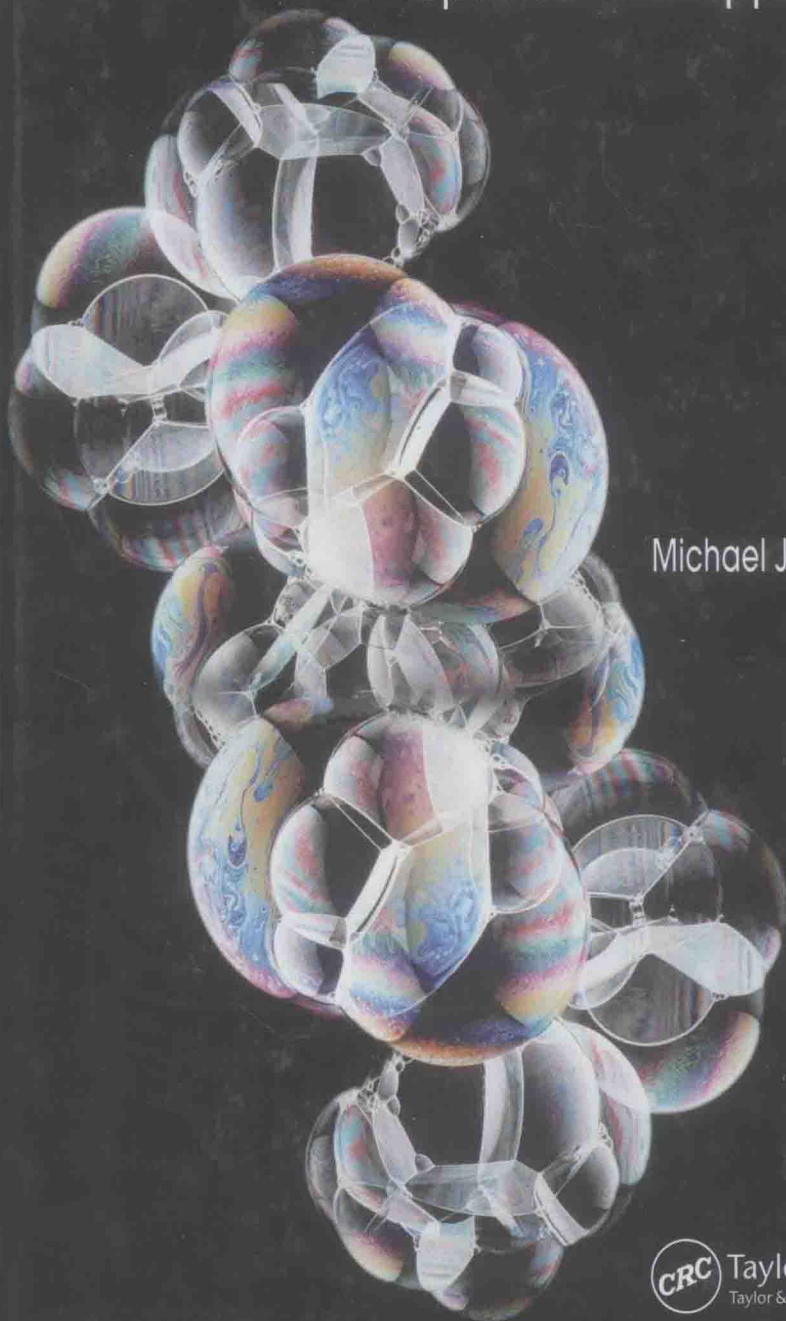


# Carbon Nanotubes

Properties and Applications

Edited by  
Michael J. O'Connell



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## Properties and Applications

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# **Carbon Nanotubes**

## Properties and Applications

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# Preface

In 1985, a molecule called buckminsterfullerene was discovered by a group of researchers at Rice University. This molecule consisted of 60 carbon atoms in  $sp^2$  hybridized bonds arranged in a surprisingly symmetric fashion. The Nobel Prize was awarded to Richard Smalley, Robert Curl, and Harry Kroto for their discovery of this new allotrope of carbon. This discovery was groundbreaking for the now vibrant field of carbon nanotechnology.

Carbon nanotubes, discovered in 1991 by Sumio Iijima, are members of the fullerene family. Their morphology is considered equivalent to a graphene sheet rolled into a seamless tube capped on both ends. Single-walled carbon nanotubes (SWNTs) have diameters on the order of single-digit nanometers, and their lengths can range from tens of nanometers to several centimeters. SWNTs also exhibit extraordinary mechanical properties ideal for applications in reinforced composite materials and nanoelectromechanical systems (NEMS): Young's modulus is over 1 TPa and the tensile strength is an estimated 200 GPa. Additionally, SWNTs have very interesting band structures. Depending on the atomic arrangement of the carbon atoms making up the nanotube (chirality), the electronic properties can be metallic or semiconducting in nature, making it possible to create nanoelectronic devices, circuits, and computers using SWNTs.

This book introduces carbon nanotubes and the science used to investigate them. The field is progressing at staggering rates, with thousands of publications appearing in the literature each year. The current progress and the applications SWNTs have found use in are particularly impressive, since the existence of the fullerenes has only been known for 20 years. This book is a great resource for anyone new to carbon nanotube research. It can also introduce the experienced researcher to subjects outside his or her area of study. The book assumes that the reader has a basic understanding of chemistry and physics. I hope that high school students and undergraduates may stumble upon this book, find the inspiration to study science, and pursue a career in nanotechnology research.

This book was written by many expert carbon nanotube researchers. The book does not build information sequentially, but rather each chapter can be read as a mini-book of its particular subject. I encourage the reader to explore this book in the order of subject matter interest.

This book begins with an introduction and history of carbon nanotubes. The introduction was written by Frank Hennrich, Candace Chan, Valerie Moore, Marco Rolandi, and Mike O'Connell. Frank Hennrich received his Ph.D. in physical chemistry from Karlsruhe University based on his work on the producing and characterizing of fullerenes and SWNTs. His main interests at his current position in the Institute of Nanotechnology (Research Center Karlsruhe) include Raman spectroscopy, nanotube separations, and nanotube electronic devices. Candace Chan received a B.S. in chemistry from Rice University, where she worked on SWNT cutting and functionalization. She is currently pursuing a Ph.D. at Stanford University as a National Science Foundation Fellow and Stanford Graduate Fellow in the departments of chemistry and materials science and engineering. Her current research interests are synthesizing new nanowire materials and incorporating them into memory, electronic, and sensor devices. Valerie Moore recently completed her Ph.D. in chemistry at Rice University in the areas of characterization and application of colloidal SWNT suspensions and novel methods toward (n, m)-selective SWNT growth. She holds a B.S. in chemistry from Centenary College of Louisiana, where she was able to conduct undergraduate research at NASA Glenn Research Center on carbon nanotube growth in flames. Marco Rolandi recently received his Ph.D. in applied physics from Stanford University, where he characterized carbon nanotubes using Raman spectroscopy. He also holds an M.Sci. in physics from Queen Mary and Westfield College, University of London.

Following the introduction is a discussion on the various ways to synthesize carbon nanotubes, written by David Mann and Mike O'Connell. While SWNTs had been discovered as a by-product in 1991, they were not controllably synthesized until 1993. David Mann is busy completing a Ph.D. in applied physics from Stanford University, where he conducts research on nanotubes covering a wide variety of topics, including novel synthesis methods as well as electrical and thermal characterization. He received a B.S. in physics from Harvey Mudd College.

The next chapter is about another type of nanotube material synthesis. Satishkumar B. Chikkannanavar, Brian W. Smith, and David E. Luzzi look at the carbon nanotube as a volume of space capable of transporting or containing other materials inside. These amazing structures, commonly known as peapods, have interesting properties and great potential in many useful applications. Satishkumar B. Chikkannanavar finished his undergraduate from Karnataka University and Ph.D. at Indian Institute of Science, Bangalore. He did his postdoctoral research at the University of Pennsylvania, working on carbon nanotubes and fullerene hybrid materials, and currently he is at the Los Alamos National Laboratory. His research interests include near-infrared optical characteristics of carbon nanotubes, optical sensing of biomolecules, and device applications. Brian W. Smith received his Ph.D. in materials science from the University of Pennsylvania, where he was instrumental in the discovery, synthesis, and characterization of carbon nanotube peapod materials. He is currently a member of the technical

staff at the Fox Chase Cancer Center (Philadelphia). His research program is focused on applications of nanotechnology in cancer treatment, specifically in the area of radioimmunotherapy. David E. Luzzi received his Ph.D. in materials science and engineering from Northwestern University in 1986. His Luzzi Research Group at the University of Pennsylvania synthesizes novel nanoscale materials based primarily on SWNTs, and his research interest includes structure and properties of carbon nanotubes, interface in structural materials, and mechanical properties of Laves phases.

The next few chapters discuss the properties of SWNTs. Marcus Freitag begins with the description of the electronic properties and band structure of nanotubes, and then moves on to the electronic properties of devices made with SWNTs. Marcus Freitag is a research staff member at the IBM T.J. Watson Research Center in Yorktown Heights, New York. He received his Diplom degree at the University of Tuebingen, Germany, his M.S. at the University of Massachusetts, and his Ph.D. in physics at the University of Pennsylvania. He joined IBM's research division in 2004 after 2 years of postdoctoral work with Carbon Nanotechnologies. His research is focused on electronic transport and electro-optic interactions in carbon nanotubes.

Carbon nanotubes can be paramagnetic or diamagnetic depending on their chirality. Junichiro Kono and Stephan Roche cover the magnetic properties of nanotubes. Junichiro Kono currently serves as an associate professor of electrical and computer engineering at Rice University. His research interests include optical studies of low-dimensional solids and nanostructures; spintronics, opto-spintronics, and optical quantum information processing; nonlinear, ultrafast, and quantum optics in solids; physical phenomena in ultrahigh magnetic fields; and physics and applications of terahertz phenomena in semiconductors. He holds a Ph.D. in physics from the State University of New York–Buffalo and an M.S. and B.S. in applied physics from the University of Tokyo. Stephan Roche completed his Ph.D. at French CNRS in 1996. He worked as an EU research fellow in the department of applied physics at Tokyo University, Japan, and in the department of theoretical physics at Valladolid University, Spain, before being appointed as assistant professor at the University of Grenoble. He is now research staff of the Commissariat à l'Énergie Atomique in Grenoble, focusing on charge transport in nanoelectronics and mesoscopic systems from a theoretical perspective.

The next chapter discusses using Raman spectroscopy to probe the electronic and chemical behavior of SWNTs. This chapter was written by Stephen K. Doorn, Daniel Heller, Monica Usrey, Paul Barone, and Michael S. Strano. Stephen K. Doorn received his B.S. in chemistry (with honors) from the University of Wisconsin and holds a Ph.D. in physical chemistry from Northwestern University. He is currently a technical staff member in the chemistry division at Los Alamos National Laboratory. His research efforts are focused on spectroscopic materials characterization and fundamental studies and biosensor applications of nanoparticle assemblies. His specific interests in carbon nanotubes include fundamental spectroscopy, separations, redox chemistry,

and sensors. Daniel Heller is a graduate student in the department of chemistry at the University of Illinois–Urbana/Champaign in the laboratory of Michael S. Strano. He studies the chemistry and physics of nanoscale materials and their interactions with biological systems. Monica Usrey is a graduate student in the department of chemical and biomolecular engineering at the University of Illinois–Urbana/Champaign working with Michael S. Strano. She works with the functionalization of single-walled carbon nanotubes with diazonium salts, with emphasis on electronic structure separation. She holds a B.S. in chemical engineering from the University of Louisville. Paul Barone is completing work for a Ph.D. in chemical and biomolecular engineering at the University of Illinois–Urbana/Champaign. He studies the photophysics of single-walled carbon nanotube/protein systems. He received his B.S. in chemical engineering from the University of Missouri–Columbia. Michael S. Strano is an assistant professor in the department of chemical and biomolecular engineering at the University of Illinois–Urbana/Champaign. His research focuses on the chemistry of nanotube and nanowire systems and the photophysics of such systems. Daniel Heller, Monica Usrey, Paul Barone, and Michael S. Strano also include a discussion on the optical properties of nanotubes and separations.

Next, Randal J. Grow discusses some of the electromechanical properties of SWNTs and their applications in NEMS devices. Randal J. Grow recently completed a Ph.D. in applied physics from Stanford University, where he conducted research on the electromechanical properties of carbon nanotubes and germanium nanowires, among other things. He also holds a B.A. in physics from Colorado College.

Carbon nanotubes are the strongest material known. In their chapter, Han Gi Chae, Jing Liu, and Satish Kumar discuss the mechanical properties of SWNTs spun into fibers. Han Gi Chae is working toward his Ph.D. degree in polymeric materials at the Georgia Institute of Technology, where he conducts research on polymer/nanotubes composite fibers. Prior to joining Georgia Tech, he conducted research on high-performance polymer hybrids at Korea Institute of Science and Technology, Seoul, Korea. He received his B.S. and M.S. in polymer engineering from Hanyang University, Korea. Jing Liu is working toward her Ph.D. degree in polymeric materials at Georgia Institute of Technology, where she conducts research on carbon nanotubes/polymer composites and novel structured materials by electrospinning. She received her M.E. degree in polymer materials from Zhejiang University, China. Satish Kumar is a professor in the School of Polymer, Textile and Fiber Engineering at the Georgia Institute of Technology. His research interests are structure, processing, and properties of polymers, fibers, and composites. His current research focus includes carbon nanotube composites, electrospinning, and electrochemical supercapacitors.

Covalent sidewall functionalization opens new doors for nanotube research. Christopher A. Dyke and James M. Tour include their chapter on the synthesis and applications of covalently modified SWNTs. Christopher A. Dyke is currently the chief scientific officer of NanoComposites, Inc.



(NCI). NCI employs carbon nanotube functionalization technology for the enhancement of polymeric materials. He received his Ph.D. in synthetic organic chemistry from the University of South Carolina with postdoctoral research at Rice University, where he worked on carbon nanotube technology. James M. Tour is the Chao professor of chemistry, professor of computer science, and professor of mechanical engineering and materials science at Rice University's Center for Nanoscale Science and Technology. He received his B.S. in chemistry from Syracuse University and his Ph.D. from Purdue University, with postdoctoral research at the University of Wisconsin and Stanford University. He presently works on carbon nanotubes and composites, molecular electronics, and nanomachines.

C. Patrick Collier's chapter discusses the use of SWNTs as tips for scanning probe microscopy. He includes the fabrication of these tips, the properties of the SWNTs on the tips, and applications in biosensing. C. Patrick Collier is an assistant professor of chemistry at the California Institute of Technology. His research interests include single-molecule spectroscopy, scanning probe microscopy using carbon nanotube tips, and nanolithography. He obtained his Ph.D. from the University of California–Berkeley, where he was involved in the discovery of a reversible metal–insulator transition in ordered two-dimensional superlattices of silver quantum dots under ambient conditions. In his postdoctoral work at University of California–Los Angeles and Hewlett-Packard Labs, he was involved in some of the first demonstrations of defect-tolerant computation in molecular electronics. He received a B.A. in chemistry and a B.Mus. from Oberlin College.

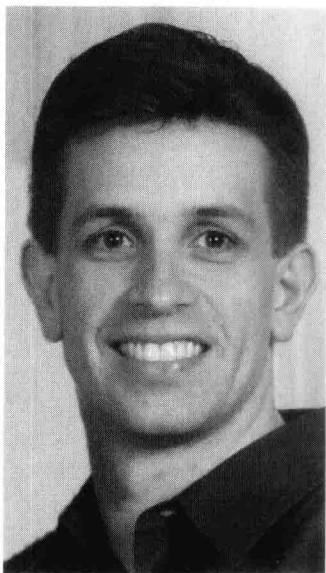
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I am sincerely thankful for the time and effort put in by all of the authors. I also acknowledge the Director of Central Intelligence Fellowship Program for its support during my postdoctoral fellowships at Los Alamos National Laboratory and Stanford University, and Theranos, Inc., for my current support. Finally, I honor my Ph.D. advisor at Rice University, the recently departed Rick Smalley. Rick was a good friend and mentor to me. He shared his vision for the success of carbon nanotechnology with so many people around the world. His passion for science helped to make carbon nanotechnology the vibrant research field it is today. He is gone, but not forgotten. Rick left behind in many, including myself, a deep fascination and respect for the curious molecules known as carbon nanotubes.

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## About the Editor



**Dr. Michael J. O'Connell** graduated with a B.S. in biochemistry and molecular biology from the University of California in 1998 and developed an interest in the emerging field of nanotechnology. He went on to Rice University and received his Ph.D. in physical chemistry in 2002 for research with Richard E. Smalley on aqueous phase suspensions of carbon nanotubes. O'Connell then joined Los Alamos National Laboratory in 2003 as a postdoctoral researcher with Stephen K. Doorn, working on carbon nanotube spectroscopy and sensors. In 2004 he transferred as a postdoctoral fellow to Stanford University to work with Hongjie Dai on biological applications of carbon nanotubes. He has numerous patents and publications in the nanotech field. He is now leading a team of nanotech researchers at Theranos to create future generation products.

O'Connell's many accomplishments include the Director of Central Intelligence Postdoctoral Fellowship from 2003 to 2005. He also wrote "4-Centimeter-Long Carbon Nanotubes" for *Nanotech Briefs* that won the Nano 50 Award in 2005. He has been a Los Alamos National Laboratory Director's Postdoctoral Fellow in 2003, a Los Alamos National Laboratory Postdoctoral Fellow in 2003, a Welch Fellow of Rice University from 2000 to 2002, and a President's Undergraduate Fellow of the University of California-Santa Cruz from 1997 to 1998. O'Connell was honored with the College Eight Research Award from the University of California-Santa Cruz from 1997 to 1998 and is a member of the Phi Lambda Upsilon Honor Society.

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# *chapter one*

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## *The element carbon*

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Carbon is the most versatile element in the periodic table, owing to the type, strength, and number of bonds it can form with many different elements. The diversity of bonds and their corresponding geometries enable the existence of structural isomers, geometric isomers, and enantiomers. These are found in large, complex, and diverse structures and allow for an endless variety of organic molecules.

The properties of carbon are a direct consequence of the arrangement of electrons around the nucleus of the atom. There are six electrons in a carbon atom, shared evenly between the 1s, 2s, and 2p orbitals. Since the 2p atomic orbitals can hold up to six electrons, carbon can make up to four bonds;

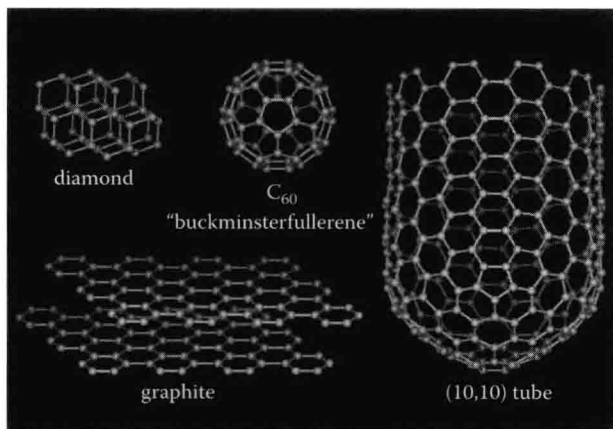
however, the valence electrons, involved in chemical bonding, occupy both the 2s and 2p orbitals.

Covalent bonds are formed by promotion of the 2s electrons to one or more 2p orbitals; the resulting hybridized orbitals are the sum of the original orbitals. Depending on how many p orbitals are involved, this can happen in three different ways. In the first type of hybridization, the 2s orbital pairs with one of the 2p orbitals, forming two hybridized  $sp^1$  orbitals in a linear geometry, separated by an angle of  $180^\circ$ . The second type of hybridization involves the 2s orbital hybridizing with two 2p orbitals; as a result, three  $sp^2$  orbitals are formed. These are on the same plane separated by an angle of  $120^\circ$ . In the third hybridization, one 2s orbital hybridizes with the three 2p orbitals, yielding four  $sp^3$  orbitals separated by an angle of  $109.5^\circ$ .  $sp^3$  hybridization yields the characteristic tetrahedral arrangements of the bonds. In all three cases, the energy required to hybridize the atomic orbitals is given by the free energy of forming chemical bonds with other atoms.

Carbon can bind in a sigma ( $\sigma$ ) bond and a pi ( $\pi$ ) bond while forming a molecule; the final molecular structure depends on the level of hybridization of the carbon orbitals. An  $sp^1$  hybridized carbon atom can make two  $\sigma$  bonds and two  $\pi$  bonds,  $sp^2$  hybridized carbon forms three  $\sigma$  bonds and one  $\pi$  bond, and an  $sp^3$  hybridized carbon atom forms four  $\sigma$  bonds. The number and nature of the bonds determine the geometry and properties of carbon allotropes.

## 1.1 Allotropes of carbon

Carbon in the solid phase can exist in three allotropic forms: graphite, diamond, and buckminsterfullerene (Figure 1.1). Diamond has a crystalline structure where each  $sp^3$  hybridized carbon atom is bonded to four others



*Figure 1.1* The three allotropes of carbon. (From [http://smalley.rice.edu/smalley.cfm?doc\\_id=4866](http://smalley.rice.edu/smalley.cfm?doc_id=4866).)



in a tetrahedral arrangement. The crystalline network gives diamond its hardness (it is the hardest substance known) and excellent heat conduction properties (about five times better than copper).<sup>1</sup> The  $sp^3$  hybridized bonds account for its electrically insulating property and optical transparency. Graphite is made by layered planar sheets of  $sp^2$  hybridized carbon atoms bonded together in a hexagonal network. The different geometry of the chemical bonds makes graphite soft, slippery, opaque, and electrically conductive. In contrast to diamond, each carbon atom in a graphite sheet is bonded to only three other atoms; electrons can move freely from an unhybridized p orbital to another, forming an endless delocalized  $\pi$  bond network that gives rise to the electrical conductivity.

Buckminsterfullerenes, or fullerenes, are the third allotrope of carbon and consist of a family of spheroidal or cylindrical molecules with all the carbon atoms  $sp^2$  hybridized. The tubular form of the fullerenes, nanotubes, will be the subject of this book, and a detailed description of their history, properties, and challenges will be given in the next section.

## 1.2 History

Fullerenes were discovered in 1985 by Rick Smalley and coworkers.<sup>2</sup>  $C_{60}$  was the first fullerene to be discovered.  $C_{60}$ , or “bucky ball,” is a soccer ball (icosahedral)-shaped molecule with 60 carbon atoms bonded together in pentagons and hexagons. The carbon atoms are  $sp^2$  hybridized, but in contrast to graphite, they are not arranged on a plane. The geometry of  $C_{60}$  strains the bonds of the  $sp^2$  hybridized carbon atoms, creating new properties for  $C_{60}$ . Graphite is a semimetal, whereas  $C_{60}$  is a semiconductor.

The discovery of  $C_{60}$  was, like many other scientific breakthroughs, an accident. It started because Kroto was interested in interstellar dust, the long-chain polyynes formed by red giant stars. Smalley and Curl developed a technique to analyze atom clusters produced by laser vaporization with time-of-flight mass spectrometry, which caught Kroto’s attention. When they used a graphite target, they could produce and analyze the long chain polyynes (Figure 1.2a). In September of 1985, the collaborators experimented with the carbon plasma, confirming the formation of polyynes. They observed two mysterious peaks at mass 720 and, to a lesser extent, 840, corresponding to 60 and 70 carbon atoms, respectively (Figure 1.2b). Further reactivity experiments determined a most likely spherical structure, leading to the conclusion that  $C_{60}$  is made of 12 pentagons and 20 hexagons arranged to form a truncated icosahedron<sup>2,3</sup> (Figure 1.3).

In 1990, at a carbon-carbon composites workshop, Rick Smalley proposed the existence of a tubular fullerene.<sup>4</sup> He envisioned a bucky tube that could be made by elongating a  $C_{60}$  molecule. In August of 1991, Dresselhaus followed up in an oral presentation in Philadelphia at a fullerene workshop on the symmetry proposed for carbon nanotubes capped at either end by fullerene hemispheres.<sup>5</sup> Experimental evidence of the existence of carbon nanotubes came in 1991 when Iijima imaged multiwalled carbon nanotubes