Response to the referee's remarks and questions

Reviewer:

Emília Tálas

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

1. **It is written (page 57): Energy-dispersive X-ray spectroscopy (EDS) (Figure 5.3) confirmed that pristine g-C_3N_4 contains approximately 42.9 % carbon and 57.1 % nitrogen". How were these values obtained?**

Answer. Thank you for your query regarding the elemental composition values reported on page 57.

These values (42.9 at% C and 57.1 at% N) for pristine g-C_3N_4 were obtained by converting the measured EDS weight percentages (39.2 wt% C, 60.8 wt% N) into atomic percent using standard atomic masses (C: 12.01 g/mol, N: 14.01 g/mol).

The calculation proceeds as follows:

Moles of C = 39.2/12.01 ≈ 3.26,

Moles of N = 60.8/14.01 ≈ 4.34,

Total moles = 7.60; then C at% = (3.26/7.60) × 100 = 42.9%, and N at% = (4.34/7.60) × 100 = 57.1%.

This standard approach accurately reflects the materials stoichiometry as shown in Figure 5.3.

2. **Regarding the chemical state of the silver in the Ag-g-C_3N_4 nanocomposites, the following sentence can be found (page 80): „ …the Ag 3d spectrum (Figure 5.17/d) shows two spin-orbit split peaks at 368.3 and 368.4 eV, corresponding to the Ag 3d5/2 and 3d3/2 levels of metallic silver, as reported in the literature [197]". However, the cited work wrote: "Fig. 7B shows Ag 3d spectrum which could be resolved into two peaks (3d5/2 and 3d3/2) due to the spin-orbit coupling with binding energies of 368.21 and 374.17 eV, respectively. These binding energy components are attributed to metallic silver …"[O. J. Achadu, I. Uddin, and T. Nyokong, "The interaction between**

graphene quantum dots grafted with polyethyleneimine and Au@Ag nanoparticles: Application as a fluorescence 'turn-on' nanoprobe," Journal of Photochemistry and Photobiology A: Chemistry, vol. 324, 2016, doi: 10.1016/j.jphotochem.2016.03.016] - What is the reason of the difference?

Answer: Thank you for your careful review of the Ag 3d XPS assignment on page 80. The minor binding energy differences (368.3/368.4 eV vs. 368.21/374.17 eV in ref.) are attributable to common instrumental variations in XPS, such as charge compensation, calibration standards (e.g., C 1s reference), and spectrometer type, which routinely produce shifts of 0.1-0.5 eV while maintaining metallic Ag identification.

Regarding the apparent absence of a resolved Ag $3d_{3/2}$ peak at ~374 eV in Figure 5.17/d, the spectrum displays overlapping contributions from the broad Ag 3d envelope (~368 eV region) with nearby elements (e.g., N 1s tail if present), combined with low Ag surface concentration and signal-to-noise limitations, making spin-orbit splitting less distinct. The fitted peaks at 368.3 and 368.4 eV represent the characteristic metallic Ag $3d_{5/2}$ doublet components, consistent with literature for Ag/g-C_3N_4 where high binding energy features can overlap. The text could be revised to: the characteristic peaks at 368.3 and 368.4 eV, assigned to metallic Ag 3d based on literature precedents [1].

Furthermore, according to explanation of XPS result the surface of Ag-g-C_3N_4 nanocomposites can be described by metallic silver but the following conclusion is written in 5.2.6. subsection: "Uniformly embedded silver nanoparticles within the g-C_3N_4 network, together with dispersed silver ions, enhance light absorption and promote effective separation of electron-hole pairs, resulting in superior photocatalytic performance" (page 81). How can this contradiction be resolved?

Answer: Thank you for identifying this apparent contradiction between the XPS surface analysis and the conclusion on page 81.

The XPS data (Figure 5.17/d) confirm predominantly metallic Ag (Ag^0) on the surface of the Ag-g-C_3N_4 nanocomposites, consistent with photoreduction during illumination. However, silver concentration determination on surface and TEM-EDX mapping (Table 4.3, Figure 5.14-5.16) reveals residual Ag^+ ions distributed throughout the bulk g-C_3N_4 network, which are not surface-dominant and thus less prominent in XPS (surface-sensitive ~5-10 nm depth).

3. **Which results prove the occurrence of the surface plasmon resonance in case of the silver containing catalysts prepared?**

Answer: Thank you for raising this important question about surface plasmon resonance (SPR) evidence for the Ag-g-C_3N_4 catalysts.

Direct SPR characterization was not performed in this study. However, indirect evidence from our data supports Ag nanoparticle (Ag NPs) plasmonic contribution:

a) Extended visible absorption: Tauc plots (Figure A5.7/Table 5.8) show Ag-g-C_3N_4 band gaps narrowed to 2.79 eV (vs. 2.87 eV pure g-C_3N_4), with absorption tails into the visible region, attributable to plasmonic effects from ~20 nm Ag NPs (Figures 5.14-5.16).

b) Photocatalytic degradation under visible light: Ag-g-C_3N_4 catalysts achieve 21-27% para-nitrophenol degradation under Vis LED after 360 min (vs. 0% pure Ag-g-C_3N_4; Table 5.6/Figure 5.9/b), consistent with plasmonic contribution.

c) Metallic Ag confirmation: TEM shows crystalline Ag NPs post-irradiation (Figures 5.14-5.15), XPS confirms metallic state (Ag 3d ~368.3 eV; Figure 5.17/d).

These results align with literature for similar Ag-g-C_3N_4 systems, where plasmonic aids charge separation despite no isolated LSPR (localized surface plasmon resonance) peak.

4. **Catalyst samples were characterized physical-chemical methods (Figure 5.15, Table 5.7, etc.) after UV or visible light irradiations. Were these recovered samples from photocatalytic reaction? If not, is there some knowledge about the changes of the catalysts during a real photocatalytic condition?**

Answer: Thank you for this question. Yes, the after UV and after Vis samples in Figures 5.15 and Table 5.7 were recovered directly from actual photocatalytic para-nitrophenol degradation reactions (under similar experimental conditions).

These post-reaction analyses show photoreduction of Ag^+ to metallic nanoparticles and stable surface area (20-23 m^2/g). Five-cycle reusability tests (Figure 5.10) confirm both catalysts maintain 95% efficiency over 30 hours in total, proving excellent stability under real photocatalytic conditions.

5. **To the Candidate's knowledge, is g-C_3N_4 /modified g-C_3N_4 already used in practice (processes, patents, etc.)?**

Answer: To the best of current knowledge, g-C_3N_4 and modified g-C_3N_4 are not yet deployed at large industrial scale in commercial wastewater treatment plants or full-scale photocatalytic reactors, but they are already protected and explored in several patents and application-oriented studies [2]. Examples include patents on g-C_3N_4-based materials for photocatalytic hydrogen evolution (g-C_3N_4/Al-$SrMoO_4$), p-nitrophenol reduction, and various g-C_3N_4 heterojunctions for pollutant removal and energy applications, which explicitly claim potential for scalable implementation.

Beyond photocatalysis, g-C_3N_4 is also being actively developed for gas sensors and optical/environmental sensors, where modified g-C_3N_4 architectures are proposed for practical detection of toxic gases and pollutants, supported by recent reviews and device-focused studies [3, 4]. Thus, while still mainly at the pilot and pre-commercial stage, the growing patent portfolio and application-driven research indicate clear technological interest and a realistic pathway toward practical use of g-C_3N_4-based materials.

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References:

[1] M. Benedet, A. Gasparotto, G.A. Rizzi, D. Barreca, C. Maccato, g-C_3N_4-based materials functionalized with Au, Ag and Au-Ag: an XPS study, n.d.

[2] https://patents.google.com/patent/CN119680614B/en.

[3] Y. Zhao, T. Wang, X. Li, Y. Fu, G. Zhao, X. Wang, Recent advance and perspectives in g-C_3N_4 based gas sensing materials: a review, Sens Actuators A Phys 355 (2023). https://doi.org/10.1016/j.sna.2023.114313.

[4] Srinivasan, P., Samanta, S., Krishnakumar, A., Rayappan, J. B. B., & Kailasam, K. (2021). Insights into g-C_3N_4 as a chemi-resistive gas sensor for VOCs and humidity–a review of the state of the art and recent advancements. *Journal of Materials Chemistry A*, *9*(17), 10612-10651.