Nanoscale Phenomena

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**Introduction**

The advance of nanoscience has been strongly connected with research carried out on nanoscale materials with sizes far smaller than can be seen by the human eye or with an optical microscope. At the nanoscale, which is below 1 µm (or $10^{-6}$ m), materials exhibit different properties than the same materials exhibit in bulk form. This is in part due to the much larger surface-to-volume ratio of nanoscale materials, which for example has had a great impact on the development of catalysts. Tiny catalytic particles a few nm in size have a huge impact nowadays in the chemical industry in the production of ever-increasingly novel nanomaterials which are designed to improve our quality of life. Beyond this, the new physical phenomena that are discovered at the nanoscale, year by year and at an accelerated rate, are a central focus of this paper.

The first part of the paper discusses my 50-year adventure with sp$^2$-carbon-based nanomaterials. This research area has attracted increasing attention in the last two decades, in part because carbon-based materials have become prototypes for the study of nanoscale materials properties. The second part of the paper discusses the impact of nanoscale materials on the conversion of thermal energy to electrical energy, as occurs when waste heat is converted to electricity which can be used directly by consumers. Whereas the carbon studies of nanostructures were inspired by curiosity, the studies on thermal energy conversion were inspired by societal need.

**Nanoscale Carbon Research**

The active study of nanoscale carbons started with the 1947 paper of Wallace$^1$ on a single layer of graphite, which is known today as graphene. The novelty of his work was the linear dispersion relation $E^\pm(k) = \pm\hbar v_F k$ for the energy of an electron in graphene as a function of wavevector $k$ and velocity $v$ at the Fermi level. In 1960, when I started my independent research career, I chose to study the electronic structure of three-dimensional graphite, highly inspired by the work of Wallace on the linear $E(k)$ relation in two-dimensional graphene, largely because of its novelty. Although we often used sticky tape in the 1960s to generate a beautiful shiny surface on our graphite samples, we never had an idea to try to study the single-layer graphene left behind on the sticky tape.

In 1960 the electronic structure of three-dimensional graphite was just in a discovery phase, and I had an opportunity to work on early experimental studies of this fascinating materials system. Theoretical models of the electronic band structure for graphite had been developed by Slonczewski and Weiss in 1956$^2$ and by McClure in 1957$^3$ in zero magnetic field, and in 1960 McClure$^4$ extended his calculations to a magnetic field. My research addressed experimental studies of the electronic band structure of graphite in a magnetic field with the intention of getting a far more complete picture of the electronic band structure than was then available. This research was important in evaluating the various parameters of the
Slonczewski-Weiss-McClure band structure, and the study using circularly polarized light yielded the proper location of electrons and holes in the graphite Brillouin zone.\(^5\) As can be seen from Figure 1, the publication of papers on sp\(^2\) carbons during the 1960s was sparse, although the research by H. P. Boehm on the 1962 observation of monolayer graphene,\(^6\) though very important historically, was not widely known to those working in the sp\(^2\) carbon field at that time. In my case, I first met Boehm in 1977 at the first international meeting of sp\(^2\) carbon researchers, which was held in La Napoule, France.\(^7\) This conference was the first international conference on graphite intercalation compounds. At that time, international travel and international conferences were not yet common, and the most common communications medium was through the postal system. Intercalation compounds (see Figure 2) allowed study of graphene monolayers, bilayers, trilayers, etc., sandwiched between the intercalant layers, but also as somewhat modified by the interaction with these intercalant layers between adjacent graphene layers.

Methods for generating clusters and for studying nanoscale carbon cluster properties became available in the early 1980s and the clusters produced by laser ablation that we were studying turned out to be larger than 50 carbon atoms in size. Such large clusters were unexpected at that time.

In 1984 I visited the Exxon Research Labs to discuss the large carbon clusters that we were observing with international experts on large carbon clusters. Soon after this visit, the Exxon group reported their results on large carbon clusters\(^8\) (see Figure 3), showing carbon clusters up to C\(\text{100}\) but with only even numbers of carbon atoms per cluster above about C\(\text{24}\). These results were also observed independently by Richard Smalley at Rice University\(^9\), who interpreted the large observed intensities for the C\(\text{60}\) and C\(\text{70}\) species to be connected with the early observation of all-carbon fullerene molecules. As can be seen in Figure 1, the discovery of fullerenes attracted much interest from the science community.

Our involvement in fullerene research was mostly in carrying out detailed symmetry-based infrared and Raman spectroscopy studies in collaboration with Peter Eklund who was at the University of Kentucky at that time; this collaboration and resulting extensive research program was reported in a large book on fullerene spectroscopy published by Academic Press.\(^10\) Fullerenes were a manifestation of nanodot nanocarbons, in comparison with graphite intercalation compounds which had a two-dimensionality within large planes of few-layer graphene and a one-dimensionality in the direction of the superlattice perpendicular to these graphene planes.
Through the intercalation research program, I attended the Second International Conference on Graphite Intercalation Compounds. It was there in 1980 that I met Professor Morinobu Endo of Shinshu University and heard him speak about carbon fibers. This talk gave me the idea of intercalating carbon fibers, and started a long-term collaborative program on nanocarbon research. My heavy involvement in the field of intercalated carbon fibers led to my giving a review talk on carbon fibers\textsuperscript{11} at a Nanocarbon Meeting in Washington, DC, where Richard Smalley gave a review talk on fullerenes. When Professor Smalley and I were both asked about the connection between carbon fullerenes and carbon fibers, he responded that we could perhaps think of a C\textsubscript{60} molecule elongating to form a C\textsubscript{70} fullerene and then elongating to C\textsubscript{80} and eventually reaching a tube-like shape (see Figure 4). I could see that this concept excited the audience.

**Carbon Nanotube Studies**

The idea of fullerenes reaching a long tube-like shape suggested to me the idea in September 1991, when Matsutaka Fujita and Riichiro Saito, two very young physics faculty members from Japan, came to MIT for a year’s sabbatical, that I ask them if they would like to calculate the electronic structure of what is now called a single-wall carbon nanotube to see whether, if we could ever make such a nanocarbon material experimentally, such a structure might have interesting properties (see Figure 5).
Their calculation of the rolling up of a monolayer graphene sheet to form a single wall carbon nanotube (SWCNT) (Figure 5) showed that the linear E(k) relations for graphene electrons would be subjected to the boundary conditions of the cutting lines on the Dirac cone for both the valence and conduction bands, as shown in Figure 5. If the cutting lines would go through the apex of the cones, then a metallic nanotube would be formed, but if the cutting lines did not go through the apex, then a semiconducting nanotube with a bandgap would be formed. The prediction that nanotubes could be either semiconducting or metallic, depending on the orientation of the hexagons of carbon atoms relative to the nanotube axis became very controversial between 1992 and 1998. This controversy remained until experiments in 1998 directly identified semiconducting and metallic nanotubes. Once researchers became successful in synthesizing carbon nanotubes, many experimental and theoretical researchers entered the carbon nanostructure field (see Figure 1) and found many challenging topics related to the overall behavior of electrons, phonons, and the electron-phonon interaction between them.

Our group became heavily involved with Raman spectroscopy studies explained in Figure 6a, and results on Raman spectra from bundled and individual SWCNTs shown in Figure 6b. The reason for the entry of large numbers of researchers into the nanotube field can be understood when considering the complexity of carbon nanotubes, largely due to their chirality, which denotes the (n,m) index pair that is used to describe the orientation of the nanotube hexagons relative to the nanotube axis (see Figure 5).
This complexity generated a very large literature devoted to the study of the chirality dependence of the many interesting carbon nanotube properties that have been demonstrated in the literature.\textsuperscript{18}

Recent studies on carbon nanotubes have included more in-depth chirality studies,\textsuperscript{18} investigations of the electronic Raman effect in carbon nanotube’s,\textsuperscript{19} combination modes and overtones in the Raman spectra,\textsuperscript{20} and electrochemical studies of the Raman effect.\textsuperscript{21} In general, major advances have occurred in the general control of the chirality of carbon nanotubes in the last two or three years. Control of the synthesis process has been achieved both for producing only metallic nanotubes,\textsuperscript{22} only semiconducting nanotubes,\textsuperscript{22} and specific (n,m) nanotubes to reasonable purities,\textsuperscript{23} with further work ongoing mostly in industry and government laboratories to achieve ever-higher purity levels, and likewise for the characterization of nanotube samples for their metallicity (S,M) and chirality (n,m). Photoluminescence techniques for the identification of the (n,m) of nanotubes have also advanced greatly and are now commercialized.\textsuperscript{24} The observation of coherent phonon relaxation processes has greatly advanced both experimentally\textsuperscript{25} and theoretically.\textsuperscript{26} Optical processes in nanotubes have been shown to be highly sensitive to both excitonic excitation\textsuperscript{27} and dielectric screening effects;\textsuperscript{28} these effects need to be characterized in specific samples and controlled where these effects are at issue. Recent nanotube studies have been extended to double wall\textsuperscript{29} and triple wall\textsuperscript{30} nanotubes, with studies also done on individual (n,m) nanotubes and bundles of nanotubes with mixed or with similar chiralities.

**Graphene Studies**

The discovery of graphene in 2004 by Geim and Novoselov\textsuperscript{31} as a stable single layer of carbon atoms with sp\textsuperscript{2} bonding had a profound effect on nanocarbon science, transforming the Wallace 1947 conceptual picture\textsuperscript{1} of monolayer graphene into a physical reality. The demonstration of a unique quantum Hall effect in graphene, never seen before for any materials system, aroused great interest in the physics community\textsuperscript{32}. This was soon followed by the demonstration of a series of remarkable properties, such as very high current densities, very high thermal conductivity, very similar behavior of the hole and electron carriers regarding band parameters, and very high carrier mobilities. My involvement with graphene has been largely with exploiting the relative simplicity of the electronic structure, allowing study of symmetry-breaking phenomena that had previously been somewhat neglected in condensed matter systems such as substrate effects, and edge effects.

One powerful tool that the lattice vibrations provide is the ability to use isotopes to distinguish surface and environmental effects from bulk material effects. Since the \textsuperscript{12}C and \textsuperscript{13}C isotopes have masses that differ by almost 10 per cent, the phonon vibrations will occur at different frequencies according to the relation

\[
\frac{\omega_0 - \omega}{\omega_0} = 1 + \left(\frac{(12+C_0)}{(12+C)}\right)^{1/2}
\]

where \(\omega_0\) and \(\omega\) are, respectively, the frequencies of the \textsuperscript{12}C graphene G-band carbon-carbon vibrational frequency and that of a \textsuperscript{13}C-enriched carbon sample, C\textsubscript{0} = 0.0107 is the natural abundance of \textsuperscript{13}C, while C = 0.99 is the concentration of \textsuperscript{13}C in an enriched sample. Since the \textsuperscript{12}C and \textsuperscript{13}C isotopes have the same electronic structure, use of isotopes allows the separation of the phonon-related effects from electronic structure phenomena, since phonon-related phenomena are sensitive to the different isotopes while the
electronic structure is not. Thus if a trilayer graphene sample is prepared such that the $^{13}$C-enriched layer is placed on a substrate, a $^{12}$C/$^{13}$C layer of mixed $^{12}$C and $^{13}$C composition is placed in the middle (where the $^{12}$C/$^{13}$C ratio could be varied from one sample to another), and a $^{12}$C layer is placed on the top, then we can distinguish the environments of each of the three layers independently. Figure 7 shows the Raman spectrum for the $^{12}$C top layer taken at a laser excitation energy of 2.33 eV which is similar to other traces in the literature showing a strong intensity for the second-order $G'$ feature and a much weaker intensity for the first-order $G$-band vibration due to the optical phonon modes of monolayer graphene. The anomalously large intensity of the second-order feature in Figure 7 has been explained by the double resonance process in sp$^2$ carbon systems, but the $I_{G'}/I_G$ intensity ratio for the $G'$ and $G$ band features in monolayer graphene is especially large because every step in the double resonance process is in resonance.

Electrochemistry allows us to put a controlled voltage across the layers using both negative and positive voltages, which is equivalent to varying the Fermi level. These results (Figure 7b) show that the middle
layer is protected by the two surrounding graphene layers, so that it is possible to clearly see features in Figure 7b in the G band peak frequency for both positive and negative potentials at electrode potentials corresponding to the G-band vibrational frequency, but this effect is not well seen for the bottom layer or for the top layer in the triple layer sample in Figure 7b.

Raman spectra taken as a function of applied potential, ranging from –1.5V to +1.5V, are highly informative in showing the effect of chemical doping on the sample itself as well as asymmetries in the valence and conduction bands. These effects are shown in Figure 8 for both the G band and the G’ band. The G band reflects intraband transitions in a first order process, while the G’ band is highly sensitive to interband transitions. The G’ band is a second order process, which is sensitive to the wave vectors of the phonons involved in the transition.21

My involvement with graphene edges started in 1996 when a visiting student, Nakada, worked with me and her Japanese supervisor, Fujita, on armchair and zigzag edges (Figure 9). They had shown theoretically that a zigzag edge had a high density of electron states at the Fermi level but armchair ribbons did not have a similar singularity in the electronic density of states. Armchair ribbons could instead be either metallic or semiconducting depending on the ribbon width34 as shown in Figure 10. Here we can see a correspondence between one-dimensional armchair graphene ribbons and carbon nanotubes insofar as armchair ribbons can be either semiconducting or metallic depending on their width.34 Differences between the Raman spectra of zigzag and armchair edges in the Raman spectra were demonstrated in terms of the D-band Raman intensity35 which was also confirmed by theory. Studying edges experimentally is difficult because of difficulties in separating edge roughness artifacts from intrinsic edge effects. We have more recently shown that joule heating within a transmission electron microscope of graphitic ribbons (Figure 11) can yield atomically sharp edges, as can be seen in the high resolution TEM image in Figure 11.36,37

Graphene has also provided a vehicle for identifying the physical origin of the weak features in the Raman spectra such as the weak G* mode in the Raman spectra. In this case by varying both the gate voltage (V_g) and the laser excitation energy (E_laser) we have been able to identify specific low-intensity features in the Raman spectrum of monolayer graphene with specific harmonics and phonon combination modes as in molecular spectroscopy. The same approach appears to be promising more generally. One benefit of studying such features in graphene is that related spectral features appear in the Raman spectra of sp² nanocarbons generally, but they are complicated by metallicity issues and chirality phenomena that are not present in graphene. In this sense, graphene provides a useful metrology tool for studying a whole range of related sp² nanocarbons, and this is another reason people care about graphene.
There is an abundance of sources of thermal energy that could be used to improve our quality of life which instead is often considered to be waste heat and a pollutant to our environment. Thermoelectric processes offer opportunities to convert some of the waste heat from automobiles and commercial industrial processes into useful electrical energy. Such conversion could become more attractive if the efficiency of the energy conversion process could be enhanced. It was proposed starting in 1992, under encouragement by the US and French navies, that the use of nanostructures could significantly enhance the efficiency of the thermoelectric conversion process. This proposal came after a 30-year history from 1960-1990 when thermoelectric research was mostly inactive. More specifically, the 1992 suggestion to the Navy was that nanomaterials in the form of thin films and quantum wires could show better performance than the same materials in bulk form. The merit of the proposal was discussed within the research community in the 1990s and strategies were next developed for testing of this concept. The following few years involved proof-of-principle studies, followed by implementation at the pilot scale study level. Once commercial implementation of nanothermoelectric materials started in the last five years, new concepts for further enhancing the thermoelectric performance came to the fore. This 20-year development of nanothermoelectricity is briefly summarized in this review.

Thermoelectric energy conversion depends on the temperature difference between a hot junction and a cold junction as shown in Figure 12, thereby creating a voltage between them because of the difference in carrier concentration between the two ends of the rod. This voltage difference results in a Seebeck effect with a Seebeck coefficient S for thermoelectric materials which we try to make as large as possible for improved thermoelectric performance. It is important for the thermal conductivity $\kappa$ to be as low as possible to maintain the temperature difference between the hot and cold junctions, but at the same time we need electrons to carry electricity so that a large carrier density and a large electrical conductivity $\sigma$ are used. The thermoelectric figure of merit $Z = S^2\sigma/\kappa$ is the quantity which controls the performance of thermoelectric devices, and is normally reported as a dimensionless quantity $ZT = S^2\sigma T/\kappa$. Since $S$ is a decreasing function of carrier density and $\sigma$ increases with carrier density, as shown in Figure 12, and
since $\kappa$ increases when $\sigma$ increases because of the Wiedemann-Franz law, it had been difficult in bulk materials to increase ZT beyond the value of 1 using bulk thermoelectric materials.

However, the introduction of composite nanothermoelectric materials (Figure 13) increased the performance of many thermoelectric materials in the past 15 years. In Figure 13 both the bulk nano composite material and nanostructural inclusions-based material are shown. To make three-dimensional (3D) bulk material with useful heat-carrying capacity, it is necessary to assemble large amounts of nanomaterials into some kind of composite. This consolidation process produces, with some optimization, bulk thermoelectric materials with enhanced ZT, as obtained from measurement of the constituent thermoelectric quantities $S$, $\sigma$, $\kappa$ (Figure 14). The most important scattering mechanism here is the boundary scattering at the boundaries of the nanoparticles contained in the composite material, which in practice implies that the particles should be $\sim$10 nm in size. The PbTe-based material containing nanostructural precipitates (Figure 13) also is effective as a bulk nanostructural thermoelectric material. This boundary scattering approach had been the main driving force during the 1990s and into the following decade for improving the performance of thermoelectric materials.

More recently four other research strategies have been implemented to enhance ZT. First came the concept of using resonant states in the energy dependence of the Seebeck coefficient by Heremans. Although first demonstrated as a Tl dopant in PbTe, this effect is expected to be quite general and can be extended to other dopants and to other host materials. The concept of modulation doping, taken originally from the doping of III-V semiconductors such as GaAs, was recently successfully extended to thermoelectrics by Zebarjadi. According to this concept, dopants are introduced in one special region of a sample (see Figure 15) and the carriers from this special region are transported across a very thin spacer
region to the active channel that is doped. In modulation-doped thermoelectric materials, the host material is a 3D bulk composite, and the dopant is located inside tiny nanoparticles which donate carriers to the host semiconductor to enhance its conductivity with highly mobile carriers. These carriers maintain high mobility because the carrier pathway is predominantly through the high-mobility material with only a small amount of scattering by the tiny nanoparticles containing dopants. The measured ZT enhancement of a Si80Ge20 composite material is shown in Figure 16 using this concept. Other novel methods for ZT enhancement have been proposed and these are also in an early demonstration stage, such as energy filtering, nanoparticle doping,44 and the spin Hall effect.45

Since nanostructures have different properties from their bulk counterparts we can expect a continuing stream of novel concepts for various energy conversion strategies both within the thermal energy to electrical energy conversion initiative and more generally, for thermal energy, solar energy, and perhaps even wind energy conversion as independent technologies. Our planet has a large untapped renewable energy resource available from both waste heat and solar energy. The potential for the utilization of nanoscience for both enhanced renewable energy recovery and for the control of global warming is large, and is mostly untapped, offering many opportunities for the younger generation to contribute strongly to these very active current research areas.

References


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