



Supporting Online Material for

Carbon Nanotubes as High-Pressure Cylinders and Nanoextruders

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1. Supporting Figures

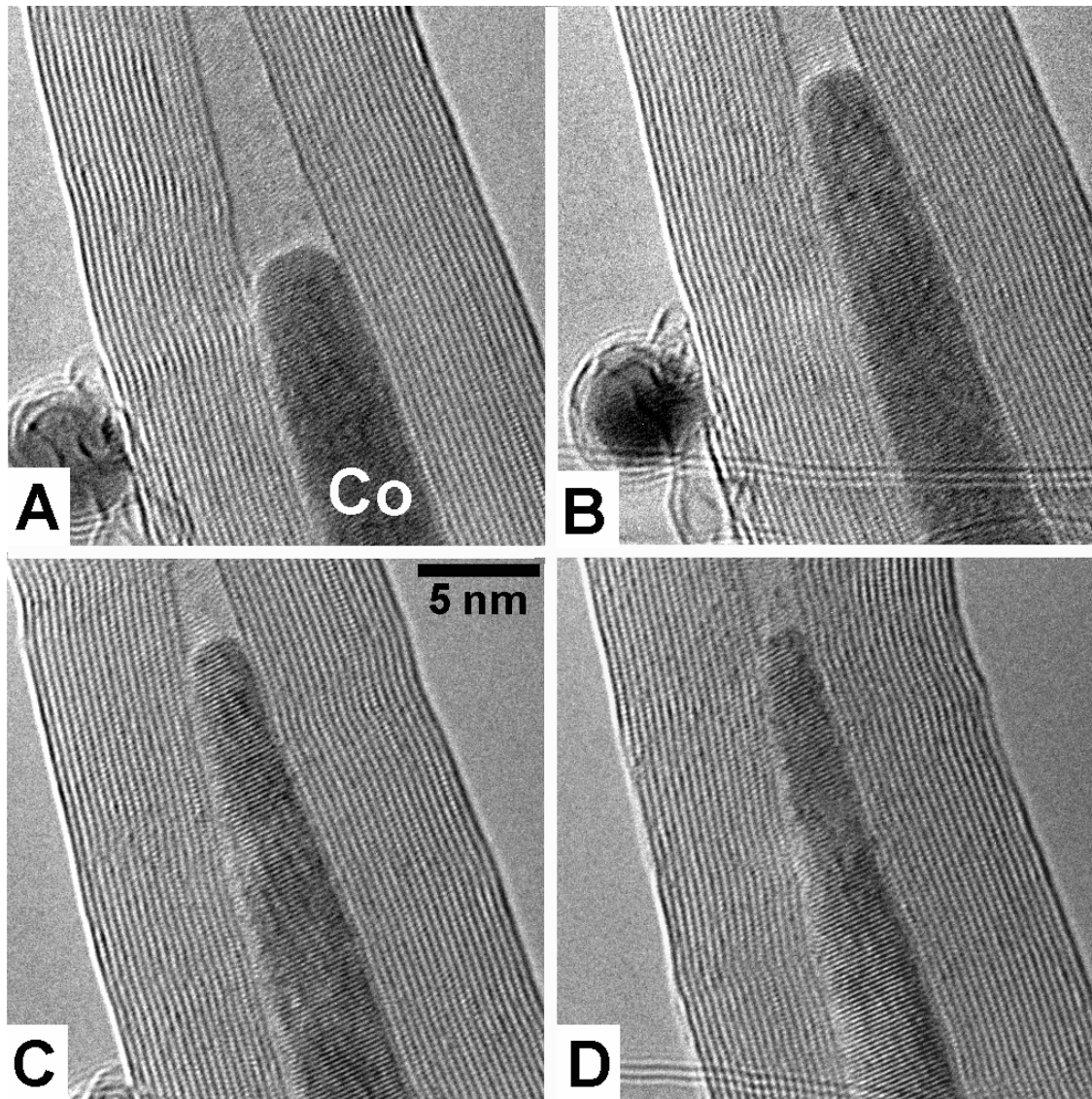


Figure S1:

Deformation of a β -cobalt crystal (fcc lattice structure) in a collapsing carbon nanotube. While the tube collapses, the Co crystal slides in the axial direction (upwards) which can be seen by taking the small particle on the surface of the tube (left hand side) as a reference point. The Co crystal is getting thinner and experiences deformation, but no visible crystallographic defects appear. This example shows how nanotubes can be used to study the deformation behavior of individual nanometer-sized crystals. Irradiation intensity: 260 A/cm^2 , irradiation times: A: starting point ($t=0$), B: 2 min, C: 4 min, D: 9 min. Specimen temperature: 600°C .

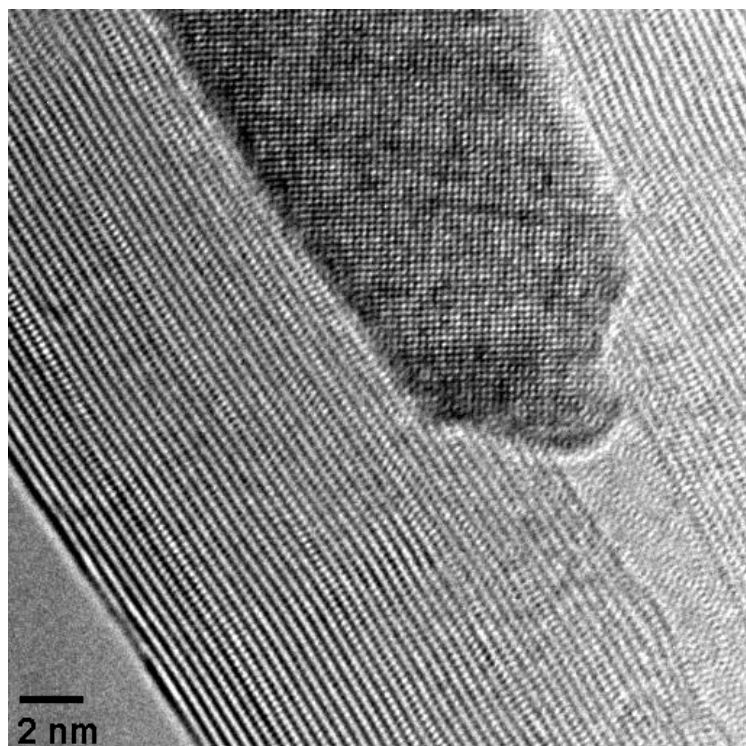


Figure S2:

Lattice resolution transmission electron microscopy image of a 40-shell nanotube with a Fe₃C core which has already undergone strong deformation (both thinning and widening due to collapse of the tube and following axial sliding of the crystal). The lattice shows no crystallographic defects. The additional graphite layers ending at the carbide crystal originate from interstitials that are transported into the tube ("sputtering inwards"). The deformation of the end of the crystal due to compressive forces is clearly visible. A tentative analysis of the vertical (002) fringes and the horizontal (220) fringes (seen here in a $\bar{1}10$ -projection of the crystal) shows a compression of the (002) fringes by approximately 6% whereas the (220) fringes appear to be slightly stretched (~1%). Furthermore, the lattice image (which should be a rectangular pattern in the unstrained state) is sheared by an angle of 3-4°. The measurement of the actual pressure is difficult, however, due to the non-uniform confinement of the crystal, plastic relaxation, and possible irradiation effects in the crystal. (Specimen temperature: 600°C)

2. Materials and Methods

Simulation Technique

We used a non-orthogonal density functional theory-based tight-binding (DFTB) method (S1) to calculate the forces acting on atoms as a function of the atom separation. As we recently showed (S2), the DFTB method gives the values of formation energies for vacancy-type defects, which are in an excellent agreement with the results obtained from ab initio calculations. At the same time, the DFTB method being computationally less expensive than the ab initio approach, makes it possible to model nanotubes with relatively big diameters and lengths composed of hundreds of atoms.

We modeled the innermost shell of multi-wall carbon nanotube as a 1.7nm-long (10,10) single-wall nanotube (SWNT) with an equilibrium radius of 0.684 nm (intact nanotube). We consecutively created one, two, three etc. double vacancies in the nanotubes and ran simulations as follows. In the first set of calculations, we first fully relaxed the atomic network of the SWNT with a given number of double vacancies which were randomly created. We repeated several runs to make sure that the results are almost independent of vacancy distribution. We defined the concentration of double vacancies as half the ratio of the number of missing atoms to the number of atoms in the pristine tube. In the second set of calculations, we also created double vacancies in the SWNT, but contrary to the first set, we originally relaxed the atomic structure assuming that the tube radius remains the same (a hard-wall potential inside the tube). Thus we directly calculated the pressure as a function of vacancy concentration. For low vacancy concentration, we obtained essentially the same results as in the first set. However, when the concentration of double vacancies was high and the strain, correspondingly, large, the pressure calculations failed, as the system frequently got stuck in metastable configurations as double vacancies did not reconstruct.

References:

- S1 T. Frauenheim et al., *J. Phys.: Condens. Matter* **14**, 3015 (2002).
- S2 A. V. Krasheninnikov, P. O. Lehtinen, A.S. Foster R. M. Nieminen, *Chem. Phys. Lett.* **418**, 132 (2006).