Response to the referee's remarks and questions

Reviewer:

Dr. Dániel Zámbó

First of all, I would like to thank the Reviewer very much for the valuable and important remarks, comments, and questions.

1. **It is stated that para-nitrophenol enables the assessment of a photocatalyst's efficiency in real-world pollutants. What are the advantages of para-nitrophenol over the colored dyes which make it a better model pollutant? Can the degradation mechanism of PNP molecule be used in the explanation of other (real) pollutants' behavior?**

Answer: Thanks to the Reviewer for this insightful question, which makes a good point about how important it is to choose model pollutants that really show the problems that researchers face in photocatalysis.

Para-nitrophenol offers several key advantages over coloured dyes as a model pollutant for photocatalyst evaluation. Unlike dyes such as Rhodamine B or methylene blue, para-nitrophenol is colourless, eliminating spectral interference from chromophore degradation or byproduct formation. Degradation is measured cleanly at 318 nm by direct pollutant loss (<3% self-photolysis in blanks; Figure 5.9). Para-nitrophenol also better represents real-world nitroaromatic pollutants from industrial sources (explosives, pesticides, pharmaceuticals), which are toxic, persistent, and environmentally relevant, unlike synthetic dyes that are used primarily for visual decolorization tests. Its single nitro (-NO_2) group enables clear mechanistic tracking of specific pathways (hydroxylation, nitro-reduction) without the complexity of multiple chromophores.

The way that para-nitrophenol breaks down, starting with $^{\bullet}OH$ radicals accumulating across the ring, changing the nitro group to amino forms, and finally cleaving the structure, is similar to how other complex pollutants like phenols, chlorophenols, or nitrobenzene found in industrial effluent break down [1]. The study of para-nitrophenol indicates that our photocatalyst can use holes, electrons, $^{\bullet}OH$, and superoxide to break down tough aromatics. This gives us a good idea of how to deal with actual effluents that are more complex than simply dyes.

2. **In case of modification with silver species, can the Candidate imagine charge transfer processes from the AgNPs/clusters towards the g-C_3N_4 under UV illumination fulfilling the resonance energy of the Ag NPs plasmon mode? If yes, which process could be more probable: plasmon-induced charge transport or hot electron injection?**

Answer: Thank you for this insightful question on plasmonic charge transfer in Ag-modified g-C_3N_4 under UV light.

Yes, charge transfer from Ag nanoparticles or clusters to g-C_3N_4 conduction band is feasible under UV illumination. UV photons (around 3.3 eV, 374 nm LED) exceed Ag LSPR (localized surface plasmon resonance) energy (~2.5-3.0 eV), exciting plasmon oscillations that generate hot electrons above Ag Fermi level. These can inject into g-C_3N_4 conduction band via Schottky barrier, supplementing g-C_3N_4 intrinsic bandgap excitation (~2.7 eV). Our Tauc plots (Figure A5.7) show narrowed band gaps (2.79-2.88 eV) and visible extension, with Ag acting as a dual electron sink (UV trapping from g-C_3N_4) and donor.

Hot electron injection is more probable than plasmon-induced charge transport. Hot electrons from LSPR decay directly tunnel to g-C_3N_4 conduction band (<1 ps timescale), creating long-lived carriers for redox (evidenced by 21-27% para-nitrophenol degradation under visible source vs. 0% pure g-C_3N_4; Table 5.6). Plasmon field enhancement plays a secondary role here [2].

3. **Ag-loaded samples can be catalytically active due to the surface silver ion clusters or the formed Ag nanoparticles. It is obvious from the TEM-EDX that light irradiation facilitates the formation of nanoparticles, but what is the form of silver in the beginning of the reaction? If silver binds to the surface as ion clusters, how stable they can be in aqueous solution during the catalytic reaction itself?**

Answer: Thanks to the Reviewer for this extremely important question concerning the stability and nature of silver in the Ag-modified samples.

Prior to irradiation (dark conditions), silver is expected to be present predominantly as surface-anchored Ag^+ species and very small Ag^+ clusters coordinated to electron-rich nitrogen (and possibly oxygen-containing) sites of g-C_3N_4, together with a minor fraction of pre-formed metallic Ag^0 originating from the synthesis step. These silver species are therefore mainly immobilized at the catalyst surface through electrostatic interactions rather than existing as free Ag^+/Ag^0 in the aqueous phase.

During photocatalysis, photogenerated electrons from $g\text{-}C_3N_4$ progressively reduce the surface Ag^+ species to metallic Ag^0, which explains the clear growth of Ag nanoparticles observed after UV/Vis irradiation in our TEM-EDX results (Figure 5.14-Figure 5.16). Regarding stability, the initial Ag^+/Ag^+-cluster species can be sufficiently stable at the beginning of the aqueous reaction because anchoring to the $g\text{-}C_3N_4$ surface suppresses leaching, and cardamom extract further aids binding and stabilization through its polyphenolic compounds that coordinate with silver ions. However, these species remain photo-labile and are driven under irradiation toward the formation of metallic Ag^0 clusters/nanoparticles. As a result, the ionic silver state serves as a transient precursor, while metallic Ag nanoparticles become the dominant, more stable catalytic form under operating light conditions.

4. **What type of other, earth-abundant photocatalyst could show similar electronic structure for utilizing both UV- and visible light excitation? Can p-type Cu_2O or n-type $\alpha\text{-}Fe_2O_3$ also be considered with or without metal/metal-chalcogenide decoration?**

Answer: Thanks to the Reviewer for this forward-looking query on earth-abundant alternatives to $g\text{-}C_3N_4$ that could use both UV and visible light in the same way as $g\text{-}C_3N_4$ does.

Earth-abundant photocatalysts, such as CdS (2.4 eV), $ZnIn_2S_4$ (2.3-2.7 eV), and $BiVO_4$ (2.4 eV), have electronic structures similar to $g\text{-}C_3N_4$, with moderate band gaps (2-3 eV) allowing strong UV and visible-light response and suitable band positions for photocatalysis. CdS offers high visible absorption and a favorable conduction band for pollutant degradation and H_2 evolution, but needs photo corrosion protection. $ZnIn_2S_4$ offers layered stability and high charge separation for sustained activity, while $BiVO_4$ excels in water oxidation with strong n-type behavior. These three photocatalytic alternatives effectively imitate $g\text{-}C_3N_4$ dual-light flexibility and often boost performance with metal or heterojunction decorations [3].

Yes, both p-type Cu_2O (band gap 2.0-2.2 eV) and n-type $\alpha\text{-}Fe_2O_3$ (hematite, 2.1 eV) are excellent options that are easy to find on Earth and work well for UV/visible photocatalysis, just like $g\text{-}C_3N_4$. Cu_2O has strong visible absorption and a conduction band that is well-positioned for reductions. It works well on its own but lasts longer when decorated with metals (Ag, Au) or metal-chalcogenides (Cu_2S) to prevent photo corrosion [4]. α-Fe_2O_3, on the other hand, has great stability and visible response and works well on its own in many cases but is greatly improved by cocatalysts like NiFe oxides, MoS_2, or even g-C_3N_4 heterojunctions to overcome short hole diffusion lengths [5,6]. Both are very useful for breaking down pollutants or making solar fuel, just like our Ag-modified system.

5. **What extent can the concentration of the active ingredients (phenols, flavonoids, etc.) be kept constant or controlled in case of extracting them from biological sources? Can the concentration and ratio of these active molecules change from batch-to-batch?**

Answer: No, it is not possible to maintain completely consistent amounts of phenols, flavonoids, and other active compounds derived from biological sources throughout several batches. Plants naturally change because of things like the quality of the soil, the weather, the time of year, and their genes. This can cause the overall content and the ratios between different chemicals to change by 20% to 50%. Although extraction protocols can be standardized (e.g., fixed solvent ratios, temperature, and time) and each batch can be tested using HPLC or total phenol/flavonoid assays to reduce variation, true constancy is unattainable without controlled cultivation or chemical synthesis, rendering biological extracts inherently variable despite quality control measures [7].

6. **Which nanostructure of g-C_3N_4 can provide more efficient charge carrier separation and utilization: granular or sheet-like? Melamine as precursor provides rather granular, while urea provides sheet-like carbon nitride. Can the extraction depth of the charge carrier change if the morphology changes?**

Answer: Thanks to the Reviewer for this insightful question about g-C_3N_4 morphology effects.

Sheet-like g-C_3N_4 nanostructures separate and utilize charge carriers much more effectively than granular forms [8]. In my thesis, I chose melamine as the precursor because of its high product yield (under our synthesis conditions) along with good photoactivity, which naturally produces the more compact granular morphology (with lower surface area compared to sheet-like nanostructure). Urea, by contrast, creates exfoliated sheets with much higher surface area that shorten charge diffusion paths and cut down recombination, leading to better photocatalytic activity [8].

Yes, charge extraction depth changes with morphology. Thin sheets let carriers reach the surface much faster (nanometres away) compared to thick granules (micrometres away), improving efficiency 2-5 times in photocatalysis [9].

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