Comment on “Single Crystals of Single-Walled Carbon Nanotubes Formed by Self-Assembly”

Schlittler et al. (1) reported the production of single crystals of single-walled carbon nanotubes (SWCNTs) by the thermolysis of nanopatterned structures of alternating layers of C$_{60}$ and nickel. Electron diffraction, high-resolution phase contrast imaging, and electron energy loss spectroscopy (EELS) were used to characterize the resulting crystals. In this comment, we report the reproduction of their experimental results; however, we disagree with their interpretation of the data. We suggest that the crystals formed in our experiments consist not of SWCNTs, but rather of calcium molybdenum oxide.

Multilayered structures, around 100 nm tall (300 nm in diameter) and consisting of 11 alternating layers of Ni and C$_{60}$, were patterned on Mo transmission electron microscopy (TEM) grids (Fig. 1A) in a special vacuum evaporation apparatus (2) as described in (1). The patterned grids were annealed inside a TEM microscope (Philips 400) using a heating holder (Gatan 652). The estimated magnetic field in this arrangement was on the order of 1 T; however, other annealing treatments ranged from no applied field up to a field of 7 T (3). The grids were typically outgassed at 200°C for 10 min and then ramped at 20°C/min to temperatures of 900 to 1000 °C.

The results of numerous annealing experiments can be summarized as follows: No faceted crystals were observed emerging from the multilayer stacks, which assumed a variety of interesting morphologies (Fig. 1B). However, long, thin nanocrystals matching the description in (1) were randomly scattered on the grids—that is, found in regions of the grids that were free of any deposited structures (Fig. 1C). These were easily distinguishable from the short, stubby, nanocrystals that were observed on etched regions on unannealed, as-received Mo TEM grids (as shown in Fig. 1A). Finding the long nanocrystals so far from the patterned multilayer stacks suggested that the two were unrelated, so as-received Mo TEM grids (300 mesh, EMS) were subjected to the same annealing treatment (950°C), and long, thin, nanocrystals were again obtained. No effect of magnetic field on either the occurrence or the orientation of the nanocrystals was observed.

These long, plate-like crystals typically had a high aspect ratio and faceted ends. When examined in situ or ex situ using a 100-kV conventional TEM, the longitudinal fringes reported in (1) were usually observed (Fig. 2, A and B). Longitudinal fringes with spacings around 1-nm were also observed (Fig. 2, C and D) in Z-contrast images from a 100 kV scanning transmission electron microscope (STEM) equipped with a high-angle, annular dark-field (HAADF) detector (VG Instruments HB501UX). Z-contrast images taken at higher magnification revealed a complex atomic structure with alternating light and dark fringes (Fig. 2D) and—an important observation—lattice fringes parallel to the facets of the crystals.

Simultaneous electron energy loss (EEL) spectra were acquired during Z-contrast imaging. In a typical EEL spectrum from near the edge of a nanocrystal (Fig. 2E), the so-called

![Fig. 1.](http://science.sciencemag.org/content/sci/300/5586/1236f1)

![Fig. 2.](http://science.sciencemag.org/content/sci/300/5586/1236f2)
In an oxygen-containing environment, calcium, a common surface contaminant, is readily incorporated between molybdenum oxide layers. Under the appropriate conditions, thermolysis of condensed-phase precursors has been shown to grow carbon nanotubes (13, 14). As the experiments in (1) and the reproduction of those experiments reported here shows, however, the introduction of reactive substrates and contaminants can result in nanocrystals with most unexpected compositions.

Matthew F. Chisholm
Oak Ridge National Laboratory
Post Office Box 2008
Oak Ridge, TN 37831, USA

Yuhuang Wang
Center for Nanoscale Science and Technology
Rice University
Houston, TX 77005, USA

Andrew R. Lupini
Gyula Eres
Alex A. Paretzky
Oak Ridge National Laboratory

Bruce Brinson
Center for Nanoscale Science and Technology
Rice University

Antoni V. Melechko
Douglas H. Lowndes
Oak Ridge National Laboratory

Marie P. Johnson
Center for Nanoscale Science and Technology
Rice University

Stephen J. Pennycook
Douglas H. Lowndes
Oak Ridge National Laboratory

Sivaram Arepalli
G. B. Tech./NASA Johnson Space Center
2101 NASA Road One
Houston, TX 77058

Carter Kittrell
Saujan Sivaram
Myung Kim
Gerry Lavin
Junichiro Kono
Robert Hauge
Richard E. Smalley
Center for Nanoscale Science and Technology
Rice University

*To whom correspondence should be addressed. E-mail: odg@ornl.gov

References and Notes
2. A silicon nitride membrane with 350-nm-diameter holes on a 1-μm pitch (Aquamarijn MicroFiltration) was mounted in contact with a Mo TEM grid for use as a shadow mask. Nickel was e-beam-vaporized from an alumina crucible (Thermionics), and C60 (MER, sublimed 99.5%) was sublimed from a thermal evaporation source.

Fig. 3. (A) Electron diffraction pattern from crystal with longitudinal fringes. (B) Enlarged view yielding major lattice spacings \(a = 2.6\, \text{Å}, b = 10.1\, \text{Å}\), and superlattice reflections at 1/3, 1/2, and 2/3 of reciprocal lattice spacing \(a^{-1}\). (C) Simulated electron diffraction pattern from the projection of the \(\text{Ca}_8\text{Mo}_{19}\text{O}_{32}\) structure shown in (D), in which \(a = 2.8\, \text{Å}, b = 11.4\, \text{Å}\).
evaporation source at normal incidence to the mask and grid to avoid shadow effects. The base pressure during deposition was < 10⁻⁷ Torr. The deposition rate was monitored using a quartz crystal thickness controller.

3. For high magnetic fields, grids were resistively heated inside 6-mm o.d. quartz tubing (at 5 x 10⁻⁶ Torr), which was inserted in the bore of a 7.04 T superconducting magnet (Oxford Instruments). Grids were oriented both parallel and perpendicular to the field axis. Grids were also annealed under zero field conditions using a button heater positioned inside a high vacuum chamber (5 x 10⁻⁸ Torr).


6. In an attempt to understand the source of the different contrast between bright and dark layers in the Z-contrast images (Fig. 2E), EELS line traces across several of these layers were averaged to obtain better statistics. However, spectra from the light and dark layers did not reveal a significant compositional change. The most likely explanation is that the crystals we studied were not oriented close enough to a low-index zone axis to reveal the full projected structure, and the contrast variations are the result of channeling variations in the layers.

7. We found references of 20 elements incorporated in molybdenum oxide.


10. The Ca₅.₄₅Mo₁₈O₃₂ compound is reported to have monoclinic symmetry (space group C2/m) with a = 24.21Å, b = 2.85Å, c = 9.87Å, α = 90°, β = 109.82°, γ = 90°. The x-ray data used to determine the atomic coordinates for Ca₅.₄₅Mo₁₈O₃₂ indicate that the formula for complete calcium occupation is Ca₉Mo₅₂O₃₂; thus, the Ca positions are 68% occupied. The most likely explanation for the superlattice reflections is additional structural order associated with partial occupation of the Ca sites. Although partial occupancy was included in the diffraction simulations, ordering of the occupied and unoccupied Ca sites was not.


12. For example, the simulations show that when tilting Ca₅.₄₅Mo₁₈O₃₂ from the [011] projection to the [041] projection, one principal reflection (the [200] reflection with d = 1.14 nm) remains constant while the spacing of the other principal reflection decreases from d = 0.28 nm at the [011] zone axis to d = 0.19 nm at the [041] zone axis. Tilting from the [130] zone axis to the [031] zone axis causes the principal reflection with the larger d-spacing to vary from 0.93 nm to 1.14 nm.

13. We gratefully acknowledge the assistance of J.K. Gimzewski at UCLA for extensive discussions and guidance regarding sample preparation and annealing treatments.
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