Discovering Properties of Nanocarbon Materials as a Pivot for Device Applications

by Tetyana Ignatova and Slava V. Rotkin

It is rare in the history of modern science that a single area will be so productive for both fundamental research and its applications as in the field of nanocarbon materials. During last few decades several breakthrough discoveries in synthesis and fabrication of these materials have happened. Enabling materials technology has inspired thousands of scientists and engineers around the world working in physics, materials science, nanotechnology, chemistry, and other fields: 140,000 papers were published since 1991 (Fig. 1). Successes in these fields were celebrated by three major prizes,[1] the 1996 Nobel Prize in Chemistry (R. F. Curl, H. Kroto, R. E. Smalley), the 2010 Nobel Prize in Physics (A. Geim, K. Novoselov), and the 2012 Kavli Prize in Nanoscience (M. S. Dresselhaus).

Multiple applications of nanocarbon materials are anticipated to follow from their unique properties. The latter range from high mechanical stability and stiffness to unusual interfacial thermal conductance and optical performance. At the most basic levels all of these properties are related to the special type of carbon–carbon chemical bonding, so called sp[2] hybridization, present in all nanocarbons.[2] These bonds are natural in the flat, two-dimensional (2D) network, connecting carbon atoms and making a honeycomb-shape atomic lattice. The resulting material appears in the form of infinitesimally thin (just one atomic layer thick) although extremely strong film. Scrolls[3] of such a film could have a spheroidal shape (fullerenes), cylindrical shape (nanotubes), may form flat or conical flakes (graphene and nanocones) or a combination of those shapes. Furthermore, these clusters may be placed in each other, making "matryoshka" (nesting doll) fullerenes and multi-wall nanotubes, "peapods" (fullerenes inside nanotubes), nested cones, fishbone whiskers, and multi-layer graphene flakes. Physical peculiarities of hexagonal lattice, and an intrinsically small size of the objects, give rise to all the advantages but also to the challenges of nanocarbon materials to be briefly outlined below.

Significant mechanical strength and very high 2D electric conductance—two major physical properties of sp[2]-carbons—are due to the high chemical stability of sp[2]-bonds of a carbon atom and the delocalization of the last non-hybridized valence π-electron of the atom. These π-electrons are mobile within the whole lattice and their dynamics in a particular configuration determines electronic, optical, and interfacial thermal conductance properties of the material. Such

2D "electronic layers" are germane not only to nanocarbons: several other semi-metal materials, including new class of topological insulators[4a] and MAX-phases[4b], share a common physics.

The honeycomb lattice with two equivalent carbon atoms in the unit cell generates a semi-metal (or zero-gap semiconductor) band structure in the flat graphene monolayer. Electronic states form valence and conduction bands which touch each other in the Dirac point in the momentum space. By symmetry, two equivalent Dirac cones exist in nanocarbons.[5] The energy dispersion is linear near these points, like for an electron-positron pair in vacuum, except for the characteristic (Fermi) velocity of charge carriers in nanocarbons is approximately 300 times smaller than the speed of light, the fundamental constant for Dirac electrons in space. This rich physics and beautiful symmetry makes the nanocarbon materials so attractive for fundamental studies.

From the practical point of view, production of a large quantity of nanoscale materials, well characterized and easy to

handle, is challenging. Several methods proved to be efficient in nanocarbon synthesis, including chemical vapor deposition (CVD), laser ablation and arc discharge, as well as their modifications.[6] As produced nanocarbon materials may include contaminants from the synthesis (such as catalytic particles and side products) but more importantly, even for the best tuning of the parameters of the synthesis, they include multiple varieties of nanocarbon shapes.

The shape controls all important physical properties: by scrolling flat graphene in a tube the valence electrons are confined on the circumference of the cylinder. This so called "space quantization" creates discrete electron states. Indeed, a free quantum particle placed in the box of length $2\pi R$ must have wavelength compatible with the box size. Thus the nanotube electrons should have a discrete quantum number associated with the orbital motion, while for the fullerenes both components of 2D momentum are quantized.[5] Discretization of orbital states of an electron in nanocarbons,
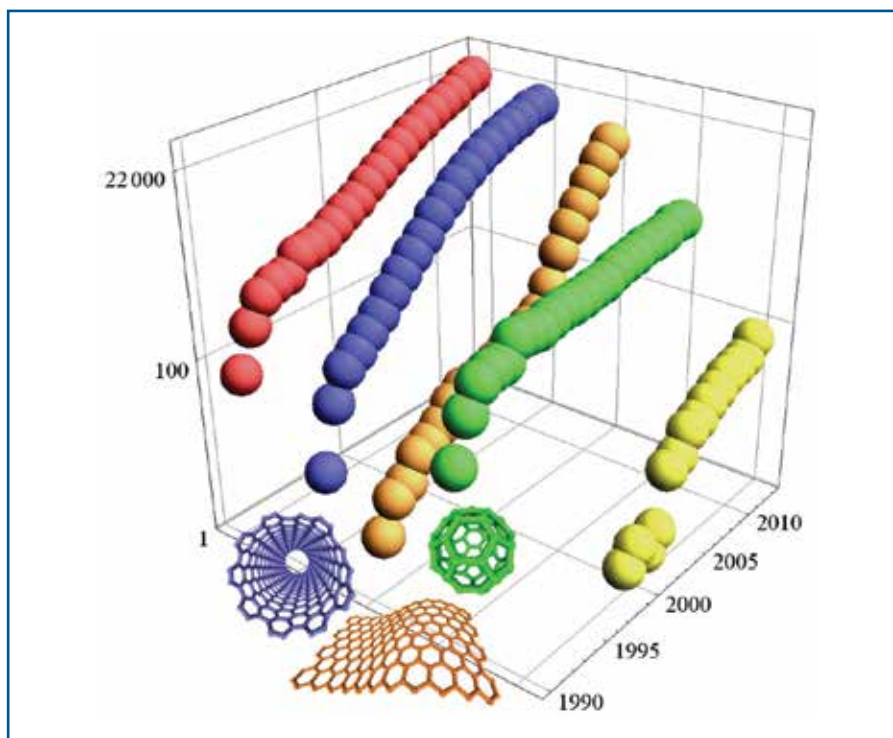
Fig. 1. *Publication rates for papers containing keywords: "nanotube" (blue), "graphene" (brown), "fullerene" (green), "nanocarbon" (yellow), and all of the above (red). Note log-scale of the vertical axis. (data from* Web of Knowledge, *2013).*

inferred from a "particle-in-a-box" analogy, leads to energy gaps between such states, like in semiconductors. This has two major experimental manifestations: similar to atoms, fullerenes and nanotubes show distinct optical properties, dominated by sharp optical transitions. Secondly, since the size of the band gap depends on the quantization length, which in turn depends on the inverse scrolling curvature of nanocarbons, by varying their shape one can obtain a class of semiconductor materials with variable band gap,[7] potentially tunable for particular optical or electronic applications.

This specific band structure of nanocarbons leads to both the major advantages of these materials and the main challenges of their technology. For example, large versatility of electronic properties of different forms of fullerenes and nanotubes, that can be considered as different chemical species, naturally mixed during the synthetic stage, is detrimental for some applications: an easy and inexpensive way of separating the nanocarbon species is required. A little difference in density and chemical properties of nanocarbons made this as formidable as the separation of isotopes and organic macromolecules in the past. Fortunately, several solution-based methods were successfully borrowed from these fields to achieve a high purity fullerene and, most recently, nanotube species. Before that could happen, it was important to achieve water solubility of nanocarbon materials. The lattice of a good quality raw nanocarbon is almost defect free. Their surface is mostly chemically inert, similar to graphite, making them hydrophobic, except for edges of nanotubes or graphene flakes. On the other hand, van der Waals (vdW) interactions between two graphite-like clusters are strong and result in bundling them together, precluding good solubilization and affecting materials properties. For example, first quantitative measurements of the nanotube photoluminescence became possible only after successful use of surfactants such as SDS and SDBS.[8] Later studies showed that many polymers[9] and several other surfactants can efficiently break the nanotube bundles and suspend them in water solutions as well as in other solvents.[10] Then, standard chromatography methods were applied[11] and tuned to extract the species of interest, such as nanotubes sorted by their diameter and length.

So far we have discussed the electronic structure of nanocarbons in terms of the size quantization, where the size was related to the scrolling curvature or length. There are two more important aspects of physics of these materials that need to be accounted for. One reflects a natural high surface-to-volume ratio of nanoscale systems, which reaches the ultimate limit of S/V=1, for single atomic shells. This leads to

extreme sensitivity of nanocarbons to their environment to be discussed later. Secondly, going beyond the simplest approximation of the space-quantized/scrolled graphene, the electronic structure shows dependence on the particular symmetry of the nanocarbon cluster, such as the existence and exact placement of non-hexagonal rings and/or carbon bonds other than of sp^2-type, the chirality (screw symmetry) of nanotubes, and the commensurability between the graphene layers in multi-shell matryoshka structures. Each of these perturbations influences all materials properties, including mechanical strength and chemical stability but most importantly for device applications it greatly expands our control on their electronic properties. One can potentially change the type of nanocarbon material without adding any other chemical element, a rare case in nature. The best known examples are the symmetry of chiral (or finite length) nanotubes (or graphene ribbons): increasing diameter (or length of a short nanotube, or width of a narrow graphene ribbon) by one atomic layer one may abruptly change its electronic properties. It switches from metal to semiconductor, and then to semiconductor and to metal again (Fig. 2): 1/3 of possible nanotube scrolling symmetries lead to a metal-like band structure, though adding or subtracting just one winding string of carbon atoms changes such a nanotube into a semiconductor.

Sorting metallic from semiconductor nanotubes was one of the major requirements for using them as field-effect transistor channels.[12] Nowadays it is achieved either with the density gradient ultracentrifugation method[13] (earlier used for separating DNA species) or multi-stage chromatography (analogous to isotope

separation technique). In 2013 two-phase liquid extraction[14] (applied for protein separation in the past) was proposed. An interesting aspect of strong interaction between organic macromolecules and nanocarbons—chirality specific wrapping of nanotubes by a single-strand DNA—was implemented to enhance the selectivity of the chromatographic separation.[15]

What are the forces[16] responsible for such "recognition"? To what extent the electronic properties of the hybrid[17] resemble those of the pristine material? The nature of the DNA-nanotube interaction is still to be understood as well as for other nanoscale complexes in solution. It is the development of advanced sorting methods that makes such a study possible in the near future. For example, analytical ultracentrifugation in isotopically different solvents[18] was proposed recently and allowed to measure the size of the solvation shell for a number of surfactants.

Since the mechanical properties of nanotube and graphene materials rely mostly on the crystal lattice perfection and absence of defects and not on the details of its symmetry or electronic structure, several device applications emerge that are not sensitive to coexistence of similar nanocarbon species and surface interactions. Durable nanocarbon electrodes and contacts should mostly require materials of good metallic conductance and strength, which has been already achieved.[13,14,15,19] Such electrodes can be applied in photovoltaic cells (PVC),[20] liquid crystal devices,[21] batteries and supercapacitors,[22] electron field emitters, and electronics. The physics explored in these devices is rather simple: small nanotube diameter and graphene thickness result in very large surface density
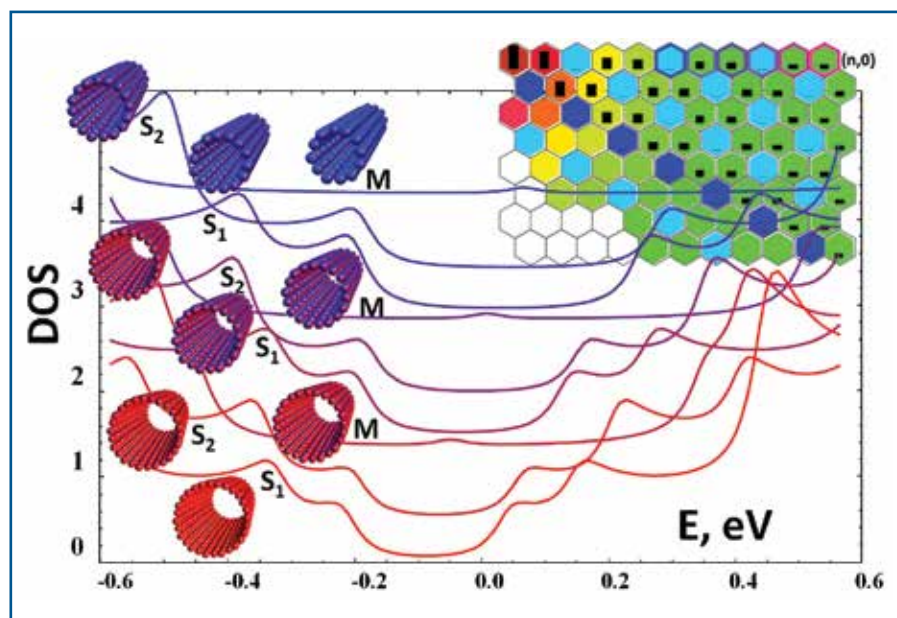

Fig. 2. *Density of states (DOS) for a sequence of nanotubes (n,0), for n = 6–14. The family splitting of DOS is clearly seen: 1/3 of the nanotubes have large DOS at E = 0, which corresponds to metals (M); 2/3 of the nanotubes are semiconductors (S_1 or S_2). Top inset shows a "periodic table" of nanotubes: band gaps are shown by color code and bar length; upper row corresponds to (n,0) tubes.*

of the nanocarbon material and thus to the large electric conductance or capacitance. High conductance, light weight, and great strength make it superior to other existing materials.

Additional advantages may follow from electromagnetic response of nanoscale objects: high aspect ratio of nanotubes leads to large enhancement of the electric field in their local vicinity. In devices based on the charge carrier extraction under electric bias, such as a field emission source[23] or fullerene/nanotube PVC,[24] one may achieve higher performance at the same applied voltage due to the field concentration. Same effect combined with intrinsic plasmonic response of a nanotube or graphene may lead to modification of the photoluminescence of a dye, making a complex with nanocarbon,[25] or may change its thermal contact conductance properties.[26] Large electric fields at the nanotube tip, their flexibility and high mechanical strength allow nano-electromechanical memory applications.[27] Although the vdW interactions, typical for nanocarbon devices, must be properly accounted for.[28]

Given the proper separation of the nanocarbon species of interest can be achieved, what are the other technological challenges for device fabrication? First of all one needs a capability for controllable placement (and orientation) of nanoscale objects in desired locations or within the macroscopic nanocarbon material. Also such nanofabrication methods should not alter the properties of individual clusters, bearing in mind extreme sensitivity of "all-on-surface" electrons to their environment. DC/AC dielectrophoresis,[29] oriented CVD growth,[30] and meniscus-drag alignment[31] have been successfully applied so far.

Many device properties of nanocarbon materials are solely due to their geometric size. Electronics and optical applications, on the other hand, rely on specific quantum behavior of charge carriers in graphene and its scrolled derivatives, specific symmetry of honeycomb lattice, chiral breaking of this symmetry due to curvature and space quantization. Great strength of the optical transitions in fullerenes and nanotubes is due to confinement of charge carriers in a small volume. In addition to the physical confinement provided by a small lateral size of the clusters, the Coulomb interaction between the charges is very important. It is well known that attraction of the electron, being promoted into conduction band from the valence band, to the electronic hole which it leaves behind, results in an appreciable modification of the optical response of 3D semiconductors. All these effects are greatly enhanced in low dimensions. The physics is transparent: the electric field transmitting such an interaction is not limited to the volume of the cluster, it propagates in the space around it and cannot be easily screened. Thus the Coulomb interaction in low dimensional systems often becomes dominant and cannot be neglected. This explains a number of phenomena in nanocarbons: excitons, plasmons, Luttinger liquid, Oosawa-Manning condensation, quantum capacitance, and Auger recombination, to name just a few. The fundamental physics underlying these effects is important for some applications. For example, excitonic narrowing of the near infrared optical transitions in nanotubes and extreme spatial confinement of the exciton provide unique opportunities for using nanotubes as inorganic dyes, with no photobleaching and being compatible with the biological environment due to the chemical inertness of graphene-like surfaces.[32] Strong plasmon-polariton coupling (Fig. 3) enhances the contact thermal conductance in nanocarbons[33] and makes them attractive for heat removal.[34]

High symmetry of the graphene lattice leads to interesting rules for scattering of charge carriers: external perturbations that are not atomically sharp cannot break certain quantum symmetry of charge carries, and so called long range scattering in nanocarbons is severely restricted. For the perfect material one may expect extremely high electron mobility, as it was experimentally demonstrated for both nanotubes and graphene. Furthermore, breaking such a symmetry in a controllable way, for example with electric or magnetic fields,[35] may result in novel device operation principles.[36] Here the largest challenge remains in fabrication. Often the beautiful physics of nanocarbon material is masked by non-intrinsic effects: the issue of making electrical contacts,[37] the lowering of performance by strong interaction with the environment. This is natural consequence of the same principles—in the absence of self-screening in nanocarbons, the Coulomb interactions with the surrounding material becomes critical.[38,39] Nanocarbons placed on a surface of the polar dielectric or a metal interact with the electromagnetic modes of the surface so strongly that it drastically changes charge and heat conductance properties.[40] While degradation of the former is not desirable, the increase of the interfacial heat conductance and, even more, appearance of new thermal effects, such as remote Joule losses,[41] opens new ways of using nanocarbons for cooling technologies.[42]

In conclusion, nanocarbons represent a broad class of materials with unique properties enabling an appreciable number of applications, while many of them are still awaiting their discovery. ■

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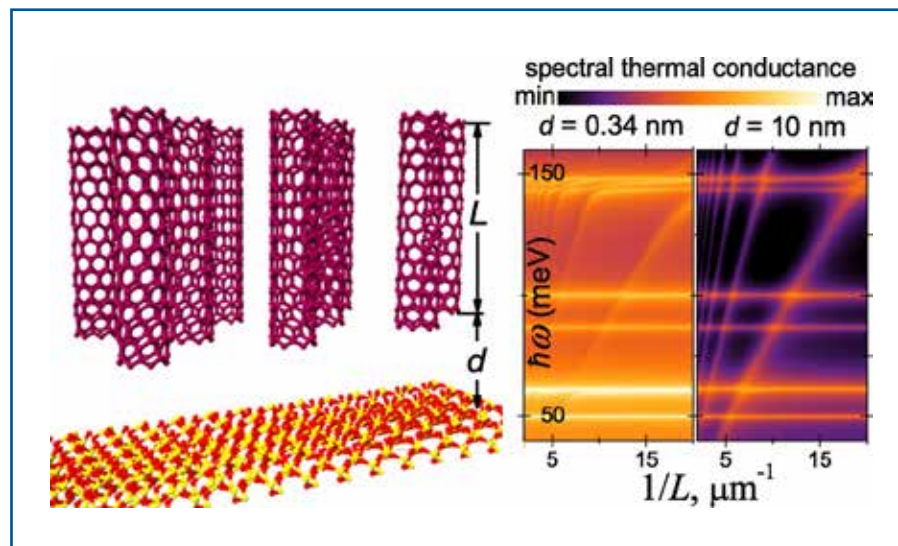
Fig. 3. *Calculated spectral density of the interface thermal conductance for a nanotube forest on the quartz substrate for values of the gap at the interface. (Reprinted with permission from* ACS Nano, **6**, *4298 2012). © 2012 ACS.)*

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