Growth of Ionic Crystals in Carbon Nanotubes

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Received October 23, 2000
Revised Manuscript Received December 27, 2000

A molecular electronics technology based upon networks of carbon nanotubes whose electronic properties have been modified by the incorporation of electroactive materials has been proposed, and the chemistry for developing suitable materials is making rapid progress.[1−5] Sloan and co-workers[1,6] have recently shown how single-walled nanotubes (SWNT) of 1−2 nm diameter may be filled with perfect crystals of ionic materials in a remarkably simple way. A selection of SWNTs formed by the arc vaporization method are immersed in a suitable molten salt (under vacuum) and recovered after cooling. On examination with high-resolution transmission electron microscopy some of the tubes were found to be completely filled with ionic crystals only two or three atoms wide. In the case of KI the arrangement of atoms is the same as that of bulk KI crystals (rocksalt), and the crystalline order is almost perfect along the tube axis over (apparently) the whole tube length of ∼100 nm. Differences between the K−I distances parallel and perpendicular to the tube axis were resolved, whereas all K−I separations would be equal in a fragment of the bulk crystal. Similar observations have been made for a variety of ionic materials.

It is known that the tubes are “uncapped” by the chemical reaction of the salt with the more reactive carbon atoms in the domes which cap the tubes.[1] To explain how an inorganic material can then penetrate a carbon pore only two or three atomic diameters wide to form a perfectly coherent crystal is more difficult. An ionic melt is highly charge-ordered, and it is difficult to see the interactions between the ions and (uncharged) carbon atoms of the tube compensating for the disruption of this structure, allowing the melt to “wet”[7−9] the interior of the tube and therefore to enter it without the imposition of a large external pressure. An alternative scenario might be that isolated KI *molecules* enter the tube, so that the crystal forms by vapor epitaxy. The experiments themselves do not distinguish between such possibilities, which might influence the nature and quality of the materials which can be grown. Instead, we look to computer simulation to suggest a plausible mechanism.

We have performed molecular dynamics simulations of the process using a potential appropriate to nonbonding interactions. The interactions between the ionic species are described by standard Born−Mayer pair potentials,[10] with the ions carrying their formal (integer) charges. These potentials are supplemented by a representation of dipole polarization effects, using techniques described elsewhere.[11,12] Polarization effects occur at the low-symmetry sites of crystal surfaces and corners, and become important in the nanocrystals formed inside the tubes. The interactions between the ions and the nanotube are described by Lennard-Jones potentials, with parameters derived from potentials for the interactions of the isoelectronic inert gas atoms (i.e., Ar for K^+, Xe for I^-) with the carbon atoms of a graphite surface.[13] All parameters are specified in Supporting Information.

Calculations were performed to determine the initial minimum energy structure of elongated KI crystals which are two (2 × 2) and three (3 × 3) atoms wide and which are either free (isolated), embedded inside nanotubes of varying diameters, or embedded inside tubes which are themselves encased in amorphous KI. The structural distortions, uncovered by the experiments, are conveniently described in terms of the ratio of two lengths $R = a/b$, illustrated in Figure 1. In the bulk crystal, the ratios of these lengths would be unity. The SWNTs are formed by wrapping graphene sheets into tubes.[14] We will only discuss a limited subset of results here—those obtained for (8,8), (10,10), and (12,12) tubes, in the standard notation.[14] These give diameters of 10.9, 13.6, and 16.3 Å; the (8,8) and (10,10) can accommodate the 2 × 2 crystal, and the (12,12), the 3 × 3. Throughout the calculations the relative positions of the carbon atoms in the tubes were held fixed. The consequences of this restriction[15] will be examined in future work.

From the results in Table 2 we see that the free crystallites deform in the same direction as observed in the experiments, but to a much smaller extent. Enclosing them in an isolated tube can either enhance the effect (2 × 2 in (10,10) or 3 × 3 in (12,12)) or oppose it (2 × 2 in (8,8)), depending upon the relationship of the width of the crystallite to the tube diameter. In the latter case the K^+ and I^- ions lie on the repulsive wall of the interaction potential with the tube walls, and the crystallite is squashed. In the former cases, the outermost ions lie in the régime of attractive forces and are drawn toward the wall so that, in the 3 × 3 case, the crystallite acquires a more circular cross section. The attractive forces are increased if the tube itself is immersed in amorphous KI (see below) to account for the material present during preparation (such material also appears on the tube exterior in the HRTEM images[1]). In the 2 × 2 in (10,10) case this results in a deformation which agrees well with the HRTEM results. In the 3 × 3 in (12,12) case the ratio is larger than that found experimentally although it should be noted that this ratio is very sensitive to the degree of deformation for the 3 × 3 crystal.

These calculations indicate that the actual deformations seen in an experiment will depend sensitively on the diameter of the actual tube selected for examination. It would seem that there will be tubes whose radii do not match the natural sizes of possible crystallites and for which the interactions between the tube and any possible crystallite will be so repulsive as to prevent the tube filling.

We turn now to the mechanism by which the tubes fill. A starting configuration was created by removing 98 ions from a cylindrical region of a molten KI simulation containing 1728 ions in periodic boundary conditions. A (10,10) SWNT of length 22.2 Å (≡9 unit cells, 360 atoms) was then inserted. The tube ends were then blocked while the melt was reequilibrated at 954 K

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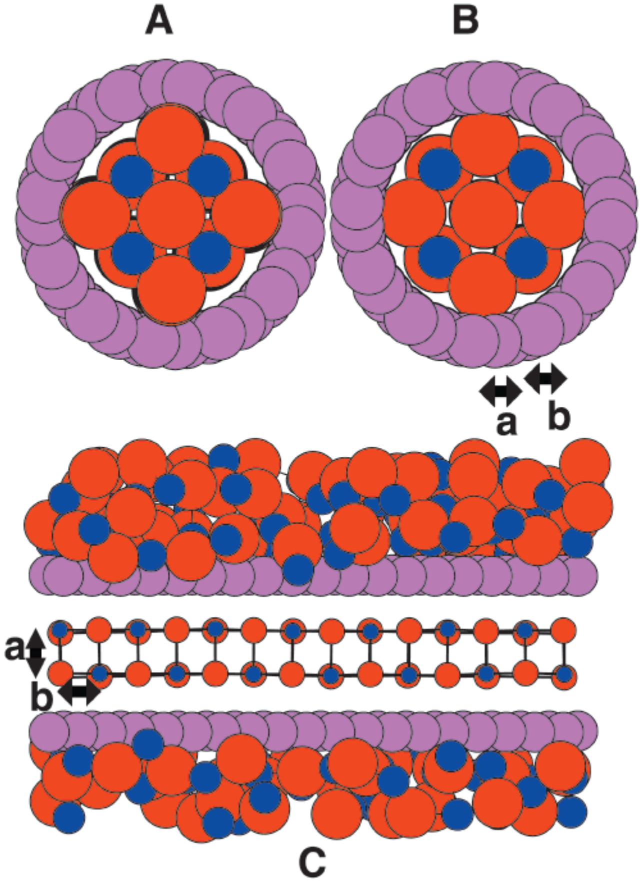

Figure 1. Aspects of the minimum energy configurations obtained for nanocrystals of KI in various environments. The lower panel is a side view of a 2 × 2 crystal in a (10,10) SWNT encased in amorphous KI (obtained from a single liquid configuration). For clarity the enclosed ions are drawn with reduced sizes and bonds are drawn if ions are separated by less than 4.0 Å. The upper panels show end-on views with realistic atomic radii of a 3 × 3 crystal enclosed in an isolated (12,12) SWNT (panel a) and a KI-encased (12,12) SWNT (panel b, the exterior atoms are omitted from this figure). Note the greater degree of deformation evident in the more circular cross-section in the latter case.

Table 1. Values for the Ratio *a*/*b* of Lengths Illustrated in Figure 1 Obtained on ($n \times n$) Nanocrystals which Are Either Free, Enclosed in an Isolated SWNT, or Enclosed in a SWNT Itself Surrounded by Molten KI (Obtained from the Liquid around a Tube at High Temperature)[a]

	free	tube	tube*
2 × 2 in (8,8)	1.03	0.92	-
2 × 2 in (10,10)	1.03	1.05	1.13
3 × 3 in (12,12)	0.94	0.84	0.68

[a] The ratios are to be compared with experimental values of 1.14 for 2 × 2 and 0.75 for 3 × 3 obtained for enclosed samples in tubes of unknown type. This ratio is 1 for bulk crystal.

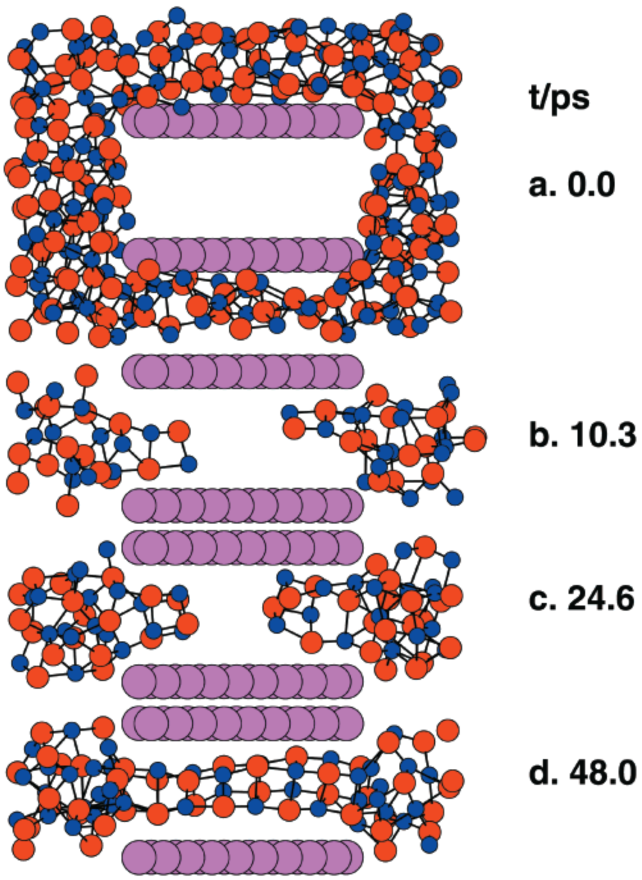

Figure 2. The time evolution of an initially empty tube immersed in molten KI at 954 K and zero pressure. Panel a shows a cross-section through the initial configuration: in the lower panels the exterior atoms above and below the tube are omitted and bonds drawn between ions closer than 4.0 Å. Panels b and c show that the KI only enters the tube when oppositely charged ions are paired and that substantial progress only occurs alter these pairs are arranged like a finger of the 2 × 2 crystal (note the time delay between panels b and c). The final configuration (panel d) shows the large amplitude vibrations (at 954 K) of the final embedded crystallite. Time averaging these vibrations gives the well-ordered crystal as illustrated in the lower part of Figure 1.

and zero pressure using thermostated, barostatted molecular dynamics.[16] Figure 2 shows snapshots of the simulation cell at various times after the tube ends were opened. Initially, the melt was slow to enter the empty space within the tube. This only occurred after the ions at the entrances to the tube had acquired the spatial arrangement of the 2 × 2 crystallite. Penetration of these ordered fingers was then rapid (panels b and c) until they met (panel d). Although the charge ordering of the interior material is apparent from the snapshot, its true nature only becomes clear after time averaging the ion positions to remove the thermal motion. The averaged positions are perfectly crystalline, as already illustrated in Figure 1. Thus, even at 954 K, where the exterior material is still fluid (as evidenced by the diffusivities), the ions inside the tube have crystallized. Radhakrishnan et al.[9] have discussed the thermodynamics of freezing of van der Waals fluids in pores in terms of the relative strength of the fluid−fluid and fluid−pore interactions. It will be of interest to see if these considerations can be extended to Coulombic systems, where the requirement of local charge-ordering has a major influence on interfacial energies.

The implication of these figures is that the ions have to adopt a crystalline arrangement to reduce the Coulombic interaction energies on entering the pore. Thus, these Coulombic interactions *facilitate* the formation of well-ordered crystals, rather than inhibiting tube filling, as anticipated in the introduction. Any defects due, for example, to mismatches of the crystalline fingers growing from the tube ends, anneal out at the high temperatures at which the crystallites form. It will be of interest in future work to see how these considerations are affected by bulk crystal structure, and whether selective absorption from mixtures is possible.

Acknowledgment. We thank Professors R. G. Denning and M. L. H.Green for alerting us to these experiments. We also thank Adam Palser for help with generating the carbon nanotubes. M.W. thanks the Royal Society for a Research Fellowship. The work was supported by EPSRC Grant GR/L/49369.

Supporting Information Available: Table specifying potential parameters (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA003737X

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