Chemical Reactions within Single-Walled Carbon Nanotube Channels

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The discovery of single-walled carbon nanotubes (SWNTs) has sparked worldwide ever-increasing interest arising from their unusual electronic, chemical, optical, and mechanical properties as well as a great potential for application in nanoelectronics and nanotechnology.[1,2] It is generally accepted that all the properties of SWNTs strongly depend on the tube's diameter and atomic structure[2,3] and can be successfully influenced by chemical modification of tubular external surface (e.g., decoration or coating)[4,6] or their internal channels (e.g., intercalation).[5,6] Loading guest compounds into nanotube voids leads to the development of a novel class of functional nanocomposites (1Dcrystal@SWNT), consisting of a carbon shell and a one-dimensional (1D) crystal of encapsulated material.

For example, filling of SWNT channels with electron-donor or electron-acceptor compounds will increase or, accordingly, decrease the electron density on nanotube walls and, therefore, allow one to control the electronic properties of the system.[7]

Unfortunately, an extensive application of SWNT-based composites is limited due to the absence of universal synthetic approaches for filling in nanotube channels, which narrows the range of chemical compounds suitable for intercalation.[6] The traditional techniques include in situ filling of nanotubes by catalytic metals during the chemical vapor deposition (CVD) process (e.g., Ni, Co, or Fe) or an ex situ procedure

(so-called capillary technique) via impregnation of preopened SWNTs with gaseous or liquid medium.[5,9,10] However, in most cases the preferential formation of discrete spherical or oviform clusters inside carbon nanotubes instead of continuous one-dimensional nanocrystals becomes a fundamental problem. Homogeneous and continuous filling of nanotube channels can be achieved by an intercalation of molten guest compounds into SWNTs followed by crystallization under a slow cooling (so-called molten media method).[8,11] This approach requires a low surface tension of the guest compound ($\gamma = 130-170$ mN/m) to wet the nanotube surface and a low melting point (< 800 °C) to prevent the destruction of carbon nanotubes during the impregnation.[9] However, these conditions prohibit direct filling of SWNTs by most metals (due to high surface tension) and covalently bonded compounds. To our knowledge, no appropriate technique for the preparation of SWNT-based composites with continuous 1D crystals of high-melting compounds inside nanotube channels have been developed so far. At the same time, the encapsulation of wide-gap semiconductors into metallic nanotubes or metal nanoparticles into semiconducting ones can cause the most significant changes in the electronic structure of SWNTs. Therefore, in the present study we focused on the formation of 1D $A^{II}B^{VI}$ and $A^{IV}B^{VI}$ nanocrystals (namely, cadmium, zinc, and lead chalcogenides) within SWNT channels.

The first experiments were aimed to grow 1D CdS nanocrystals inside SWNT channels. Though CdS has a rather high melting point (1750 °C at 100 bar), which forbids direct impregnation of nanotubes using the molten media method, this compound can be easily formed from low-melting precursors (e.g., $Cd(Hal)_2 + S$, where Hal = F, Cl, Br, I). However, to perform a chemical reaction inside a SWNT, first, it is necessary to deliver reactants to the reaction zone in the nanotube channel and avoid their interaction at the exterior medium. Obviously, the delivery of the precursors could not be realized through the nanotube endings due to their possible intermixing previous to the intercalation process. On the other hand, recently, we observed the destruction of one-dimensional CuI nanocrystals within SWNT channels, which was accompanied by an escape of both copper and iodine atoms from the nanotube interior through the defects in the SWNT wall.[12] This effect could be utilized for incorporation of the material into SWNT

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and performing chemical reaction inside the nanotube channel. If one has success with an intercalation of the first precursor into the nanotube, it could be possible to proceed with second precursor delivery to the SWNT interior (from the external surface) through the defects in the nanotube wall. In this case, the location of the reaction product will be governed by the "diffusion" rates of the precursors (or precursor components) and reaction products through the graphene layer. For example, intercalation of $Cd(Hal)_2$ into nanotube channels with subsequent treatment by sulfur melt will result in the formation of CdS@SWNT composite, due to the higher chemical affinity of SWNTs to electron acceptors rather than donors. This implies higher anion mobility through the grathene layer. The reverse order of melt treatments (impregnation of S@SWNT composite with $Cd(Hal)_2$ melt) will lead to decorating of nanotubes by cadmium sulfide nanoparticles.

To realize the approach discussed, we performed an impregnation of single-wall carbon nanotubes (inner tube diameter 1−1.4 nm) with low-melting cadmium iodide (T_m = 388 °C) followed by sulfidizing in molten sulfur (T_m = 112.8−120 °C) at 288 °C. All operations were carried out under a static vacuum (1 Pa). To avoid the formation of amorphous product in the channels, the cooling rate was set to 0.4°/min. During the treatment, an excess of sulfur was evaporated and transported to the cooler part of the quartz ampule as defined by a slight temperature gradient in the furnace. The general synthetic procedure for preparation of $A^{II}B^{VI}$ and $A^{IV}B^{VI}$ semiconductor nanocrystals within SWNT channels is provided in the Supporting Information.

The evidence for filling nanotubes and the structure of encapsulated particles was investigated using JEM-3000F JEOL and FEI Titan 80-300 Cs-corrected field emission transmission electron microscopes (TEMs) equipped with an INCA Energy + Oxford EDX analyzer. The images were acquired at acceleration voltage of 80−300 kV. Figure 1 illustrates clearly the formation of continuous one-dimensional fine crystals in SWNT channels. To determine the chemical composition of the composite, local energy dispersive X-ray (EDX) analysis of CdS@SWNT composite was carried out (Figure 1). The detection area was chosen to disjoin any sample non-idealities, impurities, or the microscopy carbon grid. Cadmium, sulfur, and carbon Kα and Kβ spectral lines were detected by EDX, while no evidence for the presence of iodine was observed. The atomic Cd:S ratio in the area of interest was found to correspond to 1:1.5, which reveals some excess of sulfur, possibly enveloping the tube's surface. To exclude the probable oxidation of composite, X-ray photoelectron spectroscopy (XPS) studies were carried out for the CdS@SWNT sample, which detected no oxygen lines in the overview spectrum.

The iodine formed during substitution reaction was found by mass spectrometry of sublimate byproduct collected on the cooler part of the quartz ampule. These data give conclusive evidence for reaction 1, taking place at 288 °C:
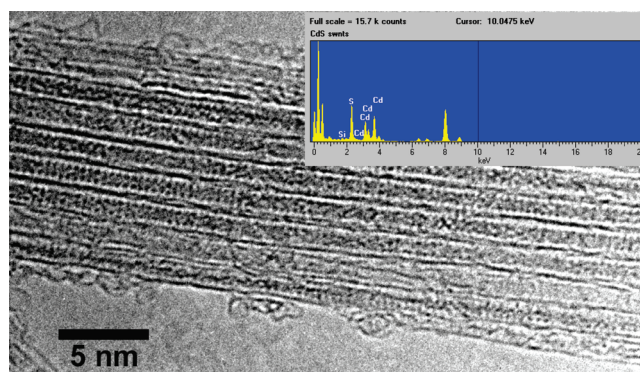
$$CdI_{2(s)}@SWNT + S_{(l)} = CdS_{(s)}@SWNT + I_{2(v)} \quad (1)$$

Figure 1. High-resolution (HR) TEM imaging and EDX spectra of CdS@SWNT nanocomposite.

To our knowledge, this is the first chemical exchange reaction observed in the spatially confined zone of the SWNT channel. Earlier the reduction reaction of ReO by hydrogen in the nanotube interior was reported in the literature, which resulted in the formation of rhenium clusters in the SWNT channel.[15] On the other hand, the suggested approach opens a pathway for homogeneous and continuous filling of nanotubes by high-melting compounds not discussed in the literature previously.

Only one well-defined projection of the one-dimensional CdS crystal@SWNT was observed by HRTEM. The image for this projection (Figure 2b) is formed by two modulated rows of rather dense "subunits" running with the periodicity of ∼0.74 nm along the sides of the one-dimensional nanocrystal. The modulation interval consists of two sets of subunits shifted slightly relative to each other in the direction perpendicular to the tube axis. The distance between the nearest subunits of 0.37 nm (the minimal interlayer spacing) corresponds rather well to the interplanar spacing between sulfur (or cadmium) planes in bulk greenockite (3.57 Å). The average distance between the rows equals 0.44 nm, which is consistent with a nearest-neighbor Cd−Cd or S−S distance for the above-mentioned structure ($D_{Cd-Cd} = D_{S-S} = 4.12$ Å). The mismatch in experimentally observed data and lattice constants of greenockite can arise from a spatial confinement of the growth zone in SWNT channel, as it was earlier observed for one-dimensional crystals of iodine, potassium, and copper iodides and many compounds synthesized in SWNT channels.[16−19]

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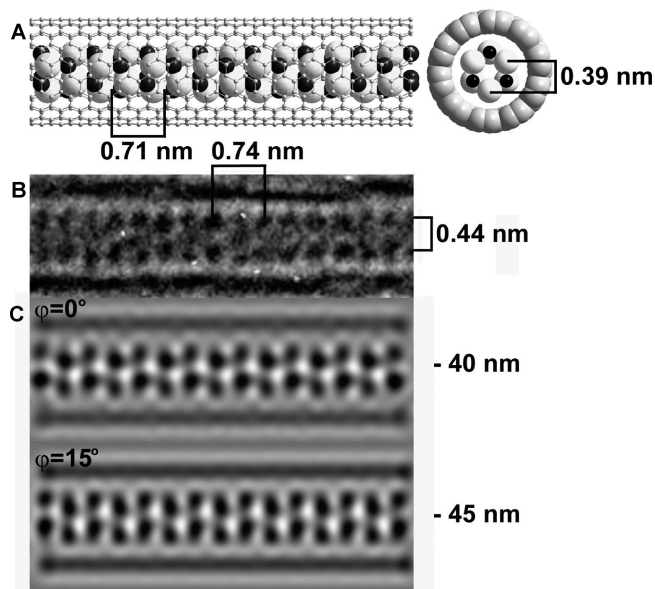
Figure 2. (A) Structural model of CdS one-dimensional crystal inside an SWNT channel (black spheres, cadmium atoms; light gray spheres, sulfur atoms; small gray spheres, carbon atoms). (B) Filtered HRTEM image of CdS@SWNT sample. (C) Simulated images for the proposed model at different Δf.

To prove the proposed structure of CdS one-dimensional nanocrystals, we built a model of the CdS@SWNT composite and performed an TEM image simulation using the "Diamond" and "SimulaTEM" software packages (Figure 2a and c). The model of 1D nanocrystals corresponds to a structural type of greenockite, represented by a hexagonal two-layer closest packing of sulfur and cadmium ions. From the cross-view of the CdS@SWNT composite, the structure can be imagined as a Star of David inscribed into the tube circumference. Hexagonal lattice parameters are $a = 0.42$ nm and $c = 0.67$ nm, space group $P6_3mc$. The direction $\langle 001 \rangle$ of bulk greenockite crystal was chosen to coincide with the SWNT axis. An excess of atoms from the CdS unit cell was cut away. As a result, the tentative symmetrical atomic model was obtained (Figure 2a). Viewed along the nanotube axis, the model illustrates just enough room to accommodate a one-dimensional CdS crystal in the tube channel.

The simulated images for the proposed CdS@SWNT model are in a good agreement with experimental micrographs at the wide range of Δf (Figure 2c). The only deviation concerns ~10% increase of interatomic distances as compared to bulk $P6_3mc$ CdS and a slight distortion of hexagonal packing appearing due to the spatial confinement of crystal by SWNT walls. As a crystal possess 3-fold inversion symmetry, the side view of the model gives only three characteristic projections ($\varphi = 0°$, $\varphi = 15°$, and $\varphi = 30°$). According to image simulation, two of them ($\varphi = 0°$ and $\varphi = 15°$) give nearly the same pictures, corresponding well to the structure observed by HRTEM. Unfortunately, we were unable to experimentally detect the third ($\varphi = 30°$) projection of the CdS@SWNT structure which is possibly related to a low contrast emerging for this type of image.
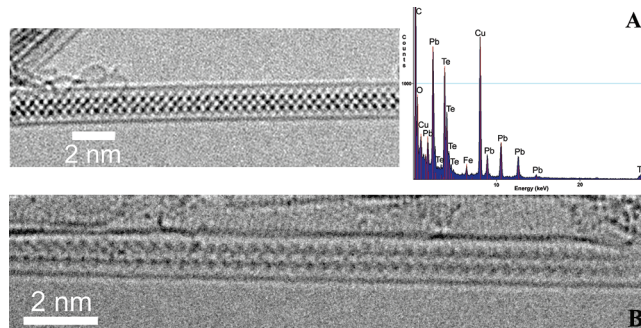

Figure 3. HRTEM imaging and EDX spectra of PbTe@SWNT (A) and ZnTe@SWNT (B) nanocomposites.

Modification of the SWNT channel by intercalation of semiconductor crystal leads to a change of the electronic structure of nanotubes, as was observed by Raman spectroscopy of CdI$_2$@SWNT and CdS@SWNT composites (see the Supporting Information for details). The composites exhibit the upshift of RBM and G vibrational frequencies as compared to raw SWNTs, which is attributed to depletion of electrons from the SWNT walls to the intercalated compound.[7,19] Moreover the efficiency of charge transfer was found to depend on the electron affinity of the acceptor atom (sulfur or iodine) and nanotube chirality.

The same synthetic approach was extended to form 1D nanocrystals of cadmium, zinc, and lead chalcogenides within SWNT channels (see the Supporting Information for details). Figure 3 illustrates a perfect structure of intercalated 1D crystals, while EDX spectra reveal the formation of desired compounds inside SWNT channels. The structure and electronic properties of obtained nanocomposites would be issues for further studies.

To conclude, in the frame of the present study, a simple two-step approach for the assured filling of SWNT channels with A^{II}B^{VI} and A^{IV}B^{VI} chalcogenide 1D nanocrystals was suggested. The method is based on the formation of intermediate metal iodide in SWNTs using a molten media technique with subsequent chalcogenation reaction performed in molten chalcogen. Local EDX of CdS@SWNT composite together with mass spectrometry of byproduct gave us the conclusive evidence of the reaction taking place between cadmium iodide nanocrystal and molten sulfur inside the tube interior. This is the first chemical exchange reaction observed in the spatially confined zone of SWNT channels. The suggested approach opens a pathway for homogeneous and continuous filling of nanotubes by high-melting compounds of A^{II}B^{VI} and A^{IV}B^{VI} semiconductor nanocrystals.

Supporting Information Available: General preparation procedure for A^{II}B^{VI}@SWNT and A^{IV}B^{VI}@SWNT composites and electronic properties of CdI$_2$@SWNT and CdS@SWNT composites investigated by Raman spectroscopy. This material is available free of charge via the Internet at http://pubs.acs.org.