Synopsis

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Nanoscience and nanotechnology have a vast potential in the modern world since these exciting fields help to explore and understand the fundamental properties of matter in the nanoscale dimension. Since nanomaterials exhibit distinctive behaviours which significantly differ from their bulk equivalents, this enables scientists, engineers, and researchers to design and develop innovative solutions with extraordinary precision. This interesting branch of science has immense prospective for environmental applications, like in wastewater remediation. Nanomaterials can be employed to remove contaminants like heavy metals, organic impurities, pathogens, and other pollutants from water resources with excellent efficiency. Moreover, nanocatalysts can significantly contribute to enhancing the efficiency of wastewater treatment procedures by converting contaminants into less toxic or non-toxic products. The present dissertation encompasses the synthesis and characterization of carbon- and nitrogen-based polymeric nanomaterials in their pristine and doped forms. The physiochemical properties of these nanomaterials have been modified by varying the synthesis techniques. Finally, the suitability and applicability of the as-synthesized nanomaterials in the fields of wastewater remediation have been extensively investigated following different methodologies.

Carbon- and nitrogen-based nanomaterials consisting of triazine cores as the fundamental building blocks have immense potentiality in numerous targeted applications owing to their fascinating characteristics. The reason for choosing this class of materials is their low cost of synthesis, straightforward synthesis technique, large yield of production, and the raw materials required for their synthesis purposes are cheap and easily available. Moreover, these materials are non-toxic in nature, which facilitates their utilization in environmental applications. Their two-dimensional conjugated matrix provides a stable support for anchoring metal nanoparticles, and their covalent network gives rise to chemical and thermal stability. These nanomaterials have abundant reactive sites on their surface owing to their nitrogen-rich nature, which is highly beneficial for sensing and catalytic applications. A novel triazine-based organic polymeric material (MEG_{10}) possessing some interesting features like crystallinity, thermal stability, and nanodendrite-like morphology, along with abundant surface functional groups, was developed in this dissertation. Graphitic carbon nitride (GCN) belongs to the class of triazine-based polymeric materials, which has colossal significance for implementation in the fields of environmental remediation. In the present dissertation, GCN was synthesized in its pristine form with substantial modification in its surface and physiochemical properties through thermal treatment and exfoliation procedures. Moreover, GCN was decorated with transition metal ions like Cu and Ni to modify its surface properties and to enhance its effectiveness in rapidly degrading hazardous wastewater contaminants. All the triazine-based nanomaterials synthesized during the research works were thoroughly characterized employing modern characterization techniques to unravel their intrinsic properties in details.

Fluorescence detection technique is a highly selective, sensitive, and rapid method for the detection of heavy metals from aquatic environment. Until now, the majority of previous studies have indicated that triazine-based polymers used for sensing mercury ions (Hg^{2+}) necessitate the incorporation of sulfur-based functional groups due to the strong affinity of Hg^{2+} towards sulfur. Nonetheless, MEG_{10} polymer sensor demonstrated an impressive level of sensitivity, with a value of approximately $8.18x10^{6}$ M^{-1}, and ability to selectively detect Hg^{2+} ions at an incredibly low concentration (1.95 nM) without the requirement of any sulfur-mediated modifications. This is because the covalent MEG_{10} polymer is rich in nitrogen and oxygen functional groups, which facilitated the ultra-trace level detection of mercury ions. The underlying sensing phenomenon was thoroughly elucidated to comprehend the material's practicality and potential applications.

Until now, the majority of reports on enhancing the photocatalytic activity of GCN have necessitated complex procedures involving the creation of heterojunctions or the integration of metals or non-metals into the GCN framework. However, these approaches often introduce toxicity to GCN, which can lead to secondary contamination, rendering the utilization of such materials impractical and challenging in real-world scenarios. In contrast, a straightforward synthesis method for metal-free pristine GCN was undertaken in the present dissertation. It focused on modifying GCN through exfoliation, eliminating the need for intricate functionalization while achieving remarkable catalytic properties. The conventional bulk GCN suffers from a limited surface area, resulting in clustered sheets that poorly adsorb pollutants on its surface. To overcome this limitation, the surface area of GCN was successfully increased to a value of 88.735 m^2/g through exfoliation; thereby creating a greater number of active sites. This enhancement led to improved adsorption of contaminants, ultimately resulting in superior catalytic activity. This exfoliated GCN (GCX) was subsequently implemented in the photocatalytic reduction of some conventional harmful pollutants found in aquatic environments, specifically targeting the removal of rhodamine B dye (RhB) and hexavalent chromium (VI) (Cr(VI)) heavy metal. By harnessing visible-light source, GCNX was capable of rapidly degrading RhB dye within just 30 min when combined with the electron-capturing reagent H_2O_2. Additionally, it could efficiently convert chromium from its hexavalent to trivalent form in less than 2 h when FA was introduced into the system as the hole-capturing reagent. In order to comprehend the intricate interplay between the factors influencing catalytic activity, a comprehensive statistical assessment was conducted using the response surface methodology. Additionally, first-principles calculations based on density functional theory was undertaken to further investigate the reduction efficiency of the GCN catalyst.

Though metal nanoparticles exhibit remarkable potentiality in catalysing the reduction of hazardous pollutants following catalytic hydrogenation technique, nevertheless, metal nanoparticles are costly, prone to agglomeration with repeated usage, and exhibit poor stability. These factors hinder their practical application as catalysts in wastewater treatment. To address these limitations, researchers have sought to immobilize or anchor nanoparticles onto the two-dimensional matrix of GCN. The majority of existing studies focus on incorporating noble metals (like Au, Ag, Pt) into the GCN sheets, which poses practical limitations due to their high cost, limited availability, and the need for controlled synthesis approaches. In contrast, transition metals such as Cu and Ni are widely abundant on earth and offer a more cost-effective solution for practical applications. In the present dissertation, promising catalyst materials were developed by integrating Cu and Ni into the GCN conjugated network. The as-synthesized nanomaterials were extensively employed to catalytically degrade a wide spectrum of pollutants commonly present in wastewater, including textile pollutants and nitrophenol compounds, utilizing the $NaBH_4$-mediated catalytic hydrogenation method. The catalysts decorated with metals exhibited an impressive ability to rapidly and completely reduce these pollutants in just a matter of minutes, demonstrating nearly 100 % decolourizing efficiency in all the cases. The effectiveness of the catalyst was confirmed by conducting detailed first-principles-based rigorous theoretical calculations. By exploring atomic-level reactions, the most viable reaction pathways for selected pollutants were identified, highlighting the crucial role of $NaBH_4$ in facilitating the electron-relay process.

Therefore, the inexpensive nanomaterials discussed earlier can serve as highly effective sensors and catalysts for identifying and breaking down various pollutants commonly found in wastewater. In wastewater remediation, these polymeric materials exhibit exceptional performance, making them viable substitutes for certain conventional catalysts.

Keywords: nanomaterials, polymers, triazine-core, metal-doping, exfoliation, heavy metals, organic dyes, nitrophenols, sensing, photocatalysis, catalytic hydrogenation, first principles calculation, DFT, reaction pathways.

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