Nanocrystal cleaving

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We report on the virtually perfect cleaving of a nanoscale crystal within the confines of an atomically smooth-bore BN nanotube, performed *in situ* inside a high-resolution transmission electron microscope. The cleaving-induced gap region between the two nanocrystal subunits could then represent a near-perfect (i.e., atom-free) vacuum. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1695635]

It has long been known, at least since the stone age, that many crystalline solids have special cleavage planes which facilitate the physical shaping of material. Examining the way a relatively defect-free macroscopic crystal can be cleaved often gives insight into the underlying atomic structure. The cleaving of rocksalt is a classic example.[1] An important issue is thus if nanoscale crystals, for which high surface area and quantum confinement effects may dominate, behave similarly.

Here, we report on the cleaving of a salt nanocrystal, performed *in situ* inside a high-resolution transmission electron microscope (HRTEM). To insure an ultraclean environment, the nanocrystal has been cleaved while residing within the atomically smooth bore of a multiwalled boron nitride nanotube (BNNT).

High-structural-quality pure (unfilled) BNNTs were first synthesized[2] and then sealed, together with high-purity KCl, in an evacuated quartz ampoule. The ampoule was heated at 740 °C for 3 h. Through a vapor-transport process, KCl nanocrystals formed in the interior of the nanotube. Related nanocrystal growth within carbon nanotubes has been previously reported.[3]

Figure 1(a) shows a HRTEM image (obtained using a Phillips CM200 field emission gun HRTEM operating at 200 keV) of a KCl nanocrystal within a BNNT; the nanocrystal appears to efficiently fill the BNNT cross section. Energy dispersive x-ray spectroscopy confirmed the composition of the nanocrystal, and electron diffraction identified the crystallographic ***a*** axis of the cubic KCl nanocrystal as aligning with the BNNT cylinder axis, with the ⟨001⟩ axis parallel to the electron beam.

Because BNNTs are semiconductors with band gaps in the 4–5 eV range,[4] they are easily charged by the transmission element microscope (TEM) imaging beam. As a consequence, during imaging, there occur charge fluctuations on and within the BNNT; these in turn induce electrostatic force fluctuations on the encapsulated KCl nanocrystal. During TEM imaging, the nanocrystal was observed to undergo a more or less random walk along the axis of the nanotube, moving at speeds up to 20 nm/s. This motion demonstrates that the interaction between the atomically smooth nanocrystal and the surrounding atomically smooth BNNT is small or, at the very least, that there is little position dependence on the system energy (the lattice parameters are incommensurate). The image shown in Fig. 1(b) was recorded a few seconds after that of Fig. 1(a), and an axial repositioning of the KCl nanocrystal is readily apparent.

We found that under conditions of continuous (but hardly extreme) HRTEM electron irradiation (current density 500 nA/μm^2, exposure time typically 10 s), the KCl nanocrystal could be induced to cleave under the influence of the electron beam alone, resulting in two smaller independent KCl nanocrystals within the common BNNT housing. Figure 1(c) illustrates the system after cleaving. The original nanocrystal has cleanly separated along a (100) plane. Continued irradiation of the BNNT/KCl system of Fig. 1(c) resulted in

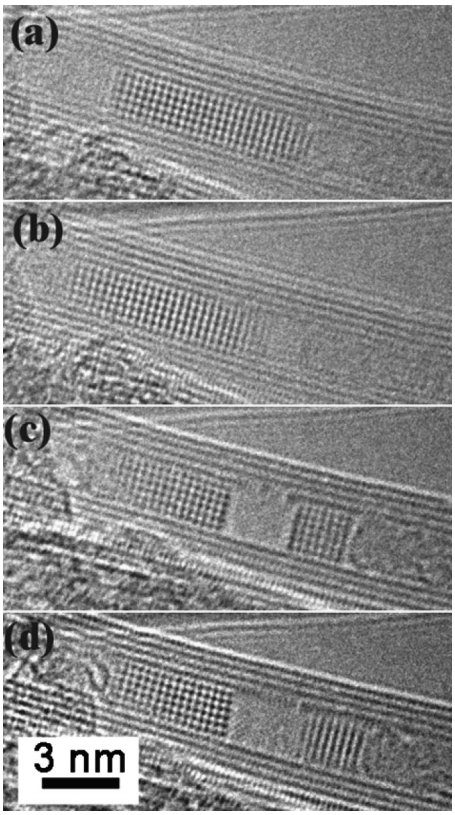

FIG. 1. HRTEM images of KCl nanocrystal(s) within a BNNT. The single KCl nanocrystal observed in (a) and (b) has been cleanly cleaved into two independent subunits, as seen in both (c) and (d).

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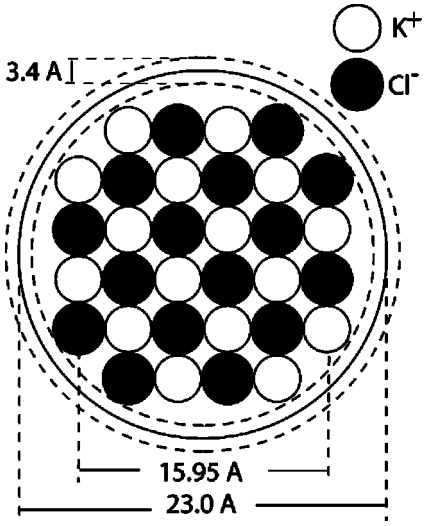

FIG. 2. Simulation image of the cross section of KCl-filled BNNT. In comparing this image to Fig. 1, the vertical direction (⟨100⟩ axis) would be parallel to the imaging electron-beam direction.

the two nanocrystal subunits moving roughly independently of one another along the axis of the nanotube. For example, in Fig. 1(c) the gap between the two subnanocrystal units is 2.86 nm, while in Fig. 1(d) (taken 2 s later), the gap has increased to 3.14 nm. The above-described experiments have been repeated for different KCl nanocrystals contained within BNNT nanotubes.

Using a simple geometrical model (Fig. 2), we find that, relevant to the system described in Fig. 1, a 1.59 nm width cylindrical KCl nanocrystal fits exceedingly well within a 2.3 nm (inner) diameter BNNT. This suggests that the original KCl nanocrystal in Fig. 1(a) is a ''near-perfect'' fit to the cylindrical BNNT core, and that the contact interface between the nanocrystal(s) and the BNNT likely forms an atomically tight seal. The cleaving-induced gap region between the two nanocrystal subunits in Figs. 1(c) and 1(d) could then represent a near-perfect (i.e., atom-free) vacuum. This vacuum chamber is created by an ideal cleaving process conducted in a tailor-made atomic-scale ''UHV'' environment. The cylindrical walls of the vacuum chamber consist of ultrastrong sp^2-bonded boron nitride, while the end caps of the chamber consist of atomically perfect ionically bonded KCl sheets created by separation at the cleavage plane. Assuming a temperature $T=300$ K and using the binding energies[1,5] of surface atoms of appropriately-structured BN and KCl, we estimate a pressure within the cavity of 10^{-84} Torr. Residual electrostatic fields can easily maintain end-cap separation, and prevent an immediate spontaneous fusing or ''recrystallization'' of the original nanocrystal.

In preliminary studies, we have not observed related cleaving of nanocrystals housed within multiwall carbon nanotubes. This suggests that the wide band gap of BNNTs may be crucial in facilitating the electron-beam-induced cleaving process. It should be possible to cleave and/or fuse other nanocrystal types within BNNTs, leading to interesting sub-or-superstructure nanocrystalline units.

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