Supplementary Information

Synergistic design of graphene oxide mediated polyaniline/α-Fe₂O₃ ternary heterostructure: Advancing photocatalytic degradation and adsorption efficiency

Iftekhar Ahmad[#a], Mohammad Saud Athar[#a], Mohammad Muneer[a]*, Hatem M. Altass[b], Raad Felemban[c], Saleh A. Ahmed[b]*

[#]Both authors have equal contributions to this work

[a]Department of Chemistry, Faculty of Science, Aligarh Muslim University, Aligarh 202002, India

[b]Department of Chemistry, Faculty of Applied Sciences, Umm Al-Qura University, 21955 Makkah, Saudi Arabia

[c]Research Laboratories Unit, Faculty of Applied Science, Umm Al-Qura University, Makkah, Saudi Arabia

*Corresponding Author E-mail: m.muneer.ch@amu.ac.in; saleh_63@hotmail.com

---

S2.1. Chemicals requirements

Brilliant green, Ciprofloxacin, graphite, 1,2-propanediamine was bought from Sigma-Aldrich. Aniline, hydrochloric acid and ethanol were purchased from Fisher Pvt. Ltd. Thiourea, $FeCl_3 \cdot 6H_2O$, benzoquinone, ammonium persulfate and isopropyl alcohol were acquired from Merck India Pvt Ltd.

S2.2. Materials characterization

An X-ray beam diffractometer (Shimadzu XRD model 6100) with monochromatic copper radiation [Cu Ka=1.544414 Å] at a scanning angle of 5° to 80° of 2θ was used to investigate the crystalline natures and phases of all the photocatalytic materials. The Perkin-Elmer-

Lambda 35 UV–vis spectrophotometer was used to measure diffuse reflectance spectra (DRS) in the ultraviolet-visible (UV-vis) range of 300–800 nm. The FTIR spectra of the synthesized materials in the KBr pellet were obtained using the PerkinElmer Spectrum 2 model. X-ray photoelectron spectroscopy was used to obtain a quantitative elemental composition and chemical state information from the surface of the samples using a PHI-5000 VersaProbe III Model with AlKa monochromatic radiation (h=1486.6 eV). To identify the morphological appearance of the materials, FESEM (JEOL JSM-7600 F) and FEG-TEM (FEI, TECNAI G2, F30) were used. Additionally, the BET surface area and porosity of the photocatalytic materials was analyzed using the TriStar II 3020 Version 3.02 instrument. The photoluminescence (PL) spectra of the synthesized samples were measured using a PerkinElmer LS 55 fluorescence spectrometer. Electrochemical impedance spectroscopy (EIS) and Mott–Schottky experiments were conducted using the electrochemical workstation (Metrohm Autolab), which was performed in a 0.1 M Na_2SO_4 solution with a pH of 7.

S2.3. Active species generation experiments

Trapping investigations were conducted in order to identify the principal reactive species responsible for pollutant degradation over the 10PGF ternary composite. Under illumination, various scavengers such as benzoquinone, isopropyl alcohol, and EDTA were introduced to the aqueous suspension of pollutants to capture the $O_2^{\bullet-}$, $\bullet OH$, and h^+, respectively. The reaction conditions were the same as in the photodegradation experiment, with the difference that the scavengers were added before the photocatalyst. The concentrations of all scavengers were 2.0 mM, and the reactions were monitored by Perkin-Elmer-Lambda 35 UV–vis spectrophotometer.

To estimate the concentration of superoxide radicals ($O_2^{\bullet-}$), nitro blue tetrazolium (NBT) transformation experiments were conducted in the presence of 10PGF ternary composite. The

experimental procedure was similar to the degradation experiment, except that 0.015 mM nitro blue tetrazolium NBT) in an aqueous solution was used instead of the organic pollutants. The decrease in NBT concentration was tracked by recording the absorbance at around 259 nm with a Perkin-Elmer Lambda 35 UV–vis spectrophotometer.

To determine the involvement of hydroxyl radicals ($^{\bullet}$OH) in the degradation processes, the PL terephthalic acid probe method was employed. A solution was prepared by dissolving terephthalic acid (3 mmol L^{-1}) and NaOH (3 mmol L^{-1}) in 200 mL of double-distilled water. After incorporating 200 mg of the 10PGF ternary composite into the solution, the mixture was subjected to 15 min of sonication. The solution was then exposed to irradiation under the same conditions as the photocatalytic experiments. Samples were collected periodically from the reaction mixture, and their fluorescence was measured using a PerkinElmer LS 55 fluorescence spectrometer.

S2.4. Adsorption experiments

A study was carried out to evaluate the pollutant adsorption efficiency of the 10PGF ternary composite, focusing on BrG removal. In the experiment, 10 mg of the composite was added to 10 mL of BrG solutions with varying concentrations (5 to 40 mg/L) and agitated in the dark for 8 h. For kinetic analysis, 1 g/L of the composite was mixed with 100 mL of 15 ppm BrG solution, with samples collected at regular intervals over 8 h. The absorbance of the samples was measured using a Perkin Elmer UV-Vis spectrophotometer.
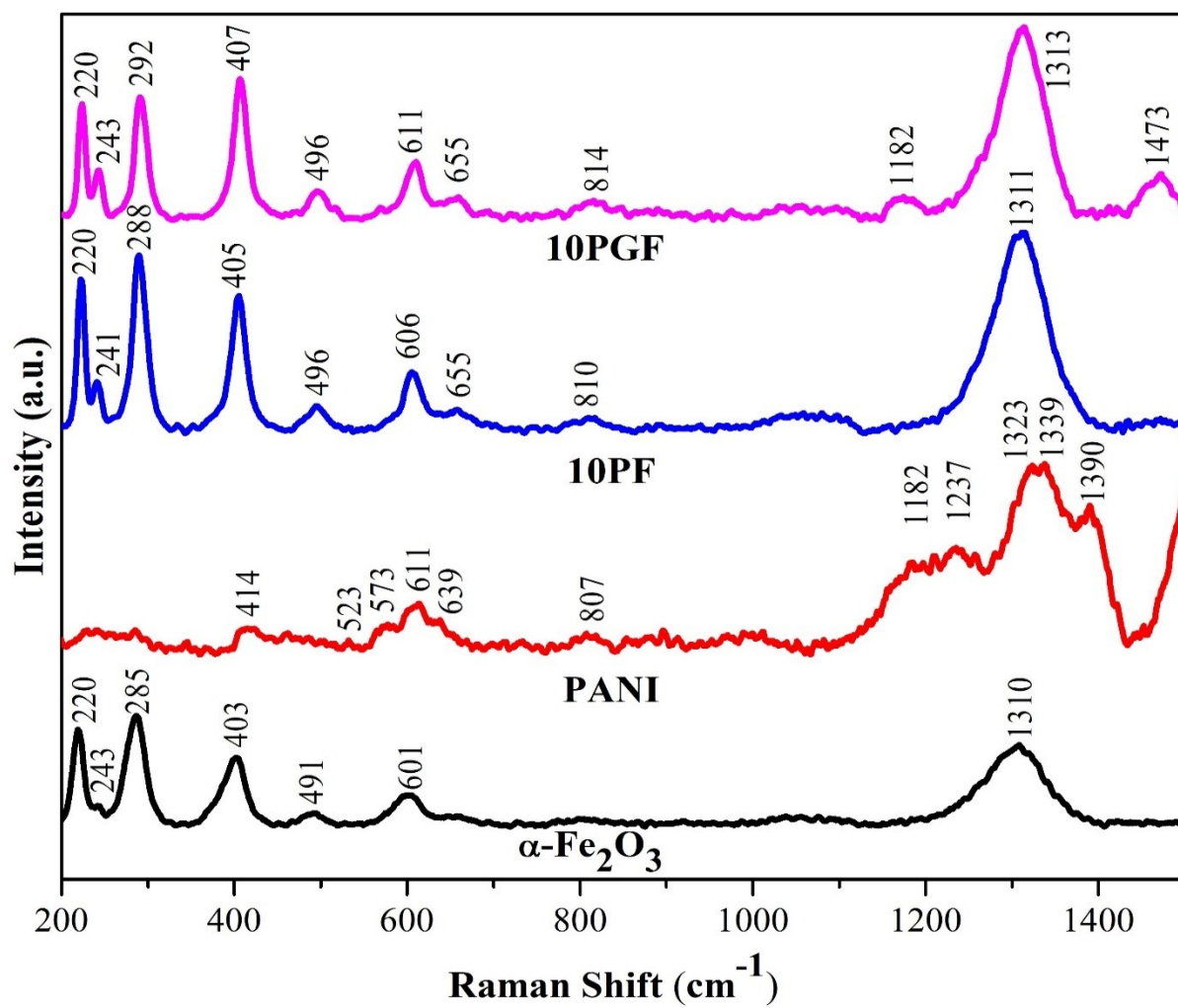
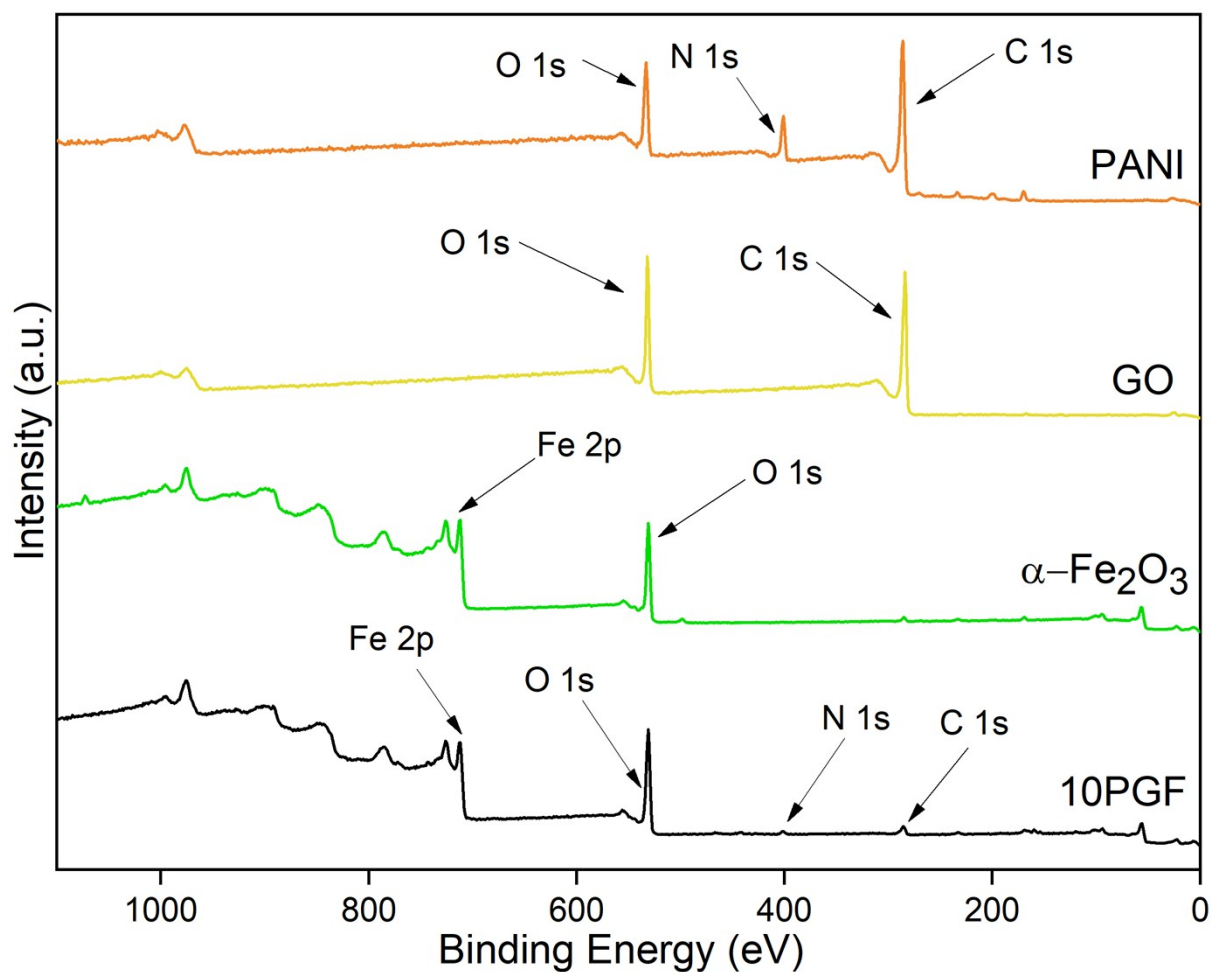**Fig. S1.** Raman spectra of PANI, α-Fe$_2$O$_3$ 10PF and 10PGF ternary composite.

Fig. S2. Survey scan XPS spectra of PANI, GO, α-Fe$_2$O$_3$ and 10PGF ternary composite.
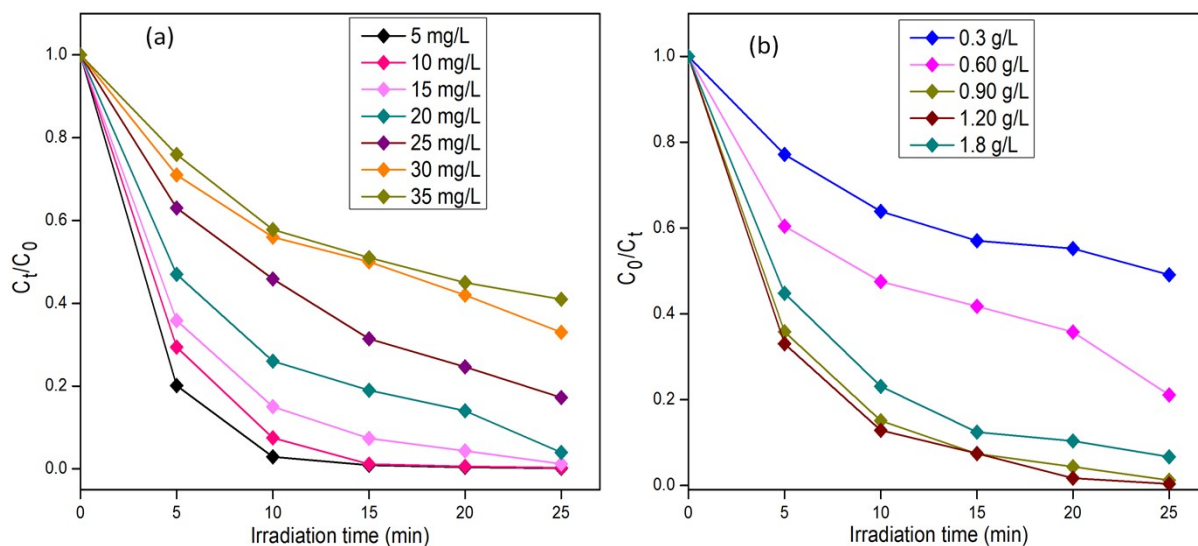

Fig. S3. Effects of initial concentration of BG dye over 10PGF ternary composite (a) and effect of varied doses of 10PGF ternary composite for BG degradation (b).
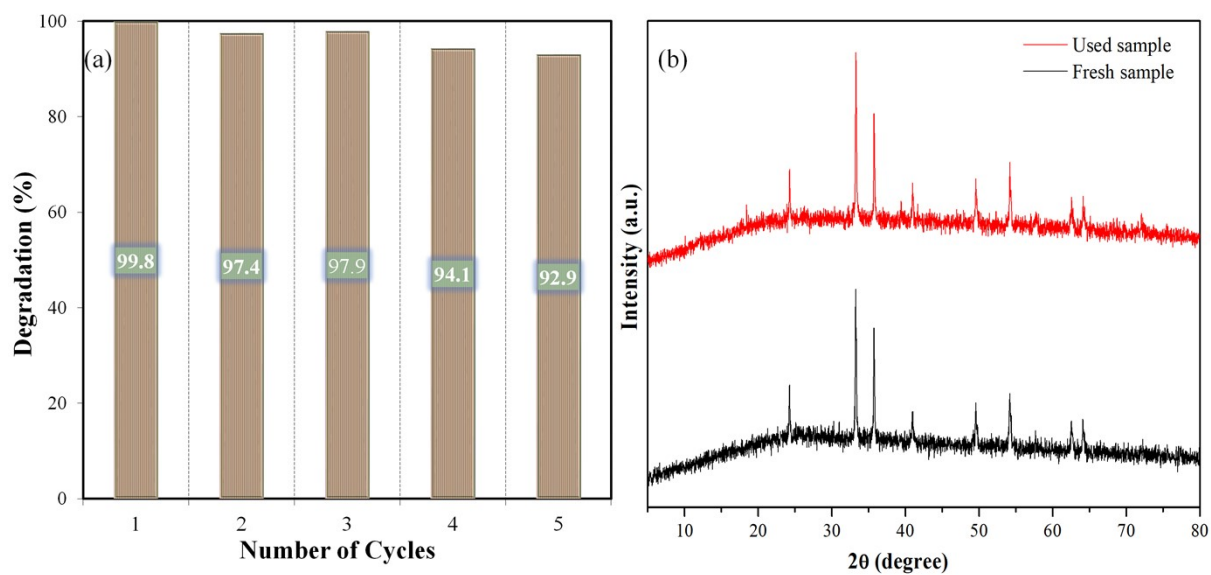
Fig. S4. Reusability study of the 10PGF ternary composite (a) and XRD patterns comparing fresh and used 10PGF samples (b).

Table S1. Pseudo-first order rate constants along with their respective R^2 values obtained with the various photocatalysts used in degradation of BrG.

Sample	Apparent rate constant (k_{app})(min^{-1})	R^2
Blank	0.0025	0.9808
PANI	0.01474	0.93461
$\alpha-Fe_2O_3$	0.02227	0.94375
10PF	0.04819	0.93926
5PGF	0.12226	0.9578
10PGF	0.22204	0.95276
30PGF	0.07857	0.93218
40PGF	0.05537	0.89393

Table S2. Pseudo-first order rate constants along with their respective R^2 values obtained with the various photocatalysts used in degradation of CIP.

Sample	Apparent rate constant (k_{app})(min^{-1})	R^2
Blank	0.00065	0.9834
PANI	0.00332	0.92153
$\alpha-Fe_2O_3$	0.00481	0.88509
10PF	0.00822	0.90571
5PGF	0.02151	0.96989
10PGF	0.02955	0.9893
30PGF	0.0129	0.88676
40PGF	0.00997	0.89521

Table S3. Parameters of Langmuir and Freundlich isotherm models for BrG adsorption on the 10PGF composite.

Model	Parameters	BrG
Langmuir	K_L	1.328
	q_m	28.974
	Reduced- χ^2	1.8415
	R^2	0.97407
Freundlich	K_F (L mg^{-1})	15.17
	1/n	0.2755
	red- χ^2	3.124

	R^2	0.9559

Table S4. Langmuir separation factor (R$_L$) values for BrG adsorption over 10PGF composite at various initial concentrations.

Initial Concentration of BrG (mg L^{-1})	R$_L$ Values
5	0.1315
10	0.07
15	0.048
20	0.0365
25	0.0294
30	0.0246
35	0.0212
40	0.0186

Table S5. Pseudo-first and pseudo-second order parameters for BrG adsorption over 10PGF composite.

Kinetic models	Parameters	BG
Pseudo-first order	K$_1$	0.01932
	q$_e$	13.449
	R^2	0.94274
	Red-χ^2	0.77878
Pseudo-second order	K$_2$	0.00171
	q$_e$	15.159

	R^2	0.98892
	Red-χ^2	0.15318