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Energy storage device utilising garlic skin and carbon fibre derived from agricultural and industrial waste: A review

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ABSTRACT

Carbon quantum dots (CQDs) are small-sized nanoparticles (1 – 10 nm) with unique properties such as high conductivity, thermal stability, and fluorescence capability, making them superior materials for energy applications. This research develops an energy storage device based on garlic skin waste and carbon fiber from agricultural and industrial waste. Garlic peel was processed into CQDs using pyrolysis method, while carbon fiber was obtained from methylcellulose. Analytical results showed that CQDs increased the specific capacitance of the gel electrolyte to 110.57 F/g, with excellent cycling stability reaching 96% after 2000 cycles. In addition, the carbon fiber-based electrode showed the highest specific capacitance of 155.58 F/g, energy density of 10.59 Wh/kg, and power density of 4047 W/kg, making it an economical alternative to carbon nanotubes and graphene. Material characterization via TGA, UV-Vis, FTIR, SEM, and TEM confirmed the high thermal stability and quasi-round particle morphology with an average size of 7 nm. The results of this study highlight the potential of CQDs from garlic skin as a sustainable solution for advanced energy storage applications.

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1. INTRODUCTION

Energy demand has experienced significant growth parallel to economic expansion and societal progress in recent years. The conservation and efficient storage of energy have emerged as significant subjects in technological advancement [1]. A primary difficulty in the shift to sustainable energy sources is the creation of efficient, cost-effective, and eco-friendly. Supercapacitors are essential in energy storage. Nevertheless, the raw materials utilised in these devices are sometimes unsustainable and costly. To resolve this issue, extensive research has concentrated on utilising natural and waste materials to create more cost-effective and eco-friendly. A viable material source is garlic peel, an agricultural byproduct, along with carbon fibres derived from industrial waste [2].

Garlic skin comprises carbon compounds that can be converted into active materials for energy storage, including supercapacitors. Furthermore, the utilisation of carbon fibres derived from industrial waste presents promise for the development of high energy storage. Utilising these wastes mitigates environmental damage and fosters more cost-effective alternatives in the advancement of future energy.

2. THEORITICAL REVIEW

2.1. Energy of Storage Devices

An energy storage device is engineered to retain energy in several forms for subsequent utilisation. Supercapacitors are essential in energy storage. Energy storage devices operate inside the

electrical system as reservoirs to retain surplus energy during periods of high output and serve as a backup by discharging energy when required.

2.2. Supercapacitors

Supercapacitors are a category of capacitors characterised by a significantly greater energy storage capacity than traditional capacitors. Supercapacitors provide a significantly greater storage capacity compared to traditional electrolytic capacitors. They are utilised in applications necessitating immediate energy storage and elevated power, including as electric automobiles and energy recovery systems [3, 4].

2.3. Quantum Dots and Carbon Fibres

Quantum dots (QDs) are semiconductor nanostructures whose dimensions are diminished to the scale of inter-atomic distances. In these miniaturised structures, the dimensions in all three axes (x, y, and z) are proportionate to the de Broglie wavelength. This results in the quantisation of electron energy in all three dimensions, restricting degrees of freedom. Figure 1 illustrates the 0D fullerene.

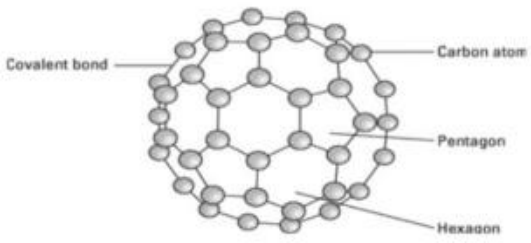


Figure 1. Structure of zero-dimensional fullerene.

Figure 1 displays a picture of the 0D fullerene structure. Common characteristics of carbon quantum dots (CQDs) include minimal toxicity, chemical inertness, exceptional biocompatibility, high crystallinity, favourable dispersibility, photo-induced electron transfer, and commendable conductivity. They also demonstrate superconductivity, rapid electron transport, and favourable photonic and photoelectronic characteristics [5].

3. RESEARCH METHODS

3.1. Techniques for Characterising Materials

Material characterisation is a procedure employed to ascertain the physical, chemical, structural, and mechanical qualities of a material.

3.2. Thermogravimetric Analysis

Thermogravimetric analysis (TGA) is a thermal analytical technique that measures the mass of a sample over time as temperature varies. These measurements yield insights into physical events, including phase transitions, absorption, adsorption, and desorption, as well as chemical phenomena. TGA is conducted with a thermogravimetric analyser, which continually monitors the mass variation as the sample temperature fluctuates. The temperature is often elevated at a consistent rate, or in certain instances, it is regulated to sustain a steady rate of mass loss to initiate a thermal reaction. The data acquired from the TGA analysis is subsequently illustrated in graphical format, with the sample mass represented on the y-axis and temperature or time on the x-axis. This graph, frequently flattened, is referred to as a TGA curve [6].

3.3. Scanning Electron Microscopy

Scanning electron microscopy (SEM) is a prevalent method for examining the morphology and topography of membrane surfaces. In SEM, a concentrated electron beam traverses the membrane surface and penetrates further inward. The resultant image is produced by a mix of secondary electrons, which are responsive to surface topography, and backscattered electrons, which convey

information regarding the specimen's composition. SEM can elucidate the microstructure of membrane materials and necessitates little sample preparation, including drying and coating with conductive substances such as gold or carbon. The resolution of SEM generally varies from 10 to 50 nm, contingent upon the apparatus utilised. SEM is employed to characterise the membrane structure and analyse the production of hollow fibre membranes [7, 8].

3.4. Transmission Electron Microscopy

Transmission electron microscopy (TEM) is a method wherein a stream of electrons traverses a highly thin specimen, engaging with it during passage. The resultant image is produced from the interaction of transmitted electrons and is magnified and focussed onto a display medium, such as a fluorescence screen, photographic film, or charge-coupled device (CCD) camera. Carbon molecular sieve (CMS) membranes are sophisticated materials produced from the pyrolysis of polymer precursors. It possesses a highly advanced ultra-microporous architecture that enables the separation of tiny gas pairs with minimal diameter variation. Consequently, CMS membranes demonstrate enhanced gas permeability and selectivity relative to polymer membranes [8].

3.5. Fourier Transform Infrared Spectroscopy

Fourier transform infrared (FTIR) spectroscopy is a method employed to examine molecules, yielding significant biochemical data without modifying the biological specimen. FTIR spectroscopy is a technique that examines the interaction between infrared radiation and a sample, which may be in solid, liquid, or gaseous form. When infrared radiation traverses a sample, a portion is absorbed and the remainder is transmitted. FTIR measures both the frequency of radiation absorption by the sample and the strength of that absorption. These frequencies are crucial in determining the chemical composition of the sample, as distinct chemical functional groups absorb radiation at particular frequencies. The absorption intensity can also be utilised to ascertain the concentration of a component. The resultant spectrum yields a molecule absorption and transmission profile, establishing a molecular fingerprint that is unique to the sample, akin to the uniqueness of human fingerprints. FTIR was developed to address the limitations of dispersive devices. An interferometer generates a unique signal that encapsulates all the infrared frequencies included within it. Owing to its simplicity and efficiency, FTIR has been extensively utilised in herbal analysis as well as in domains like as environmental research, cancer detection, forensics, food analysis, and toxicology [9, 10].

3.6. Ultraviolet-Visible Spectroscopy

The phrase ultraviolet-visible (UV-Vis) spectroscopy typically refers to radiation with wavelengths ranging from 200 – 800 nm. Numerous groups absorb wavelengths below 200 nm. This segment of the spectrum is challenging to analyse, as oxygen absorbs UV radiation below 200 nm, unless the spectrum is captured in a vacuum or UV-Vis vacuum. UV-visible spectroscopy operates on the premise of light absorption or reflection in the ultraviolet or visible spectrum, namely within the wavelength range of 160 – 780 nm, by a material, leading to the generation of an absorption spectrum, which is contingent upon the interaction between light and matter. UV-Vis spectroscopy is mostly employed for the quantitative analysis of molecules in solution, inorganic ions, or complexes. Molecules absorb UV or visible wavelengths, and the spectrum produced by the absorption bands reveals the molecular structure [11].

4. RESULTS AND DISCUSSIONS

4.1. TGA of Garlic Skin and Fibre Carbon

The thermal stability of garlic peel and carbon fibre was assessed using TGA analysis from ambient temperature to 600°C. The outcomes are illustrated in Figure 2. The thermogravimetric analysis of carbon fibre exhibited negligible loss, with a residual weight of 97.82% at 600°C. The TGA of garlic skin revealed three primary stages of heat deterioration. The first weight loss ranged from 50°C to 140°C, attributed to the evaporation of water in the garlic skin. The residual weight of garlic skin was 24.5% at 600°C in this investigation; accounting for an 8% water loss, the actual residual weight was 32.5%, consistent with existing references. Additionally, the garlic peel was

transformed into a CQDs precursor at 240°C for 2 hours, with the residual weight of the CQDs precursor exceeding 80%, as indicated in Figure 2. This substantiates that the conversion rate was notably high and can yield adequate carbon content for CQDs in energy storage devices.

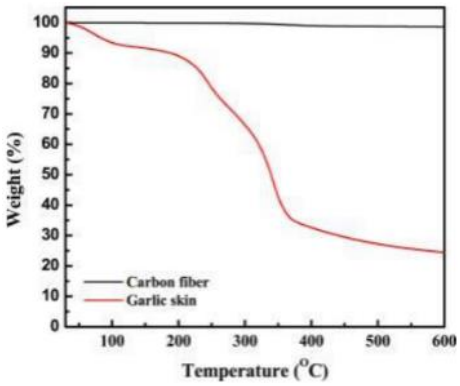


Figure 2. TGA graph depicting garlic skin and carbon fibre.

4.2. Results of QDs Surface Analysis

CQDs are typically zero-dimensional, quasi-spherical nanoparticles with dimensions under 10 nm, demonstrating quantum confinement phenomena. The mean particle size of paper-coated garlic CQDs is 7 nm, as determined by particle size and potential analysis. Figure 3 (a) illustrates the histogram of the measured size distribution. The surface potential of garlic carbon quantum dots was assessed using zeta potential measurement, as illustrated in Figure 3 (b). The measured zeta potential was 0.00364 mV. Incorporating a minimal quantity of garlic CQDs into the electrolyte can enhance its electrical characteristics.

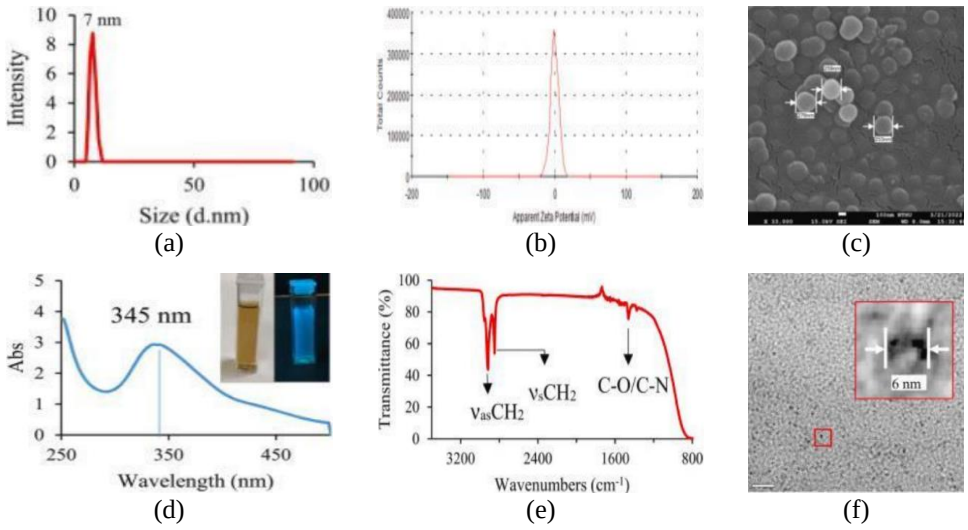


Figure 3. Carbon quantum dots derived from garlic skin: (a) analysis of particle size; (b) analysis of surface zero potential; (c) SEM; (d) UV-Vis spectrum of CQDs; (e) FTIR spectrum of garlic skin CQDs, and (f) TEM.

The incorporation of garlic carbon quantum dots into the gel electrolyte yielded specific capacitances of 0.002, 51.53, 110.57, 32.57, and 23.98 F/g at a scan rate of 0.02 V/s. The incorporation of 0 CQDs exhibits the greatest value in this investigation, likely due to the minimal doping of CQDs enhancing the charge transfer capacity of the electrolyte, which reduces internal resistance and consequently elevates specific capacitance. The surface morphology indicates the emergence of spherical carbon particles following the carbonisation process. The diameter of spherical CQDs is approximately 250 nm, as illustrated in Figure 3 (c). The collected spheres were diluted 1000-fold, revealing that the CQDs were effectively distributed in water without aggregation. The

dimensions of the synthesised CQDs were verified to be around 6 – 10 nm, as ascertained by TEM, illustrated in Figure 3 (f).

4.3. UV-Vis and FTIR Analysis of Garlic CQDs

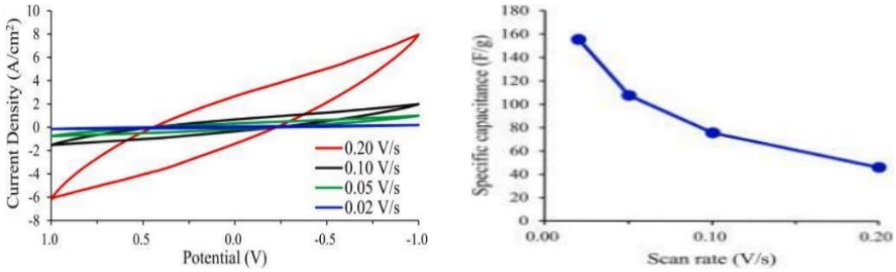
Figure 3 (d) illustrates the UV-Vis spectra of a solution of carbon quantum dots diluted 1000-fold. The absorption peak of the synthesised sample in the UV-Vis spectrum corresponds to the absorption of CQDs. A characteristic n-π* electronic transition peak is detected at 345 nm, attributable to the presence of oxygen-containing functional groups. Figure 3 (e) illustrates the aqueous solution of CQDs exposed to sunshine. The former appears yellow-brown under sunlight, while the latter is blue due to the CQDs being activated to generate fluorescence under ultraviolet irradiation.

4.4. Cyclic Voltammetry Analysis of Methylcellulose-Based Carbon Fibre Electrodes

In a three-electrode electrochemical cell, the optimal cyclic voltammetry curve should exhibit a form like a rectangle. Contact resistance or internal resistance of the electrolyte arises from the interaction between the electrode and the electrolyte, leading to a rapid ideal cyclic voltammetry curve of the desired form. Figure 4 presents cyclic voltammetry curves of methylcellulose-based C-fiber electrodes evaluated in phosphoric acid at scan speeds ranging from 0.20 – 0.02 V/s. All curves exhibit symmetrical forms at varying scan rates, indicating that the electrodes possess better capacitance attributes and optimal redox qualities. The specific capacitance of the methylcellulose-based C-fiber electrode at a scan rate ranging from 0.20 – 0.02 V/s.

Table 1. Specific capacitance values of methylcellulose-derived carbon fibre electrodes at various scan rates.

Scanning velocity (V/s)	Electrolytes	Specific capacitance (F/g)	Energy density (Wh/kg)	Power density (W/kg)
0.20	PVA/H_3PO_4	46.68	3.18	1214
0.10	PVA/H_3PO_4	76.10	5.18	1979
0.05	PVA/H_3PO_4	107.90	7.34	2806
0.02	PVA/H_3PO_4	155.58	10.59	4047



(a) (b)

Figure 4. Recycled carbon fibre electrode based on methyl cellulose in phosphoric acid electrolyte: (a) cyclic voltammetry curves at different scan speeds; and (b) Specific capacitance at varying scan rates.

The findings are illustrated in Figure 4 and enumerated in Table 1. The specific capacitance of the methylcellulose-based carbon fibre electrode augmented as the scan voltage diminished, yielding values of 46.68, 76.10, 107.9, and 155.58 F/g at scan rates of 0.02, 0.10, 0.05, and 0.02 V/s, respectively. The methylcellulose-based C-fiber electrode exhibits the best specific capacitance at a scan rate of 0.02 V/s compared to all other rates. This phenomenon may occur from the elevated surface area of the C-fiber electrode, facilitating a greater influx of ions into the carbon fibre electrode at reduced scan speeds, akin to our prior findings. Furthermore, the energy density and power density of methylcellulose-based carbon fibre electrodes at various specific capacitances may be computed using equations energy density and power density. The energy density and power density of methylcellulose-based carbon fibre electrodes are 4.18, 5.18, 7.34, and 10.59 Wh/kg, and 1214, 1979, 2806, and 4047 W/kg, corresponding to specific capacitances of 46.68, 76.10, 107.9, and 46.68, respectively 155.58 F/g, as indicated in Table 1. The methylcellulose-based C-fiber electrode

demonstrated superior performance relative to other documented modified activated carbons, specifically carbon nanotubes and graphene. C-fiber demonstrates significant potential to supplant costly carbon nanotubes and graphene.

4.5. Electrochemical Assessment of Supercapacitors

The capacitance retention rate of supercapacitors utilising carbon fibre electrodes is maintained at 96% of the initial capacitance. The supercapacitor constructed with a carbon fibre electrode and a 0.1% CQDs-infused gel electrolyte exhibits a capacitance retention of 96%, indicating exceptional cyclic stability in comparison to previously documented biomass-derived carbons, such as potato starch-based activated carbon, which demonstrates 86% capacitance retention after 900 cycles, and CQDs integrated with ferrous-coordinated polypyrrole (CQDs/PPy-Fe) as a supercapacitor electrode, which retains 94.6% capacitance after 2000 cycles. The findings validated that the elevated capacitance retention rate of the carbon fibre electrode signifies excellent electrochemical performance and cycle stability. This can enhance the optimal concentration of CQDs in the electrolyte, diminish internal resistance, and augment charge transfer efficiency when including carbon fibre electrodes. This work indicates that carbon quantum dots derived from agricultural garlic skin and electrodes made from industrial waste carbon fibre may possess potential for future applications in flexible and wearable electronic devices, as well as energy storage systems.

5. CONCLUSION

Garlic peel waste, often disposed of, comprises carbon compounds that can be converted into usable materials with significant energy storage potential by pyrolysis. This approach generates CQDs that improve the specific capacitance of gel electrolytes to 110.57 F/g and support sustainable energy solutions like supercapacitors. These supercapacitors have exceptional longevity, maintaining 96% of their capacity after 2000 cycles. Moreover, carbon fibre electrodes synthesised from methylcellulose exhibit remarkable performance, attaining a specific capacitance of 155.58 F/g, an energy density of 10.59 Wh/kg, and a power density of 4047 W/kg, indicating their potential as economical substitutes for carbon nanotubes and graphene. Thermal investigation verifies the elevated thermal stability of carbon fibres and the substantial carbon content in garlic peels, affirming their appropriateness for CQDs manufacture. Characterisation indicates quasi-spherical garlic CQDs with an average diameter of 7 nm and superior dispersion characteristics, rendering them advantageous for enhancing the electrical properties of energy storage systems. This research highlights the promise of garlic peel-derived CQDs as a sustainable and effective alternative for advanced energy storage applications.

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