The exciting world of carbon nanotubes

Small Wonder

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THE PAST DECADE HAS WITnessed tremendous progress in the field of nanotechnology, which is broadly defined as the creation and application of nanometer-scale materials. One nanometer is one billionth of a meter, and materials at this length scale exhibit distinctively different properties from their bulk counterparts. Among the various nanomaterials studied thus far, carbon nanotubes (CNTs) stand out due to their remarkable electrical, mechanical, optical, and chemical properties. Since their discovery by Sumio Iijima at NEC Corporation in Japan in 1991, CNTs have stimulated enormous interest for both fundamental research and future applications.

CNTs can be viewed as long graphene sheets rolled into seamless cylinders, and a single walled carbon nanotube (SWNT) can be as long as several centimeters, while the diameter is only 1–2 nm. The excitement and opportunity come from the fact that the property of the nanotube depends on how one rolls the graphene sheet to make a nanotube. As shown in Figure 1, we can cut the graphene along the lines of OB and AC and then roll it up into a nanotube, so that O meets A and C meets B. The chiral vector $\overrightarrow{OA}$ is defined on the hexagonal lattice as $\overrightarrow{OA} = m\boldsymbol{a} + n\boldsymbol{b}$, where $\boldsymbol{a}$ and $\boldsymbol{b}$ are two basic vectors shown in Figure 1 and n and m are two integers that can be used

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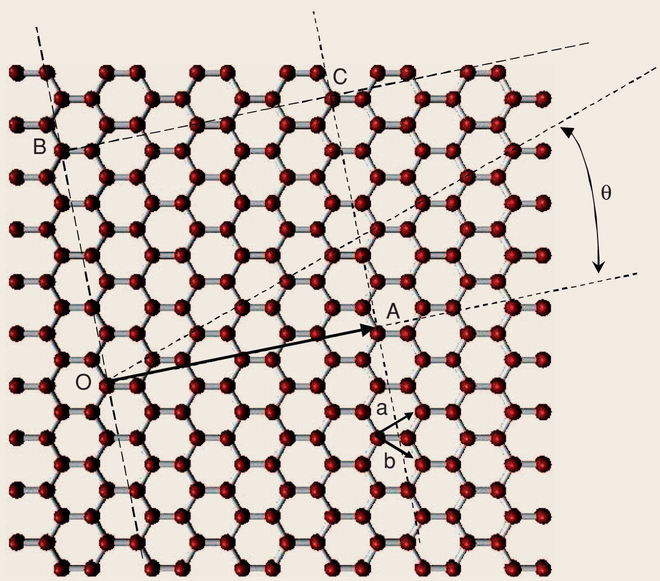

FIGURE 1 A CNT can be constructed by cutting a graphene layer along lines OB and AC, and then rolling it up into a tube, so that O meets A and C meets B. Vector $\overrightarrow{OA}$ is called the chiral vector.

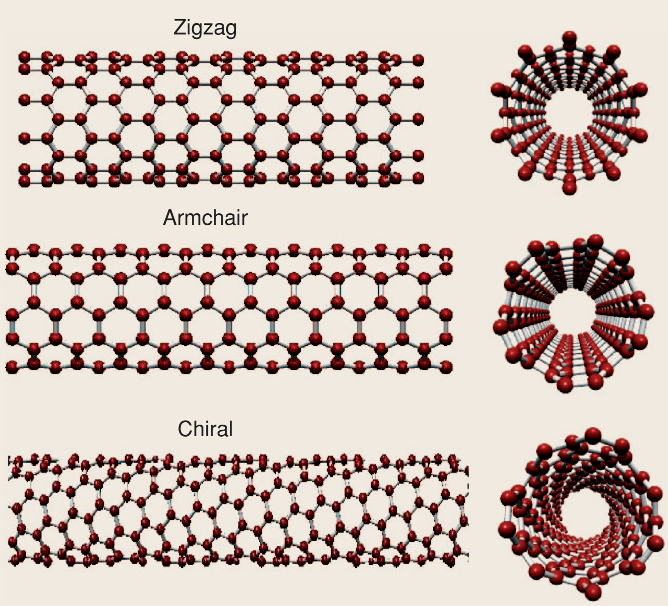

FIGURE 2 Schematic diagrams of zigzag, armchair, and chiral nanotubes.

to fully define the structure of this nanotube. The chiral angle, θ, is measured relative to the direction defined by $\boldsymbol{a}$. The diagram in Figure 1 has been constructed for $(m, n) = (4, 2)$, and the unit cell of this nanotube is bounded by $OACB$.

Different types of CNTs have different values of n and m. Figure 2 displays the schematic diagram of three kinds of CNTs: zigzag, armchair, and chiral nanotubes. Zigzag nanotubes correspond to either m or n equal to 0 and have a chiral angle of 0°. Armchair nanotubes (named so because the configuration is similar to an armchair) have $n = m$ and a chiral angle of 30°, while other nanotubes are generally called chiral nanotubes.

WHAT MAKES CNTS SO INTERESTING?

CNTs boast a wide variety of remarkable properties. For instance, CNTs can be either metallic or semiconductive, depending on their structures. In addition, CNTs have high current-carrying capability, high carrier mobility, high saturation velocity, excellent thermal conductivity, ultra-thin geometry, and the potential to integrate with mainstream silicon-based semiconductor electronics. Furthermore, CNTs exhibit extraordinary mechanical properties, with Young's modulus over 1 TPa and tensile strength ~200 GPa. Due to the ultra-high surface-to-volume ratio of CNTs, they can be further employed to work as high-performance chemical and biosensors. It is possible to attach other chemical groups to the tip or sidewall of the CNTs and alter the property to suit the application.

CNT SYNTHESIS

Different kinds of CNTs can be synthesized using a variety of techniques. The most commonly used techniques include arc discharge, laser ablation, and chemical vapor deposition (CVD). CNTs were first discovered when Iijima examined the products from an arc discharge between two graphite electrodes and observed tube-like structures. Laser ablation was subsequently developed to produce both high-quality multiwalled and single-walled CNTs.

The past decade, however, has witnessed tremendous progress in nanotube synthesis using chemical vapor deposition, which has become the technology of choice for most nanoelectronics and similar applications. Figure 3(a) shows the schematic diagram of a typical CVD system used in our lab. A substrate coated with metal catalyst nanoparticles (such as iron, nickel, or cobalt) is placed in a quartz tube furnace and the temperature is then raised to the growth temperature ($\sim 900\ ^\circ$C). The carbon feedstock is typically made of a mixture of methane, ethylene, and hydrogen, all controlled by mass flow controllers. The hydrocarbon decomposes on the surface of the catalyst particles at high temperature, and the carbon diffuses into the catalyst particles and then grows in the tubular form with continuous supply of the feedstock.

A schematic diagram showing the growth mechanism is found in Figure 3(b). The metal particle can be either at the starting position of the nanotube (base growth), or at the growing end of the nanotube (tip growth). Figure 3(c) shows a scanning electron microscope (SEM) image of single-walled nanotubes grown on a silicon substrate, while Figure 3(d) shows a patterned growth of vertical multiwalled CNT towers.

Recent advances in nanotube synthesis have led to aligned growth of single-walled CNTs, which can work as a platform for integrated nanotube circuits and high-

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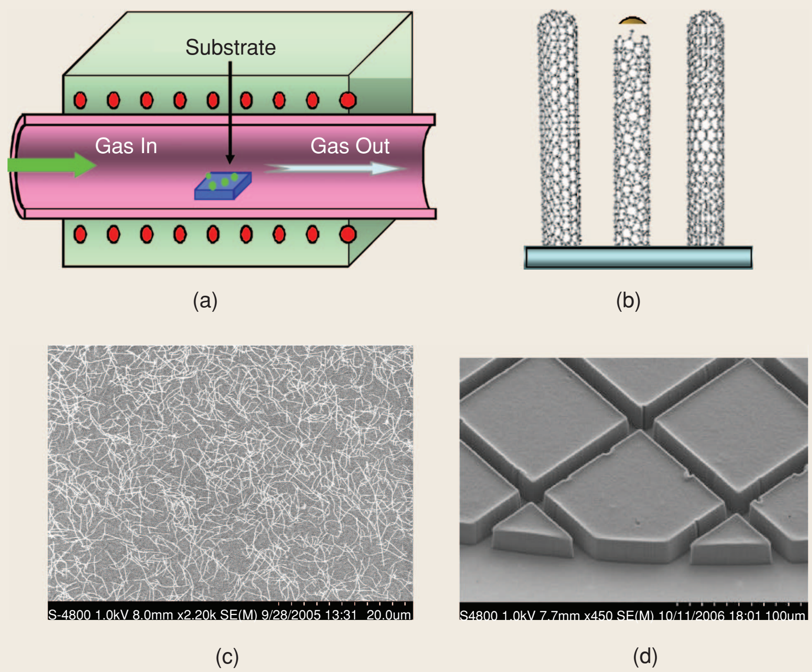

FIGURE 3 A (a) Schematic diagram of a chemical vapor deposition setup for nanotube synthesis. (b) Base growth versus tip growth. (c) An SEM image of single-walled CNTs synthesized atop a silicon substrate coated with silicon dioxide. (d) An SEM image of CVD-synthesized multiwalled CNT towers.

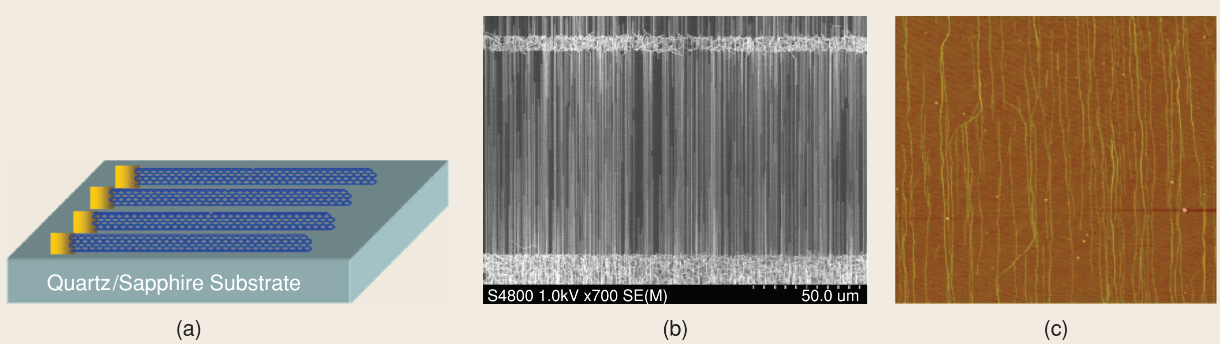

FIGURE 4 (a) Schematic diagram of aligned nanotube synthesis, and images of aligned single-walled CNTs on (b) quartz and (c) sapphire.

> The property of the nanotube depends on how one rolls the graphene sheet to make a nanotube.

performance nanotube radio-frequency electronics. Alignment can be achieved on various substrates, as shown schematically in Figure 4(a). For example, Figure 4(b) shows an SEM image of aligned nanotubes grown on a miscut quartz substrate, where the step edges are believed to work as the template for nanotube growth. In contrast, Figure 4(b) shows aligned nanotubes grown on an a-plane sapphire substrate without intentional miscut. Here the atomic layout of the sapphire substrate is believed to guide the nanotube orientation.

APPLICATIONS

Fundamental and applied CNT research has revealed the great potential of using nanotubes for various applications, including nanoelectronics, biosensor, chemical sensor, field emission, energy storage and conversion, composite materials, and nanophotonic devices.

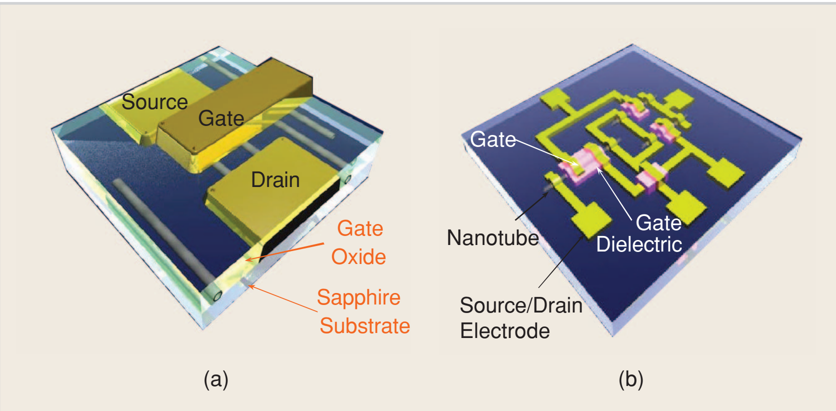

FIGURE 5 Schematic diagrams of (a) a CNT field-effect transistor and (b) an integrated nanotube circuit.

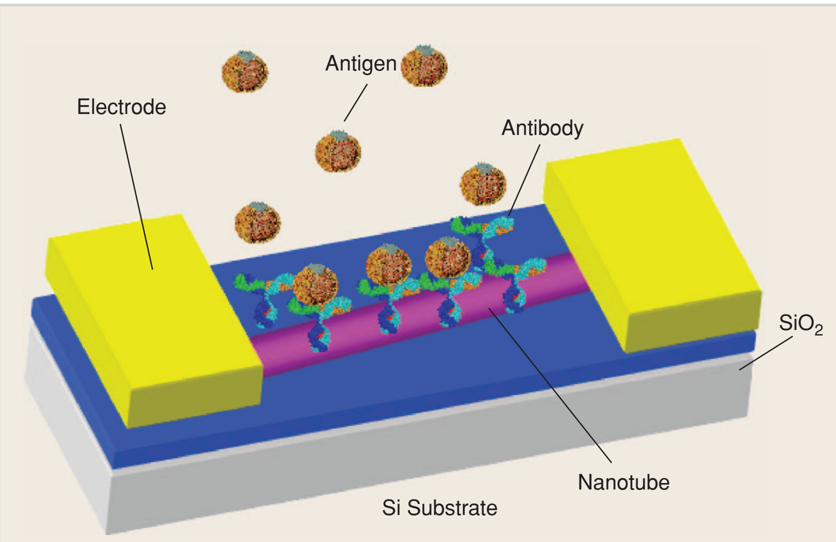

FIGURE 6 Schematic diagram of a CNT biosensor.

NANOELECTRONICS

As mentioned earlier, different CNTs exhibit very different electronic properties. For instance, depending on their chiral vector, CNTs can be either semiconducting or metallic. A nanotube with chiral vector (n, m) is metallic when $n = m$ or $(n - m) = 3i$, where i is an integer; otherwise, the nanotube is semiconducting with a nonzero bandgap. These semiconducting nanotubes can work as the active channel in a field-effect transistor and, thus, play a role similar to silicon for the semiconductor industry. Figure 5(a) shows the schematic diagram of a transistor based on several aligned nanotubes. Current flows from the source to the drain and its magnitude can be modulated by the gate electrode, separated from the nanotubes by a thin dielectric layer. These transistors can have on/off ratios up to 10^6 and carrier mobility superior to traditional silicon-based transistors. In addition, by fabricating a large number of nanotube transistors on the same chip, one can form integrated nanotube circuits after removing unwanted nanotubes and patterning interconnects. A schematic layout of the CNT circuit architecture is shown in Figure 5(b).

CHEMICAL AND BIOSENSING

Single-walled CNTs are made of one layer of carbon atoms, and thus boast a unique structure in which all the conductive electrons are exposed to the ambient. As a result, the conductance of a nanotube can be significantly modulated by the binding or unbinding of various charged molecules to the nanotube outer surface. This makes the nanotubes ideal materials for various sensing applications. For instance, CNTs have been demonstrated to detect NO_2 down to sub parts per billion (ppb) concentrations. They can also be used to detect other hazardous chemicals such as ammonia and hydrogen. Furthermore, CNTs can be employed to work as highly sensitive and selective biosensors, which may find broad applications for bio-threat detection, healthcare, and medical research. Figure 6 depicts the typical structure of a nanotube biosensor. To achieve selectivity, receptor molecules that can selectively bind to specific DNA or proteins are first attached to the nanotube surface. The conductance of the nanotube is then measured between source and drain and monitored, while the biosensor is exposed to the biological assays to be analyzed. Once the target molecules bind to the receptors, a change in conductance can usually be detected due to the chemical gating effect. The magnitude of the conductance change can be analyzed to decipher the concentration of the target molecules. CNT biosensors have been utilized to detect a variety of important biomolecules including low-density lipoprotein, a protein important for cardiovascular study, and prostate specific antigen, an important biomarker for prostate cancer.

There is no doubt that CNTs have great potential to revolutionize many aspects of scientific research and engender applications that affect daily life.

ENERGY CONVERSION AND STORAGE

CNTs can be used for energy conversion and storage applications. A transparent conductive nanotube paper can be produced by filtering purified nanotubes through a filtration membrane. The nanotube paper can then be transferred to either a glass substrate [Figure 7(a)] or a plastic substrate [Figure 7(b)]. One can clearly see that these nanotube films are highly transparent, and the conductance of these nanotube films can approach tens of Ω per square. Figure 7(c) shows an SEM image of the CNT strands inside the nanotube film. These nanotube films can work as transparent conductive electrodes for various energy conversion or display applications, including organic light-emitting diodes and organic solar cells. Figure 7(d) illustrates the details of an OLED made with nanotube film electrodes. Nanotube films can inject holes into the organic multilayers, and the injected holes recombine with electrons injected from the aluminum cathode, resulting in light emission that can easily escape the transparent nanotube film. In parallel to the advance in nanotube transparent electrodes, energy storage using CNTs has also been extensively studied, including the areas of electrochemical hydrogen storage, gas phase intercalation, electrochemical lithium storage, and charge storage in supercapacitors.

Overall, there is no doubt that CNTs have great potential to revolutionize many aspects of scientific research and engender numerous applications that will affect our daily lives. The excitement of application development for CNTs continues.

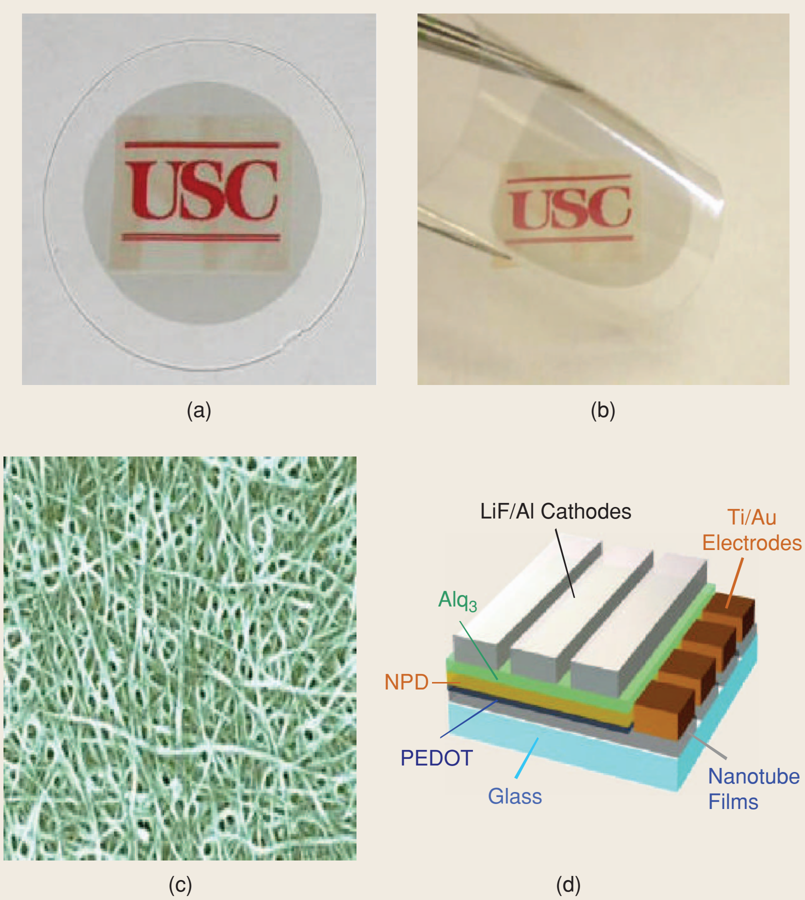

FIGURE 7 Transparent CNT films on (a) glass and (b) plastic. (c) An SEM image of CNTs in the nanotube film. (d) A schematic diagram of a demonstrated organic light-emitting diode with nanotube films as the anode.

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