Encapsulation and Polymerization of White Phosphorus Inside Single-Wall Carbon Nanotubes

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Abstract: Elemental phosphorus displays an impressive number of allotropes with highly diverse chemical and physical properties. White phosphorus has now been filled into single-wall carbon nanotubes (SWCNTs) from the liquid and thereby stabilized against the highly exothermic reaction with atmospheric oxygen. The encapsulated tetraphosphorus molecules were visualized with transmission electron microscopy, but found to convert readily into chain structures inside the SWCNT “nanoreactors”. The energies of the possible chain structures were determined computationally, highlighting a delicate balance between the extent of polymerization and the SWCNT diameter. Experimentally, a single-stranded zig-zag chain of phosphorus atoms was observed, which is the lowest energy structure at small confinement diameters. These one-dimensional chains provide a glimpse into the very first steps of the transformation from white to red phosphorus.

The discovery of phosphorene, a single, two-dimensional sheet of black phosphorus,[1] has sparked a renewed interest in the highly diverse chemistry and complex structures of this important main-group element. Unlike graphene, phosphorene possesses a direct band gap that can be tuned by the number of stacked layers, and future applications in electronics and optoelectronics are therefore envisaged.[1a,b,2] Other nanostructured phosphorus allotropes are attracting considerable attention as well. Most recently, blue phosphorus has been grown on gold substrates using molecular beam epitaxial growth,[3] and a ring-shaped fibrous structure with alternating P₄ and P₃ structural units has been obtained from a chemical vapor reaction inside multi-wall carbon nanotubes.[4] Other allotropes of phosphorus include white phosphorus, which consists of tetrahedral P₄ molecules,[5] the amorphous red phosphorus,[6] Hittorf’s violet phosphorus,[7] fibrous phosphorus,[8] phosphorus nanorods,[9] and finally black phosphorus,[6a,10] which is the most stable form at ambient pressure.[11]

Apart from the current quest for new phosphorus nanomaterials, efforts have been made to stabilize P₄ molecules against the infamous spontaneous combustion with atmospheric oxygen. Recently, P₄ was successfully encapsulated within supramolecular materials,[12] which may be useful for mitigating dangerous phosphorus spills, or conversely, for controlled release of P₄ into chemical reactions or for heat generation.[13] Single-wall carbon nanotubes (SWCNTs) offer an appealing potential encapsulation environment, with an inert, light-weight, cylindrical pore well-matched to the diameter of P₄ molecules. SWCNTs have been filled with a wide range of materials,[13] molecular species can be stabilized sufficiently to allow direct electron microscopy imaging, including of simple chemical reactions.[14]

Herein, we fill SWCNTs with white phosphorus and explore the stability of the resulting structures. Along with the experimental approaches, the possible chain structures arising from phase transformations are evaluated using density functional theory (DFT).

Successful filling was achieved by stirring tip-opened CoMoCat SWCNTs[15] with average diameter of about 8.1 Å, in liquid phosphorus at 50°C under inert gas conditions, followed by vacuum sublimation of the excess solid phosphorus at room temperature. The encapsulated P₄ molecules were imaged by high-resolution transmission electron microscopy (HRTEM) (Figure 1a), showing long strings of P₄ beads. At high magnification (Figure 1b), the images are in good agreement with the simulated HRTEM image obtained from the corresponding molecular structure (Figure 1c,d). The presence of phosphorus in the SWCNT samples was also confirmed by X-ray photoelectron spectroscopy (XPS) measurements (Figure 1e); the filled SWCNT sample contains 15 at% phosphorus, 32 at% of which can be attributed to elemental phosphorus as shown in the inset of Figure 1e. This corresponds to 9.5% elemental phosphorus by weight in the sample as a whole. Prolonged exposure of the sample to air at room temperature did not change the proportion of elemental phosphorus stabilized within the SWCNTs. The oxidized phosphorus species are therefore assumed to form upon the first exposure of the sample to air; any remaining white phosphorus, either trapped between SWCNT bundles or...
The enthalpy of combustion of P₄ to P₄O₁₀ is remarkably exothermic (−2971 kJ mol⁻¹ P₄), implying that the new P₄@SWCNT hybrid may be considered to be a potentially interesting high-energy material. Previous attempts to stabilize P₄ achieved a maximum loading of 3.5 wt% P₄,[12] whereas the encapsulation within SWCNTs reported herein reached 9.5 wt% according to XPS analysis. Assuming a 100% filling yield and complete removal of phosphorus oxide by-products, up to 17 wt% could be achieved in principle, as estimated from the available space within the CoMoCat SWCNTs and the van der Waals volume of P₄.

Differential scanning calorimetry (DSC) data (Figure 1f) shows that the combustion of the encapsulated P₄ can be conducted in a controlled fashion by heating the material in air. The strongest exothermic feature is observed above 50°C, which is just above the melting point of white phosphorus at 44.1°C.[11] The two weaker exotherms at 110 and 200°C, respectively, are assigned to the combustion of P₄ that has either undergone conversion towards red phosphorus or been heavily passivated by phosphorus oxides. The exotherms above 300°C are attributed to the burning of the SWCNTs. In line with these assignments, the thermogravimetric analysis (TGA) in Figure 1f shows that the first three exotherms occur along with mass increases as the phosphorus converts to phosphorus oxide, whereas the burning of the SWCNTs to give CO₂ gas is accompanied by a mass decrease. Integration over the first three exotherms shows that the combustion of the encapsulated P₄ releases −2.77 J per milligram of sample. Considering that the combustion enthalpy of pure P₄ is −23.98 J mg⁻¹,[16] it follows that the filled SWCNT sample contains 11.6 wt% elemental phosphorus, which is in good agreement with the value of 9.5 wt% obtained from XPS.

Extensive investigation of the new nanomaterial with HRTEM showed that the encapsulated elemental phosphorus is not always present in the form of P₄ molecules. On several occasions, the P₄ molecules had undergone polymerization reactions to form chain structures. Presumably, the transformation is aided by the exposure to the electron beam, the result of previous thermal treatments, or promoted by the presence of the SWCNTs. Surprisingly, it was not possible to observe the highly Raman-active breathing mode[17] of the encapsulated P₄ molecules (Supporting Information, Figure S1). This failure may lend support to the idea that both the electron beam or the incident photons of the Raman laser may drive the polymerization of the encapsulated P₄ molecules. It is well-known that the conversion of bulk white to red phosphorus can be induced by exposure to visible light.[13]

The HRTEM image in Figure 2a shows the coexistence of P₄ molecules and linear chain structures in the fashion of a nanoscale “Morse code”. In general, the atomic structure of the chains was difficult to resolve with HRTEM. Considering the high-temperature α phase of white phosphorus is a plastic crystal with dynamic reorientations of the P₄ molecules,[18] it is likely that both the encapsulated P₄ molecules, as well as the associated chain structures, also display pronounced dynamic behavior, which makes it difficult to achieve atomic resolution with HRTEM. However, analysis of a successful image (Figure 2b) with the aid of a simulated HRTEM image is consistent with a single-stranded zig-zag chain of phosphorus atoms (Figure 2c–e). Furthermore, the line features shown in Figure 2a are consistent with the simulated HRTEM image of a rotationally averaged single-stranded zig-zag chain (Supporting Information, Figure S2). A tendency for the formation of chain structures inside SWCNTs has also been observed for other elements including iodine,[13] sulfur,[19] selenium,[14] and even carbon itself in the form of encapsulated carbonyl[13b] or chains of nanodiamonds.[10]
Insights into charge transfer processes between phosphorus and carbon nanomaterials can be obtained from Raman spectroscopy. As demonstrated in Ref.[4], the presence of phosphorus oxides leads to hole-doping and consequently to a blue-shift of the G band of multi-wall carbon nanotubes, whereas the electron-doping from the lone pairs of elemental phosphorus results in small red-shifts. Consistent with this, a SWCNT sample containing predominately oxidized phosphorus species, according to XPS analysis, showed a pronounced blue-shift of the G band of 11 cm⁻¹.[18] Depending on the excitation wavelength, the G bands of P₄-filled SWCNTs were either slightly red-shifted (−1.5 cm⁻¹) or unchanged within the error of the measurement compared to the empty SWCNTs (Supporting Information, Figure S3). This implies that the phosphorus oxides present in our samples do not significantly influence the electronic properties of the SWCNTs.

In addition to the experimental work, ab initio random structure searches (AIRSS)[19] were used to identify the possible chain structures and the most relevant structures are shown in Figure 3a. Starting from different packings of P₄ molecules, a single bond formation between neighboring P₄ molecules gives chains of “butterfly” units in which the zero-atom bridges can be either trans or cis–trans with respect to the newly formed P–P bonds. Pauling proposed that these structures are the first step in the phase transition from white to red phosphorus[20] and isolated P₄ “butterflies” have been stabilized in a number of molecular compounds.[21] Further rearrangement of the butterfly chains lead to ladder structures. The zig-zag ladder is interesting as this structural motif is found in the fibrous and Hittorf polymorphs[7a,8] as well as in the recently discovered ring-shaped phosphorus.[4] Yet, in those cases, the zig-zag ladder motifs are stabilized with additional “roof” atoms which cannot be accommodated within the confinement of SWCNTs. Finally, the single-stranded zig-zag chain can be considered to be the final state of a polymerization reaction achieved by successive deconstruction of the initial P₄ tetrahedra and it is the only structure in Figure 3a with free valencies.

Figure 3b shows the DFT energies of the various chain structures, including contributions from binding and confinement, as a function of the SWCNT diameter. Generally speaking, the energy differences between the various chain structures are quite small for a given SWCNT diameter. At
larger diameters, the free P₄ molecules are most stable. Yet, the energy difference between the free molecules and in particular the trans butterfly chain is very small. Interestingly, towards smaller SWCNT diameters, the single zig-zag chain becomes most stable.

Using nudged-elastic-band DFT calculations[31] the activation energy for the reaction from P₄ molecules to the trans butterfly chain was determined as 0.07 eV mol⁻¹ (Figure 3c). Considering that kT has a value of 0.0257 eV at room temperature, it is now understandable that confined P₄ molecules are likely to undergo transformations. Furthermore, considering the small energy differences between the various chain structures, it seems reasonable to assume that the polymerization reactions are, at least to some extent, reversible within the confinement of SWCNTs. Owing to the different space requirements of the various chain structures (Figure 3a), it is even conceivable that different extents of lateral pressures could affect the local equilibria. Considering that complicated chemical equilibria may exist between the various one-dimensional structures, it is important to stress that our TEM observations may not necessarily show the lowest energy structures for a given SWCNT diameter.

In summary, SWCNTs have been filled with P₄ molecules at filling yields of up to about 10 wt%. The encapsulated white phosphorus is stable at room temperature in air. Yet, upon heating above 50°C, the highly exothermic reaction with oxygen takes place. This small temperature window makes our new composite material well-suited for applications where controlled releases of heat are required. A tendency for the confined P₄ molecules to polymerize has been observed. According to DFT calculations, a range of possible chain structures is expected to exist, including a single zig-zag chain of phosphorus atoms, which has been observed in HRTEM. These polymerizations are thought to be the very first steps in the transformation from white to red phosphorus. Future explorations of their electronic properties and chemical interactions will be of great interest. Their encapsulation provides an exciting opportunity to isolate and study highly reactive intermediates in the phase behavior of phosphorus.

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Conflict of interest
The authors declare no conflict of interest.

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