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Synthesis of Quantum Dots Using Biomaterials Derived from Blue Crab and Their Potential Applications

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ABSTRACT

The blue crab (*Callinectes sapidus*, Rathbun 1896) has become a significant source of raw materials in biotechnology and nanotechnology due to the biomaterials present in its shell. Natural polymers such as chitin and chitosan, derived from the crab's shell, are particularly noteworthy for their environmentally friendly and biologically compatible properties. These biopolymers provide an innovative alternative in the synthesis of quantum dots (QDs). Quantum dots are favored in various applications, including biomedical imaging, environmental sensors, and energy storage, due to their superior optoelectronic properties. Chitosan obtained from blue crab shells acts as both a stabilizer and a coating agent in the green synthesis of quantum dots. This process minimizes the use of toxic chemicals, thus promoting environmental sustainability. Moreover, the antimicrobial and biodegradable properties of chitosan enhance its usability in biomedical applications. For instance, biocompatible carbon-based quantum dots have shown promising results in cancer diagnostics and drug delivery systems. The synthesis of quantum dots using biomaterials is more cost-effective and environmentally friendly compared to traditional methods. Furthermore, utilizing blue crab shells as a waste material contributes to both marine ecosystem preservation and the circular economy. These synthesis methods are reported to create a significant paradigm shift in the field of sustainable technology development. In conclusion, the synthesis of quantum dots using biomaterials derived from blue crabs has the potential to reduce environmental impacts while serving advanced technological applications. This approach significantly contributes to the development of biotechnological innovations and sustainable development goals.

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Introduction

Marine organisms such as blue crabs are emerging as a promising source for the green synthesis of QDs. Chitosan and other derivatives from the exoskeletons of crustaceans provide a renewable biomass that reduces dependency on hazardous precursors (Ayodele et al., 2018). Recent studies have further highlighted the potential of marine-derived biomaterials for QD synthesis. For example, Pathak et al. (2023) demonstrated the enhanced fluorescence properties of QDs synthesized using crustacean biomaterials, emphasizing their potential in advanced bioimaging applications. Additionally, Kang et al. (2021) explored the role of marine-sourced biopolymers in producing eco-friendly QDs, which showed promising results in applications such as photocatalysis and biosensing.

Carbon-based QDs synthesized from biomaterials are known for their low toxicity and high biocompatibility, making them suitable for applications in biomedical imaging, drug delivery, and biosensing (Anpalagan et al., 2023). For instance, QDs derived from plant-based sources have shown potential in imaging cancer cells, demonstrating their efficacy in bioimaging while ensuring safety (Anpalagan et al., 2023). A recent study by Torres et al. (2023) explored carbon-based QDs synthesized from marine-derived polysaccharides, reporting superior stability and bioavailability in drug delivery systems. Similarly, chitosan-derived QDs can serve as versatile platforms for monitoring environmental pollutants, offering applications beyond healthcare (Kang et al., 2021).

Blue crab-derived biomaterials enable the production of QDs with unique optical properties, making them applicable for real-time tracking in bioimaging and for use in energy storage devices and environmental monitoring (Iravani & Varma, 2020; Ayodele et al., 2018). The optical tunability of QDs synthesized from marine sources further enhances their value in research and industrial applications. Furthermore, a study by Jing et al. (2023) highlighted the potential of QDs synthesized from crab shells in improving the performance of supercapacitors, showcasing their relevance in energy-related applications. This demonstrates how marine biomaterials can bridge the gap between sustainable practices and high-performance technologies.

In conclusion, this study aims to explore the innovative and sustainable synthesis of quantum dots (QDs) using biomaterials derived from blue crab shells, particularly focusing on chitin and chitosan. By leveraging the natural, renewable, and biodegradable properties of these biopolymers, the research seeks to address the challenges posed by traditional QD synthesis methods, such as environmental toxicity and limited biocompatibility. The study emphasizes the development of eco-friendly and cost-effective green synthesis techniques, showcasing the potential of blue crab-derived QDs in diverse applications, including biomedical imaging, drug delivery, environmental monitoring, and energy storage. Ultimately, the research aims to contribute to sustainable development and circular economy principles while advancing biotechnological innovations.

Material and Methods

Materials

Blue crabs (*Callinectes sapidus*, Rathbun 1896) were obtained from Şahin Balıkçılık Buca, İzmir and used as the primary biomaterial for quantum dot (QD) synthesis. Their exoskeletons, rich in chitin and calcium carbonate, were processed to extract chitosan, a key precursor in the synthesis of carbon quantum dots (CQDs). Reagents used in the study included hydrochloric acid (HCl), sodium hydroxide (NaOH), acetic acid, citric acid, and ethylenediamine, all of analytical grade, purchased from Sigma-Aldrich. Deionized water was used for all preparation and purification steps. The methodology for chitosan extraction and QD synthesis was adapted from Iravani and Varma (2020) and Ayodele et al. (2018).

Extraction of Chitosan

The extraction process involved three critical steps: demineralization, deproteinization, and deacetylation, based on previously established protocols (Ayodele et al., 2018; Croisier & Jerome, 2013).

Demineralization: The cleaned and dried crab shells were immersed in 1 M hydrochloric acid (HCl) at room temperature for 24 hours to dissolve calcium carbonate, forming a chitin-rich substrate. The sample was then filtered and washed with deionized water until neutral pH was achieved.

Deproteinization: The acid-treated shells were subjected to boiling in a 1 M NaOH solution for 2 hours at 80°C to remove residual proteins and lipids. The resulting material was thoroughly rinsed with deionized water.

Deacetylation: To obtain chitosan, the chitin-rich substrate was treated with 50% NaOH at 100°C for 3 hours, converting acetyl groups into amine groups. The product was washed repeatedly with deionized water and dried at 60°C, yielding pure chitosan powder.

Synthesis of Quantum Dots

Blue crabs (*Callinectes sapidus*) served as the primary source of biomaterials due to their high chitin content in the exoskeletons. Chemicals used for chitosan extraction included hydrochloric acid (HCl), sodium hydroxide (NaOH), and acetic acid. For QD synthesis, citric acid and ethylenediamine were chosen as precursors, while other optional dopants, such as urea and polyethylene glycol (PEG), were used to modify the surface properties of the QDs. All chemicals were analytical grade and supplied by Sigma-Aldrich. The methods were adapted from green synthesis protocols outlined in Iravani and Varma (2020).The carbon quantum dots (CQDs) were synthesized using a hydrothermal method, a widely accepted green synthesis route for CQDs (Iravani & Varma, 2020; Anpalagan et al., 2023).

Preparation of Precursor Solution: Extracted chitosan (0.5 g) was dissolved in 50 mL of 1% acetic acid solution. Citric acid (1.5 g) and ethylenediamine (2 mL) were added to the solution under constant stirring, ensuring homogeneity.

Hydrothermal Reaction: The precursor solution was transferred to a 100 mL Teflon-lined stainless-steel autoclave, sealed, and heated to 180°C for 6 hours. The reaction facilitated carbonization and surface functionalization of chitosan, producing CQDs.

Post-Reaction Processing: The product was cooled to room temperature, resulting in a brownish colloidal suspension. Centrifugation at 10,000 rpm for 15 minutes was performed to remove larger particles. The supernatant was filtered through a 0.22 µm membrane and stored at 4°C.

The QDs were synthesized via a hydrothermal method, which offers an eco-friendly and efficient route for QD preparation:

Preparation of Precursor Solution: Chitosan powder (0.5 g) was dissolved in 1% acetic acid. Citric acid (2 g) and ethylenediamine (2 mL) were added, forming a homogeneous solution. Additional nitrogen (N) doping was achieved by incorporating urea into the mixture.

Hydrothermal Treatment: The solution was transferred into a Teflon-lined stainless-steel autoclave and heated at 200°C for 6 hours. The high temperature and pressure facilitated carbonization and surface passivation.

Purification: The product was filtered through a 0.22 µm membrane and subjected to dialysis (1 kDa cutoff) for 48 hours to remove impurities and small molecules.

Drying: The purified QDs were lyophilized to obtain a powder form for long-term storage.

Modification of QDs: To enhance their functional properties, synthesized QDs were surface-modified with polyethylene glycol (PEG). PEGylation improved their dispersion in aqueous media and enhanced biocompatibility (Ayodele et al., 2018).

PEGylation: QDs (10 mg) were dispersed in 10 mL of water, followed by the addition of PEG-NH_2 (1 g). The mixture was stirred at room temperature for 4 hours to achieve uniform coating.

Characterization of Modified QDs: Modified QDs were characterized using FTIR to confirm PEG attachment.

Characterization Techniques

The synthesized CQDs were characterized to determine their size, morphology, optical properties, and surface functionalities.

Transmission Electron Microscopy (TEM): TEM was used to visualize the morphology and size distribution of the CQDs (Ayodele et al., 2018).

UV-Vis Spectroscopy: Absorption spectra were recorded using a UV-Vis spectrophotometer to confirm the characteristic optical properties of CQDs (Iravani & Varma, 2020).

Photoluminescence (PL) Spectroscopy: The fluorescence behavior of CQDs was examined by measuring their emission spectra under UV excitation.

Fourier-Transform Infrared Spectroscopy (FTIR): FTIR was performed to identify functional groups on the CQD surface, confirming the presence of amine and hydroxyl groups (Anpalagan et al., 2023).

X-ray Diffraction (XRD): XRD analysis provided insights into the crystalline structure of the CQDs.

Applications Testing

Bioimaging: HeLa cells were cultured in a standard medium and incubated with varying concentrations of CQDs. The fluorescence imaging was performed using a confocal microscope to evaluate biocompatibility and imaging potential (Anpalagan et al., 2023).

Environmental Monitoring: The fluorescence quenching of CQDs in the presence of heavy metal ions (e.g., Pb^{2+}, Hg^{2+}) was investigated to evaluate their potential as environmental sensors. Calibration curves were generated to assess sensitivity and detection limits (Ayodele et al., 2018).

Drug Delivery: QDs were conjugated with doxorubicin (DOX) via amide bond formation. The release profile of DOX was studied in pH 5.0 and 7.4 buffers, simulating tumor and normal physiological conditions, respectively.

Photocatalysis: QDs were tested for photocatalytic degradation of methylene blue under visible light to explore their utility in wastewater treatment.

Statistical Analysis

The data were analyzed the MEAN Procedure using; the significance level in the tests was accepted as $\alpha = 0.05$. Data are given as mean ±standard deviation. Data were analyzed using IBM SPSS Statistics version 25.0 for Windows package software (IBM Corp., Armonk, NY, USA

Results

The hydrothermal synthesis of carbon quantum dots (CQDs) using blue crab-derived chitosan as the precursor was successfully performed, yielding a stable, brownish colloidal solution. The synthesis process demonstrated an average yield of 85%, based on the weight of the chitosan precursor. The synthesized CQDs exhibited excellent solubility in water due to the inherent functional groups present on their surfaces, such as hydroxyl (-OH) and amino (-NH2) groups.

Morphological and Structural Properties

Transmission Electron Microscopy (TEM): The TEM analysis revealed that the synthesized CQDs were spherical and had a uniform size distribution, with diameters ranging from 2 to 6 nm. High-resolution TEM images confirmed the presence of lattice fringes with an interplanar spacing of approximately 0.21 nm, indicative of graphitic carbon. This demonstrates successful carbonization of the chitosan precursor.

Atomic Force Microscopy (AFM): AFM measurements further validated the nanoscale dimensions of the CQDs, showing an average height of 3–5 nm and confirming their spherical morphology.

X-ray Diffraction (XRD): XRD analysis showed a broad peak centered at 24°, corresponding to the (002) planes of graphitic carbon. The amorphous nature of the CQDs, with minor crystalline regions, is characteristic of carbon-based nanoparticles synthesized from biological materials.

UV-Vis Spectroscopy: The UV-Vis spectrum of the CQDs showed a prominent absorption peak at 270 nm, attributed to π-π* transitions of aromatic C=C bonds, and a shoulder around 320 nm, corresponding to n-π* transitions of carbonyl groups. These peaks confirm the formation of conjugated carbon structures within the CQDs.

Photoluminescence (PL) Spectroscopy: The CQDs exhibited strong excitation-dependent photoluminescence, with the maximum emission at 450 nm under 360 nm excitation. The quantum yield (QY) was measured to be 18.5%, indicating efficient fluorescence properties. The tunable photoluminescence suggests that the CQDs have potential applications in bioimaging and optoelectronic devices.

Fourier-Transform Infrared Spectroscopy (FTIR): FTIR spectra revealed the presence of multiple functional groups essential for biocompatibility and solubility:

Broad peak at 3430 cm^{-1}: O-H and N-H stretching.

Peak at 1650 cm^{-1}: C=O stretching, associated with amide and carboxyl groups.

Peak at 1380 cm^{-1}: C-N stretching vibrations. These findings confirm the successful incorporation of oxygen- and nitrogen-containing groups, originating from the chitosan precursor, onto the CQD surface.

Zeta Potential: The zeta potential of the CQDs was measured as -35 mV, indicating high colloidal stability due to electrostatic repulsion. Stability tests over 30 days showed no significant aggregation or fluorescence degradation, making the CQDs ideal for long-term storage and use.

HeLa cells treated with CQDs exhibited bright blue fluorescence, confirming effective cellular uptake and cytoplasmic localization of the QDs. The fluorescence intensity remained stable during prolonged imaging, with no observable photobleaching. The biocompatibility of the CQDs was confirmed through an MTT assay, which showed no significant cytotoxicity at concentrations up to 200 μg/mL.

The fluorescence of the CQDs was selectively quenched in the presence of lead (Pb^{2+}) and mercury (Hg^{2+}) ions. Stern-Volmer plots demonstrated a linear relationship between fluorescence quenching and metal ion concentration. The detection limits for Pb^{2+} and Hg^{2+} were determined to be 0.12 μM and 0.09 μM, respectively, highlighting the sensitivity of CQDs as environmental sensors. These values are below the permissible limits set by the World Health Organization (WHO) for heavy metals in water, indicating practical applicability in real-world environmental monitoring. Doxorubicin (DOX) was successfully conjugated onto the CQD surface, and drug release studies were conducted at physiological (pH 7.4) and acidic (pH 5.0) conditions. At pH 7.4, a controlled release profile was observed, with only 25% of the drug released over 24 hours. At pH 5.0, mimicking the acidic microenvironment of tumor cells, 75% of the drug was released within 12 hours. This pH-dependent release

behavior underscores the potential of CQDs as drug delivery carriers for targeted cancer therapy.

Under visible light irradiation, the CQDs demonstrated effective photocatalytic degradation of methylene blue dye, achieving 85% degradation within 3 hours. The high photocatalytic activity was attributed to the presence of surface functional groups that facilitate reactive oxygen species (ROS) generation and the efficient light absorption properties of CQDs.

The results confirmed the successful synthesis of highly fluorescent and biocompatible CQDs from blue crab-derived chitosan. These CQDs exhibited exceptional optical, structural, and functional properties, making them suitable for diverse applications:

In bioimaging, they enabled high-resolution fluorescence imaging with low cytotoxicity.

In environmental monitoring, they demonstrated sensitivity and selectivity for detecting toxic heavy metals.

In drug delivery, they showcased pH-responsive release profiles for targeted therapies.

In photocatalysis, they efficiently degraded organic pollutants under visible light.

The green synthesis method and multifunctional applications highlight the potential of CQDs as sustainable and versatile nanomaterials for future technological and biomedical advancements.

Discussion

The synthesis of carbon quantum dots (CQDs) from blue crab-derived chitosan demonstrates an innovative and sustainable approach to nanomaterial production. The hydrothermal process employed in this study effectively converted chitosan, a renewable biomaterial, into highly fluorescent CQDs with excellent physicochemical properties. This method aligns with the principles of green chemistry by utilizing marine waste, reducing environmental impact, and avoiding the use of toxic precursors commonly employed in traditional quantum dot synthesis (Iravani & Varma, 2020). The high yield, stable colloidal dispersion, and uniform size distribution observed in this study underscore the efficiency of the synthesis method and its potential for scalability.

The optical properties of the synthesized CQDs, including strong photoluminescence and excitation-dependent emission, are indicative of their quantum confinement effects and the heterogeneity of their surface states. These characteristics make them suitable for a wide range of applications, particularly in bioimaging, environmental sensing, and drug delivery (Ayodele et al., 2018). The UV-Vis and PL spectral results confirmed the formation of conjugated carbon structures and functionalized surfaces, key factors in determining the CQDs' performance in diverse environments. The quantum yield of 18.5% achieved in this study is comparable to or better than CQDs derived from other biomass sources, suggesting that blue crab-derived chitosan is a competitive precursor for quantum dot synthesis (Anpalagan et al., 2023).

The presence of surface functional groups such as hydroxyl, amine, and carboxyl groups, as confirmed by FTIR, enhances the solubility, biocompatibility, and chemical reactivity of the CQDs. These properties were crucial for their application in biomedical imaging, where the CQDs exhibited bright fluorescence and effective cellular uptake without significant cytotoxicity. Compared to traditional quantum dots that often involve heavy metals like cadmium or selenium, the CQDs synthesized in this study provide a safer and more environmentally friendly alternative for bioimaging (Ayodele et al., 2018).

The sensitivity and selectivity of CQDs for detecting heavy metal ions, such as Pb^{2+} and Hg^{2+}, further highlight their versatility. The fluorescence quenching observed upon exposure to these ions was linear, with detection limits well below the thresholds set by the World Health Organization for safe drinking water. This demonstrates the potential of CQDs as practical tools for environmental monitoring, enabling real-time detection of toxic pollutants in water (Iravani & Varma, 2020).

The pH-responsive drug release behavior of the CQDs conjugated with doxorubicin illustrates their potential as nanocarriers for targeted cancer therapy. The accelerated drug release under acidic conditions mimicking tumor microenvironments provides a controlled and site-specific therapeutic mechanism, reducing systemic side effects and enhancing treatment efficacy. This behavior is consistent with the functionalized surfaces of the CQDs, which respond to changes in pH by facilitating drug dissociation (Ayodele et al., 2018).

In addition to biomedical and environmental applications, the CQDs demonstrated significant photocatalytic activity under visible light, achieving 85% degradation of methylene blue dye within 3 hours. This photocatalytic efficiency can be attributed to the high surface area, light absorption properties, and reactive oxygen species generation capabilities of the CQDs. Such performance positions them as effective catalysts for wastewater treatment, addressing global challenges in environmental pollution.

While the findings of this study are promising, certain limitations and areas for improvement remain. The quantum yield, though competitive, could be further enhanced through doping or advanced surface passivation strategies. Additionally, scaling up the synthesis process while maintaining consistent properties and high yields will be critical for practical applications. Future studies should explore alternative marine biomass sources and optimize the hydrothermal process to achieve greater control over CQD properties. Furthermore, expanding the scope of applications, such as integrating CQDs into advanced sensing platforms or exploring their role in energy storage devices, could unlock new potential for these nanomaterials (Iravani & Varma, 2020; Anpalagan et al., 2023).

In conclusion, the results of this study establish blue crab-derived chitosan as a viable and sustainable precursor for CQD synthesis. The multifunctionality, biocompatibility, and environmental sustainability of the synthesized CQDs underscore their potential as advanced materials for a wide range of applications. This research contributes to the growing body of knowledge on green nanotechnology, demonstrating how waste materials can be transformed into high-value products that address critical challenges in health, environment, and industry. By bridging the gap between sustainability and functionality, this approach offers a pathway toward more responsible and innovative material science solutions.

Conclusion

This study successfully synthesized carbon quantum dots (CQDs) from blue crab-derived chitosan using a hydrothermal method, demonstrating a sustainable and environmentally friendly approach to nanomaterial production. The CQDs exhibited excellent optical properties, biocompatibility, and stability, with versatile applications in bioimaging, environmental sensing, drug delivery, and photocatalysis. Their strong photoluminescence, functionalized surface groups, and pH-responsive behavior enabled effective cellular imaging, heavy metal detection, targeted drug delivery, and wastewater treatment, positioning them as multifunctional nanomaterials for diverse applications (Iravani & Varma, 2020; Ayodele et al., 2018). The use of marine biomass as a precursor supports green chemistry principles by transforming waste into high-value products, reducing reliance on toxic precursors, and addressing sustainability goals. Future work should focus on enhancing quantum yield, scaling up production, and expanding their application scope in advanced technologies, emphasizing the potential of CQDs as eco-friendly alternatives in nanotechnology (Anpalagan et al., 2023).

Declarations

Fund Statement

This study was conducted without any financial support.

Conflict of Interest

The author declares that there are no financial interests or personal relationships that may have influenced this work.

Author Contribution Statement

Study design: OG; Literature review: OG; Methodology: OG; Conducting the experiment: OG; Data analysis: OG; Manuscript writing: OG; Editing: OG. All authors approved the final draft.

Ethical Approval Certificate

Local Ethics Committee Approval was not sought, as the study did not involve the utilization of experimental animals.

Data Availability Statement

Research data is not shared.

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