



Research Review on Synthesis of Bio-waste Graphene Quantum Dots for Super Capacitor Applications

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Abstract

This comprehensive study delves into the fabrication of Graphene Quantum Dots (GQDs) sourced from organic waste for their application in supercapacitors, addressing the growing demand for sustainable and effective energy storage solutions. GQDs exhibit distinctive characteristics, including remarkable surface area and superb conductivity, offering considerable potential for augmenting supercapacitor efficiency. Various methodologies for GQD synthesis, such as hydrothermal and solvothermal techniques, chemical exfoliation, carbonization, pyrolysis, as well as microwave-assisted processes, are meticulously examined alongside diverse characterization methodologies aimed at assessing GQD attributes. The utilization of organic waste-derived GQDs showcases significant advancements in enhancing specific capacitance and endurance in supercapacitor electrodes. Nevertheless, scalability hurdles and material purity concerns persist, necessitating further research endeavors. Future endeavors are directed towards elevating energy density, prolonging cycle life, and optimizing cost-efficiency to expedite the integration of organic waste-derived GQDs into mainstream energy storage applications.

Keywords: Graphene Quantum Dots (GQD); Super capacitor; Energy storage; Power storage; Zero dimensions' materials

Introduction

The rapid advancement of technology and increasing energy demands have spurred significant interest in developing efficient and sustainable energy storage devices [1]. Super capacitors have emerged as promising candidates due to their high power density, fast charge-discharge rates, and long cycle life [2]. However, to fully harness their potential, innovative materials with exceptional electrical properties are required [3].

Graphene Quantum Dots (GQDs) have garnered considerable attention for their unique attributes, including high surface area, excellent electrical conductivity, and tunable electronic properties [4]. These nanoscale fragments of graphene combine the advantageous

characteristics of both graphene and quantum dots, making them ideal for a variety of applications, including energy storage, sensing, and optoelectronics [5].

Traditionally, the synthesis of GQDs involves complex and costly methods that often rely on hazardous chemicals [6]. In response to environmental and economic concerns, researchers have explored the use of biowaste as a precursor for GQD production. This approach not only provides a sustainable and cost-effective alternative but also addresses the pressing issue of biowaste management.

Biowaste, which includes agricultural residues, fruit peels, leaves, and other organic waste, is abundant and renewable [7]. Utilizing these materials for the synthesis of GQDs aligns with the principles of green chemistry and circular economy, promoting the conversion of waste into valuable products [8]. The process of converting biowaste into GQDs typically involves methods such as hydrothermal treatment, chemical exfoliation, carbonization, and microwave-assisted synthesis [9].

The biowaste-derived GQDs exhibit properties that are highly beneficial for supercapacitor applications [10]. They offer numerous active sites for charge storage, enhance electrical conductivity, and contribute to the structural stability of the electrodes [11]. As a result, supercapacitors incorporating GQDs demonstrate improved energy and power densities, as well as excellent cycling stability [12].

This review aims to provide a comprehensive overview of the synthesis of GQDs from biowaste and their application in supercapacitors. It will cover the various synthesis methods, the characterization of GQDs, and their performance in supercapacitor devices. Additionally, the review will address the challenges and future prospects in this burgeoning field, highlighting the potential of biowaste-derived GQDs to revolutionize energy storage technologies (Figure 1).

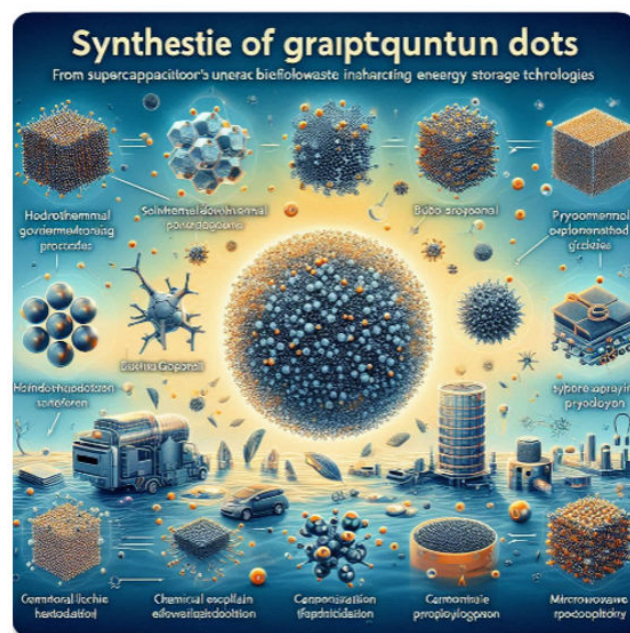


Figure 1: Graphical abstract of graphene quantum dots for supercapacitor applications.

Materials and Methods

The synthesis of GQDs from bio-waste involves several methods, primarily categorized into top-down and bottom-up approaches. The

selection of biowaste material and the synthesis method significantly influence the properties of the resultant GQDs (Table 1-6) [13].

| Method | Process | Examples | Advantages | Challenges |
|---|---|---|--|---|
| Hydrothermal and solvothermal processes | Biowaste is dispersed in water or an organic solvent and heated in a sealed vessel (autoclave) under high-pressure and high-temperature conditions. | Orange peels, citric acid from fruit peels, spinach leaves. | Simple setup, environmentally friendly, controlled size and functional groups. | Requires precise control of reaction conditions, limited scalability due to autoclave capacity. |
| Chemical exfoliation | Carbon-rich biowaste is treated with strong acids or bases to exfoliate it into graphene layers, which are then broken down into GQDs. | Cow manure, soybean waste, sugarcane bagasse. | High yield, straightforward process. | Use of hazardous chemicals, potential impurities or defects in GQDs. |

Table 1: Top-down methods.

| Method | Process | Examples | Advantages | Challenges |
|------------------------------|---|--|--|---|
| Carbonization and pyrolysis | Thermal decomposition of biowaste at high temperatures in an inert atmosphere (nitrogen or argon) to form carbon structures, further processed into GQDs. | Chicken feathers, peanut shells, coconut shells. | Inexpensive, abundant materials, good electrical conductivity. | High energy consumption, potential non-uniform GQDs. |
| Microwave-assisted synthesis | Microwave radiation rapidly heats and decomposes biowaste into GQDs, involving mixing the biowaste with a solvent and irradiating with microwaves. | Banana peels, sugarcane bagasse, coffee grounds. | Fast, energy-efficient, scalable, desirable size and surface properties. | Requires precise control of microwave parameters to avoid over-heating or incomplete decomposition. |

Table 2: Bottom-up methods.

| Property | Description | Characterization technique | Details |
|---------------------------|--|--|--|
| Size and morphology | The dimensions and shape of the GQDs. | Transmission Electron Microscopy (TEM) | TEM provides detailed images, allowing for precise measurement of GQD size and observation of their morphological characteristics. |
| Crystalline structure | The arrangement of atoms in the GQDs. | X-Ray Diffraction (XRD) | XRD is used to assess the crystalline structure, determining the presence of graphitic layers and crystalline phases. |
| Degree of graphitization | The extent to which the GQDs are composed of graphitic carbon. | Raman spectroscopy | Raman spectroscopy evaluates the degree of graphitization by analyzing the D and G bands, which indicate defects and graphitic structure respectively. |
| Surface functional groups | Chemical groups present on the surface of the GQDs. | Fourier Transform Infrared spectroscopy (FTIR) | FTIR identifies functional groups on the GQD surface, providing information on chemical bonding and surface chemistry. |
| Optical properties | The behavior of GQDs in response to light. | Photoluminescence (PL) spectroscopy | PL spectroscopy analyzes the emission of light from GQDs, which is crucial for applications in optoelectronics and bioimaging, by studying their luminescent properties. |

Table 3: Properties and characterization.

Super capacitor applications

A super capacitor, also known as an ultra-capacitor or electrochemical capacitor, is an energy storage device that combines the properties of traditional capacitors and batteries [14]. Unlike conventional capacitors, which store energy through electrostatic

charge separation, supercapacitors store energy through both electrostatic and electrochemical processes [14]. This dual mechanism allows them to have much higher energy storage capacity than traditional capacitors, while also offering faster charge and discharge rates compared to batteries.

| Characteristic | Description | Benefits |
|----------------------------------|--|---|
| High power density | Ability to deliver and accept charge quickly. | Ideal for applications requiring rapid energy bursts, such as power tools and regenerative braking systems. |
| Long cycle life | Can withstand millions of charge-discharge cycles without significant degradation. | Offers much longer lifespans compared to batteries, reducing the need for frequent replacements. |
| Fast charge and discharge | Low internal resistance allows rapid charging and discharging. | Enables quick energy availability, useful in applications like emergency power backup and peak load leveling. |
| Wide operating temperature range | Effective operation over a broad range of temperatures. | Suitable for use in extreme environments, from cold climates to hot industrial settings. |
| Environmentally friendly | Often use less harmful materials and have simpler recycling processes compared to batteries. | Reduces environmental impact and aligns with sustainable and green technology goals. |

Table 4: Key characteristics of super capacitors.

| Application | Description | Examples |
|----------------------|--|---|
| Energy storage | Supplementing batteries in hybrid and electric vehicles, renewable energy systems, and grid storage. | Hybrid and electric vehicles for regenerative braking and acceleration. Solar and wind energy systems for smoothing out power fluctuations. Grid storage for load balancing and peak shaving. |
| Consumer electronics | Providing quick bursts of energy in various electronic devices. | Cameras for flash systems. Laptops for quick boot operations. Portable speakers for high-power sound bursts. |
| Industrial uses | Used in heavy machinery to provide quick energy for lifting and moving. | Cranes and forklifts for lifting heavy loads. Uninterruptible Power Supplies (UPS) for industrial systems. |
| Backup power | Offering reliable power in case of short-term outages. | Computers to prevent data loss during power interruptions. Medical devices to ensure continuous operation. Telecommunications equipment to maintain service during power failures. |
| Transportation | Enhancing performance and energy efficiency in various transport systems. | Electric buses for energy recovery and acceleration. Trains for auxiliary power systems. Aerospace for fast-acting power needs. |
| Military and defense | Providing robust and reliable power in critical defense applications. | Powering communication devices. Energy systems in drones and other unmanned vehicles. Rapid-deployment power supplies for field operations. |

Table 5: Applications.

Importance of bio-waste-derived GQDs in super capacitors

The integration of Graphene Quantum Dots (GQDs) derived from biowaste into supercapacitors offers numerous advantages, including

enhanced performance, cost-effectiveness, and environmental sustainability [15]. These GQDs provide a high surface area, excellent electrical conductivity, and good structural stability, which are crucial for improving the overall efficiency and capacity of supercapacitors [16]. By utilizing biowaste as a source material, this approach also promotes recycling and reduces waste, aligning with green chemistry principles and supporting the development of eco-friendly energy storage solutions [17].

Results and Discussion

Types of super capacitors

Supercapacitors are classified into various types based on their electrode materials and mechanisms of energy storage [18]. The main types include Electric Double-Layer Capacitors (EDLCs), pseudocapacitors, and hybrid capacitors [19]. Each type has distinct characteristics and advantages, making them suitable for different applications (Table 6).

| Type | Description | Key characteristics | Applications |
|--|---|---|---|
| Electric Double-Layer Capacitors (EDLCs) | Store energy through electrostatic charge separation at the electrode-electrolyte interface. | High power density Long cycle life Fast charge and discharge No chemical reactions involved | Energy storage Consumer electronics Power backup Electric vehicles |
| Pseudocapacitors | Store energy through fast and reversible redox reactions at the surface of the electrodes. | Higher energy density than EDLCs Involves Faradaic (redox) reactions Moderate power density Shorter cycle life compared to EDLCs | Renewable energy systems Portable electronics Power tools Sensors |
| Hybrid Capacitors | Combine the properties of EDLCs and pseudocapacitors, typically using different materials for each electrode. | Balanced energy and power density Improved performance. Combination of electrostatic and Faradaic mechanisms | Electric vehicles Grid storage Industrial |

Table 6: Types of super capacitors.

Electric Double-Layer Capacitors (EDLCs)

Mechanism: EDLCs store energy by forming an electric double layer at the interface between the electrode and the electrolyte. This electrostatic separation of charges does not involve any chemical reactions [20].

Materials: Commonly used materials include activated carbon, carbon nanotubes, and graphene.

Advantages: High power density, long cycle life, and rapid charge-discharge capability.

Disadvantages: Lower energy density compared to pseudo-capacitors and batteries.

Pseudo-capacitors

Mechanism: Pseudocapacitors store energy through fast and reversible redox (Faradaic) reactions at the electrode surface. These reactions involve electron transfer and result in higher energy storage capacity.

Materials: Typically use transition metal oxides (such as RuO₂, MnO₂) and conducting polymers (such as polyaniline, polypyrrole).

Advantages: Higher energy density compared to EDLCs.

Disadvantages: Lower cycle life and power density compared to EDLCs.

Hybrid capacitors

Mechanism: Hybrid capacitors combine the mechanisms of EDLCs and pseudo-capacitors, using different electrode materials to optimize both energy and power density. They often use a carbon-based material for one electrode and a pseudo-capacitive material for the other.

Materials: Can include a combination of activated carbon and transition metal oxides or conducting polymers.

Advantages: Balanced performance, offering a compromise between the high power density of EDLCs and the high energy density of pseudo-capacitors.

Disadvantages: Complexity in design and potentially higher costs.

Challenges and future perspectives

Supercapacitors have made significant strides in energy storage technology, but several challenges remain to be addressed for their widespread adoption and further advancement. Future research and development efforts are focusing on overcoming these challenges and unlocking the full potential of supercapacitors in various applications (Table 7).

| Challenge | Description | Potential solutions |
|----------------|---|---|
| Energy density | Super capacitors have lower energy density compared to batteries, limiting their use in long-duration energy storage. | Development of advanced electrode materials. Innovations in electrode design and architecture. |

| | | |
|---------------------------------------|--|--|
| Cycle life and durability | Super capacitors can degrade over time, especially under high cycling conditions, impacting their long-term reliability. | Improved electrode materials and electrolyte formulations. Enhanced cell design for durability and stability. |
| Cost-effectiveness | High material and manufacturing costs hinder widespread adoption of super capacitors in commercial applications. | Scalable synthesis methods for cost-effective production. Recycling strategies for electrode materials. |
| Temperature range | Super capacitor performance can be limited by extreme temperatures, affecting their applicability in harsh environments. | Development of electrolytes and materials with wide temperature tolerance. Thermal management strategies. |
| Integration into systems | Efficient integration of super capacitors into existing energy storage systems and electronic devices requires tailored designs. | Collaborative efforts between material scientists, engineers, and system integrators. Standardized interfaces and protocols. |
| Advancements in nanomaterials | Continued research on advanced nanomaterials to enhance energy and power density while maintaining stability. | Exploration of graphene, carbon nanotubes, and metal oxides for improved performance. Nanomaterial synthesis innovations |
| Hybrid energy storage systems | Integration of supercapacitors with batteries for hybrid systems combining benefits of both technologies. | Development of hybrid architectures for optimized performance. Control algorithms for seamless integration. |
| Smart and flexible devices | Design of flexible and lightweight supercapacitors for wearable electronics and IoT applications. | Development of flexible electrode materials and packaging, Integration with flexible electronics and sensors |
| Environmental sustainability | Emphasis on sustainable manufacturing processes and recycling strategies to minimize environmental impact. | Use of renewable materials and green synthesis methods. Recycling programs for spent electrode materials. |
| Standardization and commercialization | Establishment of industry standards and regulations to facilitate wider adoption and integration of supercapacitors. | Collaborative efforts among stakeholders to define performance metrics and safety standards. Market-driven policies for incentivizing adoption and investment |

Table 7: Challenges and future perspectives.

Future research should focus on optimizing synthesis methods, exploring new biowaste sources, and enhancing the understanding of the relationship between GQD properties and supercapacitor performance. Interdisciplinary approaches combining materials science, chemistry, and engineering will be crucial in overcoming these challenges.

Conclusion

The synthesis of graphene quantum dots from biowaste represents a sustainable and economically viable approach to producing high-performance materials for supercapacitor applications. By leveraging abundant and renewable biowaste resources, this strategy not only addresses environmental concerns but also advances the development of next-generation energy storage devices. Further research and technological advancements are needed to fully realize the potential of biowaste-derived GQDs in commercial supercapacitors.

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