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Structure and Performance Analysis of New Carbon Nanomaterials Based on Microscopic Imaging Technology

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Abstract
Carbon nanomaterials are widely used in metallurgy, chemical engineering, energy and other disciplines due to their unique structure and properties. The huge potential application of carbon nanomaterials makes it very popular among researchers. The performance of the new carbon nanomaterials is much higher than that of the previous nanomaterials. Therefore, the research on nanomaterials is the top priority. Microscopic imaging technology is an important technical means for studying carbon nanomaterials. Microscopic imaging technology has better detection functions in the field of microscopic detection. Microscopic imaging technology can explore the molecular arrangement and structural functions of new carbon nanomaterials in the microscopic field. This study summarizes and analyzes the application of microscopic imaging technology in the field of carbon nanomaterials research. On this basis, the structure and properties of a new type of carbon nanomaterials-carbon nanotubes were analyzed.

Keywords: Microscopic Imaging Technology, Carbon Nanomaterials, Carbon Nanotubes

1. Introduction

Nanomaterials are a kind of emerging materials which have developed rapidly in recent years. At present, it has been widely used in the fields of metallurgy, chemical industry, food storage, paint, energy and daily necessities. Nanoscience and technology are the study of the properties and interactions of substances on the nanoscale. And multi-disciplinary high-tech that makes use of these characteristics. In recent years, the research and application of carbon nanomaterials in nanomaterials have developed rapidly. Since the discovery of carbon nanotubes, its unique electrical, mechanical and other physical and chemical properties have made it a great potential application in field emission displays, microelectronic devices, hydrogen storage materials, composite material additives and other fields [1, 3]. As a result, carbon nanomaterials have received much attention from many scientists at home and abroad for nearly two decades.

There are many ways to study nanomaterials. Such as electron microscopy technology, diffraction technology, spectroscopy technology, thermal analysis technology and various magnetic spectrum, surface analysis spectrum and dynamic structure spectrum. Among these analysis methods, electron microscopy is the earliest, most widely used and most commonly used nanomaterial research method. This study is based on microscopic imaging technology to further analyze the structure and properties of carbon nanomaterials.

2. Application of Microscopic Imaging Technology in the Research of Carbon Nanomaterials

2.1. Application Characteristics of Various Microscopic Imaging Techniques

Electron microscopy technology uses electron beams as the light source. It is an analysis technology that uses a certain shape of electrostatic field or magnetic field to focus imaging. It has a higher resolution than ordinary optical microscopes. According to the different signals detected, According to the different signals detected, electron microscopy mainly includes transmission electron microscope (TEM), scanning electron microscope (SEM), scanning transmission electron microscope (STEM), scanning tunneling microscope (STM). In addition, the electron microscope also includes atomic force microscope (AFM), electron probe (EPM), Auger electron spectroscopy (AES), field emission microscope (FEM) and field ion microscope (FIM). In this study, the following comprehensive analysis of the application of these microscopy techniques in nanomaterials was conducted:

SEM is widely used in the analysis of nanomaterials. It can be used for particle size analysis, morphology analysis and microstructure analysis of nanomaterials. SEM generally only provides micrometer or submicron topography information, and its resolution is lower than that of TEM. Therefore, the characterization results are not as accurate as transmission electron microscopy. But the current SEM is equipped with X-ray energy spectrometer device. It can simultaneously observe the microstructure morphology and analyze the micro-components. It is a scientific research instrument commonly used today.

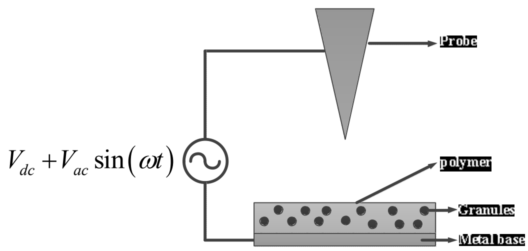
Transmission electron microscopes are generally divided into analytical transmission electron microscopes and high-resolution transmission electron microscopes. The high resolution of TEM can be used to research the crystallization of nanomaterials and observe the morphology of nanoparticles. It is an important instrument for studying the microstructure of materials. Transmission electron microscopy is one of the most intuitive methods to measure the particle size and distribution of nanomaterials. The reliability of this method is high, but the accuracy depends largely on the representativeness of sampling and the selection of scanning area.

STM uses tunnel current to study the surface morphology and surface electronic structure of materials. It is currently the highest resolution microscope in the world. One of the most striking achievements of STM in nanotechnology is the operation and control of single atoms [13]. STM can not only observe the atomic or electronic structure of the surface of the nanomaterial, but also reconstruct the surface and the surface covered with adsorbate. It can also observe structural defects such as atomic steps, platforms, pits, and mounds on the surface.

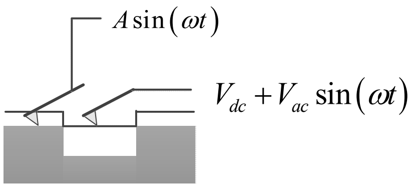
The working principle of atomic force microscope is similar to STM. And AFM makes up for the shortcomings that STM can only directly observe conductors and semiconductors. AFM can study the surface of insulators with very high resolution. Its horizontal and vertical resolutions exceed those of ordinary scanning electron microscopes. Moreover, AFM requires much less working environment and sample preparation than electron microscope. In the study of nanomaterials, AFM can be used to analyze the morphology of nanostructured materials, including nanocrystalline solid films, LB films, and nanostructured ceramic materials. Generally, AFM can be combined with TEM or STM technology to study nanoparticles. In addition, the use of conductive AFM can study the electrical properties of nanomaterials, and can also manipulate atoms, molecules, nanoparticles and nanotubes.

2.2. Application and Working Principle of KPFM in the Research of Carbon Nanomaterials

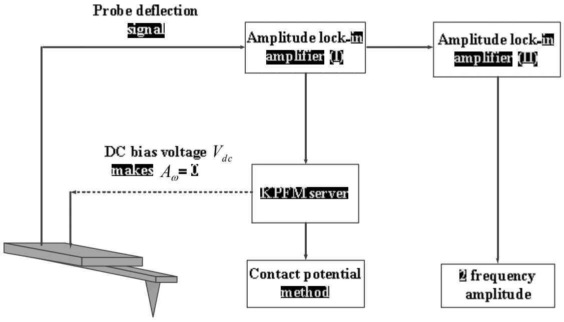
Kelvin probe force microscopy (KPFM) is a tool developed in the 1990s to measure the contact potential difference between the tip of the atomic force microscope and the sample. KPFM is commonly used in the study of nanoscale electrical properties such as semiconductor surfaces and semiconductor devices[4,5]. The simplified structure of KPFM includes a conductive probe and a sample to be tested, as shown in Figure 1 (a). In use, first the probe vibrates at the first-order resonance frequency, and the surface morphology of the sample is obtained in a conventional tapping mode. Then, the probe scans along the measured surface profile and lifts a constant height z_{offset}. A DC bias voltage V_{dc} and an AC voltage $V_{ac}\sin(\omega t)$ are added between the probe and the sample. The distribution of work function on the sample surface is obtained from the vibration signal of the probe under the action of electrostatic force, as shown in Figure 1 (b). In the figure, ω_{res} is the probe resonance frequency. Figure 1 (c) is a schematic diagram of the structure of KPFM in amplitude modulation mode. The amplitude lock-in amplifiers I and II resolve the ω and 2ω components of the probe amplitude signal, respectively A_{ω} and $A_{2\omega}$.



(a) Schematic diagram of probe-sample interaction



(b) Schematic diagram of imaging mode



(c) Schematic diagram of KPFM

Figure 1. Schematic diagram of KPFM

The electrostatic force between the KPFM conductive probe and the sample can be expressed as:

$$F_{ts} = -\frac{1}{2}\frac{\partial C}{\partial z}\Delta V^2 \tag{1}$$

In formula (1): z is the distance between the probe tip and the sample. ΔV is the potential difference between the probe and the sample. $\frac{\partial C}{\partial z}$ is the gradient of the capacitance between the probe and the sample with respect to the distance z.

When a voltage $V_{ac}\sin(\omega t)+V_{dc}$ is applied to the probe, the potential difference ΔV between the probe and the sample is:

$$\Delta V = V_{dc} - V_{cpd} + V_{ac}\sin(\omega t) \tag{2}$$

Where V_{cpd} is the contact potential difference between the probe and the sample. Substituting ΔV into equation (1) gives:

$$F_{ts} = -\frac{1}{2}\frac{\partial c}{\partial z}\left[\left(V_{dc}-V_{cpd}\right)+V_{ac}\sin\left(\omega t\right)^2\right] \tag{3}$$

Expanding equation (3), it can be seen that the electrostatic force between the probe and the sample is composed of three parts, respectively：

$$F_{dc} = -\frac{1}{2}\frac{\partial c}{\partial z}\left[\left(V_{dc}-V_{cpd}\right)^2+\frac{1}{4}V^2{}_{ac}\right] \tag{4}$$

$$F_{\omega} = -\frac{\partial c}{\partial z}\left(V_{dc}-V_{cpd}\right)V_{ac}\sin\left(\omega t\right) \tag{5}$$

$$F_{2\omega} = \frac{1}{4}\frac{\partial c}{\partial z}V^2{}_{ac}\cos\left(2\omega t\right) \tag{6}$$

F_{dc} is a constant electrostatic force, which causes the static bending of the conductive probe. F_ω has the same frequency as the applied AC voltage $V_{ac}\sin(\omega t)$ and is proportional to the difference $(V_{dc}-V_{cpd})$ between the DC voltage V_{dc} and the contact potential difference V_{cpd}. F_ω drives the conductive probe to vibrate with an amplitude of A_ω. To measure V_{cpd}, the KPFM controller changes the magnitude of V_{dc} in real time to make the amplitude A_ω zero. At this time, $V_{cpd} = V_{dc}$. After obtaining the contact potential difference on the sample surface, the local work function can be calculated by formula $\varphi_{sample} = \varphi_{tip} - eV_{cpd}$. In the formula, φ_{sample} and φ_{tip} are the work functions of the sample and the probe, respectively, and e is the electron charge. The force $F_{2\omega}$ is proportional to the square of the capacitance gradient $\partial C/\partial z$ and the AC voltage V_{ac}. In this way, the capacitance gradient $\partial C/\partial z$ between the probe and the sample can be measured. The presence of sub-surface nanomaterials will change the local capacitance gradient, causing the corresponding force $F_{2\omega}$ to change. So that the detectable probe vibration signal changes. Therefore, an image contrast reflecting the subsurface structure and material properties is formed in the probe vibration amplitude image at the frequency doubling.

3. Carbon Nanotube Structure

Because of its unique structure and performance, carbon nanotubes（CNTs） have become the most widely studied new materials. In this study, the structure and properties of the new carbon nano materials will be analyzed in detail.The ratio of the length and diameter of CNTs is much larger than that of ordinary fiber materials, so it is often called "super fiber". And CNTs can be regarded as nanotubes formed by single or multiple layers of graphite sheets curled around the central axis according to a certain degree of helix. The ends of the tube are generally sealed by a carbon pentagonal hemispherical grid.Carbon nanotubes can be divided into single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) according to the number of curled graphite layers[7]. SWCNTs can be regarded as a single-layer graphite sheet curled, with good symmetry and simplicity. Due to its unique quasi-one-dimensional structure, SWCNTs exhibit excellent mechanical, electrical, optical and thermal properties. And many research results show that SWCNTs is a very ideal nanoelectronic device, and has great potential applications in single electron transistors, field effect transistors and sensors. The schematic diagram of the structure of SWCNTs is shown in Figure 1. The transmission electron micrograph of SWCNTs is shown in Figure 2.

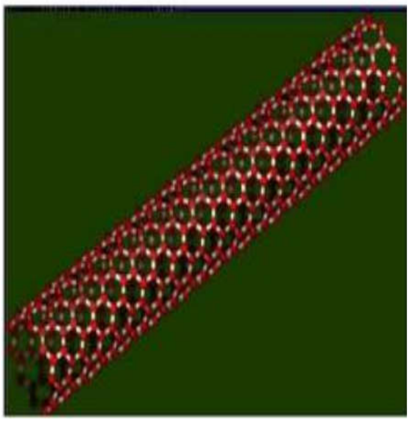


Figure 1. Schematic diagram of SWCNTs structure

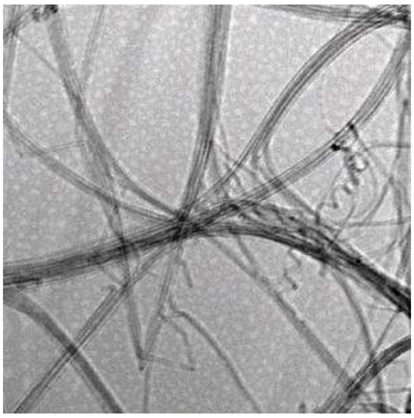


Figure 2. Transmission electron micrograph of SWCNTs

MWCNTs can be seen as curled multilayer graphite sheets. The diameter of MWCNTs is between a few nanometers and tens of nanometers, and the length can be up to several millimeters. The fixed distance between adjacent layers is about 0.34 nanometers, which is equivalent to that of graphite. The structure of MWCNTs is shown in Figure 3. The transmission electron micrograph of MWCNTs is shown in Figure 4.

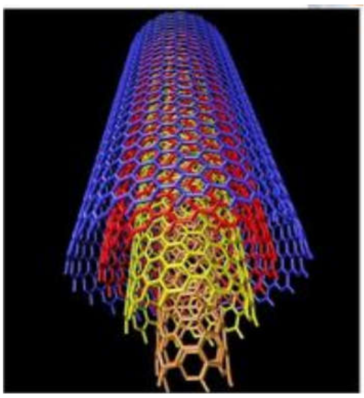


Figure 3. The structure of MWCNTs

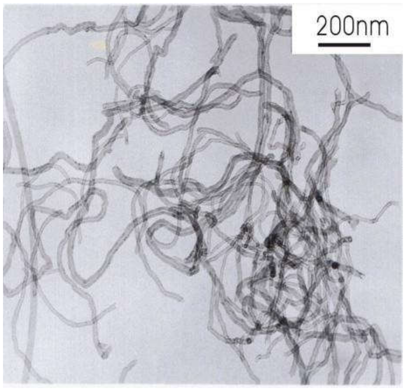


Figure 4. Transmission electron micrograph of MWCNTs

4. Performance of Carbon Nanotubes

4.1. Mechanical Properties of Carbon Nanotubes

Carbon nanotubes have unique spatial structural integrity and the strongest σ chemical bond between -C-C atoms in nature. Therefore, carbon nanotubes have many unique physical and chemical properties, especially the high strength and high elastic modulus in terms of mechanical properties. The strength and toughness of carbon nanotubes are far superior to any fiber[6]. Its strength is about 200 times higher than other fibers, and it can withstand about 1 million atmospheres without breaking.

So far, we have mainly used TEM and AFM to test the mechanical properties of carbon nanomaterials. The main methods are as follows:

1. erved by TEM to calculate the Young's modulus.
2. The Young's modulus is obtained by measuring the fluctuation of the current after the heat causes the tube to vibrate. This method generally only targets large-sized nanotubes with vibration frequencies on the order of a few megahertz.
3. TEM directly observes the performance of single carbon nanomaterials by observing the electric field leading to a mechanical response.
4. For carbon nanotubes fixed at one end, the force and static displacement are measured under AFM to obtain the Young's modulus.
5. For ultra-long carbon nanotubes (2mm), it can be directly measured with a small stretching device.

4.2. Electromagnetic Properties of Carbon Nanotubes

In CNTs, due to the quantum confinement effect of electrons, electrons can only move along the axial direction of the carbon nanotubes in the graphite sheet, and their radial motion is limited. Carbon nanotubes can exhibit both metallic and semiconducting properties. Even in different parts of the same carbon nanotube, they can exhibit different electrical conductivity as their structure changes[8,9]. Therefore, carbon nanotubes have very unique electrical properties. Because carbon nanotubes have a large length-to-diameter ratio, their tips have nano-scale curvature, and can be excited at a relatively low voltage to emit a large number of electrons. Therefore, carbon nanotubes also exhibit very excellent field electron emission characteristics. Carbon nanotubes have very stable chemical properties and extremely high mechanical strength. A large number of research results indicate that carbon nanotubes are an ideal field emission electron source. The schematic diagram of carbon nanotubes as ultrafast emitters with narrow frequency energy diffusion is shown in Figure 5.

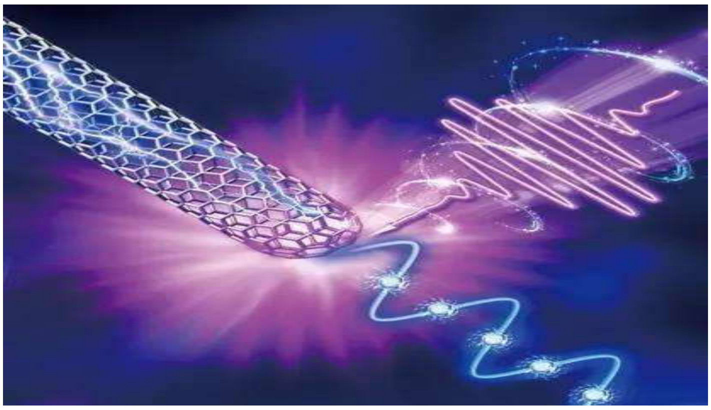


Figure 5. Carbon nanotubes as ultrafast emitters with narrow frequency energy diffusion

In addition, the magnetic and magnetic susceptibility of carbon nanotubes are higher than graphite, fullerene, activated carbon and so on. And certain types of carbon nanotubes exhibit diamagnetic properties.

4.3. Optical Properties of Carbon Nanotubes

Due to the strange optical properties exhibited by CNTs, such as optical polarization, correlation, good luminous performance, and sensitivity to infrared radiation, etc. The optical properties of carbon nanotubes have attracted more and more attention. Carbon nanotubes can emit strong visible light under the excitation of infrared laser, which has excellent photoluminescence and electroluminescence characteristics. In addition, carbon nanotubes have high sensitivity and low noise to infrared radiation detection, and have the potential to be high-quality infrared detectors.

In addition, in the research of the optical response of carbon nanotubes, it is found that its optical properties are closely related to its shape and structure. Periodic carbon nanotube arrays can exhibit properties such as photonic band gap, plasmon resonance, and Bragg diffraction. The interaction of non-periodic carbon nanotube arrays and light waves is similar to the interaction of radio antennas and radio waves.

4.4. Thermal Properties of Carbon Nanotubes

Because carbon nanotubes are made of graphite sheet curled. The unique structural characteristics of carbon nanotubes have a great influence on their thermal properties, and are considered to be one of the best known thermally conductive materials in the world. It relies on ultrasonic waves to transmit heat at a transmission speed of up to 10,000 meters per second. And research found that carbon nanotubes can only transfer heat in one dimension. Even if carbon nanotubes are bundled together, heat will not be transferred from one to another nanotube. Because carbon nanotubes exhibit a quasi-one-dimensional nanostructure. Its thermal conductivity shows a great difference in the direction parallel to the axis and perpendicular to the axis. The thermal conductivity in the direction parallel to its axis is twice that of diamond, and its value is as high as 6600W/(m·k), which is the highest value of materials known in nature. But in the direction perpendicular to its axis, its thermal conductivity is very small. This feature makes carbon nanotubes likely to become the basic raw materials for the production of protective materials and controllable thermally conductive materials for various high-temperature components in the future.

4.5. Chemical Properties of Carbon Nanotubes

Carbon nanotubes have a relatively large specific surface area. Carbon nanotubes have a special pipe structure and a graphite-like layered structure. Therefore, carbon nanotubes have become the most potential hydrogen storage materials, and have a very important role in fuel cells[10]. And the unique tubular structure of carbon nanotubes makes carbon nanotubes have extremely strong capillary properties, and can be filled with metal or oxide into the open carbon nanotube template to form a unique one-dimensional nanomaterial. These low-dimensional nanomaterials and technologies may allow microelectronic devices to enter the nano age. And because carbon nanotubes have the characteristics of nanotube cavity structure, extremely high specific surface area and good conductivity, when they are used to promote electrode reactions, electron transfer reactions can occur. Therefore, as a new generation of electrode materials, carbon nanotubes are widely used in energy storage devices such as supercapacitors. The SEM image of the electrode materials based on CNTs is shown in Figure 6.

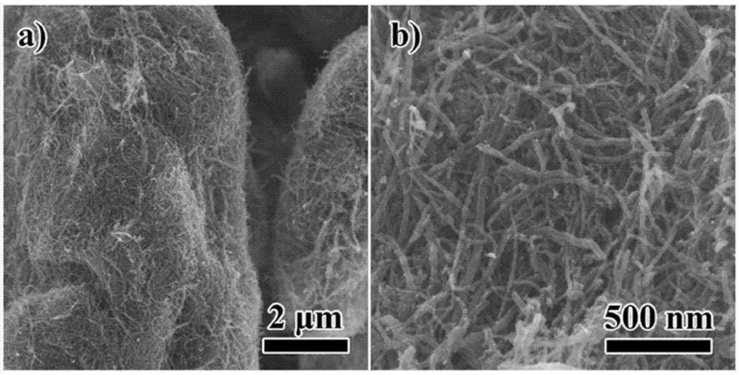


Figure 6. SEM image of the electrode materials based on CNTs

5. Summary

With the application of micro imaging technology, the structure and properties of carbon nanotubes are gradually mastered by us. This makes carbon nanotubes play an important role in many fields.Although the research of carbon nanotubes has attracted much attention in the past two decades. Research scholars have also done a lot of breakthrough work. However, research on other new types of carbon nanomaterials such as carbon nanoribbons, carbon nanospheres, etc. is very rare. We need to combine microscopic imaging based on nanomaterial research. It helps researchers more intuitively recognize the structure of carbon nanomaterials. At the same time, it promotes researchers to more fully understand and prepare new carbon nanomaterials. It will be better applied to various fields such as chemical industry, energy, metallurgy and so on.

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