Executive Summary of the Ph.D. thesis Entitled

"INVESTIGATION ON GRAPHENE BASED COMPOSITES OF METAL OXIDES FUNCTIONALIZED BY SURFACTANTS"

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By

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❖ Introduction:

Rapid industrialization and urban expansion have significantly increased the discharge of wastewater, leading to substantial water pollution, notably from dye release. This poses a grave threat to both terrestrial and aquatic ecosystems. Effluent disposal containing used dyes exacerbates water pollution, necessitating treatment to mitigate its harmful effects before disposal. However, dye removal remains a formidable challenge due to its potential health hazards, including allergic reactions, skin irritation, and carcinogenicity. Various methods such as physical, photocatalytic, electrochemical, chemical, adsorption, and biological treatments have been employed to address this issue. Among these, adsorption emerges as the most effective technique due to its simplicity, affordability, and adaptability in selecting and modifying adsorbent materials. Additionally, it generates no harmful by-products and can efficiently treat large water volumes[1]. Analytical instruments like GC–MS[2], LC-MS[3], and HPLC-DAD[4] have been established for dye detection, offering rapid and precise results. However, these techniques are hindered by high costs, complex instrumentation, and the use of organic reagents, necessitating a more sustainable approach. UV-visible spectroscopy presents itself as a viable alternative detection method, offering user-friendly operation, quick and accurate results, and cost-effectiveness, thus promoting sustainability throughout the process[5].

Graphene oxide (GO) is preferred over pure graphene due to its functional groups and exceptional properties **(Figure 1)**. However, challenges such as surface energy-induced agglomeration and higher costs are encountered. These issues are addressed by incorporating metallic oxides through nanocomposite (NC) formation[6–8]. Titanium (IV) oxide (TiO_2) has garnered significant attention in the research community for NC formation due to its easy availability, long-term stability, cost-effectiveness, non-toxic nature, biocompatibility, environmental friendliness, and high chemical stability[9–12]. These qualities render it a promising precursor for nanomaterial in large-scale industrial wastewater treatment[13]. Currently, NCs are being modified or functionalized with various compounds or mixtures, including polymers (both synthetic and natural), surfactants, or ionic liquids among others [14–19].

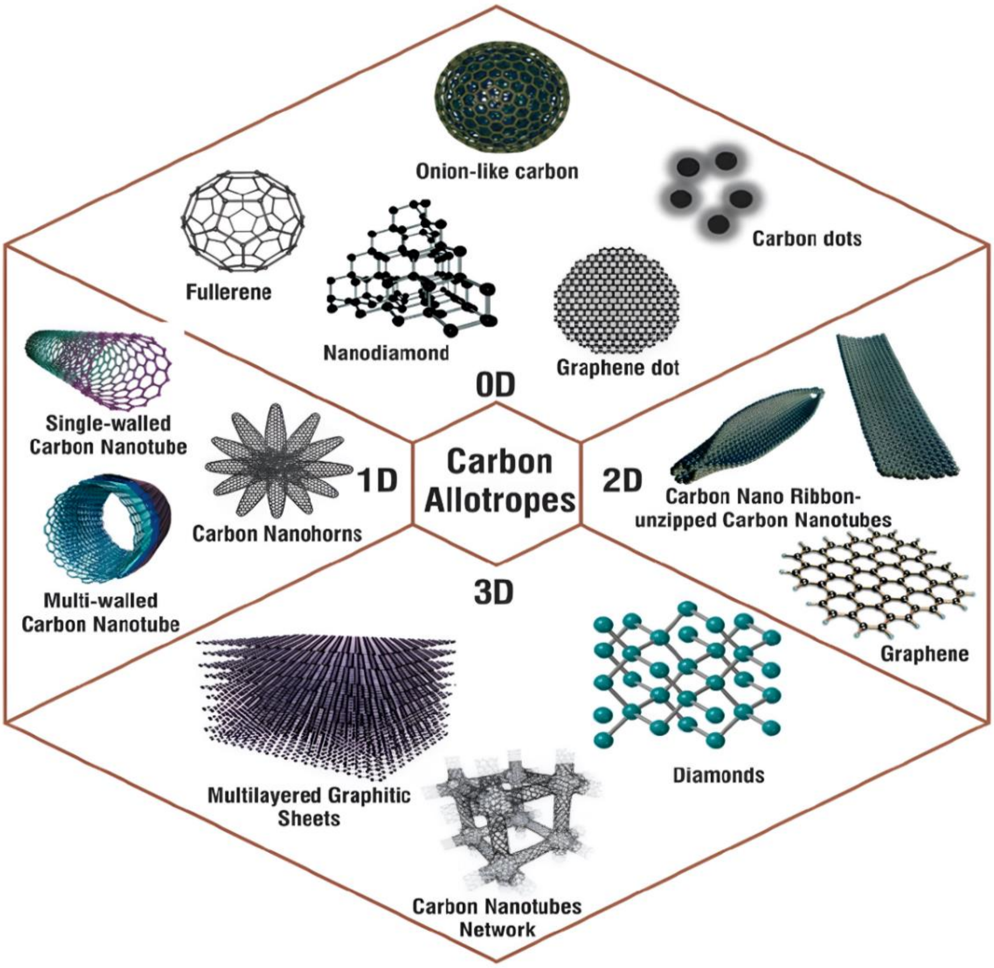

Figure 1: Illustration of carbon-based materials[20].

GO can undergo modification through the addition of other groups via either covalent or non-covalent bonding. Covalent functionalization is feasible due to the presence of carboxylic and carbonyl groups at the edges, as well as epoxy and hydroxyl groups on the surface of GO. These functional groups serve as active sites for the addition of other organic functionalities onto the GO surface[21]. For the functionalization of GO with organic molecules, achieving orthogonality in the reaction conditions is ideal for selectively functionalizing one site over another[22]. On the other hand, non-covalent functionalization can be accomplished through intercalation and doping. Small molecules, such as surfactants[18], pyridine[23], proteins[24], DNA[25], RNA, peptides, deep eutectic solvents (DES)[26], and complex compounds like anticancer drugs, can be functionalized onto graphene surfaces[27]. This process enhances solution processing capability, as well as optical, electronic, and biological properties (**Figure 2**)[28].

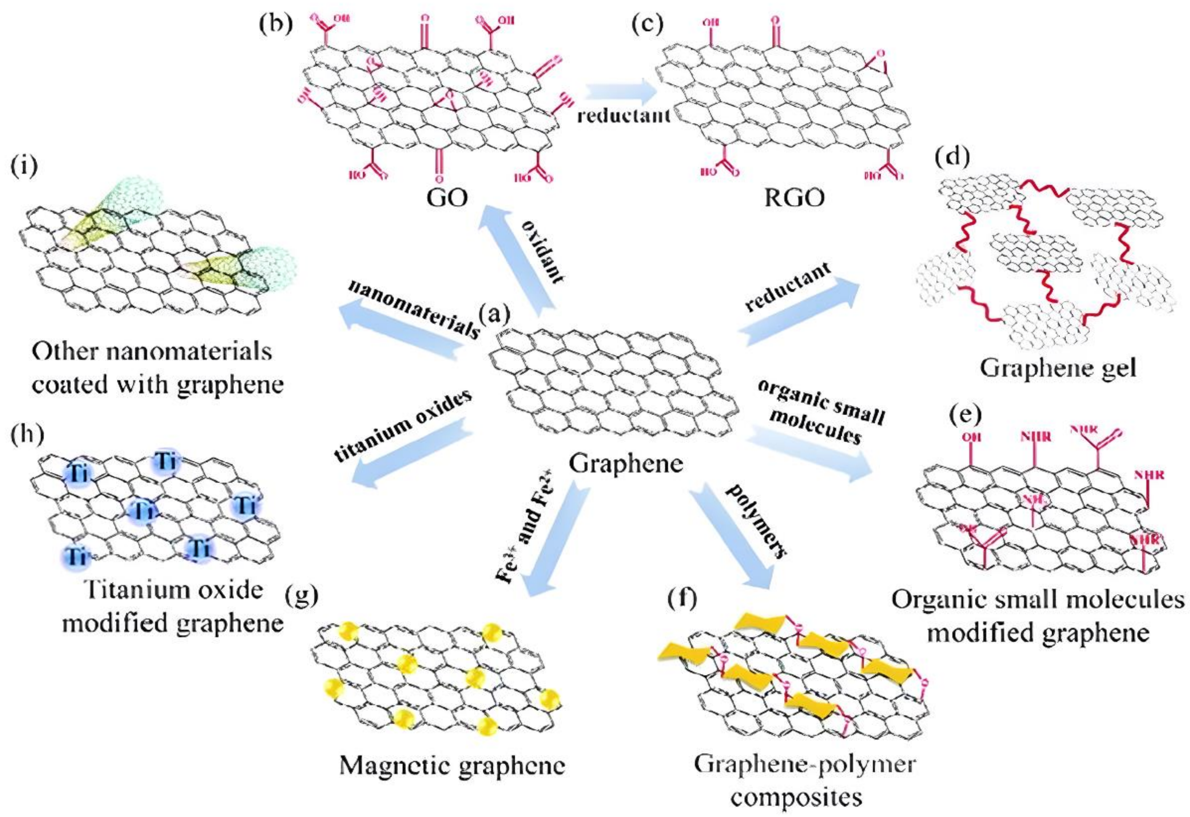

Figure 2: Functionalization of graphene (a) Graphene; (b), (c), and (d) are GO, rGO and graphene gel; (e) and (f) are organic small molecules and polymers modified graphene materials; (g), (h), and (i) are NPs functionalized graphene materials[29].

❖ **Brief Research Methodology:**

Carbon allotropes have received considerable attention over the past few decades due to their unique properties and wide-ranging applications. One notable allotrope, graphene, consists of a single layer of carbon atoms arranged in a two-dimensional lattice with sp_2 hybridization. Graphene is extensively utilized, both in its pure form and as part of composites, across various scientific and engineering fields due to its outstanding mechanical, electrical, and thermal properties. Despite these impressive characteristics, GO is often favored because of its functional groups. GO disperses readily in aqueous solutions, making it particularly useful for treating polluted water. However, its high surface energy can cause agglomeration, reducing its dispersibility. To overcome this challenge, GO is frequently combined with metallic oxides to create NCs. These NCs, which are multicomponent materials with distinct phase nano-domains, possess specific structural and photochemical properties that enhance their effectiveness in water treatment technologies.

The thesis entitles "**Investigation on Graphene Based Composites of Metal Oxides Functionalized by Surfactants**" consists of seven chapters including: ***Chapter 1*** : General introduction; ***Chapter 2*** *:* Materials, methods, and characterization techniques; ***Chapter 3*** : Synthesis and characterization of surfactant/DES modified GO@ZrO_2 NC for adsorption of dye from aqueous background; ***Chapter 4*** : Synthesis and characterization of surfactant/DES modified GO@TiO_2 NC for adsorption of dye from aqueous background; ***Chapter 5*** : GO/surfactant-inspired photophysical modulation of dye in DESs with or without additives; ***Chapter 6*** : Polymer blend NCs for the separation and purification of gases for different applications; ***Chapter 7*** : Conclusion and future perspective. The salient features of each chapter are given as under.

Chapter 1 delves into the realm of nanotechnology and nanocomposites, with a special focus on GO, a carbon-based two-dimensional material. This chapter provides a concise overview of graphene oxide, highlighting its unique properties. It also underscores the benefits that come from functionalizing GO with metal oxide NCs.

Chapter 2 delves into the synthesis routes, principles, and applications of characterization techniques utilized in the creation of nanocomposites with metal oxides. GO was synthesized in the laboratory using Hummer's method. Additionally, the discussion covers the functionalization of graphene-metal oxide nanocomposites with surfactants and DESs. Subsequently, major characterization techniques for structural, chemical, microscopic, and physical evaluations of nanocomposites were developed. These techniques include Fourier transform infrared spectroscopy (FTIR), X-ray diffraction studies (XRD), UV-visible absorption spectroscopy (UV-Vis), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), energy dispersive X-ray (EDX), contact angle measurement, and tensile strength analysis.

In **Chapter 3** and **Chapter 4**, the synthesis of nanocomposites continued with graphene oxide–zirconium oxide (GO@ZrO_2) and graphene oxide–titanium oxide nanocomposites (GO@TiO_2), respectively. Subsequently, these nanocomposites underwent modification using a cationic gemini surfactant (CGS, specifically butanediyl-1,4-bis(N,N-hexadecyl ammonium) dibromide (16-4-16)), dodecyl trimethyl ammonium bromide (DTAB), or DES (reline, ChCl; urea, in a 1:2 molar ratio). Following synthesis and modification, the resulting adsorbent materials underwent thorough characterization using various physicochemical techniques. To evaluate their effectiveness, methylene blue (MB) was utilized as a model adsorbate to investigate its adsorption and removal from aqueous solutions employing the modified nanocomposites. The adsorption data obtained were then compared with those of other similar reported adsorbents. Interestingly, the DES-based advanced material demonstrated ultrafast MB adsorption compared to the surfactant-modified nanocomposites. These findings underscore the promising potential of the developed nanocomposites for efficient and rapid adsorption applications.

Chapter 5 delves into the photophysical behavior of rhodamine B (RB) within DESs, both in the presence and absence of GO or ionic surfactants. The chapter provides a comprehensive analysis of how GO, surfactants, or their combination affect the movement of RB across various sites, including the GO surface, surfactant micelles, DES surface, and the background solvent, using fluorometric analysis. Furthermore, it is observed that modifications induced by reline in DESs alter the interactions between RB and GO, sodium dodecyl sulfate (SDS, an anionic surfactant), or cetyltrimethylammonium bromide (CTAB, a cationic surfactant). The DES environment controls whether RB adopts a cationic or zwitterionic form, which significantly influences its interactions and sustained movement toward the GO surface, micellar surface, or the formation of negatively charged ion pairs with SDS monomers. These findings offer a deeper understanding of the complex interactions among DES components, surfactants, and GO in shaping the photophysical behavior of RB. This knowledge is valuable for potential applications in controlled-release systems and sensing devices.

In **Chapter 6**, the fabrication of Mixed Matrix Membranes (MMMs) was achieved using the standard phase inversion technique, known for its cost-effectiveness and time efficiency. This process involved blending polycarbonate (PC) and polystyrene (PS) with nanofillers, such as GO and ZrO_2, in concentrations ranging from 2 wt% to 20 wt%. Additionally, membranes incorporating DES were produced. The resulting MMMs were thoroughly characterized using various techniques. Leveraging the excellent surface characteristics of ZrO_2, the high sorption capacity of GO, and the enhanced thermal stability provided by DES, the MMMs demonstrated significantly improved gas permeability and selectivity compared to conventional membrane materials. Permeability data for various environmental gases, including CO_2, N_2, O_2, and CH_4, were collected and used to determine selectivities, highlighting the potential of these MMMs for advanced gas separation applications.

In **Chapter 7** provides a comprehensive summary of the research, highlighting key findings and outcomes. It concludes by discussing potential future research directions in related areas, offering insights into the possibilities for further exploration.

❖ **Key Findings:**

This thesis proposes a comprehensive approach to synthesize GO via a modified Hummer's method, integrating metal oxides to create nanocomposites. Functionalization with surfactants and DES enhances these nanocomposites, which are meticulously characterized for their structural, chemical, and optical properties. Dye adsorption experiments demonstrate their efficacy in wastewater treatment. Additionally, polymer-modified nanocomposites show promise in enhancing gas separation for energy storage and green hydrogen production. The study also explores photophysical modulation of dyes in DESs, with and without additives, leveraging GO and surfactants to reveal significant insights for advanced material applications.

❖ Conclusion:

In conclusion, this thesis presents a detailed investigation of graphene-based composites, emphasizing metal oxide functionalization and surfactant/DES modification. It begins by highlighting the fundamental properties of GO and the advantages of functionalizing NCs with GO and metal oxides. The synthesis of nanocomposites involved preparing GO and functionalizing graphene-metal oxide nanocomposites with surfactants and DESs. Characterization techniques such as FTIR, XRD, UV-Vis, TGA, DSC, FESEM, TEM, EDX, contact angle measurements, and tensile strength tests elucidated their structural, chemical, and physical properties. GO@ZrO_2 and GO@TiO_2 NCs were synthesized and modified using a cationic gemini surfactant, DTAB, or DES (reline). These materials showed ultrafast MB adsorption, highlighting their potential for efficient wastewater treatment. The thesis also explores the photophysical behavior of RB in DESs with and without GO or ionic surfactants, revealing intricate interactions valuable for controlled-release systems and sensing devices. Additionally, the fabrication of MMMs using PC and PS with nanofillers like GO and ZrO_2 demonstrated improved gas permeability and selectivity. These advancements indicate the potential of MMMs for advanced gas separation applications. Overall, the thesis successfully integrates graphene-based nanocomposites, showcasing their versatility in wastewater treatment, gas separation, and photophysical studies, paving the way for future innovations in nanotechnology and material science.

❖ Recommendation and Suggestions:

For future research, it is recommended to explore the long-term stability and reusability of the synthesized nanocomposites in real-world applications. Investigating the environmental impact and biodegradability of these materials will be crucial for sustainable development. Additionally, expanding the range of metal oxides and surfactants could further enhance the properties and applications of the nanocomposites. Advanced computational modeling could provide deeper insights into the interaction mechanisms at the molecular level. Lastly, scaling up the synthesis process while maintaining the material's efficacy and consistency should be prioritized to facilitate industrial applications and commercialization.

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