

RECENT PROGRESS AND FUTURE APPLICATIONS OF CARBON QUANTUM DOT SYNTHESIS

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ABSTRACT

Fluorescent carbon nanoparticles, also known as carbon quantum dots (CQDs), have attracted a lot of attention due to their potential applications in chemical sensing, biomedical imaging, nanotechnology, photovoltaics, light-emitting diodes (LEDs), and electrochemistry, especially when compared to traditional semiconductor quantum dots. CQDs have beneficial optical properties in addition to their beneficial toxicity, ecological friendliness, low cost, and easy production processes. To further tailor CQDs to specific applications, surface passivation and functionalization are other viable options. Because of their exceptional qualities and broad applicability, CQDs are the subject of this review. Several methods for synthesising CQDs, as well as their advantages and disadvantages, and potential applications in sensors, bioimaging, drug administration, solar cells, and supercapacitors, are discussed in the article.

Keywords - Carbon quantum dots, a synthetic method, biomedical uses, energy storage, and biosensors are some of the relevant terms.

INTRODUCTION

Around the past decade, carbon quantum dots (CQDs) have attracted the interest of scientists all around the world. Recently, there has been a lot of focus on carbon nanomaterials (CNMs). Carbon nanotubes (CNTs), graphene, nanodiamonds, and fullerenes are only a few examples (Rao., 2018, Lin., 2018, Clancy., 2018; Georgakilas., 2015). However, nanodiamonds are more challenging to prepare and separate. As of 2020 (Chauhan et al.). Because of their limited applications and poor water solubility, carbon nanotubes (CNTs), graphene, and fullerenes are unable to generate stronger fluorescence in visible regions. (Zhang., 2011).

The flexibility to tailor their size and surface chemistry makes them useful in many different contexts. Aqueous solubility and fluorescence brightness are two areas where CQDs stand well when compared to other carbon-based nanomaterials (Jeevanandam., 2018).

Not only are CQDs less harmful to cells and the environment than their semiconductor counterparts, but they are also more energy efficient. Because of this, they have great potential in the life sciences for uses like as biological imaging and medication administration (Smith and Nie, 2010).

It will be fascinating to see how CQDs, which have been the subject of much study and development, are further investigated and put to use in the future of nanotechnology and materials science (Baker and Baker, 2010; Li et al., 2012; Shen et al., 2012).

Due to its potential uses in many different sectors, such as biomedicine, optoelectronics, and catalysis, carbon-based quantum dots (CQDs) have received a lot of interest in recent years. The unique characteristics of CQDs, such as superior biocompatibility (Maiti et al., 2019), low toxicity, environmental friendliness, and cost-effectiveness, make them appealing for a variety of uses. The superior electronic characteristics of CQDs as donors and acceptors of electrons result in chemiluminescence and electrochemical luminescence due to the quantum size-effect (Chen et al., 2020).

However, there are still certain difficulties in maximising the effectiveness and efficiency of CQDs in real-world settings. Adding new functional groups to the surface of CQDs is a popular method used to improve their qualities. Despite their widespread use, customised CQDs may not always exhibit better performance than conventional semiconductor quantum dots (SQDs). Since the qualities of CQDs are inferior to those of SQDs, more study is required to bring them up to par (Lim et al., 2015).

Researchers are always working to find better ways to produce carbon quantum dots, fine-tune their features, and uncover new areas in which they may be useful (Baker and Baker, 2010; Li et al., 2012; Shen et al., 2012)..

From their synthesis to their possible uses in numerous sectors, the essay covers it all. This will be useful for scientists who are interested in learning more about the applications of CQDs. This review can shed light on the characteristics and possible applications of CQDs by examining the various synthesis techniques and applications. Moreover, dividing the post into subsections might help readers discover the specific details they're looking for. In conclusion, this study might serve as a helpful reference for scientists who are considering using CQDs into their studies.

2. CQDS Synthesis Techniques

Bottom-up approaches entail constructing CQDs from smaller molecules via chemical processes, whereas top-down methods require breaking down a bulk carbon source into smaller-sized CQDs using physical or chemical methods (Carbonaro et al., 2019). Arc-discharge, laser ablation, and acidic oxidation are examples of top-down approaches (Pillar-Little et al., 2018), whereas microwave pyrolysis, combustion pathways, electrochemical methods, and hydrothermal/solvothermal synthesis are examples of bottom-up methods (Singh et al., 2018) (El-Shabasy et al., 2021).

Schematic showing how CNTs and CQDs are formed by means of a laser ablation technique

2.1 Top-Down Methods

2.1.1 Arc-Discharge

In the gas plasma approach, gas plasma is generated in a sealed reactor to break down bulk carbon sources (Arora and Sharma, 2014). .An anodic electrode supplies power to the reactor, increasing the temperature inside to as high as 4000 K and creating highly energetic plasma as a byproduct. CQDs are formed when carbon vapour condenses in the cathode (Dey et al., 2014).

Hydrothermal synthesis is another technique for producing CQDs. To facilitate the creation of CQDs, bulk carbon sources are dissolved in a solution and subjected to high pressure and temperatures (often between 100 and 300°C) (Zuo et al., 2016). High-quality CQDs with a high degree of monodispersity may be made using the hydrothermal technique.

Microwave-assisted synthesis, electrochemical synthesis, and laser ablation synthesis are some of the other techniques for synthesising CQDs. There are benefits and drawbacks to each approach, and selecting one relies on the needs of the given application.

The water solubility of CQDs can be enhanced by adding hydrophilic carboxyl groups on their surface using HNO₃. While the arc-discharge approach can produce CQDs, they may have a greater particle size and poorer yield, making it more difficult to filter and remove complex components (Chao-Mujica et al., 2021).

Submerged arc-discharge synthesis of CQDs in water by Chao-Mujica et al. yielded 16% quantum yield CQDs that consistently emitted two bands in the spectrum at 320-340 nm (band A) and 400-410 nm (band B) for 275 nm (band A) and 285 nm (band B) excitation wavelengths. These CQDs were used as a fluorescent biomarker in cell culture experiments with L929 murine fibroblasts for in-vitro research. These CQDs showed strong photoluminescence (PL) capabilities and can be employed in bio-imaging applications despite their poor quantum yield and restricted particle size scaling.

2.1.2 Laser Ablation Method

Due to its capacity to produce CQDs with a regulated size distribution, excellent water solubility, and intense fluorescence, laser ablation is a common approach for manufacturing CQDs. This technique involves irradiating a carbon precursor in an organic solvent with a high-energy laser pulse, creating a high-pressure, high-temperature thermodynamic state. Carbon nanomaterials, such as CQDs, are formed after the process's vapour cools and crystallises. However, the first synthesised carbon nanoparticles are frequently aggregated and do not exhibit any detectable photoluminescence (Hu et al., 2011).

The problem may be solved by reacting the sample with polyethylene glycol (PEG) after it has been treated with diluted HNO₃ (Zuo et al., 2016). This results in visible and controllable photoluminescence. CQDs with high PL and a diameter of roughly 5 nm may be manufactured by manipulating their surface characteristics with the help of suitable organic solvents. Laser-ablated CQDs have QYs in the fluorescence range of 4% to 10% when stimulated at 400 nm (Desmond et al., 2021).

The N-doped micro-pore CQDs Ren et al. synthesised through pulsed laser ablation had a QY of 32.4%, a fluorescence lifetime of 6.56 ns, and were therefore well suited for cellular staining and imaging. However, Cui et al. made CQDs from inexpensive carbon textiles using dual beam laser ablation, and they achieved a QY of 35.4%; these CQDs were also put to use in cell bioimaging.

It has been shown that the solvent and precursor employed affect how much PL is emitted from CQDs, and that laser ablation procedures result in the highest PL emissions. Low QY may occur from the method's utilisation of a lot of raw materials and the fact that particle sizes can't be controlled. The surface condition of CQDs may be controlled, and the process is fast and efficient.

2.1.3 Acidic Oxidation

Exfoliating and dissolving bulk carbon into nanoparticles while concurrently introducing hydrophilic functional groups on the surface is one method of synthesising carbon quantum dots (Shen and Xia, 2014). The combination of acidic oxidation and hydrothermal reduction is one method for the large-scale synthesis of hetero-atom-doped CQDs. Hydrothermal reactions with nitrogen, sulphur, or selenium sources resulted in the formation of N-CQDs, S-CQDs, and Se-CQDs, respectively, from carbon nanoparticles derived from Chinese ink (Yang et al., 2014). To boost the CQDs' photoluminescence (PL) performance and quantum yield (QY), these highly doped hetero-atoms can alter their electronic structure (Hassan and Saleh, 2021).

In addition, due to their high electrocatalytic activity, strongly doped CQDs may find use in a variety of contexts as electrocatalysts. Jiang et al. (2015) found that CQDs' electrocatalytic performance may be improved by adding active hetero-atoms to the surface. Single-atom catalysts (SAC) can be produced by doping N-CQDs, S-CQDs, or Se-CQDs with metal ions like Fe³⁺, Co²⁺, or Ni²⁺. The characteristics and uses of strongly doped CQDs may be altered by their interactions with metal ions (Feng and Zhang, 2019).

FIGURE 4 | Schematic showing how the CNT/CQDs are formed by laser ablation. Research by Lu Zan et al.

In several cases, acidic oxidation procedures have been used to synthesise carbon quantum dots (CQDs) and graphene quantum dots (GQDs). The research shows that coke, multi-walled carbon nanotubes, and graphene oxide can all be used to synthesise CQDs and GQDs.

Drug delivery, electrochemical detection, and catalysis are just a few of the many uses for the CQDs and GQDs that arise. Lannazzo et al. added RTIs to GQDs for targeted HIV therapy and drug delivery, as just one example. Peroxidase-like catalytic activity and high-sensitivity H₂O₂ detection were demonstrated for GQDs synthesised from graphene oxide by Tang et al. (Lannazzo et al., 2018).

However, the acidic oxidation procedure may need the use of powerful oxidizers, which are potentially dangerous and necessitate extensive post-processing processes for synthesising these carbon quantum dots. in e (Tang et al., 2016). Despite this, the approach is seen as easy and useful for mass-producing CQDs and GQDs.

2.2 Bottom-Up Methodology

2.2.1 Path of Combustion

As a result of its accessibility, scalability, and low cost, combustion approach has been embraced by numerous researchers for the synthesis of carbon quantum dots (CQDs). To create CQDs with the appropriate characteristics, the initial molecules are burned at high temperatures (Varma et al., 2016). N/S-co-doped CQDs were synthesised from cellulose-based bio-waste willow catkin, while GQDs containing carboxyl groups were generated by burning citric acid and functionalizing with acetic acid. The combustion process produced CQDs with a consistent size and a high concentration of carboxyl groups. However, during burning, tiny polycyclic aromatic hydrocarbons (PAHs) are released into the atmosphere, which is harmful to the environment (Cheng et al., 2019).

Using thermal pyrolysis of citric acid and urea, Xiang et al. have discovered a simple and scalable process for synthesising multicolor emissive carbon dots (CDs). The CDs' blue, green, and red emissions had very high photoluminescence quantum yields (QY) of 52.6%, 35.1%, and 12.9%, respectively (Miao et al., 2018).

Further, the CDs may be uniformly dispersed in epoxy resins to make transparent CD/epoxy composites that emit several hues and white light, making them useful for optoelectronics. The CDs synthesised using this approach have good PL intensity and high QY, suggesting their potential utility in bioimaging and other fields (Li S. et al., 2017).

2.2.2 Pyrolysis in Microwave Ovens

Because of its ease of use, efficiency, and low environmental impact, microwave pyrolysis has great promise as a route to the synthesis of high-quality CQDs. The biomedical, sensing, and optoelectronics industries might all benefit greatly from this method's use. More study is needed to determine the best response conditions and identify the underlying processes at play in this technique. Good photoluminescence characteristics and a consistent size distribution were observed in the resulting CQDs (Wang et al., 2019).

FIGURE 6 | Microwave-assisted pyrolysis synthesis of CQDs. With the authors' blessing, this was reworked and adapted from Monte-Filho et al. (2019).

CQDs have demonstrated significant potential for improving the efficiency of dye-sensitized solar cells (DSSCs) and quantum dot-sensitized solar cells (QDSSCs). High photoconversion efficiency and photocurrent density have been achieved with a single solar irradiance with the use of NCQDs as a co-photoactive layer. Power conversion efficiency has been enhanced by using CQDs as a co-sensitizer and a sensitizer, surpassing the efficiency reached using NCQDs alone (Tungare et al., 2020).

CQDs are appealing for usage in DSSCs and QDSSCs due to their physiochemical and optical properties, which include wide spectrum absorption, high charge carrier extraction, quick charge carrier transportation, and tunable emission. The one-stop approach utilised to manufacture CQDs is not only ecologically beneficial, but also practical, scalable, inexpensive, and easy to implement. It is worth noting, nonetheless, that this approach does not allow for regulation of CQD size (Zhu et al., 2021).

One interesting approach to enhancing the efficiency and performance of DSSCs and QDSSCs is the incorporation of CQDs into their construction. To improve the synthesis and use of CQDs in DSSCs and QDSSCs, more study is required.

2.2.3 Procedures Using Electrochemistry

Since it can be carried out at room temperature and pressure, the electrochemical technique for CQD synthesis is a practical option. The capacity to modify particle size and PL performance has led to its widespread reporting in the literature. Ahirwar et al. (2017) report that blue-emission CQDs were synthesised by electrochemical carbonization of sodium citrate and urea in DI water, which may be employed as a very sensitive detector for Hg²⁺ in wastewater.

Fig. 7 Electrochemical oxidation of the graphite electrode in alkaline alcohols is depicted schematically as the means through which CQDs are produced.

The notion of using an electrochemical technique to simultaneously produce CQDs and electrocatalysts seems appealing. Three electrodes—a graphite working electrode, a platinum foil or Pt wire counter electrode, and a silver/silver chloride reference electrode—are used in this method. An inert nitrogen atmosphere is maintained while an alkaline alcohol electrolyte and a steady voltage of 5 V are provided to the graphite electrode for 3 hours. Unlike previous reports that used graphite rods or other carbon materials as the working electrode and resulted in a brown CQD dispersion and an enlarged electrode, our electrolyte remains transparent throughout the electrochemical oxidation process, and the graphite electrode surface does not enlarge significantly.

Therefore, the electrochemical approach to CQD synthesis provides a simple and practical way for generating CQDs with versatile characteristics. Optimisation of the synthesis conditions and elucidation of the underlying processes of this technique require more study (Tian et al., 2020; Sun et al., 2021).

2.2.4 Hydrothermal/Solid-State Heat Transfer

Hydrothermal processes produce particles that are uniform in size, have a high quantum yield, and may be made with minimally complex equipment. The hydrothermal method is a popular choice for synthesising CQDs (Thambiraj and Shankaran, 2016). The reaction precursor is made up of small organic molecules floating in water or an organic solvent. Hydrothermal methods are often performed in a laboratory using an autoclave made of stainless steel and lined with Teflon, as shown in Figure 8 (He et al., 2018). Organic molecule fusion at high temperatures produced carbon seeding cores that were utilised to generate CQDs with widths of less than 10 nm (Azam et al., 2021).

In comparison to fluorescent dyes, the highest QY of CQDs was very near to 80%. In a high-yield hydrothermal procedure, CQDs were effectively made from citric acid and ethylenediamine, respectively serving as carbon and nitrogen sources. As-prepared CQDs were used to create biosensors for the detection of Fe³⁺ in living cells (Pu et al., 2019). Hydrothermal circumstances

allowed us to control the quantity of graphitic nitrogen, producing full-color CQDs with wavelength-tunable photo-luminescence.

The CQDs' limit of detection (LOD) for Ag⁺ is 0.5 M (Arumugam and Kim, 2018). Mahani et al. synthesised CQDs by hydrothermal carbonization of citric acid and then modified them with transferrin (TF) to increase water solubility and interaction with certain cell receptors. Doxorubicin was loaded onto a TF-CQD carrier and then used to treat MCF-7 breast cancer cells (Mahani et al., 2021).

The hydrothermal method stands out as the simplest approach for producing CQDs with high QY, regulated particle size, and without the need of expensive chemicals. Hydrothermally synthesised CQDs have found applications in bio-imaging, drug delivery, sensor R&D, solar cells, and supercapacitors. The hydrothermal method has the added bonuses of being inexpensive, risk-free, and good for the planet. CQDs of varied sizes and low quality might be created using this method.

3. CQDS CHARACTERISTICS

3.1 UV-Visible Absorption

The size, morphologies, and surface functionalization of CQDs all influence their UV-visible absorption spectra. CQDs have broad UV-to-visible absorption spectra with a peak at 300-400 nm. This peak is due to the π - π^* transition in the carbon nucleus (Azam et al., 2021).

CQDs' absorption spectra may be modified by controlling their size and surface chemistry. For instance, increasing the size of CQDs causes a red shift in their absorption spectra, whereas introducing functional groups to their surfaces causes a blue shift (Kang et al., 2020).

CQDs can have their absorption spectra altered by doping with other elements like nitrogen or sulphur. For instance, nitrogen-doped CQDs show promise for application in biological imaging due to their absorption peaks in the visible to near-infrared region. Since CQDs' UV-visible absorption spectra are highly dependent on their manufacturing and functionalization (Holá et al., 2017), they are a versatile material with several applications.

3.2 Photoluminescence

Photoluminescence (PL) occurs when an object emits light in response to being exposed to another light. Carbon quantum dots (CQDs) have several uses because to their strong PL characteristics in fields such as bioimaging, sensing, and optoelectronics (Chu et al., 2019).

Photon absorption in CQDs generates PL by generating electron-hole pairs. Exactly how PL occurs in CQDs is still being investigated, however it is thought that both surface and core states have a role (Cao et al., 2013).

The PL emission spectrum of CQDs can range from the ultraviolet (UV) through the visible (visible) to the near-infrared (NIR), depending on their size, surface chemistry, and doping. Smaller CQDs have a higher PL quantum yield and emit at shorter wavelengths than larger CQDs, which have a lower PL quantum yield and emit at longer wavelengths (Sun et al., 2006).

The PL of CQDs may be tuned by modifying their synthesis and surface functionalization. Adding functional groups to the surface of CQDs, such as amino or carboxyl groups, can increase their PL quantum yield. (Wang R. et al. 2017).

Doping CQDs with other elements, such as nitrogen or sulphur, can potentially alter their PL properties. Increased quantum yield and a red-shifted PL emission spectrum are two features of nitrogen-doped CQDs that make them useful for bioimaging (Zhu et al., 2015).

3.3 Photoluminescence with an Upward Transition

Upconversion photoluminescence (UCPL) is a nonlinear optical phenomenon that occurs when a material absorbs two or more low-energy photons and emits a higher-energy photon. The unique electrical and optical properties of carbon quantum dots (CQDs) have made them a promising material for UCPL applications in recent years (Zong et al., 2011).

It is possible to achieve UCPL in CQDs by two-photon absorption, energy transfer, and photon upconversion. UCPL in CQDs is theorised to include energy transfer from surface states to core states, albeit this is only a hypothesis (Zheng et al., 2015).

The UCPL properties of CQDs may be modified by tinkering with their size, surface chemistry, and doping. CQDs with a higher surface-to-volume ratio, for instance, exhibit a more dramatic UCPL. It has been shown that functional groups, such as amino or carboxyl groups, added to the surface of CQDs can enhance their UCPL properties (Zuo et al., 2016).

Doping CQDs with lanthanides or rare-earth metals improves their UCPL performance. Lanthanide-doped CQDs exhibit UCPL emission in the visible to near-infrared range, making them useful for bioimaging and photodynamic therapy.

3.4 The Effect of Light on Electron Transfer

An excited electron is transferred from a donor molecule to an acceptor molecule using light in a process called photo-induced electron transfer (PET). Carbon quantum dots (CQDs) are a promising material for usage in a variety of sectors because of its PET features, which include sensing, energy conversion, and catalysis (Roy et al., 2015).

CQDs' PET properties are mostly determined by their size, surface chemistry, and doping. Because of their larger surface area and greater number of surface states, smaller CQDs are able to transmit electrons more quickly. Adding functional groups to the surface of CQDs, such as carboxyl or amino groups, can increase the number of electron donors and acceptors, hence enhancing their PET properties (Xia et al., 2016).

3.5.1 Electroluminescence

Electroluminescence (EL) is a phenomena in which a substance emits light when an electric current is passed through it. Carbon quantum dots (CQDs) are a promising new material for usage in electronics, lighting, and displays since their EL properties were discovered (Xu et al., 2018).

The EL properties of CQDs are mostly determined by their size, surface chemistry, and doping. CQDs can serve as either an emissive layer component or a phosphor material in electroluminescent devices (Sk et al., 2014).

The EL emission spectrum of CQDs may be modified by changing their size, surface chemistry, and doping. For example, the EL efficiency of smaller CQDs is higher for a variety of reasons, including increased surface area and the availability of surface states that may permit charge transfer. Doping CQDs with other elements, like as nitrogen or sulphur, can potentially alter their EL properties. For instance, the EL emission spectra of nitrogen-doped CQDs have been shown to be shifted towards the blue (Wang et al., 2014).

3.6 Chemiluminescence

Chemical reactions that produce light are known as chemiluminescence (CL). Carbon quantum dots (CQDs) have been shown to possess CL properties, making them a promising material for application in biosensing, imaging, and lighting (Lin et al., 2012).

Many factors, including surface chemistry, doping, and reaction conditions, affect the CL properties of CQDs. The CL properties of CQDs may be enhanced by adding functional groups to their surfaces, such as amino or carboxyl groups, which increases the total number of reactive sites accessible for the reaction (Teng et al., 2014).

Doping CQDs with other elements, such as nitrogen or sulphur, can alter their CL properties. Claims have been made that nitrogen-doped CQDs are more effective in catalysing chemical reactions (Zhao et al., 2013). This is because the surface states of these materials are based on nitrogen.

4. Potential Applications Of CQDS

Carbon quantum dots (CQDs) have shown a lot of promise due to their peculiar optical, electrical, and surface features, and they've been used in a lot of different ways. CQDs may be used for a variety of purposes, such as:

- a. Bioimaging - CQDs are being used as fluorescent probes in cellular and in vivo imaging due to their high brightness, low toxicity, and easy functionalization. CQDs are a viable solution for multiplexed bioimaging due to their selectivity (Liu et al., 2018).
- b. CQDs can be used for drug delivery due to their high surface area and their amenability to being functionalized with a wide variety of medications and targeting moieties. By delivering drugs directly to cancer cells, CQDs have been shown to boost therapeutic efficacy and lessen side effects (Molaei, 2019).
- c. Sensing: CQDs may be employed as sensing platforms for a wide range of biomolecules, including glucose, DNA, and proteins, because of their outstanding sensitivity, selectivity, and stability. CQDs can be used as a biosensory for a wide variety of diseases and conditions, including cancer, Alzheimer's, and Parkinson's (Zhou C. et al., 2021; Zhang et al., 2020).
- d. As a new generation of lighting materials, CQDs may be utilised due to their high efficiency, longer lifespan, and low toxicity. Displays, backlighting, and ambient lighting are just a few of the many possible applications for CQDs in the lighting sector (Ouyang et al., 2021).

- e. Energy conversion - CQDs can be used as photocatalysts in the energy-conversion processes of water splitting and carbon dioxide reduction because of their unique electrical properties. CQDs have the potential to enhance the efficiency and durability of solar cells due to their photoactive properties (Rasal et al., 2021; Zhang et al., 2017).
- f. Environmental remediation - CQDs are effective in a variety of environmental remediation applications, such as wastewater treatment and air purification, due to their unique surface characteristics and high adsorption capacity for pollutants (Xu et al., 2017).

CONCLUSION

Numerous methods have been devised for the production of carbon quantum dots, and these newly discovered materials have proven to have a number of desirable qualities. They have been put to good use in the sensor, biomedical, optoelectronic, and energy industries, to name a few. To aid in the delivery of medications to a specific area, CQDs have been "doped" with electromagnetic or magnetically driven material. In addition, they have been utilised to create supercapacitors with high power and energy densities. Osmotic power generation (OPG) employing pressure-retarded osmosis (PRO) is a relatively new use for CQDs. However, even with the correct synthetic methods, elemental doping, and surface passivation, mass manufacturing of CQDs is still a major challenge. For specialised uses in analytical and bio-analytical science, drug delivery, solar cells, and energy storage devices, further research is needed to construct geometrically, compositionally, and structurally well-defined CQDs with greater quantum yield (QY).

REFERENCES –

- Arsalani, N., Nezhad-Mokhtari, P., and Jabbari, E. (2019). *Microwave-assisted and One-step Synthesis of PEG Passivated Fluorescent Carbon Dots from Gelatin as an Efficient Nanocarrier for Methotrexate Delivery*. *Artif. Cells, Nanomedicine, Biotechnol.* 47, 540–547.
- Arunragasa, S., Seekaew, Y., Pon-On, W., and Wongchoosuk, C. (2020). *Hydroxyl Edge-Functionalized Graphene Quantum Dots for Gas Sensing Applications*. *Diam. Relat. Mater.* 105, 107790.
- Atchudan, R., Kishore, S. C., Edison, T. N. J. I., Perumal, S., Vinodh, R., Sundramoorthy, A. K., et al. (2021c). *Highly Fluorescent Carbon Dots as a Potential Fluorescence Probe for Selective Sensing of Ferric Ions in Aqueous Solution*. *Chemosensors* 9, 301
- Bao, R., Chen, Z., Zhao, Z., Sun, X., Zhang, J., Hou, L., et al. (2018). *Green and Facile Synthesis of Nitrogen and Phosphorus Co-doped Carbon Quantum Dots towards Fluorescent Ink and Sensing Applications*. *Nanomaterials* 8, 386.
- Cai, R., Xiao, L., Liu, M., Du, F., and Wang, Z. (2021). *Recent Advances in Functional Carbon Quantum Dots for Antitumour*. *Ijn Vol.* 16, 7195–7229.
- Carbonaro, C., Corpino, R., SalisMocci, F., Mocci, S., Thakkar, C., Olla, P. C., et al. (2019). *On the Emission Properties of Carbon Dots: Reviewing Data and Discussing Models*. *C* 5, 60
- Chao-Mujica, F. J., Garcia-Hernández, L., Camacho-López, S., Camacho-López, M., Camacho-López, M. A., Reyes Contreras, D., et al. (2021). *Carbon Quantum Dots by Submerged Arc Discharge in Water: Synthesis, Characterization, and Mechanism of Formation*. *J. Appl. Phys.* 129, 163301.
- Chen, H., Gao, Q., Li, J., and Lin, J.-M. (2016). *Graphene Materials-Based Chemiluminescence for Sensing*. *J. Photochem. Photobiol. C Photochem. Rev.* 27, 54–71.
- Chen, Y., Cao, Y., Ma, C., and Zhu, J.-J. (2020). *Carbon-based Dots for Electrochemiluminescence Sensing*. *Mat. Chem. Front.* 4, 369–385.
- Cheng, C., Shi, Y., Li, M., Xing, M., and Wu, Q. (2017). *Carbon Quantum Dots from Carbonized Walnut Shells: Structural Evolution, Fluorescence Characteristics, and Intracellular Bioimaging*. *Mater. Sci. Eng. C* 79, 473–480.
- Clancy, A. J., Bayazit, M. K., Hodge, S. A., Skipper, N. T., Howard, C. A., and Shaffer, M. S. P. (2018). *Charged Carbon Nanomaterials: Redox Chemistries of Fullerenes, Carbon Nanotubes, and Graphenes*. *Chem. Rev.* 118, 7363–7408.
- Cui, B., Yan, L., Gu, H., Yang, Y., Liu, X., Ma, C.-Q., et al. (2018). *Fluorescent Carbon Quantum Dots Synthesized by Chemical Vapor Deposition: An Alternative Candidate for Electron Acceptor in Polymer Solar Cells*. *Opt. Mater.* 75, 166–173.
- Deng, Y., Chen, M., Chen, G., Zou, W., Zhao, Y., Zhang, H., et al. (2021). *Visible Ultraviolet Upconversion Carbon Quantum Dots for Enhancement of the Photocatalytic Activity of Titanium Dioxide*. *ACS Omega* 6, 4247–4254.

- Desmond, L. J., Phan, A. N., and Gentile, P. (2021). *Critical Overview on the Green Synthesis of Carbon Quantum Dots and Their Application for Cancer Therapy*. *Environ. Sci. Nano* 8, 848–862.
- Devi, P., Saini, S., and Kim, K.-H. (2019). *The Advanced Role of Carbon Quantum Dots in Nanomedical Applications*. *Biosens. Bioelectron.* 141, 111158.
- Dong, Y., Wang, R., Li, G., Chen, C., Chi, Y., and Chen, G. (2012). *Polyamine Functionalized Carbon Quantum Dots as Fluorescent Probes for Selective and Sensitive Detection of Copper Ions*. *Anal. Chem.* 84, 6220–6224.
- Feng, H., Xie, P., Xue, S., Li, L., Hou, X., Liu, Z., et al. (2018). *Synthesis of Three Dimensional Porous Reduced Graphene Oxide Hydrogel/carbon Dots for High-Performance Supercapacitor*. *J. Electroanal. Chem.* 808, 321–328.
- Gai, W., Zhao, D. L., and Chung, T.-S. (2018). *Novel Thin Film Composite Hollow Fiber Membranes Incorporated with Carbon Quantum Dots for Osmotic Power Generation*. *J. Membr. Sci.* 551, 94–102.
- Guo, Q., Yuan, F., Zhang, B., Zhou, S., Zhang, J., Bai, Y., et al. (2018). *Passivation of the Grain Boundaries of CH₃NH₃PbI₃ Using Carbon Quantum Dots for Highly Efficient Perovskite Solar Cells with Excellent Environmental Stability*. *Nanoscale* 11, 115–124.
- Han, C., Zhang, X., Wang, F., Yu, Q., Chen, F., Shen, D., et al. (2021). *Duplex Metal Co-doped Carbon Quantum Dots-Based Drug Delivery System with Intelligent Adjustable Size as Adjuvant for Synergistic Cancer Therapy*. *Carbon* 183, 789–808.
- Holá, K., Sudolská, M., Kalytchuk, S., Nachtigallová, D., Rogach, A. L., Otyepka, M., et al. (2017). *Graphitic Nitrogen Triggers Red Fluorescence in Carbon Dots*. *ACS Nano* 11, 12402–12410.
- Hu, S., Liu, J., Yang, J., Wang, Y., and Cao, S. (2011). *Laser Synthesis and Size Tailor of Carbon Quantum Dots*. *J. Nanopart Res.* 13, 7247–7252.
- Huang, P., Xu, S., Zhang, M., Zhong, W., Xiao, Z., and Luo, Y. (2020a). *Carbon Quantum Dots Improving Photovoltaic Performance of CdS Quantum Dot Sensitized Solar Cells*. *Opt. Mater.* 110, 110535.
- Huo, X., Liu, L., Bai, Y., Qin, J., Yuan, L., and Feng, F. (2022). *Facile Synthesis of Yellowish-Green Emitting Carbon Quantum Dots and Their Applications for Phoxim Sensing and Cellular Imaging*. *Anal. Chim. Acta* 1206, 338685.
- Iannazzo, D., Pistone, A., Ferro, S., De Luca, L., Monforte, A. M., Romeo, R., et al. (2018). *Graphene Quantum Dots Based Systems as HIV Inhibitors*. *Bioconjugate Chem.* 29, 3084–3093.
- Jeevanandam, J., Barhoum, A., Chan, Y. S., Dufresne, A., and Danquah, M. K. (2018). *Review on Nanoparticles and Nanostructured Materials: History, Sources, Toxicity and Regulations*. *Beilstein J. Nanotechnol.* 9, 1050–1074.
- Jiang, Y., Han, Q., Jin, C., Zhang, J., and Wang, B. (2015). *A Fluorescence Turn-Off Chemosensor Based on N-Doped Carbon Quantum Dots for Detection of Fe³⁺ in Aqueous Solution*. *Mater. Lett.* 141, 366–368.
- Kang, C., Huang, Y., Yang, H., Yan, X. F., and Chen, Z. P. (2020). *A Review of Carbon Dots Produced from Biomass Wastes*. *Nanomaterials* 10, 2316–2324.
- Li, G., Pei, M., and Liu, P. (2020). *DOX-conjugated CQD-Based Nanosponges for Tumor Intracellular pH-Triggered DOX Release and Imaging*. *Colloids Surfaces A Physicochem. Eng. Aspects* 603, 125258.
- Liu, H., Xu, H., and Li, H. (2022). *Detection of Fe³⁺ and Hg²⁺ Ions by Using High Fluorescent Carbon Dots Doped with S and N as Fluorescence Probes*. *J. Fluoresc.* 32, 1089–1098.
- Liu, J., Li, R., and Yang, B. (2020). *Carbon Dots: A New Type of Carbon-Based Nanomaterial with Wide Applications*. *ACS Cent. Sci.* 6, 2179–2195.
- Maiti, D., Tong, X., Mou, X., and Yang, K. (2019). *Carbon-Based Nanomaterials for Biomedical Applications: A Recent Study*. *Front. Pharmacol.* 9, 1401.
- Matea, C., Mocan, T., Tabaran, F., Pop, T., Mosteanu, O., Puia, C., et al. (2017). *Quantum Dots in Imaging, Drug Delivery and Sensor Applications*. *Ijn Vol.* 12, 5421–5431.
- Miao, X., Qu, D., Yang, D., Nie, B., Zhao, Y., Fan, H., et al. (2018). *Synthesis of Carbon Dots with Multiple Color Emission by Controlled Graphitization and Surface Functionalization*. *Adv. Mat.* 30, 1704740.
- Niu, F., Xu, Y., Liu, J., Song, Z., Liu, M., and Liu, J. (2017). *Controllable Electrochemical/electroanalytical Approach to Generate Nitrogen-Doped Carbon Quantum Dots from Varied Amino*

- Acids: Pinpointing the Utmost Quantum Yield and the Versatile Photoluminescent and Electrochemiluminescent Applications. Electrochimica Acta* 236, 239–251.
- Pardo, J., Peng, Z., and Leblanc, R. (2018). *Cancer Targeting and Drug Delivery Using Carbon-Based Quantum Dots and Nanotubes. Molecules* 23, 378.
- Permatasari, F. A., Irham, M. A., Bisri, S. Z., and Iskandar, F. (2021). *Carbon-Based Quantum Dots for Supercapacitors: Recent Advances and Future Challenges. Nanomaterials* 11, 91.
- Pu, Z.-F., Wen, Q.-L., Yang, Y.-J., Cui, X.-M., Ling, J., Liu, P., et al. (2020). *Fluorescent Carbon Quantum Dots Synthesized Using Phenylalanine and Citric Acid for Selective Detection of Fe³⁺ Ions. Spectrochimica Acta Part A Mol. Biomol. Spectrosc.* 229, 117944.
- Quan, Y., Wang, G., Lu, L., Wang, Z., Xu, H., Liu, S., et al. (2020). *High performance Pseudocapacitor Energy Storage Device Based on a Hollow Structured Copper Sulfide Nanoflower and Carbon Quantum Dot Nanocomposite. Electrochimica Acta* 353, 136606.
- Ren, X., Zhang, F., Guo, B., Gao, N., and Zhang, X. (2019). *Synthesis of N-Doped Micropore Carbon Quantum Dots with High Quantum Yield and Dual Wavelength Photoluminescence Emission from Biomass for Cellular Imaging. Nanomaterials* 9, 495.
- Riaz, R., Ali, M., Maiyalagan, T., Anjum, A. S., Lee, S., Ko, M. J., et al. (2019). *Dye sensitized Solar Cell (DSSC) Coated with Energy Down Shift Layer of Nitrogen Doped Carbon Quantum Dots (N-CQDs) for Enhanced Current Density and Stability. Appl. Surf. Sci.* 483, 425–431
- Shah, S. N. A., Zheng, Y., Li, H., and Lin, J.-M. (2016). *Chemiluminescence Character of ZnS Quantum Dots with Bisulphite-Hydrogen Peroxide System in Acidic Medium. J. Phys. Chem. C* 120, 9308–9316.
- Shen, P., and Xia, Y. (2014). *Synthesis-modification Integration: One-step Fabrication of Boronic Acid Functionalized Carbon Dots for Fluorescent Blood Sugar Sensing. Anal. Chem.* 86, 5323–5329.
- Teng, P., Xie, J., Long, Y., Huang, X., Zhu, R., Wang, X., et al. (2014). *Chemiluminescence Behavior of the Carbon Dots and the Reduced State Carbon Dots. J. Luminescence* 146, 464–469.
- Tyagi, A., Tripathi, K. M., Singh, N., Choudhary, S., and Gupta, R. K. (2016). *Green Synthesis of Carbon Quantum Dots from Lemon Peel Waste: Applications in Sensing and Photocatalysis. RSC Adv.* 6, 72423–72432.
- Varma, A., Mukasyan, A. S., Rogachev, A. S., and Manukyan, K. V. (2016). *Solution Combustion Synthesis of Nanoscale Materials. Chem. Rev.* 116, 14493–14586.
- Wang, B., Wang, S., Wang, Y., Lv, Y., Wu, H., Ma, X., et al. (2016). *Highly Fluorescent Carbon Dots for Visible Sensing of Doxorubicin Release Based on Efficient Nanosurface Energy Transfer. Biotechnol. Lett.* 38, 191–201.
- Wang, C., Wu, X., Li, X., Wang, W., Wang, L., Gu, M., et al. (2012). *Upconversion Fluorescent Carbon Nanodots Enriched with Nitrogen for Light Harvesting. J. Mat. Chem.* 22, 15522–15525.
- Wu, F., Yang, M., Zhang, H., Zhu, S., Zhu, X., and Wang, K. (2018). *Facile Synthesis of Sulfur-Doped Carbon Quantum Dots from Vitamin B1 for Highly Selective Detection of Fe³⁺ Ion. Opt. Mater.* 77, 258–263.
- Xu, J., Sahu, S., Cao, L., Bunker, C. E., Peng, G., Liu, Y., et al. (2012). *Efficient Fluorescence Quenching in Carbon Dots by Surface-Doped Metals – Disruption of Excited State Redox Processes and Mechanistic Implications. Langmuir* 28,
- Yang, S.-T., Cao, L., Luo, P. G., Lu, F., Wang, X., Wang, H., et al. (2009). *Carbon Dots for Optical Imaging In Vivo. J. Am. Chem. Soc.* 131, 11308–11309.