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# On the bonding environment of phosphorus in purified doped single-walled carbon nanotubes

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ABSTRACT

In this work, phosphorous-doped single-walled carbon nanotubes have been synthesized by the thermal decomposition of trimethylphosphine using a high-vacuum chemical vapor deposition method. Furthermore, a modified density-gradient-ultracentrifugation process has been applied to carefully purify our doped material. The combined use of Raman and X-ray photoelectron spectroscopy allowed us to provide the first insight into the bonding environment of P incorporated into the carbon lattice, avoiding competing signals arising from synthesis byproducts. This study represents the first step toward the identification of the bonding configuration of P atoms when direct substitution takes place.



## 1. Introduction

Fine-tuning the electronic properties of single-walled carbon nanotubes (SWCNTs) via different functionalization paths is highly desirable for applications. The direct replacement of C atoms by heteroatoms is an ideal method, but also the one presenting the largest difficulties [1,2]. Experimentally, substitutional nitrogen doping has already been extensively explored and the bonding configurations that N atoms can have in the graphitic network of a nanotube have been studied by various methods [3,4]. In a more limited number of publications, boron has also been reported as a feasible substitutional element [5–8]. Another dopant candidate is phosphorus. Calculations have indicated that P can incorporate in the nanotube wall, taking the place of a C atom through direct substitution. It has been suggested that P incorporation allows the modulation of the transport properties of CPx-SWNTs [2,9]. Although the experimental incorporation of P in carbon materials such as diamond and fullerenes was reported more than a decade ago [10,11], the theoretical prediction of P-doped single-walled carbon nanotubes (CPx-SWNTs) has been followed only much later by experimental results using aerosol-assisted chemical vapor deposition (CVD) [12] and arc discharge [13]. Similarly to other doped SWCNTs, even in the optimal conditions, the properties of produced CPx-SWNTs depend on the specific P precursor and the catalytic method used for synthesis.

In this context, it has been reported that P and N working as co-dopants can favor the oxygen reduction in proton exchange membrane fuel cells [14]. Enhanced charge carrier spin scattering compared to pristine SWCNTs has been reported from nuclear magnetic resonance measurements [13]. Nevertheless, the field is still in its initial stages, and an understanding of the material's properties as well as the optimization of the synthesis processes is needed before CPx-SWNTs can find their way into applications. It is necessary to understand the incorporation of P atoms in the nanotube to analyze whether the overall morphology of the tubes

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is affected by the purification process, i.e. the tube diameter and the sample diameter distribution.

To address this matter, we have used for the first time a non-diluted trimethylphosphine feedstock for the synthesis of CPx-SWNTs using a high-vacuum based CVD method. We have noticed that for the specific case of CPx-SWNTs, the yield of nanotubes is reduced in comparison to previously reported CVD methods. However, the possibility to use a non-diluted precursor provides a great advantage towards understanding the bonding environments in which P bonds to the carbon atoms in the graphitic lattice as well as to the catalytic byproducts. Only indirect techniques, namely Raman spectroscopy and transport measurements, had so far been used to infer the incorporation of P in the nanotubes [9,13]. To the best of our knowledge, none of the reports on CPx-SWNTs have been able to provide direct evidence for the incorporation of P atoms in substitutional configuration in a single-walled nanotube sample nor an estimation of the bulk percentage of P heteroatoms.

In this context, the purification of CPx-SWNTs we report here has allowed analytically disentangling the role of P in the nanotubes exclusively. We have benefited from the use of a purified material to apply the full capability of X-ray photoelectron spectroscopy (XPS) to understand the bonding environments of P in a SWCNT doped sample.

## 2. Experimental

A high-vacuum (HV) CVD, was used for the thermal decomposition of trimethylphosphine ($PMe_3$) in the presence of an iron-based supported catalyst. This is the first work to report the use of this precursor and HV-CVD system to synthesize CPx-SWNTs nanotubes. This method has been used previously for the synthesis of pristine and doped SWCNTs as described in detail elsewhere [15–17]. The optimal growth temperature for CPx-SWNTs was found to be ~900 °C. The samples were purified using a modified density gradient ultracentrifugation (DGU) method [18–20] using a mild acid solution of HCl in water (30 wt.%). The metallic catalytic particles were eliminated by tip sonication in a 1% sodium deoxycholate (DOC) aqueous solution for 4 h and later ultracentrifugation for 30 min at ~150,000*g*. From the centrifugation tube, only ~70% of the supernatant was collected, since the upper ~10% is typically constituted by remaining amorphous carbon and the bottom ~20% of metallic particles. To clean the surfactant from the nanotubes, the solution was filtrated through PTFE membrane filters (Milipore, pore size 0.2 μm) and rinsed thoroughly with methanol, water and toluene. The overall morphology of the samples was inspected by scanning electron microscopy (SEM; Zeiss Supra 55 VP, 1.00 kV gun acceleration voltage) and transmission electron microscopy (TEM; FEI Tecnai F30, operating at 100 keV). A JY-Horiba HR800 Raman spectrometer with a liquid nitrogen cooled CCD detector was used for multifrequency measurements using 488, 568 and 632 nm excitation wavelengths. All data were collected in ambient conditions. XPS was used to inspect the elemental composition of the samples, with the spectra recorded using a Scienta spectrometer equipped with a MX650 monochromatic X-ray source.

## 3. Results and discussion

The optimal growth temperature was identified to be ~900 °C. However, the growth temperature is practically limited to a T 50 °C window. Out of this range the growth of nanotubes was practically voided. Based on this fact, we focused on the quality of the experiments with steps of T 10 °C. The yield was indeed slightly compromised away from 900 °C but no significant morphology changes were identified. The first remarkable result regards the possibility to obtain a buckypaper of purified doped material. The limited number of works related to the purification of either *in situ* or post synthesis doped tubes had previously highlighted this as a problem [20,21]. SEM and TEM micrographs, as well as the schematics of the purification procedure are shown in Fig. 1.

The low magnification image displays highly compact bundles of CPx-SWNTs with no visible impurities. To provide a rough estimation of the distribution of diameters in the raw and purified samples, a multifrequency resonance Raman spectroscopy inspection of the radial breathing mode (RBM) region is shown in (Fig. 2a). It is well understood that the Raman response in this region, $\omega_{RBM}$, is inversely proportional to the diameter of the tubes $d_t$. We have made use of the environmental parameters and force constant reported in Ref. [22]) for our estimation. From our measurements with the three laser lines, the highest diameter populations were found in the range between ~0.85 and ~1.4 nm (dotted vertical lines). The spectra in Fig. 2 are normalized to the maximum peak intensity for ease of comparison. However, comparing the spectra of the raw material with the purified one with the intensity normalized to the laser power (not shown here) reveals a particularly pronounced elimination

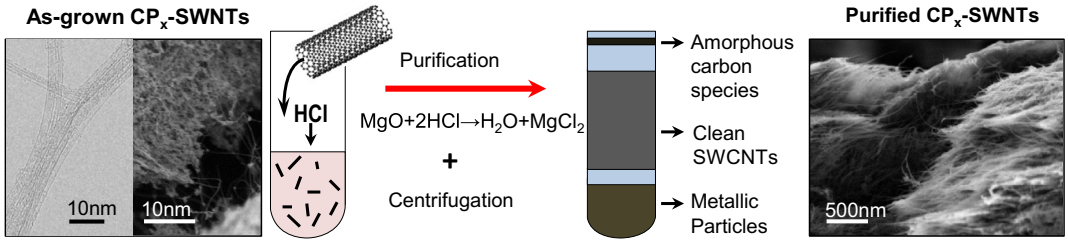


**Fig. 1 – Intermediate magnification TEM image and SEM micrograph of the sample as grown (left), schematics of the DGU purification process (middle), and SEM micrograph of the material after purification (right). (A color version of this figure can be viewed online.)**

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