**Graphene Quantum Dots -Polyacrylic Acid Hybrid   
Hydrogel as Heaven for Wound Healing**

**The rationale behind this work.**

Using the binary cooperative complementary principle to design self-assembly-confined unusual nanostructures is firmly entrenched in biomimetic materials, which exhibit hierarchical cooperation and complementarity, laying the groundwork for synthetic polymers. Self-assembly architecture using nanoparticle-mediated-polymer techniques can be used to understand well-organized supramolecular networks with the goal of leveraging intelligent macromolecular design. Nanostructures with precisely regulated size, orientation, shape, and adaptability utilising graphene-based fillers have been a long-sought goal, however high-dimensional nanoparticles can cause perturbations in polymeric chain formation. Understanding the relationships between synthetic polymer structure and function are of great importance. As technology requires more advanced materials with cutting-edge qualities, zero-dimensional (0D) analogues are becoming more popular. Graphene Quantum Dots (GQDs) have emerged as a critical functional material with applications in optoelectronics, and biomedical applications. Biocompatibility, high solubility, sustained photoluminescence, and improved surface grafting are all characteristics of GQDs, making them ideal entity for a variety of applications.

Transformative advances in hydrogel nanocomposite system leads to rational design of both the chemistry (framework’s nature and crosslinking approach) and the morphology (matrix structure) to append new end-groups in polymers and further harvesting the interaction of colloidal nano-regime carbon-structure *i.e.* GQDs with hydrogel matrix with numerous unique and distinct properties. GQDs have functional groups (hydroxyl, carbonyl and epoxy/ether) on their edges which make them fluorescent, soluble in water, and reactive towards other molecules. Click or tap here to enter text. Herein, we aim to elucidate the synthesis of graphene quantum dot-polyacrylic acid (GQD-PAA) and their further application for normal(diabetic) wound healing.

Various covalent and non-covalent forces *i.e.* spatiotemporal aspects at molecular level and corresponding interactions in order to scrutinize and infer correlation between the hydrogel matrix and GQDs is also crucial. ***Although, several excellent work exist in literature highlighting the successful impregnation of graphene family members such as GO/rGO/CNT/ Fullerene/CQDs within the hydrogel polymers matrix, however, there are very rare reports on the GQDs, a newly born candidate from the same family group communicating with the “host” polymer in functional hydrogel assisted colloidal system unravelling the underlying mechanisms.*** This sowed the seeds of unexplored vistas in the concerned regime. ***Till date, the dispersion behaviour of GQDs with respect to hydrogels at molecular levels is poorly studied. Hence, a conceptual framework of GQD-hybrid hydrogel and their interesting nexus has paved the way for a new horizon in the theranostic field.***

Interestingly, photoluminescent properties of the integrated GQDs can not only remain intact in the hybrid hydrogel Click or tap here to enter text.but hydrogel also provide protection to GQDs against degradation/denaturation in the harsh milieu. Nanoparticles like GQDs help to regulate the molecular arrangements during gelation by reducing phase separation and immobilizing a significant amount of solvent and hosting GQDs in solvent pockets, thus creating unique nano/microscopic domains.

In the current context, vested with excellent properties, GQDs' inclusion into hydrogel matrices has attained its pinnacle. **The superiority in the features of the hydrogel polymer matrix is the outcomes of physical interactions, polar-polar anchoring, surface enhanced physisorption, hydrogen bonding, and polymeric entanglement.** **At minimal nanofiller loading, mechanical strength is augmented and justified as a percolation threshold whose decreased value is attributed to the lesser filler fraction to improve the elastic modulus.** GQDs compared to other nanoscale fillers enhance certain physical properties of GQD-hybrid hydrogels. **GQDs, due to their nanoconfinement in all the three dimensions, offer more surface area for the polymer attachment and consequently better reinforcement effect.** Owing to the immense surface area and surface energy, a plethora of parameters have to be considered while planning a nano-inclusion into a polymer matrix. **GQDs are colloidal in nature and possess a great amount of surface charges that are counterbalanced by a hydrogel network chain or its pendant groups leading to better stability inside the hydrogel matrix.** Physical anchoring of GQDs through adsorption within the hydrogel matrix can extemporize its ﬂexibility, hydrophobicity, durability, and strength. **One of the major challenges of the polymer nanocomposites is the uniform distribution and intercalation of nanomaterials within the polymer matrices as nanomaterials are susceptible to agglomeration. Properties like surface polarities and functionalities of GQDs can overcome this challenge by proper insertion of the nanofiller within the polymer matrix.** **Now the question is why the idea behind the dispersion of nanodots inside a polymer matrix is of prodigious importance? The answer to this question is that polymers can pacify the high surface energy of nanoparticles by diffusing through their surface, indemnifying their ravenous nature and thereby stabilizing them.** **The free space within the porous structures of the hydrogel matrix acts as a nanoscopic room for the synthesis and growth of nanoparticles without accretions/disintegration**

Synthesis of GQD-polyacrylic acid hydrogel nanocomposite



GQD-HAA hybrid (a) PAA, (b) 0.05 % GQD PAA, (c) 0.1 % GQD PAA, (d) 0.3% GQD PAA, (e) 0.5% GQD PAA, (f) 1 % GQD PAA

* GQDs were incorporated in the polyacrylic acid PAA matrix
* Fluorescent hydrogels were obtained
* Hybrid acts as superabsorbent but with poor mechanical strength.

The attributes upon which GQD hybrid hydrogels hinge on is the information inscribed on the GQD surface. Nanomaterials, upon incorporation, can change the nanostructure of gelators and align themselves within the polymer chains, with its directionality being swayed by the interdigitation of surface functional groups present on the GQD surface and the polymer. The upsurge in dispersibility of nanofillers for the synthesis of nanocomposite gels can be achieved through non-covalent functionalization strategies and in aromatic-based gelators *via* π–π stacking. Easy dispersion, and hence the nanocomposite formation, can be achieved through the phenomenon of van der Waals interactions *via* alkyl chains and/or polymer chain wrapping. The degree of functionalization and the successful coalescence of nanofiller with the host gelator is subjugated by the magnitude of non-covalent interactions between the two. Intimate interactions between GQDs and hydrogels can witness an upsurge by appropriate surface modification. Therefore, the polymer microenvironment can act as “host” to harbour GQDs as “guests” to form GQD hybrid hydrogels. The formation of GQD hybrid hydrogels experience an interplay of numerous non-covalent interactions encompassing π-π stacking, van der Waals, dipole-dipole, electrostatic interactions through polar groups, hydrogen bonding and covalent interactions leading to the formation of nanocomposite gels with superior properties in comparison to the native gels.