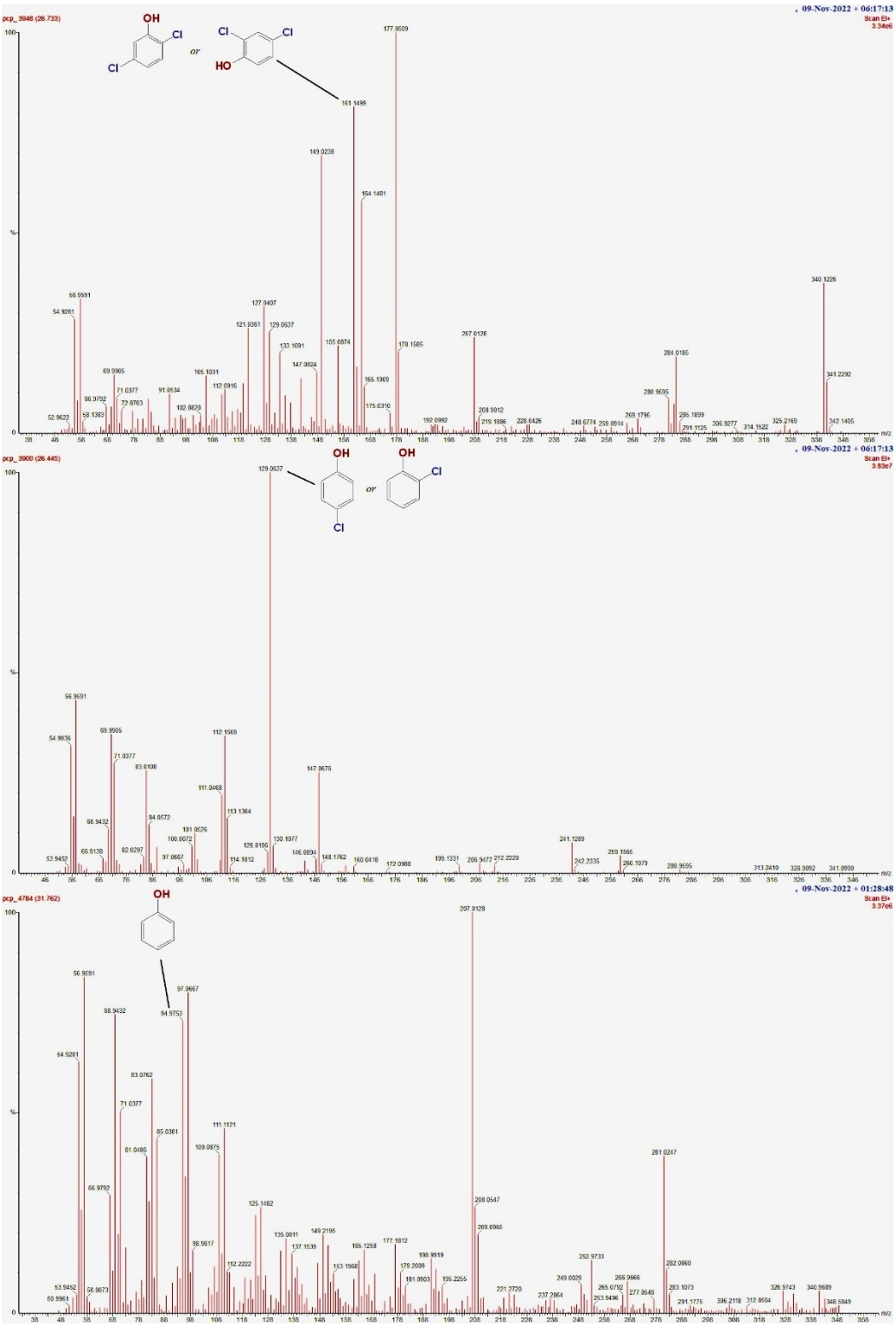


Fig. S9. Mass spectra of transformed products of PCP under photocatalytic degradation using CGBT nanocomposites.

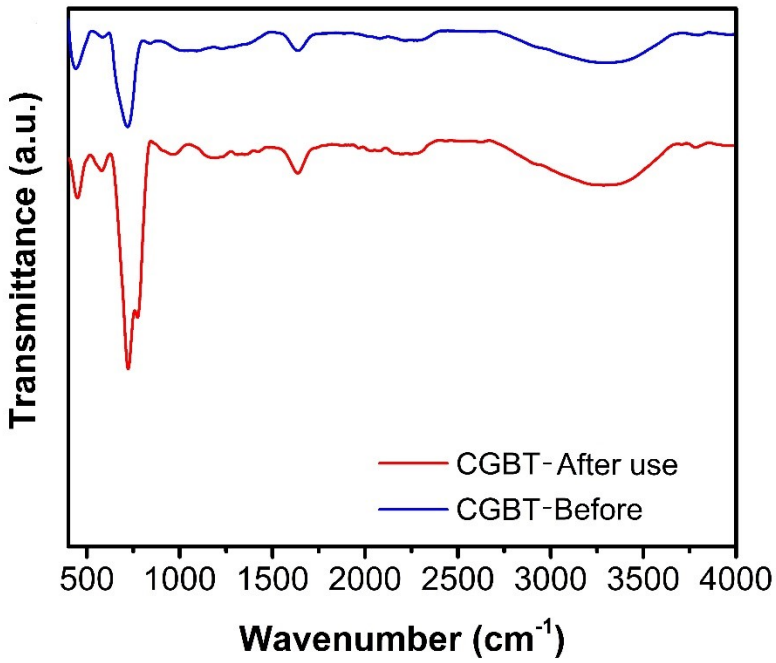


Fig. S10. FT-IR spectra of fresh and used CGBT nanocomposites after 5 consecutive cycles.

Table S1. Properties of pentachlorophenol

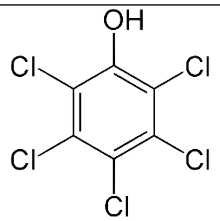
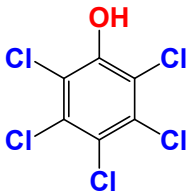
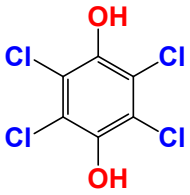
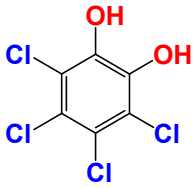
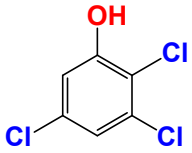
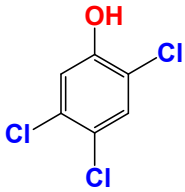
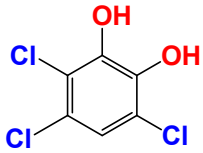
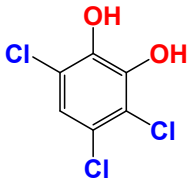
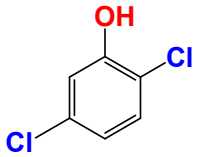
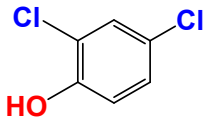
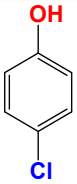
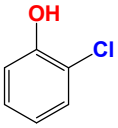
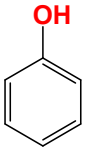
Name of clinical form	Pentachlorophenol
Molecular formula	C_6HCl_5O
Molecular weight	266.34 g mol^{-1}
Aqueous solubility	0.020 g L^{-1} at 30 °C
Chemical structure	

Table S2. Identified transformed products of pentachlorophenol by GC-MS

Substrate	Rt (min)	Chemical formula	Chemical structure	m/z fragments (% Similarity)
PCP	18.04	C_6HCl_5O		[M⁺] 265.86 (100); 267.87 (90); 263.77 (70)
Tetrachloro-hydroquinone (TCHC)	18.21	$C_6H_2Cl_4O_2$		[M⁺] 247.02 (95); 245.81 (70); 249.78 (20)
Tetrachloro-pyrocatechol (TCPC)	18.21	$C_6H_2Cl_4O_2$		[M⁺] 247.02 (95); 245.81 (70); 249.78 (20)
2,3,5-trichlorophenol (TCP)	16.86	$C_6H_3Cl_3O$		[M⁺] 197.04 (100)
2,4,5-trichlorophenol (TCP)	16.86	$C_6H_3Cl_3O$		[M⁺] 197.04 (100)
3,5,6-trichloro-1,2-pyrocatechol	16.74	$C_6H_3Cl_3O_2$		[M⁺] 213.06 (80)

(TCPC)				
3,4,6-trichloro--1,2-pyrocatechol (TCPC)	16.74	$C_6H_3Cl_3O_2$		[M⁺] 213.06 (80)
2,5-dichlorophenol (DCP)	26.73	$C_6H_4Cl_2O$		[M⁺] 161.14 (80); 164.14 (80); 165.19 (10)
2,4-dichlorophenol (DCP)	26.73	$C_6H_4Cl_2O$		[M⁺] 161.14 (80); 164.14 (80); 165.19 (10)
4-chlorophenol	26.44	C_6H_5ClO		[M⁺] 129.06 (100); 128.01 (10); 130.10 (10)
2-chlorophenol	26.44	C_6H_5ClO		[M⁺] 129.06 (100); 128.01 (10); 130.10 (10)
Phenol	31.72	C_6H_6O		[M⁺] 94.97 (65)
Ring opening products				

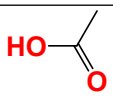
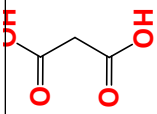
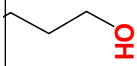
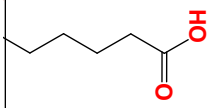
Formic acid	
Acetic acid	
Malonic acid	
1,3-Propanediol	
Adipic acid	

Table S3. Performance based comparison of our synthesized biochar-TiO_2 hybrid material with the reported biomass derived-TiO_2 photocatalysts and the photocatalyst utilized for the degradation of PCP.

Biomass derived-TiO_2 photocatalysts						
Photocatalyst	Target pollutant	Experimental conditions*	QY# (molecule/photon)	STY (molecules/photon/g)	FoM (L/g/mol/J/h)	Ref.
Coffee-ground biochar-TiO_2 (CGBT)	Pentachloro phenol (PCP)	C_o=10 mg/L; *t* = 60 min; pH 5; $[Cat.]_o$= 1 g/L; Light source: Hg lamps (UV light); $t_{vol.}$ = 50 mL; Degradation=96.1%	3.07E-07	6.14E-06	3.24E-09	This study
Commercial TiO_2	PCP	C_o=10 mg/L; *t* = 60 min; pH 5; $[Cat.]_o$= 1 g/L; Light source: Hg lamps (UV light); $t_{vol.}$ = 50 mL; Degradation=49.3%	1.58E-07	3.15E-06	8.53E-10	This study
Synthesized TiO_2	PCP	C_o=10 mg/L; *t* = 60 min; pH 5; $[Cat.]_o$= 1 g/L; Light source: Hg lamps (UV light); $t_{vol.}$ = 50 mL; Degradation=57.8%	1.85E-07	3.70E-06	1.17E-09	This study

Soft wood pellets biochar-TiO_2	Phenol	C_o=50 mg/L; t = 240 min; $[Cat.]_o$= 1 g/L; Light source: Hg lamps (UV light); $t_{vol.}$ = 150 mL; Degradation=64.1%	7.94E-08	5.30E-07	5.59E-10	5
TiO_2/Soft wood pellets carbon composite	Phenol	C_o=50 mg/L; t = 240 min; $[Cat.]_o$= 3.3 g/L; Light source: Hg lamps (UV light); $t_{vol.}$ = 150 mL; Degradation=44.3%	5.49E-08	1.10E-07	8.01E-11	6
Ag/TiO_2/ walnut shell biochar	Methylene orange dye	C_o=20 mg/L; t = 60 min; $[Cat.]_o$= 0.25 g/L; Light source: Hg lamps (UV light); $t_{vol.}$ = 40 mL; Degradation=97.4%	4.02E-08	4.02E-06	1.70E-09	7
Peanut shells biochar/TiO_2	Methylene blue dye	C_o=30 mg/L; t = 90 min; $[Cat.]_o$= 1 g/L; Light source: Hg lamps (UV light); $t_{vol.}$ = 40 mL; Degradation=98%	2.72E-08	6.80E-07	2.92E-10	8
TiO_2/Coconut shell biochar composite	Reactive Brilliant Blue	C_o=30 mg/L; t = 80 min; $[Cat.]_o$= 6 g/L; Light source: Hg lamps (UV light); $t_{vol.}$ = 200 mL; Degradation=81.1%	2.18E-08	1.82E-08	3.24E-11	9
TiO_2/Walnut shells biochar composite	Methylene orange dye	C_o=20 mg/L; t = 150 min; $[Cat.]_o$= 0.25 g/L; Light source: Hg lamps (UV light); $t_{vol.}$ = 40 mL; Degradation=96.8%	6.39E-09	6.39E-07	2.68E-10	10
Paper mill Sludge biochar-	Methylene orange dye	C_o=5 mg/L; t = 840 min; $[Cat.]_o$= 0.1 g/L; Light source: Hg lamps	6.14E-09	1.23E-06	5.86E-10	11

TiO_2 magnetic		(UV light); $t_{vol.}$ = 50 mL; Degradation=87%				
Sugarcane bagasse biochar/H_2-TiO_2	Enrofloxacin	C_o=3.6 mg/L; t = 180 min; $[Cat.]_o$=0.1 g/L; Light source: Xe lamps (Visible light); $t_{vol.}$ = 200 mL; Degradation=95.6%	1.22E-09	6.08E-08	1.47E-10	12
Macroalgae-based biochar/TiO_2	Methylene blue dye	C_o=5 mg/L; t = 240 min; $[Cat.]_o$=2 g/L; Light source: Xe lamps (Visible light); $t_{vol.}$ = 50 mL; Degradation=99.4%	7.02E-10	7.02E-09	4.41E-12	13
TiO_2/Corn cob biochar composite	Sulfamethoxazole	C_o=10 mg/L; t = 360 min; pH 4; $[Cat.]_o$= 5 g/L; Light source: Hg lamps (UV-C); $t_{vol.}$ = 100 mL; Degradation=91%	2.96E-10	5.91E-10	4.11E-13	14
		Photocatalysts for pentachlorophenol removal				
Ag_2CrO_4	Sodium pentachlorophenate (PCP-Na)	C_o=50 mg/L; t = 60 min; pH 9.5; $[Cat.]_o$= 0.75 g/L; Light source: Xe lamps (Visible); $t_{vol.}$ = 200 mL; Degradation=100%	1.98E-07	1.32E-06	3.34E-09	15
Graphene- TiO_2 nanocomposites	PCP-Na	C_o=50 mg/L; t = 120 min; $[Cat.]_o$= 0.2 g/L; Light source: Hg lamps (UV light); $t_{vol.}$ = 500 mL; Degradation=97%	3.15E-08	3.15E-07	1.68E-09	16
Vanadium-N-TiO_2	PCP-Na	C_o=20 mg/L; t = 120 min; $[Cat.]_o$= 0.4 g/L; Light source: Xe lamps (Visible light); $t_{vol.}$ = 500 mL;	3.11E-08	1.56E-07	8.05E-10	17

		Degradation=82%				
Nanoporous Ti-doped *β*-Bi_2O_3	PCP	C_o=10 mg/L; *t* = 60 min; pH 11.2; $[Cat.]_o$= 0.5 g/L; Light source: Xe lamps (Visible); $t_{vol.}$ = 100 mL; Degradation=98%	2.10E-08	4.21E-07	5.21E-10	18
Bi/SnO_2/TiO_2-graphene nanocomposite	PCP	C_o=20 mg/L; *t* = 120 min; pH 3; $[Cat.]_o$= 0.3 g/L; Light source: Hg lamps (UV light); $t_{vol.}$ = 100 mL; Degradation=84%	1.04E-08	3.46E-07	3.19E-10	19
Mesoporous TiO_2 microspheres	PCP	C_o=10 mg/L; *t* = 135 min; pH 9; $[Cat.]_o$= 1 g/L; Light source: Hg lamps (UV-C light); $t_{vol.}$ = 100 mL; Degradation=98%	6.88E-09	6.88E-08	5.14E-11	20
N–F–TiO_2	PCP	C_o=5 mg/L; *t* = 120 min; pH 5; $[Cat.]_o$= 0.5 g/L; Light source: Xe lamps (Visible light); $t_{vol.}$ = 250 mL; Degradation=95%	4.42E-09	3.54E-08	1.06E-10	21
Ag/TiO_2 nanoparticles	PCP	C_o=20 mg/L; *t* = 160 min; $[Cat.]_o$= 0.15 g/L; Light source: Hg lamps (UV light); $t_{vol.}$ = 20 mL; Degradation=98%	4.16E-09	1.66E-06	3.58E-10	22
$Bi_{12}SiO_{20}$	PCP	C_o=4 mg/L; *t* = 120 min; pH 6.1; $[Cat.]_o$= 0.25 g/L; Light source: Xe lamp (Visible light); $t_{vol.}$=200 mL; Degradation=95%	4.09E-09	8.17E-08	1.97E-10	23
$FeNi_3$/SiO_2/	PCP	C_o=10 mg/L; *t* = 120 min; pH 3;	3.62E-09	1.45E-08	9.14E-	24

ZnO magnetic nanocomposite		$[Cat.]_o$= 0.5 g/L; Light source: Xe lamps (Visible light); $t_{vol.}$ = 500 mL; Degradation=100%			11	
Ag/TiO_2 nanotubes	PCP	C_o=10 mg/L; t = 180 min; $[Cat.]_o$= 1 g/L; Light source: Xe lamps (Visible light); $t_{vol.}$ = 500 mL; Degradation=99%	2.48E-09	4.96E-09	3.10E-11	25
α-Fe_2O_3/ZnO composites	PCP	C_o=10 mg/L; t = 240 min; pH 9; $[Cat.]_o$= 1.5 g/L; Light source: Xe lamps (Visible light); $t_{vol.}$ = 100 mL; Degradation=98%	1.31E-09	8.76E-09	1.08E-11	26
$Bi_2O_3/TiO_{2-x}B_x$	PCP	C_o=10 mg/L; t = 300 min; $[Cat.]_o$= 1 g/L; Light source: Xe lamps (Visible light); $t_{vol.}$ = 50 mL; Degradation=85%	3.65E-10	7.30E-09	3.92E-12	27

C_o: Initial concentration of pollutants; t: treatment time; $[Cat]_o$: Catalyst dosage; Hg: Mercury; Xe: Xenon; t_{vol}: Treatment volume.

** In calculating the photon flux, light intensity (mW cm^{-2}) was considered based on the reported in the cited studies and where not mentioned, the common conditions of 100 mW cm^{-2} were assumed as a reference value for performance evaluation.*

 # QY values were calculated based upon the peak wavelength of the light source reported in the cited papers. For the reference without specific wavelength information, the common UV light (λ=365 nm) and visible light (λ=420 nm) conditions were assumed as a reference value for performance evaluation.

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