Functionalized Graphene Oxide Quantum Dots based Hybrid Materials for Diverse Applications

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Abstract

Graphene, a “wonder material” with a potential to revolutionize the existing field of technology, is presently the most promising material for the future.[1] Recently, graphene quantum dots or GQDs (first reported in 2008) have attracted much attention after their cousin sister material i.e., carbon dots.[2] They are single or few-layered graphene sheets with lateral dimensions less than 100 nm being composed of a regular hexagonal lattice of sp² carbon atoms edged with heteroatomic functional groups[3] decorated with oxygenated groups including hydroxyl, epoxide and carboxyl at their edges similar to graphene oxide.[4] Surface modification via introduction of different chemical functionalities allows for favorable solubility, enhanced interaction of graphene sheets with polar polymer matrices, various biomolecules, or inorganic precursors in order to be applicable as potential materials in the field of bio-medical science, polymer composites, catalysis, nanoelectronics, sensors, batteries and supercapacitors.[5] Although many surfactant based methods are available, the presence of stabilizers is often undesirable and since practical applications require the presence of functional groups, therefore development of easier ways for better dispersibility and proper functionalization of graphene materials is the need of the hour.[6] On the other hand reinforcement of polymers with functionalized carbon nanomaterials has been an area of recent interest as a route to designing new materials with new and improved structural and functional properties thereby enabling enhanced performance of the material in a broad range of technological fields such as telecommunications, electronics, energy, biomedicine, transport industries and as chemosensors and biosensors with enhanced sensitivity and selectivity.[7]

Herein we report the synthesis, functionalization of Graphene Oxide Quantum Dots (GOQDs) and their subsequent applications as optical switching materials via in situ growth of CoNPs on the GOQDs and as sensors (based on colorimetric and UV-Visible detection) for detection of heavy metal ions(Fe²⁺, Co²⁺ and Cu²⁺) in aqueous media.

GOQDs were prepared from graphene nanoplatelets using a simple chemical method employing acid mixture oxidants (mixture of H₂SO₄ and HNO₃) and were subsequently characterized. Subsequently, a simple method for one step reduction cum functionalization of graphene oxide quantum dots using ethylene diammine followed by ethylene diammine mediated immobilization of Co²⁺ on the graphene oxide GQDs via in situ formation of Co₃O₄ nanoparticles is being reported. Ethylene diammine gets attached to the layers of graphene oxide quantum dots via ring opening of epoxides and acts as the driving force to pull the Co²⁺ ions into the interlayer spacings such that the ions get immobilized onto the GOQDs (as shown in Figure 1). Functionalization of GOQDs with ethylene diammine led to an enhanced fluorescence intensity of the graphene oxide quantum dots with a huge blue shift and this was tremendously increased upon in situ Co-nanoparticle formation on the GOQDs with further blue shift in PL emission. All the experimental evidences suggest the successful formation of GOQDs-CoNPs nanocomposite. Moreover, in our work we tried to prepare quantum level GQDs-inorganic hybrid material by using a very simple solution based strategy and we observed that the optical property i.e., fluorescence of GQDs could be greatly enhanced at the same time. Since this aspect has not been highly explored, therefore we feel our system can prove to be a model for opening up new possibilities for synthesis and possible applications of such systems in future.

On the other hand four different GOQDs were prepared using various chemical reactions viz. oxidation, reduction, esterification and amination and were successfully characterized. Functionalized Graphene Oxide Quantum Dots were then introduced as cross-linking agents into the Poly(vinyl alcohol) matrix (the polymer of interest) thereby resulting in gelation to form four different hybrid hydrogels. After careful experimental characterization, it was observed that the hybrid hydrogel prepared with amine functionalized graphene oxide quantum dots was the most stable. The potential applicability of this material was then subsequently explored in an easy, simple, effective and sensitive method for optical detection of Mg²⁺ (Fe²⁺, Co²⁺ and Cu²⁺) in aqueous media involving colorimetric detection. Amine functionalized graphene oxide quantum dots-poly(vinyl alcohol) hybrid hydrogel when put into the
corresponding solution of Fe$^{2+}$, Co$^{2+}$ and Cu$^{2+}$ renders brown, orange and blue coloration respectively of the solution detecting the presence of Fe$^{2+}$, Co$^{2+}$ and Cu$^{2+}$ ions in the solution (as shown in Figure 2). The minimum detection limit observed was 1x10$^{-7}$ M using UV-Visible spectroscopy. Insight into the probable mechanistic pathway involved in the detection process is also being discussed.

References

Figures

Figure 1: The schematic representation of the complete process of oxidation-exfoliation of graphene nanoplatelets to form GOQDs, reduction-functionalization of GOQDs to form GOQDs-en and ethylene diammine aided in situ formation of CoNPs to give GOQDs-en-CoNPs.

Figure 2: Schematic representation for fabrication of functionalized GOQDs-PVA hybrid hydrogels and the corresponding hydrogen bonding interaction between PVA and different functionalized GOQDs leading to cross-linking of PVA chains to form the three-dimensional hydrogel structure and photographs of metal salt solutions before and after dipping in of GOQDs-en-PVA hydrogel showing characteristic colour changes exclusively for Fe$^{2+}$, Co$^{2+}$ and Cu$^{2+}$ ions whereas the other metal solutions remain unaffected.