Thesis Abstract

Two-Dimensional Films and Three-Dimensional Macrostructures from the Aqueous Dispersions of Graphene Oxide: Synthesis, Rheology and Applications

Abstract

The 'graphene era', started in 2004 following the discovery of graphene by Geim and Novoselov, has laid interest in Graphene oxide (GO) research first as a starting material for the graphene synthesis and later as a unique material itself due to its structure and functionalities. GO is a two-dimensional (2D) material with plenty of oxygen-containing functional groups like carboxyl, epoxy, hydroxyl, carbonyl groups that play an exciting role in deciding properties of GO.

A single layer of GO, due to its homogeneity, large surface area (2630 m^2g^{-1}) and occupancy of chemically active surface functional groups, are also manifested to have a high adsorption capability. Utilizing these properties, the scientific community has established its decontamination potential for a spectrum of organic substances related to various industries. However, the recovery of GO from water requires ultrahigh centrifugation for an extended time, which significantly increases the process costs and difficulty. Further, the long term exposure to these graphene-family nanomaterials (GFN's) to water is reported to be toxic. To overcome these many biopolymers and chemicals are said to cross-link the individual GO sheet and make 3D networks. However, despite being too costly, all these cross-linked nanostructures show either weak mechanical strength or have very low efficiency towards the adsorption or removal of hazardous organic substances. Thus there is a constant requirement for the materials with higher mechanical strength, reasonable adsorption capacity, and minimum toxicity.

In this thesis work, we tried to investigate graphene-based two-dimensional (2D) and three-dimensional (3D) nanostructures with tunable mechanical strength and good adsorption capacity; further we report the rheological tuning mechanism for these gel-like aggregated nanostructures for the first time. We studied the microstructure, rheology and adsorption properties of aqueous dispersions of GO at an optimized volume fraction (ϕ_{GO})

= 0.018, which can be transformed into gels by cation induced charge shielding and cross-linking between the GO nanosheets. At similar ϕ_{GO}, cations of varying size and valence are systematically introduced with a range of electrolytes. Our results suggest that depending on the electrolyte concentration, size and the valence of the cation: low viscosity suspensions, fragile gels, and solid-like GO-electrolyte cross-linked gels are formed. These GO-electrolyte gels are shown to adsorb high quantities of oils and other organic contaminants. Along with higher oil and dye adsorption efficiency, GO-electrolyte gels are easy to recollect after the adsorption, thus avoiding the potential toxicity for bio-organisms in water caused by GO nanosheets.

Next to this, we explored the effect of size reduction and electrolyte addition on the rheology, microstructure, and adsorption capacity of the GO suspensions. We show that increasing the time of ultrasonication without any chemical treatment can promote aggregation of GO nanosheets reflected by the increase in the storage modulus (G'_p). The presence of electrolytes (NaCl, $MgCl_2$) increases the elastic moduli for GO aqueous dispersions by depending on the extent of aggregation and cross-linking. Stable gel-like suspensions with maximum G'_p are formed for GO nanosheets with the largest aspect ratio and maximum tested electrolyte concentration. The detailed XPS analysis is used to demonstrate the Mg^{2+} mediated bridging of GO is the primary factor of aggregation and the subsequent large G'_p. Moreover, ultrasonication for prolonged time not only causes a reduction in the size of GO nanosheets but also leads to a reduction in the Mg^{2+} mediated crosslinking and hence a decrease in overall G'_p.

We further synthesized composite photocatalysts using graphene-based nanomaterials GO and rGO as matrix components with TiO_2 using heat treatment and hydrothermal process. The unique feature is that these composites also show significant degradation efficiency for both the dyes in white light, making them suitable for practical applications requiring a wide range of the spectrum. In sum-up, lower bandgap, very efficient separation of e^-/h^+ pair, and the availability of d-π electron cloud for the excellent e^- shuttling between the conduction band of TiO_2 and graphene matrix are some of the features that enhance the photocatalytic efficiency. One more unique feature of these photocatalysts is that they are equally efficient for the degradation of both MB and Eosin Y dyes with >95% efficiency in the extended wavelength region of the light spectrum.

Our next work reports the self-assembly of GO nanosheets at air-water interface using the LB method and obtained both monolayers and multi-layer films of graphene

oxide at specific experimental conditions. We further explore the reproducibility of forming these GO films at similar experimental conditions by performing multiple compression-decompression cycles and observed the potential effect of various cycles on the hysteresis obtained. We also studied the impact of a significant factor, temperature, on the stability and properties of obtained GO LB films.

In conclusion, the first aspect of the thesis work has presented a new perspective on the science of graphene oxide suspension rheology. It is indeed the first study to explain the effects of systematic cation addition on the rheological properties of aqueous GO dispersions. It also establishes that the microstructural transformation of GO suspensions is actually governed by the hydrodynamic size of participating monovalent cation and the valence in case it's a multivalent cation. The second aspect of the thesis work emphasizes mostly on the nanosheets properties responsible for anchoring the cations from electrolyte dispersion to form cross-links between the adjacent GO sheets. The experimental results are evidencing that the carboxyl functionalities available on the rim of the nanosheets are indeed responsible for creating cross-links between the nanosheets. Thus, exposing the GO sheets to ultrasonication reduces their size and cross-linking efficiency that results in the GO suspension of low average storage modulus (G'_p). This forms a fundamental discovery related to an aspect that has been associated with several research areas, yet remains unexplored. On the other hand, the third aspect of the thesis reveals the potential of graphene and its derivatives to be used as a suitable matrix material for the efficient anchoring of titania nanoparticles and form composites that are efficient to degrade both positively and negatively charged industrial dye wastes. In the end, the fourth aspect of the research reveals the ability to form monolayers on the air-water interface in optimized conditions. The monolayers of desired properties are of great scientific importance in designing the sensors and supercapacitors.

Overall, this thesis establishes a scope for using rheology as a modulation method for cation cross-linked GO-based macrostructures. It affirms that the mechanical strength and stability of these GO-based macrostructures depends on not only the external ionic conditions but also the size and functionalities of the GO sheets and can be optimized by controlling these critical factors. It not only provides certain fundamental additions to the current state of knowledge in 2D materials research but also raises so many questions in relevant contexts that open up new avenues of research in this domain.