Carbon Nanotube: Property, application and ultrafast optical spectroscopy

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Introduction

Aside from diamond, graphite and \( C_{60} \), a new form of carbon was found in 1991, which is multi-walled carbon nanotube. Ever since the finding of single-walled carbon nanotube which is two years later, carbon nanotubes have attracted the attention of researchers’ world around. Significant amount of work has been done to reveal the chemical, mechanical, and electrical properties of this interesting material; and all kinds of applications have been proposed on carbon nanotube to fully utilize its unique properties. In this review paper, the properties and the applications of carbon nanotube are presented, and the challenge and future of this area are discussed.

The structure of this review will be as follows. First, the definition of carbon nanotube is given. Second, we will describe the mechanical and electrical properties of carbon nanotube. Third, we will describe the ultra-fast optical spectroscopy of carbon nanotube. After that, the applications of carbon nanotube are discussed. And we mainly cover its biological applications. Lastly, we briefly summarize and speculate its future applications.

Definition of CNT (carbon nanotube)

A SWNT (single wall carbon nanotube) is formed by rolling up a layer of grapheme sheet into a seamless cylinder. Its diameter is in the range of 1~ 2 nm and it can be as long as hundreds of microns. Figure 1 shows the rolling up process for a layer of grapheme sheet to form a SWNT. In the figure, \( a_1 \) and \( a_2 \) are the fundamental vectors of the grapheme sheet. The beginning and the end of vector \( \overrightarrow{OA} \) join together to form a SWNT cylinder, and \( \overrightarrow{OA} \) is called the rolling up vector. This rolling up vector can be decomposed as: \( \overrightarrow{OA} = na_1 + ma_2 \), and the corresponding nanotube is labeled as \((n, m)\) tube. This \((n, m)\) vector sets the diameter of a nanotube, and the so called
“chirality”. In the following chapters, we will see that this index determines the band structure of a carbon nanotube.

Properties

1. Mechanical properties

Compared to conventional carbon fiber, carbon nanotubes are composed of the same carbon-carbon bond but are highly organized. Thus they are believed to be the “ultimate carbon fiber” human have ever made. Since traditional carbon fiber have specific strength fifty times higher than that of steel, it is reasonable to deduce that carbon nanotube can outperform carbon fiber easily and expected to be used in high strength, light weight and high performance composite materials.

It is known that carbon-carbon bonds are one of the strongest chemical bond in nature, and carbon nanotube is based on a perfect arrangement of these bonds oriented along the tube axis, we can expect the carbon nanotube to be extremely strong. In fact, theoretical work showed that the Young’s modulus of SWNT is as high as 1TPa, which is that of in-plane non-defect graphite crystal. However, experimental measurement of a single SWNT is difficult and experiments are still in progress.

2. Electrical properties

As we mentioned in previous chapter, a carbon nanotube is label with (n, m) index. This index is important because the diameter and the chirality are determined by it. Theoretical works show that, if \( n = m \) SWNT is a metal; if \( n - m = 3j \) while j is a non-zero integer, SWNT is a tiny-bandgap semiconductor; and for all the rest of (n, m) combinations, SWNT are large bandgap semiconductor. And for semiconductor SWNT, its bandgap is determined by the diameter of the
nanotube. For tiny-bandgap SWNT, it is shown that $E_g \propto 1/R^2$; and for large-bandgap SWNT, it is shown that $E_g \propto 1/R$. **Figure 2** shows the electrical band structure of a $(7,0)$ SWNT and that of a $(7,7)$ SWNT, the difference between a metallic SWNT and a semiconductor SWNT is clearly shown here.

It is obvious that a carbon nanotube is 1D confined material, thus we should expect spikes in the DOS (density of state) of SWNT due to its 1D nature. Current vs voltage measurement of SWNT is performed, and the $dI/dV$ curve is used to characterize the DOS. **Figure 3** shows the experiment result and the corresponding theoretical calculation. One graph shows very good agreement between the experiment and the theoretical result, but the other one shows some deviation between the two. Further investigation is needed to resolve this discrepancy; however, a spike-like 1D DOS is clearly shown here.

**Ultra-fast optical spectroscopy of SWNT**

Although carbon nanotube has shown excellent mechanical and electrical properties, its optical properties are still not quite clear, and many important questions for carbon nanotube still remain unsolved. Among them, the exciton effects on the optical properties are crucial, because excitons have significant effect on quantum confined material system. In this chapter, excitonic properties of SWNT are studied through ultra-fast optical spectroscopy. Both auger recombination and many-body effect of confined excitons are studied, and the possibility of nanotube-based optoelectronics devices is discussed.

1 Auger recombination of excitons
Auger recombination is the non-radiative recombination of electron-hole pairs, in which the recombination energy is transferred to a third particle (electron or hole) that is excited to a higher energy state. **Figure 4** shows the schematic diagram of an Auger process. In bulk materials, the Auger recombination process is suppressed due to the energy and momentum conservation requirement. However, in reduce dimension systems, especially 0D quantum dot and 1D quantum wire, the requirement of momentum conservation is relaxed and thus Auger recombination can be the dominant non-radiative process. Auger recombination in reduced dimension materials also differs from that of bulk material in the regime of a few excitons per particle, for which Auger recombination occurs at a sequence of quantized steps from N excitons to N-1 excitons, and finally to 1 exciton in the particle. In this quantized Auger recombination picture, Auger recombination rate is characterized by a set of discrete recombination time constants instead of a continuum of density-dependent recombination time constants as in bulk materials.

Experiments based on ultra-fast optical spectroscopy have been performed to study the Auger-like exciton-exciton recombination processes in SWNT. **Figure 5** shows the experiment setup for the pump-probe experiment, the ultra-short laser pulse is used as the pump laser for the SWNT sample; probe beam at several wavelength passes through the sample which is already excited by the pump beam. By changing the variable time delay between the pump beam and the probe beam, transient absorption data were obtained by measurement of the transmission of the probe beam. Useful information such as Auger recombination life time, population decay dynamics can be obtained by studying the pump-probe experiment data.

**Figure 6** shows a typical pump-probe experiment result. Different curves are measured at different pump intensity, starting from $2,4,8,20 \times 10^{13}$ photons/cm$^2$ for lowest curve groups, to
5.8,10,20×10^{14} \text{photons/cm}^2 \text{ for middle curve group, and } 3.4,5×10^{15} \text{photons/cm}^2 \text{ for top curve group. From the curve, it is easy to extract the Auger recombination lifetime information. And conclusions are:}

a) Although the pump beam intensity is increased in a continuous way, the transient absorption curves are clearly clustered into three groups. This grouping behavior shows the quantized Auger recombination at several excitons per particle levels. In fact, the number of exciton per SWNT changes in discrete steps from 3, to 2, and finally to 1 exciton; and each step is characterized by a specific Auger recombination lifetime.

b) The pump-probe curve shows that the Auger recombination time constant for 2 excitons and 3 excitons are extremely small, in the range of 2-3 ps. This suggests a very strong Auger-effect, compared to other quantum confinement systems. For example, Auger recombination life time for CdSe quantum rods and quantum dots are on the order of tens of ps or hundreds of ps depending on the numbers of excitons in each particle.

The ultrafast optical spectroscopy results show that Auger recombination process dominates the e-h pair recombination process, and this process is characterized by a life time in the order of several ps time scale. This rapid loss of e-h pair due to Auger recombination limits the possibility of generating population inversion in SWNT, and thus the application of SWNT in optoelectronics is quite limited. However, research also shows that the engineering of the dimension of quantum rods can actually slow down the Auger recombination rate at certain wavelengths. Thus further research may be needed to investigate the optoelectronic application of SWNT.

2. Blue-shifted exciton resonance
Aside from Auger recombination of excitons, at high exciton concentration, many-body interactions significantly affect the excitonic properties of semiconductors. Originally, exciton effects are studied through simple Hydrogen atom model, and exciton energy levels are stable when the exciton Bohr radius is smaller than the exciton-exciton distance – where this simple model is still accurate. However, at intense laser excitation level, large amounts of excitons can be created within one particle or SWNT, and the confinement of these excitons in one particle leads to the reduction of exciton distance. At this limit, many-body effects dominate and exciton energy level is renormalized.

Many-body effects have been exploited in 2D or 3D semiconductor materials, both experimentally and theoretically. Study shows that with increasing densities of excitons, the excitonic absorption spectrum can shift, broaden or saturate due to many-body effect. Intuitively, we should expect a stronger many-body effect on the exciton energy level in 1D SWNT or 0D quantum dots, because of the exciton spatial confinement. To study this effect, frequency resolved transient absorption measurement was performed for SWNT samples, because SWNTs have smaller tube diameters and thus higher spatial confinement than quantum wires. Thus we are expecting to see even strong many-body effect for SWNTs.

The experiment setup is the same as in Figure 6; the differential transmission of the probe at zero delay is plotted in Figure 7 as a function of probe wavelength; the excitation wavelength is chosen to resonantly excite the low excitonic state of SWNTs; and the excitation intensity is chosen to be $\sim 5 \times 10^{15}$ photons/cm$^2$, which corresponding to an excitonic density of $\sim 5$ excitons per SWNT. The “dip” of the transmission spectrum curve is explained by the author photon-induced absorption; this absorption is only observed in the blue-side of the pump and only at high excitation intensity level. Time-resolve measurement also shows that this absorption
reverses after ~600 fs, which corresponds to the life time of Auger recombination for 5 excitons per SWNT. These observations are explained by the blue-shift of excitonic energy level for multiple excitons confined in a single SWNT, due to many-body effect. And as multiple excitons quickly recombined due to Auger process within ~1ps, many-body effect disappears and the transmission of probe signal recovers. However, further investigation for this subject is still needed to determine the effect of multiple excitons confined with in one SWNT.

Applications

Ever since the discovery of carbon nanotube, the small dimension, strength and unique electronic band structure of carbon nanotubes make them unique for all kinds of applications. In this part of the review paper, we describe some of the important applications of carbon nanotubes, especially the applications in nano-electronics and biological applications. Other potential applications, such as composite material applications and applications in energy will not be covered here.

1. Biological applications

   a) Functional AFM tips

As shown in Figure 8, a typical AFM (atom force microscope) is composed of a cantilever-tip assembly; a laser that shines laser beam onto the cavalier; and a detector to monitor cantilever displacement through the displacement of reflected laser beam. Clearly, from the figure we can see that the resolution of the AFM will be highly dependent on the nature of the cantilever-tip, such as the size, stiffness and curvature at the tip. In fact, it is proposed that for an ideal AFM tip, it should have a high aspect ratio, the tip radius should be as small as possible, and it should be mechanically and chemically robust so that its structure is not changed when imaging in fluid environments. And in fact, carbon nanotube seems to be the
only candidate to satisfy all the requirements mentioned above because of its superior mechanical and chemical properties. In this part of this review paper, carbon nanotube as functional AFM tips for biological applications will be discussed.

First, Carbon nanotubes are attached to silicon tip through manual assembly or by direct growth through CVD. And it is shown that, the direct growth method provides the possibility of mass production, and thin, individual SWNTs tips that are difficult to achieve through other methods.

Research reports by Lieber group have shown that, CVD nanotube tips for structural imaging have been used in structural biology to image aggregation pathway of amyloid proteins, to address ATP-dependent nucleosome remodeling, and for DNA sequence determination. However, it is also possible to utilize the high sensitivity of AFM to normal forces for biological and chemical sensitive measurement. In fact, the AFM tip is simply modified with specific chemical groups, and the force between the chemical group and the sample can be measured at the same time as the surface topography. Once again, carbon nanotube tips are proven to be the perfect candidate for this kind of application. They have small radius of curvature at the tip, and the tip can be specially modified only at the ends. Research work already shows that modified SWNT could lead to sub-nm resolution in chemical bonding site recognitions.

b) Bio-sensing based applications

In traditional electrochemiluminescence (ECL), a label is first excited to higher energy state by electron transfer reactions near the surface of an electrode. And a photon is emitted when the label relaxed to the ground state. For biosensing applications, an ECL label is coupled to
an analyte of interest and then excited to higher energy state. Since the number of photons emitted in this process scales with the number of excited labels, it is possible to quantitatively measure the concentration of analyte that is of interest.

It is already shown that carbon nanotubes have several characteristics that make them useful for ECL-based biosensing applications. First, carbon nanotubes are conducting, thus it can act as electrode and generate ECL in liquid solution. Secondly, carbon nanotubes can be derivatized with functional groups that allow immobilization of biomolecules. And thirdly, carbon nanotubes have high surface area to weight ratio, and most of the surface areas can be utilized for ECL and immobilization of biomolecules. In fact, carbon nanotubes based ECL biosensing systems have already been fabricated, and they have the ability to quantitatively measure a wide range of biological analytes.

2. Electrical applications
   a) Field emission device

As we all know, nanotubes are the best field emitters among all the material because of their high electrical conductivity, and the insuperable sharpness of their tip which also means that they emit at especially low voltage, the most important feature for building electrical devices that utilize this feature. Nanotubes can carry an amazingly high current density, possibly as high as $10^{13}$ A/cm$^2$. What is even more, the current is extremely stable according to the latest research.

A direct application of this feature of nanotubes is in field-emission flat-panel displays. What is filed emission? Field emission is emission of electrons from the surface of a condensed phase into another phase usually vacuum, under the action of a high electrostatic field (108
V/cm). It is a quantum effect. Instead of a single electron gun, here there is a separate electron gun (or many) for each pixel in the display, which has high current density, low turn-on and operating voltage, and steady, long-lived behavior. **Figure 9** shows the diagram of carbon nanotube based field emission devices.

b) Molecular electronics

In any electronic circuit, especially the ones in microelectronic level, the interconnections between switches and other active devices become increasingly important. As the result of wonderful geometry, electrical conductivity, and ability to be precisely derived, Nanotubes become the ideal candidates for the connections in molecular electronics. Moreover, they have been demonstrated as switches themselves. The reason is that nanotubes conductivity is determined by surrounding environments. In different environment, it can present as conductor, semiconductor and insulator respectively. That is to say, we can easily control the conductivity of nanotubes via changing the conditions nanotubues face. Based on this feature, we can easily adjust the whole characteristics of the circuits without adding any other electronic devices. At the present time, nanotubes have been widely used in microelectronics. **Figure 10** shows the picture of a carbon nanotube based molecular device.

3 Energy applications

Recent research has shown that nanotubes contain the highest reversible capacity of any carbon material for use in lithium-ion batteries. Nanotubes also have applications in a variety of fuel cell components. They have a number of properties including high surface area and thermal conductivity that make them useful as electrode catalyst supports in PEM fuel cells. Nanotubes' high strength and toughness to weight characteristics may also prove valuable as
part of composite components in fuel cells that are deployed in transport applications where durability is extremely important.

Conclusion

Ever since carbon nanotube was found in 1991, it has attracted much attention because of its excellent mechanical and electrical properties. Although ultrafast optical spectroscopy of carbon nanotube shows that its optoelectronic applications are limited due to Auger recombination, carbon nanotube is still quite promising in nano-electronics, biological applications and composite material applications. The method for industrial mass production of high quality carbon nanotube is still missing, thus the application for carbon nanotube is still in its childhood. However, carbon nanotube will have a bright future in the emerging nano-technology age.
References

5. Carbon nanotubes : synthesis, structure, properties, and applications; Springer, c2001
1 Figures

Figure 1: The forming of a carbon nanotube

Figure 2: Band structure for different carbon nanotubes

(7,7) (7,0)
Figure 3: Carbon nanotube density of state

Figure 4: Diagram of Auger process and quantized Auger recombination
Figure 5: Pump-probe experiment setup

Figure 6: Pump-probe experiment result
Figure 7: Absorption spectrum at zero delay

Figure 8: Schematic of AFM
Figure 9: Carbon nanotube based field emission device

Figure 10: Testing of a carbon nanotube