

Review

Graphene Quantum Dots from Synthesis to Innovation for Advanced Optics and Bio-Optics Trends

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Abstract

The generation of non-classical light with improved performances within tiny sizes, intervals of lengths, and diameters is still a challenge. The generation of variable wavelengths associated with different frequencies of energy modes produced from new sources of emitters within confined scales from the Quantum to Nano-and Micro-scales are of high impact. It is noted here that the concept of the generation of non-classical light related to electronics and photonics interactions with different topological matter constitutions could be tuned by the use of new optical carbon-based active materials. When the light is produced below the Nanoscale, other phenomena are involved where Quantum phenomena and Optics are present. In this regard, there are a lot of materials that could achieve these types of new modes of energy from different sources. However, there are not so many from organic based materials. This does not originate from the electron density, and the potential tuning of their properties due to carbon and incorporation within varied chemical structures



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is associated with interesting optoelectronic properties. These properties are based logically on the electronic configuration and orbitals involved. Therefore, Carbon-based Nanomaterials and Quantum materials achieved the high impact and new Nano-Optical emitters. In this context, Carbon dots, Carbon-based Laser dyes, and Carbon Quantum Dots appeared to be of interest for Optoelectronics developments contemplating from fundamental studies to applications. Thus, Graphene showed improved performances for Optical perspectives with varied types of applications. Graphene Quantum dots appeared in the developments of high interest based on their homogeneous electronic distributions produced by well-organized chemical structures controlled spatially and contemplating sizes. Both characteristics are not so easily found in other materials. For this reason this short Review of Graphene Quantum Dots and new Carbon Dot structures presented the classical and new trends in the synthesis of these types of materials to open further discussion toward fundamental studies with targeted new Optics based on fine chemical modifications and Quantum and quantum coupling, electromagnetisms, electron and photon conductions, as well as other modes of photonics, plasmonics, and quantum energy modes such as phonons, polaritons, bosons, excitons, electromagnetic fields, magnetism, Qbits, and quarks, etc. In this manner, the concept of quantum coupling was always considered in the Research, showing the electronic waves and related phenomena were under focus and analysis to show and demonstrate enhanced interferences based on their interactions. Therefore, there are many new modes of energy that are of interest to new studies and further applications. In these perspectives this short Review intends to show trends in progress.

Keywords

Quantum semiconductors; quantum emitters; quantum optoelectronics; bioconjugation of quantum dots; graphene QDots; carbon dots; quantum dots (QDots)

1. Introduction

Quantum Dots (QDots) are tiny dots with particular Opto-active properties based on their confined electronics, showing a high interest from many points of view [1]. There are many well-known inorganic Quantum materials within dot scales; however, in recent years, increased interest in Carbon Dots (CDots) [2] and CQDots [3] was shown. In particular, it highlighted allotropes of Carbon, such as Graphene, within the Quantum scale. Graphene QDots showed very stable emission properties accompanied by semiconductive properties based on their electronic band gaps [4]. Thus, graphene, derivatives, and further carbon-based allotropes augmented the attention from the synthetic point of view, considering the enhancement of quantum Optoelectronics and biocompatibility in imaging and biophotonics applications. In this manner, the perspectives were opened to hard and soft materials developments. 2D Graphene QDots structures showed accurate and well-organized atomic distributions that afforded the development of varied new properties based on their inter-layer interactions that enhanced pseudo-electromagnetic fields. In this context, it is noted that the nomination of pseudo-for electromagnetics fields is due to the non-classical electronic movement of organic layers that

produce this property. Thus, the manipulation of these scales could contribute to the generation of bright emitters with varied applications, and for electron shuttle functions as well. This last particular function requires the electrons to flow through chemical structures capable of receiving and letting them move through the structure. In graphene and derivatives, it occurs based on their high conjugated electron densities, often forming part of more complex sized bottom up such as decorated metallic nanoparticles, and semiconductors, and incorporated within heterojunctions. In addition, electronic movements and pseudo-electromagnetic fields could modify the electronic orbitals of laser dyes and other emitters, generating positive interferences with enhanced properties. So, the versatility of tuning new Quantum Optics from dots to higher-sized surfaces and incorporating them within devices is under continuous development. In this regard, the synthesis and design of modified CQDots showed a trend towards the use of different Carbon bio-sources such as varied natural ones looking for new passivating agents and final biocompatible perspectives.

Carbon-based structures are stable chemical architectures that require high energy to transform their covalent bonds. However, it is not the only challenge to overcome; in addition, it should be confined and shaped below the nanoscales. Therefore, it is not a trivial new synthetic proposal to obtain carbon-based Dots and QDots. Thus, it highlighted the synthesis of Graphene and Graphene QDots developed within strong acidic media to convert 3D Carbon-based structures into exfoliated 2D structures with available carboxylic groups produced in the oxidation pathways of synthesis. These important functional groups opened the possibility to modify them (Figure 1). For example, covalent modifications by carbon functionalization could be proposed. From controlled oxidations, it is possible to lead carboxylic and aldehyde groups [5] in drastic and mild conditions, respectively. Moreover, other types of modifications, such as polymeric films, highlighting boron-, nitrides- and silicon-based monomers, are incorporated due to their targeted known functions as well as potential new phenomena developed by proper optical matter tuning. In this way, organoboranes [6] and organosilanes [7] permitted chemical functionalization with the incorporation of further Quantum and Optical active materials within devices, heterojunctions, optical fibers, and waveguides.

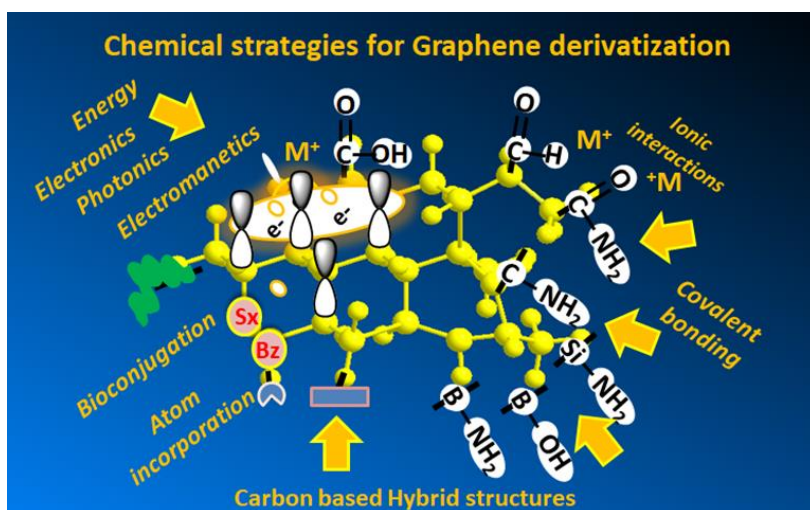


Figure 1 Schema of chemical modifications on Quantum Dots by incorporating varied organic, inorganic, and hybrid linkers. Reprinted with permission from A. G. Bracamonte et al. Copyright 2025.

The versatility is achieved by summarizing the reported strategies; and, in this manner, from an overview standpoint, it checks possibilities and evaluates new ones in the context of the design of the generation of hybrid optical active nanocomposites, where Graphene Quantum based materials could play important roles Nanotechnology, Biotechnology and Life Sciences applications.

By combining different chemical strategies for Graphene Quantum Dots modifications, it is possible to generate varied new linking sites based on i) covalent bonding, ii) non-covalent linking, iii) ionic interactions, iv) π - π stacking, v) Vander Walls interactions, vi) polar interactions, vii) electromagnetic fields, magnetic and electrostatic interactions, etc. These variable linking forces should be done by tuning the material with chemical or physical modifications. Therefore, different types of molecules and materials could be added.

However, new trends of synthesis applying surprising natural sources of carbon such as fruits and similar biocompatible materials produced by the application of highly intense thermal energy processes such as pyrolysis within controlled conditions within furnaces produced interesting Carbon-based Dots as well as Quantum Dots. In this manner, it opened new Bio-green perspectives toward Life Sciences applications.

Moreover, Carbon-based Quantum materials could be part of new Metamaterials and Hybrid Nanomaterials by tuning the design of hybrid structures from below and beyond the Nanoscale. It highlights new nano emitters by accurately confined QDots within the nanoscale, with unique emission properties not obtained by other synthetic methods. In a similar manner, advanced highly stable Nano-Optics by controlling Plasmonic and Quantum emitter interactions showed different and improved Quantum properties. Thus, it was applied QDots of varied sources. However, there are not many focused on new ones based on carbon-based quantum materials and derivatives.

In this regard, it was presented in this short-Review a potential point of view from the state of the Art focusing on the design of Quantum structures: synthesis and chemical modifications of Carbon and Quantum Dots with high-impact perspectives in Quantum and Nanotechnology focusing on Life Sciences developments. In this manner, insights within imaging, Bioimaging, Bioelectronics, Optoelectronics, Chips, and devices were shown. Therefore, it was introduced from the properties of Graphene Quantum Dots, contemplating basic synthetic pathways to innovative green approaches. So, bioconjugation and Bioimaging research were presented for advanced Optics and Bio-Optics trends.

2. Design of Quantum Structures: Synthesis and Chemical Modifications of Carbon-Based Quantum Dots and Derivatives

The synthesis of Graphene Quantum dots could be achieved by varied methodologies that it is not expected to develop here in detail due to there is a huge amount of literature related. However, it could be mentioned the main synthetic pathways such as; i) hydrothermal pathways, ii) electrochemical strategies, iii) other exfoliation techniques, and iv) by oxidation cleavages [8, 9]. Moreover, the importance of the shape and structure based on graphene and related carbon-based materials could also be of interest for the proposal of new or alternative strategies for the synthesis and design of further 3D architectures below and beyond the nanoscale. In this regard, it is highlighted the optical, electronic, and quantum properties that stimulate still focusing work on

that. So, before discussing synthetic pathways, chemical modifications, and manipulation of these tiny Carbon-based materials it is noted some important properties and considerations that show the high sensitivity offered by apparently inert materials against media modifications. It highlights the combination with other well-known and excellent semiconductors, such as perovskites within photonics layers and heterojunctions, for enhanced photonics and photocatalysis performances [10]. Thus, tuning 2D perovskite-graphene layered composites afforded exceptional performances in photocatalytic H₂ production, exhibiting the highest activity, achieving a hydrogen evolution rate of 835 mmol g⁻¹ under light illumination, attributable to optimal interfacial effects. This particular surface effect was explained by optimized optoelectronics developed predominantly influenced by modified charge densities at the materials' interface, required by the charge transfer dynamics. The stimulation of light provides energy for varied electron movements that could be smoothed, and developed with diminished energy losses by the presence of electronic waves. This model could be found in many research works in literature. So, sizes, shapes, and chemical modifications on tiny Quantum dimensions are of interest when looking for coupling phenomena and electronic density modifications from the atom to Quantum dot sizes and the Nanoscale (Figure 2).

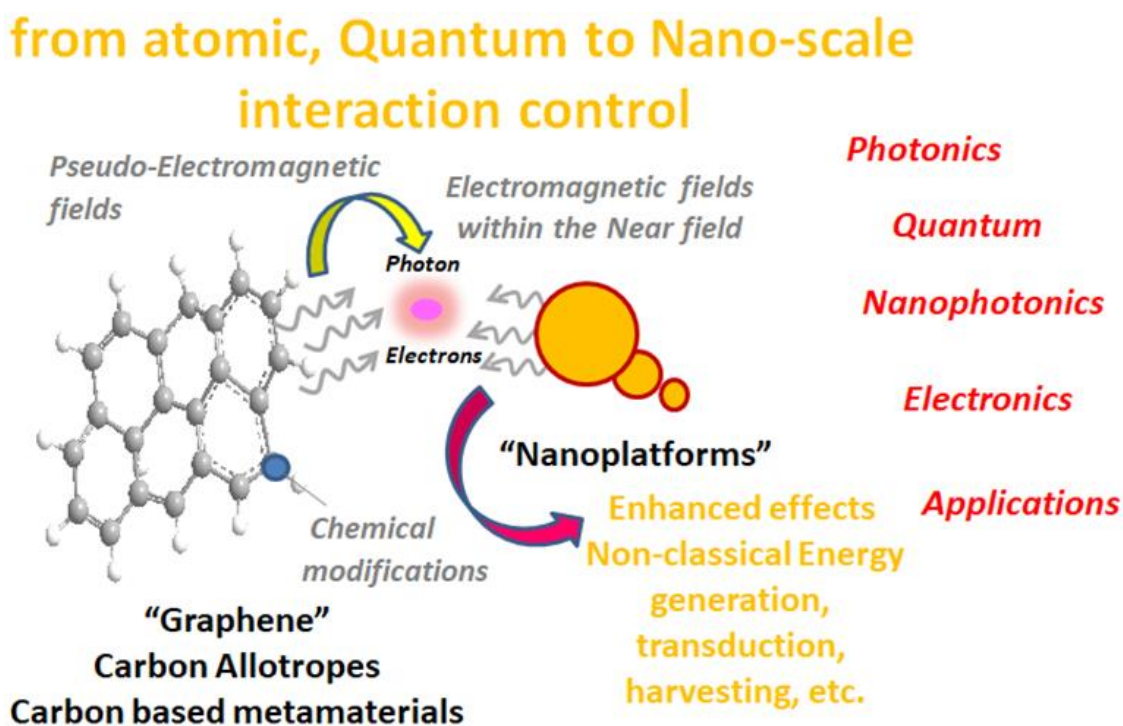


Figure 2 Schema of hybrid graphene Quantum Dot composites for the design of new metamaterials by joining different sources of pseudo-electromagnetic fields. Nanomaterials of different compositions could be proposed, for example, metallic nanoparticles with high electromagnetic fields within the near field related to closer distances in the nanoscale intervals. In this manner, the generation of new matter properties and applications, such as the generation of Enhanced Non-classical Light, could be achieved. Reprinted with permissions of A. G. Bracamonte et al. 2025.

To understand some important properties associated with these variables, for example, stable bi-layered chemical structures based on electronic orbital interactions produced varied Quantum

phenomena. It is noted the particular electronic structure generated from the accurate coupling of electronic sp^2 orbitals that produces lineal dependences on the correspondent waves vectors [11]. Thus, particular semiconductor properties are shown as semiconductor material. These interactions are characterized as symmetric Dirac electronic energies in relation to quantum mechanics, explained by the existence of antiparticles. So, these phenomena are explained by spin wave functions that could be affected by modifications in the symmetry of Graphene structures when the intrinsic 2D material is modified. In this regard, any change in the 3D structure affects magnetic oscillations produced from variations of interactions that generate different phenomena nominated, such as Haas van Alphen or Schubnikov de Haas effects [12]. These mentions are just only to highlight the importance of the design and bottom-up of the next generation of materials or contemplate them to propose new Quantum studies within the Nanoscale. The manipulation of multilayered Graphene in 2D and 3D permitted the advancement of many important effects, such as the generation of pseudo-electromagnetic fields [13] and opened the interest to couple with other types of optically active materials. This could be one of the potential challenges that could produce different effects depending on the materials within the Nanoscale and beyond. There Graphene Quantum Dots, due to their tiny sizes and different shapes in comparison to multilayered materials, are of high interest. The tunneling of electrons and chiral particles through electronic wave barriers affects the physics of electronic devices such as carbon-based transistors [14]. The future technology from the bench to the transistors and incorporated in devices showed how soft materials such as graphene and derivatives could provide tiny modifications from the Quantum scale to Nanostructured matter [15]. Thus, as mentioned, the design of voltage gate pitches with 48 nm sizes by tuning, vertical metalized drain local interconnects, and back-side gate contacts [16].

Moreover, about well defines structures from graphene, it is known that Graphene, a unique type of semiconductor, is a two dimensional crystal with a zero bandgap and a zero effective mass of charge carriers [17]. However, it was highlighted as well that even within these scales the mentioned phenomena showed a high sensitivity against the size scaling following Quantum physics laws. Thus, these invisible laws affected the Nanoscale and microscale Optics. The synthesis of graphene Quantum Dots permitted by well controlled organic chemistry reactions showed the versatility to vary sizes, stabilizing agents, and chemical surface modifications. In this manner, variations in electron mobility are afforded to different photonics and photovoltaics applications.

Recently, we developed a new solubilizing strategy that led to the synthesis of stable colloidal graphene QDs with more than 100 conjugated carbon atoms, allowing us to study their properties in a new size regime. In these perspectives it was recently highlighted variation in their energy relaxation dynamics. In particular, it was observed unconventional slow “electron cooling” related to the relaxation of electrons from high excited states to lower ones. These high-energy electrons could potentially be harvested in solar energy applications. At this level, the modifications from the source of Carbons to chemical surface passivating agents affect Quantum phenomena considering the interaction of confined 100 Carbon atoms.

The innovation in the synthesis of Carbon-based materials from Carbon dots with varied sizes to Quantum Dots is based on managing Carbon sources and energy to break and form covalent bonds. The theory was developed experimentally by different strategies where both variables were combined.

In this regard hydrothermal processes permitted to manage aqueous media and energy delivery. It also combines highly conjugated carbon-based molecules such as Rhodamine B and o-Phenylenediamine, as well as similar molecules with bifunctional linkers. The use of o-Phenylenediamine with varied precursors and changes in the reaction media was afforded to N-doped Carbon Nanodots (N, S-doped in case of thiourea addition) with less than 10 nm spherical diameters [18]. In brief, the synthesis was achieved by solvothermal heating of the precursors solution in acidic media at pH = 2.00 and 200°C using a Teflon-lined stainless-steel autoclave reactor. The combination of the main precursor with benzoic acid and thiourea produced Nanoemitters within the interval of 300-600 nm spectral regions depending on their reagent composition. Sonication, centrifugation, filtering, and cleaning by applying varied solvents could be used in order to separate different fractions and sizes of carbon-based materials. Thus, as was shown in this previous report, the synthesis could be developed within less intense acidic media. However, to modify surfaces by functionalizing them with carboxylic acids, the application of more potent oxidant agents is required [19]. In this manner, the chemical surface affects the interaction with media by additional strong polar non covalent interactions such as hydrogen bridges. Further examples are developed based on this simple strategy of chemical modification that opens Carbon-based materials to be used within aqueous media.

In order to have an idea about the efficiency of emitters that could be developed by this synthetic pathway, orange emitting carbon dots (CDs) were synthesized by a hydrothermal process, showing strong and stable emissions at 574 nm by 555 nm Laser excitation with a fluorescence quantum efficiency of 46% [20]. This high quantum yield was drastically affected by the presence of Hg, which opened the interest to develop a quenching base Nanosensor for Hg within aqueous samples, rivers, and oceans with different ionic strengths. Moreover it was designed a modified Carbon Nanodots paper test and a cellulose acetate film to detect this ion. This approach, or smart Optical active modified Carbon Nanodot paper, showed the concept of a functional device extending this setup in many other Research fields. Finally, the low Limit of Detection (LOD) achieved was highlighted, such as below 2.5 nM.

Then, to highlight the importance of the varied sources with different structures, it is mentioned how reduced sizes of dots, such as Graphene Quantum Dots, varied sources selection based on intrinsic structure needs that could influence the product obtained. As it is known graphene could be generated with the incorporation of other heteroatoms within the 2D surface or covalent linked on their surfaces. In this way, recently it was showed the synthesis of Graphene quantum dots by the use of bio-waste Carbon material source to produce amine-terminated GQDs (Am-GQDs), which have higher dispersibility and photoluminescence intensity than those of GQDs in the absence of amines groups as well as further passivating agents provided from the complex natural source. In contrast to the previous example described, in this case, the presence of Ag ions and L-Cysteine switched on the emission; however, replacing another bunch of ions afforded the emission quenching. So, in this manner, it was controlled emissions from single Carbon Quantum Dots depend on the ionic media and the presence of a targeted amino acid.

From previously mentioned Research works it was highlighted that a factor in common governed all the synthesis related to the control of energy application on varied sources of Carbon-based materials. Specific conditions only conduct to reduced sized chemical and quantum structures. These architectures were governed by their intrinsic double bonds with the capability to form stable conjugations through space within 2D layers. In addition, these layers could interact

to form 3D structures. In this manner, the material goes from transparent properties to higher light scattering and high molar absorptivity. But after the next step, further covalent bonds and modifications could be achieved. Some strategies were mentioned; however it could be mentioned other ones such as from carbon allotropes. The functionalization of monofunctional linkers as amines on Carbon Nanotubes was achieved by forming hybrid polymeric composites PANI with Multi-Walled Carbon Nanotubes (MWCNTs) [21]. Moreover, it is mentioned other strategies for Graphene Quantum Dots [22], such as forming covalent bonds on the CNTs through photochemical oxidation processes [23].

So, as shown, the chemical synthesis of Carbon-based dot materials, Graphene Quantum Dots, and derivatives could be conducted by varied pathways that affect the chemistry developed on surfaces for further uses. Thus, the surfaces should be modified by additional methods where it is applied the addition of organic matter, covalent linkers, non-covalent interactions, and joining biomaterials as well. It highlighted new trends using natural biomaterials that perform biocompatible Quantum surfaces. But, it was also highlighted that there needs to be further studies depending on the variables and the huge world of applications that can be proposed. In this manner, it was intended to focus attention on these related different synthetic pathways and future uses. In these perspectives, in the next section, it was developed the approach and concept of Bioconjugate of Graphene and derivatives to optimize incorporations within new materials.

3. Bioconjugation Strategies for Quantum Dots Incorporations within Functional Substrates

Carbon-based materials within the Nanoscale and Quantum dimensions are exciting as Optical active platforms for varied applications [24]. The development of platforms with smart and versatile surfaces is a challenge for the targeted functions. Thus, first of all, the Quantum Dots should show chemical groups and atoms ready for covalent link or non-covalent interactions. In this manner, the Quantum regime is required to disperse the Quantum Dots within colloidal dispersions by the use of aqueous or mix of solvents with intermediate polar media to target the application then [25]. By this way of thinking it is possible to go for aqueous media within Bio-compatible and soft matter applications where in general is desired the manipulation of water as solvent [26]. However, for other types of applications, such as challenging matter designs and bottom-ups considering hydrophobic surfaces, metallic substrates, and non-polar chemical surfaces, the manipulation of colloids within organic solvents is required [27]. So, in this context, from this brief introduction, it is known that for biological uses, it needs the bioconjugation of the Quantum and Nanomaterial [28]. In particular, graphene, as it was described previously, has a highly hydrophobic surface and is relatively inert or non-reactive in comparison to other carbon-based structures [29]. In this context, it is noted that there is a lack of biocompatibility if they are not modified with biocompatible molecules, biomolecules, and higher-sized biostructures. In this context, recently, the effect of graphene quantum dots interactions was studied by directly covering the active site of the anterior gradient homolog 2 (AGR2) protein, a key protein capable of protecting the intestine. In this study it was used a molecular dynamics (MD) simulation approach to systematically investigate the potential toxicity of both Graphene Quantum Dots and Graphene Oxide Quantum Dots on the protein. Thus, the MD results demonstrated that both can directly make contact with and even cover the active site over a specific Cys81 amino acid. In this manner, the capability to inhibit or interfere with the normal biological interaction of the AGR2

active site with its target protein showed potential detrimental effects on the focused AGR2 protein [30].

For this reason, Graphene Quantum Dots, Carbon-based dots, and Nanoparticles are functionalized by the incorporation of different organic groups depending on needs and interests [31]. Modifications of these types of materials are relatively new and still under study. Thus, Bioapplications require the modification of biocompatible materials on nanoplatforms [32]. It could be contemplated from single small molecules, such as citric acids, and polymeric chains, such as polyethylene glycol chains, to supra-molecules, such as RNA, DNA, etc. [33]. There are many bioconjugation techniques available offered from fundamental research to the market [34]. However, there are constant challenges with each new application. Always each case it is the case that should be tuned conditions. In order to highlight some of the most used as for examples it could be mentioned the following highlights. There are more significant types of reactions that could be applied for covalent bonding; however, not so many within aqueous solutions and Colloidal dispersions. For Bio-applications, it should be applied biocompatible conditions to avoid any problems in their use. Thus, within these groups of reactions, there are many variable polar media with organic, aqueous, and mixed solvents. Reactions can occur based on differences in the electronic densities of involucred heteroatoms and Organic functional groups, for example [35]. In this manner, nucleophilic reactions by the use of nucleophiles such as amines, thiols, and hydroxyl groups in the presence of organic groups with electronic deficiencies showed covalent bonding between heteroatoms. In this manner, for example, alkoxides could lead to oxidation as well as to nucleophilic reactions depending on the conditions. Thus, using activated carboxylic groups with the right esters formations or similar could be easily replaced by other nucleophiles with variables secondary chemical structures. It is mentioned the carboxylic activation with *N*-Hydroxysuccinimide (NHS) [36] in aqueous media, the *EDC* (1-ethyl-3-(3-dimethylaminopropyl) carbodiimide) in intermediate solvent polarities or mixed solvents with a high reactivity for inter-cross linking [37]. Moreover, *N,N'*-Dicyclohexylcarbodiimide (*DCC* or *DCCD*) is used in apolar solvents [38]. These reagents could activate carboxylic groups for nucleophilic reactions by lowering the Energy of activation of the concerted nucleophilic attack and leaving groups such as for the Bi-molecular Substitution Nucleophilic reaction (SN_2) [39]. Further examples from the literature could be found within the conjugation of different functional molecules, such as Laser dyes with modified organosilanes [40]. It was assayed the activation of the carboxylic group of laser dyes with NHS, EDC, with a combination of both, and DCC to react with (3-Aminopropyl) trimethoxysilane (APS) to form fluorescent modified organosilanes (Figure 3) [41]. This strategy permitted the incorporation within tiny sizes close to the Quantum regime [42] as well as in the Nanoscale [43, 44]. Another example was using bifunctional modified Laser dyes with Isocyanate groups to react with APS and other types of mined hydrocarbons and other chemical structures. In this case, it is noted how varying organic groups could be tuned polarities of high conjugated organic molecules as well as allotropes of carbon. Moreover, the hydroxyl groups could form ester bonds, modifying reagents, and conditions used when it is needed. These examples from Laser dyes could be transferred to further Graphene Quantum materials.

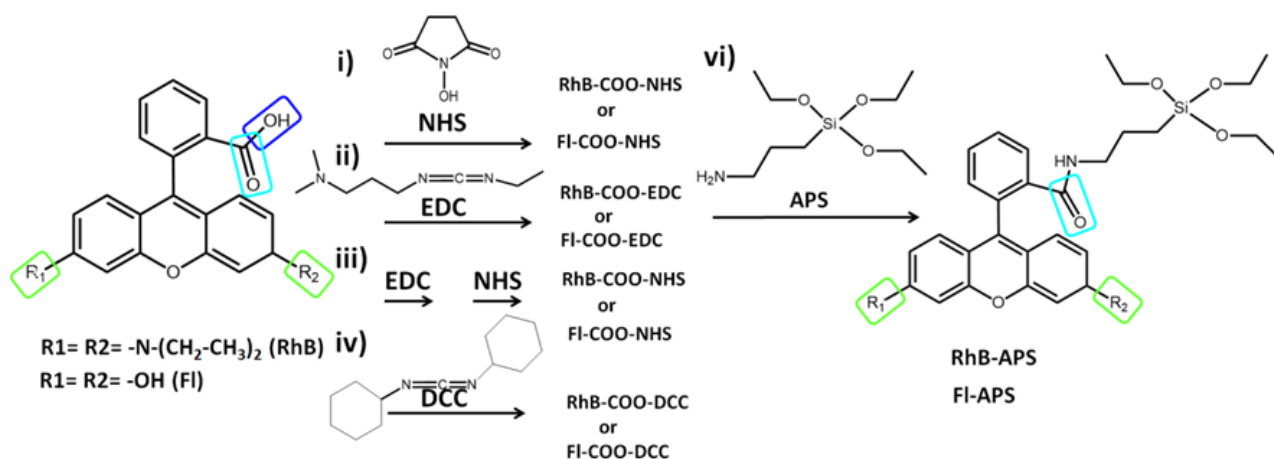


Figure 3 Scheme of conjugation reaction of Laser dyes based on Xanthene derivatives by activation of the carboxylic group for nucleophilic reaction with Aminopropyltriethoxysilane (APS). Reprinted with permissions of A. G. Bracamonte et al., Ref. 37 Journal of Chemical Research Advances, Open Access (CC) 2020 [37].

Taking as example Graphene oxides, it is possible to activate and modify Carbon based surfaces easily by these synthetic pathways. However, as it was noted previously, the biological counterpart should contain the nucleophile available and non-hindered by any constraint. So, the close contact could produce the covalent bioconjugation. It is just a simple bottom-up that could provide an idea of what is involved experimentally and how it could be managed by the design and higher-sized Quantum, Nano-Bio-architectures, and assemblies.

In order to show one strategy based on the bioconjugation with small molecules within polymeric supports, it is noted that recent designs incorporate graphene within hydrogels in combination with other biocompatible materials in order to apply it where it is required with relatively easy applications. Thus, biocompatibility was improved, aggregation avoided, and highly valuable and potential bioelectronics perspectives on other new hybrid materials were added. For example, alginate bioconjugate with graphene oxide in Multifunctional Hydrogels for Versatile Biomedical Applications was developed [45]. It was combined electrically-conductive graphene oxides and sodium alginate caffeic acid conjugates to then be incorporated within acrylate hydrogel networks (Figure 4). In this manner, it was added a versatile and malleable material to obtain multifunctional materials designed to perform multiple tasks in biomedical research. Within the multiple promising performances, it was highlighted the toleration of human fibroblast lung cells (MRC-5) (viability higher than 94%) and swelling properties upon application of an external electric field. These characteristics are enough to understand how the intrinsic semiconducting properties of Graphene materials could be available in direct contact with Life Science uses. Otherwise, the material could show a negative cellular response because its surface chemistry is naturally intrinsically hydrophobic.

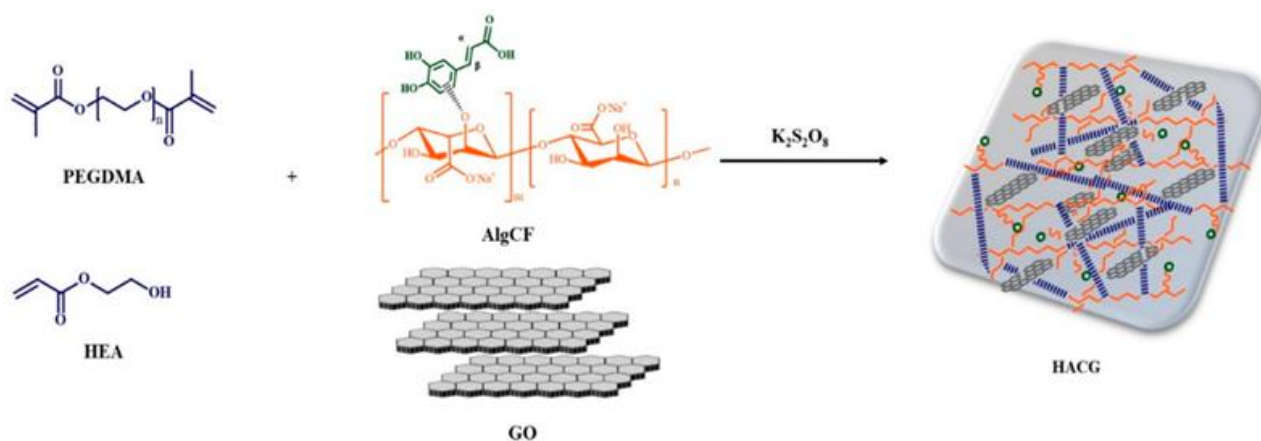


Figure 4 Schematic representation of the synthesis of multifunctional hybrid hydrogels. Reprinted with permission from Fiore Pasquale Nicoletta et al. Copyright 2021 Molecules, MDPI [38].

The malleability and biocompatibility are two essential characteristics for the bottom up in the next step of design and fabrication of a device or miniaturized instrumentation. High-sensitivity sensors applied in various diagnostic systems for Biosciences uses require these characteristics. In particular, it highlighted biosensor technology for clinical chemistry, biochemistry, food chemistry, and medical sciences [46]. From these perspectives, highly sensitive electrical characteristics of carbon nanotubes were applied to develop electron transfer processes on electrochemical biosensors. It essentially showed electrochemical biosensors applied with various receptors such as antibodies, DNA fragments, and other nanomaterials for Biosensing, nutrients, food preservatives, additives, toxins, etc., for food evaluation. Carbon nanotube-based biosensors supported within silicon wafers showed excellent properties to fabricate biosensor templates due to their properties serving as field-effect transistors (FET), increasing high sensitivity.

Moreover, it is highlighted that graphene properties and electrochemical behavior perfectly match in close contact with biocompatible peptides within Peptide-Modified Graphene Oxide Screen-Printed Carbon Electrodes bottom ups [47]. It showed how graphene acted as an electron shuttle in contact with a peptide-modified surface with a high sensitivity against the interaction with a small molecule and natural polyphenol antioxidant compound, namely rosmarinic acid. It is mentioned that glutaraldehyde was chosen as the cross-linking agent because it is able to bind the peptide. In this manner, the analytical performances were optimal for rosmarinic acid detection. However, Graphene and derivatives could act as single, highly sensitive Optical dots or particles. In these perspectives and looking for single particle spectroscopy it is required the manipulation of tiny sizes in the bioconjugation and chemical modifications. This fact opens up many related considerations. Thus, the incorporation of reduced sizes of Carbon-based chemical structures, such as Graphene Quantum Dots, is of high interest due to their tiny sizes and higher surface interactions from the bulk. Even if they are below the standard nanoscale, graphene quantum dots should be bioconjugated or conjugated to be introduced within substrates or deposited on surfaces. In this context, it is noted that for all bioconjugations, the proximity or accessibility of the biological structure should be in close contact with covalent linkers, spacer linkers, mono-functional-linkers and bi-functional linkers involved in Carbon-based structure conjugation [48]. So, it is a challenge within colloids all these apparent standardized methodologies where it should

avoid aggregation, non-desired inter-cross-linking, drastic polar media modifications, and all uncontrolled phenomena that could modify the intrinsic material properties. In this regard, there are many examples where bioconjugation played an essential role in the next step of the functional bottom-up system or targeted device. Thus, it is noted the manipulation of small biomolecules such as aminoacids and peptides that provide biocompatibility, dispersibility, linkers, non-covalent interactions from different structural domains, etc. In these perspectives, if it is focused on colloids and achieved homogenous distributions of Quantum Dots in order to provide optimal conditions for bioconjugation reactions, the probability of obtaining single modified dots is high [49]. And by this manner it is available quantum dots with versatile and particular properties that could be transferred to varied Nanotechnologies applications focusing light and electronic conductions within different soft and hard matter interactions.

4. New Perspectives of Quantum Dots for Biolabelling and Bioimaging Applications

Graphene and Carbon Quantum Dots could provide improved solutions towards Bioapplications due to their smaller sizes accompanied by smaller non-classical light emissions, providing higher bio-resolutions at different levels. Thus, it is mentioned the need to improve from single Biostructure analysis the definition of the whole structure as well as target reduced-sized components of membranes and biomolecules. In these perspectives, even if, in the last few years, many insights and applications have been developed, there still exist needs. The Nanoscale produced sub-nanometer resolution managing emissions and sizes of light hot spots generated. This concept looks easy; however, it is not all control of the parameters for accurate tuneable Nano-Optics [50]. In a similar manner, it should be specific for targeted tissues and cells, in particular for tracking biological events where Biostructures are moved from one place to another. For example, studies related to cellular trafficking, migrating, and any other type of space modifications with pass of time require tiny sizes such as Quantum Dots well incorporated within the Biostructure [51]. Moreover, other challenges require tracking imaging modifications of biomolecules and receptors. In this regard, it is highlighted that by treating colorectal cancer, it was shown that inhibition of the oncogene-activated mitogen-activated protein kinase (MAPK) signaling pathway was often more effective if the activity of the epidermal growth factor receptor [52]. Thus, applying a controlled approach to the study, it was chosen single-cell imaging of the activity of the MAPK extracellular signal-regulated kinase (ERK) in patient-derived organoids. In this manner, the oncogene-induced signaling showed that oscillations in ERK activity were amplified by the epidermal growth factor signaling. Therefore, important outputs were achieved by focusing light on single Biostructures considering from cells to proteins could be achieved. The important fact that should be shown for a given application is the demonstration of the incorporation of the Carbon-based structure in the close surroundings of the targeted structure to interact and resolve developing variable signaling depending on the optical setup used. But, before any example presentation, it should be highlighted that Graphene and related carbon allotropes could show deep interactions within the membrane and single lipidic layers within biological media. Thus, recently, mass spectrometry imaging (SIMS) of untreated wet cell membranes in solution using single-layer graphene was reported [53]. It was showed i) graphene-covered cells prepared on a wet substrate with a cell culture medium reservoir are alive, ii) cellular membranes do not disintegrate, iii) it was demonstrated interactions based on a transient hole

generated in the graphene layer, iv) moreover it was shown that Graphene single layers permitted the deposition of other molecules such as cholesterol and fatty acids that enabled spatial resolution of enriched regions in cell membranes by SIMS. It is important to note how techniques that afford to know about molecular constitutions joined to theoretical calculations permitted the 3D generation of images. However, in addition to these types of studies, there are other ones, such as different Microscopy techniques under study. Thus, by Epifluorescence Microscopy imaging it was generated cell membrane imaging at different times after Graphene incorporation, such as 5, 20, and 40 min. Therefore, it was possible to track green and magenta colors associated with live and dead cells before graphene capping. Interesting membrane resolution was achieved from modified Graphene hot spots incorporated within the membrane structure, while dark images were produced from non-labeled hot spots. These images were stable and well resolved over time in a similar manner as other inorganic Quantum Dots as Metallic Phase Transition Metal Dichalcogenide Quantum Dots as Promising Bio-Imaging Materials and Nanomaterials for Life Sciences applications [54]. It was noted from Metal Dichalcogenide Quantum Dots that when the diameters were decreased, the emission peaks blue-shifted from 436 to 486 nm under excitation by a He-Cd laser (325 nm). This was explained by the density function, which led to an increase in the bandgap because of quantum confinement effects. This effect could then transfer to the bio-imaging of HeLa cells, which had bright luminescence and low toxicity. These are just examples of the variables managed from other Quantum structures; however, graphene and derivatives also show variable properties and performances. For example, it was reported that a tunable broadband terahertz absorber based on a star-shaped ring graphene metasurface has potential properties for detection applications [55]. Thus, it was shown the design of periodic arrays of star-shaped ring graphene resonators along with a silicon dioxide substrate acting as high sensitive absorbing structure. In this manner, the absorption rate is more than 90% in the 0.8 to 2.4 terahertz frequency range. Moreover, it was shown that the proposed structure retains its absorption bandwidth with an absorption level of more than 75% up to a 60-degree elevation angle for different wave polarizations. In addition, by increasing the chemical potential of graphene in the proposed structure from 0.1 to 0.9 eV, the absorption rate of the structure can be tuned from 40% to nearly 100%. Therefore, the surface showed high sensitivity to interactions with light and could afford new Optical setups with varied applications.

It is noted from previous examples how different instruments, techniques, and methods associated could participate in the fundamental Research looking to highlight the chemical modification to the development of Nano-Optics. In this regard, the combination of Quantum materials as tiny optical tools with Optical instrumentations based on different techniques for sensing varied quantum phenomena could have an important impact on the market of photonics and optics for life sciences uses. For example, for high-resolved imaging applications, the optical setup is essential, as well as the Quantum and Nano-Optics. And, even if they are claimed to be toxic graphene quantum dots were proposed in many Research works as potential for biological imaging if they are properly bioconjugated. This fact opened further research on the effect of biomolecules on optical properties that could vary depending on the intrinsic optical active matter incorporated. It highlighted their intense visible photoluminescence that has shown several benefits over conventional organic photosensitizers, such as chemical inertness, high water solubility, photostability, the interaction between optoelectronic features and shape/size, good donors in the fluorescence resonance energy transfer process, and high stability in physiological

conditions. All these characteristics merit the bioconjugation and biocompatibility study to proceed on exploiting specific accumulation at the target site, and straightforward over varied surface functionalization [56]. In this context, it is reminded of the key concept associated with the design of the synthetic pathway where green chemistry could play an important role in final optimal results [57].

As observed from all the previous reports, it demonstrated the chemical versatility of Graphene and its uses by their incorporation within different media and optical setups. However, it should be highlighted that the varied resolutions developed and properties were by different and controlled optical excitations. Further examples could be obtained from current Advanced Optical Research where combined Graphene modified substrates under the focus of different Optical techniques applying techniques such as electromagnetic fields and photonics excitations. There, the objectives overcome standard resolutions and go towards Super-Resolution Imaging with Graphene [58]. For example, using hyperlens to track the Mid-Infrared interval of wavelengths permitted a resolution of 10 nm based on tuneable conductivities with Graphene [59]. Further data by focusing light on graphene Plasmonics and analyzing parameters such as ultra-high wave vectors combining Graphene Metasurfaces (GMS) and Plasmonic Structured Illumination Microscopy (PSIM) was achieved using the Finite Difference Time Domain Method (FDTD) method to model GMS structure and found that the standing wave of surface plasmons (SW-SPs) with an 11 nm period can be achieved on graphene (Figure 5) [60]. This important spectroscopic and chemical structure correlation permitted enhanced resolution, arriving close to 5 nm by 980 nm illumination, which was improved 39.6-fold in comparison with the conventional microscopy technique with a resolution of 283 nm at the best optical conditions. It was noted that the imaging system achieved two-point objects separated by 6 nm from periodical Nanopatterns directed by graphene.

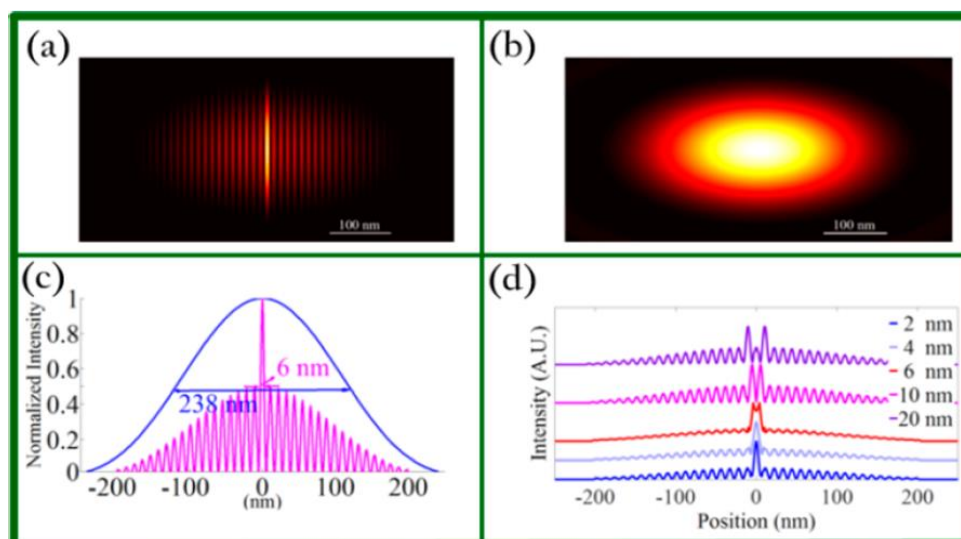


Figure 5 a) The reconstructed image of a point object in the x direction. b) The image of the point object in the conventional fluorescence microscopy system. c) FWHM comparison between (a) (red line) and (b) (blue line). d) Illustration resolving capability of GMS-PSIM system of two point objects separated with different distances of 2, 4, 6, 10, and 20 nm. Reprinted with permission from T. Zhang et al. Copyright 2013 Optical Express [59].

In this case, it is noted that the analysis is from the far field; however, there are many other approaches proposed by focusing optics on the near field of pseudo-electromagnetics and Plasmonics properties applying Surface Near Field Optic Microscopy (SNOM) [61]. This technique permitted sensing with a tip of the near field generated from Graphene incorporated with a similar resolution. These approaches could be transferred towards different needs, looking for modified tissues with new Carbon-based structures where they afford to add to the Optical system new properties that could achieve optical information based on the Optoelectronic properties incorporated. These are all very important and high-impact results that not all are transferred to Biological systems yet, and they merit being known to be applied for further Quantum and Nano-Bioimaging systems.

5. Concluding Remarks and Discussion

The design of Graphene Quantum Dots could be stated as mentioned, based on the knowledge developed by the vast amount of Research related to the control of Carbon-based materials from varied sources of Carbon. This concept requires adding energy to break and form new structures with tiny sizes. The tiny sizes could be achieved by confining defined inter-cross-linked molecules highly conjugated as well as other chemical structures. Graphene, in particular, and carbon dots required hydrothermal methodologies with biocompatible finished materials unless there was a modifiable surface for biological studies and applications. The oxides were the most common Quantum surfaces by carboxylates and carboxylic acid additions by oxidative processes during the synthetic pathways. Then, reduction reactions and further linking reactions could afford to tune surfaces. It is noted that surface interactions of Graphene could drastically affect inter-layered interactions, and, in this manner, the properties of Graphene. So, Graphene Quantum Dot's properties could vary their emissions and Optoelectronics depending on the state of multi-layer assembling. In addition, chemistry and additional molecules or ions deposited on Graphene Quantum Dots as well could modify Quantum properties and semiconductive behaviours. It is known that Graphene is a 2D material that could be incorporated within further 3D bottom ups within technological approaches and Optical set ups such as Heterojunctions and Light Emitting devices (LEDs).

Moreover, graphene Quantum dots have been used for fluorescence imaging to visualize tumors and monitor therapeutic responses in addition to magnetic resonance imaging applications. Therefore, interesting perspectives towards multi-modal imaging dots are opened. In addition, photoluminescence to develop biosensing applications such as hydrogen peroxide, micro RNA, DNA, horse radish peroxidase, heavy metal ions, negatively charged ions, and cardiac troponin were recently reported. Thus, varying media is essential, always depending on the methodology, that quantum materials show biocompatible behaviors [62].

In addition, it highlighted the last trends related to green methodologies for synthesizing carbon-based structures using varied sources of natural carbon materials. These insights showed interesting perspectives towards Bioapplications with diminished or lower toxicity. However, these mentions are wishes in many cases because they have not been studied yet. Similarly, green photonics should be highlighted from where compatible and green photonic components are required. These are related to Green chemistry methodologies; therefore, multidisciplinary Research work should be contemplated to propose new Quantum approaches. So, the future is

green and will have a high impact in introducing quantum non-classical light within green applications and biophotonics developments with potential perspectives toward clinical translation. Thus, many are based on the developments and analysis of imaging approaches to real technology on the market. However, it was noted that fundamental research is essential to show simple facts that could be exploited in bioimaging technology. This is the case of the simple incorporation of luminescent dots within the membrane or deposition on membrane surfaces. Similarly, it is not all developed, and the design and synthesis of single Carbon Quantum dots, such as Graphene Quantum Dots or any related derivative, is exciting.

It is noted the importance of contemplating the design and synthesis of the biocompatibility and green perspectives to improve the incorporation of Biophotonics approaches by quantum-based devices, looking for further solutions to current challenges related to early diagnoses, resolutions, quantifications, and Theranostics.

In these perspectives, for example, varied imaging modes and strategies could be as well proposed by the application of synthetic Carbon-based materials on the environment depending on the chemistry of surfaces, in particular, within aquatic organisms with Graphene-based nanomaterials and their interactions [63]. Moreover, focusing attention below and beyond the Quantum and Nanoscales, it is necessary first to analyze confined interactions between materials and biomaterials. In this manner, it will be possible to extrapolate potential biological dangers. So, multidisciplinary work is required at different levels of life sciences and technology development. Regarding new proposals and experiments in order to study light Bio-matter interactions, such as with varied tissues and cells based on Graphene properties, it was highlighted the importance of the chemical structure, derivatization, bioconjugation, and combination with other materials to tune nonclassical physics with perspectives for new modes of imaging. Quantum and nano-biophysics are involved in opening the interest from different points of view. Thus, graphene and Carbon-based materials could vary in size, shape, and composition when they are combined with other materials and logical properties. In this manner, their incorporations within Biological systems and varied apolar systems with different optical matter properties could produce new phenomena of interest to study and exploit for Bioimaging perspectives.

To afford new Quantum-, Nano-Biosystems, interactions are required where different variables could affect the incorporation of carbon-based matter. From this level of chemistry it is just only the beginning to produce new assemblies. For example, non-covalent interactions and hydrogen bridges from silanized Nano-emitters produced Nano-Bio-assemblies with different dynamics and non-classical light generation with a pass of time. Varied shapes recorded from the Nano-to the Microscale were observed in the presence of silicon Nanophotonic structures and *Escherichia Coli* bacteria [64]. It is noted that both materials are used for different reasons. Silicon-based materials are highly conjugable with varied matter compositions, while bacteria, unicellular organisms, and cells towards organs are logically well receptors of Quantum and Nanomaterials [65]. Moreover, it should be noted that shapes could affect the deep introduction within the membrane. Thus, it was recently developed a theoretical study focusing light on the effect of shape on the entering of Graphene Quantum Dots into a Membrane by Molecular Dynamics Simulations [66] (Figure 6). In this study it was focused on the translocation mechanism of Graphene with different shapes where the permeation was evaluated through a 1-palmitoyl-2-oleoylphosphatidylcholine membrane. The results showed that all small-sized Graphene Quantum Dots with different shapes translocated through the lipid membrane at a nanosecond timescale. In this process, the tendency

to remain on the surface of the cell membrane was noted first; then, the corners of the structures spontaneously entered within the cell membrane, and finally, the entire structure entered the middle of the cell membrane. If all the steps are biocompatible, it is attended to don't produce any damage, low toxicity and to be a biocompatible material for Bioimaging from inside the cell structure.

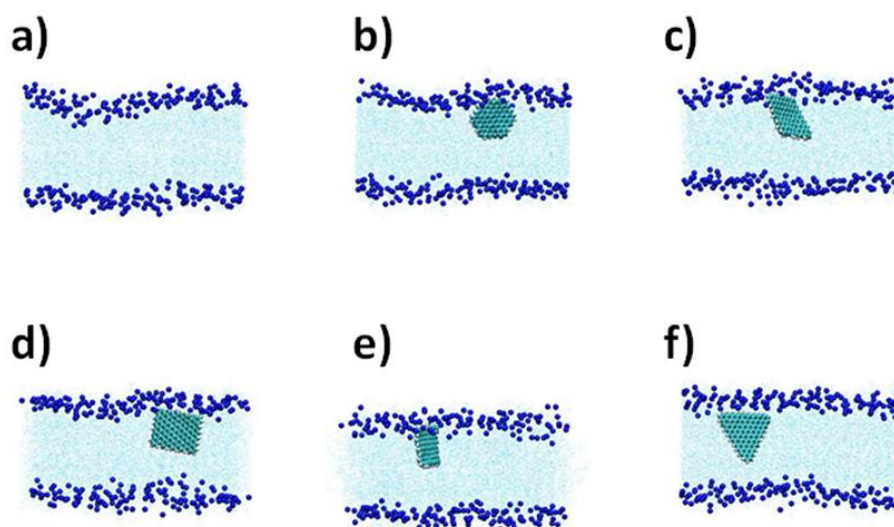


Figure 6 Snapshots at ultimate time GQDs with different shapes in the membrane after 100 ns MD simulation: a) protocell membrane, b) Cir-GQD37, c) Par-GQD49, d) Rec-GQD50, e) Squ-GQD46, and f) Tri-GQD45. The GQD and POPC are shown by the VMD model. GQDs are represented by a red VMD model, and the P atoms in the membrane are represented by a blue VMD model. Water molecules are hidden for clearer display. Reprinted with permission from L.-J. Liang et al. Copyright 2021 ACS Omega, ACS [48].

So, joining theoretical studies towards re-thinking new synthetic methods could afford the required control of sizes, shapes, and chemical surfaces. Therefore, it is iterated in a retrospective manner of the synthesis and further designs of materials. In this way, it was achieved other similar modified methodologies such as the hydrothermal method, but applying a strong basic media to obtain Carbon-Nitride luminescent dots (g-C₃N₅-dots) [67]. The reported g-C₃N₅-dots displayed bright blue fluorescence properties with a high quantum yield of 12%. Moreover, it was shown particular catalytic activities on their surfaces like peroxidases. In addition, it showed good biocompatibility and low cytotoxicity, opening very interesting perspectives toward cell imaging developments. In this regard, it should be noted that Hybrid Carbon-based materials such as Silicon-Carbides, Silicon-Nitrides, and tiny silicon Quantum dots with very interesting conjugation perspectives with Carbon dots and Graphene Quantum Dots. These last concluding remarks are just to open the attention to the design of new materials and properties generated.

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Author Contributions

The author did all the research work of this study.

Competing Interests

The authors confirm that this article content has no conflict of interest.

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