Review

2025 International Conference on Science Technology, Architecture, Power and Intelligent Information Technology （APIIT 2025）

Preparation and Capacitive Performance Study of Graphene/Carbon Nanotubes

Yutong Zhu [1,*]

[1] College of Chemistry (Normal), University of Nantong, Nantong, Jiangsu, China
* Correspondence: Yutong Zhu, College of Chemistry (Normal), University of Nantong, Nantong, Jiangsu, China

Abstract: Graphene and carbon nanotubes, as representatives of novel carbon materials, have demonstrated immense application potential in the field of energy storage owing to their distinctive structures and excellent physicochemical properties. Graphene boasts high electrical conductivity, a large specific surface area, and favorable mechanical properties, while carbon nanotubes are renowned for their high aspect ratio and outstanding electrical performance. Combining the two not only enables the utilization of their respective advantages but also further enhances the comprehensive performance of the material through a synergistic effect. As a highly efficient energy storage device, the performance of a supercapacitor largely depends on the characteristics of the electrode material. The graphene/carbon nanotube composite material, with its large specific surface area, excellent electrical conductivity, and good electrochemical stability, emerges as an ideal choice for supercapacitor electrode materials. This paper investigates the preparation methods of graphene/carbon nanotubes and their capacitive performance, which not only contributes to a profound understanding of the structure-property relationship of the material but also provides theoretical basis and technical support for the development of high-performance supercapacitors.

Keywords: graphene; carbon nanotubes; preparation method; capacitive properties

Received: 21 April 2025
Revised: 29 April 2025
Accepted: 16 May 2025
Published: 02 June 2025

1. Introduction

The energy crisis and environmental issues have spurred the rapid development of novel energy-storage technologies. Supercapacitors have emerged as a focal point of research owing to their high power density and long cycle life. The design of electrode materials directly impacts the performance of supercapacitors. Traditional carbon materials are constrained by their specific surface area and electrical conductivity, making it arduous to meet the demand for higher energy density. The advent of graphene and carbon nanotubes has offered a new direction for the innovation of electrode materials. The two-dimensional structure of graphene can provide abundant active sites, while the one-dimensional channels of carbon nanotubes accelerate ion transport. The combination of the two can construct a three-dimensional conductive network, remarkably enhancing the charge-storage efficiency. However, the performance of composite materials is significantly influenced by the preparation methods: the physical method is easy to operate but has weak interfacial bonding, while the chemical method strengthens the interaction through functional group modification but may introduce structural defects. Electrochemical characterization techniques such as cyclic voltammetry have revealed the synergistic mechanism of the electric double-layer and pseudocapacitance of composite materials, and the galvanostatic charge-discharge test has quantified their cycle stability. Current research needs further addressing of the uniformity issue in large-scale preparation and exploring green synthesis routes to facilitate its transition from the laboratory to practical applications.

2. Overview of graphene/carbon nanotubes

2.1. Structure and properties of graphene

Graphene is a two-dimensional honeycomb lattice structure formed by carbon atoms with sp^2 hybrid orbitals. Its single-layer thickness is merely 0.34 nanometers, making it one of the thinnest materials discovered to date. This distinctive structure endows graphene with a series of excellent physical and chemical properties. Graphene exhibits extremely high electrical conductivity, with an electron mobility reaching up to 200,000 $cm^2/V \cdot s$, far exceeding that of traditional semiconductor materials. Its mechanical strength is also remarkably prominent, with a tensile strength as high as 130 GPa, more than 100 times that of steel. Moreover, the specific surface area of graphene is as high as 2630 m^2/g, which offers immense potential for its application in the field of energy storage. The optical properties of graphene are equally eye-catching, with a light transmittance of up to 97.7%, making it almost transparent. In terms of chemical stability, graphene exhibits good corrosion resistance and oxidation resistance, enabling it to maintain stable performance even in harsh environments. These properties enable graphene to demonstrate broad application prospects in fields such as electronic devices, energy storage, and sensors. The structure and properties of graphene not only bring new research hotspots to the field of materials science but also provide new ideas for solving energy and environmental problems [1].

2.2. Structure and Properties of Carbon Nanotubes

Carbon nanotubes are one-dimensional tubular structures formed by the curling of graphene sheets. Their diameters are typically on the nanoscale, while their lengths can reach the micrometer or even millimeter level. According to the number of tube walls, carbon nanotubes can be classified into single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). SWCNTs are formed by the curling of a single layer of graphene, exhibiting an extremely high aspect ratio and excellent electrical conductivity, with an electron mobility of up to 100,000 $cm^2/V \cdot s$. MWCNTs are formed by the coaxial curling of multiple layers of graphene, featuring enhanced mechanical strength and thermal stability. Their tensile strength can reach as high as 150 GPa, and their thermal conductivity can reach 3000 $W/m \cdot K$. The tubular structure of carbon nanotubes provides them with a unique electron-transport channel, enabling them to demonstrate rapid charge-transport capabilities in electrochemical energy storage. Additionally, the high specific surface area and abundant surface active sites of carbon nanotubes endow them with extensive applications in the fields of adsorption and catalysis. However, the dispersibility and interfacial bonding ability of carbon nanotubes pose major challenges in their practical applications. Their performance can be effectively improved through surface functionalization or compounding with other materials. The structure and characteristics of carbon nanotubes have brought new possibilities to the fields of energy storage, electronic devices, and composite materials, and research on them is still deepening continuously.

2.3. Advantages of graphene/carbon nanotube composites

Graphene/carbon nanotube composites combine the distinctive advantages of the two materials and demonstrate immense potential in the field of electrochemical energy storage. The two-dimensional structure of graphene offers a high specific surface area and abundant active sites, while the one-dimensional tubular structure of carbon nanotubes constructs an efficient electron transport channel. The combination of the two forms a three-dimensional conductive network, which not only enhances the charge transfer efficiency but also strengthens the mechanical strength of the material. Graphene sheets can effectively prevent the agglomeration of carbon nanotubes, and carbon nanotubes act as "pillars" to support the graphene sheets, preventing them from restacking and thus maintaining a high specific surface area. This synergistic effect significantly improves the electrochemical performance of the composite material, enabling it to exhibit higher specific capacitance and cycling stability in supercapacitors. Moreover, the preparation methods of the composite material are flexible and diverse, and the performance can be optimized by adjusting the proportion and interface structure. The research on graphene/carbon nanotube composites provides new insights for the development of high-performance energy storage devices, and its application prospects are broad. However, how to achieve large-scale preparation and cost control remains the focus of future research.

3. Preparation methods of graphene/carbon nanotubes

3.1. Physical Preparation Methods

The physical preparation method is one of the key approaches for the synthesis of graphene/carbon nanotube composites. Its core lies in utilizing mechanical force or physical action to achieve the dispersion and combination of materials. The ball-milling method is a common physical approach. Through high-energy ball milling, graphene and carbon nanotubes are mixed, and their uniform dispersion is realized by means of mechanical shear force. This method is simple to operate and relatively low-cost, yet it may cause partial damage to the material structure. The ultrasonic dispersion method exploits the cavitation effect of ultrasonic waves to exfoliate and uniformly mix graphene sheets and carbon nanotubes, enabling the acquisition of composites with excellent dispersibility in a relatively short period. The vacuum filtration method, via physical adsorption, allows graphene and carbon nanotubes to self-assemble into a thin film on the filter membrane, which is suitable for preparing flexible electrode materials. The advantage of physical methods is that there is no need to introduce chemical reagents, thus avoiding the contamination of the material surface and preserving the inherent properties of graphene and carbon nanotubes. However, the interface bonding of composites prepared by physical methods is relatively weak, which may affect their electrochemical performance [2]. Therefore, physical methods are often combined with other methods to further enhance the comprehensive performance of the materials. The research on physical preparation methods provides a technological foundation for the large-scale production of graphene/carbon nanotube composites, but further exploration is still required for process optimization and performance improvement.

3.2. Chemical Preparation Methods

Chemical preparation methods are important techniques for synthesizing graphene/carbon nanotube composites. The core of these methods lies in achieving the compounding and functionalization of materials through chemical reactions. Chemical vapor deposition is a typical approach. At high temperatures, the carbon-source gas is decomposed, enabling the simultaneous growth of graphene and carbon nanotubes on the substrate to form a tightly-bonded composite material. This method can precisely control the structure and morphology of the material, yet it incurs relatively high equipment costs and involves complex processes. The solution-chemistry method realizes the compounding through the self-assembly of graphene oxide and functionalized carbon nanotubes in solution. It is simple to operate and easy to scale up. The reduced graphene oxide method utilizes chemical reducing agents to reduce graphene oxide while combining it with carbon nanotubes, which can effectively improve the electrical conductivity of the material. The composites prepared by chemical methods feature strong interfacial bonding and stable performance. However, they may introduce impurities or defects, which could affect the material's performance. Functionalization treatment is one of the advantages of chemical methods. By introducing functional groups or doping elements, the electrochemical properties of the material can be regulated. The research on chemical preparation methods provides an important avenue for optimizing the performance of graphene/carbon nanotube composites. Nevertheless, their development towards being more environmentally friendly and cost-effective remains the direction for future development.

3.3. Other Preparation Methods

Apart from physical and chemical methods, the preparation of graphene/carbon nanotube composites also includes other innovative techniques. These methods demonstrate unique advantages in specific scenarios. The electrochemical deposition method is an efficient approach. By applying a voltage on the electrode surface, graphene and carbon nanotubes are simultaneously deposited to form a uniform composite film. This method is suitable for preparing high-performance electrode materials, yet the process parameters need to be precisely controlled. The hydrothermal method utilizes a high-temperature and high-pressure environment to react graphene oxide with carbon nanotubes in a solution, thereby forming a composite material with a stable structure. The hydrothermal method is simple to operate, but the reaction conditions are relatively harsh. The template method relies on the confinement effect of porous templates to guide the ordered growth of graphene and carbon nanotubes, enabling the acquisition of composite materials with specific morphologies. The biological template method takes advantage of the self-assembly characteristics of biomolecules to provide an environmentally friendly way for the synthesis of composite materials. Each of these methods has its own characteristics and can meet the requirements of different application scenarios. However, their large-scale production and cost control still need further optimization. The research on other preparation methods provides new ideas for the diversified development of graphene/carbon nanotube composites and promotes the exploration of their applications in fields such as energy and catalysis [3].

3.4. Comparison and Selection of Preparation Methods

There are a wide variety of preparation methods for graphene/carbon nanotube composites, and each method has its own unique advantages and limitations. To select an appropriate preparation method, one must comprehensively consider factors such as material properties, process conditions, cost, and application requirements. Physical methods, such as ball-milling and ultrasonic dispersion, are simple to operate and relatively low-cost, making them suitable for large-scale production. However, the interfacial bonding of the materials is relatively weak, which may affect the electrochemical performance. Chemical methods, such as chemical vapor deposition and solution chemistry, can achieve precise control of the material's structure and functionalization, with strong interfacial bonding and stable performance. Nevertheless, the processes are complex and may introduce impurities or defects. Other methods, such as electrochemical deposition and hydrothermal synthesis, demonstrate unique advantages in specific scenarios, but large-scale production and cost control still need to be optimized. When choosing a preparation method, material properties are the primary consideration. For instance, for high-performance electrode materials, chemical vapor deposition and electrochemical deposition can provide high conductivity and strong interfacial bonding, yet they are relatively costly. For flexible electronic devices, vacuum filtration and templating methods can prepare uniform thin-film materials, but the process conditions are rather demanding. Cost-effectiveness and production efficiency are also key considerations. Physical methods are suitable for large-scale production, but their performance may be limited; chemical methods offer excellent performance but at a higher cost. Application requirements also influence the method selection. In the field of energy storage, composites with high conductivity and large specific surface area are required, and chemical and electrochemical methods are more suitable; in the field of catalysis, functionalization treatment and environmentally friendly preparation routes are needed, and biological templating and hydrothermal methods have more advantages. Comparing different preparation methods requires balancing multiple factors, as no single method can satisfy all requirements. Future research should focus on developing low-cost, efficient, and environmentally friendly preparation technologies, while exploring the combination and optimization of multiple methods to further enhance the comprehensive performance and application potential of graphene/carbon nanotube composites.

4. Characterization of Capacitive Properties of Graphene/Carbon Nanotubes

4.1. Cyclic voltammetry (CV)

Cyclic voltammetry (CV) stands as a crucial electrochemical characterization method for investigating the capacitive properties of graphene/carbon nanotube composites, which can intuitively reflect the charge-storage behavior and electrochemical activity of the materials. This method entails applying a linearly varying voltage to the electrode and measuring the resulting current response to obtain the cyclic voltammogram. The shape and area of the curve directly mirror the capacitive performance of the material. An ideal electric double-layer capacitor presents a rectangular shape in the CV curve, indicating its ideal capacitive behavior and rapid charge-discharge capability. The CV curve of the graphene/carbon nanotube composite typically shows a shape between rectangular and quasi-rectangular, indicating the presence of both electric double-layer capacitance and pseudocapacitance. The CV method can effectively evaluate the specific capacitance, electrochemical stability, and charge-transfer kinetics of the material. The specific capacitance can be calculated by integrating the area of the CV curve; a larger value implies a stronger charge-storage capacity of the material. Electrochemical stability is evaluated through multiple cyclic tests. The smaller the changes in the curve shape and area, the higher the stability of the material. Charge-transfer kinetics can be analyzed by examining the influence of the scan rate on the CV curve. At a low scan rate, the curve shape can better reflect the intrinsic capacitive behavior of the material, while at a high scan rate, it can reveal the material's rapid charge-discharge ability. The CV curve of the graphene/carbon nanotube composite typically exhibits a relatively high specific capacitance and favorable electrochemical stability, which can be attributed to the high specific surface area of graphene and the high conductivity of carbon nanotubes [4]. The synergistic effect of the composite enables more efficient charge transfer and significantly enhances the capacitive performance. The research using the CV method provides an important basis for optimizing the structure and performance of the material. However, its results are highly influenced by the testing conditions, and thus need to be comprehensively analyzed in combination with other characterization methods. The application of the CV method in the study of the capacitive properties of graphene/carbon nanotube composites offers strong support for the development of high-performance supercapacitor electrode materials.

4.2. Constant current charge/discharge (GCD)

The galvanostatic charge-discharge (GCD) method is another crucial electrochemical characterization technique for evaluating the capacitive performance of graphene/carbon nanotube composites, which can directly reflect the charge-storage capacity and electrochemical stability of the materials. This method measures the change in voltage over time by applying a constant current to the electrode to obtain the charge-discharge curve. The curve shape and duration directly reflect the capacitive characteristics of the materials. An ideal electric double-layer capacitor exhibits a symmetric triangular shape in the GCD curve, indicating its ideal capacitive behavior and reversible charge-discharge process. The GCD curves of graphene/carbon nanotube composites typically fall between a triangular and a quasi-triangular shape, suggesting that they possess both electric double-layer capacitance and pseudocapacitance characteristics. The GCD method can effectively calculate the specific capacitance, energy density, and power density of the materials. The specific capacitance can be calculated from the charge-discharge time and current density. A larger value indicates a stronger charge-storage capacity of the material. Energy and power densities are calculated from the voltage window and discharge duration. Higher values signify stronger energy-storage and energy-release capabilities of the material. Electrochemical stability is evaluated through multiple cycle tests. The smaller the changes in the shape of the charge-discharge curve and the specific capacitance, the higher the stability of the material. The GCD curves of graphene/carbon nanotube composites usually exhibit high specific capacitance and good electrochemical stability, which benefits from the high specific surface area of graphene and the high conductivity of carbon nanotubes. The synergistic effect of the composite enables more efficient charge transfer and significantly enhances capacitive performance. The research on the GCD method provides an important basis for optimizing the structure and performance of the materials. However, its results are greatly affected by the test conditions and need to be comprehensively analyzed in combination with other characterization methods. The application of the GCD method in the study of the capacitive characteristics of graphene/carbon nanotube composites provides strong support for the development of high-performance supercapacitor electrode materials [5].

4.3. Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) serves as a crucial characterization method for investigating the capacitive properties of graphene/carbon nanotube composites, capable of delving deep into the charge-transport mechanism and interfacial characteristics of the materials. This method measures the impedance response of the system at different frequencies by applying a small-amplitude alternating voltage, thereby obtaining Nyquist and Bode plots. The semicircle and straight line in the Nyquist plot respectively reflect the charge-transfer resistance and diffusion impedance, while the Bode plot can intuitively demonstrate the influence of frequency on the phase angle and impedance modulus. EIS can comprehensively evaluate the charge-transport kinetics, interfacial characteristics, and electrochemical stability of the materials. The EIS spectrum of graphene/carbon nanotube composites typically exhibits a small semicircle in the high-frequency region and a straight line in the low-frequency region. A smaller semicircle indicates lower charge-transfer resistance and thus higher charge-transport efficiency. The straight line in the low-frequency region reflects the diffusion impedance of ions in the electrode material; the closer the slope is to 45 degrees, the more efficient the ion diffusion. The synergistic effect of the composites significantly reduces the charge-transfer resistance and diffusion impedance, remarkably enhancing the capacitive performance. EIS can effectively evaluate the equivalent series resistance, charge-transfer resistance, and diffusion impedance of the materials. The equivalent series resistance reflects the total internal resistance of the system; the smaller the value, the lower the energy loss. Lower charge-transfer resistance corresponds to faster electron transport at the electrode/electrolyte interface. The diffusion impedance reflects the transport ability of ions in the electrode material; the smaller the value, the faster the ion diffusion. Electrochemical stability is evaluated through multiple cycle tests. The smaller the change in the impedance spectrum, the higher the material stability. The application of EIS in the study of the capacitive properties of graphene/carbon nanotube composites provides an important basis for optimizing the material structure and performance. EIS can comprehensively reveal the charge transport mechanisms and interfacial characteristics of the materials, offering strong support for the development of high-performance supercapacitor electrode materials. The research on EIS provides a new perspective for understanding the capacitive performance of graphene/carbon nanotube composites, yet its results are greatly influenced by the testing conditions and thus need to be comprehensively analyzed in combination with other characterization methods.

5. Conclusion

Graphene/carbon nanotube composites exhibit tremendous potential in the field of supercapacitor electrode materials owing to their distinctive structures and excellent properties. Various preparation methods enable control over the material's microstructure and surface properties, thereby optimizing its capacitive performance. Electrochemical testing methods, such as cyclic voltammetry, galvanostatic charge-discharge, and electrochemical impedance spectroscopy, provide powerful tools for evaluating the capacitive performance of the materials. In the future, with the continuous advancement of preparation technologies and the increasing refinement of characterization means, the application prospects of graphene/carbon nanotube composites in supercapacitors and other energy-storage fields will be even broader. In-depth research on the structure–property relationship and the development of efficient, low-cost preparation methods will be essential for advancing the field.

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