

One-dimensional Arsenic Allotropes: Polymerization of Yellow Arsenic Inside Single-wall Carbon Nanotubes

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Abstract: The pnictogen nanomaterials, including phosphorene and arsenene, display remarkable electronic and chemical properties. Yet, the structural diversity that these main group elements are capable of is still poorly explored. Here we fill single-wall carbon nanotubes with elemental arsenic from the vapor phase. Using electron microscopy, we find chains of highly reactive As₄ molecules as well as two new one-dimensional allotropes of arsenic: a single-stranded zig-zag chain and a double-stranded zig-zag ladder. These linear structures are important intermediates between the gas-phase clusters of arsenic and the extended sheets of arsenene. Raman spectroscopy indicates weak electronic interaction between the arsenic and the nanotubes which implies that the formation of the new allotropes is driven primarily by the geometry of the confinement. The relative stabilities of the new arsenic structures are estimated computationally. Band-gap calculations predict that the insulating As₄ chains become semiconducting, once converted to the zig-zag ladder, and form a fully metallic allotrope of arsenic as the zig-zag chain.

Despite its infamous toxicity, arsenic is considered to be an essential element and up to 25 µg per day are thought to be required for human health.^[1] In the electronics industry, arsenic is found in a wide range of semiconducting materials^[2] and it is used in car batteries to strengthen the lead components.^[3] The recent discovery of phosphorene,^[4] a single, two-dimensional sheet of black phosphorus, has sparked tremendous interest in the nanomaterials of the pnictogens including arsenic.^[5] In fact, arsenene, the single-layer arsenic equivalent to graphene, has been predicted to display a large bandgap^[6] which, combined with a low thermal conductivity, makes it a highly desirable material for thermoelectric applications.^[7] A large number of other electronic, optoelectronic, spintronic and sensing applications are also envisaged.^[5a] The first experimental steps towards the isolation of

arsenene have recently been taken including the plasma-assisted deposition of arsenic on an InAs substrate^[8] as well as aqueous shear exfoliation.^[9]

Gray arsenic (α-As) is the most stable allotrope at ambient conditions and it consists of layers of puckered hexagons in a rhombohedral crystal structure.^[10] Black arsenic (β-As) is metastable with an orthorhombic layered crystal structure similar to that of black phosphorus.^[11] Amorphous arsenic, with a wide range of different densities, has also been isolated.^[10, 12] Finally, yellow arsenic (γ-As) consists of tetrahedral As₄ molecules, analogous to white phosphorus (P₄).^[13] However, due to its extreme sensitivity to light and X-rays, which trigger the conversion to gray arsenic, no crystallographic data has been collected so far for the bulk material.^[14] In addition to the bulk allotropes, clusters in size up to As₅ have been found experimentally.^[15] Nanostructures that may exist between these small clusters and the two-dimensional sheets of arsenene have so far not been identified.

Carbon nanotubes have recently been used as molds to prepare new one-dimensional allotropes of a range of elements including carbon in the forms of carbyne,^[16] nano-diamond^[17] and graphene nanoribbons,^[18] iodine,^[19] sulphur,^[20] selenium^[21] and phosphorus.^[22] In the case of phosphorus, fibrous chains with alternating P₈ and P₂ units^[22a] as well as single-stranded zig-zag chains have been identified so far, depending on the tube diameter.^[22b] Furthermore, confinement within carbon nanotubes stabilizes the highly reactive P₄ molecules against reaction with atmospheric oxygen.^[22b] The stabilization of individual As₄ molecules has been achieved by intercalation between polymeric chains,^[23] using a copper ligand^[24] and supramolecular tetrahedral cages,^[25] as well as in the confinement environments provided by activated carbon.^[26]

Herein, we investigate the filling of single-wall carbon nanotubes (SWCNTs) with arsenic from the vapor phase in order to achieve the stabilization of As₄ molecules and to search for new one-dimensional arsenic structures. In addition to the experimental work, density functional theory (DFT) is used to estimate the relative stabilities and electronic properties of the various arsenic nanostructures.

The successful filling of SWCNTs with arsenic (As@SWCNT) was achieved by exposing tip-opened HiPco (high-pressure carbon monoxide) SWCNTs, with a diameter range of about 0.8 to 1.2 nm, to arsenic vapor at 615°C in an evacuated and sealed quartz-glass ampoule. Upon subsequent exposure to light and air, the excess arsenic is expected to either oxidize to give arsenic(III) oxide or to convert to gray arsenic. To remove the external arsenic materials, the crude As@SWCNT product was treated with dilute nitric acid, followed by washing with water. Full details of the filling and purification procedures are given in the Experimental section.

As₄ molecules remained encapsulated within the SWCNTs and were successfully imaged using high-resolution transmission

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electron microscopy (HRTEM), as shown in Figure 1(a-d). The 'beads' of As_4 molecules are spaced 0.53 ± 0.06 nm apart from one another. X-ray photoelectron spectroscopy (XPS) confirmed the presence of elemental arsenic. The As@SWCNT sample was found to contain 20 wt% As(0) , 5 wt% As(III) , 69 wt% C and 6 wt% O (see Figure 1(e)). It is proposed that elemental arsenic closest to the ends of the SWCNTs is oxidized by exposure to atmospheric oxygen. The oxidized arsenic then acts as a 'cork' to the SWCNTs preventing further oxidation of the confined material. According to powder X-ray diffraction, only 1.2 wt% of bulk gray arsenic is present in the sample after the final purification step which suggests that around 94% of the elemental arsenic is encapsulated within the SWCNTs (see Figure S1). A completely filled SWCNT with a 0.9 nm diameter is predicted to contain 30 wt% As, considering the available space of the SWCNT cavity and the van der Waals volume of As_4 .

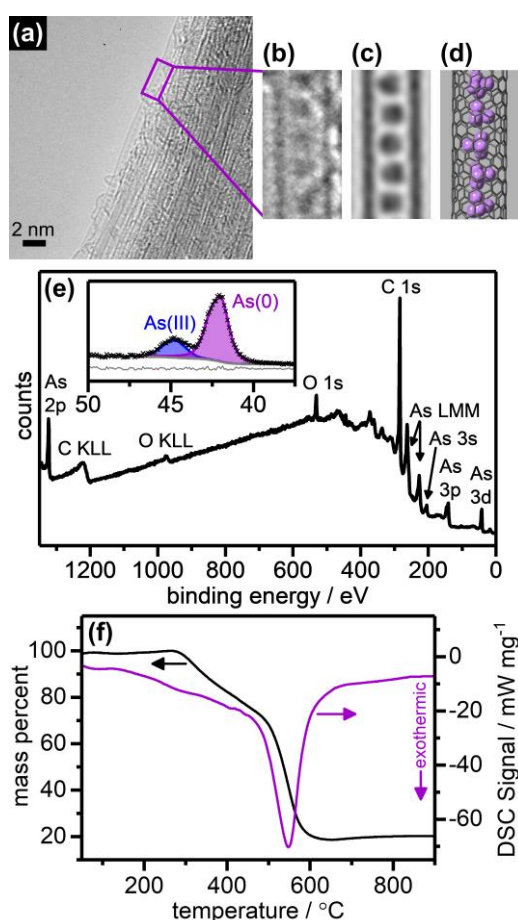


Figure 1. Successful filling of SWCNTs with elemental arsenic. (a) HRTEM image of As_4 molecules contained within a SWCNT. (b) Zoom of region highlighted in (a). (c) Corresponding HRTEM simulation using the structure shown in (d). Panels (b-d) are shown on the same scale. (e) XPS analysis of As@SWCNT with a high-resolution spectrum of the As 3d region shown in the inset. (f) Thermogravimetric analysis / differential scanning calorimetry (TGA/DSC) of As@SWCNT in air.

The TGA/DSC analysis of As@SWCNT in air shows that the exothermic oxidation of the elemental arsenic is signaled by a

small mass increase that starts at around 130°C (see Figure 1(f)). The mass loss in the $300 - 500^\circ\text{C}$ range is then due to the sublimation of arsenic oxide. This process is followed by the exothermic burning of the carbon at around 550°C . Analysis of this feature shows that -22.8 J are released per milligram of sample. Since graphitic carbon has an enthalpy of combustion^[27] of -33.2 J mg^{-1} it follows that this sample is comprised of 70 wt% carbon which is in very good agreement with the XPS analysis of the sample. Figure S2 shows that elemental arsenic can be released from As@SWCNT upon thermal annealing under high-vacuum conditions illustrating the reversibility of the filling process.

In addition to the encapsulated As_4 molecules, novel one-dimensional (1D) arsenic structures were observed inside the SWCNTs: either single-stranded zig-zag chains or double-stranded zig-zag ladders, as shown in Figure 2.

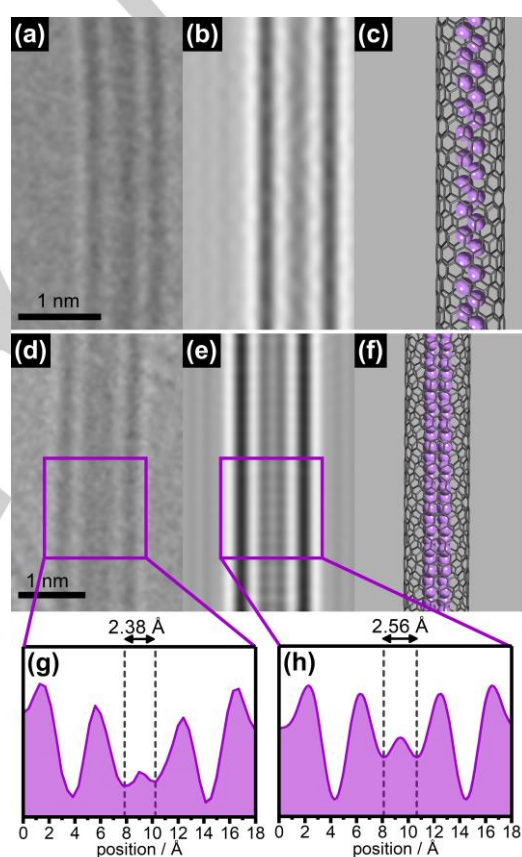


Figure 2. New one-dimensional arsenic allotropes inside SWCNTs. (a) HRTEM image, (b) HRTEM simulation and (c) structure of a SWCNT filled with a single zig-zag chain. (d) HRTEM image, (e) HRTEM simulation and (f) structure of a SWCNT filled with a zig-zag ladder. Panels (a-c) and (d-f) are shown on the same scale, respectively. (g,h) Line profiles taken across the highlighted areas in (d) and (e).

The HRTEM simulations shown in Figure 2(b,e) were generated by using filling materials rotationally-averaged about the axis of the SWCNTs. Stills of the structures can be seen in Figures S3 and S4, respectively, which show highly defined features that are not observed in any of the collected HRTEM images, supporting the interpretation that the arsenic chains spin dynamically about

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the nanotube axis. Similar dynamic rotations of filling materials have previously been observed for graphene nanoribbons.^[18] The zig-zag ladder displays a faint gap between the two strands in both the experimental as well as calculated HRTEM images (see Figure 2(g,h)). The average width of this gap was measured as 2.38 Å which closely matches the value obtained from the simulation. The single zig-zag chain on the other hand does not show such a feature and is defined by a narrow band in the center of the host SWCNTs.

A statistical analysis shows that the occurrence of the various 1D arsenic nanostructures is a function of the SWCNT diameter (see Figure 3). The most frequently observed structures are zig-zag ladders in the diameter range typical for HiPco SWCNTs between 0.8 and 1.2 nm. Single zig-zag chains and individual As₄ tetrahedra were most common in the 0.8 – 0.9 and 0.7 – 0.8 nm ranges, respectively. It is interesting to note that empty tubes are observed most frequently for diameters above 1.1 nm. This finding suggests that the arsenic structures must be confined in a narrow enclosure to prevent leakage and oxidation. The filling yield calculated from the data in Figure 3 is 73% which is consistent with estimates from the XPS data. Several more HRTEM images of the As@SWCNT nanostructures are shown in Figure S7.

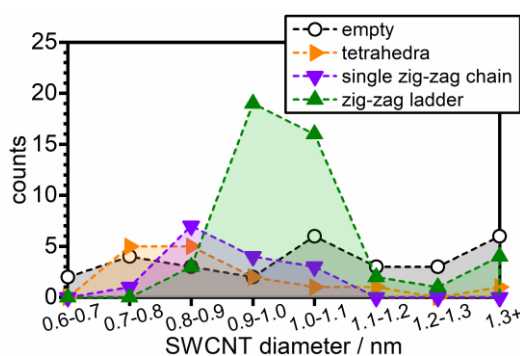


Figure 3. Occurrence of the various 1D arsenic nanostructures observed in HRTEM as a function of the SWCNT diameter.

To gain information about the relative stabilities of the various 1D arsenic nanostructures, DFT calculations were conducted using the structures shown in Figure 4(a). These types of structures were previously identified in work on 1D phosphorus structures^[22b]; chains of As₈ clusters which have been proposed elsewhere^[28] were also considered. The confinement provided by the SWCNTs was described with an empirical cylindrical potential as outlined in more detail in the Supporting Information. The resulting DFT energies of these structures are shown as a function of the nanotube diameter in Figure 4(b). According to DFT, the single zig-zag chain is most stable at small diameters whereas the zig-zag ladder becomes increasingly more stable with increasing nanotube diameters, in agreement with the experimental observations. The individual As₄ molecules are never the most stable structures. However, experimentally they are expected to enter the SWCNTs from the gas phase and may then persist in a metastable state.

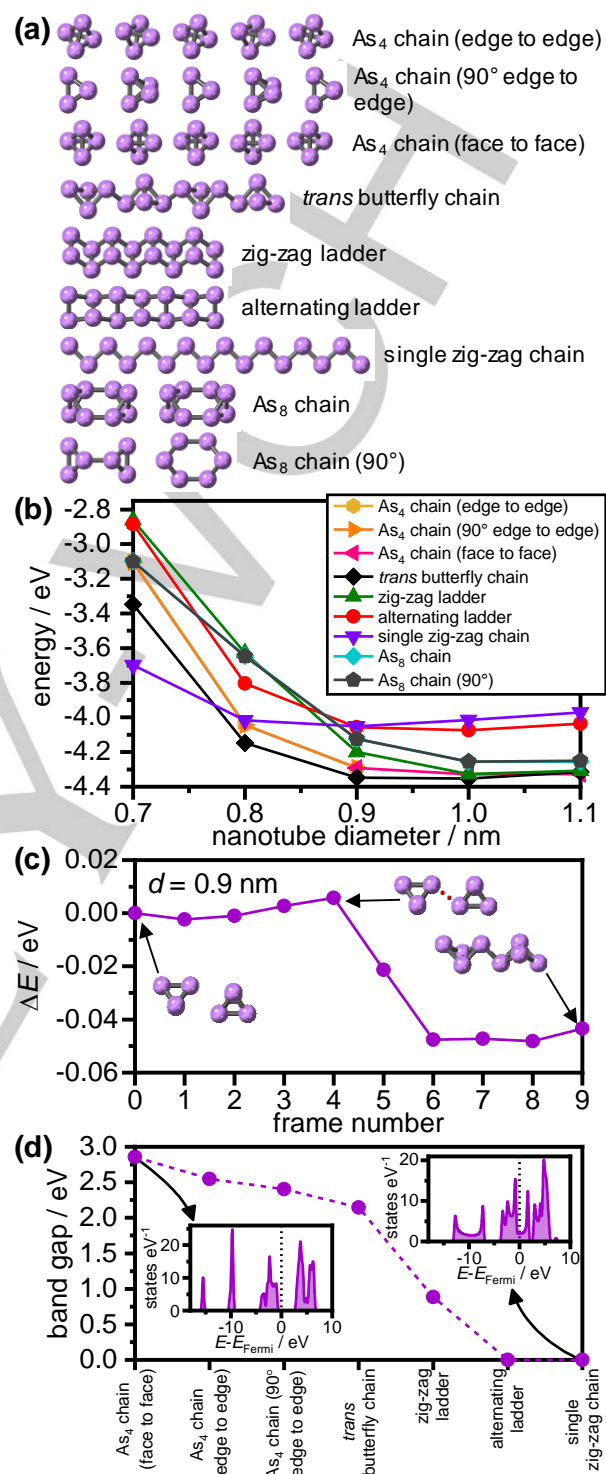


Figure 4. DFT analysis of one-dimensional arsenic structures within a nanotube. (a) Geometry-optimized arsenic structures. (b) Energies of the structures shown in (a) as a function of the nanotube diameter and defined as the per-atom binding energy relative to an isolated arsenic atom plus the confining energy. (c) Energy differences relative to the starting structure along a computationally optimized reaction pathway from face-oriented As₄ to the *trans* butterfly chain calculated using climbing-image nudged-elastic band calculations (cNEB) with a nanotube diameter of 0.9 nm. (d) Electronic band gaps of the confined arsenic structures. The insets show the density-of-states for the face-to-face As₄ chain and the single zig-zag chain, respectively.

No Raman features were observed from the encapsulated As₄ molecules, which are expected to display an intense Raman feature at around 340 cm⁻¹ according to gas-phase measurements^[29] (see Figure S8). This absence suggests that the Raman lasers may induce the conversion of As₄ molecules to the two types of linear chains, analogously to the conversion of yellow to gray arsenic triggered by light.^[14] Overall, the Raman spectra of empty and As@SWCNT recorded with three different excitation wavelengths are very similar, suggesting weak electronic interactions between SWCNTs and the arsenic filling material.^[30] Therefore, the new arsenic nanostructures are stabilized primarily by the geometry of the cylindrical confinement.

Although the *trans* butterfly chain is predicted to be the most stable structure over a range of diameters, it has not been possible to find any experimental evidence for this structure in HRTEM. The simulated HRTEM images of the *trans* butterfly chain are shown in Figures S5 and S6. Figure 4(c) shows that the reaction pathway between individual As₄ molecules and the *trans* butterfly chain has a very small activation energy which enables rapid interconversion between these two structures. In contrast to the various chain structures, the individual As₄ molecules are expected to be stabilized due to entropic factors, which are not captured in the current DFT calculations, since the As₄ molecules are free to rotate about three axes. It seems therefore possible that the *trans* butterfly chain has remained elusive so far due to a rapid and entropy-driven conversion to individual As₄ molecules.

DFT calculations of the electronic band gaps of the 1D arsenic structures predict an interesting trend for the experimentally observed 1D allotropes (see Figure 4(d)): the individual As₄ molecules form insulating chains which are converted to semiconducting (zig-zag ladder) or fully metallic (zig-zag chain) structures. The electronic densities of states of all 1D structures are shown in Fig. S9.

In summary, SWCNTs have been filled with up to 20 wt% elemental arsenic. Individual As₄ molecules have been imaged for the first time with HRTEM, illustrating that these extraordinarily reactive molecules can be stabilized at room temperature within the 1D confinement of SWCNTs. In principle, As@SWCNT offer the potential to use As₄ molecules as a reagent by safely releasing them into a reaction mixture; the empty SWCNTs can be easily removed by subsequent filtration. Furthermore, two new 1D allotropes of arsenic have been discovered inside the SWCNTs including the single-stranded zig-zag chain and the double-stranded zig-zag ladder. As@SWCNT provides an excellent model system for studying polymerization equilibria inside 1D confinements. Structurally speaking, the two new linear chains provide an important missing link between small arsenic clusters and the 2D sheets of gray and black arsenic. Further investigations of the electronic and chemical properties of the new 1D allotropes are warranted. In particular, analogous synthesis in insulating confining structures, such as boron nitride single-wall nanotubes, will allow the predictions of the diverse electronic properties of the new 1D arsenic allotropes to be tested and possibly even exploited.

Experimental Section

HipCo single-wall carbon nanotubes (SWCNTs) were purchased from Nanointegris Inc. in ethanol-wet cake form. These were dried at 100°C and 10⁻² mbar for 4 days, and then tip-opened by heating to 400°C in air.^[22b] 20 mg SWCNTs and 20 mg gray arsenic were ground for 5 minutes to create a homogenous mixture. The mixture was then placed in a 200 mm long quartz ampoule which was pumped down to 10⁻⁶ mbar, heated to 200°C at 7°C min⁻¹ and held for 2 hours. The ampoule was sealed under dynamic vacuum, heated in a tube furnace to 615°C at 10°C min⁻¹ and held for 12 hours with the sample end in the center of the furnace. The ampoule was reheated three more times, each time rotating the ampoule by 180° to sublime the arsenic along the ampoule. The fourth and last heat treatment sublimed the arsenic onto the SWCNTs located at the cool end of the ampoule. After recovering the sample from the ampoule, excess arsenic was removed by stirring in 100 mL 0.5 M nitric acid solution for 4 hours followed by filtration and washing with water. Full details of the sample characterizations and DFT calculations are given in the Supporting Information.

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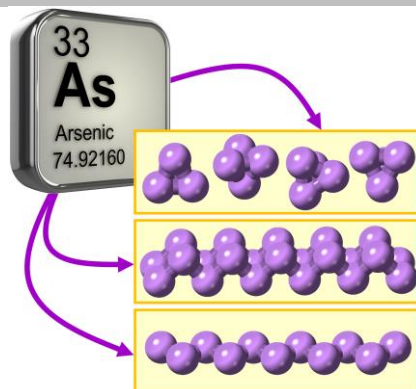
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