



## What's Next for Low-Dimensional Materials?

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## What's Next for Low-Dimensional Materials?

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I start this perspectives article with a brief historical review about how graphene logically fits into the nanoscience field from my own perspective in contrast to the actual history of graphene research. This is followed by comments on the current perceived importance of graphene research and potential graphene applications along with my perspectives on research opportunities. These discussions naturally lead to a summary of my views on the present status of the field and where it is heading as we look to the future.

Logically, graphene is almost as simple as a nanostructure can be. Graphene as a material consists of only carbon atoms, all being of the same atomic species, with the same relatively simple  $sp^2$  bonding arrangements, and occurring in nature with high abundance and quite high purity. Because of the relative simplicity of graphene, study of this material started at an early time, with a highly influential publication by Wallace in 1947[1] predicting a unique linear electronic dispersion relation for  $E(k)$ . The experimental preparation of monolayer graphene goes back to the work of Boehm who reported his synthesis method based on graphene oxide in the 1961–1962 timeframe.[2,3] Logically, I would have expected some follow-up to this line of research by Boehm and readers of these publications. This could logically have led to a detailed development of the synthesis of graphene (by the scotch tape method or by other methods) and followed by detailed property studies of this material in its pristine form using all experimental and theoretical tools available in the 1960s and 1970s. The actual historical developments of nanocarbon research, however, took a somewhat different turn, with only the *graphene concept* remaining in our minds. Correspondingly, the

actual research path followed other directions for the next 40 years, perhaps due to a lack of a theoretical driving force to pursue graphene-based calculations as such, and for this reason there was little motivation to try to study monolayer graphene experimentally.

Other distractions also seemed to interfere with graphene research progress as such. In the 1960s, the industrial labs associated with several large companies—Bell Telephone, IBM, General Electric, Union Carbide, and others—established major research laboratories that contributed strongly to publications on materials research at that time, but their own industrial interests somewhat affected their actual research directions. Also in this time frame, Europe and Asia were still rebuilding their infrastructures following World War II and were not yet as strongly involved in materials research as they are today.

There were also other carbon-related scientific distractions in the 1960s that did not involve graphene explicitly. The big push at that time was silicon and the closely related semiconductor electronics industry along with the communications industry. At that time, the III–V semiconductors were still discussed as materials of the future. We must remember that Sputnik occurred in 1957, and the launch of this first satellite into outer space not only gave much impetus to the space program in the USA, but to science and engineering education and research generally. The advent of Sputnik also gave opportunities for young women like myself to find a possibility for employment in good research positions because of the large perceived national need in the USA to catch up to the Russians.

Carbon-based research in the 1960s was a backwater research area. Carbon-related research, however, saw

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the development of highly oriented pyrolytic graphite (HOPG) at Imperial College in the UK by Professor Ubbelohde and his research group.[4–6] This synthetic form of bulk graphite was further developed and commercialized at the Union Carbide company in the USA by Moore et al.,[7] Diefendorf and Tokarsky.[8] The availability of high quality HOPG,[7,8] originally commercialized for use in monochromators and other device applications such as batteries for energy storage, fostered studies of graphite intercalation compounds (GICs).[9]

From a structural viewpoint, GIC materials are superlattices (see Figure 1) with unit cells consisting of an intercalate layer and  $n$  graphene layers (where  $n$  is a small integer). These graphene layers normally show the AB Bernal layer stacking of graphite (Figure 2), and in GICs the few graphene layers are sandwiched between a monolayer of intercalant ions or molecules. The intercalants typically transfer either electrons or holes to the few-layer graphene stacks, thereby making them n-type or p-type, and imparting interesting electronic properties to these graphene layers. Research on GICs started actively in the 1950s [12] and became much more active starting in 1977 when the first international conference on GICs was held at a historic chateau in La Napoule, France. This was to my knowledge the first important international conference in the nanocarbon field, and gave researchers like myself the opportunity to meet their counterparts internationally for the first time. In the 1970s, international travel was rare and the communication was slow between researchers and largely took place by air mail letters and also through the journal articles that were eventually published. The contacts made at La Napoule greatly facilitated international exchange and this conference was followed by other international GIC conferences subsequently, with the second conference held in Provincetown, MA, in the USA in 1980,[13] with a somewhat larger audience than at the first conference.

Within the GIC setting, graphene as a research topic was not significantly pursued, though the graphene concept played a large role in the development of concepts for all nanocarbons generally. Research on GICs was very active in the 1970s and 1980s and attracted the interest of chemists, physicists, and engineers, and benefitted from collaborative research both in academic and industrial settings as well as in national laboratory environments. Within the larger nanocarbon research field, the early 1980s witnessed increasing interest in carbon fibers [14] and carbon clusters.[15] The carbon fibers eventually led to carbon nanotubes [16] and the clusters led to fullerenes.[17] Overall, the large scientific interest in nanotubes and fullerenes led to the growth of a large scientific community ready to both appreciate the importance of the synthesis of monolayer graphene and of its unique properties when this advance was finally reported in 2004 by Novoselov et al., and Geim and co-workers [18,19] in Manchester in the UK and at about the same time by

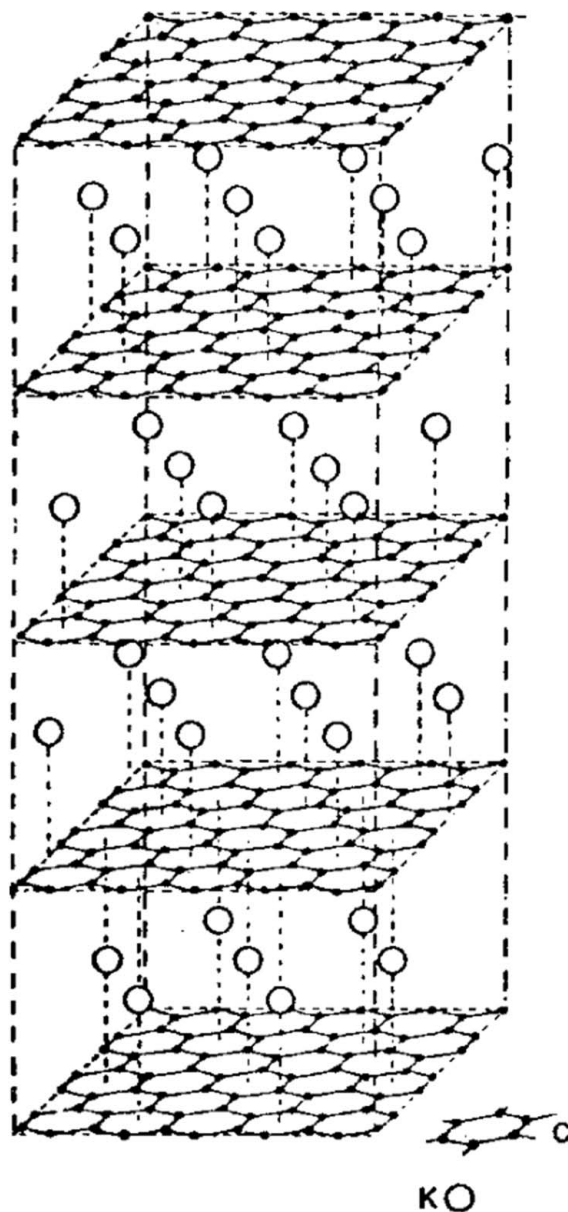


Figure 1. Model for  $C_8K$  according to Rüdorf and Schulze [10] showing the stacking of graphite layers (networks of small solid balls) and of potassium layers (networks of large hollow balls). The graphite and intercalate layers are arranged in an  $A\alpha A\beta A\gamma A\delta$  stacking sequence, where A refers to the graphite layers and the Greek letters to the intercalate layers.[9] The actual layer stacking is, however, more complex and takes into account the Herold–Daumas intercalation process.[9]

Kim and co-workers [20] at Columbia University in the USA. Many of the researchers who were also knowledgeable in GICs, fullerenes, and nanotubes quickly entered the graphene research field and brought with them many others from other research backgrounds, thereby strongly enriching the graphene field and greatly accelerating the early advance of graphene-related research.

We now review some perspectives on the status of the graphene field today. The method used by Novoselov et al.[18] to prepare monolayer graphene suitable for

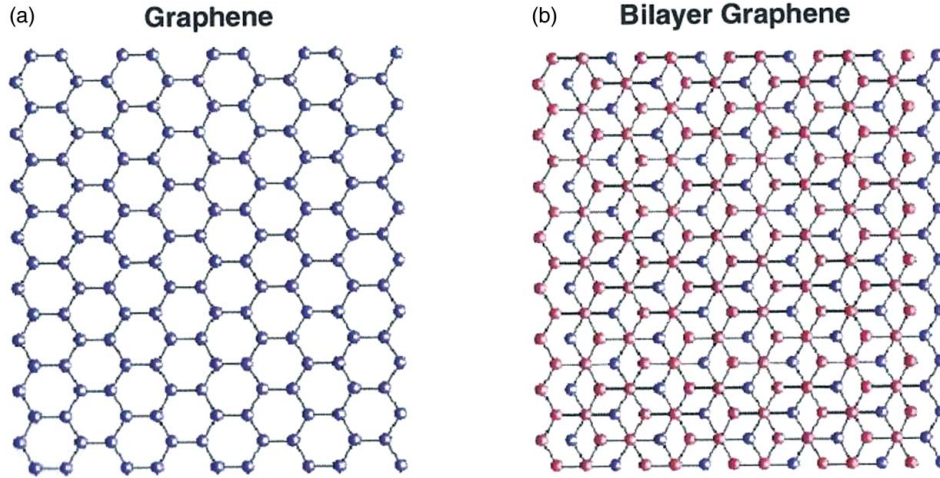


Figure 2. Model for the atomic arrangements of (a) monolayer graphene where there are two inequivalent sites (usually called the A and B sites in the literature); (b) bilayer graphene where the carbon atoms show the so-called Bernal AB stacking: the A' sites in the second layer lie over the A atoms in the first layer and the B' atoms of the second layer lie over the empty centers of the hexagons of the first layer. Figure is modified from Raza [11].

characterization and property measurements was the scotch tape method applied to a bulk graphite crystal, whereby a few layers of graphene were peeled off. By repeating the thinning procedure many times, small flakes of monolayer graphene could be identified optically when placed on an oxidized Si/SiO<sub>2</sub> substrate by the 2.3% absorption of light by a graphene monolayer.[21] Many researchers had used the scotch tape method in the past to work on clean graphite surfaces for optical and magneto-optical studies of the electronic structure and lattice vibrations in graphite.[16] But these researchers worked on the bulk samples and threw away the few-layer graphene pieces left behind on the scotch tape.

The electronic structure of graphene is associated with the four valence electrons, forming  $\sigma$ -bonds and  $\pi$ -bonds. The  $\sigma$ -bonds in graphene come from the  $sp^2$  covalent bonding of a carbon atom to its three nearest neighbor carbon atoms in the planar honeycomb hexagonal lattice. The remaining fourth carbon bond is related to the weak out-of-plane carbon  $2p_z$  bond. These  $p_z$  bonded electrons half fill the  $\pi$  band to form an occupied conduction band and an empty valence band which are degenerate at the  $K$  point zone corner [16] of the two-dimensional Brillouin zone of graphene (Figure 3).[19] The electronic structure of the valence and conduction  $\pi$  bands in graphene is described by a simple tight binding model,[23–26] which provides a satisfactory model for understanding many of the basic fundamental properties of monolayer and few-layer graphene. Based on the lattice symmetry of the honeycomb lattice, the tight binding approximation can be used to solve the resulting linear  $E(k)$  electronic dispersion relation.[16,26] This dispersion relation can be conveniently expanded in a Taylor series in which the first term is  $E^\pm(k) = \pm \hbar v_F k$ , where  $v_F$  is the Fermi velocity of the electrons and holes,  $\hbar$  is

Planck's constant divided by  $2\pi$ , and  $k$  is the wave vector for both electron and hole carriers. Since the valence and conduction bands are degenerative at the  $K$  point, graphene is a zero gap semiconductor. But graphene is an unusual material from an electronic structure point of view, with a linear  $E(k)$  relation that is symmetric about the Fermi level which goes through the  $K$  and  $K'$  points of the Brillouin zone (see Figure 3(a)). These  $K$  and  $K'$  points are related by time reversal symmetry, so that the Fermi surface has two valleys with a Dirac point of degeneracy between the valence and conduction bands imposed by symmetry [18,19] and backscattering is forbidden for these electrons.[27]

In practice, for many applications the capability to produce large-area high-quality graphene samples under controlled conditions is important. In addition, many applications require the ability to vary the carrier concentration (or Fermi level) and carrier type (n-type or p-type). The high mobility of carriers in graphene is another special property of monolayer graphene.[18,19] However, the absence of a band gap [19,27] restricts its utility for many practical applications commonly associated with semiconducting optoelectronic materials. For all these reasons, we should not think of graphene as a material that will replace silicon along the timeline for Moore's law for advancing the functionality of semiconductor electronics as the device size continues to get smaller and smaller. We should instead consider graphene as a special novel material with interesting and unique properties of its own, with many potential applications based on its own unique properties.

Once early samples of monolayer graphene prepared by the mechanical scotch tape method mentioned above revealed the special and very interesting graphene properties of high mobility,[27,28] electron and hole

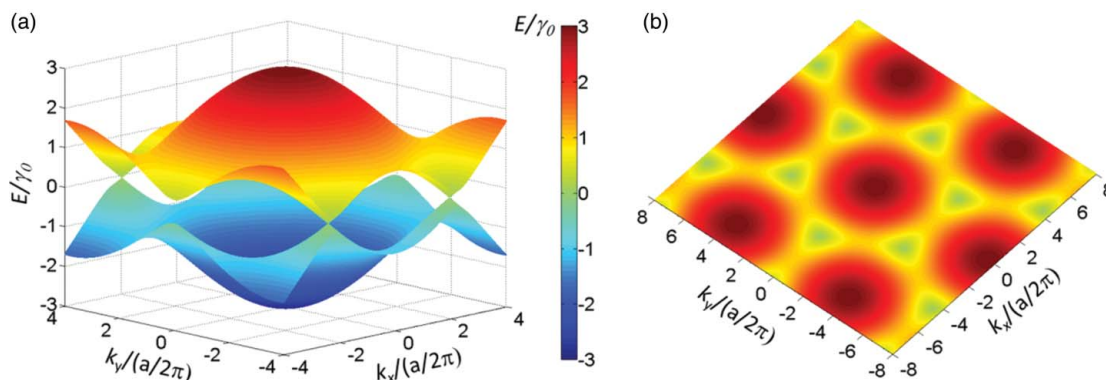


Figure 3. The 2D energy dispersion relation of monolayer graphene. (a) The energy dispersion relation for monolayer graphene.[19] The conduction band and valence band touches at the  $\bar{K}$  and  $K'$  points. (b) Top-view of the  $E - k$  relation showing correspondence with the hexagonal reciprocal lattice. Figure is modified from Wang [22].

symmetry,[27,28] Klein tunneling,[28,29] unconventional quantum Hall effects,[30,31] and suppression of backscattering effects, the graphene research field was launched.[27]

Large efforts were soon exerted to develop controlled laboratory synthesis methods for large-area graphene materials.[32,33] This effort resulted in growth techniques for monolayer graphene based on chemical vapor deposition methods on a Si/SiO<sub>2</sub> substrate.[32–34] In some of the more successful attempts, special molecules with structural components that are related to the graphene structure were used to seed the growth process,[35,36] and copper was used as the metal to promote the formation of sp<sup>2</sup> carbon bonds during a monolayer graphene growth process.[32,37,38] taking advantage of the very low solubility of carbon in copper. If few-layer graphene is desired then nickel can, for example, be used as the transition metal to promote preferential bilayer graphene growth.[39] Furthermore, some authors have found hydrogen effective for promoting the growth of larger crystalline graphene flakes.[40] An annealing step [33] is often used to improve the crystallinity and carrier mobility of chemical vapor deposition (CVD) graphene.

Once the CVD graphene is grown, it is necessary to transfer the graphene sample to the desired location where it will be incorporated into a device or into an experiment. The technology for graphene transfer from one location to another was therefore developed by several groups.[41–44] Two problems were however introduced in the CVD graphene growth method and these involved (1) removal of the remains of the poly(methyl methacrylate) and other agents used in the transfer process, and (2) mitigation of the defects introduced by the CVD growth process. The growth process is normally initiated by a graphene nucleation process involving growth seeds forming graphene islands or grains.[45] When one graphene grain grows into an adjacent grain, a grain boundary is formed because the crystalline orientation

of adjacent grains are in most cases crystallographically incoherent on an atomic scale.[45,46] The grain boundary defect is thus a natural consequence of the CVD synthesis process. Another graphene growth problem that has received attention is the patterning of graphene samples [47,48] to appropriate size, shape, and location on a substrate for use in further characterization or property measurements for device applications.

A wide variety of property measurements have already been carried out on monolayer graphene, including transport,[19,20,49,50] optical absorption,[21] reflectivity and luminescence,[21,51] Raman scattering,[52,53] magnetic properties,[54] doping,[55–58] electrical properties,[49,50] X-ray photoemission spectroscopy,[59,60] defects,[61,62] strain,[63] pressure effects,[64] quantum Hall effects,[19,20,30,31,49] and more. The unusual properties of graphene have attracted many theoretical studies directed toward gaining an understanding of the fundamental size and dimensionality dependence of the special properties of layered materials.[19,27,65] Another popular research direction has been the detailed study of the effect of the substrate on each of the properties that had been studied previously, leading to studies on freely suspended graphene.[66]

Variations on many properties of graphene have been probed by systematic studies of their dependence on the Fermi level, since the Fermi level controls the carrier concentration and the balance of electrons and holes. Control of the Fermi level has been achieved by gating,[67–69] doping,[55,57] and electro-chemistry.[70–73] The simplicity of the graphene system and the interesting and unique properties of graphene promoted more detailed and controlled experiments than would normally be carried out on another materials system. The tendency to carry out systematic studies of fundamental issues by applying electric fields,[18,20,50] magnetic fields,[74] strain,[63] pressure,[64] substrate effects,[59] and any conceivable perturbation greatly enriches our

understanding of graphene as a material, as well as our understanding of the capabilities of each of the probe techniques normally used in materials research to study graphene in particular. In this sense, graphene can be used as a metrology tool for layered materials generally, and this is another reason for the importance and interest in this materials system.

The absence of a bandgap in graphene has historically provided another driving force for the choice of research directions. In particular, the fact that the application of an electric field could generate a band gap stimulated particular interest in bilayer graphene,[75] which also led to studies looking for a bandgap in trilayer graphene.[68] Since graphene has two atoms per unit cell, the interlayer stacking in bilayer graphene could be either AA stacking or AB stacking or random layer stacking, systematic studies of layer stacking have been actively pursued by many groups, including the stacking of three-layer graphene,[76,77] stimulated by the fact that each carbon atom in the graphene lattice has three neighbors, with the ABA and ABC interlayer stacking arrangements being of particular interest.[76,77] Doping studies with p and n dopants, such as with boron and nitrogen substitutional impurities, have been carried out widely,[56–58] including the development of preferred doping on one of the lattice sites [57] in a sample (i.e. the A site or the B site) because of the repulsion of the same dopant on neighboring lattice sites.

Layer stacking also stimulated studies on twisted graphene layers and the special stacking of twisted layers where moiré patterns form.[78,79] Closely related to twisted layer stacking is the folding of a graphene layer and the correlated effects produced by layer folding.[79] This research direction has also been pursued actively and fruitfully.

Another related frontier area involves the physical properties of the layered compound hexagonal BN [80] which is a wide gap semiconductor but composed of III–V elements with very similar lattice constants to those of graphene. Fruitful studies have been pursued using hexagonal BN as a substrate for growing high-quality graphene by the CVD method.[81] Furthermore, BN has been studied because of its own interesting properties as a monolayer wide bandgap semiconductor.[80,82] This similarity in lattice constants between graphene and hexagonal BN also suggests the growth of superlattices containing periodic sandwiches of graphene and h-BN.[82,83] Although early work in this research direction has been carried out, many potentially interesting studies await such future investigation, along with related studies on few-layer graphene, BN, superlattices of graphene, and BN together with other layered materials,[83] If nanotubes are also included, we could have a superlattice that would nicely combine one-dimensional and two-dimensional objects in larger frameworks, taking advantage of materials having similarities in lattice constants

but with different symmetry constraints imposed by their different geometries and dimensionalities.

Studies on double-wall [84,85] and triple-wall nanotube bundles and individual double-wall and triple-wall carbon nanotubes [84] strongly complement advances in bilayer and trilayer graphene and the synergy between these two research directions awaits future exploration. Theory is badly needed to explain the many advances that have occurred both in graphene studies and in the beyond graphene studies. We are just at the beginning of the beyond-graphene field of nanoscience and because of the many recent entrants to this field we can expect many advances to occur in the near future.

As stated above, few condensed matter systems have been studied in as much detail and as systematically as graphene. This may be in part due to the fact that the preparation of few-layer graphene took place so much later than the intense studies of silicon and III–V compounds occurred. By the time graphene became an active field of study, condensed matter physics and materials physics were mature research fields and many experimental and theoretical techniques had already been developed. Furthermore, as a result of all of this activity in the nanocarbon field discussed above, a large cadre of people had been trained with extensive research experience and know-how in the condensed matter and materials research fields, including the nanocarbon field, and these researchers were ready to advance the graphene field rapidly, taking advantage of an interesting material receiving much press coverage and having a broad readership.

As we look to the future, we see the graphene field expanding to other layered compounds and to the investigation of new phenomena. These new research directions have been stimulated by the intense graphene studies that have taken place in the past decade. From my own perspective, my research group has also started studies of few layer transition metal dichalcogenides, and we are looking for the occurrence of Dirac cones in other materials systems, especially in systems with other crystalline symmetry properties than graphene. It is likely that other researchers have been inspired by graphene to move along yet different paths, and this variety of activities will enrich the materials research environment for layered materials for the next few years. However, in this perspectives article, I have limited myself to the areas of my own greatest familiarity.

What I see is that conferences are now being held on the subject of ‘beyond graphene’, and this is telling the research community that a significant number of people are moving into research on other layered materials at this time and to my thinking this is a good idea for the exploration of new ideas and techniques that we learned from working with graphene. One research direction frequently studied in this connection is the trilayered transition metal dichalcogenides,[86,87] such as MoS<sub>2</sub>

and WS<sub>2</sub> and other-related layered compounds containing the dichalcogenides Se and Te.[83] These materials have in fact been investigated for many years in their bulk form.[86,87] I personally worked on the trilayer transition metal dichalcogenides in the 1990s because they formed nanotubes [87] and had many properties that paralleled those of carbon nanotubes.

Another category are the five-layered V–VI compounds related to the Bi<sub>2</sub>Te<sub>3</sub> family.[88,89] I also worked on bismuth and bismuth-antimony nanowires more than a decade ago to study the semiconducting and semimetallic phase transitions,[90,91] and the special phenomena related to these nanowires. More recently, my research group has been studying Bi–Sb thin films as two-dimensional systems which are of potential interest for their thermoelectric properties for cooling electronics at low temperatures.[92] The advent of graphene led to our study of the possibility of Dirac cones in the Bi<sub>1–x</sub>Sb<sub>x</sub> system in two dimensions, and this has resulted in our location of Dirac cones in this system under special ranges of antimony concentration, film thickness, and normal to certain crystallographic orientations in this highly anisotropic crystalline material.[92–94] What is special about Dirac cones in the Bi<sub>1–x</sub>Sb<sub>x</sub> system is the high degree of anisotropy of these Dirac cones,[92–94] which introduces new symmetries to the problem and new physical properties.

Another future direction is inspired by combining two different nanostructures. For example, graphene provides an interesting conducting substrate for the deposition of other nanostructures and the subsequent studies of two-dimensional films.[95] Spectroscopic studies, as for example by Raman spectroscopy, show strongly enhanced Raman scattering intensities that are observed when single wall carbon nanotubes are placed on graphene substrates through a graphene-enhanced Raman signal effect.[95] New physics and interesting effects are observed when certain molecules are placed on the outer walls of nanotubes or placed within the internal cavity of a carbon nanotube.[96] In such experiments, double-wall nanotubes are of particular interest for separating effects occurring on the inner tube relative to the outer walls of individual double wall nanotubes. For example, in the case of a carbon nanotube containing two strands of Eu rare earth atomic nanowires within the nanotube core,[85] a large enhancement in the Raman intensity of the single wall nanotube was observed. Such studies could lead to interesting new research directions. A number of these resonant properties of double-wall carbon nanotubes have already been demonstrated,[97] though detailed investigation [98] remains at an early stage. It is likely, based on rapid recent progress as is reported annually at conferences such as the international NTxx conference series for carbon nanotubes,[99] that further interesting discoveries will be occurring in the coming years in this general research area.

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