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Review

Degradation Efficiency of Organic Dyes on CQDs As Photocatalysts: A Review

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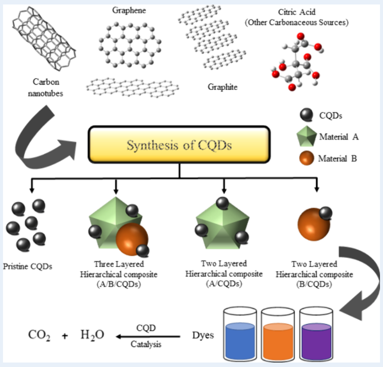
ABSTRACT: Across the globe, the task of providing clean and safe drinking water is getting harder. Organic contaminants, including dyes and pharmaceutical medications, are a significant environmental threat, especially in aquatic bodies due to their uncontrolled emission. Therefore, a method for their degradation in water bodies that is both environmentally friendly and commercially feasible must be developed. In the realm of photocatalysis, carbon-based nanomaterials have drawn more attention in the last ten years. Due to their exceptional and distinct qualities, metal-free carbon-based photocatalytic systems have received a lot of attention recently for their ability to degrade organic contaminants into semiconductor quantum dots, which are already available. A class of nanomaterials with a particle size between 2 and 10 nm showing distinct optoelectrical characteristics is among the variety of catalytic quantum dots. This review covers several synthesis techniques such as electrochemical, laser ablation, microwave radiation, hydrothermal, and optical features of CQDs such as the photoluminescent (PL) property and quantum confinement effect. The uses of CQDs in the degradation of various dyes as well as the difficulties that still exist and the opportunities that lie ahead have also been explored.



INTRODUCTION

Undoubtedly, environmental contamination is a major issue in today's society.[1] Untreated waste is released into water bodies by industries like pulp, plastic, paper, and textiles.[2] Aquatic environments frequently contain harmful chemicals such as textile dyes, pesticides, herbicides, heavy metals, and surfactants.[1] This waste frequently contains significant volumes of organic dyes, which are usually nonbiodegradable and exhibit higher stability in the presence of light and high temperatures, leading to detrimental effects on the environment.[3] The removal of organic compounds requires highly efficient, stable, and reasonably priced photocatalysts to meet the growing demand to protect the environment. Pollutant dyes are hazardous to human health and the environment, thus eliminating them from wastewater is crucial because of their tenacity.[4] Most of the dyes have one or more benzene rings, which are poisonous and resistant to degradation by microorganisms. If neglected, they have the potential to permanently damage the ecosystem by increasing the chemical oxygen demand (COD) and blocking sunlight from entering the water's depths, which negatively affects aquatic life.[5]

NEED FOR SUSTAINABLE DEVELOPMENT

Given the finite amount of water resources and the ever-increasing population that depends on them, water scarcity is a major environmental concern. Access to energy, a clean environment, and clean water are essential conditions for both human survival and economic advancement.[6] The adoption of ecosystem-friendly techniques to promote a sustainable environment is the key to combat this contamination and meet the unavoidable industrial demand for synthetic dyes. In this quest, scientists have investigated environmentally benign techniques, taking traditional, physical, and chemical treatment methods into account, such as desalination, membrane filtration, chemical separation, adsorption on activated carbon, coagulation, flocculation, precipitation, etc. These methods, however, have some restrictions as they may result in incomplete degradation and the production of secondary pollutants.[2] One extremely promising area holding significant potential for the advancement of sustainability is nanotechnology. This is a field that continues to mature and has helped tremendously in the development of innovative substances and applications that have paved the way for mankind toward a better, brighter future. Nanochemistry is mainly associated with designing newer materials at a molecular scale having novel properties and functionalities

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enabling the materials to have new ground-breaking applications.[7]

QUANTUM DOTS (QDS)

A family of nanomaterials known as quantum dots (QDs) comprises particles ranging between 2 and 10 nm in size. They are materials in which the excitons, i.e., the charge pair of a positive hole and the negatively charged electron are constrained in all three spatial dimensions by electrostatic forces.[8] Their electrical and optical properties are highly tunable. The properties of QDs deviate significantly from their bulk counterparts if their size becomes less than the electrons of the de Broglie wavelength present in the dot. This effect is known as the quantum confinement effect.[9] The development of semiconductor QDs with controllable and confined emission spectrum characteristics due to the quantum confinement effect is seen as a big breakthrough. However, due to them being nonbiocompatible and highly toxic, early conventional QDs like Zn/Se QDs, Ag_2S QDs, Pb/Se QDs, and Cd/Se QDs are considered to be an environmental hazard. Carbon is one of the most abundant and environmentally friendly elements found on the Earth. The recent development in the field of carbonaceous QDs as substitutes for semiconductor QDs has sparked intense research attention.[10]

CARBON QUANTUM DOTS (CQDS)

Carbon-based quantum dots have received significant attention because of their exceptional optical, mechanical, and electrical properties. CQDs are a subtype of nanoparticles that are smaller than 10 nm in size[11,12] and are usually zero-dimensional, sp^2 hybridized carbon nanomaterials exhibiting affinity for oxygen-bearing functionality like carboxylic and hydroxyl groups on their surface.[7] Unlike other semiconductors, CQDs are low cost and show excellent photostability, low toxicity, chemical inertness, and ease of functionalization with other photocatalysts (such as Ag_3PO_4, TiO_2, and Fe_2O_3), which allows them to absorb a wide range of light photons, which is the key requisite for photocatalysis.[13,14] These CQDs are known for their high water solubility and biocompatibility; furthermore, they cause almost no cytotoxicity,[15] which makes them a good candidate for modern applications focusing on sustainable developmental goals.

CQDs not only have the electrical properties that are associated with nanoparticles, i.e., the bandgap tuning and electronic transitions, but also possess distinctive optical characteristics including very sharp fluorescence.[16] As the fluorescence is size dependent because of the quantum limiting effect, the smaller CQDs show blue fluorescence which is a smaller wavelength but bigger sizes show fluorescence way up even in the IR region of the electromagnetic radiations.[17] Surface passivation is another key aspect when it comes to CQDs and the modifiability of these CQDs is unparalleled. Different functional groups on the CQDs surface lead to different interactions with the substrates and hence, they have found their application in being biosensors,[18] catalysts,[19] biomaging,[20] contrasting agents,[21] drug delivery agents,[22] and even optoelectronics[23] such as photovoltaic cells and LEDs.[24]

CQDs are one of the materials that can be produced by using a whole world of materials, as long as they can act as a carbon precursor. Some of these materials are low cost such as citric acid,[25] proteins, and carbohydrates; but can also be produced from waste materials such as bagasse of Sugar cane,[26] Sugar cane juice,[27,28] peels of fruits and vegetables,[26] nuts,[29−31] other organic[32] and plastic waste,[33,34] juices of fruits and vegetables.[26] It can even be produced from ashes.[32] The process of removal of water and then the occurrence of carbonization under extreme temperature and pressure conditions, followed by the passivation of the CQDs surface is the usual approach for CQDs synthesis using a natural source.[35] Some other precursors include carbonaceous nanomaterials such as carbon nanotubes,[19] graphene, or bulk molecules such as graphite and coal.[22] In this regard it will not be wrong to say it can be synthesized from any possible organic material one can find lying around.[18]

PHOTOCATALYSIS

The long-term viability of solar energy makes photocatalysis an attractive solution to the energy crisis. Using various types of catalysts, solar energy can be harvested, and this energy is absorbed by materials of different kinds to undergo electronic transitions. The excitation of electrons results in a charge pair (an electron in the conduction band and a hole generated in the valence band).[36] This charge pair created in the catalyst results in the breakdown of different organic and inorganic pollutants as the excited electron gets transferred to the substrate causing a chain of various chemical reactions and turning the substrate e.g., organic dyes into smaller nonharmful constituents such as water and carbon dioxide.[37] Metal semiconductors are the most widely used photocatalysts; however, certain metals, such as Pb and Co, are hazardous to human health and the environment. Consequently, photocatalysts with no metals, such as graphene QDs, carbon QDs, and carbon nitrite QDs, have garnered significant attention.

CARBONACEOUS PHOTOCATALYSTS

Carbon materials of different types such as carbon nanotubes (CNTs), carbon nanofibers (CNFs), hydrochar, and graphene have been studied throughout the years to show photocatalytic properties.[36] Although these carbon materials have the electronic properties to act as catalysts, the photocatalytic activity shown by them is quite low. CNTs and CNFs are remarkable when it comes to conduction and absorption abilities and naturally act as very good charge transfer materials by absorbing energy, which is in electromagnetic radiation form and results in catalysis. However, these materials require some metals or other chemical species to be paired up with them by creating a synergic effect.[38,39] Hydrochar is similar to CNTs and CNFs in this nature and shows catalytic performance after pairing up with good semiconductor materials or light-sensitive nanoparticles.[40] Sometimes, hydrochar, CNTs, and CNFs are to be modified with different functionalities such as doping with nitrogen and sulfur to amplify the band separation, resulting in better catalytic performance.[39] Only graphene and graphene oxide (GO) nanoparticles are found to have photocatalytic properties worth considering when used in their pristine form. Graphene and graphene oxide nanoparticles are also doped and paired with various other materials to increase the performance of catalysis; however, Ahuja et al.[41] studied the photocatalytic degradation of methylene blue using pristine graphene oxide nanoparticles, along with its composite with polyaniline and NiO. Ahuja reported that the pristine reduced GO nanoparticles degraded 32% of methylene blue in 100 min, while the composite of NiO-polyaniline-RGO showed 98% degradation in only 11 min.[41] The GO being a carbonaceous material also follows a similar rule, and the catalytic activity is enhanced by doping of GO with various other elements. Mukhtar et al. reported that GO in pristine form can be doped with materials like nitrogen and boron. The nitrogen-doped GO (NGO) degraded 93% methylene blue in 150 min, while the boron-doped GO (BGO) and nitrogen and boron-doped GO (NBGO) showed 38% and 25% degradation, respectively.[42]

CQDS AS PHOTOCATALYST

Carbon QDs are a zero-dimensional conductive material that exhibits good size effects and electrical conductivity. Because their surface is highly modifiable with required functional groups, semiconductors can be paired with CQDs to get the appropriate band positions, which will result in an efficiency boost of photocatalysis. Furthermore, carbon QDs have a great adsorption capacity for reactants, because of their excellent surface area specificity and surface functional groups abundance, which supports the interaction of the substrate with the catalyst and hence, the photocatalytic process.[10]

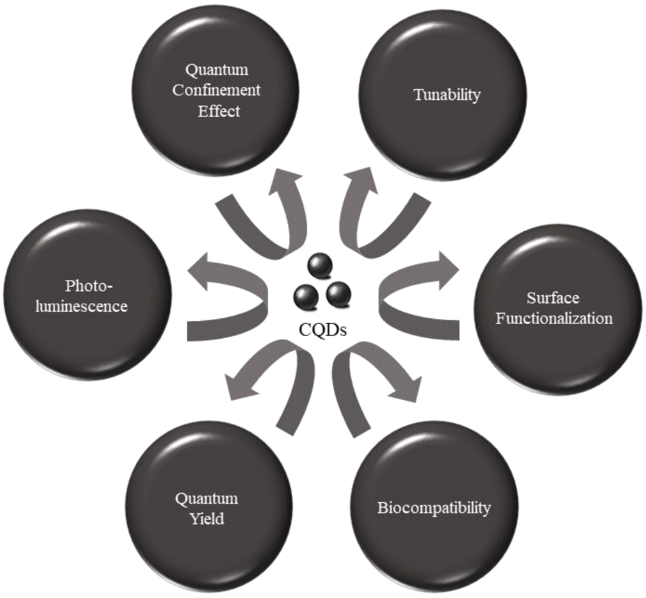

Figure 1. Photocatalytic properties of CQD.

CQDs show a quantum confinement effect and hence show unique optical properties which conventional nanomaterials do not possess. This very quality sets them apart from the rest of the carbonaceous nanomaterials. Furthermore, because of the large surface area to volume ratio, it can be more functionalized with groups that both increase the interaction of the substrate and increase the band separation, as already discussed when addressing other nanomaterials. CQDs also show photoluminescence and emit light once they are excited and undergo electronic transitions. This allows the CQDs to have a quantum yield, a property no other carbonaceous material has shown so far. This crucial property along with photoluminescence allows the CQDs to show more photocatalytic activity than conventional materials, as it allows CQDs to emit light in a process where the utilization and absorption of light are essential. As the QDs are still nanoparticles, they retain the good properties of nanomaterials such as the bandgap tunability which makes the CQDs just as tunable as other materials and the properties of CQDs making them suitable photocatalysts are shown in Figure 1.

A range of synthesis procedures, such as the hydrothermal/solvothermal approach, chemical ablation, laser ablation, and pyrolysis, have gradually been explored for CQD production.[43] However, different synthesis processes come with pros and cons of their own.

This thorough review attempts to give the reader a better understanding of carbon quantum dots by summarizing the ideas of synthesis, characterization, applications in photocatalysis as a decontaminant (dye removal), drawbacks and unfilled research requirements, and possible prospects for future development.

SYNTHESIS METHODS

The techniques for the synthesis of CQDs are classified into two categories: “top-down” and “bottom-up” approaches. In the first type, coal, graphene oxide (GO), carbon nanotubes, graphene, graphite powder, and other carbonaceous materials are broken down via physical, chemical, or electrochemical processes, leading to CQDs as represented in Figure 2. The bottom-up strategies are based on chemical synthesis and use pyrolysis as well as reactions that will result in the carburization of simple organic compounds.[44] In this section, the most

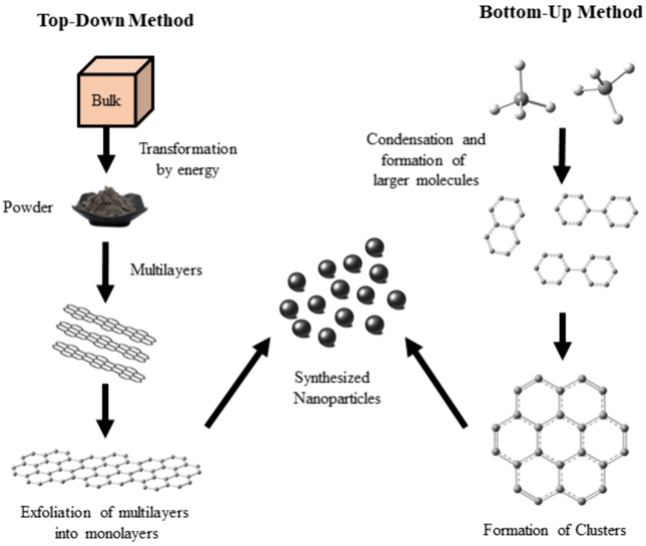

Figure 2. Synthetic approaches for CQDs. Modified and reprinted with permission from ref 45. Copyright 2018 Elsevier.

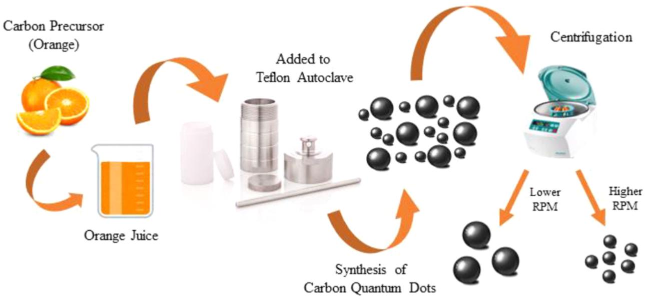

Figure 3. Hydrothermal Method for CQDs synthesis.

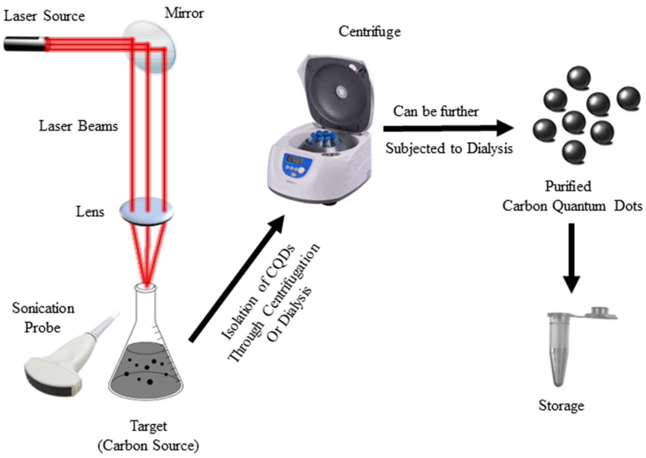

Figure 4. Laser Ablation Method for CQDs synthesis

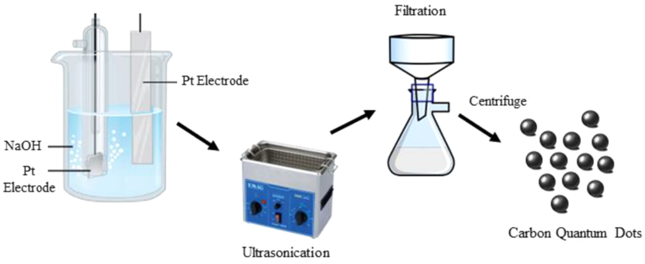

Figure 5. Electrochemical Synthesis of CQDs.

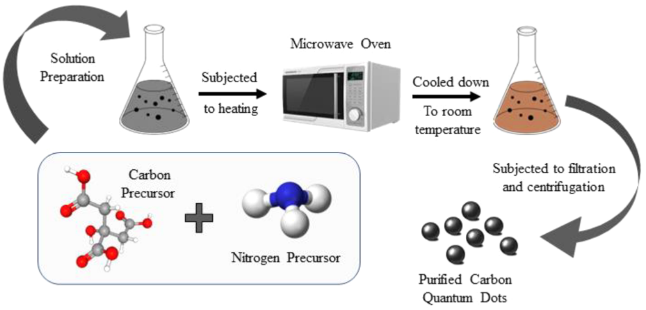

Figure 6. Pyrolysis or Microwave assisted CQD synthesis.

widely used techniques for the synthesis of CQDs are explored in detail.

Hydrothermal and Solvothermal Method. The hydrothermal method, which involves a customized autoclave for building pressure and heating of a reaction system, is a top-down method for synthesizing catalysts. Precursors are dissolved, and desired products are synthesized in an environment with relatively high temperature and pressure that is created using an aqueous solution. Because of its high specificity, ease of use, good selectivity, high accuracy, and outstanding reproducibility, this method is the most widely used to prepare CQDs.[10] It is an inexpensive, environmentally friendly, and nontoxic technique, that is capable of employing a variety of carbon precursors, including glucose, sucrose, maltol, chitosan, citric acid, banana juice, and orange juice.[44] This method is also known to produce CQDs having multiple sizes, which can be further separated using dialysis and centrifugation at different speeds. Sahu et al. used orange juice to prepare CQD showing high photoluminescence with a quantum yield of 26% in a single step using hydrothermal carbonization and centrifuged the mixture that was left over[46] as shown in Figure 3.

Other organic solvents with higher boiling points, such as benzene, dimethylformamide, and dimethyl sulfoxide, are utilized in place of water in the solvothermal process. Carbon sources are usually dissolved in these types of solvents, after which they undergo heat treatment at high temperatures, extraction, and concentration.[44]

Chemical Ablation. In this method, the carbonaceous materials are carbonized into smaller molecules using strong oxidizing acids, and these molecules can be specifically cleaved into much smaller sheets using oxidation in a controlled environment.[47] Peng and Travas-Sejdic demonstrated a way to produce CQDs in the presence of water by first exposing carbohydrates to concentrated sulfuric acid which results in dehydration, followed by the treatment with nitric acid resulting in the formation of individual CQDs by the breakage of carbonaceous source and finally modifying CQDs with amine-terminated compounds (4,7,10-trioxa-1,13-tridecanediamine).[48]

Laser Ablation. One of the most widely used production method for carbon-derived nanomaterials is laser ablation, which involves the ablation of solid target materials using a high-energy laser beam. For the evaporation of the substance, a large quantity of energy is focused at one specific location on a solid surface during this process which is shown in Figure 4. This approach can produce exceedingly pure particles, as the purity of the final output is essentially determined by the purity of the media being used and the precursor acting as the target in this process. Cao et al. synthesized pure CQDs using laser ablation.[49−51] The laser ablation process was carried out using carbonaceous materials as a target while having argon, performing as the carrier gas, and H_2O vapors present under 75 kPa at 900 °C. CQDs were produced and further modified with organic polymers and 12 h of refluxing in HNO_3.[49−51]

Electrochemical Carbonization. One of the most popular technique for producing CQDs using various bulk carbon sources as precursors is the electrochemical method. Typically, an electrolyte consisting of water is submerged in two electrodes made of carbon which can also be seen in Figure 5. Water electrolysis and the formation of $H^{\bullet}$ and $OH^{\bullet}$ radicals on the electrodes are facilitated by applying redox potential, and the electrode defects work as electrochemical scissors to generate CQDs. This technology has several advantages, i.e., it is cost-effective, can be produced in large quantities, and is nontoxic and simple and easy to use.[44]

Zhang et al. reported a method of synthesizing CQDs by using alcohols having low molecular weight and carbonizing them using an electrochemical cell. As the working and auxiliary electrodes, they used two Pt sheets. The reference calomel electrode was fixed to a Luggin capillary that could be adjusted. Once the alcohols were electrochemically carbonized in a basic environment, they were converted into CQDs. As the applied potential increases, the CQD sizes and graphitization degrees also increases.[52]

Microwave Irradiation Synthesis/Pyrolysis Method. Several methods have been developed to generate CDs, but most of them are mainly labor-intensive and require specialized equipment. Therefore, a uniform heating technique that is easy to use, quick, and selective is crucial for large-scale synthesis. All of these objectives are achieved by the microwave (MW) irradiation/pyrolysis technique, which allows large-scale and quick manufacturing.[44] The diagram is shown in Figure 6.

High temperatures are used in microwave-assisted method to force molecules to recombine and reorganize, creating completely new compounds. This bottom-up approach is hence used to combine extremely microscopic substances and turn them into relatively macroscopic moieties, however, still being in the nano range.[10]

Zhai et al. examined the production of CQDs using citric acid by microwave irradiation utilizing variety of amine functionality-containing compounds, including ethylenediamine and thiourea. The performance of the CQDs was enhanced by the molecules having primary amines in their structure, which resulted in them acting both, as surface passivating agents and N-doping starting material.[53]

■ ADVANTAGES AND DISADVANTAGES OF THE SYNTHESIS METHOD

The summary of all the pros and cons of different methods used to synthesize CQDs are listed in Table 1.

Table 1. Pros and Cons of Different Methods Employed to Produce CQDs

Methods	Advantages	Disadvantages	References
Hydrothermal/solvothermal	Highly specific	Reaction is slow and time-consuming	10
	Easy to operate		
	Highly selective		
	Extremely accurate	Yield is low	
	Reproducible product		
	Nontoxic	Required reaction conditions are harsh	
	Size controllability		
Chemical ablation	Easily available	Reaction conditions are harsh	47
		Rigorous and extreme modification	
	Can be done using a number of sources	A number of steps	
		Size is not controllable	
Laser ablation	Facile and rapid synthesis	Low quantum yield	44,47
	Cost effective	Size not controllable	
	Eco- friendly		
	Scalable	Surface modification is essential	
	Monodispersed concerning size		
Electrochemical carbonization	Various types of starting material	Few small molecule precursors	44
	controllable size		
	One-step and facile	Complicated operation	
	High purity		
	Stable product	Tedious purification process	
	High yield		
Microwave irradiation synthesis/pyrolysis method	Performance can be controlled	Heat treatment with high temperature is required	10,44,47
	Highly efficient		
	Microstructure can be adjusted	Low quantum yield	
	Readily available	Poor size control	
	Time saving	Post-modification needed	
	Highly economically efficient	High cost and energy consumption	

■ PHOTOCATALYTIC APPLICATION FOR THE DEGRADATION OF DYES (MB)

For Wastewater Treatment. Photocatalysis is the acceleration of a chemical reaction by light in the presence of a catalyst.[14] The majority of photocatalyzed reactions use free radicals. It is a green and sustainable energy conversion method with significant applications in addressing environmental pollution and energy scarcity. One major problem was figuring out how to remove a wide range of toxins from wastewater by combining photocatalytic and adsorption approaches.[1] The application of CQDs in photocatalysis has certain benefits. When it comes to low toxicity, chemical stability, and water solubility, CQDs surpass other common photocatalysts (such as ZnO, TiO_2, and CdS).[54]

■ DEGRADATION OF METHYLENE BLUE (MB) DYE

Synthesis Procedure for CQD-Based Heterostructures. To degrade methylene blue (MB), several methods have been used to produce CQD-based heterostructures. Simply adding the CQDs as-prepared to the suspension of TiO_2 microspheres allowed for the formation of CQDs/TiO_2 heterostructures. Ascorbic acid was hydrothermally treated to yield CQDs for this purpose, which is represented in Figure 7.[55]

Mechanism. The proposed mechanism states that photogenerated electrons in the CQDs are moved to the TiO_2 conduction band (CB) and valence band (VB) when the nanocomposite is subjected to visible light. The mechanism is observed in Figure 8. Moreover, higher frequency photons produced by the up-conversion process in CQDs aid in the charge pair production in TiO_2. The combined effects of these processes greatly increase the nanocomposite's photoactivity.

The mechanism of photocatalytic degradation of MB utilizing CQD/TiO_2 as the photocatalyst is summarized below:[57]

$$\mathrm{CQDs/TiO_2} + h\nu \rightarrow \mathrm{eCB^-} + \mathrm{hVB^+}$$

$$\mathrm{h^+} + \mathrm{MB_{dye}} \rightarrow \text{Oxidation of dye}$$

$$\mathrm{h^+} + \mathrm{H_2O} \rightarrow \mathrm{H^+} + {}^{\bullet}\mathrm{OH}$$

$$\mathrm{h^+} + \mathrm{OH^-} \rightarrow \mathrm{H^+} + {}^{\bullet}\mathrm{OH}$$

$${}^{\bullet}\mathrm{OH} + \mathrm{MB_{dye}} \rightarrow \text{Degradation of}\ \mathrm{MB_{dye}}$$

Furthermore, by behaving as electron traps, CQDs are essential for enhancing the photoactivity of CQDs/TiO_2 nanocomposite photocatalysts, which in turn causes the MB dye to degrade completely.[55]

CQDs as Photosensitizers. CQDs have been employed as photosensitizers for semiconductors like TiO_2, and GQDs.[55] TiO_2 has an energy bandgap of about 3.1 eV.[58] Ke et al. exploited the phenomenon by combining CQDs with TiO_2 microspheres resulting in a remarkably high photocatalytic degradation of MB.[56] This resulted in a nanocomposite showing 3.6 times more degradation than pristine TiO_2 and degraded 90% of the MB. (Figure 9).

CQDs Nanocomposites. Semiconductors like TiO_2 and SiO_2 were paired up with CQDs to form nanocomposites, and the composite showed an effective and stable response in visible light for the breakdown of methylene blue (MB), an organic dye. After 25 min of exposure to a 300 W halogen

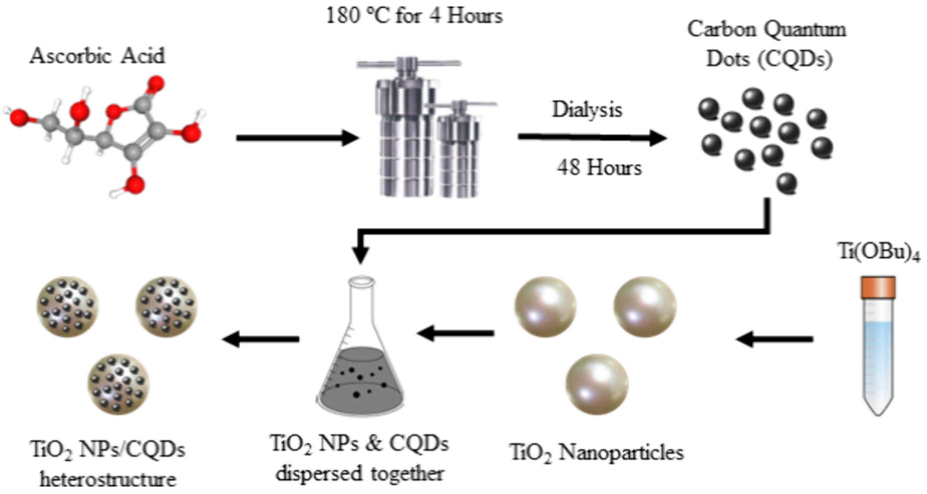

Figure 7. Synthesis of CQDs/TiO$_2$ Composite for MB degradation modified and reprinted from Ke et al. work.[56] Copyright 2017, Elsevier

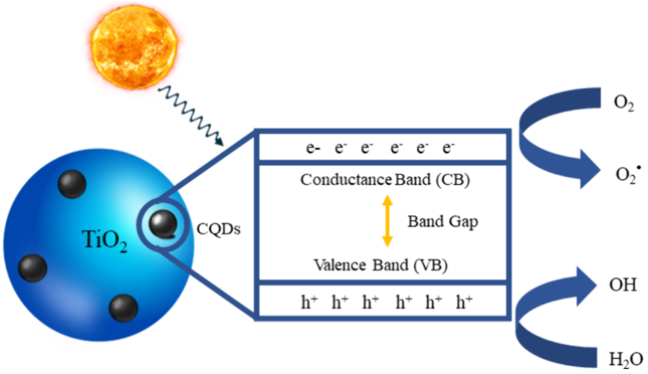

Figure 8. Mechanism of MB degradation using CQDs/TiO$_2$ composite. Modified and reprinted with permission from ref 56. Copyright 2017 Elsevier.

lamp, the results indicated that the composites of TiO$_2$ with CQDs and SiO$_2$ with CQDs showed maximum degradation of dye and even reached up to 100% degradation. It was also noticed that the control comprising of pure CQDs, pure TiO$_2$,

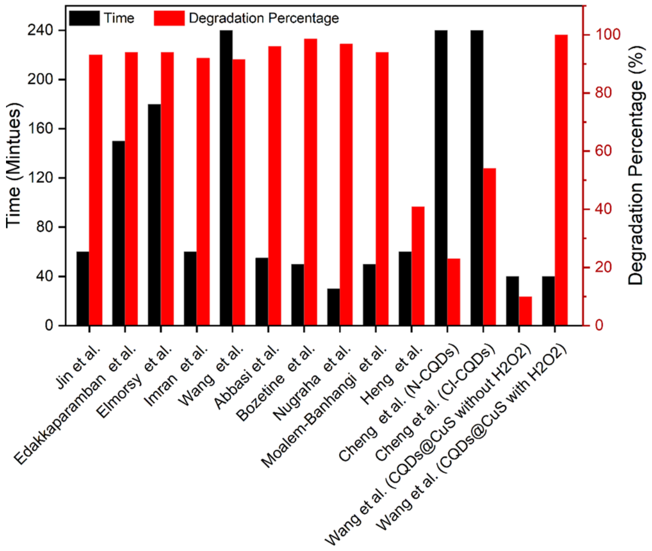

Figure 9. CQDs used for the degradation of MB in recent years.

Table 2. CQDs Used for the Degradation of MB in Recent Years

Authors	Year	Nanovomposite	Methods	Degradation percentage (%)	Time (min)	Ref
Jin et al.	2023	N-CQDs/TiO$_2$	Facile hydrothermal-calcination synthesis approach	93.1	60	59
Edakkaparamban et al.	2023	N-CQDs	Hydrothermal treatment	94	150	60
Elmorsy et al.	2023	ZIF-8@N-CQDs/ZIF-67	Solvothermal methods	94	180	61
Imran et al.	2023	CQDs	Solvothermal methods	92	60	62
Wang et al.	2021	CQDs/CeO$_2$/SrFe$_{12}$O$_{19}$	The hydrothermal method and gamma-ray-assisted polyacrylamide gel method	91.5	240	63
Abbasi et al.	2023	Undoped bare CQDs	Pyrolysis method	96	55	64
Bozetine et al.	2021	ZnO/CQDs/AgNPs	In situ hydrothermal method	98.6	50	65
Nugraha et al.	2021	WO$_3$/N-CQDs	Simple mixing process	96.86	30	28
Moalem-Banhangi et al.	2021	N-doped ZnO/Fulvic acid (FA)/CQDs	Hydrothermal method	94	50	66
Heng et al.	2020	CQDs/TiO$_2$	In situ hydrothermal method	40.9	60	67
Cheng et al.	2019	N-CQDs	Hydrothermal method	23	240	68
		Cl-CQDs		54		
Wang et al.	2018	CQDs@CuS (without H$_2$O$_2$)	Hydrothermal treatment	10	40	69
		CQDs@CuS (with H$_2$O$_2$)		100		

and pure SiO_2 respectively, showed minimum degradation and 0% dye degradation was observed.[6]

This outcome suggested two possibilities. First, photoexcited TiO_2 or SiO_2 is required for high-frequency photon emission resulting from photoluminescence up-conversion in CQDs. Second, the band position of CQDs created a synergic effect in which electron transfer took place between CQDs and their semiconductor counterparts in the composite. The photoluminescence up-conversion phenomenon in CQDs holds great potential in the context of creating smart visible light-active photocatalysts.[7] The degradation of methylene blue carried out by different types of CQDs is reported in Table 2 and can also be observed in Figure 9.

DEGRADATION OF NAPHTHOL BLUE BLACK AZO DYE

Prasannan et al. reported the synthesis of CQDs/ZnO composite as a photocatalyst to degrade naphthol blue-black azo dye when exposed to UV light by synthesizing CQDs from orange peels.[7] Figure 10 provides a schematic representation of the CQDs/ZnO degrading pathway of naphthol blue black azo dye.

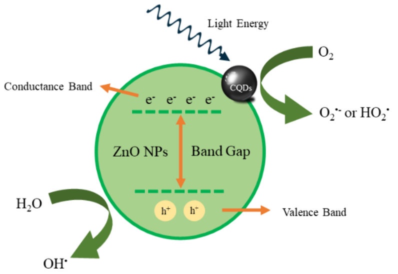

Figure 10. Degradation pathway of naphthol blue black using ZnO NPs/CQDs composite. M0odified and reprinted with permission from ref 70. Copyright 2013 American Chemical Society.

It has been observed that the use of CQDs in the composite caused almost 100% degradation of the dye in 45 min, which is significantly greater than what the pure CQDs and pure ZnO managed. The ZnO nanoparticles managed to degrade 84.3% in 45 min, while CQDs were able to perform only 4.4% dye degradation in 45 min when used alone. This proves that the use of NPs and CQDs in a system to make a composite creates a synergic effect that immensely increases the degradation abilities and enhances the material properties as a photocatalyst.

Mechanism. The degradation process in the nanocomposite starts with the charge pair (a positive hole and an electron) production due to the excitation of electrons by a photon:[54]

$$ZnO + h\nu \rightarrow ZnO\ (eCB^{-} + hVB^{+})$$

$$CQDs + h\nu \rightarrow CQDs\ (eCB^{-} + hVB^{+})$$

The dyes are readily oxidized just by the immense oxidative potential caused by the hole (hVB^{+}):

$$hVB^{+} + dye \rightarrow \text{Oxidation of dye}$$

This hole also disintegrates water and produces hydroxyl ions which can further be converted into hydroxyl radicals, which are known for their extreme reactivity. Because of the hydroxyl radical's inherent instability, organic compounds began to degrade.

$$hVB^{+} + H_2O \rightarrow H^{+} + OH^{\bullet}$$

$$hVB^{+} + OH^{-} \rightarrow OH^{\bullet}$$

The conductance electrons (eCB^{-}) combine with oxygen to form superoxide anions by reduction of O_2:

$$eCB^{-} + O_2 \rightarrow O_2^{\bullet-}$$

In the presence of organic scavengers or hydrogen peroxide (H_2O_2), the radical may generate organic peroxides:

$$O_2^{\bullet-} + \text{Dye/Scavengers} \rightarrow \text{Dye/Scavengers} + O - O^{\bullet}$$

$$O_2^{\bullet-} + HO\text{-}O^{\bullet} + H^{+} \rightarrow H_2O_2 + O_2$$

$HO\text{-}O^{\bullet}$ is created when holes and hydroxyl radicals combine with excess H_2O_2.

$$H_2O_2 + OH^{\bullet} \rightarrow HO\text{-}O^{\bullet} + H_2O$$

$$H_2O_2 + hVB^{+} \rightarrow H^{+} + HO\text{-}O^{\bullet}$$

The conductance electrons (eCB^{-}) also produce hydroxyl radicals, which as a result cause degradation in dyes.

$$H_2O_2 + eCB^{-} \rightarrow HO^{-} + OH^{\bullet}$$

$$H_2O_2 + O_2^{\bullet-} \rightarrow HO^{-} + OH^{\bullet} + O_2$$

$$OH^{\bullet} + \text{Dyes} \rightarrow \text{Degraded dye by-products}$$

DEGRADATION OF CONGO RED DYE

There have been several studies that have produced CQDs to remove methylene blue and Congo Red in the past. These included CQDs formation from rice husk waste, using bismuth and nitrogen to dope CQDs for better photoluminescence, and to increase its quantum yield. Production of CQDs from sugar cane bagasse, having an amine group on the surface, and then using it for dye removal and degradation. Having these amines modified CQDs paired up with tungsten dioxide to make a composite, but quite recently in 2023, Nizam et al. produced CQDs using rubber seed which is considered to be biomass waste and used it for CR and MB removal and photodegradation.[71]

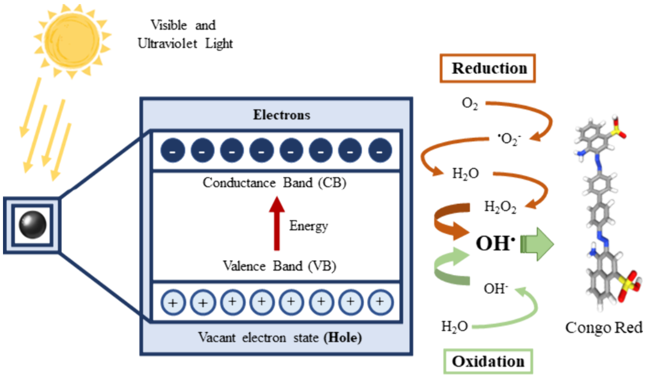

Figure 11. Degradation mechanism pathway of Congo Red (CR) using CQDs. Reprinted with permission from ref 71. Available under a Creative Commons CC BY license.

Table 3. CQDs used for the degradation of CR in recent years

Authors	Year	Nanocomposite	Methods	.Degradation percentage (%)	Time (min)	Ref
Rahman et al.	2023	$CaFe_2O_4$/CQDs	Hydrothermal method	90	140	[72]
Abbasi et al.	2023	Undoped bare CQDs	Pyrolysis method	98	60	[64]
Vyas et al.	2023	CuSe@CQDs	Green synthesis using oxidation	97.8	60	[73]
Lu et al.	2023	N, S-CQDs@Fe_3O_4@HTC	Green synthesis from lignin	95.43	120	[74]
Wei et al.	2023	N-CQDs/TiO_2	Hydrothermal method	100	40	[75]
Nizam et al.	2023	Pristine CQDs	Graphene oxide using Hummers' method	90	100	[71]
Padervand et al.	2021	CQDs/BiOCl	Microwave irradiation synthesis	96.8	180	[76]
Hu et al.	2020	N-CQDs (4 different types based on precursor)	Solvothermal method	82.32	120	[77]

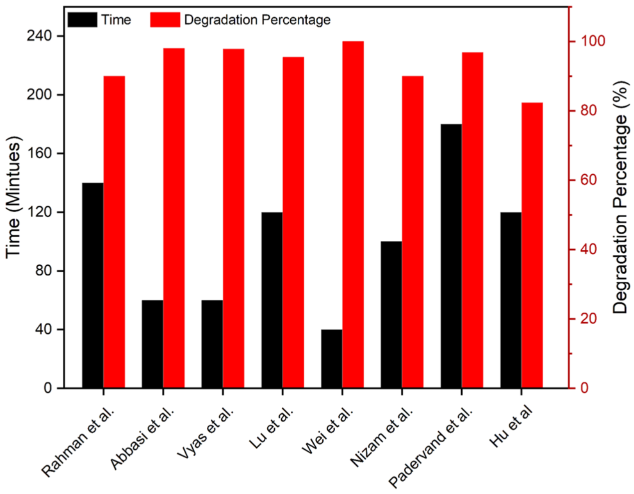

Figure 12. CQDs used for the degradation of CR in recent years.

Congo Red was degraded under a solar simulator, and the data was used to assess the photocatalytic properties of CQDs. It was observed that the CQDs managed to remove almost 30% of the CR dye in just 30 min, and when tested for MB, it also removed 20% of the dye in the same period. Furthermore, it was noted that in 90 min, the CQDs had removed the Congo red completely from the source, which accounts for its strong adsorption properties, because of the Oxygen functionality present on these carbon-based materials. These Oxygen groups attracted the N-functionalities on the dyes, making it an efficient material for dye removal and photocatalysis. A complete discoloration of CR in the sample, in 90 min, indicates the strong capability of CQDs as a photocatalyst and a sorbent.[71] The mechanism pathway for CR degradation is diagrammatically shown in Figure 11, and Table 3 reports various types of CQDs produced over the years to degrade CR. CR degradation can also be observed in Figure 12.

■ DEGRADATION OF INDIGO CARMINE (IC) DYE

Using aqua mesophase pitch (AMP) and a hydrothermal method, Cheng et al. developed Carbon quantum dots and created two different types by doping them with nitrogen (N-CQDs) and chlorine (Cl-CQDs) to enhance their properties like fluorescence. For the production of CQDs, the AMP reaction mixture was subjected to centrifugation for 10 min at 8×10^3 rpm in an autoclave lined with polytetrafluoroethylene maintained at 120, 150, and 180 °C for 12, 24, and 48 h,

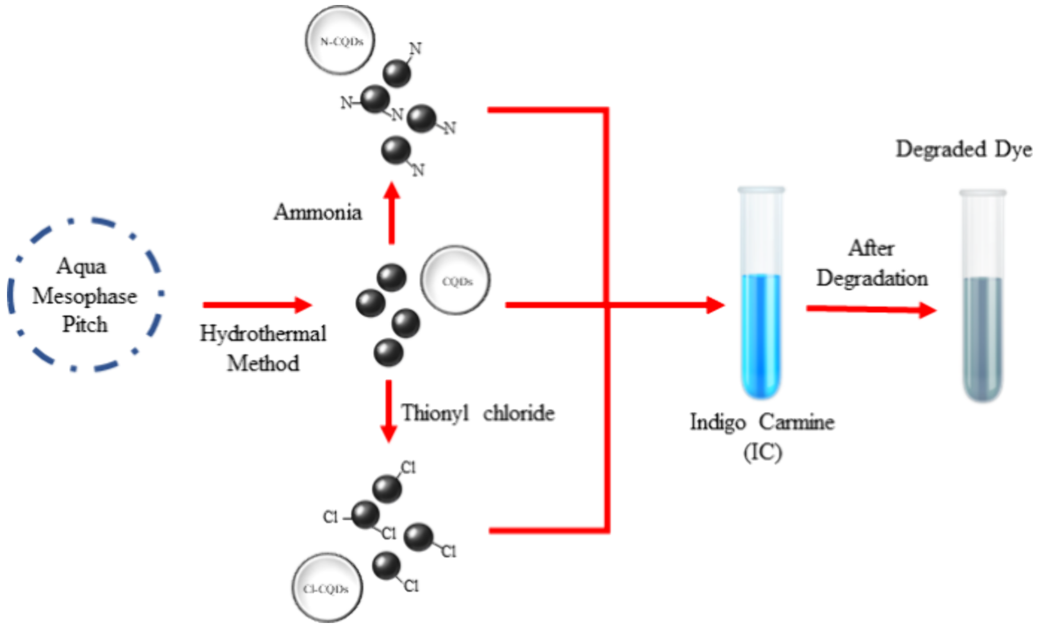

Figure 13. Synthetic pathway for N and Cl doped CQDs for IC degradation. Modified and reprinted with permission from ref 68. Copyright 2019 Elsevier.

Table 4. CQDs Used for the Degradation of IC in Recent Years

Authors	Year	Nanocomposite	Methods	Degradation percentage (%)	Time	Ref
Liu et al.	2023	Surface modified CQDs	Hydrothermal method	99.13	15 Days	81
Hu et al.	2020	N-CQDs (4 different types based on precursor)	Solvothermal method	97	120 min	77
Sharma et al.	2019	α-Bi_2O_3/CQDs	Sonication method	86	120 min	82
Cheng et al.	2019	N-CQDs	Hydrothermal method	56	240 min	68
		Cl-CQDs		60		

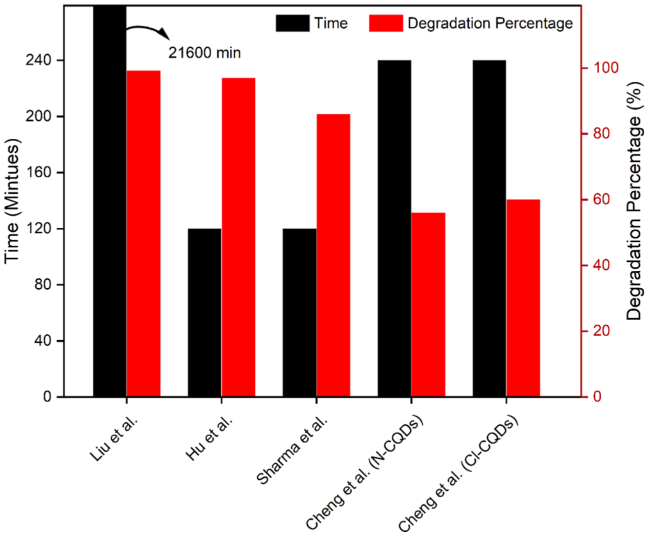

Figure 14. CQDs used for the degradation of IC in recent years.

respectively. To generate N-CQDs, the CQDs that had been maintained at 120 °C for 24 h were added to an autoclave and ammonia was added to the system. The system was heated for 12 h at 120 °C and then at 80 °C for almost 30 min, in a well-ventilated area. Thionyl chloride and CQDs undergo the same process, for the synthesis of Cl-CQDs.[68,78−80] The formation of these CQDs can be seen in Figure 13. The quantum yield (QY) of CQDs was 27.6%, and the QY of the chlorine- and nitrogen-doped CQDs was much lower. The Cl-CQDs degraded the highest amount of Indigo carmine and the degradation percentage of the dye was reported to be 60%.[78−80] The composites of CQDs that have been used for the degradation of IC are reported in Table 4 and can be seen diagrammatically in Figure 14.

DEGRADATION OF RHODAMINE B (RHB)

Zhang and colleagues produced a nanocomposite (CQDs/N-TiO_2) having nitrogen-doped titanium dioxide nanoparticles (N-TiO_2) and carbon quantum dots (CQDs) as its hierarchical components. For carbon dots synthesis, ascorbic acid and ethanol were kept at 160 °C for three h in a high-pressure reactor. To form N-TiO_2, a combination of urea $(NH_2)_2CO$, nitric acid (HNO_3), and anhydrous ethanol was mixed with tetra butyl titanate and was maintained at 240 °C for 10 h in a high-pressure reactor, dried and for 6 h, it was subjected to calcination at 200 °C. For the formation of the composite, CQDs and N-TiO_2 were mixed for 1 h, and put through the process of centrifugation, washing, and drying for an entire night at 90 °C.[78,80] The degradation mechanism of RhB using N-doped TiO_2 NPs/CQDs composite is shown in Figure 15, while Table 5 and Figure 16 contain different types of CQDs and their composites used for the degradation of RhB in recent years.

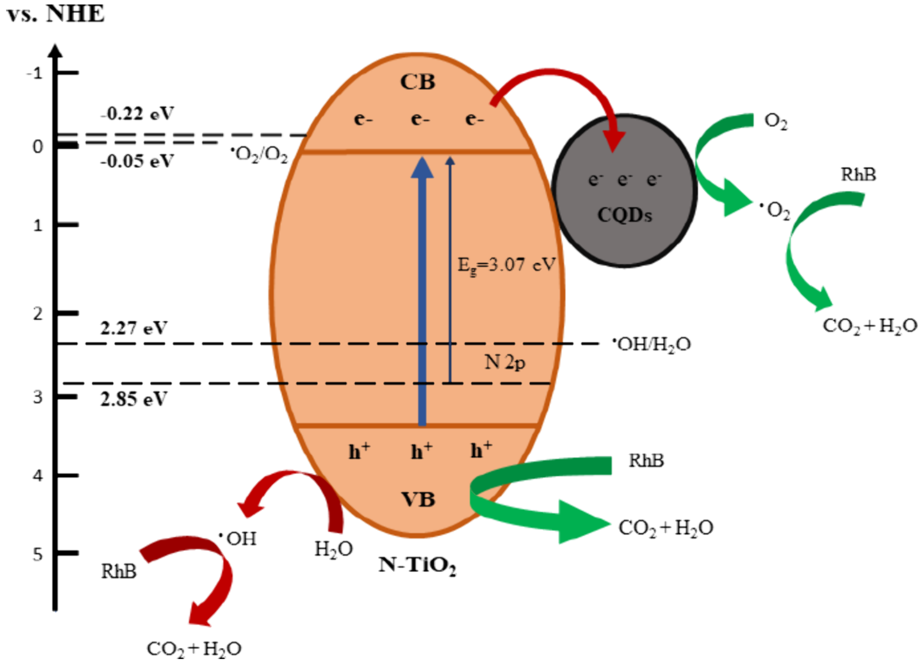

Figure 15. Degradation mechanism of RhB using nitrogen-doped TiO_2 NPs/CQDs composite. Reprinted and modified with permission from ref 80. Copyright 2020 Elsevier.

Table 5. CQDs Used for the Degradation of RhB in Recent Years

Authors	Year	Nanocomposite	Methods	Degradation percentage (%)	Time (min)	Ref
Wang et al.	2023	Ag_3PO_4/g-C_3N_4/CQDs	Ball-milling-assisted H_2O_2 oxidation method	99	120	11
Yi-di et al.	2023	$LaFeO_3$/CQDs-g-C_3N_x	Hydrothermal method for CQDs and $LaFeO_3$ NPs, C_3N_x with alkali treatment, ultrasonication for composite	95.2	60	83
Rahmani et al.	2023	MIL-Cr/N-CQDs	Hydrothermal for the CQDs, solvent deposition method for composite	95	160	84
Ahlawat et al.	2023	CQDs-1 (Precursor: Polyethylenimine and Urea)	Pyrolysis method	98.4	100	85
		CQDs-2 (Precursor: Polyethylenimine and Citric acid)		99.63		
Chen et al.	2023	Fe_3O_4@CQDs	Hydrothermal method	98	35	86
Tong et al.	2022	TiO_2/CQDs	Sol−gel hydrolysis	85.47	120	87
Preethi et al.	2022	CQDs	Green synthesis-stirrer-assisted method	99.11	35	88
Zhao et al.	2022	BiOCl/CQDs	Mechanical compounding method	95.76	60	89
		BiOBr/CQDs		98.91%		
Jin et al.	2022	g-C_3N_4/CQDs	Graphitic carbon nitride	90.9	120	90
Bai et al.	2021	D-CeO_2:CQDs/BiOCl composite	Hydrothermal method	97.7	25	91
Mandal et al.	2021	N-CQDs/ZnO-Nanorods	Sol−gel method for ZnO nanorods, pyrolysis for N-CQDs	90	9	92
Cheng et al.	2019	N-CQDs	Hydrothermal method	97	240	68
		Cl-CQDs		25		
Gao et al.	2019	CQDs/Ag_3PO_4/$BiPO_4$	Hydrothermal synthesis	98.41	50	93

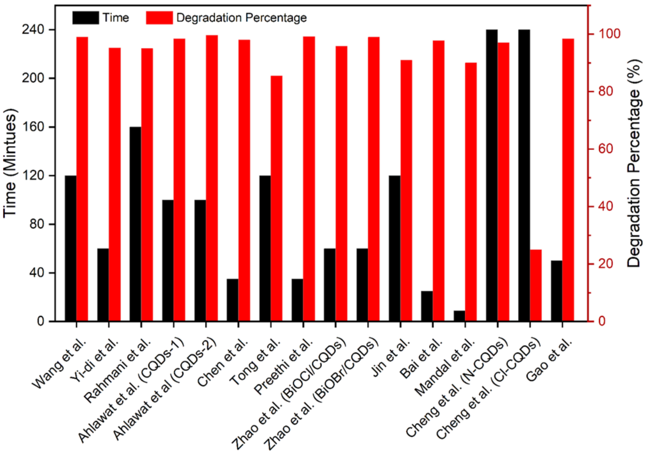

Figure 16. CQDs used for the degradation of RhB in recent years.

■ CONCLUSION AND FUTURE PROSPECTS

Water and wastewater treatment, including that of industrial water, is a major public health concern and vital to protecting both the environment and human health. Future studies should focus more on the following concerns regardless of the notable advances in synthesis and the catalytic capacities demonstrated by CQDs and GQDs:

- To reduce the cost of synthesizing QDs and improve their catalytic activity, novel and inventive synthetic methods are needed.
- Employment of nontoxic substrates and minerals for the production of CQDs for sustainable development.
- To improve the magnetization and surface properties of CQDs for water treatment.
- Development of inexpensive, water-soluble, mild conditions requiring pathways for CQD production to break down a range of contaminants.
- Animal wastes, such as bones, eggshells, and bristles, are being manipulated to create CQDs that can then be used to clean the environment.

It is possible to establish quantitative methods for quickly measuring the amounts of pollutants based on changes in intensity, in addition to the qualitative impacts of fluorescence quenching or enhancement. The process of oxidizing and using electrochemical assistance to modify carbon dots (CDs) can significantly increase their adsorption rate and capacity to remove contaminants from the environment. This could be considered an innovative approach to environmental remediation, but a thorough assessment of the toxicity issues is required. Scalable methods for the synthesis, purification, and functionalization of CDs must be established since the characteristics of CDs are highly correlated with the experimental setup, dopants, and precursors used. By creating reliable in situ characterization techniques, it will be possible to improve our theoretical knowledge of how CDs are formed, what influences their shape and photochemical characteristics, and how they interact with their surroundings. This would assist scientists in creating methods for customizing the characteristics of nanomaterials for certain uses. According to the majority of findings, CDs can identify or break down specific developing pollutants. Thus, it is imperative to focus on streamlining synthesis and purification procedures, creating a comprehensive knowledge base for the mechanisms underlying CD generation, detection, and degradation, evaluating the viability of CDs in large-scale applications, and anticipating long-term consequences.

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Notes

The authors declare no competing financial interest.

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