Contribution (Oral)

Symmetry breaking and on-tube modulated surface potentials in hybrids of Single-Walled Carbon Nanotubes with encapsulated inorganic nanostructures

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Templated confinement in carbon nanotubes has emerged in recent years as a successful route towards producing low dimensional hybrid nanomaterials with new and diverse nanoscale properties and applications, from nanothermometers, to nanofluidic attogram mass transport, to chemical sensors with enhanced sensitivity, to transport phenomena such as negative differential resistance (NDR) or spin-related, or vectors for drug delivery. It also generates phases of materials inaccessible otherwise. Effects are particularly rich when confining inorganic materials in Single-Walled Carbon Nanotubes (SWCNTs), with theoretical predictions and increasing experimental evidence of unique morphologies forming inside [1-3]: inorganic nanotubes (INTs), twisted structures, with lowered symmetry and high anisotropy, or with strong structural relaxation.

To ultimately exploit these hybrid nanomaterials controllably one needs to be able to correlate structure with physical properties, and then with functionality down to the *local (atomic) level*. This approach is essential at this degree of lateral confinement where few atom morphological variations can dramatically affect properties.

For this, we combine high resolution transmission electron microscopy (HRTEM), scanning tunnelling microscopy /spectroscopy (STM/STS), and ab-initio calculations to study structural phases of SWCNT-templated silver iodide (AgI) nanowires [4]. We show that symmetry breaking of the nanotube's surface wavefunction correlates with the electrostatic/polarization interaction from the ionic component of AgI filling (which has a mixed ionic-covalent character). This is the first direct demonstration of the capability of inorganic nanostructures to be unique sources of non-bonding on-tube *surface potentials where symmetry and magnitude can be controllably modulated*, with strong implications for electronic transport.

Here, low-dimensional AgI nanowires formed inside SWCNTs provided the first opportunity to use STM/STS to reveal more generic local effects on nanotubes caused by a long-range, non-bonding, electrostatic/polarization interaction potential. AgI is a good study system as its polymorphic nature helps select the symmetry of the resulting SWCNT-encapsulated phases. Fig.1 shows such an AgI phase with strong charge anisotropy, where charges of alternating sign are separated in rows (see Fig. 3a): 1(a) is an HRTEM image of two structural configurations stemming from the same crystallization phase, i.e. in a narrower nanotube, and a larger nanotube where structural relaxation occured; 1(c) are associated structural models derived from Density Functional Theory (DFT) simulations; 1(b) are HRTEM image simulations using the structural models from 1(c). Figure 2 shows STM/STS from AgI-filled SWCNTs. A stripe-like superstructure breaks the usual symmetry of the nanotube's wavefuction. We found that its overall characteristics and energy dependence is consistent with the ionic/polarization perturbation potential at the nanotube wall generated by the phases in Fig. 1 (and different from known superstructures). This potential has a stripe-like surface distribution, shown in Fig. 3(a); its amplitude magnitude is sizeable, of several tenths of eV, as obtained from both Discrete Dipole Approximation (DDA) and DFT calculations. Fig. 3(b) shows that the potential's distribution / symmetry and its magnitude is governed crucially by the type of encapsulated AgI phase: a different phase, with fast charge alternation and thus less anisotropic charge distribution, produces a different symmetry and a strongly reduced modulation of the potential.

This leads to the generalization that *well-chosen* encapsulated inorganic structures with regulated, "quantized" number of atomic rows can be unique sources of interaction potentials with the nanotubes where symmetry and magnitude can be controllably selected and modulated. Adding to the results of another study of ours, where permanent dipoles in the chain of a SWCNT-encapsulated KI nanocrystal were invoked to explain Negative Differential Resistance phenomena [5], such potentials can have

strong implications for the electronic transport through carbon nanotube-based hybrids. Moreover, they can provide a potential way to dominate and uniformize the nanotube's response in respect to its (n,m) type; as well as an additional, charge-based assembly mechanism for nanotube functionalization.

References

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Figures

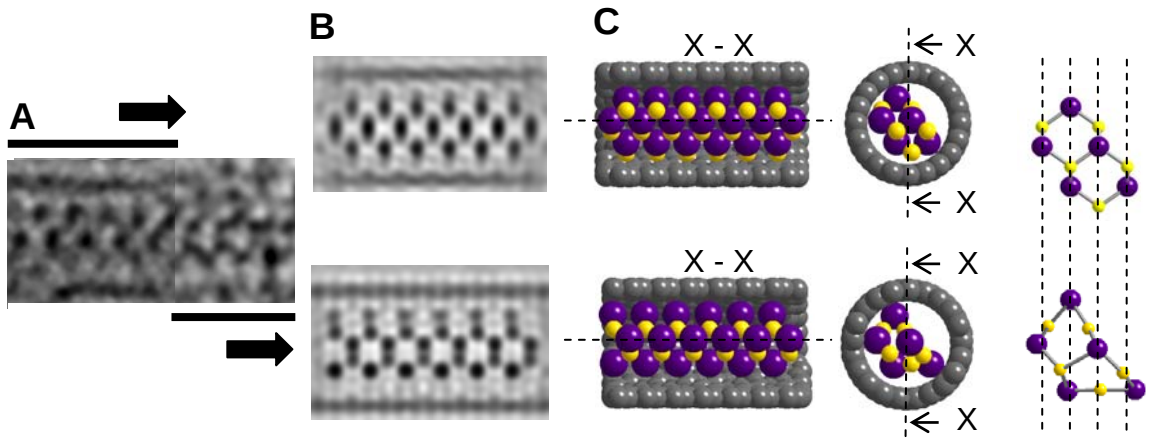

Figure 1.
(a) HRTEM of same AgI phase, without (left) and with (right) structural relaxation in a narrower (1.45 nm diameter) / larger (~1.65 nm diameter) SWCNT, respectively; (b) HRTEM image simulations using structural models from (c); (c) structural models for unrelaxed (top) / relaxed (bottom) AgI phases. DFT simulations were used to determine relaxation.

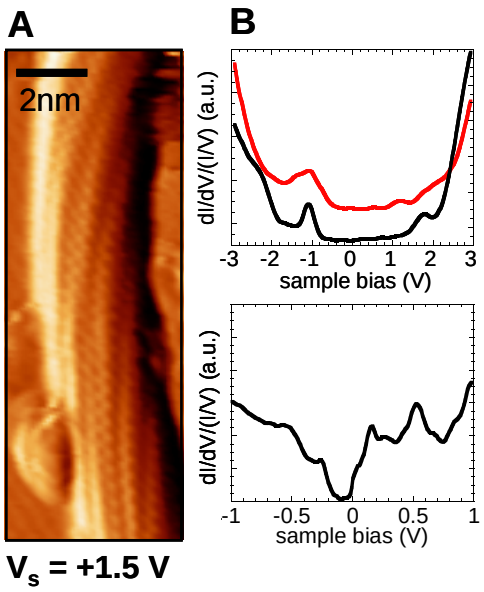

Figure 2.
(a) Bias-dependent STM showing a stripe-like superstructure; (b) Example of associated STS spectroscopy. Both STM/STS are consistent with proposed models.

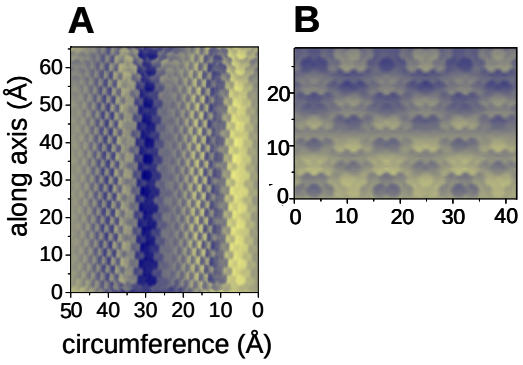

Figure 3.
Unrolled circumferential polarization potential map at the SWCNT wall resulting from associating Mulliken Population charges with the AgI filling for: (a) an AgI phase from Fig. 1; (b) a different AgI phase, with different charge distribution (see text). The maps have been obtained by unrolling the AgI@SWCNTs structures.