Extended Abstract

(For Ph.D. Open Seminar)

Design of composite materials for achieving enhanced photocatalytic performance under visible light by using various synthesis methods and DFT calculations

Presented by: **Sujeet Kumar Pandey**

Department of Chemical & Biochemical Engineering (CBE)

Rajiv Gandhi Institute of Petroleum Technology Jais, Amethi, Uttar Pradesh, India

Name of Student: Sujeet Kumar Pandey **Roll No.** 20CE0012

Email: 20ce0012@rgipt.ac.in

Degree for which submitted: Doctor of Philosophy

Name of the Supervisor: Prof. Amit Ranjan

Photocatalysis under visible light has emerged as a sustainable approach for environmental remediation and solar energy harvesting. However, conventional photocatalysts suffer from limited visible light response, low charge separation efficiency, and insufficient surface activity. To overcome these challenges, this research explores the design of composite materials through various synthesis strategies and theoretical studies using Density Functional Theory (DFT). The focus is on engineering nanocomposites that exhibit enhanced photocatalytic performance under visible light by manipulating structural, electronic, and surface properties via synthetic modifications.

Chapter 1: Introduction.

This chapter lays the theoretical and experimental foundation for synthesizing composite photocatalysts. It discusses how structural engineering, through doping, compositing with graphene-based materials, and plasma treatments, can alter electronic properties such as band gap, donor density, and surface area. The importance of DFT calculations in predicting and validating changes at the atomic level is emphasized to understand and rationalize photocatalytic performance enhancements.

Chapter 2: Synthesis and Characterization of ZTO/GO Composites.

ZTO/GO composites with 1% GO were synthesized using three different methods: solid-state, liquid-phase, and hydrothermal techniques. The hydrothermal method resulted in the highest degree of GO reduction to r-GO, as confirmed by XRD and XPS. Ambient synthesis routes led to greater Zn_2TiO_4 phase formation due to oxygen deficiency, whereas hydrothermal treatment inhibited this transformation. Hydrothermal synthesis yielded higher BET surface area (1.40 m^2/g) and broader XRD peaks, indicating lower crystallinity but more photocatalytic active sites. Among all, Composite III demonstrated the best performance, balancing reduced bandgap (2.73 eV), high surface area, and efficient charge transfer as evident from Electrochemical Impedance Spectroscopy (R_{ct}=3.1 kΩ). The strong ZTO-rGO interface played a key role in enhancing photoactivity.

Chapter 3: Plasma-Treated $ZnTiO_3$ for visible light pollutant degradation.

A custom-designed setup enabled nitrogen plasma treatment of sol-gel synthesized $ZnTiO_3$ particles. Immediate liquid immersion post-treatment preserved the plasma-induced surface modifications, including oxygen vacancy creation and surface area enhancement. These changes significantly improved photocatalytic activity, with the rate constant increasing by 1.56 times under LED light compared to untreated samples. This chapter highlights how non-conventional post-synthesis treatments like plasma exposure can effectively tailor photocatalyst properties without altering bulk structure.

Chapter 4: NiZnO/GO Nanocomposites for visible light pollutant degradation.

NiZnO/GO composites were synthesized hydrothermally with varying GO content. The inclusion of GO induced oxygen vacancies, reduced the bandgap, and increased the specific surface area of the composite materials. Among the variants, NiZnO/GO10 demonstrated superior photocatalytic efficiency under visible light, with the rate constant 1.76 times higher than that of pristine NiZnO. This enhancement is attributed to improved light absorption, increased active sites, and better interfacial charge separation facilitated by the GO matrix.

Chapter 5: Cu-Doped $ZnTiO_3$: Structural and Electronic Modifications for photocatalytic applications.

Cu doping introduced lattice strain and surface defects, as evidenced by XRD peak broadening. FESEM analyses revealed morphological transformations more porous and rougher surfaces when synthesized in Deep Eutectic Solvent (DES), indicating enhanced photocatalytic interface properties. Tauc plot and DFT results confirmed bandgap narrowing and mid-gap state formation, enhancing visible-light absorption and electron-hole separation. Cu-doped $ZnTiO_3$, especially when DES-synthesized, shows promise for use in solar energy applications due to its optimized electronic structure and surface morphology.

Chapter 6: Summary and Future Scope.

This work successfully demonstrates the role of composite formation, doping, and plasma treatment in enhancing the photocatalytic efficiency of oxide materials under visible light. These strategic synthesis of oxide-based photocatalysts proved most effective in increasing surface area, introducing beneficial defects, reduced band gaps, improved crystallinity control, and efficient charge carrier dynamics. DFT calculations supported experimental findings by explaining changes in band structure and defect-induced electronic states.

Future research directions:

Integrating multi-metal doping to synergistically tune electronic properties. Developing scalable plasma setups for industrial-level photocatalyst production. Using machine learning algorithms with DFT data for predictive design of new photocatalytic composites. Expanding application domains to water splitting, CO_2 reduction, and photovoltaic devices. This work contributes a comprehensive framework for rational design and experimental validation of next-generation visible-light-active photocatalysts.

List of publications

1. **Sujeet Kumar Pandey**, Vipin Amoli, **Amit Ranjan***, Synthesis and characterization of zinc titanate-graphene oxide composites prepared under ambient and hydrothermal conditions, *Solid State Sciences*, Volume 166, 2025, 107969. https://doi.org/10.1016/j.solidstatesciences.2025.107969.

2. **Sujeet Kumar Pandey, Amit Ranjan***, Improving zinc titanate dispersion in water and thereby its photocatalytic activity towards MB degradation by using custom designed plasma treatment set-up, *Ceramics International* **(Under Review).**

3. **Sujeet Kumar Pandey**, Bhupendra Kumar, V.S. Sistla, **Amit Ranjan*,** Photocatalytic performance of NiZnO-graphene oxide composites, towards visible light induced degradation of methylene blue dye. **(Manuscript Prepared).**

4. **Sujeet Kumar Pandey, Amit Ranjan*,** Computational and experimental investigation of Cu doped ZnTiO3 for photocatalytic applications, (**Under preparation**).

5. **Sujeet Kumar Pandey, Amit Ranjan***, First-Principles Prediction of Enhanced Photocatalytic Activity in Cu-Doped $ZnTiO_3$ by Replacing Zinc and Titanium. Proceedings 2024, 105, 71. https://doi.org/10.3390/proceedings2024105071.

6. Yogendra Yadawa, Anil Verma, **Sujeet Kumar Pandey, Amit Ranjan***, PVP assisted sol-electrospraying, unlike sol electrospinning, yields highly pure rhombohedral zinc titanate particles that reduce 4-nitrophenol under visible light, *Journal of Alloys, and Compounds,* Volume 981, 2024, 173618 2023. https://doi.org/10.1016/j.jallcom.2024.173618.