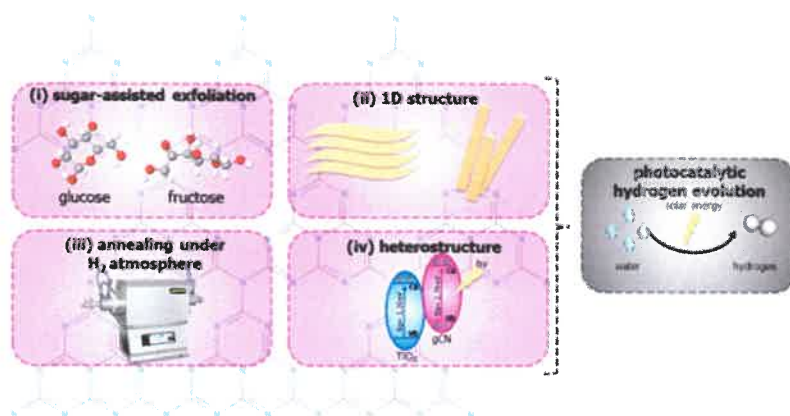


Abstract of the PhD Dissertation by M. Sc. Eng. Daria Baranowska titled “Exfoliated Graphitic Carbon Nitride and Its Composites for Photocatalytic Hydrogen Generation”

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The research conducted as part of this doctoral dissertation includes the analysis of the physicochemical properties and photocatalytic activity of catalysts based on exfoliated graphitic carbon nitride (ex-gCN) and its composites. In this work, four strategies for modifying graphitic carbon nitride were presented (see graphical abstract): (i) liquid-phase exfoliation of bulk graphitic carbon nitride (bulk-gCN) in the presence of sugars [P1], (ii) transforming the dimensionality of graphitic carbon nitride from 2D to 1D [P2], (iii) annealing of ex-gCN at elevated temperatures in a hydrogen atmosphere [P3], (iv) creating heterostructures by (a) combining ex-gCN with mesoporous titanium dioxide spheres [P4], and (b) calcining bulk-gCN with MXene ($Ti_3C_2T_x$) at 500-600 °C in an oxidizing atmosphere (unpublished data). The activity of the obtained catalysts was evaluated in the photocatalytic hydrogen generation reaction. Additionally, the physicochemical characterization of the obtained catalysts allowed me to determine the mechanism of the photocatalytic hydrogen generation reaction in the presence of the studied catalysts.



In publication P1, a series of photocatalysts based on ex-gCN, synthesized through a solvothermal process in the presence of various sugars (glucose, fructose, and sucrose) were described. The highest photocatalytic activity was observed for fructose_{6h} (1.42 $\mu\text{mol/g}$), representing a 13-fold increase in H_2 production compared to the starting bulk-gCN (0.11 $\mu\text{mol/g}$). Liquid-phase exfoliation of graphitic carbon nitride with fructose resulted in a material with an increased specific surface area, enriched with oxygen and carbon, and containing nitrogen defects, contributing to enhanced photocatalytic efficiency.

In publication **P2**, the development of one-dimensional graphitic carbon nitride (gCN_1D) from ex-gCN was presented. The synthesis of gCN_1D was achieved through a solvothermal process involving ascorbic acid. The hydrogen generation for gCN_1D reached 18.20 $\mu\text{mol/g}$, representing 4-fold and 18-fold increase compared to ex-gCN (4.32 $\mu\text{mol/g}$) and bulk-gCN (0.99 $\mu\text{mol/g}$). The resulting gCN_1D exhibited reduced charge carrier recombination, decreased resistance, and increased photocurrent response compared to its 2D counterparts (bulk-gCN and ex-gCN).

In publication **P3**, the impact of annealing parameters (temperature and time) in a hydrogen atmosphere on the physicochemical properties and photocatalytic activity of ex-gCN in hydrogen generation was described. The highest photocatalytic activity was observed for ex-gCN annealed in a hydrogen atmosphere at 400°C for 4 hours (400-4), producing 18.17 $\mu\text{mol/g}$, representing a 22.8-fold and 25.2-fold improvement compared to ex-gCN (0.80 $\mu\text{mol/g}$) and bulk-gCN (0.72 $\mu\text{mol/g}$). The 400-4 material features (1) an increased surface area, (2) enhanced visible light absorption, (3) efficient charge carrier transport and separation, and (4) reduced unfavorable recombination processes of these carriers.

In publication **P4**, a heterostructure combining mesoporous TiO_2 (mTiO₂) spheres with ex-gCN was proposed. The photocatalytic reactions demonstrated that the mTiO₂_ex-gCN heterostructure showed higher activity compared to the individual components (mTiO₂ and ex-gCN) in both hydrogen photocatalytic generation under simulated solar light and Rhodamine B (RhB) degradation under UV-Vis and visible light. The hydrogen production efficiency for mTiO₂_ex-gCN was 70 times greater (644.16 $\mu\text{mol/g}$) than that of the reference ex-gCN (9.04 $\mu\text{mol/g}$). The enhanced photocatalytic activity was attributed to a synergistic effect between the heterostructure components, resulting in (1) increased surface area, (2) improved charge mobility, (3) better separation of electron-hole pairs, and (4) reduced charge carrier recombination.

In the final studies of this doctoral dissertation (unpublished data), a synthesis method for highly active photocatalysts based on bulk-gCN and $\text{Ti}_3\text{C}_2\text{T}_x$ (MXene) for photocatalytic hydrogen generation was proposed. A mixture of bulk-gCN and $\text{Ti}_3\text{C}_2\text{T}_x$ was calcined at 500-600°C for 4 hours in an oxidizing atmosphere. The calcination temperature significantly influenced the final product's structure – either a gCN-TiO₂ heterostructure or a TiO₂ structure enriched with carbon and nitrogen. All gCN:MXene_T catalysts exhibited higher photocatalytic hydrogen generation activity than the reference materials (bulk-gCN (57.5 $\mu\text{mol/g}$) and MXene (36.9 $\mu\text{mol/g}$), with gCN:MXene_600 showing the highest activity of 37,660.4 $\mu\text{mol/g}$ of H₂. PL, CA, and EIS analyses indicated that the high efficiency of hydrogen generation with

gCN:MXene_600 is due to the reduced recombination rate of photogenerated electron-hole pairs, linked to their effective separation and transport within the material.

Keywords: graphitic carbon nitride, exfoliation, photocatalysis, hydrogen, mechanism

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