INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI
SHORT ABSTRACT OF THESIS

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Thesis Title: Synthesis of TiO_2-Based Nano-Photocatalysts for Organic Synthesis, Wastewater Treatment and Antibacterial Photocatalytic Therapy

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Thesis Submitted to the Department/ Center	:	Centre for the Environment

Date of completion of Thesis Viva-Voce Exam	:	01.08.2023
Key words for description of Thesis Work	:	TiO_2-Based Nano-Photocatalysts, Organic Synthesis, Glaser Coupling, Click Chemistry, Wastewater Treatment, Antibacterial Photocatalytic Therapy

SHORT ABSTRACT

The dissertation entitled "Synthesis of TiO_2-Based Nano-Photocatalysts for Organic Synthesis, Wastewater Treatment, and Antibacterial Photocatalytic Therapy" consists of a total of five chapters.

Chapter 1 is a review chapter focusing on the application of TiO_2-based heterogeneous photocatalysts in photocatalytic organic synthesis and wastewater treatment. Also, this chapter discusses in detail the basic understanding of heterogeneous photocatalysis and the exclusive properties of TiO_2 that is necessary to modify the crystal structure and bandgap orientation of TiO_2 for synthesizing new catalysts.

Chapter 2 elaborates on the first-ever report of heterogeneous photocatalytic Glaser coupling in green solvent. This chapter deals with the unique concept of a transient electron-generating semiconductor system that is utilized for both hetero-Glaser coupling and click reactions. The newly designed smart photocatalyst Cu^{2+}@TiO_2 could utilize the photogenerated electron and the holes, respectively, from the semiconductor material, for the reduction of Cu(II) into Cu(I) and oxidation back to Cu(II), thereby continually maintaining the catalytic cycle without needing of O_2 from the air. It also offers broad substrate scope, including the decoration of biomolecular building blocks with alkynes, and works well with aliphatic alkynes. Thus, one can achieve comprehensive temporal and spatial control over the hetero-Glasser reaction utilizing our catalyst. The catalytic efficiency is also reflected in its excellent recyclability without sacrificing product yield. Further, the same catalyst can be further explored for other challenging and unexplored photocatalytic organic transformations along with Pd-catalyst [Catal. Sci. Technol., 2023,13, 1281-1287; Patent: E-2/42/2023-KOL].

Chapter 3 is the reflection of the designing concept of Chapter 2, which deals with a judicious design of transient electron-generating Cu^{2+}@TiO_2. Inspired by the success of heterogeneous photocatalytic glaser coupling reaction we further explored the catalyst for click chemistry. Cu^{2+}@TiO_2 could successfully carry out photocatalytic heterogeneous azide-alkyne cycloaddition under mild conditions. A broad substrate scope could be achieved using our catalyst and most interestingly the reactions can be carried out without needing a base. The catalyst is efficient and useful for decorating the biomolecular building blocks with triazoles. The efficient workability with internal alkynes for highly substituted click-triazole formation is another exciting feature of the catalyst [Patent: E-2/42/2023-KOL].

Chapter 4 describes the first-ever report of I^{5+}/TiO_2 as a smart catalyst serving a dual role as sensor and photocatalyst. The chapter discusses in detail the synthesis and crystal structure of I^{5+}/TiO_2. A detailed study on the modification of the crystal structure of pristine TiO_2 by doping higher valence state I^{5+} ion, which ultimately acted as a strong electron acceptor and also help in charge compensation, is presented in this chapter. Further, the property of I^{5+} toward designing a molecular sensor for azo-dye Methyl Orange (MeO) was studied. Finally, the synthesized nanomaterial was established as an excellent photocatalyst with exceptional ability in photo-assisted catalytic degradation of MeO and MeB dyes within 60 min. The role of various active species in the photocatalytic reaction as well as the degradation pathway of the targeted dyes have also been established. Further, the study was extended to find the effect of the treated water on the germination of Vigna radiata (green gram seeds). Additionally, the treated water was also tested on HEK293 mammalian cell lines for cytotoxicity analysis. The results obtained suggested that the treated water is completely safe and devoid of any toxicity toward plants and human health. Therefore, the I^{5+}/TiO_2 assisted photocatalytic treated dye water can be utilized for agricultural and other household activities [J. Environ. Chem. Eng., 2022, 10, 108919].

Chapter 5 introduced a new and novel quantum dot ZnSe/CdSe/$FeTiO_3$ (***^{Bag}QD***) which has no prior report. The size of the quantum dot was found to be between 4-5 nm showcasing a band gap of 1.1 eV. ***^{Bag}QD*** when excited with visible light (λ >600 nm) showed excellent photophysics ultimately leading to a dual property of fluorescence-guided imaging/sensing and ROS-generated targeted photocatalytic disinfection therapy for multiple disease-causing bacteria including multidrug-resistant S. aureus without any regrowth. The excellent Fl-guided imaging/sensing and photocatalytic property of ***^{Bag}QD*** is resulted from the excellent electron transport cascade that is generated as a result of the triad heterojunction of ZnSe/CdSe/$FeTiO_3$. The positive surface charge of ***^{Bag}QD*** with respect to the negatively charged bacterial membrane has resulted in unique electrostatic interaction resulting in FL-based discriminative sensing of gm -ve from gm +ve bacteria. This interaction also facilitated the photocatalytic ROS generated in the process to directly attack the bacterial cellular membrane and cause complete damage through cytoplasmic leakage, DNA degradation including complete elimination of ARGs. The detailed mechanistic investigation of photocatalytic bactericidal properties as well as the excellent biocompatibility of ***^{Bag}QD*** is discussed in this chapter. The therapeutic application of ***^{Bag}QD*** was established from the in-vivo mice skin wound infection treatment study. With the support of all the evidence obtained through this investigation, we propose to project ***^{Bag}QD*** as a new alternative to antibiotics. Hence ***^{Bag}QD*** is a smart nanomedicine that upholds the hope to revolutionize the diagnostic and clinical avenue [Patent: E-2/85/2023/KOL].