

Graphite-Incorporated MoS₂ Nanotubes: A New Coaxial Binary System

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Graphite-filled MoS₂ nanotubes were synthesized by pyrolyzing propylene inside MoS₂ nanotubes prepared by a template-assisted technique. The large coaxial nanotubes were constituted of graphite sheets inserted between the MoS₂ layers, forming the outer part, and coaxial multiwall carbon nanotubes intercalated with MoS₂ inside. High-resolution electron microscopy (HREM) and electron energy loss spectroscopy techniques along with molecular dynamics simulation and quantum mechanical calculations were used to characterize the samples. The one-dimensional structures exhibit diverse morphologies such as long straight and twisted nanotubes with several structural irregularities. The interplanar spacing between the MoS₂ layers was found to increase from 6.3 to 7.4 Å due to intercalation with carbon. Simulated HREM images revealed the presence of mechanical strains in the carbon-intercalated MoS₂ layers as the reason for obtaining these twisted nanostructures. The mechanism of formation of carbon-intercalated MoS₂ tubular structures and their stability and electronic properties are discussed. Our results open up the possibility of using MoS₂ nanotubes as templates for the synthesis of new one-dimensional binary-phase systems.

Introduction

Since the discovery of the nanotubes by Iijima,¹ improving the methods for producing both carbon^{2,3} and inorganic^{4–7} tubular structures has been the goal of many researchers. The perspective of applications of these nanostructures has also determined the imperative necessity of understanding their morphology, composition, and physicochemical properties.^{8,9} The synthesis of metal chalcogenide nanotubes has been reported by several authors.^{6,7} One of the most controllable and inexpensive methods to produce one-dimensional nanostructured materials is the use of templates, such as Al₂O₃ nanoporous molds prepared by an anodization process.^{10,11} Utilizing the chemical and thermal stability,^{12–14} insulating behavior, and possibility of controlling the diameter of the channels and pore density through controlled anodization,¹⁵ aluminum oxide is traditionally used for preparing amorphous anodic alumina nanoporous templates (AANTs) highly suitable for generating one-dimensional nanostructure systems. The AANTs prepared in this way can further be modified by filling any material in its hollow structure and can be reused as a new cast to combine two or more different materials. Several workers have synthe-

sized MoS₂ nanotubes of controlled length and diameter utilizing AANTs. Generally, these nanotubes are of multiwall or layered structures.

The possibility of having a material with the extraordinary properties of both carbon and MoS₂ nanotubes in a host–guest configuration may open up a new field in the study of novel coaxial heterogeneous structures. Recently, the studies of host–guest intercalation between atomic and molecular species in layered matrixes such as graphite and metal dichalcogenide structures such as QS₂ compounds¹⁶ have been started. Though the intercalation chemistry of transition-metal sulfides has been well-known since the 1970s, molybdenum disulfide nanotube chemistry is relatively recent, and the synthesis of tubular structures of MoS₂ and their physicochemical properties are still under study.^{17–19} However, the synthesis of tubular nanostructures of binary phase utilizing the layered morphology of metal chalcogenides is still a challenge.

The design and manipulation of the nanostructured materials involve a complete study of the atomic distribution and its corresponding effects on the electronic structure. Chemical, photonic, and electronic properties of nanostructure materials^{20–23} have been determined routinely utilizing their crystallographic structures. Therefore, a combination of methods such as high-resolution electron microscopy and molecular dynamics simulation permit nanostructured materials to be studied with enough detail of their structural and physicochemical characteristics.^{24–26}

In the present work, we report on the synthesis and characterization of new MoS₂–C coaxial mixed nanotube structures with several morphologies. The nanostructures were characterized using high-resolution electron microscopy (HREM) and

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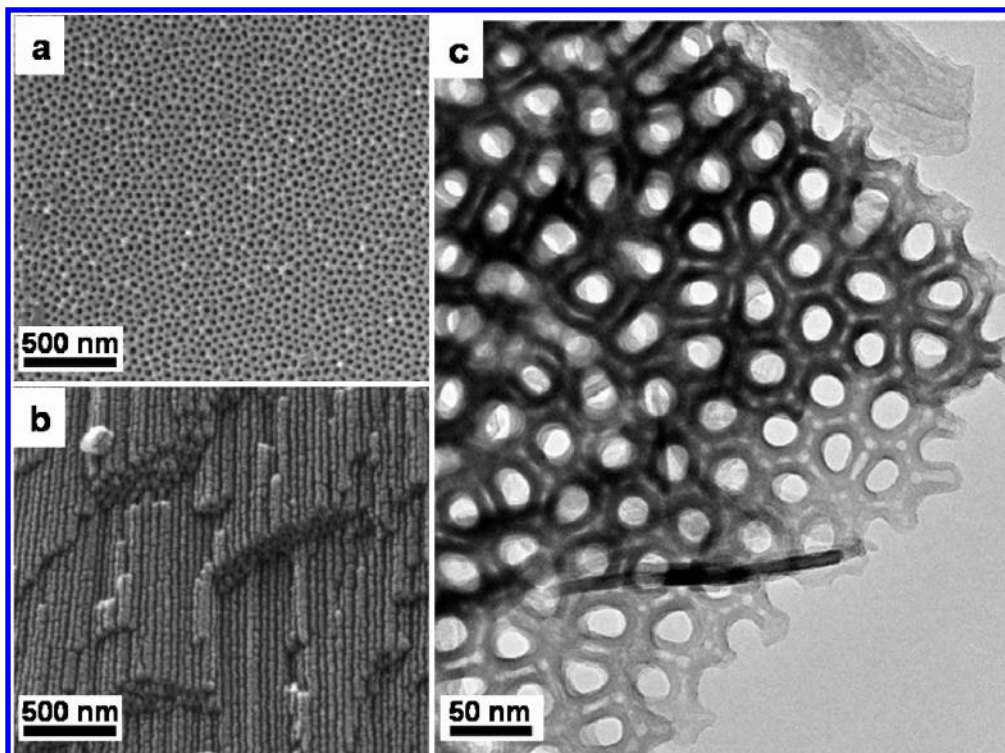


Figure 1. Typical SEM micrographs. (a) Planar and (b) cleaved section of the anodized alumina template used in this study. Formation of hexagonal pores of about 30 nm average diameter and 50 μm average length were observed. (c) TEM micrograph of the AANT cross section.

electron energy loss spectroscopy (EELS) techniques. Molecular dynamics (MD) simulations and quantum mechanics calculations were performed to understand the mechanism of formation of the nanostructures and their stability and electronic properties.

Experimental Procedure

Large coaxial and intercalated nanotubes of MoS₂ and carbon (MoS₂-C) were synthesized through a template growth approach using AANTs. Amorphous AANTs were prepared in an electrolytic cell using two aluminum electropolished sheets as electrodes immersed in an aqueous H₂SO₄ solution (5%) at a controlled dc voltage (5 V). To obtain homogeneous AANTs, the temperature of the electrolytic cell was kept in the range of 0–5 °C and the anodization was carried out for 8 h. The polarity of the electrolytic cell was reverted to separate the AANTs from the aluminum anode. The impervious layer of the film was then removed by immersing it in a 20% sulfuric acid solution for 10 min. Layers of several micrometers thickness with local hexagonal close-packed structure were obtained. The AANTs prepared in this way are thermally and structurally stable up to 900 °C.^{12–14} In Figure 1, typical microscopic views of planar and sectional surfaces of the template used in this study are shown.

The first step of generating the MoS₂-C nanotubes was the synthesis of the host structure. MoS₂ nanotubes were obtained by pyrolyzing (NH₄)₂MoS₄ inside the template using a solution of (NH₄)₂MoS₄ (0.1 M) and dimethylformamide (DMF) as the solution-phase precursor.¹⁰ A nanoporous alumina template 1 cm² in size and 50 μm in thickness was immersed in the precursor solution for 5 min and then dried at 70 °C to evaporate the remaining solvent at the surface. The precursor was pyrolyzed at 450 °C for 1 h inside a programmable horizontal furnace under the flow of a hydrogen and nitrogen gas mixture (10% H₂, 20 mL/min). The details of the synthesis technique have already been reported by Zelenski²⁸ and P. Santiago et al.¹⁰ The special feature of the MoS₂ nanotubes synthesized in the present

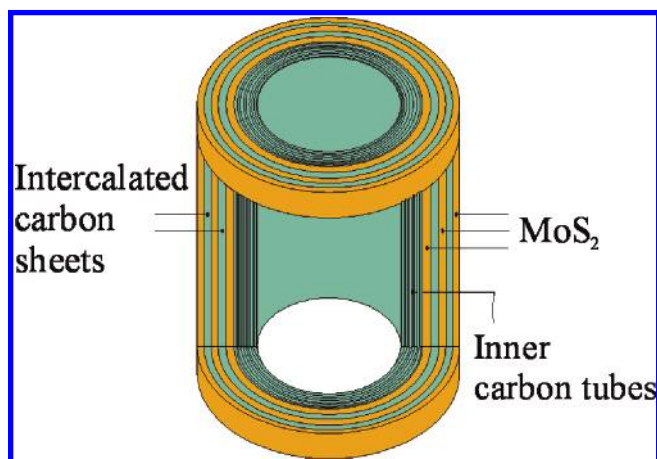


Figure 2. Schematic diagram of a coaxial intercalated MoS₂-C nanotube with a pure graphite phase inside.

case is that over 90% of them had a morphology of a chain of interconnected bent segments, while the rest had a long straight tubular structure.

Once the AANT was filled with MoS₂ nanotubes, the sample was again loaded into the furnace for the graphitization and intercalation process. A propylene/N₂ mixture flux (1:8 v/v, 2 mL/min) was passed through the furnace at 800 °C for 1 h. To isolate the synthesized nanostructures from the template, it was loaded into an acid digestion bomb filled with 1 M sodium hydroxide solution. The system was heated at 120 °C on a hot plate for 12 h. This alumina-dissolving process generates aluminum oxyhydroxide residues in the form of a gel suspended in the sodium hydroxide solution. The reaction products [2NaOH + Al₂O₃·3H₂O → 2NaOH + 2Al(OH)_{3(gel)}] were carefully removed with a syringe and substituted with distilled water several times to separate the nanotubes from these residues. Finally, distilled water was substituted with methanol, and the resultant solid material was dispersed in an ultrasonic bath for

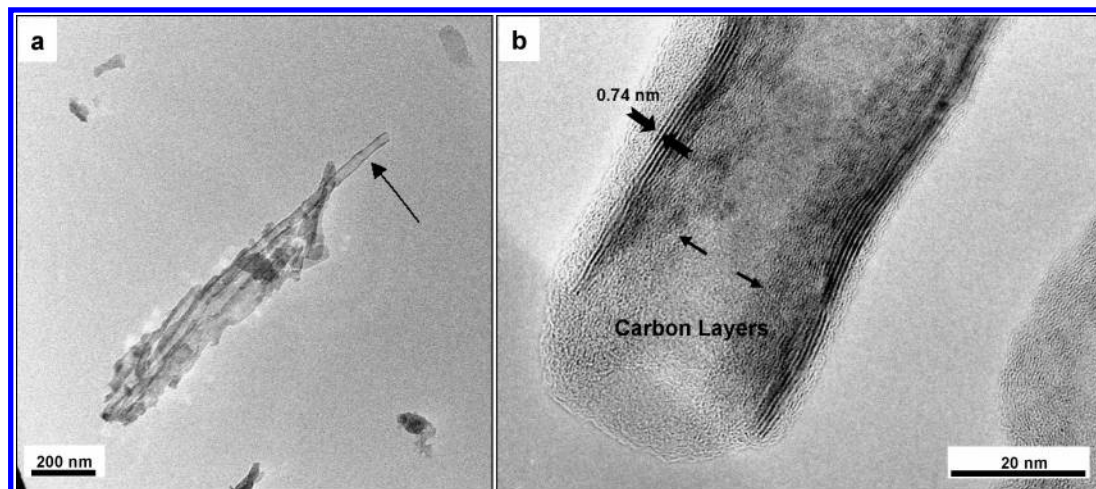


Figure 3. (a) A typical low-magnification TEM micrograph of the binary-phase nanotubes and (b) an HREM micrograph showing their layered structures.

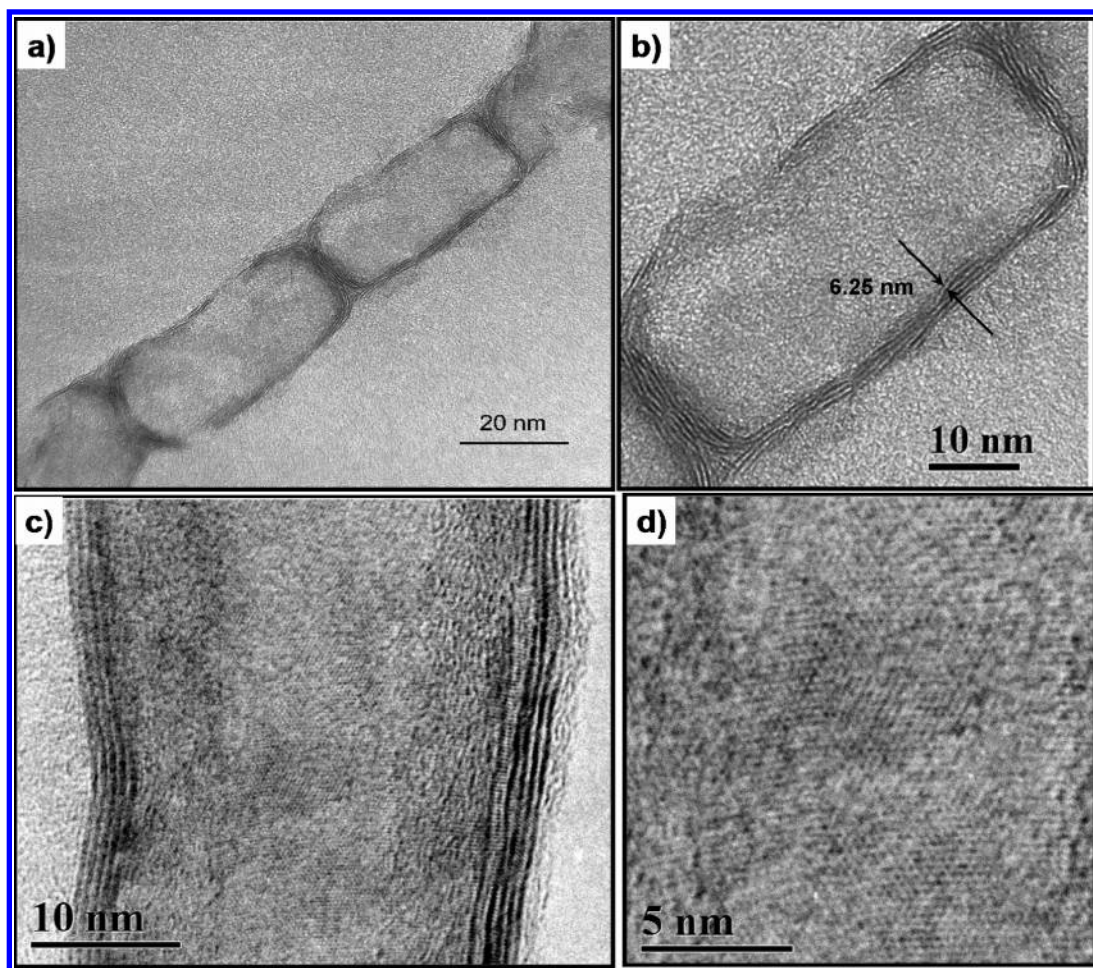


Figure 4. (a, b) Typical HREM micrographs of pure MoS_2 nanotubes. (c) HREM micrograph of $\text{MoS}_2\text{-C}$, showing hexagonal Moire fringes at the central part of the nanotubes. (d) A closer view of the selected area marked in (c).

5 min. A drop of the suspension was put on a carbon-coated copper grid for TEM analysis.

TEM observations were performed in a JEM 2010 FasTem analytical microscope equipped with a GIF (Gatan image filter) and Z-contrast annular detectors. High-resolution images were obtained at the optimum focus condition (Sherzer condition), and a defocus condition was used to improve the contrast of the nanotube walls. The chemical composition of the nanotubes was analyzed through the GIF detector, acquiring an EELS spectrum in diffraction mode.

Crystal Builder, Force-Field, and HRTEM modules of the Cerius² simulation software of Accelrys were used to simulate the crystalline nanotube structures and corresponding HREM images.²⁴ The crystalline models were generated using the Crystal Builder module based on the MoS_2 and C atomic positions, symmetry conditions, and lattice parameters. The most stable models for $\text{MoS}_2\text{-C}$ nanotubes were obtained using a force field method.^{25,26} The corresponding simulated HREM images for these models were obtained using the SimulaTEM software²⁹ based on the multislice method.

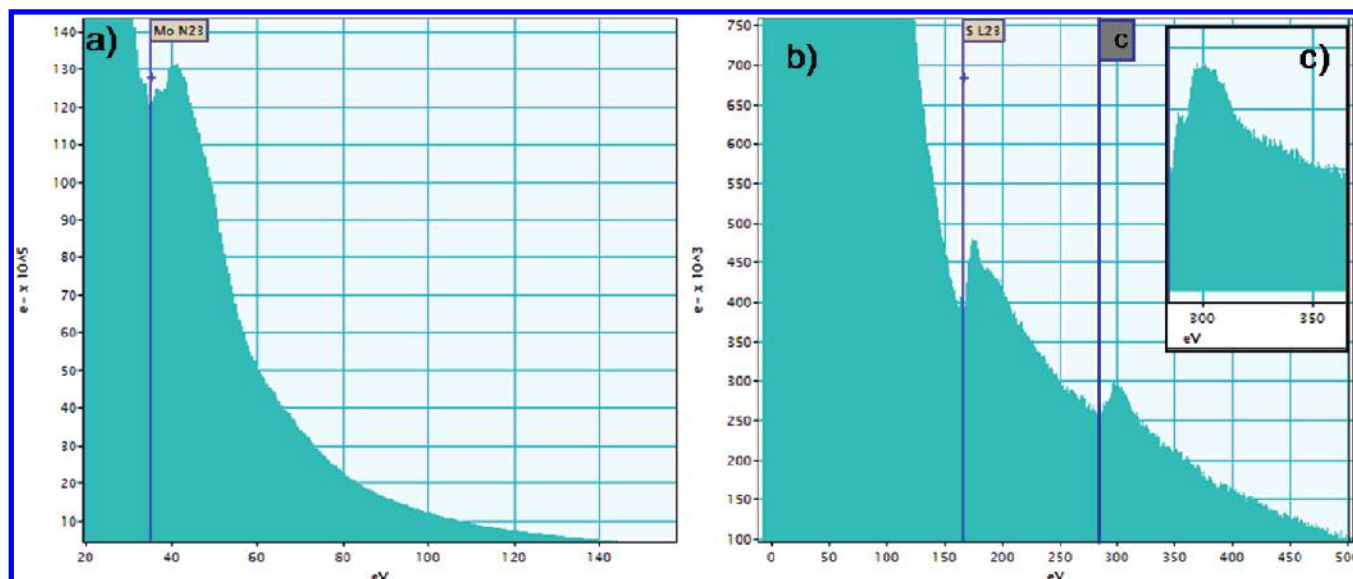


Figure 5. EELS spectrum obtained from a single tube in diffraction mode: (a) magnification of the spectrum at the Mo edge (35 eV), (b) zoomed spectrum at the sulfur and carbon edges (165 and 284 eV, respectively), and (c) magnified part at the carbon zone showing a typical graphite spectrum.

A theoretical analysis of carbon-intercalating effects in the MoS₂ structure was initially made for a periodic structure using the CASTEP software.³⁰ This module is based on a wave plane method using the gradient-corrected approximation (GGA) and the Perdew–Burke–Ernzerhof functional.³¹ To determine the density of states and changes in electrostatic potential in carbon-intercalated MoS₂, a geometry optimization procedure was considered with convergence tolerance steps of 5×10^{-6} eV/atom, a self-consistent field tolerance of 5×10^{-7} eV/atom for each single-point energy calculation, and a $9 \times 9 \times 2$ *k*-point set.

Results and Discussion

Layered compounds such as MoS₂ have a good hosting capacity because of their intercalating spaces.³² The intercalation process is associated with the weakening of the van der Waals forces between the metal dichalcogenide layers.³³ In the present work, the graphitization process through the pyrolysis of propylene gas generated the intercalation of carbon sheets between the layers of MoS₂ host nanotubes. Through this mechanism, multiwall nanotubes of binary phase containing pieces of carbon layers intercalated between the MoS₂ walls were produced. Additionally, single-phase carbon nanotubes were formed inside the intercalated nanotubes, generating coaxial binary entities. A schematic diagram of this one-dimensional structure is shown in Figure 2.

Figure 3a shows a low-magnification TEM micrograph of the sample, illustrating the presence of several nanotubes of different sizes. The contrast differences at the edges of the tubes are evident in the micrograph. The length of the tubes varied from 500 to 1000 nm with a mean internal diameter of around 30 nm. The tubular structures observed in this particular sample are exceptionally straight compared to the elliptical cage linked chain structures, generally observed in MoS₂ nanotubes produced by the template mechanism.¹⁰ Such a difference in morphology might be due to the difference in the mechanical properties between the nanostructures. In contrast to the binary phase, the pure MoS₂ nanotubes were more flexible (revealing folded structures in SEM micrographs). The HREM contrast observed at the external layers of the tubes (Figure 3b) is very similar to the usual contrast of pure MoS₂ nanotube walls and

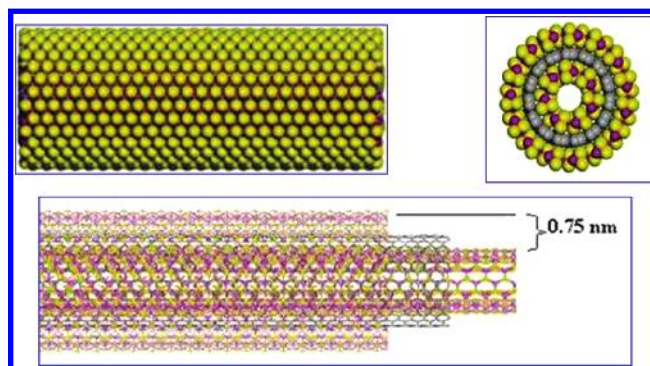


Figure 6. Lateral and sectional views (right corner and bottom) of a stable configuration of intercalated graphite slabs with a stoichiometric MoS₂ nanotube, generated using the molecular dynamics simulation process. The distance between the MoS₂ layers after the energy minimization procedure is 7.5 Å.

alkali-metal-intercalated MoS₂ layers.³³ The average interatomic layer distances were obtained using AnalySIS software from Soft Imaging System,³⁴ taking measurements at 10 different locations in 10 different tubes. Our estimated average interlayer distance for the external layers was 7.4 ± 0.05 Å in comparison with the 6.25 Å value reported for pure MoS₂ nanotubes.¹⁰ The disordered features surrounding the nanotubes shown in Figure 3a might be the fragments of aluminum hydroxide remaining on them after washing, during the template separation process. In Figure 4, typical HREM images of pure MoS₂ and graphite-incorporated MoS₂ nanotubes are presented. The contrast difference between the two samples is clear from the images. A closer view of the graphite-incorporated MoS₂ nanotubes reveals zones with highly defective graphitic layers at the inner surface of the main tube (Figure 4c). The average interplanar spacing estimated for this region was about 3.5 ± 0.05 Å, which is higher than the interplanar spacing of common (0002) graphite planes. However, such an expansion of interplanar distance has been observed previously in disordered graphite sheets.^{36,37}

The hexagonal contrasts of basal planes observed at the central region of the tubes (Figure 4b) are the Moiré fringes produced by the carbon layers sandwiched between the MoS₂ layers and the carbon layers of the inner tube. The average lattice spacing measured from these fringes was on the order of 0.337

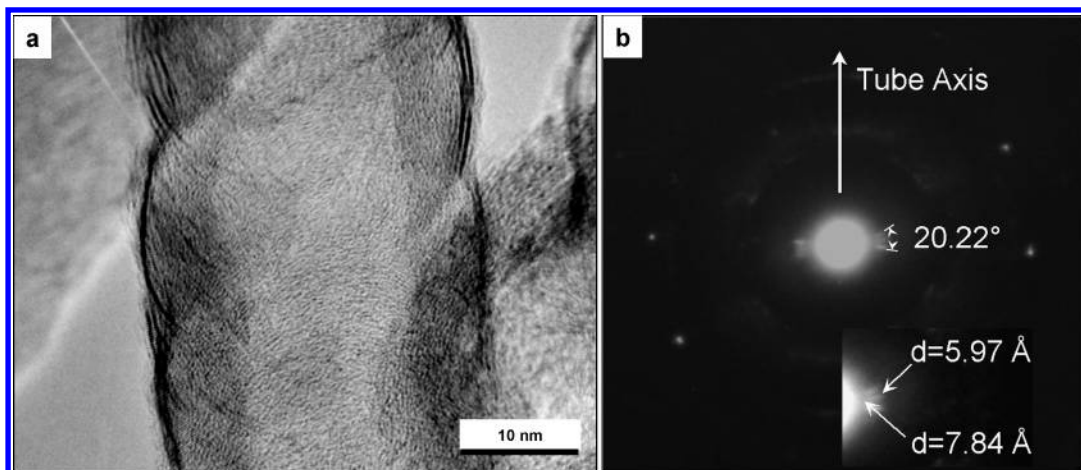


Figure 7. Local analysis of a twisted MoS₂-C nanotube: (a) TEM micrograph and (b) NBEDP obtained at 40 cm of camera length.

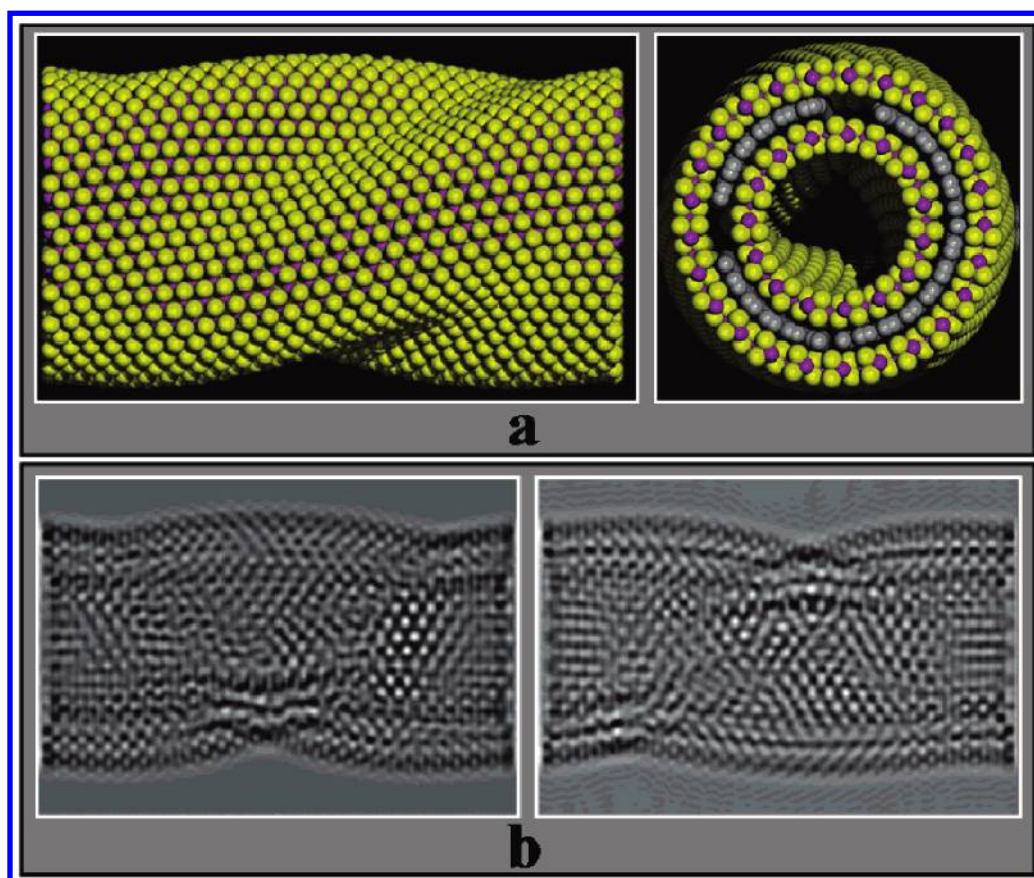


Figure 8. Stable configuration of a carbon-intercalated MoS₂ nanotube produced by sandwiching graphite sheet fragments between the MoS₂ layers: (a) perpendicular and parallel views of the theoretical model and (b) simulated HRTEM images for two different orientations of the model.

nm. This lattice spacing value is due to interference produced by two distinct lattices which has also been observed even in pure MoS₂ nanotubes with a twisted morphology.¹⁰

The presence of graphite inside the main tube is further verified by recording the EELS spectra of the samples in diffraction mode, which apart from the chemical composition reveal the nature of the chemical bonding of the atoms with their neighbors. The EELS spectrum obtained from a single tube reveals the characteristic peaks of Mo at 35 eV (N-edge) and S at 165 eV (L-edge) and the characteristic profile of graphite carbon at 284 eV (K-edge) (Figure 5). The carbon K-edge profile (Figure 5c) does not present additional fine structure associated with any Mo_xC_y compound. The effect of carbon intercalation

with MoS₂ in EELS spectra has been studied by Berhault and co-workers,³⁷ who additionally found a fine structure in the carbon K-edge profile corresponding to a Mo₂C phase at 295 eV associated with a σ^* state. However, the EELS spectra obtained from our MoS₂-C tubes revealed only the 284 eV (K-edge) peak of carbon graphite without any additional features, indicating the absence of any Mo_xC_y compound formation.

To understand the formation and growth mechanism of these intercalated nanotubes, a sequence of graphite layers intercalated with stoichiometric concentric MoS₂ sheets were simulated by molecular dynamics based on geometry manipulation and optimization.¹⁰ Once the structure was generated, the potential

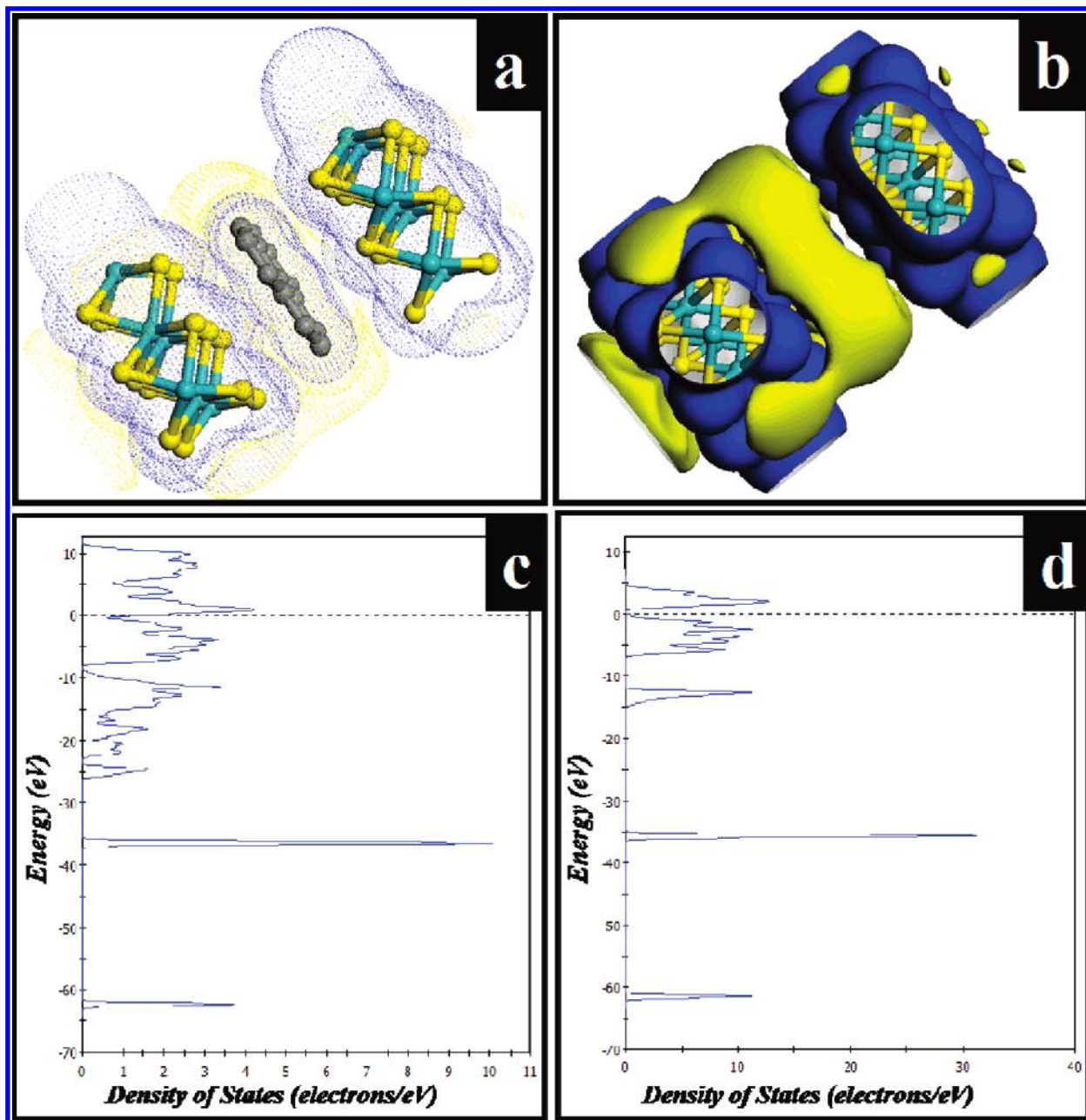


Figure 9. Quantum mechanical analysis of the (a) charge density distribution in MoS₂ + C, (b) electrostatic potential isosurface for MoS₂ + C, (c, d) and DOS spectrum for (c) MoS₂ + C and (d) MoS₂. Green, yellow, and gray balls correspond to Mo, S, and C atoms, while the yellow and blue surfaces correspond to negative and positive polarities, respectively.

energy was minimized using the Cerius² molecular simulation software of Accelrys. The coaxial nanotube was then relaxed by Cerius² using the Smart Minimizer method and UFF-VLBOND potential. In Figure 6, the optimized simulated structure consisting of a graphite layer between two MoS₂ layers is presented. We can see the distance between two MoS₂ layers is about 7.5 Å, which is very close to the average lattice spacing obtained from our HREM images and nanobeam electron diffraction patterns (NBEDPs) (Figure 7b).

However, our experimentally obtained nanotubes are neither perfect (see Figure 4) nor of homogeneous morphology (see Figure 7a). The local contrast at the nanotube boundaries presented in Figure 7a shows several waistlines with an interlayer distance of about 7.4 Å which corresponds to MoS₂ layers intercalated with carbon. Also a lighter contrast zone inside the main tube that corresponds to the graphite lattice fringes of the coaxial multiwall carbon nanotubes is visible in

the figure. The contrast and morphology of the bent walls correspond to the typical twisted hollow cylindrical structure as supported by our electron diffraction results.

NBEDPs of the twisted structures were taken at 40 cm of camera length in a JEOL 2010 microscope. The helical nature of the coaxial MoS₂-C nanotubes is clearly evident in the (0002) reflection (Figure 7b) of the sample. The knob features of the (0002) reflection reveal internal structure with two linear spots symmetric with respect to the equatorial line. The appearance of such split reflections in NBEDPs is well-known for chiral nanotubes. In the present case, the appearance of split reflections in NBEDPs is the consequence of the chiral behavior of our coaxial multiwall nanotubes of the binary irregular phase. As the intercalated graphite did not fill the MoS₂ slabs completely, several mechanical defects were generated in the intercalation process, causing a change in the curvature of the one-dimensional host structure. The appearance of a line

structure in the (0002) reflection in NBEDPs of multishell chiral MoS₂ nanotubes is demonstrated by L. Margulies and co-workers.³⁸ Nevertheless, in the particular case of a binary multiwall nanotube, the interpretation of the NBEDP is not easy. To index the diffraction pattern, internal and external diameters of each symmetric pair of linear spots along the equatorial reflection are measured. The *d* spacings measured through internal and external diameters were 7.84 ± 0.05 and 5.97 ± 0.05 Å, respectively, while the angle between the linear spots was $20.2 \pm 0.05^\circ$.

To explain the chirality in our MoS₂–C binary nanostructures, several model structures were constructed by introducing graphite sheets into the walls of a MoS₂ nanotube host. We introduced graphite sheets into the layers of a MoS₂ nanotube to induce a mechanical stress in it. Generation of positive and negative curvatures due to induction of topological defects in chiral MoS₂ nanotubes was demonstrated theoretically by Seifert and co-workers³⁹ recently. On relaxation, our model structures revealed torsions on its one-dimensional configuration. Parallel and perpendicular views of the lowest energy configuration along with a couple of simulated HREM images³⁰ for a structure formed by introducing a discontinuous graphite sheet between two MoS₂ layers are shown in Figure 8. The configuration is obtained when graphite fragments are internally distributed in the MoS₂ nanotube sheets, generating mechanical stress in the regions where there is no carbon. The contrasts observed in the simulated HREM images are in good agreement with the contrasts obtained in the experimental micrographs (Figure 8b). Particularly, the contrast at the nanotube borders argues well for the experimental observation of varied interlayer distances between (0002) planes in our system.

To explore the possible electronic changes that occurred by the intercalation process in our MoS₂ nanostructures, we performed quantum mechanical calculations for a system consisting of a graphite layer between two MoS₂ layers. The calculated charge density and electrostatic potential distribution for the system are shown in parts a and b, respectively, of Figure 9. In addition, the densities of states (DOS) for MoS₂+C and MoS₂ layered materials are plotted in parts c and d, respectively, of Figure 9. From the charge density and electrostatic potential distributions, it is clear how the presence of the graphite layer generates a high concentration of electrons between the MoS₂ layers. Furthermore, comparing the calculated DOS results for MoS₂+C and MoS₂ (Figure 9c,d), it is possible to observe that while the main features in the DOS spectrum for MoS₂ remained unchanged, the number of electrons in the occupied bands increased drastically on incorporation of the graphite sheet between MoS₂ layers. In fact, the presence the carbon layer between MoS₂ layers changes the perturbation condition and facilitates electrons to move from one MoS₂ layer to the other. Furthermore, the introduction of excess charge into the MoS₂ layers can lead to mechanical deformation as observed in the case of carbon nanotubes.⁴⁰

Our quantum mechanical calculations indicate that some energetically stable structures can be formed by putting graphite fragments between MoS₂ slabs. However, the incorporation of carbon layers causes a drastic change in the electronic properties of MoS₂, which may affect its catalytic properties. A further study is needed to explore the catalytic behavior of this MoS₂–C binary-phase nanostructure.

Conclusions

We could synthesize graphite-incorporated MoS₂ tubular nanostructures. These micrometer long nanostructures consist

of alternating carbon and MoS₂ layers at the outer walls and multiwall carbon nanotubes inside. While the van der Waals interlayer interaction allows the intercalation of carbon with MoS₂ layers, the interlayer spacing of MoS₂ increases due to incorporation of carbon sheets between them. Incorporation of a fragmented carbon sheet inside MoS₂ layers introduces mechanical strain, induces deformation in the linear tubular structure of MoS₂, and originates chiral properties in them. Our theoretical calculations predicted the formation of stable carbon-intercalated MoS₂ tubular structures with a drastic change in their electronic properties which may favor their catalytic and optoelectronic applications. However, a detailed theoretical analysis is needed to explore the possible applications of these materials. The use of MoS₂ nanotubes as a template for the synthesis of new binary-phase tubular structures is demonstrated.

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