Advanced electron microscopy techniques in structure characterization of mercury dichloride one-dimensional encapsulated crystals

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Carbon nanotubes (CNTs) possessing a confined inner space protected by chemically resistant shells are promising for delivery, storage, and desorption of various compounds, as well as carrying out specific reactions. Here, we show that single- and multi-walled CNTs interact with molten mercury dichloride ($HgCl_2$) and guide its transformation into dimercury dichloride (Hg_2Cl_2) in the cavity. The chemical state of host CNTs remains almost unchanged except for a small p-doping from the guest Hg_2Cl_2 nanocrystals. The absence of chemical modification of the CNT surface after the filling reveals a mechanism for redox transformation of the $HgCl_2$ in the nanotube cavity, which is completely different from that proposed for activated carbon. Transfer of electron density from CNTs to encapsulated molecules is a crucial stage in this transformation, as is shown by density functional theory (DFT) calculations. The encapsulated $HgCl_2$ molecules become negatively charged and start interacting via chlorine bridges when local concentration increases. This reduces the bonding strength in $HgCl_2$, which facilitates removal of chlorine, finally leading to formation of Hg_2Cl_2 species. The present work demonstrates that SWCNTs and MWCNTs not only serve as a template for growing nanocrystals but also behave as an electron-transfer catalyst in the spatially confined redox reaction by donation of electron density for temporary use by the guests.
The TEM study was carried out on a FEI Titan 60-300 TEM/STEM microscope equipped with an x-FEG, monochromator and an image side Cs spherical aberration corrector. The images were acquired at an 80 kV accelerating voltage for TEM and 300 kV for STEM and processed in Digital Micrograph software using custom-made scripts. HRTEM image simulations were performed by a standard multislice algorithm at the Musli software package. The filling ratio of SWCNTs, presented in Figure 1a, is between 20% and 50%, while the length of encapsulated crystals varies from 1 to 150 nm. An energy-dispersive X-ray (EDX) spectroscopy study of filled SWCNTs detected signals from mercury, chlorine, carbon, oxygen, and copper (Fig. 1b). The presence of mercury and chorine is unambiguous, but the exact Hg/Cl ratio cannot be determined precisely due to a low signal-to-noise ratio. The X-ray diffraction (XRD) analysis of the product obtained after the reaction of SWCNTs with $HgCl_2$ showed a transformation of $HgCl_2$ to Hg_2Cl_2 (Fig. 1c). The structure of the encapsulated nanocrystals was evaluated using high-resolution TEM images acquired with a short exposure time of 100 ms for the detection of possible nanocrystal rotation and motion under an electron beam (Fig. 2). HAADF STEM data allowed to obtain additional information about the structure of encapsulated crystals. Detailed information could be found in [1].

[1] Fedoseeva Y.V., Orekhov A.S., Chekhova G.N. et al. ACS Nano, 2017, 11 (9), pp 8643 - 8649

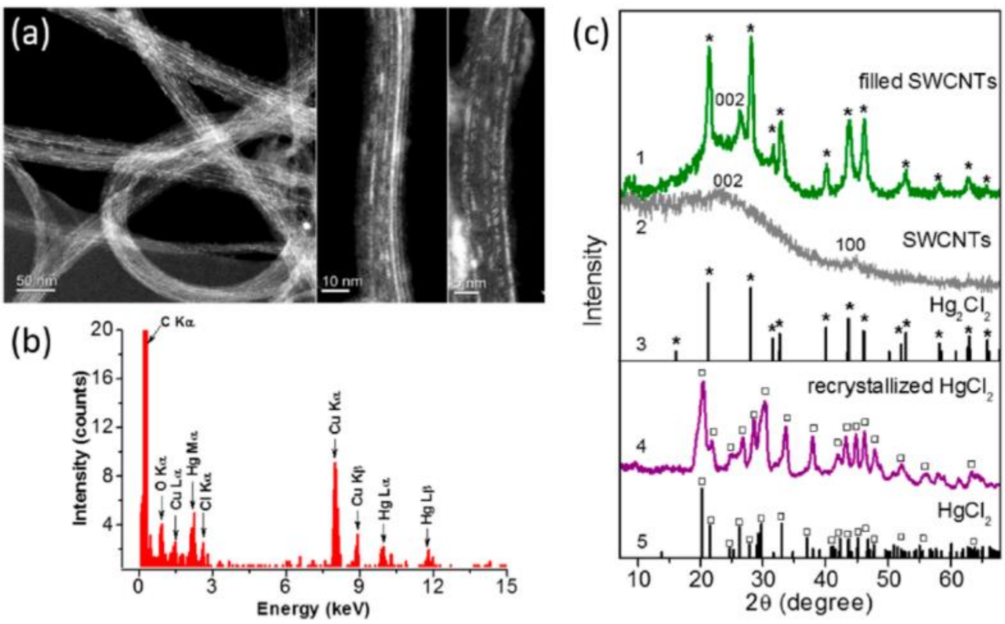

Figure 1. (a) HAADF/STEM images and (b) EDX spectrum of filled SWCNTs. (c) XRD patterns of filled (1) and initial SWCNTs (2), polycrystalline Hg2Cl2 (3), mercury chloride recrystallized without addition of SWCNTs (4), and polycrystalline HgCl2 (5).

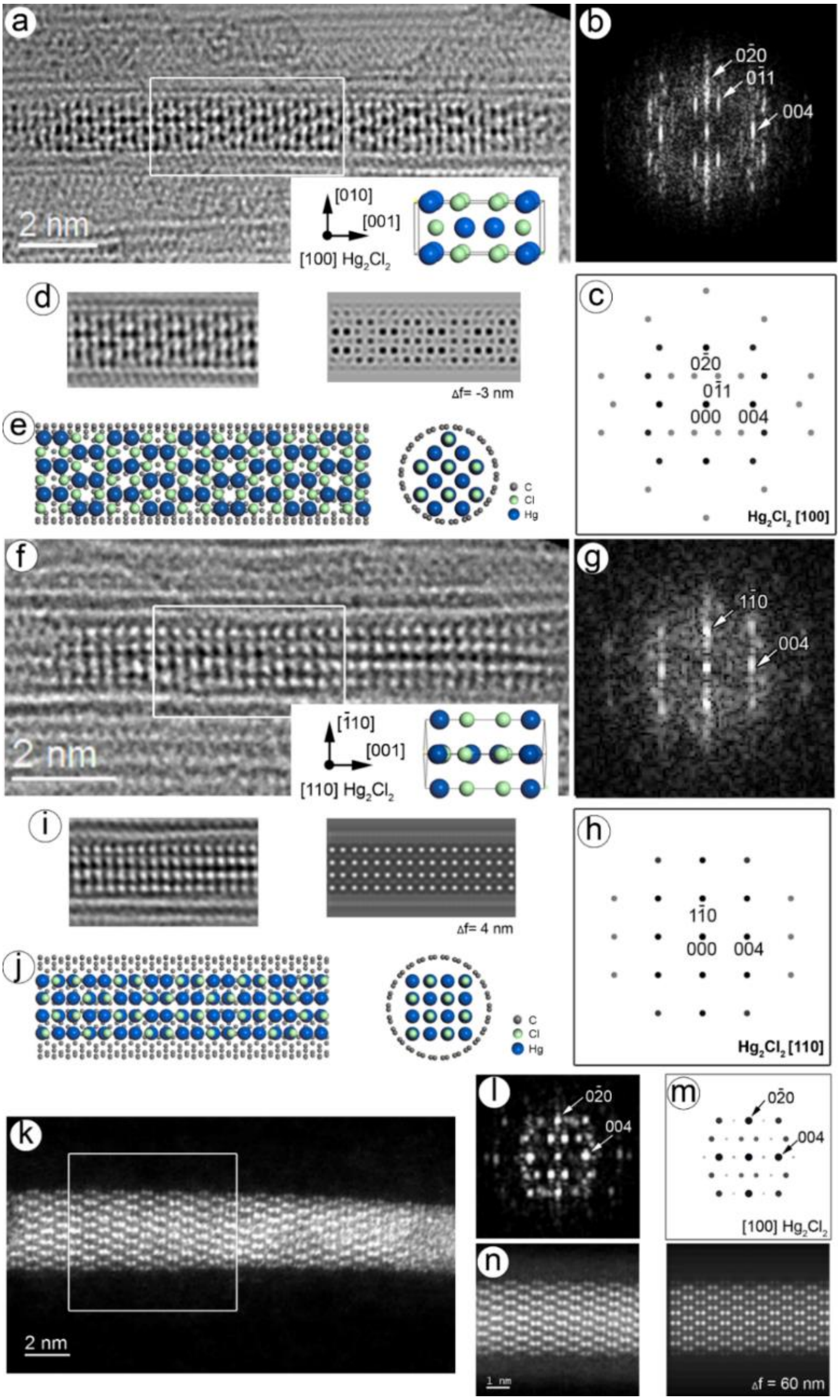

Figure 2. (a, f, k) HRTEM and HRSTEM images of filled SWCNTs viewed in [100] Hg_2Cl_2 (a, k) and [110] Hg_2Cl_2 (f) projections. (d, i, n) Filtered and simulated HRTEM images of a selected area (white box). (b, c, g, h, l, m) Diffractograms and calculated electron diffraction patterns for a Hg2Cl2 crystal along the [100] and [110] directions. (e, j) Atomic model of Hg2Cl2@SWCNT viewed in [100] Hg2Cl2 and [110] Hg2Cl2 projections and cross section of filled nanotube.