Theses of Doctoral (PhD) Dissertation

University of Pannonia
Doctoral School of Chemistry and Environmental Sciences

Synthesis and characterization of UV- and visible-light-driven photocatalysts for the degradation of organic pollutants

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Introduction

Heterogeneous photocatalysis has emerged as a transformative approach for environmental remediation, garnering significant attention for its ability to degrade a wide range of organic pollutants in water and air. This advanced oxidation process (AOP) employs photocatalysts, typically photoactive semiconductors that utilize solar radiation, a renewable and abundant energy source, to drive chemical reactions.

Among the notable benefits of photocatalysis are its cost-effectiveness, environmental friendliness, and potential for large-scale applications. However, many conventional photocatalysts, such as TiO_2, ZnO, and SnO_2, exhibit limitations, including excitation restricted to ultraviolet (UV) light, which constitutes only 5 % of solar radiation. This limitation has driven the search for visible-light-responsive materials to better utilize the solar spectrum.

Graphitic carbon nitride ($g\text{-}C_3N_4$) has emerged as a highly promising photocatalyst due to its unique properties. As a conjugated polymer composed of carbon, nitrogen, and trace amounts of hydrogen, $g\text{-}C_3N_4$ is metal-free, environmentally benign, and sustainable. Its graphite-like layered structure, formed by sp^2 hybridization of carbon and nitrogen atoms and held together by van der Waals forces, enhances its stability and durability.

The $g\text{-}C_3N_4$ narrow bandgap of 2.7-2.8 eV enables visible-light absorption and renders it suitable for a wide range of photocatalytic applications. However, pristine $g\text{-}C_3N_4$ suffers from drawbacks such as limited visible-light absorption (up to ~450 nm) and rapid recombination of photogenerated electron-hole pairs, which significantly limit its photocatalytic efficiency.

To address these challenges, extensive research has focused on modifying $g\text{-}C_3N_4$ through doping, heterojunction formation, and hybridization with other materials. Among the most effective strategies is the incorporation of metal and metal sulfide nanoparticles, which enhance light absorption, suppress electron-hole recombination, and introduce additional reactive sites.

This research aligns with the laboratory's focus on developing advanced materials for sustainable environmental technologies. Leveraging the lab's expertise in semiconductor synthesis, nanomaterial modification, and photocatalysis, the project explores bio-inspired and starch-assisted green synthesis approaches for incorporating metal and metal sulphide nanoparticles into g-C_3N_4. The work supports the department's goal of producing cost-effective, eco-friendly photocatalysts for wastewater treatment and pollutant degradation under UV and visible light, while emphasizing photocatalyst stability, reusability, and mechanism studies under realistic conditions.

Experimental methods

The g-C_3N_4 photocatalyst was synthesized via thermal polymerization of melamine and urea at 5 °C per minute up to 500 °C (550 °C), keeping that temperature for different times (0.5, 1, 2, 3, 4 h). The Ag modified nanocomposites from g-C_3N_4 obtained at 550 °C (4 h) from melamine precursors were synthesized utilizing two methods (bio-inspired incorporation of Ag nanoparticles by using cardamom extract and adsorption impregnation) using $AgNO_3$ solution. Additionally, bismuth and zinc-sulfide-modified g-C_3N_4 were fabricated through a starch-assisted method, where starch acted as both a capping and stabilizing agent to regulate the formation of Bi_2S_3/Bi_2O_3 and ZnS/ZnO nanoparticles before their integration with g-C_3N_4. The resulting catalysts were comprehensively characterized to examine their structural, morphological, and photocatalytic properties.

Photochemical experiments were carried out by using a lab-scale quartz glass reactor with a volume of 50 cm^3; UV (λ_{max}=374 nm; 50 W) and Vis (λ_{max}=453 nm; 2×7 W) LEDs as light sources, respectively. The light sources were placed on the left and right sides of the reactor with about 10 cm distance between them. In all the experimental runs, stirring of the reaction mixture was done by injecting air bubbles with a flow rate of 10 dm^3 h^{-1}. The reaction mixture temperature did not change appreciably upon illumination, even though there was a slight increase of 2-3 °C, which is insignificant to adsorption, desorption, and the photochemical process.

Coumarin was employed as a molecular probe to detect hydroxyl radicals generated during photocatalysis. An initial coumarin concentration of 9×10^{-5} mol dm^{-3} was used, which was converted to fluorescent 7-hydroxycoumarin (7-OHC) upon reaction with hydroxyl radicals. Coumarin concentration was monitored using a UV-Vis spectrophotometer (Scinco S-3100) at 277 nm, where it exhibits a high molar absorption coefficient, while 7-OHC shows much weaker absorption at this wavelength and thus only minimally interfered with absorbance measurements.

The fluorescence emission of 7-OHC was measured with a spectrofluorometer (PerkinElmer LS50B) using excitation and emission wavelengths of 332 nm and 453 nm, respectively. Quantitative analysis of coumarin and 7-OHC was carried out using calibration curves constructed from UV-Vis absorbance at 277 nm (for coumarin) and fluorescence emission intensity at 453 nm (for 7-OHC). This combined absorbance fluorescence approach provided high sensitivity and good selectivity for hydroxyl radical detection.

1,4-Hydroquinone (1,4-H_2Q, 2.25×10^{-4} mol dm^{-3}) was used as a scavenger to examine the role of superoxide radicals in the photocatalytic process. Its addition served to quench superoxide radicals and to identify their contribution to the overall degradation mechanism. 1,4-H_2Q fluorescence was measured at λ_{ex}=288 nm and λ_{em}=330 nm, with linear response up to 4×10^{-5} mol dm^{-3}, and more concentrated samples were diluted tenfold to avoid self-absorption.

Para-nitrophenol (PNP, 5×10^{-4} mol dm^{-3}) was employed as a model compound for photocatalytic degradation studies. The absorption characteristics were measured using a UV-Vis spectrophotometer, showing a maximum at 318 nm. The variation in PNP concentration during irradiation was determined from calibration curves prepared with standard PNP solutions, performed in a 0.2 cm^3 quartz cuvette to ensure precision and consistency across all measurements.

Thesis Points of PhD Dissertation

I. **I systematically investigated the synthesis of well-structured g-C_3N_4, using melamine as a precursor, achieving high product yield and improved structural ordering. I developed two eco-friendly modification strategies: bio-inspired incorporation of silver nanoparticles by using cardamom extract and adsorption impregnation, and starch-assisted incorporation of metal sulfides (Bi_2S_3/Bi_2O_3 or ZnS/ZnO).**

- I quantified that melamine thermal polymerization at 500 °C yields approximately ten times more product and produces more ordered g-C_3N_4 (sharper and better-defined XRD peaks) than urea, consistent with literature but reaffirmed under my synthesis conditions.
- The synthesis was performed in two different atmospheres; air and nitrogen, where melamine with the air atmosphere was preferred due to high photocatalytic efficiency.
- I verified that cardamom extract-assisted green synthesis enabled homogeneous Ag nanoparticle distribution, enhancing photocatalytic performance through natural reducing and capping agents.
- I demonstrated that starch-assisted green synthesis promoted stable Bi_2S_3/Bi_2O_3 and ZnS/ZnO nanoparticle dispersion, further improving photocatalytic efficiency by preventing agglomeration.

Mukhtar, S., Szabó-Bárdos, E., Horváth, O., Makó, E., Juzsakova, T., & Molnár, Z. (2025). Bio-inspired synthesis of Ag-g-C_3N_4 nanocomposites and their application for photocatalytic degradation of para-nitrophenol. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *705*, 135739. (https://doi.org/10.1016/j.colsurfa.2024.135739)

Mukhtar, S., Szabó-Bárdos, E., Őze, C., Juzsakova, T., Rácz, K., Németh, M., & Horváth, O. (2025). g-C_3N_4 Modified with Metal Sulfides for Visible-Light-Driven Photocatalytic Degradation of Organic Pollutants. *Molecules*, *30*(2), 253. (https://doi.org/10.3390/molecules30020253)

II. **I systematically investigated the effect of Ag, Bi_2S_3/Bi_2O_3, and ZnS/ZnO nanoparticle modification on graphitic carbon nitride (g-C_3N_4) and revealed that the interaction between the nanoparticles and the g-C_3N_4 matrix is predominantly weak and physical in nature, leading to a notable decrease in the specific surface area.**

- XRD and FTIR analyses confirmed the preservation of the g-C_3N_4 framework, with only minor peak shifts indicating weak bonding.
- SEM and TEM observations revealed morphological changes and uniform dispersion of ~2–20 nm nanoparticles on the g-C_3N_4 surface.
- The BET surface area decreased markedly due to nanoparticle deposition.
- XPS analysis demonstrated compositional stability of the hybrid materials.

Mukhtar, S., Szabó-Bárdos, E., Horváth, O., Makó, E., Juzsakova, T., & Molnár, Z. (2025). Bio-inspired synthesis of Ag-g-C_3N_4 nanocomposites and their application for photocatalytic degradation of para-nitrophenol. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *705*, 135739. (https://doi.org/10.1016/j.colsurfa.2024.135739)

Mukhtar, S., Szabó-Bárdos, E., Őze, C., Juzsakova, T., Rácz, K., Németh, M., & Horváth, O. (2025). g-C_3N_4 Modified with Metal Sulfides for Visible-Light-Driven Photocatalytic Degradation of Organic Pollutants. *Molecules*, *30*(2), 253. (https://doi.org/10.3390/molecules30020253)

III. **I demonstrated that incorporating Ag, Bi_2S_3/Bi_2O_3, and ZnS/ZnO nanoparticles into graphitic carbon nitride significantly reduces the efficiency of the photocatalytic degradation of coumarin by Ag-loaded g-C_3N_4 and moderately reduces it by Ag-, Bi_2S_3/Bi_2O_3-, and ZnS/ZnO-loaded g-C_3N_4 under UV irradiation.**

- I showed that pristine g-C_3N_4 produces both $^{\bullet}OH$ and $O_2^{\bullet-}$ radicals under UV light irradiation and that, in the coumarin degradation, the reactions of hydroxyl radicals play considerable roles.

- I observed that Ag, Bi_2S_3/Bi_2O_3, and ZnS/ZnO nanoparticles doping reduces the band gap of g-C_3N_4, which lowers the oxidation potential of the valence band holes (h^+_{VB}), making them less effective at oxidizing adsorbed H_2O or OH^- ions and generating hydroxyl radicals under UV irradiation, decreasing the efficiency of coumarin degradation.
- I noticed that excessive nanoparticle loading blocks active sites, which ultimately reduces photocatalytic activity.

Mukhtar, S., Szabó-Bárdos, E., Horváth, O., Makó, E., Juzsakova, T., & Molnár, Z. (2025). Bio-inspired synthesis of Ag-g-C_3N_4 nanocomposites and their application for photocatalytic degradation of para-nitrophenol. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *705*, 135739. (https://doi.org/10.1016/j.colsurfa.2024.135739)

Mukhtar, S., Szabó-Bárdos, E., Őze, C., Juzsakova, T., Rácz, K., Németh, M., & Horváth, O. (2025). g-C_3N_4 Modified with Metal Sulfides for Visible-Light-Driven Photocatalytic Degradation of Organic Pollutants. *Molecules*, *30*(2), 253. (https://doi.org/10.3390/molecules30020253)

IV. I demonstrated that Bi_2S_3/Bi_2O_3 and ZnS/ZnO modification of g-C_3N_4 promotes the degradation of coumarin under visible light irradiation.

- The pristine g-C_3N_4 cannot degrade coumarin at all under visible light irradiation.
- Although no or very slight formation of hydroxyl radicals was observed in the case of Bi_2S_3/Bi_2O_3 and ZnS/ZnO modified g-C_3N_4, a considerable increase in the efficiency of coumarin degradation occurred under visible light irradiation.
- The enhanced efficiency of coumarin degradation can be attributed to the reactions of other photogenerated reactants, such as electron and/or superoxide radical.

Mukhtar, S., Szabó-Bárdos, E., Őze, C., Juzsakova, T., Rácz, K., Németh, M., & Horváth, O. (2025). g-C_3N_4 Modified with Metal Sulfides for Visible-Light-Driven Photocatalytic Degradation of Organic Pollutants. *Molecules*, *30*(2), 253. (https://doi.org/10.3390/molecules30020253)

V. I demonstrated that the degradation efficiency of a colorless pollutant (para-nitrophenol) under UV and visible light is significantly enhanced by optimal modification of g-C_3N_4 with Ag, Bi_2S_3/Bi_2O_3, and ZnS/ZnO nanoparticles.

- I showed that under UV irradiation, Ag, Bi_2S_3/Bi_2O_3, and ZnS/ZnO modifications achieved high degradation efficiencies of 82-100 % (within 6-8 hours).
- I revealed that under visible light, the best-performing composites achieved pollutant degradation efficiencies of 15-27 % (within 6-8 hours), whereas pristine g-C_3N_4 was ineffective.
- I attributed enhanced photocatalytic performance to improved charge separation and thus increased generation of reactive species other than hydroxyl radicals (electron and/or superoxide radical).
- I demonstrated catalyst stability with minor activity loss after 5 cycles of photocatalytic degradation of para-nitrophenol, indicating potential for practical wastewater treatment applications.

Mukhtar, S., Szabó-Bárdos, E., Horváth, O., Makó, E., Juzsakova, T., & Molnár, Z. (2025). Bio-inspired synthesis of Ag-g-C_3N_4 nanocomposites and their application for photocatalytic degradation of para-nitrophenol. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *705*, 135739. (https://doi.org/10.1016/j.colsurfa.2024.135739)

Mukhtar, S., Szabó-Bárdos, E., Őze, C., Juzsakova, T., Rácz, K., Németh, M., & Horváth, O. (2025). g-C_3N_4 Modified with Metal Sulfides for Visible-Light-Driven Photocatalytic Degradation of Organic Pollutants. *Molecules*, *30*(2), 253. (https://doi.org/10.3390/molecules30020253)

Scientific publications, presentations and posters

Publications serving as the basis of thesis points:

1. **Mukhtar, S.**, Szabo-Bardos, E., Horvath, O., Mako, E., Juzsakova, T., & Molnar, Z. **(2025)**. Bio-inspired synthesis of Ag-g-C_3N_4 nanocomposites and their application for photocatalytic degradation of para-nitrophenol. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *705*, 135739. (https://doi.org/10.1016/j.colsurfa.2024.135739)
   Impact factor: **5.4, Q1 (2025)**
2. Mukhtar, S., Szabó-Bárdos, E., Őze, C., Juzsakova, T., Rácz, K., Németh, M., & Horváth, O. **(2025)**. g-C_3N_4 Modified with Metal Sulfides for Visible-Light-Driven Photocatalytic Degradation of Organic Pollutants. *Molecules*, *30*(2), 253. (https://doi.org/10.3390/molecules30020253)
   Impact factor: **4.6, Q1 (2025)**

Publications related to the topic of the dissertation:

3. Khan, J. A., Ahmad, I., Jawaid, M., Meraj, A., **Mukhtar, S.**, Lakkakula, J., & Uddin, I. **(2025)**. Evolution of photocatalytic and dielectric properties of bismuth ferrite nanoparticles with Cr doping. *Journal of the Iranian Chemical Society*, *22*(2), 337-347.
   (https://doi.org/10.1007/s13738-024-03152-1)
   Impact factor: **2.3, Q3 (2025)**
4. Uddin, I., **Mukhtar, S.**, Horváth, O., & Pósfai, M. **(2024)**. Room-temperature synthesis of rGO/Ag nanocomposite as a photocatalyst for the degradation of organic pollutants in wastewater. *Materialia*, *36*, 102179.
   (https://doi.org/10.1016/j.mtla.2024.102179)
   Impact factor: **2.9, Q2 (2025)**
5. Nguyen Xuan, T., Nguyen Thi, D., Tran Thuong, Q., Nguyen Ngoc, T., Dang Quoc, K., Molnár, Z., **Mukhtar, S.**, Szabó-Bárdos, E. and Horváth, O., **2023**. Effect of

Copper-Modification of g-C_3N_4 on the Visible-Light-Driven Photocatalytic Oxidation of Nitrophenols. *Molecules*, *28*(23), p.7810.
(https://doi.org/10.3390/molecules28237810)
Impact factor: **4.6, Q1 (2025)**

6. Xuan, T.N., Thi, D.N., Ngoc, T.N., Quoc, K.D., Németh, M., **Mukhtar, S.** and Horváth, O., **2023**. Effect of ruthenium modification of g-C_3N_4 in the visible-light-driven photocatalytic reduction of Cr (VI). *Catalysts*, *13*(6), p.964.
(https://doi.org/10.3390/catal13060964)
Impact factor: **4.0, Q2 (2025)**

7. **Mukhtar, S.**, Szabó-Bárdos, E. and Horváth, O., **2024**. Sustainable synthesis of carbon-based nanocomposite for dye degradation. In *Sustainable Nanomaterials: Synthesis and Environmental Applications* (pp. 81-101). Singapore: Springer Nature Singapore **(Book Chapter)**
(https://doi.org/10.1007/978-981-97-2761-2_4)

Publications not related to the topic of the dissertation:

8. Hidalgo, J.S., **Mukhtar, S.,** Uddin, I., Horváth, O., Galambos, I., Gábor, M., Hidalgo, L., Vilasó-Cadre, J.E., Reyes-Domínguez, I.A. and Lakkakula, J., 2025. Green silver – bioinspired nanoparticles used as an electrochemical sensor – an efficient and simple method for the determination of glyphosate in surface water samples. *Ionics*, pp.1-17.
(https://doi.org/10.1007/s11581-025-06770-8)
Impact factor: **2.6, Q2 (2025)**

9. Hidalgo, J.S., **Mukhtar, S.**, Horváth, O., Kovacs, N., Hidalgo, L., Vilasó-Cadre, J.E., Reyes-Domínguez, I.A., Rácz, K., Uddin, I., Galambos, I. and Fort, C.I., **2025**. Nanocomposite matrix based on gerhardtite-type copper (II) hydroxy nitrate and ZnO/CeO_2 nanoparticles-a sensitive platform for aminomethylphosphonic acid detection. *Electrochimica Acta*, p.147255.
(https://doi.org/10.1016/j.electacta.2025.147255)
Impact factor: **5.6, Q2 (2025)**

10. **Mukhtar, S.**, Ali, A., Aryan, S., Shahid, S., Akhtar, M.N., Hidalg, J.S., Umar, M., El-Khawaga, A.M. and Khan, M.S., **2025**. Carbon-Based Smart Sensors for Environmental Pollution Detection. In *Smart Nanosensors* (pp. 143-163). Singapore: Springer **(Book Chapter)** (https://doi.org/10.1007/978-981-96-3878-9_5)

11. Mahammad, A., Akbar, I. and **Mukhtar, S.**, **2025**. Theranostic Application of Smart Nanomaterials in Target Drug Delivery. In *Smart Nanosensors* (pp. 25-54). Singapore: Springer Nature Singapore **(Book Chapter)** (https://doi.org/10.1007/978-981-96-3878-9_2)

12. Rais, S. and **Mukhtar, S.**, 2024. Facile Synthesis of Carbon Nanotubes and Its Application in Food Science and Wastewater Treatment. In *Sustainable Nanomaterials: Synthesis and Environmental Applications* (pp. 301-316). Singapore: Springer Nature Singapore **(Book Chapter)** (https://doi.org/10.1007/978-981-97-2761-2_12)

13. El-Khawaga, A.M., **Mukhtar, S.** and Shahid, S., 2024. Sustainable nanomaterials as promising antibacterial agents. In *Sustainable nanomaterials: synthesis and environmental applications* (pp. 203-225). Singapore: Springer Nature Singapore **(Book Chapter)** (https://doi.org/10.1007/978-981-97-2761-2_8)

Total impact factor: 32.

Conference (presentation):

1. **Shoaib Mukhtar,** Erzsébet Szabó-Bárdos, Ottó Horváth
   "Eco-friendly degradation of organic pollutants by the synthesis and application of a modified g-C_3N_4 nanocomposite activated by visible light"
   INASCON (International Nanoscience Student Conference)
   25-28 August, 2025, Charles University, Czech Republic

2. **Shoaib Mukhtar,** Erzsébet Szabó-Bárdos, Ottó Horváth
   "Synthesis of metal sulfide/g-C_3N_4 nanocomposite for photocatalytic degradation of organic pollutant under visible light"
   The 3rd International Electronic Conference on Catalysis Sciences session Photocatalysis
   21 April 2025 online, MDPI

3. **Shoaib Mukhtar,** Erzsébet Szabó-Bárdos, Ottó Horváth
   "Preparation of metal sulfide/g-C_3N_4 nanocomposite for visible-light photocatalytic degradation of organic pollutants"
   Materials Science Day XXIV, conference
   18th November, 2024, University of Pannonia, Veszprém, Hungary

4. **Shoaib Mukhtar,** Erzsébet Szabó-Bárdos, Ottó Horváth
   "Green and sustainable synthesis of visible light-driven photocatalyst g-C_3N_4/Ag nanocomposite for degradation of organic dyes"
   Műszaki Kémiai Napok, Conference
   20th April, 2023, University of Pannonia, Veszprém, Hungary

5. Imran Uddin, **Shoaib Mukhtar**, Zsombor Molnár, Mihály Pósfai
   "Low-temperature synthesis of graphene/Ag nanocomposite as a photo-catalyst for the degradation of organic pollutants in wastewater"
   Műszaki Kémiai Napok, Conference
   20th April, 2023, University of Pannonia, Veszprém, Hungary

6. Ottó Horváth, **Shoaib Mukhtar**, Erzsébet Szabó-Bárdos, Dien Nguyen Thi, Truong Nguyen Xuan
   "Preparation and application of g-C_3N_4-based catalysts for photocatalytic treatment of various pollutants in aqueous systems".
   The 7th International Conference on New Photocatalytic Materials for Environment, Energy and Sustainability. The 8th International Conference on Photocatalytic and Advanced Oxidation Technologies for the Treatment of Water, Air, Soil and Surfaces
   July 10-13, 2023, Varaždin, Croatia

7. **Shoaib Mukhtar,** Erzsébet Szabó-Bárdos, Ottó Horváth
   "Preparation and characterization of graphitic carbon nitride"
   PhD hallgatók anyagtudományi napja XXIII, Conference
   14 November, 2022, University of Pannonia, Veszprém, Hungary

Conference (poster):

8. **<u>Shoaib Mukhtar</u>,** Erzsébet Szabó-Bárdos, Ottó Horváth
"Synthesis of metal sulfide/g-C_3N_4 nanocomposite for photocatalytic degradation of organic pollutant under visible light"
2nd Forum of young Researcher in Heterogeneous catalysis
14-16th November 2024, University of Szeged, Hungary

9. **<u>Shoaib Mukhtar</u>,** Erzsébet Szabó-Bárdos, Ottó Horváth
"Synthesis of Ag-g-C_3N_4 nanocomposite for environmentally friendly photocatalytic degradation of para-nitrophenol under visible light"
Central European Conference on Photochemistry
18-22 February, 2024, Bad Hofgastein, Austria

10. Ákos Bendegúz Székely, Orsolya Zsirka-Fónagy, Diána Lukács, Evelin Tóth-Farsang, Erzsébet Szabó-Bárdos, **<u>Shoaib Muhktar</u>**, Ottó Horváth
"Mineralization of a fungicide by heterogeneous photocatalysis using UV and visible light"
Central European Conference on Photochemistry
18-22 February 2024, Bad Hofgastein, Austria

11. **<u>Shoaib Mukhtar</u>,** Erzsébet Szabó-Bárdos, Ottó Horváth
"Synthesis of Ag-g-C_3N_4 nanocomposite for environmentally friendly photocatalytic degradation of para-nitrophenol under visible light"
8th International Conference on Semiconductor Photochemistry
11-15 September 2023, University of Strasbourg, France

12. **<u>Shoaib Mukhtar</u>**, Ottó Horváth, Erzsébet Szabó-Bárdos, Dien Nguyen Thi, Truong Nguyen Xuan
"Preparation and implementation of g-C_3N_4-based catalysts for photocatalytic treatment of different contaminants in water systems"
8th International Conference on Semiconductor Photochemistry
11-15 September 2023, University of Strasbourg, France