Toward the Bulk, Chiral Separation of Carbon Nanotubes: Experimental Confirmation of Nanotube-Substrate Registration Effects

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Abstract

We investigate experimentally the interaction of carbon nanotubes (CNTs) with highly ordered pyrolytic graphite (HOPG) as a first step toward realizing a method for the bulk, chiral separation of CNTs. Detailed calculations [*Phys. Rev. Lett.* **92**, 85503, 2004] suggest a very strongly preferred, chirality-dependent orientation for CNTs interacting with an HOPG substrate, resulting from the registration of atoms in the CNTs with those in the substrate. Here, we report preliminary experimental results evaluating the prevalence of this orientation dependence, and find that our initial results are consistent with the calculations.

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Introduction

Since their discovery in 1991 (*1*), carbon nanotubes (CNTs) have attracted great interest. They are the stiffest and strongest materials known (*2*) and some experts have suggested that CNTs are the strongest materials we will ever know (*3, 4*). Even more important, however, are their extraordinary electrical properties. For example, some CNTs are capable of ballistic transport of electrons, while others can conduct electricity at current densities several orders of magnitude greater than conventional copper wire (*5, 6*). Still others are capable of acting as semiconductors, with a wide variety of bandgaps (*7*). Unfortunately, all known methods of manufacturing bulk samples of CNTs result in a broad mixture of these different types or "chiralities." This limits the utility of CNTs for electronic applications. In this paper, we report initial results from experiments that test a proposed method (*8, 9*) for separating these mixtures of CNTs according to that chiral type.

The electrical properties of an individual CNT depend upon the structural arrangement of its component carbon atoms. CNTs can be visualized as a sheet of graphite rolled or wrapped into a tube, although they are not synthesized in this fashion. Different wrapping angles and diameters result in different structures, or chiralities (*7*). The chirality of a CNT most commonly is expressed as a vector represented by two indices, (n,m). This chiral vector contains the fundamental information about the wrapping angle and the diameter, which determine the electrical properties of the CNT.

As discussed above, both the extraordinary and widely varying electrical behaviors of CNTs give them great potential for use in electronics. Unfortunately, this diversity also is the reason for their limited use in applications to date. To build correctly functioning electronic circuits, it is necessary to have control over the specific electrical behaviors appropriate for the component devices, e.g., the transistors, wires, resistors, etc. At present, bulk CNTs only have been produced in a mixture of chiralities, with a corresponding mixture of electrical properties. This has prevented the effective use of CNTs for most electronic applications, as it is difficult to design and build electrical devices with uniform properties out of a mixture of conducting and semiconducting constituents. This issue is of such great importance that the ability to produce bulk samples of specific individual chiralities on demand has been dubbed the "holy grail" of nanotechnology (*10*).

It is not surprising, therefore, that much research has been devoted to developing techniques for manufacturing bulk quantities of CNTs of a single chirality or for separating bulk mixtures of CNTs into their individual components. Recent review articles have discussed the state-of-the-art in this area (*11, 12*). In summary, while significant success has been achieved in separating CNTs on the basis of important physical properties, e.g., morphology, length, diameter, or conductivity, the separation of CNTs into samples of a single chirality has not yet been achieved. Nevertheless, efforts toward this goal continue.

One novel approach that has been proposed is to use the registration-dependent, preferred orientation of CNTs adsorbed on an ordered lattice as a means of separation (*8, 9*). Below, we describe our initial experimental efforts to test this method as a means to achieve the bulk, chiral separation of carbon nanotubes (CNTs).

Background

The approach to the separation of CNTs on the basis of chirality investigated in this work is based upon the registry-dependent interactions (*13*, *14*) of CNTs with an HOPG substrate upon which they are deposited. Depending upon the angle the longitudinal axis of the CNT makes with any one of the six bond axes that are defined on the HOPG lattice, the atoms of the CNT can interact more or less strongly with each of the atoms in the substrate, or with more or fewer of them. See Figure 1. Furthermore, the angle between the CNT and the substrate that produces the strongest interaction, i.e., the lowest potential energy, depends on the chirality of the CNT. If the energy function of the angle exhibits a sufficiently strong minimum at a registration angle and this minimum is sufficiently sharp, then the CNT is likely to align exclusively at or very near this minimum energy angle. Since the angle of minimum energy is dependent on the CNTs chirality, this effect could provide a means for the bulk, chiral separation of CNTs by implementing a method that preferentially selects only a specific angle.

Previous experimental observations of CNTs on HOPG suggested the existence of such a registry-dependent interaction (*15, 16*). Also, early calculations of CNT alignment on graphite showed sharp peaks in the energies every 60 degrees corresponding to the symmetry of the graphite lattice (*13*). The depths of the potential energy wells were not calculated to be very large, though. More recently, however, Kolmogorov *et al*. recalculated the interaction using an improved interlayer potential and found that the binding energy at these preferential angles was both strongly peaked around the local minimum and 5-10 times greater than previously suspected (approximately 1-3 millielectron volts per atom) (*14*). With such large per atom energy values, even CNTs

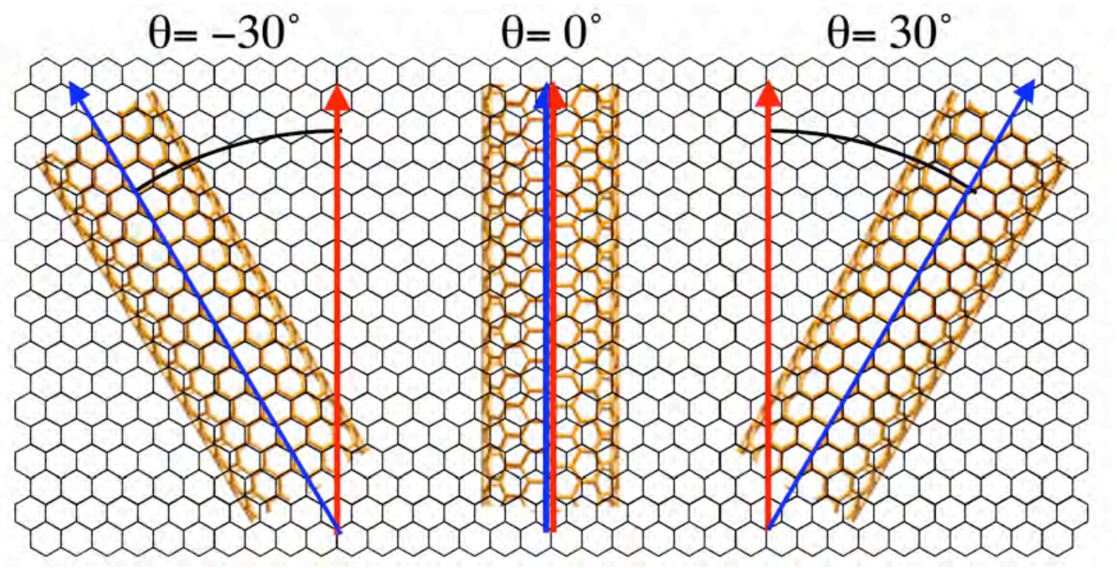

Figure 1. Schematic representation of a CNT deposited at various angles relative to an HOPG substrate. An interaction between the CNT and the substrate results when two atoms in the respective structures overlap. The more such overlaps, the stronger the energetic interaction. The angular frequency with which the overlap repeats itself depends on the symmetry of the underlying lattice. For CNTs on HOPG, the pattern repeats every 60 degrees.

of modest length, e.g., 100-200 nm, should exhibit angle-dependent binding energies that vary on the order of electron volts per CNT. These large values would suggest a strong thermodynamic tendency for the CNTs to deposit along these preferred chirality-dependent angles.

Methods have been devised that would take advantage of this effect in order to perform the bulk, chiral separation of CNTs (*8, 9*). In an effort to test the efficacy of those methods and the computational predictions of Kolmgorov *et al.* (*14*), we performed experiments to determine the preferred angles of orientation for CNTs deposited on HOPG. Below we describe the methods used in those experiments and the initial experimental results.

Sample Preparation

CNTs for the experiments were purchased from commercial vendors, Unidym and Southwest Nanotechnologies, which manufactured the CNTs via high pressure carbon monoxide processing (HIPCO) and by carbon monoxide disproportionation catalyzed by cobalt and molybdenum (CoMoCAT), respectively. The CNTs were purified by sonication in an acid bath according to the procedures prescribed in earlier work (*16-18*). Some of the CNTs then were sonicated further to reduce their length or "cut" them (*16, 19*). However, it was found that significant care must be exercised in taking at this step. The HIPCO CNTs did require sonication in strong acids, as prescribed in the literature. In contrast, however, the CoMoCAT tubes did not survive this process. Instead, they were cut by additional sonication alone.

In either case, these procedures produced four different samples: two samples of uncut CNTs, with as-manufactured lengths of 1-3 microns, and two samples of cut CNTs with lengths of 200-300 nanometers with one sample in each pair derived from CNTs from each of the two manufacturers. Expected length ranges for the two sets were confirmed experimentally using an atomic force microscope (AFM).

Once purified (or purified and cut), the CNTs were suspended in aqueous surfactant solutions (0.5% by weight of Triton 100-X) to facilitate their deposition onto the HOPG substrate. Three different deposition techniques were used: electrodeposition, drop and dry, and immersion. Electrodeposition entails confining a droplet with a 4-mm outer diameter, 1.7 mm thick viton O-ring; placing a stainless steel electrode on top of the O-ring; and, finally, supplying a steady voltage of 1 V for 5 minutes (*16*). Drop and dry involves depositing a droplet of CNT suspension on HOPG and letting it dry. Immersion simply places the HOPG substrate in a container filled with the CNT suspension.

Following each deposition procedure of any of the three types, the HOPG was washed with methanol to remove excess water and Triton-X surfactant. No substantial differences were observed in the results derived from samples prepared via any of the three deposition methods.

Measurements

Measurements were performed upon samples prepared as described above in order to examine the relationships between the CNTs and the HOPG substrate on which they are deposited or between two or more CNTs deposited on the substrate. The strength of the CNT-HOPG interaction predicted by Kolmogorov *et al.* (*14*) should limit the range of behaviors for the CNTs deposited on HOPG. For example, while long CNTs frequently occur in tangled, spaghetti-like nests, a CNT deposited on HOPG should appear to be straight due to its preferred alignment on the substrate. Further, according to the predictions from theory, if the CNT deviates from linearity, it should "bend" at angles of 60 or 120 degrees corresponding to the symmetry of the HOPG substrate, which repeats its lattice structure every 60 degrees. This behavior is seen in the experimental results shown in Figure 2.

In addition, CNTs of the same chirality should deposit on HOPG at angles that are multiples of 60 degrees relative to one another, i.e., at 60 degrees, 120 degrees, or 180 degrees (parallel to each other), due to the symmetry of the HOPG substrate. Unfortunately, there is no sample of a single chirality of CNTs upon which to test this prediction. However, Southwest Nanotechnologies's CoMoCAT process has excellent control over the diameters of the CNTs produced. Hence, the CoMoCAT process can provide samples of CNTs with only a limited number of chiralities, since chirality and diameter are coupled properties (*7*). Further, it is predicted that approximately 90% of the CNTs in their samples should have preferred orientation angles on HOPG that are within a few degrees of one another (*20, 21*). A sample of CNTs with such a distribution of orientation angles should behave much like a sample of a single chirality, and should produce the behaviors described above.

The experimental results in Figures 2 and 3 show that these behaviors are observed. For both the uncut (Figure 2) and cut (Figure 3) samples, the CNTs orient at multiples of 60 degrees relative to each other.

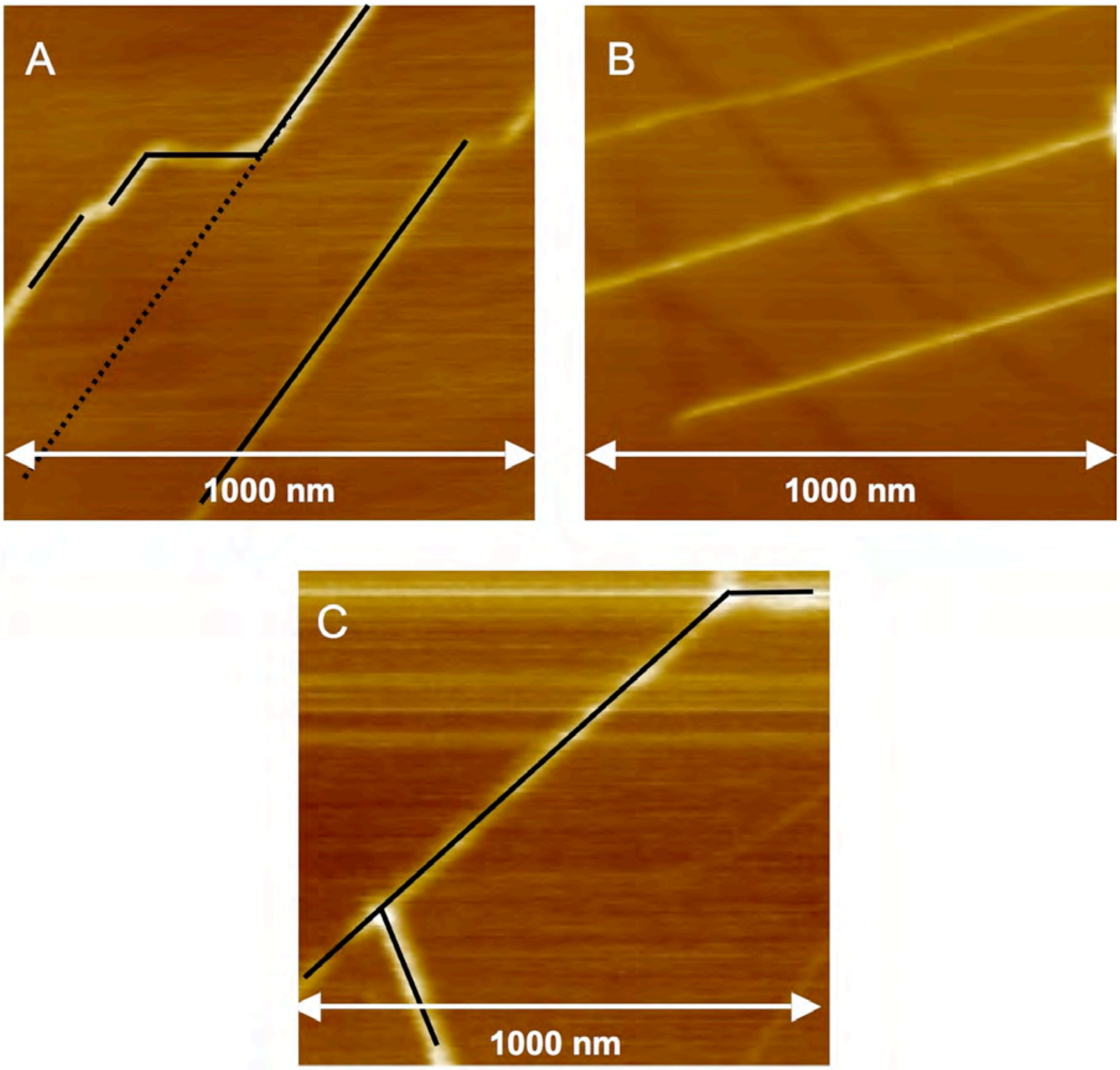

Figure 2. Atomic Force Microscope (AFM) images of uncut CoMoCAT CNTs deposited on HOPG. (A) shows a long CNT bending at approximately 120 degree angles, plus another long CNT in parallel. (B) shows three long CNTs aligned in parallel. (C) shows CNTs intersections at angles of multiples of approximately 60 degrees. Black lines overlapping the CNTs have been added to (A) and to (C) to improve clarity.

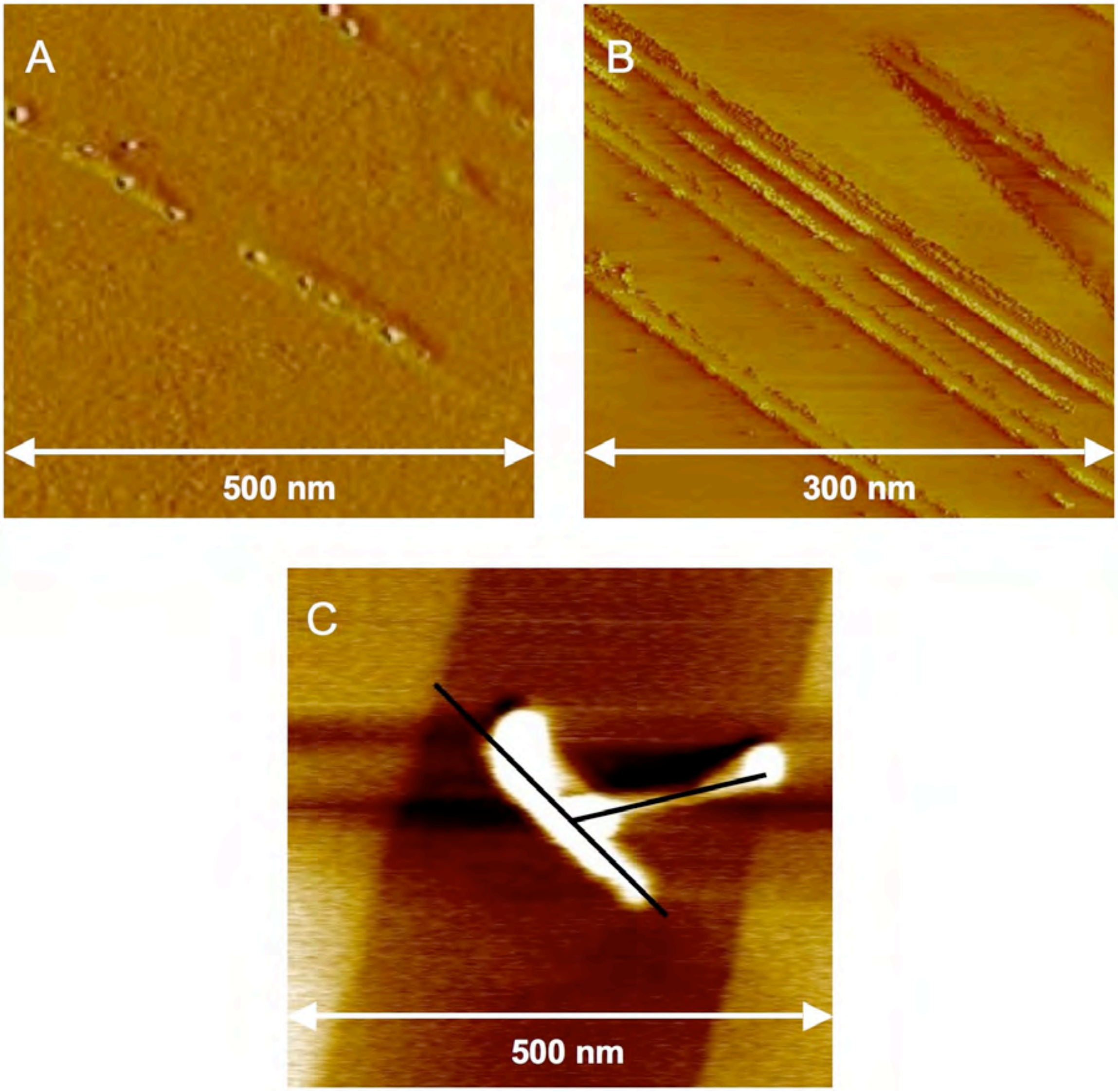

Figure 3. Atomic Force Microscope (AFM) images of cut CoMoCAT CNTs deposited on HOPG. (A) shows two CNTs aligned in parallel. (B) shows a number of CNTs aligned in parallel. (C) shows two CNTs intersection at approximately 120 degrees. Black lines designating the longitudinal axes of the CNTs have been added to (C) for clarity.

The opposite should be the case for a sample of CNTs that contains a broad distribution of chiralities. Such a sample deposited on HOPG should produce almost any arbitrary angle between CNTs. This is seen in Figure 4. The HIPCO CNT samples contain over 30 different chiralities (*22*) and produce a distribution of angles. Such measurements eliminate the possibility that the underlying HOPG forces all CNTs into a particular orientation and provides further evidence that the registration effects are chirality dependent.

The measurements described above are very encouraging. However, given the limited number of experiments to date, it is not a complete verification of the behavior predicted by the calculations of Kolmogorov *et al.* (*14*). Additional measurements are required to build a more statistically significant finding.

Further, using scanning tunneling microscopy (STM) to observe simultaneously both the atoms in the CNT and the atoms in the HOPG substrate would provide a direct probe of the preferred orientation predicted by Kolmogorov *et al.* (*14*). Such an experiment would unambiguously determine both the chirality of the CNT and its orientation relative to the HOPG substrate. Unfortunately, such a direct observation is extremely difficult under even the most highly controlled conditions. At room temperature, instabilities in the STM tip shape and drift in the piezoelectric positioning mechanisms limit the resolution of the instrument (*23*). Improved STM observation of the atoms in a CNT and the HOPG lattice might be conducted at low temperature under vacuum. Direct measurements of the chirality of a CNT at low temperature under vacuum have been made (*15*), but they have not yet included coupled observations of the underlying substrate. Additionally, under any conditions, the very narrow field of view for an STM

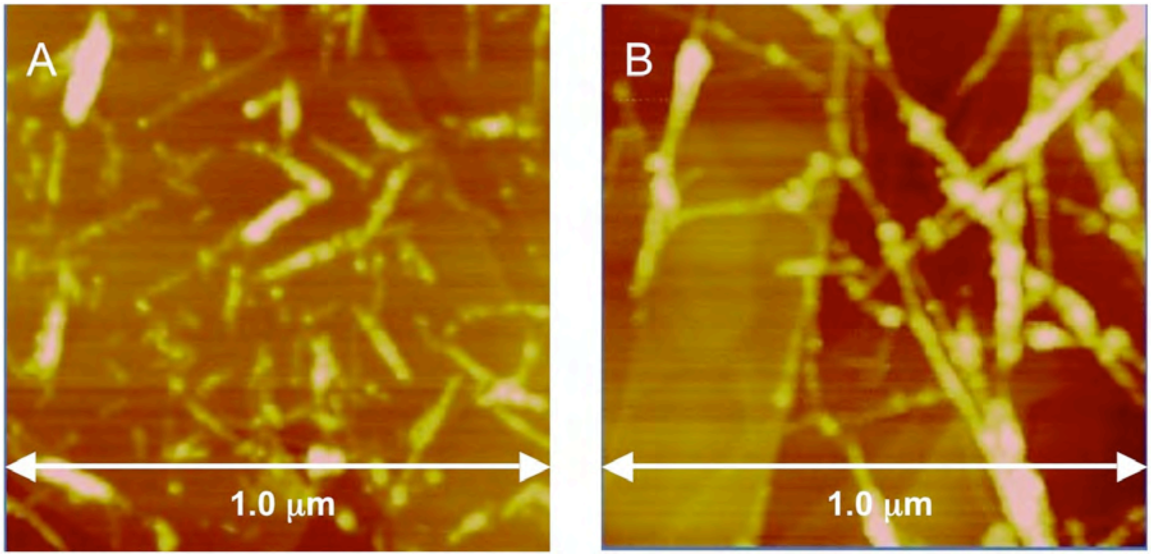

Figure 4. Atomic Force Microscope (AFM) images of HIPCO CNTs deposited on HOPG. (A) shows cut HIPCO CNTs. (B) shows uncut HIPCO CNTs. Both images have numerous examples on CNT intersections at angles other than multiples of 60 degrees.

relative to the substrate area makes it difficult to find a candidate CNT for which observations are not confounded by interfering effects such as step edges in the substrate or overlapping tubes. Because of such difficulties, it has not yet been possible to make a direct observation of the deposition angle of a CNT on a substrate for any of the samples we have prepared of CNTs deposited on HOPG. Efforts to make such an observation continue, however, because of the great value of a direct measurement and because it is believed that this experiment can be successful.

Conclusions

We have begun experimental efforts toward realizing methods for the bulk, chiral separation of CNTs by aligning them with a highly oriented substrate, as proposed by Schleier-Smith and Ellenbogen (*9*) and by Crespi *et al*. (*8*) As the first step in those efforts, we have made detailed measurements to verify experimentally the registration of CNTs on an HOPG lattice predicted by the detailed calculations published by Kolmogorov *et al*. in 2004 (*14*).

Experimental measurements have been completed that imply the existence of the strong registration effect predicted by the calculations. We have measured the orientation of CNTs deposited on HOPG relative to one another and have observed the relationships predicted by the presence of a strong registration effect. Further, long, normally spaghetti-like CNTs behave largely as rigid rods on HOPG, again in accordance with the strong registration effect predicted by theory. While further experiments must be conducted, preliminary evidence suggests the existence of a strong registration-dependent effect that could provide the basis for the bulk, chiral separation of carbon nanotubes.

In addition, we have attempted to make an unambiguous measurement using scanning probe microscopy of both the specific chirality of an individual CNT and its orientation relative to an HOPG substrate lattice. Such measurements have not yet been successful, but further work to this end is ongoing in our laboratory.

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