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Self-assembly of carbon nanotubes

Introduction

This talk addresses the self-assembly of carbon nanotubes (CNTs). In order for useful and potentially important structures and devices to be built from CNTs it is essential that the nanotubes be manipulated and organized in some way. One of the most promising routes to such structures and devices appears thus far to be self-assembly. While acknowledging that there are two types of CNTs - multiwalled (MWNTs) and single-walled (SWNTs) - the work reviewed here will deal almost exclusively with SWNTs. Within the family of SWNTs there exist nanotubes that are either metallic or semiconducting. These electronic properties are of fundamental importance when considering certain applications, but for the self-assembly work that will be discussed here the nature of the tube itself is somewhat ignored.

Background

In order to discuss any aspect of CNT research it is necessary to go back briefly to 1985 and the discovery of C_{60} (buckyball, buckminsterfullerene, fullerene).¹ This happened at Rice University by a group of scientists led by Harry Kroto and Richard Smalley, and in a roundabout way led to the discovery of CNTs in 1991, and ultimately a Nobel Prize being awarded to Curl, Kroto and Smalley in 1996.² It was while investigating the laser-induced vaporization of graphite, and carrying out mass spec.

analysis that the authors realized the most stable product had to be a closed structure comprising sixty atoms of carbon. The only feasible arrangement giving rise to such a structure is composed of 20 hexagons and 12 pentagons and came to be known as "Buckminsterfullerene", after the architect whose geodesic domes have a framework similar to that of the C_{60} molecule, Fig. 1. Each pentagon is surrounded by 5 hexagons, thus obeying the "isolated http://smalley.rice.edu/images/allot



Figure 1. Structure of C60. ropes.jpg

pentagon rule" which states that the most stable fullerenes are formed when there are no adjacent pentagons. It is now however well accepted³ that it was Osawa who, in 1970, first put forward the soccer-ball structure of C_{60} .⁴ Even earlier, David Jones writing in New Scientist under the pseudonym Daedalus, had envisioned a "closed spherical shell of a sheet-polymer like graphite, whose basic molecule is a flat sheet of carbon atoms bonded hexagonally rather like chicken-wire",⁵ thus giving us some idea of the importance of the 1985 discovery.

In 1990 Kratschmer and Huffmann reported a new synthetic route to C_{60}^{60} resulting in significantly higher yields than the laser vaporization method of Kroto and Smalley. It was while carrying out a detailed TEM study on the soot formed in this new synthesis that the Japanese scientist, Iijima discovered a prevalence of long fibers of carbon, which came to be known as MWNTs.⁷ These MWNTs have been referred to as "matrjoshka" or Russian doll structures⁸ and can be envisioned as nested graphite tubes, capped with a fullerene-type hemisphere, with a spacing of 3.4 Å between each pair of concentric tubes – identical to the spacing between flat graphite sheets.⁷

Two years later, Iijima and Ichihashi reported the successful synthesis of SWNTs, 0.7 - 1.6 nm in diameter using an iron catalyst.⁹ In the same issue of Nature, a group of researchers from IBM also reported a successful route to SWNTs, 1.2 nm in diameter using Co as a catalyst.¹⁰ Since most of the earlier theoretical studies and predictions of possible applications of CNTs had been based on SWNTs, this discovery was very significant - so much so that in 1995 Guo et al. furtively suggested using buckyballs as a continuous feedstock in the scale-up of SWNT production.¹¹ Probably the most important of the theoretical predictions made was that SWNTs would behave as either metals or semiconductors¹² depending on the diameter of the tube and it's helicity, a term which describes the arrangement of the NTs will be discussed, followed by an introduction to self-assembly and some literature examples pertaining to the self-assembly of CNTs.

Structure of SWNTs

SWNTs can be viewed as seamless cylinders rolled from a sheet of graphite, with diameters ranging from 0.5 to 5 nm and lengths greater than 1 μ m. There is a wide range

of potential applications of CNTs in the areas of electronics, plastics, catalysis and biomedical sciences. In both CNTs and graphite the carbon atoms are sp^2 hybridized. In CNTs all chemical bonds are satisfied and strong which results in extremely high chemical (no dangling bonds), mechanical (high Young's modulus), and thermal (thermal conductivity higher than diamond) graphite sheet. The tube is wrapped up so stability. Diamond on the other hand is composed of sp^3 hybridized carbon atoms and as such is less



Figure 2. Construction of a CNT from a that the point C coincides with the origin and Ch = 11a1 + 7a2. The resulting tubes is named (11, 7).14

stable. There is a standard labeling convention to differentiate between the various possible rolled-up forms of graphite. The chiral vector, $\mathbf{Ch} = n\mathbf{a_1} + m\mathbf{a_2} \equiv (n, m)$, where $\mathbf{a_1}$ and \mathbf{a}_2 are the graphitic unit vectors and *n*,*m* are integers, is used to name each and every tube.¹³⁻¹⁶ This vector determines the direction of rolling whereby a lattice point (11, 7) is superimposed on the origin (0, 0) as shown in Fig 2. It gives each nanotube a unique name which in turn refers to one of three possible structures and determines the electronic properties. Tubes named armchair (n, n), or zigzag (n, 0), have carbon-carbon bonds on opposite sides of the tube perpendicular and parallel to the tube axis respectively, Fig. 3. Both these types of tubes are achiral, while the last tube-type (n, m) are referred to as chiral SWNTs. All armchair tubes are metallic in nature; if n - m = 3q where q is an integer the tubes are small band-gap semiconductors and

all remaining tubes are medium gap semiconductors.

An in-depth analysis of the literature pertaining to the synthesis of CNTs is beyond the scope of this analysis. For this the reader is directed to some recent indepth reviews of the subject.^{17,18} Briefly, since the discovery of MWNTs in 1991⁷ scientists have been striving to find the ultimate high-yield, cheap, and reproducible synthesis of SWNTs. Last year Colbert and Smalley reported¹⁹ that there were two HiPco²⁰ reactors at different chiralities.¹⁵



Figure 3. Models of SWNTs with

Rice University running fulltime with the capability of producing 25 g of high quality

SWNTs a day. The HiPco process involves the high pressure and high temperature gasphase disproportionation of CO over catalytic clusters of Fe. The resulting perfect SWNTs, sold by Carbon Nanotechnologies Inc. (formerly Tubes@Rice), are the most abundant and widely used by research groups worldwide today.

Self-Assembly vs. Directed Assembly

It is by now a well-established fact that in order for CNTs to be turned into useful devices in such areas as molecular electronics, scientists need to develop reliable methods of organizing the nanotubes into useful structures. This is where the concept of selfassembly comes into play. Routinely used self-assembly processes in chemistry today involve the assembly of alkylsilane molecules on hydroxylated surfaces and alkanethiols on gold surfaces.²¹ Both of these architectures are referred to as self-assembled monolayers, which are spontaneously formed by immersing a solid substrate into a solution containing bifunctional molecules.²² Self-assembly may also occur in solution as is the case when surfactant molecules aggregate to form micelles, or protein-protein interactions occur. In self-assembly it is the thermal energy of the environment which produces the molecular motions necessary for assembly to occur, thus creating order from randomness. Directed assembly, on the other hand, relies on a "controller" such as a magnetic or electric field or an evaporation front, in order for the assembly process to take place. That self-assembly is important in the area of nanotechnology is apparent as it is the technique most likely to result in device fabrication and terms like "nanoarchitectonics" have been coined to refer to this developing field.²³

There is one more seminal paper that needs to be mentioned before it is possible to discuss the current research on the self-assembly of CNTs. In 1998, Smalley's group at Rice described a method which overcame one of the biggest obstacles in the path of CNT device development – the extreme hydrophobicity of nanotubes which made them difficult to disperse and organize into desired structures.²⁴ In this paper, the authors described a route to (a) large-scale purification via oxidation; and (b) ultrasonic shortening of as-prepared nanotube ropes resulting in individual macromolecules with lengths of 100 – 300 nm. These "oxidatively shortened" SWNTs were subsequently dispersed in aqueous solutions with the help of surfactants, and importantly, derivatized chemically at their carboxyl-terminated open ends. The authors demonstrated that an

amide linkage could be formed by converting the carboxyl group to the corresponding acid chloride followed by reaction with an aminoalkanethiol. The resulting SWNTs were thiol- functionalized at their ends, thus rendering them applicable for SAM formation on gold or chemically patterned surfaces. Some recent reports using this route to selfassembly will be reviewed in the following sections.

Spontaneous self-assembly of SWNTs

One of the first mentions of CNT self-assembly was in 1996 when Thess et al. noted that SWNTs with extremely uniform diameters of 13.8 ± 0.2 Å selforganized into crystalline ropes, 50 - 200 Å in diameter and up to hundreds of microns long,²⁵ Fig. 4. These Figure 4. A single nanotube rope nanotubes were prepared by a dual-pulse laser ablation



imaged end-on.25

technique using a Ni/Co catalyst. The SWNTs within the ropes were hexagonally closepacked to form a 2-D triangular lattice as evidenced from XRD studies. While the high uniformity of these self-organized ropes was confirmed by both TEM and XRD, the metallic behavior was investigated using electron spin resonance (ESR). A narrow "dysonian" line at $g = 2.001 \pm 0.001$ characteristic of metal-like conduction was observed. This particular line-shape, asymmetric about the centre and named after F. J. Dyson,²⁶ describes a metal for which the skin depth is less than the sample dimensions and the relaxation time is longer than the diffusion time. The present authors defined the van der Waals attraction between SWNTs as the driving force for the observed selforganization. This had previously been proposed by Song et al.²⁷ in their earlier study of the electronic properties of "buckybundles". The reported vdW attraction of 950 meV for every nm of overlap is sufficient thermodynamic energy for self-assembly to occur.²⁸ In their study of the structural properties of SWNTs, Tersoff and Ruoff²⁹ concluded that two distinct size-dependent regimes exist for SWNTs. The smaller of these describes individual nanotubes as rigid cylinders (diameter < 10 Å); in the larger regime (diameter > 25 Å) the tubes actually flatten against each other under the stronger vdW attraction. As it happens, the 13.8 Å SWNTs in the work of Thess et al.²⁵ fall in between the rigid and distorted cylinder regimes and this fact, along with their very uniform diameter, are the reasons such perfectly formed ropes are obtained.

Self-assembly in solution

Self-assembly has always been abundant in biology where molecules aggregate spontaneously to form complex cell membranes. Self-assembly of proteins can be driven by their amphiphilic α -helix structure whereby the helices aggregate in such a way as to favor exposure of their more hydrophilic surface to the aqueous solvent. In this way proteins behave much like surfactants forming micelles in solution. At low concentrations they exist as typical random conformers, and become helical eventually forming oligomers (usually tetramers) as the concentration is increased. In a recent report by a group from UT Dallas and Zyvex Corporation,³⁰ a peptide was designed and synthesized with a view to its having two distinct purposes: (1) to non-covalently coat and thereby increase the solubility of SWNTs in aqueous solutions, and (2) induce self-assembly of SWNTs as a result of peptide-peptide interactions. By controlling external Figure 4. SEM images of fibers conditions such as salt concentration or the addition of amphiphilic molecules that influence these interactions,



formed on addition of (a) no salt, (b) 40 mM NaCl and (c) 120 mM NaCl.30

the authors demonstrate control over the size and shape of the structures formed. Fig. 4 shows how increasing the ionic strength in an aqueous dispersion of the nanotubes and peptide led to oligomerization into ordered structures via like-charge interactions between the peptides. The diameter of the aggregates increased from 100 ± 15 nm to 38 ± 8 µm on going from 0 to 120 mM NaCl while the addition of DMF was accompanied by a change in structure from tube-like to ribbon-like. The results obtained in this work clearly demonstrate the potential of using specially designed peptides to impart desired characteristics on a system.

Self-assembly on surfaces

In 1998 Liu et al reported the controlled deposition of individual SWNTs onto a patterned substrate.³¹ The substrate comprised two different SAMs - fabricated by either e-beam lithography³² or nanolithography³³ - one of which had a terminal amine group capable of interacting with the SWNTs. Predictably, AFM studies revealed that on the mixed monolayer surface, SWNTs were only observed on the $-NH_2$ functionalized area after immersion of the patterned substrate into a SWNT dispersion. One of the most convincing AFM images shows how an SWNT actually bent in an effort to align itself with the NH₂ region of a surface patterned in the shape of a "Q". As a proof-of-concept demonstration it was also shown that two electrodes can be connected by a selectively deposited SWNT using this amine – nanotube interaction.

As mentioned earlier, the realization that oxidatively shortened SWNTs can form amide bonds is of paramount importance in the assembly of useful structures. Recently, nanotube-amine interactions and self-assembly have been used to construct nanotube cages by adsorbing oxidatively shortened single-walled nanotubes onto aminefunctionalized silica gels.³⁴ In this report, an initial layer of oxidatively shortened SWNTs was adsorbed onto amine spheres, 6 μ m in diameter. Subsequent addition of SWNTs resulted in NT-NT interaction because of van der Waals attraction, and a layered structure resulted. On etching away the silica, a nanotube cage remained the actual network structure of which was determined by the initially adsorbed layer of SWNTs. As was the case with Liu's multifarious surface,³¹ adsorption of the SWNTs does not occur unless the silica spheres have been amine-functionalized, proof that it is the initial covalent amide bond formation that initiates the self-assembly.

Cysteamine, a short-chain aminoalkanethiol, has been used to thiol-functionalize short SWNTs making self-assembly on gold surfaces possible.³⁵⁻³⁷ Of these three reports which all utilized the same basic scheme to construct arrays of SWNTs perpendicular to gold surfaces, it is only the most recent one³⁶ that demonstrated an application. The authors described the modification of a polycrystalline Au electrode with self-assembled arrays of SWNTs perpendicular to the surface, and the resulting electrocatalytic properties. A redox enzyme was covalently attached to the free end of the SWNT and its characteristic CV was observed. This supports the claim that SWNTs can act as molecular wires for electron transport between an electrode and an enzyme. This was an important conclusion as one of the proposed applications of CNTs has been their potential as electron transfer agents to redox active centers. Furthermore, this was the

first report of an electrode being modified by anything other than random deposition of SWNTs where one has no control over the extent of interaction between the redox material and the nanotube.

Obviously another possible route to the self-assembly of carbon nanotubes is via the use of complimentary DNA strands. Dwyer et al.³⁸ have demonstrated some initial success in achieving this goal whereby amino-terminated DNA strands have been tethered to open-ended carboxyl-terminated SWNTs. The authors proposed the self-assembly of molecular scale electronic systems using this technique.

One of the most widely-hyped potential application of carbon nanotubes is as field emitters in Field Emission Displays (FEDs) due to their high electrical conductivity. Compared to standard cathode-ray tubes and liquid crystal displays used in plasma display TVs, some of the advantages of CNT FEDs include faster response times, lower power consumption, wider viewing angle, and superior environmental tolerance. Among the big leaders interested in this application, Samsung has carried out the largest body of research. Researchers there have constructed display screens using a CNT/organic binder paste,³⁹ and more recently have shown the potential for thiol-Au based SAM formation in the preparation of CNT FEDs.⁴⁰

Conclusion

The field of CNT research is blooming but it has become increasingly obvious that reliable, large-scale methods of self-assembly are needed before device fabrication becomes a reality. There are currently a number of start-up companies in the U.S. pursuing the commercialization of CNT-based devices, and as many as 24 electronics companies including Samsung and Motorola are racing to develop flat-panel CNT FEDs. It is just over a decade since the discovery of the first SWNTs^{7,9} and devices such as Samsung's full-color, flat panel FEDs (www.samsung.com), and Nantero's nonvolatile random access memory chip (www.nantero.com and www.economist.com search term "carbon nanotubes") show early promise as the devices most likely to succeed in the near future.

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