CARBONACEOUS QUANTUM DOTS: SYNTHESIS AND APPLICATIONS

Editors: Kulvinder Singh Vineet Kumar

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Carbonaceous Quantum Dots: Synthesis And Applications

Edited by

Kulvinder Singh

Department of Chemistry DAV College Chandigarh India

&

Vineet Kumar

School of Bioengineering and Biosciences Lovely Professional University Jalandhar, Punjab India

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FOREWORD

Carbon-based quantum dots (CQDs) have got a lot of attention because of their bright luminescence and strong solubility. CQDs are the potential replacement for the toxic metalbased quantum dots. CQDs are characteristically quasispherical carbon nanoparticles composed of amorphous to crystalline carbon bases. CQDs can be prepared simply and inexpensively by multiple techniques such as the arc-discharge method, microwave pyrolysis, hydrothermal method and electrochemical synthesis. Additionally, CQDs exhibit excellent physical and chemical characteristics like significant crystallization, excellent dispersibility, and photoluminescence attributes. In this book, in-depth deliberation on several potent applications, such as biomedical, water treatment, energy storage, solar cells *etc.*, has been provided. These applications would affect human life quality significantly and have the potential to draw substantial commercial interest.

This book provides a comprehensive guide for researchers and students to understand the overview, properties, synthesis route and applications of carbonaceous quantum dots. This class of quantum dots has recently gained a lot of interest in various fields of basic science and technology. This could be a handbook for various professionals, researchers and students working in the field of biomedical application, green energy, sensing, energy storage, water treatment, *etc.* Most importantly, this book has proven helpful to postgraduate students in their academic studies.

Dai-Viet N. Vo Institute of Applied Technology and Sustainable Development Nguyen Tat Thanh University Ho Chi Minh City 755414, Vietnam

PREFACE

Carbonaceous quantum dots (CQDs) are an intriguing category of carbon nanoparticles with diameters of about 10 nm. Several sustainable and green characteristics of CQDs, such as low toxicity, chemical inertness, superior biocompatibility, photo-induced electron transfer, and extremely controllable photoluminescence behavior, render them to be an appealing candidate in numerous potent fields. The production of CQDs offers the benefits of basic, inexpensive synthesis processes as well as a large selection of synthetic raw materials. CQD synthesis techniques can be broadly divided into "top-down" and "bottom-up" approaches. In the former, carbonaceous materials are reduced or subdivided using chemical, electrochemical, or physical methods. The latter is accomplished either by step-by-step chemical fusion of small aromatic molecules or by pyrolysis or carbonization of small organic molecules. The worldwide significance and attention of CQDs are attributed to their unique advantages in terms of properties, such as low toxicity, chemical stability, biocompatibility, redox properties, excellent luminescence, tunable and comparable photoluminescence, fluorescent sensing, excellent solubility, and effortless environmental friendly synthesis process. In this book, the selected chapters intend to illustrate the significant potential of CQDs in numerous sectors, such as biomedical, solar cell, sensing, water treatment, and energy storage/generation, with an emphasis on prospects. This book provides a comprehensive guide for researchers and students to understand the overview, properties, synthesis route and applications of carbonaceous quantum dots. This could be a handbook for various professionals, researchers and students working in the field of biomedical application, green energy, sensing, energy storage, water treatment, *etc.* Most importantly, this book has proven helpful to postgraduate students in their academic studies. The authors of this book's chapters are renowned professionals who are enthusiastic about the rapidly emerging, crossdisciplinary fields of research, particularly material science.

We express our gratitude to all the contributors. We would like to thank Prof. (Dr) Andreas Constantinou for writing the foreword. Finally, it is a profound pleasure to thank Bentham Science for taking up the publication of this book. We hope that this book will provide recent scientific knowledge on the chemotherapeutic potential of natural products and the techniques employed for the detection of cancer and other diseases and will lead to new discussions about the global scope of nutraceuticals.

Abhinay Thakur *et al.*, in Chapter 1, discusses the basic introduction of CQDs with a round note on its potent utilization in several fields; DevikaVashisht *et al.*, in Chapter 2, elaborate on the properties of CQDs, including phosphorescence, chemiluminescence, adsorption, electrical properties, electrochemical luminescence, photo-induced electron transfer, *etc.*; Munish Kumar in Chapter 3 discusses arc discharge method, laser ablation method, acidic oxidation method and combustion/thermal method; Abhinay Thakur *et al.* in Chapter 4 mentioned about the characterization techniques of CQDs, including fluorescence spectroscopy, Fourier transform infrared spectroscopy, transmission electron microscopy, atomic force microscopy, optical analysis using photoluminescence spectrophotometer, light absorption by UV-vis spectrophotometer, *etc.*; Yarima S. García *et al.*, in Chapter 5, discusses the potential of CQDs in the biomedical field; Ekta Sharma and Vaishali Thakur, in Chapter 6, elaborated on the significance of CQDs in the solar cell; Alma Mejri *et al.*, in Chapter 7, enlighten the potential of CQDs in sensing, Garima Kumari *et al.*, in Chapter 8, mentioned about the capability of CQDs in sensing, Garima Kumari *et al.*, in Chapter 8, mentioned about the capability of CQDs in energy storage; in last, DevikaVashisht *et al.*, in Chapter 10, deeply enlighten the future aspects of CQDs in various fields.

I anticipate that the readers will find these insights and examination crucial and will inspire them to explore more about further research on Carbonaceous quantum dots in several other potent domains. I am grateful for the prompt initiatives and support provided by the editorial personnel, especially Ms. Humaira Hashmi and Ms. Rabia Maqsood at Bentham Science Publishers.

Kulvinder Singh

Department of Chemistry DAV College Chandigarh India

&

Vineet Kumar School of Bioengineering and Biosciences Lovely Professional University Jalandhar, Punjab India

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List of Contributors

Abhinay Thakur	Department of Chemistry, School of Chemical Engineering and Physical Sciences, Lovely Professional University, Phagwara, Punjab, India
Abdelmoneim Mars	Laboratory of Desalination and Natural Water Valorisation (LADVEN, Water Researches and Technologies Center (CERTE), Techno-park BorjCedria, BP 273, 8020, Soliman, Tunisia
Adelmo M. Estrada	Center for Advanced Studies, HAV, Cuba and Federal University of Pernambuco, PE, Brazil
Alma Mejri	Laboratory of Desalination and Natural Water Valorisation (LADVEN, Water Researches and Technologies Center (CERTE), Techno-park BorjCedria, BP 273, 8020, Soliman, Tunisia
Anupam Guleria	Centre of Biomedical Research, SGPGIMS Campus, Lucknow, Uttar Pradesh, India
Ashish Kumar	NCE, Department of Science and Technology, Government of Bihar, India
Ashish Guleria	Department of Applied Sciences, WIT Dehradun, India
Aseem Vashisht	Punjab State Council for Science and technology Sector - 26, Chandigarh, India
Atma Rai	Department of Applied Sciences, WIT Dehradun, Uttarakhand, India
Devika Vashisht	Department of Chemistry and Centre of Advanced Studies in Chemistry, Panjab University, Chandigarh, India
Dinesh Kumar	Centre of Biomedical Research, SGPGIMS Campus, Lucknow, Uttar Pradesh, India
Eder Lima	Institute of Chemistry, Federal University of Rio Grande, Rio Grande, Brazil
Ekta Sharma	Department of Chemistry, School of Basic and Applied Sciences, Maharaja Agrasen University, Baddi, India
Eneida R. López	Center for Advanced Studies, HAV, Cuba and Federal University of Pernambuco, PE, Brazil
Garima Kumari	Department of Biotechnology, Eternal University, Baru Sahib, Sirmaur, Himachal Pradesh, India
Hamza Elfil	Laboratory of Desalination and Natural Water Valorisation (LADVEN, Water Researches and Technologies Center (CERTE), Techno-park BorjCedria, BP 273, 8020, Soliman, Tunisia
Harpreet Kaur	Department of Chemistry, School of Chemical Engineering and Physical Sciences, Lovely Professional University, Phagwara, Punjab, India
Ivan H. Herrera	Center for Advanced Studies, HAV, Cuba and Federal University of Pernambuco, PE, Brazil
Jorge L. Neves	Center for Advanced Studies, HAV, Cuba and Federal University of Pernambuco, PE, Brazil
Mika Sillanpaa	Department of Green Chemistry, Aarhus University, Nordre Ringgade, Denmark

Munish Kumar	Department of Chemistry & Centre for Advanced Studies in Chemistry, Panjab University, Sector-14, Chandigarh, India
Nitesh Kumar	Department of Chemistry, Govt. College Jukhala, Pradesh, India
Priyanka	Department of Chemistry, Centre of Advanced Studies in Chemistry Punjab University, Chandigarh, India
Shweta Sharma	Institute of Forensic Science and Criminology, Panjab University, Chandigarh, India
Sumayah Bashir	Department of Chemistry, Central University of Kashmir, Kashmir, India
Surinder Kumar Mehta	Department of Chemistry and Centre of Advanced Studies in Chemistry, Panjab University, Chandigarh, India University of Laddakh, Leh, India
Sumayah Bashir	Department of Chemistry, Central University of Kashmir, Kashmir, India
Vaishali Thakur	Department of Chemistry, School of Basic and Applied Sciences, Maharaja Agrasen University, Baddi, India
Yarima S. García	Center for Advanced Studies, HAV, Cuba and Federal University of Pernambuco, PE, Brazil

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Introduction to Carbonaceous Quantum Dots

Abhinay Thakur¹, Ashish Kumar^{2,*} and Sumayah Bashir³

¹ Department of Chemistry, School of Chemical Engineering and Physical Sciences, Lovely Professional University, Phagwara, Punjab, India

² NCE, Department of Science and Technology, Government of Bihar, India

³ Department of Chemistry, Central University of Kashmir, Kashmir, India

Abstract: Carbonaceous quantum dots (CQDs), relatively small carbon nanoparticles (<10 nm in size), have sparked the attention over the last few decades for their potential as a promising resource in various fields, such as biomedical, solar cells, sensors, water treatment, energy generation storage because of their benign, abundant, low preparation costs, small size, non-hazardous nature, high biocompatibility, high water solubility and effective alteration nature. Numerous applications in optronics, catalysis, and sensing are made possible by the excellent electronic characteristics of CQDs as electron acceptors and donors that cause photocatalytic activity and electrochemical luminosity. This feature series aims to assess the current status of CQDs by discussing the literature in this field and deliberate the basics, applicability and advancements in the field of CQDs in both scientific and technology circles.

Keywords: Biocompatibility, Carbonaceous quantum dots, Carbon dots, Carbon nanoparticles.

INTRODUCTION

Quantum Dots (QD)

Currently, possibilities to assess the features linked to the unity of quantumconstrained features have been made possible by advancements in the manufacture of high-quality quantum dots (QDs) [1 - 3]. Acclaimed as a milestone in nanotechnology, QDs are semiconductors inorganic crystalline with adjustable quantities of electrons that can exist in distinct quantum systems. The atom arrangement in QDs is identical to that in bulk materials, but due to the 3dimensional truncation, there are more atoms on their surfaces. Since QDs frequently have small sizes and a diversity of varying element proportions, they might exhibit luminous features [4]. QDs in particular, feature unique luminous

^{*} **Corresponding author Ashish Kumar:** NCE, Department of Science and Technology, Government of Bihar, India; Tel: +91- 94784-78088, E-mail: drashishchemlpu@gmail.com

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qualities, a size-dependent emission wavelength, broad excitation spectra, and electronic characteristics like broad and persistent absorption spectrum, confined dispersion, and good light persistence [5]. After a few nanoseconds, they absorbed white light and reemitted distinct shades based on the band gaps of the materials. Furthermore, by following the quantum confinement principle, the configuration of QDs could be readily controlled. The emission and absorption spectra corresponding to the energy band gap of QDs are governed by the quantum entrapment principle, which is the energy required to stimulate electrons from the electronic range to greater energy states [6]. This excitation results in the spontaneous formation of an electron-hole pair, which enables it to discharge energy in the character of fluorescent photons. QDs could be thought of as synthetic atoms that can produce different energy states, and by adjusting their diameters, their band gap could be accurately adjusted. Smaller nanocrystals have wider band gaps, and larger nanocrystals have smaller band gaps. The usage of QDs in devices such as telecom optics, light-emitting diodes, and medicinal applications is another possibility. QDs have stable and tuneable wavelengths [7].

CARBONACEOUS QUANTUM DOTS (CQD)

Discovery of CQDs

Since carbon is normally considered a dark substance, it used to be difficult to imagine that it might be miscible in aqueous and even gloriously illuminated [8]. CDs (probably known as CQD) were found unintendedly in 2004 at the time of filtration of single-wall carbon nanotubes (SWCNTs). They were initially referred to as "carbon nanoparticles," but the name "carbon dots" was later adopted because it evoked similar properties as same that of inorganic QD. Two years after constructing stable photoluminescent carbon nanoparticles of various diameters in 2006, Sun et al. gave them the name "carbon quantum dots." Within a year, Sun et al. reported water-dispersible CDs that had been passivized using poly-propionylethylenimine-co-ethylenimine [9 - 11]. The CDs were used to detect human breast malignant MCF-7 cells and showed dual photon-induced luminescence spectra. The potential for carbon dots in biological applications has attracted significant interest. Another benefit of carbon dots in the context of nanoparticle applications is their biocompatibility. As they are predominantly composed of the abundant and non-toxic substance carbon, carbon dots stand out from other nanoparticle families due to their unique geometric and electrical characteristics [12].

CQDs are spherically symmetrical, have a size of less than 10 nm, and can have amorphous or crystalline structures. Photoluminescence and wavelengthdependent emission are interesting properties of both amorphous and crystalline materials, as are high solubility, minimal hazardous, ease of synthesis, and biocompatibility [13]. Due to their broad range of technical applications in

Introduction

various domains, including photocatalysis, solar cells, LED devices, sensors, bioimaging, and drug delivery systems, CQDs gradually became a focus of discussion among researchers. Traditional QD formulations frequently contained cadmium, however, toxicity spurred on by cadmium ions that spilled signaled the development of the more compatible QD. The goal was to create cadmium-free QDs (CFQDs) with excellent chemical resilience, minimal cytotoxicity, and simplicity in pharmaceutical activities as the demand for more biocompatible QDs expanded. As a result, different QDs were created, including graphene QDs, silicon QDs, and carbon QDs [14, 15]. CQDs compensate for the toxicological, ecological risk, and biological deficiencies of traditional semiconductor quantum dots whilst inheriting their outstanding photonic features. CQDs are also easily interface functionalized and prepared on a massive volume, and they also exhibit strong solubility in water, chemical resistance, and light absorption resilience.

In this chapter, we will critically elaborate on the advantages, limitations, and potential results of the physical and chemical features that are the main focus of our investigation. We will also discuss several syntheses and characterization methodologies. We believe that by providing guidance on the fundamentals of CQDs from a perspective viewpoint, this chapter can be helpful.

Chemical Structure of CQDs

Due to their intense brightness and robust dispersion, carbon-based quantum dots have drawn considerable scrutiny. The architectures of carbon-based quantum dots control their many characteristics [16]. The CQD surface's numerous carboxyl moieties have excellent biocompatibility and water solubility. CODs can also be used for surface modification and chemical treatment with various elastomeric, microbiological, regenerative, or inorganic substances. Surface passivation can enhance the CQDs' physical and fluorescent characteristics. CQDs are highly conductive, have a stable chemical structure, and exhibit strong photochemical resilience. CODs are spherical carbon nanoparticles that can be made with or without a crystal structure [17]. Approximately 0.34 nm separates the sections of CQDs, which is compatible with the crystalline graphite spacing of (002). A system of interconnected or altered chemical functional moieties including oxygen- and amino-based clusters, could be found at the interface of CODs. The substituent of CODs could be identified using the matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) method relying on the chemical and physical configuration of the CQDs. CQDs are created via bottomup techniques by dehydrating polycyclic aromatic molecules and carbonizing them [18]. The anticipated model architecture for the CQD DFT experiment is shown in Fig. (1). To investigate the feasibility of band edge location tweaking, the CQD configuration was synthesized with the distal carbon atoms linked by.

CHAPTER 2

Synthesis of Carbonaceous Quantum Dots

Munish Kumar^{1,*}

¹ Department of Chemistry & Centre for Advanced Studies in Chemistry, Panjab University, Sector-14, Chandigarh, India

Abstract: New class of nanocarbon materials, such as luminescent carbon quantum dots (CQDs) has gained a great deal of interest in the area of electrocatalysis, solar cells, bioimaging nanomedicine, a chemical sensor and a light-emitting diode. CQDs exhibit good physio-chemical properties, such as photoluminescence, high crystallization and good dispersibility. The rapid electron transfer, small size and superconductivity of CQDs provide the CQDs-based composite offering enhanced catalytic activity and electric conductivity. However, additional active moieties are present on the surface, which might aid in the formation of multi-component electrically activated catalysts. Additionally, the multi-component catalysts' internal interactions promote charge transfer and catalytic efficiency, both of which are essential for electrochemistry. Therefore, keeping in mind the importance of CODs, they are synthesized on the basis of two approaches: Top-down and Bottom-up. The bulk material is reduced in size by utilizing chemical and physical processes in the topdown approach. On the contrary, in the bottom-up method, the atoms are assembled and converted into CQDs using polymerization and carbonization through a chemical reaction. Hence, in this chapter, we will discuss the synthesis techniques for CQDs, such as hydrothermal/solvothermal method, laser ablation, arc-discharge method, acidic oxidation, thermal/combustion routes, electrochemical method and microwave pyrolysis method.

Keywords: CQDs, Catalyst, Polymerization, Synthesis, Solvothermal.

INTRODUCTION

At present, carbon-based nanomaterials (NMs), including fullerenes, graphene, nanodiamonds and carbon nanotubes, have attracted scientists' attention worldwide [1 - 4]. However, there are some difficulties observed in the separation and preparation of nanodiamonds, due to less water solubility of carbon nanotubes, graphene and fullerenes, which make these nanocrystals less fluorescence in the visible region and limit their application. However, CQDs are carbon-based nanomaterials having noble zero-dimensional small size and strong

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^{*} **Corresponding author Munish Kumar:** Department of Chemistry & Centre for Advanced Studies in Chemistry, Panjab University, Sector-14, Chandigarh, India; Email: munishthukral7@gmail.com

Synthesis

fluorescence nature [5]. Also, carbon quantum dots are known as carbon dots in some cases. The photoelectrochemical characteristics and dimensions of all quantum dots (including those made of graphene, carbon nano, and polymer) are comparable, but their internal structures and external chemical moieties vary. Mainly, CQDs are spherical and monodisperse in nature, and the surface is covered with a carbon-based chain, having more oxygen groups present in the skeleton [6]. In order to make these materials fluorescent and to tune the electronic structure, the surface moiety and size must be carefully familiar. CQDs' superior optical qualities make up for the material's shortcomings in regard to contamination, cytotoxic and ecological impact. Also, carbon quantum dots have shown excellent chemical stability, good water solubility, easily functionalized, scale up the reaction and photobleaching resistance [7]. Due to the superior characteristics of CQDs, they have been broadly utilized in nanomedicine, biology, photoelectrocatalysis and chemical sensing [8 - 11].

Hence, in this chapter, we will discuss the synthesis techniques for CQDs, such as hydrothermal/solvothermal method, laser ablation, acidic oxidation, arc-discharge method, thermal/ combustion routes, electrochemical method and microwave pyrolysis method. But before it, we will be discussing the chemical states and structures of the CQDs.

Chemical States of CQDs

CODs can exist in various chemical states, depending on their synthesis method, functionalization, and environmental conditions. The most common chemical states of CODs include sp2-hybridized carbon atoms, oxygen-containing functional groups, and surface defects. The sp2-hybridized carbon atoms are the core building blocks of CQDs and are responsible for their electronic properties, such as conductivity and fluorescence. The sp2 carbon atoms in CODs form a conjugated network that allows for the delocalization of π electrons, leading to their unique optical properties. The size and shape of the sp2 domains in CODs can also affect their fluorescence properties. Oxygen-containing functional groups, such as hydroxyl, carboxyl, and carbonyl groups, are commonly present on the surface of CODs. These functional groups can be introduced intentionally during synthesis or can result from surface oxidation. The presence of oxygencontaining functional groups can affect the surface charge and chemical reactivity of CODs, making them more suitable for various applications, such as sensing and catalysis. Surface defects, such as vacancies, dangling bonds, and edge sites, can also influence the electronic and catalytic properties of CODs. Surface defects can act as active sites for chemical reactions and can enhance the charge transfer between CODs and their surroundings.

Structure of CQDs

The structure of CQDs is another important factor that determines their physiochemical properties. The structure of CQDs can be classified based on their size, shape, crystallinity, and morphology.

Size: The size of CQDs typically ranges from a few nanometers to tens of nanometers. The size of CQDs can affect their fluorescence properties, with smaller CQDs exhibiting higher quantum yields due to the quantum confinement effect.

Shape: CQDs can have various shapes, such as spherical, elliptical, triangular, and hexagonal. The shape of CQDs can influence their surface area and packing density, affecting their chemical reactivity and stability.

Crystallinity: CQDs can exhibit different degrees of crystallinity, ranging from amorphous to highly crystalline. The degree of crystallinity can affect their electronic and optical properties, with highly crystalline CQDs exhibiting better conductivity and fluorescence properties.

Morphology: CQDs can have various morphologies, such as core-shell, hollow, and porous structures. The morphology of CQDs can affect their surface area, porosity, and surface charge, affecting their catalytic and sensing properties.

The structure of CQDs can also be influenced by their synthesis method. Various synthesis methods, such as hydrothermal/solvothermal, arc-discharge, thermal/combustion routes, electrochemical, and microwave pyrolysis, can result in CQDs with different structures and properties, which will be discussed beneath.

Synthesis Method

Therefore, keeping in mind the importance of CQDs, they are synthesized on the basis of two approaches: Top-down and Bottom-up [12, 13]. The bulk material is transformed into small-sized CQDs utilizing chemical and physical processes in the top-down technique. On the contrary, in the bottom-up method, the atoms are assembled and converted into CQDs using polymerization and carbonization through a chemical reaction.

Top-down Strategy

The top-down strategy is one of the most promising approaches for the preparation of CQDs. This strategy involves the fragmentation of bulk materials into small particles. In the case of CQDs, the starting material is a carbonaceous material that can be derived from natural sources such as wood, lignin, and

CHAPTER 3

Properties of Carbonaceous Quantum Dots

Devika Vashisht¹, Priyanka¹, Aseem Vashisht², Shweta Sharma³ and Surinder Kumar Mehta^{1,*}

¹ Department of Chemistry and Centre of Advanced Studies in Chemistry, Panjab University, Chandigarh, India

² Punjab State Council for Science and technology Sector - 26, Chandigarh, India

³ Institute of Forensic Science and Criminology, Panjab University, Chandigarh, India

Abstract: Carbonaceous quantum dots (CQDs) is defined as a subclass of carbon nanoparticles, which offer a size of around 10 nm, and have unique characteristics and a wide range of applications in diverse fields. CQDs have attained widespread attention due to their excellent abilities in several domains, including sensing, nanomedicine and environmental remediation. The mode of synthesis for CQDs is quite simple and inexpensive *via* methods such as microwave pyrolysis, arc-discharge, *etc.* CQDs are entitled to diverse physical, chemical and biological properties. Besides this, CQDs have various functional groups present on their surface that improve the properties, specifically the catalytic performance by a phenomenon called charge transfer. The physical, optical, electrical, and biological features of CQDs are explored in this chapter.

Keywords: Biological properties, Carbon quantum dots, Electrical properties, Optical properties, Photoluminescence.

INTRODUCTION

Carbonaceous quantum dots (CQDs) are nanoparticles of carbon with a very small size from 2 to 10 nm and have exceptional properties such as excellent conductivity, chemical stability, eco-friendly nature and strong photoluminescence (PL) emission. Xu *et al.* [1] first discovered the CQDs in 2004 while purifying carbon nanotubes. CQDs are well known for their tunable features, enabling applications in biomedicines, photocatalytic, sensing and optoelectronics applications. They improve the characteristics of semiconductor quantum dots as well as fill the gaps due to the inadequacy of conventional

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^{*} Corresponding author Surinder Kumar Mehta: Department of Chemistry and Centre of Advanced Studies in Chemistry, Panjab University, Chandigarh, India; E-mail: skmehta@pu.ac.in, ss

Properties

materials in terms of cytotoxicity, biohazard and eco-friendliness. CQDs have fascinating applications in various fields due to their good aqueous solubility and tunable fluorescence properties. During the past few years, various researchers have made substantial progress in the synthesis of the CQDs. In contrast to the traditional semiconductor QDs, the fluorescent CQDs are superior owing to their excellent solubility in an aqueous medium, resistance to photo-bleaching and facile modification.

The 'top-down' and 'bottom-up' are the two well-known approaches by which CQDs are synthesized, as shown in Fig. (1) [1]. In the top-down approach, using chemical or physical methods, the large-sized macromolecules are disintegrated into small-sized CQDs. On the other side, in a bottom-up approach, the tiny molecules carbonize *via* polymerization resulting in CQDs through a chemical reaction. Some of the methods are chemical ablation, microwave irradiation, laser ablation, hydrothermal treatment, *etc.*

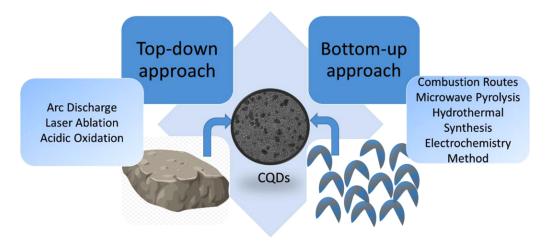


Fig. (1). Classification of methods of synthesis of CQDs [1].

The structure of the CQDs may vary depending on the mode of synthesis followed. Generally, CQDs are spherically shaped with a distance of 0.34 nm between two layers corresponding to (002) plane. Materials used to fabricate CQDs include different sources of carbon, such as citric acid, ammonium citrate, graphite, sodium hydroxide and some natural sources, such as food wastes, grass, denatured milk, broccoli *etc.* As of now, exceptional progress has been made in exploring the properties of luminescent CQDs. Thus, this chapter summarizes various properties and features of CQDs.

Optical Features

The CQDs have various applications due to their remarkable optical properties. The important optical properties have been discussed further.

Photoluminescence (PL)

The excellent feature with respect to fundamental and application-oriented perspectives is PL. In comparison to organic fluorophores, the CQDs exhibit excellent photostability and non-blinking fluorescence. According to a literature report [2], CQDs synthesized by laser ablation display PL intensity which is reduced by just 4.5% even after 4 h of irradiation. Another special property of CQDs is that λ_{ex} depends on the emission wavelength owing to quantum impact and emissive pits on its interface. Additionally, multicolor imaging technology can be achieved by using excitation-dependent PL. The fluorescent features of CQDs could be altered by the modification in experimental synthesis procedures, as shown in Fig. (2) [2]. The photoluminescence behavior of CQDs is strongly determined by size, crystallinity and functional groups. Generally, naked CQDs possess low fluorescence however; the fluorescence quantum yield is increased by chemical modification using organic moieties [2].

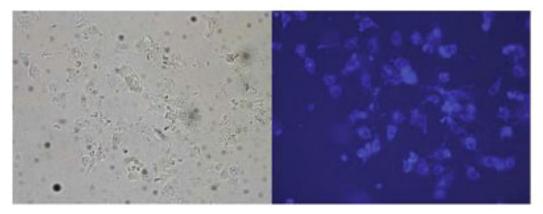


Fig. (2). Cellular scans of HUVEC experimented with carbon dots following 12 h in a spark and fluorescent field [2].

Numerous mechanisms have been reported to be responsible for the fluorescence of CQDs, including surface defects, quantum size defects and molecular states. Surface defects refer to the defects formed due to oxidation. The quantum size effect indicates the effect of radiative electron-hole pair recombination [3]. CQDs are known to possess certain specific mechanisms based on photoluminescence which have been described below.

Characterization of Carbonaceous Quantum Dots

Abhinay Thakur¹, Harpreet Kaur¹, Ashish Kumar^{2,*} and Sumayah Bashir³

¹ Department of Chemistry, School of Chemical Engineering and Physical Sciences, Lovely Professional University, Phagwara, Punjab, India

² NCE, Department of Science and Technology, Government of Bihar, India

³ Department of Chemistry, Central University of Kashmir, Kashmir, India

Abstract: Carbonaceous quantum dots (CQDs), a prominent figure of carbon materials, offer remarkable impetus in a variety of sectors, including biosensors, biomedical imaging, drug delivery, photonics, photovoltaics, and electrocatalysis, due to their distinctive physicochemical, optical, and electrical capabilities. This chapter attempts to show current advances in CQD characterization, with an emphasis on the essential multifarious function of CQDs using various techniques, such as photoluminescence and fluorescence emission spectroscopy. Additionally, with the aim of developing highly efficient and long-term sustainable CQD-based components, we explore the obstacles and potential directions of CQD-based substances in this developing research field.

Keywords: CQDs, Characterization, Energy storage, Nanomaterials, Photoluminescence, TEM.

INTRODUCTION

Carbonaceous Quantum Dots (CQDs)

Due to their intriguing properties, carbonaceous quantum dots have gained considerable attention presently. These compounds, in general, have great biocompatibility, low cytotoxicity, considerable mechanical and thermal properties, and are simple to functionalize. CQDs are also notable for their great stability, low hazardous activity, solubility in water, and transesterification accessibility [1 - 4]. Heteroatoms (functional groups) bound to a carbonised core constitute the bulk of them. Among other nanomaterials, carbon dots include carbon nanodots, polymer dots and graphene quantum dots. Particles having a small size (less than 10 nm) composed of sp^2 hybrid carbon core-shell connected among carbon (core) and organic functional groups (shell), including -C = O,

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^{*} **Corresponding author Ashish Kumar:** NCE, Department of Science and Technology, Government of Bihar, India; Tel: +91- 94784-78088; E-mail: drashishchemlpu@gmail.com

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N-H, -OH, COOH, C-N and C-O, or polymer agglomeration, are described. According to numerous studies, carbonaceous quantum dots with diverse configurations are manufactured using a variety of techniques and carbon sources. CQDs have photoluminescence (PL) qualities that are equivalent to semiconductor quantum dots, but they surpass their counterpart in terms of low cytotoxicity, environmentally friendly nature, relatively inexpensive, and a wide range of simple synthetic pathways, and a proclivity for surface functionalization. CODs sparked massive research on their synthesis, characteristics, and fabrication techniques in the disciplines of optoelectronics, electrical and chemical sensors, photocatalysis, and electrocatalysis due to their outstanding physicochemical features [5 - 7]. In 2010, the emphasis was on finding viable synthetic routes for CODs. To summarise, there are two types of synthetic techniques for CODs: "top-down" and "bottom-up." The latter deals with the oxidation of bulk carbon materials such as graphite, CNTs, carbon soot, and activated carbon using laser ablation, arc discharge, chemical reactions, and electrochemical reactions [8 - 12]. The "bottom-up" techniques use hydrothermal, microwave, and calcination to synthesize CQDs using molecular precursors like citrate, carbohydrates, and a variety of feedstock. CODs have amorphous to nanocrystalline cores and diverse surface functional groups due to the diversity of raw materials and processing processes. As the manufacturing of CQDs entails oxidation in particular, substantial quantities of oxygen-containing moieties, including carbonyl, carboxyl and hydroxyl, are added [13 - 19]. The distinctive properties of CQDs, such as their innocuous chemical structure, controllable fluorescence particulates, ease of functionalization, and outstanding physicochemical and photochemical consistency (non-photobleaching or non-photo blinking), make them extremely appealing for advanced applications when contrasted to traditional semiconductor quantum dots [20 - 24].

This chapter explores the advances made in the evolution of CQDs and their technological applications in terms of characterization approaches. In light of multiple outstanding CQD characterization techniques, such as FTIR, TEM, AFM, UV-vis, XRD, Photoluminescence, and so on, it is desired that this chapter would offer an extensive understanding of recent CQD research and expose different insights toward the research and innovation of CQDs with significantly enhanced physicochemical characteristics [25 - 27]. Taking into the consideration of the superior quality of CQDs, Vercelli *et al.* [28] gave a brief overview of the use of CQDs in organic photovoltaic devices (OPVs) in an attempt to investigate the function that nanomaterials serve in improving the devices' efficiency. They have piqued the research society's attention ever since due to their unique optical features (*e.g.*, excitation wavelength-dependent fluorescence and size-dependent), that render CQDs extremely comparable to well-recognized semiconductor QDs and appropriate for utilization in photovoltaic systems (PVs). In essence, with the

Characterization

suitable architectural design, it is feasible to manage the photoluminescence characteristics, energy levels, and band gap of CQDs, allowing for perfect charge carrier directional passage inside the PV device structure where they were embedded. Fig. (1) depicts the several green quantum dot synthesis attributes for CQDs and GQDs along with their extinctive potential applications.

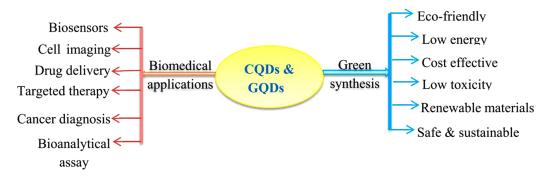


Fig. (1). Green quantum dot synthesis attributes for CQDs and GQDs along with their potential applications. Adapted from Ref [29]. Distributed under attribution-based CCBY license 4.0.

In research, Mehmandoust et al. [30] devised an electrochemical sensor for determining the azo dye tartrazine (TRT). 3D porous reduced graphene oxide embellished containing CQDs and platinum nanoparticles (Pt/CQDs@rGO/SPCE) was deposited on a screen-printed carbon electrode (SPCE). The quantity of TRT produced was measured using differential pulse voltammetry. The sensor had two main linearities under ideal circumstances, spanning from 0.01 to 1.57 M and 1.57–9.3 M, with corresponding reliability coefficients of determination of 0.991 and 0.992. 7.93 nM was also determined as the detection limit (LOD). Furthermore, in the vicinity of numerous disrupting reagents and azo dye complexes with comparable structures, the Pt/CQDs@rGO/SPCE indicated excellent selectivity. Furthermore, the Pt/CQDs@rGO/SPCE demonstrated exceptional recovery rates of 96.5-101.6 percent for candy, 96.0-101.2 percent for jelly powder, 99.7–103.5 percent for soft drinks and 98.0–103.0% for water specimens. In addition, the constructed sensor has outstanding selection, durability, reproducibility, and consistency, suggesting that it has a promising future in TRT measurement. As a result, the suggested electrode might be used to accurately quantify TRT in food specimens. Similarly, Shen et al. [31] established a simple one-step hydrothermal of m-phenylenediamine and glucose to produce nitrogen-doped CQDs (N-CQDs). The chemical structure, crystal structure and exterior functional groups of N-CQDs produced were all studied in detail. The CQDs were chemically doped with nitrogen, and the N-CQDs crystallised in a graphene configuration, according to the results. Photoluminescence (PL) studies revealed that the N-CQDs emit a significant blue light when treated with UV

Application of Carbonaceous Quantum Dots in Biomedical

Yarima S. García¹, Adelmo M. Estrada¹, Eneida R. López¹, Ivan H. Herrera¹ and Jorge L. Neves^{1,*}

¹ Center for Advanced Studies, HAV, Cuba and Federal University of Pernambuco, PE, Brazil

Abstract: Numerous research fields, including chemistry, electronics, and medical sciences, have concentrated on the production and use of novel functional nanomaterials. Carbon, a component of all organic life forms, is essential for the creation of nanomaterials. The modern carbon-based family component known as carbonaceous quantum dots (CQD) was unintentionally discovered in 2004 while single-walled carbon nanotubes were being purified. Additionally, CQDs have exceptional qualities like outstanding photoluminescence and minimal toxic effects. Outstanding in vitro and in vivo biomedical implications of CQDs include drug/gene delivery, biosensor biotherapy, and theragnostic evolution. Also, CQDs can pass through specific body sites of endothelial inflammation (epithelium of the intestinal tract, liver, for example), tumors or penetrate capillaries due to their small size. For the same reason, nanoparticles are more suitable for intravenous administration than microparticles and also prevent particle aggregation and bypass emboli or thrombi formation. This chapter describes the most contemporary applications of CQDs in diverse biomedical fields. We hope it will provide incalculable insights to inspire discoveries on CQD and delineate a road map toward a broader range of bio applications.

Keywords: Biomedical application, Biosensor, Biotherapy, CQDs, Contrast agent, Drug/gene delivery, Theragnostic.

INTRODUCTION

Throughout history, medicine and science have advanced together to improve people's life quality. However, the advancement of nanoscience and nanotechnology at the beginning of the 21st century has brought many innovations in this field [1]. Over the years, nanotechnology has focused on developing the electronic industry and the quest for new materials showing excellent attributes and new strategies for synthesizing nanomaterials [2]. The

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^{*} Corresponding author Jorge L. Neves: Center for Advanced Studies, HAV, Cuba and Federal University of Pernambuco, PE, Brazil, Email: jorge.lneves@ufpe.br

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new discipline of Nanomedicine materializes due to the growth of nanotechnology in the health sciences. In recent decades, this nanotechnology discipline has emerged with great force from the scientific sector in search of an enormous impact on today's society. That is why medicine is presented as a potential market in the nanoworld that could lead to the cure of diseases such as cancer nanotechnology is defined as the scientific-technological activity involved in the conception, synthesis, characterization, and application of materials and devices (presenting a minimum of one dimension) at the nanoscale (generally 1-100 nanometers) [2].

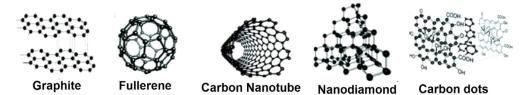
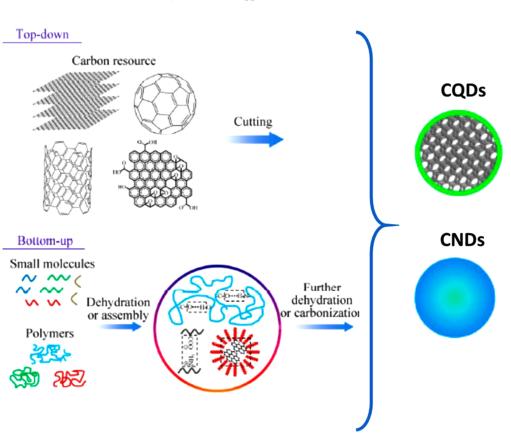


Fig. (1). Carbon nanoforms, Reproduced with permission from [3], under an open access Creative Common CC BY license.

Among the different types of nanomaterials studied for these purposes is carbon, which can take various forms see Fig. (1), the best-known being: fullerenes, graphene, nanodiamonds, carbon nanotubes and carbon quantum dots (COD), which in the last two decades have attracted much interest in biomedicine [4, 5]with excellent physical-chemical properties that are of great value. Carbon Quantum Dots (CQD) commonly refer to charming zero-dimensional (0D) carbon nanomaterials showing a diameter ≤ 10 nm. However, Scrivens and colleagues accidentally uncovered CODs (4) in 2004 by filtration of single-walled carbon nanotubes. Later on, Sun and colleagues [6] stamped the term carbon dots in 2006 for these quantum-sized nanoparticles exhibiting strong photoluminescence in solid-state and solution. Since then, CQDs' biomedical applications have achieved notable interest owing to their great advantages in optical and chemical characteristics, biocompatibility, and low toxicity [7]. Likewise, they have great aqueous stability and unique electronic features that allow them to be electron donors and receptor agents, which could be advantageous in numerous biomedical applications [8].



García et al.

Fig. (2). Top-down and bottom-up approaches for CQD synthesis. Reproduced with permission from [9], under an open-access Creative Common CC BY license.

Two main approaches have been applied to CQD synthesis see Fig. (2). On one side, the "top-down" approach comprises breaking down long carbon structures and includes methods like electrochemical oxidation, laser ablation, chemical oxidation, and ultrasound fabrication. On another side, CQD synthesis starts with molecular precursors in the "bottom-up" approach and the advantages of hydrothermal and plasma treatment, thermal decomposition and microwave synthesis [10, 11]. Hydrothermal and solvothermal approaches provided CQDs functionalized with various superficial groups (mostly carboxyl and hydroxyl groups attached to oxygen), which improves water solubility without additional surface chemical transformations. In addition, reactive groups on the border of CQDs greatly simplify passivation and functionalization of the surface, making them suitable for drug delivery.

As shown in Fig. (3), CQDs are suitable alternatives for theranostics applications

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Application of Carbonaceous Quantum Dots in Solar Cells

Ekta Sharma^{1,*} and Vaishali Thakur¹

¹ Department of Chemistry, School of Basic and Applied Sciences, Maharaja Agrasen University, Baddi, India

Abstract: Carbonaceous Quantum Dots (CQDs) are gaining the interest of various research groups owing to their significant features, including water stability, biocompatibility, minimal cytotoxicity, chemical inertness and fluorescence which make them a good candidate in solar cells applications such as photocatalysis, solar energy conversion, photovoltaic solar cells, and Photoelectrochemical cells. CQDs are used in photocatalytic reactions because they can be used as electron sinks to stop the coupling of electron void pairs. The high coefficient of absorption and the broad spectrum of absorption improve the photocatalytic activity. In solar cells, the CQDs are used as sensitizers. CQDs are employed in solar energy generation because they are non-toxic and affordable. This chapter discusses the use of CQDs in solar cells.

Keywords: Carbonaceous quantum dots, Photocatalysis, Photovoltaic solar cells, Photoelectrochemical water splitting.

INTRODUCTION

The massive usage of fossil fuels, combined with concern about worldwide warming produced by global industry, has compelled the search for clean, ecologically friendly energy sources [1 - 3]. Solar energy is among the best options for a potential source of energy [4]. With the sun contributing about 86PW of energy onto the earth's crust annually, the fundamental transition away from our inefficient and environmentally harmful petroleum-based capitalism is made possible [5]. Photovoltaic technologies such as thin-coating solar cells, silicon solar cells, dye-sensitized solar cells, perovskite solar cells and quantum dots sensitized solar cells are all common uses of solar energy [4, 6, 7]. Owing to the novel and adaptable properties of semiconductor QDs, such as extreme absorption coefficient and variable band gap, QDs solar cells are emerging as an excellent candidate among third-generation photovoltaics [8 - 11]. CdS, CdSe,

* Corresponding author Ekta Sharma: Department of Chemistry, School of Basic and Applied Sciences, Maharaja Agrasen University, Baddi, India; Email: ekta25515@gmail.com

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CdTe, PbS, PbSe, $CuInS_2$, and other low-band-gap metal chalcogenide QDs are commonly utilized as sensitizers in QDSCs [12 - 15].

In addition to semiconductor quantum dots, CQDs are attaining the interest of researchers nowadays. The CQDs were invented in 2004 by Xu *et al.* and further synthesized by Sun and Group in 2006, which resulted in better fluorescence emission [16, 17]. There are two approaches to synthesizing CQDs termed top-down and bottom-up techniques. The top-down approach includes acidic oxidation, chemical oxidation, electrochemical oxidation and laser ablation [18 - 21], whereas the bottom-up technique includes carbonization, thermal decomposition and hydrothermal synthesis [22 - 25]. CQDs are used in various applications owing to their superior attributes, including minimal cytotoxicity, high Quantum yield, easy functionalization, easy synthesis and chemical inertness [26].

Photocatalysts are supposed to ideally work in both the UV or near-infrared regions of the spectrum. There are many catalysts which fail to work in this region. Due to upconverted and downconverted PL, CQDs widely work in longer wavelength of light, which make CQDs the best candidate for photocatalysis [27]. Charge separation and photoexcitation could be the mechanism of photocatalysis in CQDs [28]. The holes and electrons would be confined at the surface locations. The fluorescent dispersion observed in CQDs is spurred on by the recombination of electrons and holes. The quantum containment effect in semiconductor QDs does not hold for CQDs, even though photoexcitation in both types of QDs is the same. Either interface imperfection entrapment regions or electron and hole interaction pathways are responsible for the wavelengths of emission in CQDs [29].

The CQDs can operate as electron donors as well as electron acceptors, allowing holes and electrons to be separated. CQDs could be utilized as the spectral converter, solitary photocatalysts, electron mediators and photosensitizers. In many circumstances, these effects can occur at the same time. Defects can scatter or trap free-charge carriers, increasing the probability of recombination. As a result, the segregation of photogenerated electrons and holes must be promoted in order to optimize photocatalytic performance. CQDs can delay recombination at junction interfaces due to their large electron storage capacity [30]. Due to their ability to down and upconversion of PL, CQDs can also operate as photosensitizers [31 - 33]. Due to upconversion PL, CQDs are also utilized as spectral converters. Surface oxygen-containing functional groups influence the photocatalytic activity of CQDs [30, 34].

Carbonaceous Quantum Dots in Photocatalysis

CQDs show superiority in features including minimal toxicity, water dispersion and chemical resilience, due to which CQDs are used in photocatalytic applications. Moreover, after particular surface modification, CQDs have outstanding and modified optical characteristics of absorbance and PL [35 - 41]. The term "UCPL with CQDs" refers to an optical phenomenon where substances produce lower wavelengths of light beyond the source of excitation and can considerably increase the absorption of wide band gap semiconductors in the visible and near-infrared. Additionally, photoinduced CQDs constitute effective electron acceptors and donors, enabling effective electron and hole separation. As a result, CQDs can be used in a variety of photocatalyst applications, including electron mediators, photosensitizers, spectrum converters, solitary photocatalysts, photo centres and catalytic centres [35 - 37, 39, 42]. In fact, in many circumstances, these many effects occur at the same time. In this section, we will highlight the many functions of CQDs in CQDs-based photocatalytic systems and their various applications.

Electron Mediator

For photocatalytic activity, photocatalysts' ability to transmit and separate photogenerated holes and electrons is crucial. Random flaws, however, can either capture or disperse free charge transfer (holes and electrons), which raises the possibility of recombination [43]. Enhancing the segregation of photogenerated voids and electrons will facilitate photocatalysis. It has been demonstrated that carbon nanostructures have a significant potential to store electrons [44]. The conductive matrix of CQDs can therefore be used to transport photo-stimulated electrons through semiconductors or similar photocatalysts, delaying photogenerated carrier splitting at the intersection junction. CQDs show substantial interest as an electron mediators due to their low toxicity and simplicity of production [45, 46].

Photosensitizer

CQDs exhibit UCPL and PL, making them suitable photosensitizers to be utilized in photocatalytic systems in addition to acting as electron mediators [31 - 33, 37, 47, 48]. CQDs, on the other hand, act as a photosensitizer in a variety of ways. To begin with, CQDs are commonly terminated at their surface by carboxylic acid groups, which provide them with great dispersion in an aqueous solution and allow for additional modification. Moreover, as organic dyes [49 - 53], CQDs can also be made on a wide scale by using eco-friendly processes at a low cost. CQDs might also be used to substitute CdS and CdSe QDs owing to their minimal cytotoxicity [54]. CQDs were used as a photosensitizer for photocatalytic CO₂

CHAPTER 7

Carbonaceous Quantum Dots as Efficient Zerodimensional Nanomaterials for Sensing Applications

Alma Mejri^{1,*}, Abdelmoneim Mars¹ and Hamza Elfil¹

¹ Laboratory of Desalination and Natural Water Valorisation (LADVEN), Water Researches and Technologies Center (CERTE), Techno-park BorjCedria, BP 273, 8020, Soliman, Tunisia

Abstract: Carbonaceous quantum dots (QDs), including carbon and graphene quantum dots, have been widely used recently in various sensing fields, such as healthcare sensing, environmental monitoring, and food safety. Owing to their exceptional electronic, fluorescent, photoluminescent, chemiluminescent, and electrochemiluminescent properties, carbonaceous QDs are essential tools for designing an ultrasensitive sensing platform. In this chapter, we summarized the applications of carbonaceous QDs in the detection of various target analysts, citing heavy metals, toxic compounds, pesticides, and proteins (DNA, aptamer, and RNA). In this regard, the authors described the effects of synthetic methods and surface functionalization on the properties of carbonaceous QDs and the analytical performance of sensors. We believe that understanding these parameters gives us better sensors that could not be obtained by other means. To give the reader a clear vision of the implementation of these zero-dimensional nanomaterials in sensor architectures, a comparative study has been developed.

Keywords: Analytic performances, Carbonaceous quantum dots, Electrochemical proprieties, Optical proprieties, Sensing applications.

INTRODUCTION

Carbonaceous nanomaterials have been a focal point of interest in the construction of various analytical tools, especially sensors and biosensors, because of their exceptional properties that are of great interest in the sensing process. Scientists have paid a great deal of attention to graphene and carbon quantum dots as viable sub-class because they have special features like high conductivity, nontoxicity, excellent chemical photoluminescence durability, and tuneable fluorescence emissions. Moreover, the existence of a variety of functional groups on the carbon

^{*} **Corresponding author Alma Mejri:** Laboratory of Desalination and Natural Water Valorisation (LADVEN), Water Researches and Technologies Center (CERTE), Techno-park BorjCedria, BP 273, 8020, Soliman, Tunisia; Email: abdelmoneim.mars@gmail.com

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core, including epoxy, hydroxyl, carboxyl, and carbonyl moieties, facilitate the functionalization of the carbonaceous QDs surface with various species, which can further open the opportunity for the fabrication of a huge variety of (bio)sensors.

Structurally, carbonaceous QDs have dissimilar structures, sizes, and surface functional groups. In regards to graphene QDs, they are made up of a thin layer (less than 10 layers) of graphene having a diameter <10 nm and are decorated with functional groups on the edges. These groups originated from carbon sources or subsequent reactions. However, carbon QDs owned spherical shapes with a crystalline graphite-like lattice. On the other hand, the methods for synthesizing carbonaceous QDs have been well reviewed in the literature, and extreme potential has been invested in pursuing the production of simple, low-cost, environmentally friendly, and controlled properties which can be monitored with QDs morphology, size, and doping type and amount [1 - 3].

To date, the literature on the applications of carbonaceous QDs in sensing fields has grown rapidly. Indeed, they have been applied in the detection of various target analytes, citing heavy metals, toxic compounds, pesticides, and proteins (DNA, aptamer, and RNA). The number of reports, described in the literature that mentioned sensing and carbonaceous quantum dots terms has increased exponentially in these ten recent years (Fig. 1). Thus, the summary of their use in detection is of considerable interest to the reading community. This chapter is thematically focused on the exploitation of the fluorescence, chemiluminescence, electroluminescence, and electrochemical proprieties of the carbonaceous QDs in the sensing and biosensing applications reaching the picomolar, nanomolar, or femtomolar region. Additionally, sensing techniques such as photo-induced electron transfer (PET), fluorescence resonance energy transfer (FRET), dynamic quench, stable quenching, energy transmission, and quenching of fluorescence, were examined.

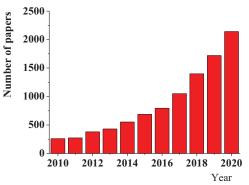


Fig. (1). Number of publications with mentioned "sensing and carbonaceous quantum dots" terms.

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Photoluminescence (Bio) Sensors

Carbonaceous QDs, with their different structures, have identical optical features based on their absorption and fluorescence behaviors (Fig. 2). Indeed, carbonaceous QDs' UV-Vis spectrum displays high optic absorption in the UV range (between 230-320 nm), having a tail ascending into the visible region. The π - π * transmission of aromatic C-C bonds present in the core carbon is responsible for the maximal spike at 230 nm, while the n- π * transmission of C=O bonds attached to the edges or other linked groups is responsible for the shoulder at 300 nm. We emphasize that discovered discrepancies in absorption spectrum data suggest variations in the compositions or structures of various derivatives of hybridized carbonaceous QDs. Concerning the emission spectra of carbon QDs, the position of the emission peaks is related to the excitation wavelengths [4]. This property can be obtained from a broad range of QD sizes, surface chemistry, and emissive traps. Interestingly, the photoluminescence color of QDs is relative to the surface groups and their molecular environment rather than the size. Fortunately, this behavior can be applied in (bio)sensing applications.

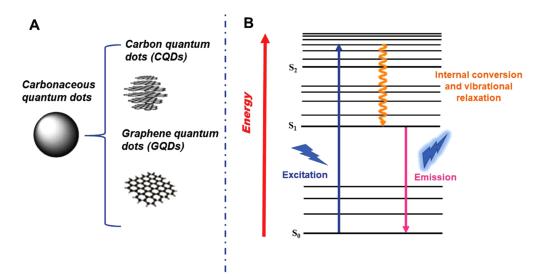


Fig. (2). (A) Structure of carbon quantum dot (CQDs) and graphene quantum dot (GQDs) (B) Schematic representation of photoluminescence principle.

Heavy Metal Ions Sensing

Currently, heavy metal pollution has become an emergent concern for global sustainability because they are highly toxic and carcinogenic, even at a trace level. These metals are nonbiodegradable and can stack up in the food chain, posing a significant environmental and human health risk [5]. Therefore, it is crucial to monitor heavy metal concentrations in drinking water, foods, and biological

CHAPTER 8

Application of Quantum Dots in Wastewaters Treatment

Garima Kumari¹, Eder Lima², Mika Sillanpaa³, Nitesh Kumar⁴, Anupam Guleria⁵, Dinesh Kumar⁵, Atma Rai⁶ and Ashish Guleria^{6,*}

¹ Department of Biotechnology, Eternal University, Baru Sahib, Sirmaur, Himachal Pradesh, India

² Institute of Chemistry, Federal University of Rio Grande, Rio Grande, Brazil

³ Department of Green Chemistry, Aarhus University, Nordre Ringgade, Denmark

⁴ Department of Chemistry, Govt. College Jukhala, Himachal Pradesh, India

⁵ Centre of Biomedical Research, SGPGIMS Campus, Lucknow, Uttar Pradesh, India

⁶ Department of Applied Sciences, WIT Dehradun, Uttarakhand, India

Abstract: Water stress and scarcity are among the primary issue that the world is witnessing in this era, as pollution of freshwater resources are increasing due to various emerging pollutants, such as pharmaceuticals, personal care products, pesticides, and household and industrial chemicals. Efficient treatment of wastewater is an important aspect of fresh water supply, and such water can also be used for different household activities and other purposes. So for wastewater treatment, different eco-friendly as well as economic approaches have been analyzed, and the use of carbon quantum dots (CQDs) for the treatment of wastewater is efficient and effective technique extensively studied in the last few years. CQDs are promising nanomaterials for water pollution treatment due to their small particle sizes, tuneable fluorescent properties and containing oxygen-based functional groups. In this chapter, the chemical and physical attributes of CQDs, raw substances and methodologies being utilized in the synthesis, and stability of CQDs, along with their effective employment in wastewater remediation and treatment, has discussed in detail.

Keywords: Heavy metals, Organic pollutants, Photo-catalysis, Quantum dots, Water pollution.

INTRODUCTION

In this current era, water contamination is an emerging issue as waste water from manufacturing and chemical processes in industries contributes to it. Heavy

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^{*} **Corresponding author Ashish Guleria:** Department of Applied Sciences WIT Dehradun Uttarakhand, India; Tel: +91-9805848660, Email: ashishchem786@gmail.com

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metals, organic dyes, phenols, pesticides, and detergents have all been linked to water contamination in past years, according to reports from all around the world. Heavy metal pollution is a global issue, and living things have been exposed to toxic metals either directly by drinking water contamination or indirectly via eating foods and drinking agricultural irrigation water polluted by toxic metals. These contaminants have a strong propensity to bioaccumulate in the food supply chain, possess significant ecological motility, and exhibit excellent resilience to chemical or biochemical destruction [1, 2]. Owing to their toxicity, perhaps at minute concentrations, the release of these contaminants into water bodies poses a serious hazard to the ecosystem and to people's health. Exposure of humans to toxic metals can cause a number of serious diseases or even death. Exposure to cadmium causes acute and chronic intoxications, and it can replace zinc ions in some metallo-enzymes, there by affecting enzyme activity [3]. Cr(VI) compounds exposure to humans is associated with a higher incidence of respiratory cancers [4]. Humans who consume excessive amounts of copper suffer lung disease, mucous inflammation, extensive vascular injury, melancholy, and necrosis alterations in the kidney and liver [5]. Additionally, microbiological degradation of water sources driven by human operations, including the release of organic waste and fecal matter contaminants, is a prevalent issue. In contrast to other forms of cleaning, chlorination is a frequently used approach for microbial rehabilitation [6, 7]. Sodium chlorite is disinfection frequently employed in drinking water treatment, fruits, vegetables and livestock cleaning, and for filtration reasons [8 - 10]. A crucial factor that is frequently overlooked is the quantity of bleach to be used. Ultrahigh disinfectant doses may result either in inefficient decontamination or major health problems such as erythrocytes and endocrine disruption [11]. Additionally, relatively tiny amounts of these toxins may result in a number of health problems, such as mortality, cancers, renal failure, eye malfunction with visual problems, neurological damage, and decreased muscle synchronization [12 - 14].

In recent years, water pollution due to inorganic and organic pollutants has appeared as global trouble as it goes through terrestrial and aquatic ecosystems imposing a relentless threat to the survival of both biotic and abiotic components. So, in order to reduce the concentrations of pollutants from wastewater, various techniques have been used, which include filtration, adsorption, ion exchange, chemical precipitation, coagulation, electrolytic treatment, electron precipitation, evaporation, electrolysis, liquid extraction, magnetic separation, membrane separation, crystallization, activated sludge, electrodialysis, ultrafiltration, chemical oxidation, aerobic and anaerobic treatment [15 - 17]. However, due to their limitation of practical utility in subsequent metal removal as a result of exacting procedures, low binding abilities, and cost-effectiveness, there remains a void for suitable nanomaterial with high metal loading capacity and facile

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synthesis, in an effort to extract heavy metal and organic pollutants through the ecosystem. Among the various nanomaterials, carbon quantum dots have been recognized as an important nanomaterial that finds extensive applications in wastewater treatment [18]. Small carbon quantum dots have an atom configuration comparable to that of bulk counterparts, only because of 3-dimensional truncation; they contain more atoms on surfaces [19]. In particular, CQDs are semiconductor NPs that display a number of uncommon qualities, including size-relied emission spectra, wide stimulation spectrum, and the ability to emit brilliant light whenever excited using UV light [20]. In recent years, the development of high-quality quantum dots seems to be an effective and more efficient approach for the treatment of wastewater and removing various pollutants from aquatic systems [21, 22]. In this chapter, we have complied the literature on the fabrication of CQDs, characterization techniques for CQDs, along with their specific applications in wastewater treatment.

APPLICATIONS OF CQDS FOR WASTEWATERS REMEDIATION

CQDs find extensive applications in the detection of metal ions in solutions, extraction of heavy metals from effluents and photocatalytic degradation of organic pollutants [23 - 31]. Due to their hydrophilicity, CQDs are a great choice for ecological water assessment. The usage of CQDs in wastewater cleanup is covered in the sections below. Carbon quantum dots (CQDs) are a new class of carbon-based nanomaterials that have gained attention due to their unique properties, such as high quantum yield, good biocompatibility, and low toxicity. The applications of CQDs in various fields, including wastewater remediation, have been extensively researched in recent years. Wastewater remediation is the process of treating contaminated water to remove pollutants and make it safe for discharge into the environment [32 - 36]. CQDs offer a promising alternative for wastewater remediation due to their unique properties, including high surface area, strong adsorption capacity, and photocatalytic activity. The applications of CQDs for wastewater remediation are based on their unique properties and mechanisms. The following section discusses the mechanism of CQDs for wastewater remediation. Photocatalysis is a process in which a catalyst is used to accelerate a chemical reaction using light. CQDs can act as photocatalysts due to their high quantum yield, which means they can absorb light and emit electrons efficiently [37 - 45]. In wastewater treatment, CQDs can be used to degrade organic pollutants such as dyes, pharmaceuticals, and pesticides. The mechanism of CQDs for photocatalysis involves the following steps:

Absorption of Light: CQDs can absorb light and convert it into excited electrons.

Application of Carbonaceous Quantum dots in Energy Storage

Vaishali Thakur^{1,*} and Ekta Sharma¹

¹ Department of Chemistry, School of Basic and Applied Sciences, Maharaja Agrasen University, Baddi, India

Abstract: Carbon quantum dots (CQDs) are a type of carbon nanomaterial that has lately received attention as a potential replacement for standard semiconductor quantum dots (QDs). CQDs feature a quasi-spherical structure and amorphous to nanocrystalline carbon cores with diameters of 10-20 nm. Based on the carbon core, CQDs are further classified as graphene quantum dots (GQDs), carbon nanodots (CNDs), and polymer dots (PDs). CQDs exhibit unique electrical and optical properties due to their bigger edge effects and quantum confinement; better than graphene oxide nanosheets, they can also be easily split into electrons and holes due to their high dielectric constant and extinction coefficient. CQDs are crucial in the sector of energy storage and transformation because CQDs offer the advantageous properties of low toxicity, environmental friendliness, low cost, photostability, favourable charge transfer with increased electronic conductivity, and comparably simple synthesis processes. Due to their superior crystal structure and surface properties, CQD nanocomposites often helped to shorten charge transfer paths and maintain electrode material cycle stability. CQDs provide cost-effective and environmentally friendly nanocomposites used for supplying high energy density and stable electrodes for energy storage applications. This chapter provides a summary of the role that CQDs play in energy transmit technologies, including solar cells, supercapacitors, lithium-ion batteries, and hydrogen and oxygen evolution reactions.

Keywords: CQDs, Hydrogen and oxygen evolution reactions, Lithium-ion batteries, Supercapacitor.

INTRODUCTION

CQDs are classified as zero-dimensional carbon-dominated nanomaterials when compared to spherical, tubular, and sheet fillers, as well as nanomaterials from the graphene family. CQDs, being a structure made up of several layers of graphene oxide (GO) nanosheets, provide many of the benefits of GO while also having their own distinct qualities. CQDs exhibit unique electrical and optical properties

^{*} Corresponding author Vaishali Thakur: Department of Chemistry, School of Basic and Applied Sciences, Maharaja Agrasen University, Baddi, India; Email: vaishalithakur137@gmail.com

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due to their bigger edge effects and quantum confinement; better than GO nanosheets, they can also be easily split into electrons and holes due to their high dielectric constant and extinction coefficient. Furthermore, long-term in-vivo testing results on CQDs showed that it is far less cytotoxic than GO sheets that are only a few micrometres in size; this suggests that it would be safer for *in-vivo* biological study. Amorphous to nanocrystalline carbon cores of CQDs are smaller than 10-20 nm in diameter and feature a quasi-spherical structure. CQDs are further subdivided into graphene quantum dots (GQDs), carbon nanodots (CNDs), and polymer dots (PDs) based on the various carbon cores [1 - 4]. A form of carbon NMs, preferably called carbon quantum dots (CQDs), has recently gained recognition as a potent alternative to conventional semiconductor quantum dots (QDs). CQDs possess several benefits over conventional semiconductors, including minimal toxicity, low price, luminescence, advantageous electrostatic interactions with increased electron mobility, and comparably simple synthesis techniques [1 - 4]. Quantum dot (QD)-based materials have been used in energy production and development to enhance the kinetic and thermodynamic features of electrochemical reactions. However, QDs' strong reactivity, chemical inertness, substance agglomeration, and limited electrical conductivity pose the biggest obstacles to their broad implementation. In this study, we merged the most recent findings on QDcarbonaceous-based nanohybrids used in rechargeable energy-storing equipment, including Sodium-ion batteries (SIBs), Perovskite, solar cells, Lithium-ion batteries (LIBs), supercapacitors, and other devices. Changes in photostability and optical properties of semiconductor QDs, such as adsorption and emission wavelength, are influenced by particle size. Semiconductor QDs, on the other hand, have several downsides, such as high toxicity, owing to the usage of heavy metals (like lead (Pb), and mercury (Hg) in their construction [2, 5 - 10]. Since then, researchers have become interested in CQDs because of their unique properties, which include good optoelectronic properties, luminescence, simple surface modification, robust biocompatibility, a sizable high surface area, and low cytotoxicity. CODs can either be amorphous or nanocrystals and have a quasi-spherical architecture with carbon centers that are less than 10–20 nm in width. Based on the carbon cores, CQDs are further split into GQDs, carbon nanodots (CNDs), and polymer dots. In the graphene family, GQDs and CQDs are 0D NMs that share characteristics of both graphene and carbon dots, such as anisotropy and horizontal lengths of less than 20 nm [11, 12]. This chapter goes into detail regarding the developments and energy applications of CODs. The part after that discussed some of the energy uses for CQDs, like solar panels, super-capacitors, and LIBs [13 - 16]. Additionally, the Shockley-Queisser performance barrier for silicon-based solar cells may be successfully exceeded by the simultaneous hot carrier gathering method of CQDs [10, 17]. The exceptional bioavailability, chemical stability, and less hazardous properties of graphene are also carried through into CQDs. CQDs, in particular, make excellent nonzero band gap and luminescence semiconductor materials because of their large number of functional units after grafting. Due to their higher conductance, high effective surface area, simplicity in loading and customizing, and superior conductance, the original CODs might be used as a conducting reagent to the electrode in energy storage systems like supercapacitors [1, 3, 18 - 20].

CQDs in the Energy Storage and Conversion Applications

CQDs were formerly thought to have only a few applications, but now that their variety of special characteristics has come to light, they are being used more frequently than first thought. The attributes of CQDS in many energy-related sectors, including supercapacitors, photovoltaic cells, solar cells, batteries, water electrolysis, photodiodes, light-emitting diodes, and other fields, are covered in this section.

CQDs in Supercapacitors

Supercapacitors are energy-storing systems that, in contrast to the battery, may sustain maximum power production for prolonged durations. Owing to their unique benefits, like extended life, environmentally friendly nature, and significant-high - power density, supercapacitors have drawn considerable attention. Supercapacitors can be replaced with an electrode made of NMs that has a higher effective capacitance and extended duration durability [21]. Inflatable electrodes for supercapacitors have been shown to be quite utilized for storing power quickly and delivering both extreme power densities and rapid recharging speeds. In contrast to continued attempts, more study is necessary to create innovative porosity, conductive, and large specific interface area carbon composites having excellent specific capacity and extended battery durability. CQDs have been utilized in power storage systems due to their high conductance and shape- and dimension characteristics [10, 14, 22 - 24]. It stands for the argument that manufacturing nanohybrid frameworks utilizing sulfide/metal oxide and CODs could be a viable method for creating powerful and reliable supercapacitors [21]. Arul et al. produced CQD-MnO nanostructures using a degraded recycling resource using an eco-benign method to achieve high energy density and electronic conductivity [25]. As per the morphological investigation, CQD-MnO had a larger surface region and superior electrical conductance than virgin MnO, which was represented by the extremely conducting CQDs. These nanohybrids showed a particular capacity of 189 F g⁻¹ when used as the electrode in symmetrical superconductors, demonstrating an extended cyclic lifetime owing to strong coulombic efficacy and quick current-voltage responsiveness discovered through electrochemical studies. While improving the electrochemical properties of energy storage devices, CQDs may also improve the electrochemical characteristics of metal oxide-sulfide composites. Binesh et al. developed manganese oxide-graphene (MnO -CDGs) nanohybrids employing an easy, green, and one-pot manufacturing method [26]. The enhanced electrical characteristics and increased electrolytic reactivity of transition metal sulphides make them more appropriate for use in energy storage devices from an electrical standpoint. These characteristics aid in the creation of extremely efficient and dependable energy

CHAPTER 10

Future Prospect of Carbonaceous Quantum Dots

Devika Vashisht¹, Aseem Vashisht², Shweta Sharma³ and Surinder Kumar Mehta^{1,4,*}

¹ Department of Chemistry and Centre of Advanced Studies in Chemistry, Panjab University, Chandigarh, India

² Punjab State Council for Science and technology Sector - 26, Chandigarh, India

³ Institute of Forensic Science and Criminology, Panjab University, Chandigarh, India

⁴ University of Ladakh, Leh, India

Abstract: Carbonaceous quantum dots (CQDs) are carbon nanomaterials offering significant contributions in the fields of sensing, biosensing, optoelectronics, and energy storage. CQDs materials with edge defects are suitable candidates for LED emitters, water splitting, optoelectronic and photodetectors devices. The role of attached functional groups and edge effects on flexible energy storage devices is discussed in this chapter. The future prospects and underlying challenges for CQD-based material for wastewater remediation, in addition to factors such as their sustainability, durability, performance and economics in the context of industrial scale-up, have also been explored in this chapter.

Keywords: Carbon dots, Energy devices, Photodetectors, Quantum dots, Wastewater remediation.

INTRODUCTION

Carbonaceous quantum dots (CQDs) are nanoparticles made up of carbon that are of extremely small size (1-10 nm). CQDs were first accidental discovery by Xu *et al.* [1] in 2004. Sun *et al.* [2] called these fluorescent nanomaterials as "carbon quantum dots" later in 2006. The CQDs have intriguing features over traditional semiconductor quantum dots (SQDs). Due to the inherent features, the possibility of using CQDs has been highlighted in countless applications in biological, material, chemical and physical sciences due to the features like biocompatibility, chemical inertness, low cost and photo stability [3 - 8]. In the recent past, numerous reviews have been reported, which are majorly concentrated on the synthesis and applications of CQDs in various fields. In the application perspective, surface passivation and functionalization for the regulation of

* Corresponding author Surinder Kumar Mehta: Department of Chemistry and Centre of Advanced Studies in Chemistry, Panjab University, Chandigarh, India and University of Ladakh, Leh, India; E-mail: skmehta@pu.ac.in

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Future Prospect

physiochemical characteristics have also been presented. The majority of CQDs reviews and chapters focus on the chemical applications rather than the exciting futuristic application of CQDs in energy and wastewater remediation.

We have already discussed the properties of CQDs in terms of structure and induced defects in their structures in previous chapters. This chapter will focus on the futuristic aspects of CQDs. This discussion is expanded to include the underlying issues as well as possible future directions.

CQDs may be synthesized by employing "top-down", "bottom-up," and "wastederived" techniques. CQDs are made from a variety of sources, including graphite powder, bulk carbon, carbon fibers and carbon nanotubes, using a top-down technique. Some of them are Arc-discharge [1], Laser ablation [2], Plasma reactor [9], Ultrasonic synthesis [10], combustion [11] and electrochemical method [12, 13]. Carbonization or Pyrolysis of organic precursors is the root of a bottom-up strategy. Microwave [14 - 16], hydrothermal [17], pyrolysis [18] and MOF template-assisted [19] are some of the bottom-up techniques. Waste-derived procedures are methods that use waste resources like leftover fruits and vegetables as a source of carbon. The waste-derived synthesis directs the environmentally responsible use of natural resources. Numerous reports on the synthesis of CQDs from waste such as watermelon peel, sweet pepper, pomelo peel, dairy waste, orange juice and cabbage have been published [20 - 24].

According to their chemical structure, the majority of CQDs contain an amorphous base with a sizable variety of functional groups. Some investigations, however, revealed the presence of sp2 carbon within the base. The electronic structure of CQDs is explained on the basis of molecular orbital (MO) theory. Every possible absorption transition among these bonding, anti-bonding and non-bonding orbitals lies in the UV-vis range. Due to a higher degree of surface oxidation, top-down-produced CQDs are known to have a higher number of defects than bottom-up-created CQDs. Surface defects increase as surface imperfections, which are referred to as molecular states. Based on the chemical and electronic structure of CQDs are energy devices and wastewater treatment, which have been discussed further in this chapter.

Photodetectors

UV Photodetectors

Based on the response wavelength, CQDs-based photodetectors can be divided into three categories: Visible light detectors, UV detectors and near mid-infrared

detectors [25 - 28]. UV photodetectors are commonly reported because $\pi \rightarrow \pi^*$ transitions produce absorption in the deep-UV region. They are majorly utilized in the transmission of signals and medical tools. In the last few decades, eco-friendly CQD detectors are more popular than the semiconductor or nitride-based detectors [29]. Due to the enormous binding energy of 60 meV, UV detectors made of high bandgap oxide materials show potential [30, 31]. Heterostructures of ZnO nanorods with CQDs/ GQDs have been studied under dark and UV light of 365 nm, revealing that ZnO-GQD has higher UV detectivity than ZnO-CQDs. The photodesorption of adsorbed oxygen under UV irradiation by trapping "hot" electrons is the process that encompasses oxide-based UV detection. However, in ZnO-CQD or ZnO-GQD-based heterostructures, the hydrophilic interface of the CQDs/GQDs extensively gathered oxygen moieties.

Broadband Photodetectors

These photodetectors often rely on substances that absorb and emit in the severe ultraviolet (UV), visible, and near-infrared (NIR) areas. CQDs may successfully simulate the absorption in the deep UV to NIR region by using the right designs and doping. This makes them great candidates for broadband photodetectors that are both efficient and affordable. Fig. (1) illustrates the mechanism underlying broadband absorption and emission. Deep UV absorption occurs when localized electrons in sp² hybridized carbon (C=C) bonds undergo a transition (v₃---c₃). On the other hand, the emission happens while the excited electron goes through an interband transmission (c₃---c₂) prior to radiative combination (v₂---c₂). Partially conjugated π -electrons give rise to visible light absorption (v₂---c₂) [32].

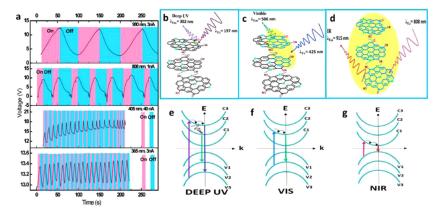


Fig. (1). N-GQD-based photodetectors: (a) The N-GQDs' reaction to different light streams (980 nm, 808 nm, 405 nm, 365 nm). The process by which N-GQDs emit wideband light is shown in (b-d). (b) Deep UV PL absorption, absorbance, and emissions for the electron in C=C. (c) The layered architecture of conjugated electrons absorbs visible light; (d) bulkier electrons are responsible for NIR absorption. (e-g) The band to-band transitions and vibrations relaxation-related emission process [32].

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Kulvinder Singh

Prof. Kulvinder Singh is an assistant professor in the Department of Chemistry, DAV College, Chandigarh, India and leads a nanotechnology group on waste management. He did Ph.D. from Panjab University, Chandigarh. He worked as an assistant professor of basic and applied sciences at PEC University of Technology, Chandigarh, India. He also worked as post-doctoral fellow at the Institute of Nanoscience and Technology, Mohali, India. His research interest lies in carbonaceous materials for supercapacitors, nanostructures for electrochemical and quantum dots for optical sensors, green chemistry, agricultural waste for sustainable development, and density functional theory for reaction mechanism studies.



Vineet Kumar

Prof. Vineet Kumar is currently working as associate professor in the Department of Biotechnology, Lovely Professional University, Jalandhar, Punjab, India. He has worked in different areas of biotechnology and nanotechnology at various institutes and universities in India namely, Panjab University Chandigarh, CSIR-Institute of Microbial Technology, Chandigarh, India, CSIR-Institute of Himalayan Bioresource Technology and Himachal Pradesh University. He has published many articles in these areas featuring in peer-reviewed journals. He is also serving as editorial board member and a reviewer for international peer reviewed journals. He has published books for different publishers such as, CRC, Taylor & Francis, Springer and Elsevier.