Observation of nm-thin spinterface-like structures in few walled carbon nanotubes by pyrolysis of sulfur/ferrocene mixtures

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Abstract

The observation of rehybridized monolayer interfacial phases between graphene-like systems and monoatomic metal phases (spin–interfaces or spinterfaces) has recently attracted significant attention. Spinterface materials result from chemical interaction between a graphene-based material and the chosen ferromagnetic metal at the atomic level. Despite the significant amount of research, controlled observation of spinterface inside carbon nanotubes (CNTs) has been elusive. Recent works have however reported evidence of monoatomic-iron diffusion within the graphene walls of CNTs produced by pyrolysis of ferrocene/sulfur mixtures. In this work we demonstrate that formation of these interfacial nm-thin Fe-based superstructures is observable only when certain critical quantities of sulfur are pyrolyzed in a ferrocene vapour (i.e. 2.5 mg to 4 mg). For lower quantities of this precursor (0.4 mg) or with vapour flow rates higher than 11 ml min⁻¹ no spinterface-nucleation could be probed. By employing complementary TEM, HRTEM, STEM and XPS methods we suggest that the concentration of sulfur can play a critical role in allowing the uniform nucleation of spinterface structures inside CNTs.

1. Introduction

Controlling the carbon content within nanocrystalline Fe-C crystal-phases encapsulated inside carbon nanotubes (CNTs) represents a major point of interest towards nanofabrication and manipulation of carbide phases at the nanoscale level. Attempts to investigate the variation of carbon-content within iron-based crystal-phases inside CNTs during pyrolysis of ferrocene have demonstrated that a wide number of crystal compositions can be obtained within single experiments [1–10]. Together with the commonly reported Fe₃C, γ-Fe and α-Fe phases, observation of atomic structures with anomalous large periodicities have been reported [7]. In this type of studies unusual diffusion effects of carbon atoms from interstitial sites of Fe₃C crystals towards the interfacial CNT-walls have been reported in conditions of high temperatures and/or high vapour flow rates [5, 6]. Nevertheless, other works have reported formation of unusual metastable carbide phases [11, 12]. Nucleation of rehybridized monolayer interfacial phases between graphene-like systems and monoatomic metal phases (spin-interfaces or spinterfaces) has been also reported [13–15]. These structures present significant advantages when compared to molecular magnet technology [16–24]. Development of the latter has been indeed limited by several issues related to environmental disturbances (i.e. thermal agitation), nuclear magnetic moment disturbances and phonon-effects [16–22].

Spinterface materials result from a chemical interaction between the graphene surface and the chosen ferromagnetic metal atomic layer [13–15]. This novel phenomenon has been reported to be driven by charge transfer effects and re-hybridization of the π-orbitals in graphene with the d-orbitals of the metal based ferromagnetic atomic layer. It has been demonstrated that such hybridized interface can induce a spin-
dependent resistance effect and a specific interface magnetoresistance in presence of magnetic fields. Also, fabrication of spinterface-like Pd/C materials has been recently shown in carbon onions and carbon foams [25] and could play an important role in the development of electromagnetic interference shielding [26, 27].

Despite the significant amount of research carried out, up to now controlled nucleation of these novel materials inside CNTs has been elusive. Interestingly, formation of unusual atomic-features within the walls of few walled CNTs was shown in an early report from Boi et al [11] by pyrolysis of ferrocene/sulfur mixtures. Existence of an anomalous monoatomic-iron-diffusion within the defects of CNT-walls was further reported [25, 28]. However, the origin of those phenomena was not explained and/or identified further.

In an attempt to elucidate the formation mechanism of such unusual CNT-based superstructures, in this work we have employed complementary transmission electron microscopy (TEM), high resolution TEM (HRTEM), scanning transmission electron microscopy (STEM) and x-ray photoelectron spectroscopy (XPS) measurements. The use of complementary TEM modes can indeed allow for the achievement of high detail imaging, specifically for samples composed of multiple elemental components. A significant feedback on the variation of the local atomic number within different areas of the analyzed sample can be indeed given in STEM mode, thanks to the Z-contrast imaging which allows direct correlation between the local contrast and local mass-thickness (which depends on the atomic number). In this work, we demonstrate that the nucleation of such interfacial superstructures with thickness of approximately 0.9–0.4 nm is observable only when certain critical quantities of sulfur are pyrolyzed within a ferrocene vapour (i.e. 2.5 mg to 4 mg). Instead, experiments performed with lower quantities of this precursor (0.4 mg) or with higher flow rates

Figure 1. SEM micrographs in (A), (B) showing the morphological characteristics of the radial CNTs structures produced by pyrolysis of ferrocene with 4 mg of sulfur.

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(100 ml min⁻¹) did not reveal nucleation of those structural features. Our results suggest that the concentration of sulfur can play a critical role in driving the uniform nucleation of this interfacial spinterface structures.

2. Experimental

2.1. Synthesis

Few wall CNTs structures filled iron-carbide crystals were produced by sublimation and pyrolysis of ferrocene/sulfur mixtures in a CVD reactor consisting of a quartz tube of 1.5 m length, 2.5 mm thickness and a one-zone electrical furnace set at the temperature of 990 °C (see ESI for details of the ferrocene/sulfur ratio used in the experiments and schematic of experimental results). The experiments were performed by changing the quantity of sulfur from 0.4 to 4 mg. The following quantities of sulfur were used in the experiments: 0.4 mg (Ar flow rate of 100 ml min⁻¹), 2.5 mg (Ar flow rates of 11 ml min⁻¹ and 100 ml min⁻¹) and 4 mg of sulfur (Ar flow rates of 11 ml min⁻¹ and 100 ml min⁻¹). Note that experiments performed with
4 mg of sulfur and vapour flow rates of 100 ml min$^{-1}$ did not reveal nucleation of CNTs structures, instead only carbon onions (CNOs) could be detected. This latter result may be attributable to disappearance of viscous boundary layer features in high flow rates conditions. The temperature of the reactor was approximately 990°C for all the experiments. The deposition substrates consisted of 1) rough quartz surfaces produced with a diamond wheel following the method in reference [11]) smooth Si/SiO$_2$ substrates with
thickness of approximately 1 mm, in analogy to those used in reference [12]. Note that experiments performed with rough surfaces revealed higher CNTs-filling rates and a continuous spinterface nucleation within the CNT-walls in proximity of the inner filled capillary of the CNTs. The obtained samples were then cooled to room temperature by removing the furnace along a rail system.

2.2. Characterization

Characterization was performed with the use of scanning electron microscopy, transmission electron microscopy (TEM), high resolution TEM (HRTEM), x-ray diffraction (XRD) and x-ray photoelectron spectroscopy (XPS) with the following instruments: a 200 kV American FEI Tecnai G2F20 transmission electron microscope (TEM), an JSM-7500F 5–20 kV scanning electron microscope and an Escalab 250Xi (XPS). Raman Spectroscopy were collected in a custom-built Raman system using a triple grating monochromator (Andor Shamrock SR-303i-B, EU) with an attached EMCCD (ANDOR Newton DU970P-UVB, EU), excitation by a solid-state laser at 532 nm (RGB lasersystem, NovaPro 300 mW, Germany) and collection by a 100 ×, 0.90 NA objective (Olympus, Japan).

3. Results and discussion

The morphology of the CNTs structures obtained by pyrolysis of 4 mg of ferrocene with sulfur in conditions of viscous boundary layer created between the rough substrate surface and the Ar flow is shown in figure 1 with SEM micrographs and at an increasing level of magnification in figures 1(A), (B). Note in figure 1(B) the high detail of a CNT bundle comprised in a radial-like CNT structure. The cross-sectional bundle-like characteristics was further evidenced in scanning transmission electron microscopy (STEM) mode, as shown in figure 2(A). HRTEM analyses of a typical filled CNT structure are then shown in figures 2(B)–(D).

Interestingly, presence of unusual nm-thick metal-based interfacial regions was found within the curved graphene layers of the CNTs. As shown in figure 3 with profile analyses in HRTEM mode, the observed interfacial structure with an amorphous like morphology can not be ascribed to an individual graphitic carbon phase. Indeed, a thickness of 0.979 nm, which is much larger than the distance between two graphene layers (∼0.40 nm), could be detected. The presence of this phase is instead an indicator of additional chemical reactions within the curved CNTs walls which appear to be triggered by a critical concentration of sulfur species in the pyrolyzing ferrocene vapour. Therefore, it is possible to assume that the nucleation mechanism of these radial CNTs structures is significantly complex and can not be described on the basis of previously reported SWCNT growth model, where formation of Fe-S-Fe eutectic areas was considered to be the critical parameter towards diameter-controlled CNT nucleation [9–11]. Specifically, considering the mechanism reported in [11], three main stages could be identified: (1) the homogeneous nucleation of supersaturated Fe3C particles, in the viscous boundary layer created between the rough substrate surface and Ar flow (2) the
Figure 6. TEM and HRTEM analyses of a few walled CNT produced by pyrolysis of ferrocene with 2.5 mg of sulfur at vapour flow rates of 11 ml min$^{-1}$. Note in this case the absence of spinterface features.
formation of agglomerates of spherical particles with Fe-S-Fe rich characteristics and (3) continuously filled CNTs nucleation.

The presence of such an unusual spinterface features reported in this work, implies that the stage 3 of the aforementioned growth mechanism is strongly dependent on the concentration of sulfur within the particles nucleated in stage 2. The concentration of sulfur appears therefore to be crucial towards control of (1) defects in CNTs walls and (2) diffusion of Fe-based monoatomic species towards the defective sites within the curved graphene layers.

In an attempt to verify these assumptions, comparative TEM measurements were considered in other types of CNTs obtained from experiments performed with lower quantities of sulfur (2.5 mg) and flow rates of 11 ml min$^{-1}$ (figures 4–7) and 100 ml min$^{-1}$ (figures 7, 8). Curiously, STEM analyses of the first type of structures revealed presence of comparable features in interfacial regions of the CNTs walls. As shown in figures 4, 5 STEM and profile analyses revealed with atomic-mass contrast the presence of an nm-thin iron-rich superstructure nucleated within the CNT walls (see also ESI for XPS and Raman Spectroscopy analyses of these structures). Such an unusual interfacial region could be detected in a large fraction of the analyzed CNTs bundles. Note that CNTs without such spinterface features were also detected in the TEM grid, as shown in figure 6. This observation appears to evidence the presence of a mixed pyrolysis product in these experimental conditions (flow rates of 11 ml min$^{-1}$). Instead, no such superstructures could be detected in CNTs fabricated at flow rates of 100 ml min$^{-1}$ (figures 7–8), which instead appeared to be characterized only by a significant amount of boundary and vacancy defects in the CNT walls. Similar results were detected for CNT produced by pyrolysis of 0.4 mg of sulfur with ferrocene, as shown in figure 9 where MWCNTs structures were found. Note that this latter result has also a significant importance because implies that
certain minimum critical quantities of sulfur are necessary in order to create Fe-S-Fe areas for activation of SWCNTs nucleation. These observations clearly confirm the critical role of sulfur concentration in ferrocene/sulfur pyrolysis experiments and imply that a change in the nucleation dynamics of CNTs phases is present for when critical quantities of sulfur (2.5 mg to 4 mg) and certain vapor flow rates conditions are used (11 ml min$^{-1}$).

4. Conclusion

In conclusion, in this work we have investigated the origin, formation mechanism and experimental conditions for the fabrication of nm-thin spinterface structures within the curved graphene layers of CNTs. By employing complementary TEM, HRTEM, STEM and XPS measurements we have shown that the formation mechanism of these spinterface structure is observable only for certain quantities of sulfur which are pyrolyzed in ferrocene.
vapour. Instead, experiments performed with lower quantities of this precursor (0.4 mg) and/or higher vapour flow rates did not reveal nucleation of such features.

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