Evidence of band gap features in Fe$_3$O$_4$ Bbmm filled carbon nano-onions

Filippo S Boi$^1$, Sameera Ivaturi$^1$, Ayoub Taallah$^1$, Shanling Wang$^1$ and Jiqiu Wen$^3$

$^1$ College of Physics, Sichuan University, Chengdu, People’s Republic of China
$^2$ Department of Physics, Guru Jambheshwar University of Science and Technology, Hisar, India
$^3$ Analytical and Testing Centre Sichuan University, Chengdu, People’s Republic of China

E-mail: fboi@sca.edu.cn

Keywords: carbon onions, iron oxide, Bbmm, magnetism

Abstract

A key challenge in the fabrication of ferromagnetically filled multilayer fullerenes (carbon nano-onions, CNOs) is the manipulation of the structure, composition and electronic band characteristics of both the carbon layers and encapsulated ferromagnetic material. Interestingly, a recent work has demonstrated that the addition of small quantities of water during the chemical vapour synthesis of Fe$_3$C filled CNOs can allow the local manipulation of the Fe$_3$C crystal-structure and induce the nucleation of a novel high pressure Bbmm Fe$_3$O$_4$ crystal-phase. In this report we propose an advanced study of such structural transition. Particularly, we investigate the morphological, optical (band-gap) characteristics and magnetic properties of the as produced CNO materials by using transmission electron microscopy, vibrating sample magnetometry, x-ray photoelectron spectroscopy and UV – vis spectroscopy.

1. Introduction

Multilayer fullerenes, also known as carbon nano-onions (CNOs) are carbon nano-structures which consist of quasi-spherical concentrically-arranged carbon-shells. Discovered by Ugarte in 1992 [1], CNOs have attracted a significant attention [1–7] for a numerous number of applications in the fields of physics, energy storage/ capacitors and materials chemistry [1–12]. Thanks to their high chemical stability, these structures have been considered also suitable candidates as nano-sized spherical containers for the encapsulation of specific materials of interest. Encapsulation of magnetic materials inside CNOs has indeed shown potential for applications in the field of high-density data-recording devices [12–14]. Up to now, CNOs have been filled with numerous ferromagnetic metals and metal-alloys such as Fe, Co, Ni, Fe$_3$C and recently FePd$_3$ [12–14]. These structures have been fabricated frequently by pyrolysis of metallocones-like precursors such as ferrocene, cobaltocene, nickelocene and dichloro-cyclo-octadiene palladium [12–14].

Although recent literature works have reported the encapsulation of Fe$_3$C within CNOs as a single reaction product, the encapsulation of ferromagnetic metal-based oxides within these structures remains a strong-challenge [15–17]. Among other metal-oxides, iron oxide as recently attracted strong attention for its unusual memory/resistive switching behavior [15–17].

Interestingly recent works have shown that mixed iron/iron-oxides Fe$_3$O$_3$ and Fe$_3$O$_4$ poly-crystals and high-pressure oxide Bbmm phases [18, 19] can be encapsulated within CNOs, carbon nanopolyhedra and carbon nanotubes by pyrolysis of ferrocene or ferrocene/Fe$_3$(CO)$_{12}$ mixtures [15]; however the difficulties in controlling/selecting (1) the desired oxide composition and (2) the desired carbon nanostructures morphology have limited up to now the development of such approaches for industrial application. In addition, the dynamics of the iron-oxide encapsulation-mechanism inside CNOs (and CNTs) remain highly controversial and have been not yet understood. However, the recently reported CVS experiments on the controlled nucleation of high pressure Bbmm Fe$_3$O$_4$ single crystals [18] show promise towards controlled reproducible fabrication of iron oxide filled CNOs as a result of an abrupt transition in the pyrolysis experiments [19]. As shown by
Taallah et al high temperature dependent x-ray diffraction (XRD) and Raman spectroscopy could not trigger such an abrupt transition, which instead was reported as a result of water-assisted pyrolysis of ferrocene [19].

In this work we propose an advanced study of such water-induced structural transition. Particularly, through a systematic transmission electron microscopy (TEM) approach we have investigated the morphological, structural properties of these novel materials. In addition, we investigated the not previously reported electronic (band gap) and magnetic properties of the as produced oxide filled CNO materials by employing magnetometry and UV spectroscopy. Existence of semiconducting band-gap characteristics is demonstrated.

2. Experimental

2.1. Synthesis

The synthesis experiments were carried out by using a CVS system composed of a quartz tube of length 1.5 m (outer diameter of 22 mm and a wall thickness of 2.5 mm), one zone electric furnace and an Ar flow rate of 10 ml min$^{-1}$. The precursor (100 mg of ferrocene) was placed in a quartz boat and sublimated/pyrolysed at the temperature of 990 °C. In order to accurately understand the effect of water in the reaction, the following quantities of water were used: 0.05 ml, 0.1 ml, 0.2 ml, 0.25 ml and 0.35 ml in analogy with [19]. In all the sets of experiments the reaction time was 5 min; the samples were cooled down by using a quench method (by sliding the furnace along a rail system).

2.2. Characterization

The characterization was carried out with: with a 200 kV American FEI Tecnai G2F20 transmission electron microscope (TEM). Raman Spectroscopy measurements were performed with an Andor SR-500i with a wavelength of 633 nm, acquisition time of approximately 100 s per sample-area at the temperature of 25 °C. XPS analyses were performed with an Escalab 250Xi. Vibrating sample magnetometry (VSM) measurements were performed with a VSM instrument Quantum Design. UV absorption measurements with a Hanon i5 UV–vis Spectrophotometer (Jinan Hanon Instruments Co., Ltd, China).

3. Results and discussion

The morphology of the CNOs obtained by pyrolysis of 0.1 ml of water with ferrocene is shown in figure 1. As shown in figures 1 and 2(A)–(C), the encapsulated crystals were found to be arranged into two main areas characterized by different lattice spacings. The area 1 with lattice spacings compatible with those of Fe$_3$C with space group Pnma (unit cell a: 0.51 nm, b: 0.67 nm and c: 0.45 nm) and the area 2 with lattice spacings
Figure 2. HRTEM micrographs (A)–(D) showing the morphology of typical filled CNOs obtained by pyrolysis of 0.1 ml of water mixed with ferrocene. In the inset in A the FFT of the encapsulated iron carbide (Fe₃C) lattice is indicated by the magenta arrow. The obtained reciprocal lattice spots can be described as follows: the dark-yellow circles indicate the 100 reflection, the red circles indicate the 200 reflection. In C more examples of the CNOs-morphology obtained in these growth conditions are shown. The blue and yellow arrows refer to areas of the CNOs with lower number of carbon layers as a consequence of oxygen-interaction.
compatible with those of Fe₃O₄ with space group Fd-3m and unit cell parameters a=b=c: 0.84 nm. The presence of a sharp change in the lattice arrangement of the encapsulated crystal was clearly found in proximity of the right region of the analyzed CNO of figures 1–2, where all the carbon shells appeared to be completely consumed by the oxygen species introduced during the pyrolysis experiment by the water molecules (see cyan arrow in figure 2(A)). The fast Fourier transform (FFT) of the lattice is indicated by the pink arrow. It is interesting to notice that the FFT analyses seems to suggest a particular role of the 100 planes of Fe₃C, which may work as a growth-seed for the nucleation of Fe₃O₄ in the form of single crystal (see figures 1, 2).

Additional analyses performed on CNOs obtained by pyrolysis of ferrocene with 0.2 ml of water are further shown in figure 3. The graphitic layers seem to decrease locally and open in some of the CNOs, creating the right conditions for the oxide nucleation. The TEM micrographs in figure 3 evidence also the presence of a

**Figure 3.** TEM micrographs (A)–(B) showing the morphology of typical filled CNOs obtained with 0.2 ml of water mixed with ferrocene.
partial detachment of the CNOs layers, as indicated by the yellow and green arrows. Additionally, the presence of single walled CNOs (blue arrow in figure 3(A)) and locally damaged multi-walled CNOs (see figure 3(B)) was found. Such an unusual detachment and local damage of the CNOs layers was observed also in the experiments performed with 0.25 ml of water as shown in figures 4(A)–(B). Also in this case the formation of iron oxide single crystals in some of the few-walled CNOs was found, as shown in figures 4(C)–(D). However, it is important to underline that the oxygen species obtained by the water pyrolysis do not seem to act uniformly within all the CNOs in the sample. Indeed, presence of thick graphitic layers could be observed (figures 4(A), (B)).

The morphological investigation of the CNOs for experiments involving pyrolysis of 0.35 ml of water is further shown in figure 5. In agreement with the report of Taallah et al [19], the majority of the analysed CNOs were found to exhibit an unusual distorted-like morphology (which can be seen in figures 5(A), (B)) together with a variable diameter. Note also the CNOs layers, which appear to be partially damaged and distorted by the exposure to the oxygen species deriving from the water pyrolysis. The effect of water concentration on these experiments is further summarized in table 1.

Further verification of the oxide nucleation dynamics was then sought by the use of XPS. As shown in figure 6, a large quantity of oxygen was found together with Fe and C confirming the presence of oxide species inside the onion structures. These measurements clearly confirm the formation of the oxide phase within the CNOs and agree with the recent observation of Taallah et al [19]. Particularly, these results suggest that when a critical concentration of water is used in the reaction, the oxidation occurs directly within the CNO core; this mechanism implies a consequent strong distortion of the graphitic-like layers, as indicated by the analyses of the C1s XPS spectrum in figure 7 where presence of a large quantity of sp3 carbon is indicated in the deconvolution.
green curve), which results from the structural transition of Fe₃C into a Fe₃O₄ Bbmm phase. Presence of C–O and C=O signals imply further the presence of partial oxidation of graphitic layers of the CNO during the aforementioned structural transition.

The attention was then turned on the magnetic characteristics of this latter type of CNOs. A typical hysteresis loop measurement performed at 300 K with VSM is shown in figure 8. Interestingly, a weak ferromagnetic-like behaviour of the Fe₃O₄/Fe-filled CNOs was found with a relatively low coercivity in the order of 100–150 Oe and low saturation magnetization of 10.4 emu g⁻¹. In the attempt to better visualize the magnetic arrangement of the sample and its possible dependence on the chosen temperature, the use of zero field cooled ZFC measurements at the field of 300 Oe was considered. The result of these measurements is shown in figure 9.

Curiously a magnetic transition is observed in the range from 100 K to 50 K. While at higher temperature, an increase of the magnetization is found. The origin of such intense magnetization peak in the range from 100K to

**Table 1.** Chart showing the morphological/structural effect of water assisted CVS as a function of water concentration.

| Amount of water | Effect |
|-----------------|--------|
| 0.05–0.15 ml    | Partial oxidation of CNO-layers, weak oxidation of the encapsulated crystals |
| 0.2–0.3 ml      | Enhanced oxidation of the CNO layers, weak oxidation of encapsulated crystals |
| 0.35 ml         | Enhanced oxidation of the CNO layers, full oxidation of encapsulated crystals and formation of a high pressure Bbmm phase |

Figure 5. TEM micrographs (A)–(B) showing the unusual distorted morphology of typical filled CNOs obtained with 0.35 ml of water mixed with ferrocene.
Figure 6. XPS analyses of Fe$_3$O$_4$ Bbmm filled CNOs showing the presence of oxygen and iron rich species.

Figure 7. XPS analyses of Fe$_3$O$_4$ Bbmm filled CNOs showing the presence sp$^3$-rich carbon species possibly resulting from the oxidation of the encapsulated crystal. Note the presence of a large quantity of sp$^3$ carbon (green curve), which results from the structural transition of the Fe$_3$C phase into a Fe$_3$O$_4$ Bbmm phase. Presence of C–O and C=O signals imply further the presence of partial oxidation of graphitic layers of the CNOs.

Figure 8. Hysteresis loops of the CNOs grown in presence of 0.35 ml of water (black) and CNOs filled with Fe$_3$C produced without water(red).
50K is currently under investigation and further studies are required to clearly attribute its magnetic origin. However possible superparamagnetic origin of such contribution can not be excluded at this stage. Additional investigations were further performed by UV–vis spectroscopy, as shown in figure 10. These investigations revealed the presence of two main absorption features, namely F1 and F2. While the first feature F1 could be attributable to the π-plasmon contribution, the second absorption feature is very unusual and appears to possibly indicate the presence of a wide energy band gap for these types of onions. Notice that the observed energy gap is mostly larger than that typically expected for Fe₃O₄ nanoparticles, 2–3 eV [20].

4. Conclusion

In conclusion we have reported an advanced study on the morphological, optical (band-gap) characteristics and magnetic properties of CNO materials filled with Bbmm Fe₃O₄ crystals by using transmission electron microscopy, vibrating sample magnetometry, x-ray photoelectron spectroscopy and UV–vis spectroscopy. Our
results demonstrate the existence of important band gap characteristics, and imply the suitability of these type of CNO-hybrid materials for possible application in semiconducting technology and devices.

Acknowledgments

We acknowledge the Sichuan Province Technology Grant No. 2019YFH0080.

ORCID iDs

Filippo S Boi https://orcid.org/0000-0002-1586-5141

References

[1] Ugarte D 1992 Nature 359 707–9
[2] Kroto H W, Heath J R, Brien S C O, Curl R F and Smalley R E 1985 Nature 318 162–3
[3] Sano N, Wang H, Chhowalla M, Alexandrou I and Amaratunga G A J 2001 NNature 414 506–7
[4] Chhowalla M, Wang H, Sano N, Teo K B K, Lee S B and Amaratunga G A J 2003 Phys. Rev. Lett. 90 155504
[5] Lau D W M, McCulloch D G, Marks N A, Madsen N R and Rode A V 2007 Phys. Rev. B 75 233408
[6] Macutkevic J, Banys J, Moseenkov S, Kuznetsov V, Nunn N and Shenderova O 2015 Polym. Compos. 36 2084–92
[7] Pawlak R, Kawai S, Fremy S, Glatzel T and Meyer E 2011 ACS Nano 5 6349–54
[8] Pech D et al 2010 Nat. Nanotechnology 5 651–4
[9] Rettenbacher A S, Elliott B, Hudson J S, Amirkanian A and Echegoyen L 2006 Chem. Eur. J. 12 376–87
[10] Chen X H et al 2001 Chem. Phys. Lett. 336 201–4
[11] Banhart F, Hernandez E and Terrones M 2003 Phys. Rev. Lett. 90 185502
[12] Ruoff R S, Lorents D C, Chan B, Malhotra R and Subramoney S 1993 Science 259 346–8
[13] Boi F S et al 2017 RSC Adv. 7 845
[14] Boi F S, Ivaturi S, Wang S and Zhang X 2017 Carbon 120 392–6
[15] Schnitzler M C, Oliveira M M, Ugarte D and Zarbin A J G 2003 Chem. Phys. Lett. 381 541–8
[16] Cava C E, Possagno R, Schnitzler M C, Roman P C, Oliveira M M, Lepiensky C M, Zarbin A J G and Roman L S 2007 Chem. Phys. Lett. 444 304–8
[17] Cava C E, Persson C, Zarbin A J G and Roman L S 2014 Nanoscale 6 378
[18] Bykova E et al 2016 Nat. Commun. 7 10661
[19] Taallah A, Odunmbaku O, Ivaturi S, Wen J, Liu M, Zhang X, Medranda D, Wang S and Boi F S 2019 Water-assisted structural manipulation of ferromagnetically filled carbon onions: the case of high pressure Fe3O4, Dae Solid State Physics Symp. 2018 (AIP Conferences Series) 030119
[20] Gilbert B, Frandsen C, Maxey E R and Sherman D M Band-gap measurements of bulk and nanoscale hematite by soft x-ray spectroscopy Phys. Rev. B 79 035108