19th International Conference on Environmental Science and Technology

CEST 2025

Kos, Greece, 3 to 6 September 2025

Synthesis and application of Z-Scheme g-C_3N_4/g-C_3N_5 heterotype homojunction for aquatic pollutants degradation

Sioulas S.[1], Lykos C.[1], Konstantinou I.[1], Albanis T.[1,*]

[1]Department of Chemistry, University of Ioannina, Ioannina 45110, Greece

*corresponding author: Albanis T.
e-mail: talbanis@uoi.gr

Abstract: Advanced oxidation processes (AOPs) are key technologies in wastewater treatment for their effectiveness and low environmental impact. Heterogeneous photocatalysis, particularly using TiO_2, has been extensively studied; however, its wide band gap (~3.2 eV) limits its efficiency under solar light. This has led to interest in visible light-activated photocatalysts, such as g-C_3N_4, which has a band gap of about 2.7–2.8 eV but suffers from high recombination rates of photogenerated e^-/h^+ pairs. Recently, nitrogen-rich graphitic carbon nitride (g-C_3N_5) has shown promise with a narrower band gap (~1.9 eV) but still faces recombination issues. Hoping to address these problems, this work evaluates the synthesis of a g-C_3N_4/g-C_3N_5 Z-Scheme heterotype homojunction, which promotes e^-/h^+ separation and broadens the catalyst response in the visible spectrum. In this concise presentation of the work, the synthesis of the materials took place through the direct calcination of urea as precursor for g-C_3N_4,and 3-amino-1,2,4-triazole (3-AT) for g-C_3N_5, utilizing water as the mixing agent. The materials were synthesized using different ratios of the two monomers, were characterized using methods such as XRD, FT-IR, and DRS, and the photocatalytic activity is being investigated, targeting Haloperidol, an antipsychotic drug, delivered as an aquatic pollutant in WWTPs.

Keywords: Heterogeneous photocatalysis, Z-Scheme, graphitic carbon nitride, Haloperidol

1. Introduction

The presence of pharmaceutical compounds in the aquatic environment at concentrations ranging from a few ng/L to μg/L is a chronic problem due to their non-removal in wastewater treatment plants (WWTPs). Antipsychotics, among other drug classes, have not received adequate attention regarding their serious toxicological effects on the aquatic environment. Haloperidol, belonging to this pharmaceutical class, is administered continuously for the treatment of chronic schizophrenia and autism and is detected both at the influents and effluents of WWTPs, as well as in various aquifers. Heterogeneous photocatalysis is among the most widespread and effective methods for removing pharmaceutical compounds from water (Ruziwa et al., 2023; Wu et al., 2021).

In this summary work, the simple synthesis of the Z-Scheme g-C_3N_4/g-C_3N_5 composite photocatalyst is presented by testing different ratios of the precursors in synthesis and its application in the photocatalytic degradation of the antipsychotic drug Haloperidol in distilled water under simulated solar radiation with the values of the degradation rate constants showing increased efficiency in the removal of the drug when smaller amounts of 3-AT are used in the preparation of the final material with the optimal content so far being 5% of the yield of the produced urea mass in g-C_3N_4.

2. Materials and methods

2.1. Synthesis of the Composite Catalyst

Composite graphitic carbon nitride (g-C_3N_4/g-C_3N_5 or CNUA) materials were synthesized by direct mixing of 10g Urea and different quantities of 3-AT (5%-CNUA, 10%-CNUA, and 25%-CNUA) in 10 mL of water, evaporating the mixture under continuous stirring at 90 °C in an oil bath not until complete dryness. The resultant was then calcined in a porcelain crucible in a muffle furnace (total time: 4 h, maximum temperature: 550 °C, temperature rate: 7 °C/min).

2.2. Characterization Techniques and Photocatalytic Experiments

The X-ray diffraction (XRD) patterns for all the synthesized materials were obtained within the 2θ range of 10◦ to 90◦ using a Bruker D8 Advance diffractometer (Billerica, MA, USA). Fourier-transform infrared spectroscopy (FT-IR) analyses for the materials were obtained in the range from 4000 cm^{-1} to 400 cm^{-1} using a Shimadzu IR Spirit QATR-S FTIR spectrophotometer (Kyoto, Japan). Diffuse reflectance spectroscopy (DRS) measurements for each photocatalyst were performed using a Shimadzu UV-2600 spectrophotometer (Kyoto, Japan). Reflectance spectra for each material were recorded in the UV-Vis region (200–800 nm).

The photodegradation of Haloperidol was conducted in an aqueous solution (5 mg/L, 100 mL) using a SUNTEST CPS^+ apparatus (Atlas, Linsengericht, Germany). This apparatus features a 1,500 W Xenon arc lamp and is

equipped with radiation cut-off filters (λ<290 nm). The intensity of the lamp was set to 500 W/m². The concentration of the catalyst was adjusted to 100 mg/L. The concentration of Haloperidol was analyzed using a Shimadzu HPLC system (Kyoto, Japan) equipped with a Supelco Discovery C18 column (15 mm × 4.6 mm, 5 µm particle size) (Bellefonte, PA, USA), utilizing a mixture of Water + 0.1% Formic Acid and Acetonitrile (60:40) as the mobile phase.

3. Results and Discussion

3.1. Material characterization

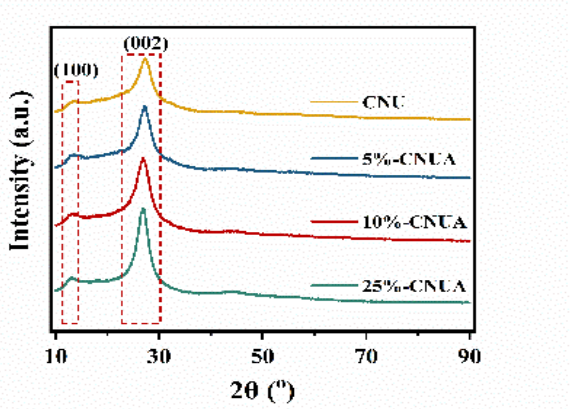

Figure 1. XRD patterns of the synthesized photocatalysts

The XRD spectra of the materials are presented in **Figure 1**, revealing the two characteristic peaks of g-C_3N_4: one low-intensity peak at 2θ = 13.1° and another significantly more intense at 2θ = 27.2°. The (100) crystal plane is attributed to the tris-s-trazine ring, while the (002) crystal plane is attributed to the stacking of the layers of conjugated aromatic hydrocarbons. Increasing the quantity of 3-AT, the intensity of the (002) peak increases, and the explanation lies in the strong electron repulsion generated by the arrangement of the 2-s-triazine ring and the triazole ring.

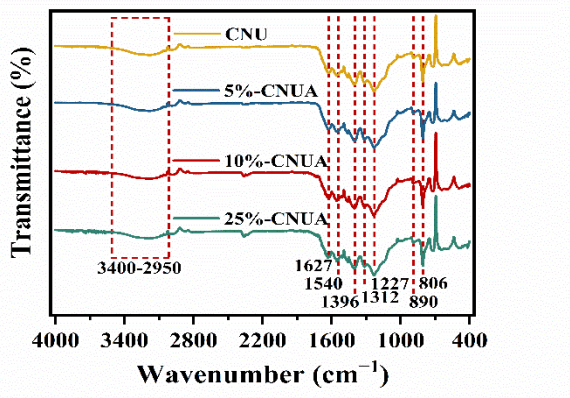

Figure 2. FT-IR spectra of the synthesized photocatalysts

In **Figure 2**, the FT-IR spectra of the synthesized photocatalysts are shown. All the spectra present a distinct band at 806 cm^{-1}, which is attributed to the bending vibration of the triazine ring. The weaker band at 890 cm^{-1} is linked to the N-H deformation mode of the cross-linked tris-s-triazines. The peaks at 1200 – 1650 cm^{-1} are typical skeletal stretching vibrations of the triazine ring. Furthermore, the presence of a broad band extending from 2950 cm^{-1} to 3400 cm^{-1}, which is typical of N-H stretching vibrations, suggests the existence of residual or terminal amino groups in the structure of g-C_3N_4.

The optical band gaps of all synthesized materials were determined as 2.79 (CNU) < 2.80 (5%-CNUA) = 2.80 (10%-CNUA) < 2.81 (25%-CNUA). It is observed that increasing the percentage of triazole in the final material does not significantly change the band gap value.

3.2. Evaluation of photocatalytic activity

The photocatalytic performance of the prepared materials was studied in the degradation of Haloperidol in distilled water. As shown in **Figure 3**, all the kinetics follow the pseudo-first order model, and the catalyst that demonstrates the fastest drug removal is 5%-CNUA (k= 0.033 min^{-1}). In fact, the drug removal slows down as the percentage of 3-AT increases during the synthesis of the catalyst. However, the composite material 5%-CNUA shows a remarkable photocatalytic activity compared to CNU (k= 0.018 min^{-1}), approximately twice higher regarding the rate constants' values.

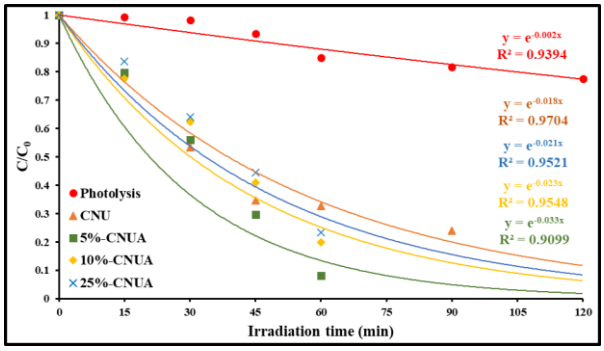

Figure 3. Photolytic and photocatalytic degradation kinetics of Haloperidol under simulated solar irradiation

Acknowledgements

This research was funded by the project "Advanced Nanostructured Materials for Sustainable Growth: Green Energy Production/Storage, Energy Saving and Environmental Remediation" (TAEDR-0535821), which is implemented under the action "Flagship actions in interdisciplinary scientific fields with a special focus on the productive fabric" (ID 16618), Greece 2.0—National Recovery and Resilience Fund, and funded by European Union NextGenerationEU.

References

Ruziwa, D. T., Oluwalana, A. E., Mupa, M., Meili, L., Selvasembian, R., Nindi, M. M., Sillanpaa, M., Gwenzi, W., & Chaukura, N. (2023). Pharmaceuticals in wastewater and their photocatalytic degradation using nano-enabled photocatalysts. In *Journal of Water Process Engineering* (Vol. 54). Elsevier Ltd. https://doi.org/10.1016/j.jwpe.2023.103880

Wu, R., Ruan, Y., Lin, H., Yuen, C. N. T., Feng, H., & Lam, P. K. S. (2021). Occurrence and Fate of Psychiatric Pharmaceuticals in Wastewater Treatment Plants in Hong Kong: Enantiomeric Profiling and Preliminary Risk Assessment. *ACS ES and T Water*, *1*(3), 542–552. https://doi.org/10.1021/acsestwater.0c00081