Supplementary Information (SI) for Journal of Materials Chemistry A.

Supplementary materials

High-energy gamma photon engineering of g-C_3N_4: low dose rate radiation as a metal-free modification enhancing solar-driven photoactivity

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1. Reactive oxygen species generation – experimental optimalization

The experimental optimalization of the conditions for scavenging superoxide anion radicals and hydroxyl radicals was conducted under solar light irradiation. The NBT concentrations used in the process were 0.011 mM, 0.025 mM, 0.038 mM, 0.05 mM, and 0.08 mM. The concentrations range was chosen based on the photocatalyst dose used in the experiments and the reported concentration for g-C_3N_4 materials in the literature (0.025 mM - 0.075 mM [S1-4]). The results obtained during the experiments are shown in Figure S1a.

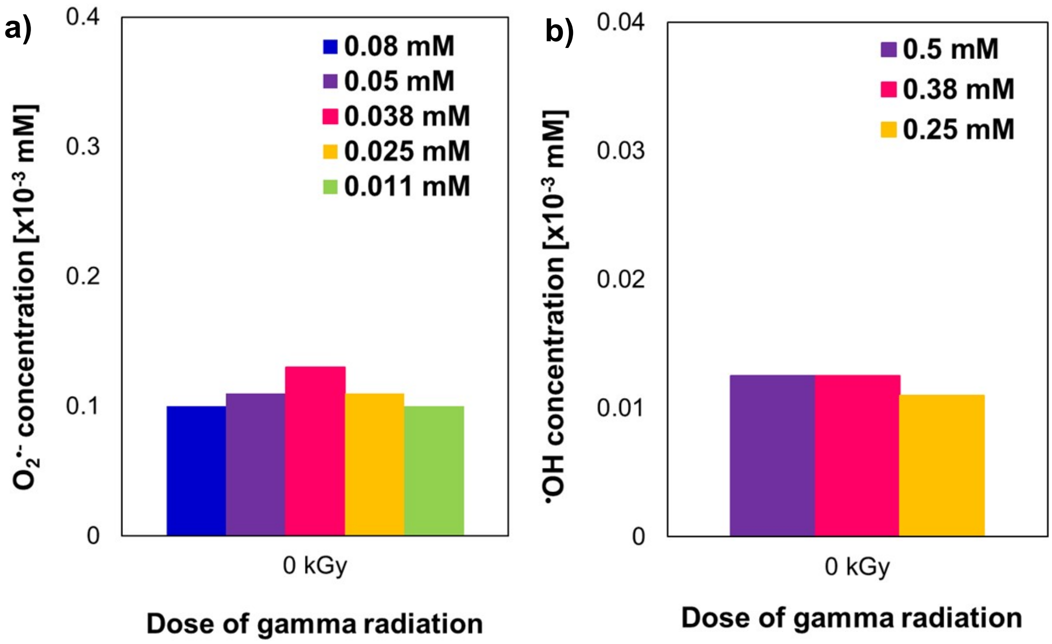


Figure S1. Detection of **a)** superoxide anion radicals and **b)** hydroxyl radicals generated by g-C_3N_4 samples using NBT and TA, respectively.

Using a 0.038 mM NBT concentration during test, the greatest reduction in NBT concentration after 60 min of solar illumination was observed, corresponding to the highest generation of superoxide anion radicals [S5]. In contrast, higher concentrations, such as 0.05 mM and 0.08 mM, resulted in a smaller decrease in NBT concentration, indicating lower superoxide anion radical production. This effect is likely due to the adsorption of NBT onto the surface of the g-C_3N_4 samples, which restricts the adsorption and subsequent reduction of oxygen to $O_2^{\bullet-}$. Moreover, NBT adsorbed on the photocatalyst surface can hinder light absorption by g-C_3N_4, further suppressing its photocatalytic activity. The optimal NBT concentration was determined to be 0.038 mM, as it enabled the highest detection of superoxide anion radicals, suggesting that inhibitory effects on photocatalytic performance were minimized.

The detection of $^{\bullet}OH$ during solar irradiation of g-C_3N_4 samples was conducted with TA in 0.25 mM, 0.38 mM, and 0.5 mM (Figure S1b). The TA concentration range reported for probing production of $^{\bullet}OH$ is 0.1 mM – 3 mM [S6-8]. All tested concentrations (0.5 mM, 0.38 mM, and 0.25 mM) indicating comparable $^{\bullet}OH$ concentrations generated by g-C_3N_4 during illumination. Based on these findings, the 0.38 mM probe concentration was selected as optimal for further experiments, as it ensured sufficient detection sensitivity while minimizing potential probe-induced interferences.

2. Mechanism of decomposition of imatinib mesylate (IMA)

The concentration of the scavengers used was selected to ensure maximum scavenging capacity for the reactive species generated *in situ*, which are involved in the degradation of imatinib. The experiments were conducted on the sample exhibiting the highest photocatalytic activity. The investigated concentration range for the hole scavenger Na_2EDTA was from 0.04 mM to 15 mM, and the results are presented in Figure S2.

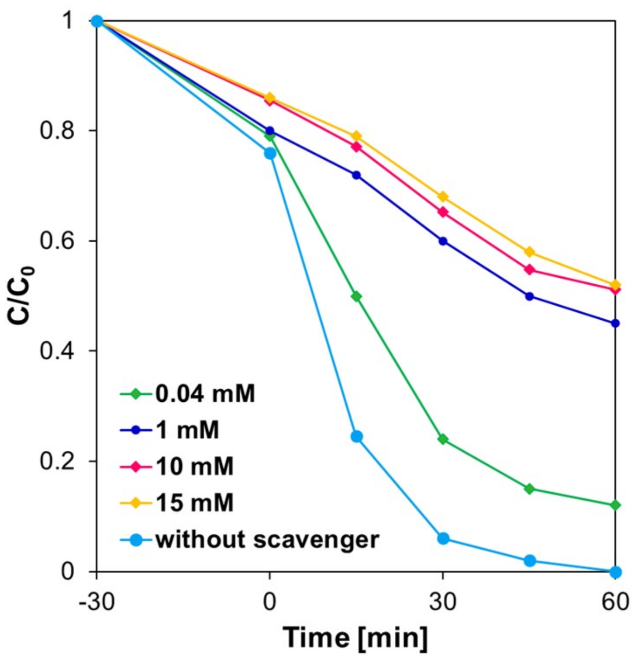
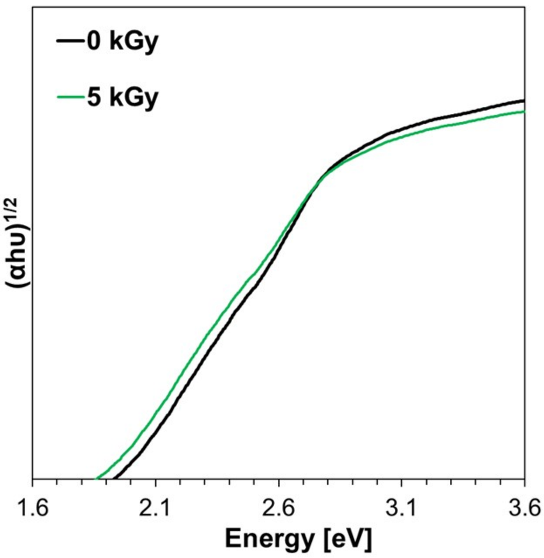


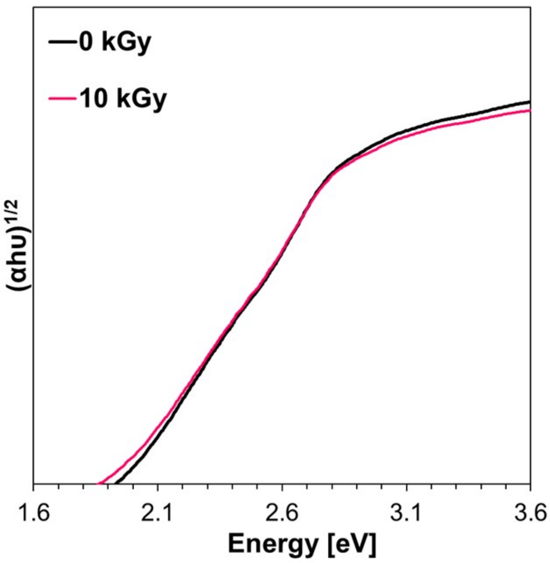
Figure S2. Effect of Na_2EDTA concentration as a hole scavenger on the inhibition of IMA degradation under solar light irradiation

In photocatalytic studies involving scavengers, each scavenger is typically used at the same concentration. Due to Na_2EDTA and tert-butyl alcohol concentration used in our experiments was 10 mM. At this concentration tert-butyl alcohol also ensure the maximum scavenging capacity. However, the use of 10 mM ascorbic acid significantly altered the solution's pH, potentially affecting the degradation conditions compared to those without scavengers. To maintain a pH comparable to the initial pH of the IMA solution, the ascorbic acid concentration was reduced to 1 mM. A control experiment was performed using both 1 mM and 10 mM ascorbic acid as scavenger of superoxide anion radical, and no differences in inhibition were observed. Thus, 1 mM ascorbic acid ensures maximum scavenging efficiency while minimizing pH-related interference. The obtained rate constants (k_{app}) for imatinib degradation in the presence of scavengers and the selected g-C_3N_4 sample are listed in Table S1.

Table S1. Rate constants k_{app} of IMA degradation in the presence of scavengers under UV-vis and solar light by g-C_3N_4 radiated in the dose of 50 kGy

Type of scavenger	Type of light					
	UV-vis			Artificial solar light		
	k_{app} [min^{-1}]	R^2	Inhibition [%]	k_{app} [min^{-1}]	R^2	Inhibition [%]
Without scavenger	0.359	0.986	-	0.081	0.998	-
Na_2EDTA	0.019	0.991	94	0.009	0.995	89
t-butyl alcohol	0.074	0.990	79	0.046	0.995	44
Ascorbic acid	0.007	0.993	98	0.002	0.990	98





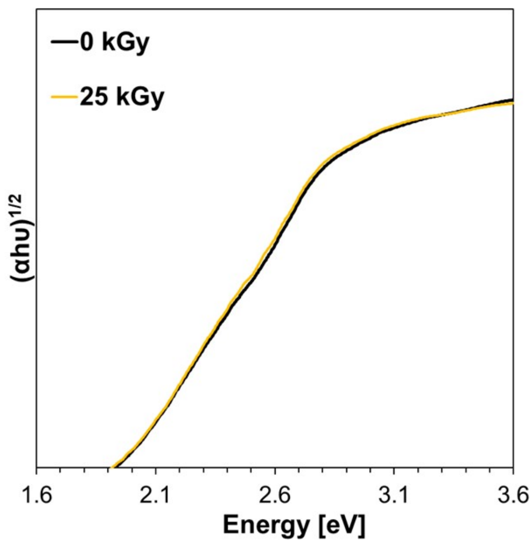


Figure S3. Kubelka-Munka transformation for selected gamma irradiated g-C_3N_4

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