Carbon 120 (2017) 392–396

Contents lists available at ScienceDirect

Carbon

journal homepage: www.elsevier.com/locate/carbon

Letter to the editor

Temperature driven structural transitions in the graphitic-arrangement of carbon onions filled with $FePd_3$ nano crystals

A B S T R A C T

Carbon nano-onions (CNOs) are fullerene-like structures which have recently attracted a great attention for numerous applications, such as magnetic data recording, energy storage, biomedicine and others. In this work we report the observation of novel temperature-driven structural transitions in approximately spherical CNOs structures filled with $FePd_3$ nano crystals through temperature dependent X-ray diffraction analyses. The Rietveld refinement method is used to demonstrate the presence of an anomalous temperature-driven increase of the 002 interplanar distance between CNOs layers from the value of approximately 0.35 nm to the value of 0.50 nm with a consequent distortion of the graphite unit-cell parameters in the temperature range of 25 °C–400 °C. These observations are confirmed also by additional high resolution transmission electron microscopy and grain-size analyses which allow to estimate the number of CNOs layers involved in the temperature driven structural transition. Specifically we find that such unusual effect is present only for the case of $FePd_3$ filled CNOs, however no structural-transition is found for the case of other types of CNOs filled with Fe_3C measured in similar experimental conditions.

Carbon nano-onions (CNOs) are fullerene-like structures characterized by a quasi-spherical arrangement consisting of $60N^2$ (N = number of carbon layers) carbon atoms, ordered in graphitic layers with concentrical shells [1–10].

For more than a decade these structures have attracted a great attention due to their structural, physical and electronic properties [1,3–14] which include giant capacitance [15–17], tribology [18,19], high surface areas (30–500 m^2/g) [17,20–23], high thermal stability [15,17,21,22,24], high conductivity (10 S/cm^2) [17] and many others [20–31]. Applications of CNOs include magnetic data recording [5,22], electrodes [5,15,22,24], energy storage [15,24], biomedicine [25], additives for aerospace [26], miniaturised fuel cells [23]. In addition to the properties above, the great chemical stability of CNOs structures can allow the encapsulation of specific materials of interest and their protection from oxidation [5,6,22]. In this context, the encapsulation of ferromagnetic materials inside CNOs has attracted a great attention for possible applications in magnetic data recording and energy storage devices [5,6,15]. Hollow CNOs can be produced in powder-form through several approaches including arc discharge [4,22] and chemical vapour deposition (CVD) [16,26]. In addition, a recent work by Boi et al. has shown that CNOs can be grown in the form of buckypaper-like films by homogeneous nucleation of Fe_3C particles in a locally-perturbed pyrolysed ferrocene vapour with high concentration of Fe and C species [32]. Up to now CNOs have been filled with numerous types of ferromagnets, including Fe, Co, Ni, Fe_3C and $FePd_3$. The distance between each of the CNOs shells has been generally reported to be graphitic, with lattice spacings of the order of 0.34 nm (corresponding to the 002 graphitic reflections) for the case of CNOs filled with Fe_3C and 0.34–0.56 nm for the case of CNOs filled with $FePd_3$ crystals [33].

However, little is known about the structural arrangement of these nano-structures at high temperature. Previous literature works have reported temperature dependent studies of melting transitions only for the case of encapsulated Sn and Pb nanocrystals inside CNOs [6]. Instead, to the best of our knowledge, no report has shown the structural arrangement of ferromagnetically filled CNOs at high temperatures. In particular the arrangement of the CNOs graphitic layers at high temperatures has not yet been investigated.

In this work we report the observation of novel and unusual temperature-driven structural transitions in approximately spherical CNOs filled with $FePd_3$ nano crystals through temperature dependent X-ray diffraction measurements. Rietveld refinement analyses of the diffractograms demonstrate the presence of an anomalous increase of the 002 interplanar distance between CNOs layers from the value of approximately 0.35 nm to the value of 0.50 nm with a consequent distortion of the graphite unit-cell parameters from 25 °C to 400 °C. Such anomalous distorted arrangement of the CNOs structure is then found to revert to the original condition after cooling in liquid nitrogen to the temperature of 25 °C, suggesting the presence of a structural-memory effect. In addition, by performing high resolution transmission electron microscopy (HRTEM) and grain-size analyses we estimate the number of CNOs layers involved in such structural transition.

http://dx.doi.org/10.1016/j.carbon.2017.05.070
0008-6223/

Also, we find that this unusual effect is present only for the case of $FePd_3$ filled CNOs. Instead no structural-transition is found for the case CNOs filled with Fe_3C measured in similar experimental conditions. This strong difference may be associated to the graphitization mechanism-differences in presence of $FePd_3$ or Fe_3C as catalyst.

The synthesis experiments were carried out by using a CVD system composed of a quartz tube of length 1.5 m, one zone electric furnace and an Ar flow rate of 10–12 ml/min. The reactor dimensions used for the production of $FePd_3$-filled CNOs were as follows: a quartz tube with an inner diameter of 44 mm and a wall thickness of 3 mm. The temperature of pyrolysis was set to that of 990 °C. The precursors (approximately 100 mg of ferrocene and 220 mg of dichloro-cyclooctadiene palladium) were evaporated with a pre-heater at a temperature of approximately 200 °C. Instead, the Fe_3C-filled CNOs were produced with a different type of CVD reactor consisting of a quartz tube of outer diameter of 22 mm, wall thickness of 2.5 mm and length of 1.5 m. In this case only ferrocene was used (300 mg) as precursor; the pyrolysis temperature was 990 °C while the sublimation temperature was of 500 °C. In both cases the samples were cooled down until the temperature of 25 °C with a fast cooling quench-approach by removing the furnace along a rail-system.

All the temperature dependent experiments were performed with a Rigaku Smartlab X-ray diffractometer (40 kv) at the temperatures of 25 °C, 100 °C, 200 °C, 300 °C, 400 °C in vacuum values below 7 Pa (for approximately 4 hours). The sample was then cooled down by fast cooling through the use of liquid nitrogen until the temperature of 25 °C. A 200 kV American FEI Tecnai G2F20 was employed to obtain transmission electron microscopy (TEM) images. The magnetic measurements were performed with a vibrating sample magnetometer (VSM) (Quantum Design). Typical hysteresis loops showing the magnetic properties of the two types of CNOs are shown in Fig.Supp.Info.10-11 for $FePd_3$ filled CNOs and Fe_3C filled CNOs respectively. Statistical Analyses of the $FePd_3$ filled CNOs and Fe_3C filled CNOs are shown in Fig.Supp.Info.12-13 respectively.

A typical example of the morphological arrangement of the CNOs filled with $FePd_3$ crystals is shown in Fig.Supp.Info.3 with SEM micrographs. Interestingly these structures are found to be arranged in mm-scale flakes. The surface-morphology of the bucky-onions can be observed in Fig.Supp.Info.3A-D, while the cross sectional morphology can be found in Fig.Supp.Info.4. The presence of a variable shape-arrangement and thickness in the CNOs is revealed by the TEM micrographs in Fig.Supp.Info.4 (C-D). As shown in Fig.Supp.Info.4 (D) the thickness and level of crystallinity is found to vary also along the same onion-structure. The use of HRTEM was then considered for the analyses of the lattice spacings within the CNOs shells. In Fig.Supp.Info.5A a selected-region of a CNO used for the analyses is shown. Typical analyses of the lattice spacings in the outer shells of the CNO are shown in Fig.Supp.Info.5B and D, while analyses of the inner shells (in proximity of the CNO core) are shown in Fig.Supp.Info.5C. Interestingly we find that the lattice periodicities of 0.614 nm and 0.473 nm in the outer layers of the CNO (Fig.Supp.Info.5B and D) are much larger than those expected for inter-atomic graphitic distances (approximately 0.34 nm).

Note that similar lattice spacings were measured also in other as grown $FePd_3$-filled CNOs analysed by TEM and HRTEM with a variable level of crystallinity. In addition in some areas a higher quantity of turbostratic-like level of disordered arrangement in the graphite layers was found. Further confirmation of the variation of the CNO-shells interplanar distances was then sought by XRD analyses. Fig. 1 shows typical examples of the diffractograms measured in the temperature range of 25 °C–400 °C. Interestingly these analyses revealed the presence of two main diffraction peaks in the range of 14–34 2θ degrees which could be attributed to two type of 002 reflections of graphitic carbon (002 peak-1 corresponding to a lattice spacing of approximately 0.50 nm and 002 peak-2 corresponding to a lattice spacing of approximately 0.35 nm). In particular the first 002 peak is found to be located in the region between 16 and 20° 2θ while the second 002 peak is found to be located in the region between 21 and 30° 2θ.

The observation of two main 002 reflections appears to confirm the HRTEM analyses outlined above and could be therefore associated to the presence of two main sets of interplanar-distances between the graphene layers in the CNOs shells (inner and outer layer-regions of the CNOs structures respectively). Note also the presence of an unusual broad-arrangement in the 002 peak-2 which could be ascribed to the presence of strain and turbostratic disorder in the CNO-structures [34,35].

In order to confirm this interpretation, the use of the Scherrer equation was considered in order to estimate the average number of CNO-shells which exhibit large periodicities (see Fig.Supp.Info.1-2 for table showing the calculated Scherrer thickness).

Interestingly the extracted Scherrer thickness values were as follow: for the 002 peak-1: 4.38 nm, for the 002 peak-2: 1.40 nm. By dividing these Scherrer-thickness values to the extracted lattice spacings corresponding to the 002 peak-1 and 002 peak-2 the approximate number of CNOs layers associated to the diffraction

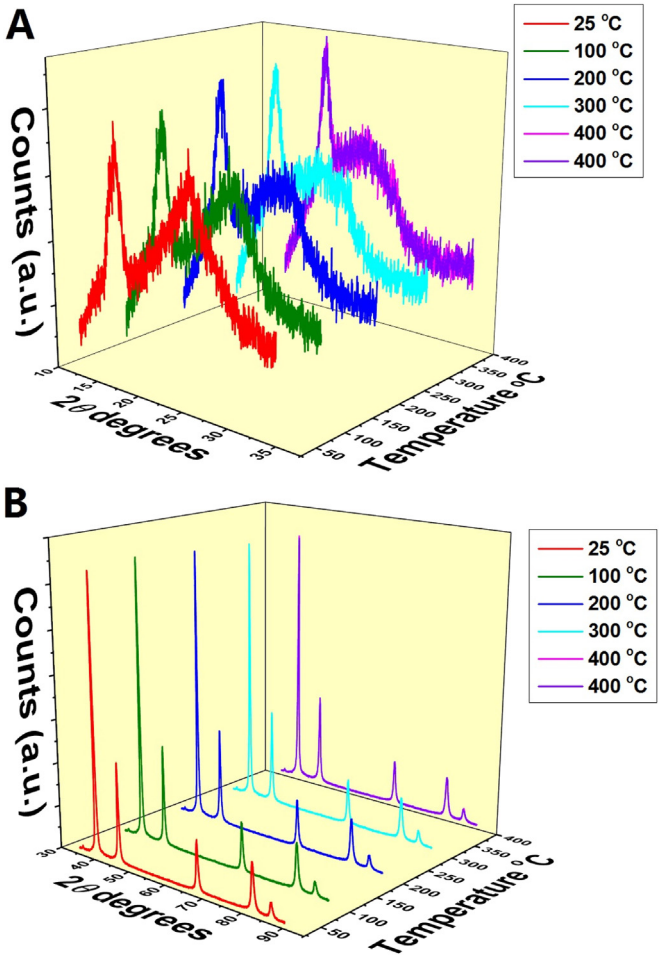

Fig. 1. Temperature dependent XRD diffractogram (in the range of 25 °C–400 °C) of the as grown CNOs filled with $FePd_3$ crystals showing in A the low angle 2θ region of the patterns and in B the high angle 2θ region of the patterns. (A colour version of this figure can be viewed online.)