Temperature-dependent c-axis lattice-spacing reduction and novel structural recrystallization in carbon nano-onions filled with Fe₃C/α-Fe nanocrystals

Filippo S Boi¹,², Jiaxiang Li¹, Omololu Odunmbaku¹, Mengjiao Liu¹, Daniel Medranda¹, Ayoub Taallah¹, Li Lei¹ and Shanling Wang⁴,⁵

¹ College of Physics, Sichuan University, Chengdu, People’s Republic of China
² College of Chemistry and Materials Science, Sichuan Normal University, Chengdu, People’s Republic of China
³ Institute of Atomic and Molecular Physics, Sichuan University, Chengdu, People’s Republic of China
⁴ Analytical and Testing Center, Sichuan University, Chengdu, People’s Republic of China
⁵ Authors to whom any correspondence should be addressed.

E-mail: fboi@scu.edu.cn and wangshanling@scu.edu.cn

Keywords: CNOs, CVD, gamma Fe, defects, percolative theory

Supplementary material for this article is available online

Abstract
Carbon nano-onions are approximately spherical nanoscale graphitic shells. When filled with ferromagnetic Fe₃C/α-Fe nanocrystals, these structures have several important applications, such as point electron-sources, magnetic data recording, energy storage, and others, that exploit the interaction of either or both the shells and the magnetic moments in the filling. Despite these applications receiving much recent attention, little is known about the structural relationship between the carbon shells and the internal nanocrystal. In this work, the graphitic c-axis lattice-spacing in Fe₃C/α-Fe-filled multi-shell structures was determined by XRD in the temperature range from 130 K to 298 K. A significant reduction in the c-axis lattice-spacing was observed in the multi-shell structures. A defect-induced magnetic transition was probed and ascribed to the formation of randomly oriented ferromagnetic clusters in the recrystallized disclination-rich regions of the CNOs-shells, in agreement with the percolative theory of ferromagnetism.

1. Introduction
Carbon nano-onions (CNOs) are quasi-spherical multi-layered structures characterized by 60N² atoms self-organized into graphitic shells (N is the number of shells) [1–10]. Since their discovery, CNOs have attracted attention thanks to these desirable physical attributes: high thermal stability and electrical conductivity (10 5 cm −1) [11–15], important mechanical properties [16–20], tuneable giant electrochemical capacitance [11, 12, 21], high surface area [11, 13], long-term field-emission stability [22], high curvature [4, 5], advantageous tribology [23, 24] and chemical stability [3, 8, 25–27]. Moreover, the interstellar optical absorption feature at wavelength 217.5 nm attributed to CNOs and the possibility of reversibly converting CNO-structure to nano-diamond has generated much interest in astrophysics and materials science [28–40].

Owing to these useful characteristics, CNOs have been considered suitable candidates for a wide range of applications, including: point electron sources [22], electrochemical energy storage electrodes [11, 12, 21], supramolecular systems [41], aerospace-additives [42] and miniaturized fuel cells [43].

CNOs have been also considered for the encapsulation of nanocrystals [3, 8, 25–27, 44–48]. The possibility of encapsulating magnetic materials, especially ferromagnetic crystals, has attracted great attention owing to possible applications in magnetic data recording and energy storage devices [25–27, 44–48]. Recent studies on these types of materials have also reported the presence of high-temperature structural memory effects, opening possible new applications of these structures in thermoelectric systems [27].
CNOs have been filled with many types of ferromagnetic nanocrystals, including metals, carbides and substitutional alloys. The c-axis spacing in the carbon shells has been reported to be 0.34–0.35 nm (corresponding to the 002 reflections of graphite) for CNOs filled with Fe3C [25] and 0.34–0.56 nm for FePd3 nanocrystal fillings [26, 27]. When filled with metal or alloy materials, the diameter of CNOs is generally much larger (in the order of one hundred nanometres) than that reported for unfilled structures (in the order of 5 nanometres) [4, 5, 25–27]. This important difference can be attributed to the different growth mechanisms of these two types. Unfilled CNOs can be produced in powder-form, mainly through arc-discharge approaches [4, 5]. Whereas, filled CNOs are grown by chemical vapour synthesis [25] or by chemical vapour deposition methods, for which the addition of sulphur to the ferrocene precursor has been identified as a means of controlling the diameter [48, 49].

Despite these important advances little is still known about the structure of these materials at low temperatures. Previous reports have been concerned with high-temperature structural changes in encapsulated Sn and Pb nanocrystals [3], and FePt3, FePd3, Fe3C and Fe7C3 fillings [25, 27, 48, 50]. The properties of ferromagnetically filled CNOs at low temperatures are yet to be investigated.

Interestingly, it was recently shown that temperature-dependent structural memory effects are present in the unit cell of Fe3C-filled carbon nanotubes [51]. This effect was attributed to cooperative behaviour of the nanotube walls and the encapsulated Fe3C nanowires, an effect of potential significance for spacesuit technology as shape memory alloy actuators [52, 53].

In this work we report an x-ray diffraction (XRD) study of the structural properties of Fe3C/α-Fe-filled CNOs in the temperature range 130 K to 298 K. Fe3C/α-Fe-filled multi-shell CNOs with variable diameter were employed in this study.

As the temperature was decreased, we observed a clear reduction in the graphitic c-axis lattice-spacing. This effect was found to be enhanced by improved inter-shell stacking and an unusual recrystallization of outer shells at low temperature. This interpretation was supported by the appearance of multiple peaks and broadening features in the XRD data in the 2θ range 15° to 18° as the temperature was lowered to 130 K. Complementary electron spin resonance (ESR) measurements revealed the presence of a defect-induced magnetic transition at 77 K in the π-electron signal. This magnetic transition was interpreted on the basis of the percolative theory of ferromagnetism and ascribed to the presence of ferromagnetic correlation (with a Tc below 150 K) originating from the recrystallized disclination-rich regions of the CNOs shells [54].

2. Experimental

2.1. Synthesis

The Fe3C/α-Fe-filled multi-shell CNOs were produced with the following synthesis method: 5 g of ferrocene were evaporated at 110 °C and pyrolysed at 990 °C under an Ar flow rate of 5 ml min⁻¹. The duration of the growth experiment at the pyrolysis temperature was 1 h. The vapour deposition reactor consisted of the following dimensions: a quartz tube with a length of 1.5 m, an inner diameter of 44 mm and a wall thickness of 3 mm. A Si/SiO2 substrate was placed in the reaction zone for the deposition of the growth product, which consisted of 3.5 g of Fe3C filled CNOs (yield of approximately 70%). A fast cooling method was used to bring the CNOs to room temperature by removing the furnace along a rail system (quench).

2.2. Characterization

Low-temperature XRD measurements were performed with a Rigaku Smartlab powder X-ray diffractometer (Cu K-α, λ = 0.154 18 nm) under vacuum of less than 10⁻³ Pa in the temperature range from 130 K to 298 K. A 200 kV American FEI Tecnai G2F20 was employed to obtain TEM/HRTEM images. ESR measurements were performed at 77 K, 150 K and 300 K using a JEOL JES-FA200 spectrometer instrument. Raman Spectra were collected in a custom-built instrument 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

A typical example of the morphology of as-produced Fe3C/α-Fe-filled CNO material is shown in figure supp. 1(A) is available online at stacks.iop.org/NANOX/1/020016/mmedia; this powder could easily be pressed into cm-scale stable pellets for easy handling, as shown in figure supp. 1(B). The cross-sectional microscopic detail is shown in figure supp. 1(C), (D).

The presence of a variable shape-arrangement and thickness in the CNOs was revealed by the TEM analyses (figures supp. 1(C), (D) and 2). Presence of variable number of carbon graphitic shells surrounding the CNOs
was found. This observation was confirmed by statistical investigations in figures Supp. 1(E), (F). A higher level of detail in the CNO structure is presented also in figure 1. Typical HRTEM confirming presence of a graphitic ordering in the CNOs-shells are shown in figures 1(C), (D). Note also the presence of defects which could be detected mostly in the outer layers (see analyses in figure 2).

A variation of the lattice-spacing in the inner, middle and outer shells of the CNO was also found, as shown in figure 2. In particular, variation in the disorientation angle between the CNOs-shells was measured when moving from the inner toward the outer layers of the CNOs. Such a variable level of structural ordering is attributable to the presence of disoriented graphitic stacks with clear disclinations in between. This interpretation can explain the observed increasing interlayer spacing and defect density in the spherical carbon shells, as a result of the disclinations, in figure 2 [55–65]. As previously indicated also by Siklitskaya et al [55] and Akatyeva et a.[56], defects can play also a significant role in altering the carbon shell curvature in this type of structures. Structural defects in CNOs have been also reported by Balaban et al [61], Blank et al [62] and Hiura et al [65].

Presence of a temperature dependent variation of the CNO inter-shells distances was revealed by temperature dependent XRD analyses. These investigations were performed in the range from 298 K to 130 K. Figure 3 shows typical examples of the XRD patterns measured in the temperature range from 298 K to 130 K. XRD data collected at 298 K revealed a diffraction peak in the range of 14°–28° 2θ which could be ascribed to the 002 reflection of graphitic carbon (corresponding to an average lattice spacing of 0.339 nm) together with a very weak broad feature in the region of 17° 2θ corresponding to an inter-shell distance of approximately 0.5–0.6 nm (i.e. outer CNOs shells). Appearance of additional 002 reflections was further found at 243 K, with two diffraction peaks arising in the region of 15° and 17° 2θ respectively (inter-shell distances of 0.513 nm and 0.592 nm respectively). The appearance of these three peaks seems to indicate the presence of a partial recrystallization of the CNOs-layers at this temperature. It is important to notice also that a variable intensity and broadening in such peak features could be found in measurements performed at lower temperatures of 200 K, 150 K and 130 K. Note that complete disappearance of such peak features was observed when the sample was taken back to the temperature of 298 K, implying the presence of a reversible transition.
Additional calculations performed by using the Scherrer equation [25] revealed the number of CNOs shells contributing to each of the observed diffraction peaks. The results of these calculations are shown in table 1. Interestingly, only a fraction of CNOs shells (average number of 38 per each CNOs in the sample) was found to contribute to the peak in the region of 26° 2θ. This result suggests that only the CNOs shells with relatively high level of graphitic ordering contribute to the pattern shown in figure 3 at 298 K, instead the shells with higher number of defects do not appear to contribute to the observed peak. Furthermore, considering the Scherrer thickness associated to the diffraction peaks in the regions of 15° and 17° 2θ, we find that a larger number of 74 and 84 CNOs layers can be at the origin of such contribution. However, the lower intensities of those peaks (lower if compared to that of the peak at 26° 2θ) may imply that a lower number of CNOs contributes to this diffraction signal in the sample. These analyses appear therefore to confirm the possible presence of a recrystallization effect as the temperature is cooled down to 243 K which could possibly be triggered by a significant depletion in the unit-cell c-axis parameter associated to the inner CNOs-shells, as shown in figures 4(A), (B). This appears to be confirmed by the observation of a shift in the inner–shells–diffraction-peak (peak at 26° 2θ) towards higher values of 2θ degrees when the temperature is lowered down below 298 K.

Figure 2. HRTEM micrographs (A)–(D) revealing significant variation in the disorientation angle between the CNOs-shells. Such a variable level of structural ordering is attributable to the presence of disoriented graphitic stacks and disclinations.
Such a temperature-induced depletion in the values of the $c$-axis has analogy with previous observations reported in multiwalled carbon nanotubes [51] and graphite [57, 58]. In particular in figure 4(B) the temperature dependent variation of the $c$-axis (as extracted from the Rietveld refinement method) reveals an approximately linear trend which is typically observed in turbostratic graphitic materials [51], [57, 58].

The additional diffraction peak features observed in this work and assigned to recrystallization appear to be most likely due to defect formation upon cooling, in agreement with previous observations from Siklitskaya et al [55], where the role of defects in altering the CNOs shell curvature and inter-shell distances was predicted through density functional theory analysis of the radial distribution of atoms.

Being interested in investigating possible existence of magnetic transitions induced by the aforementioned $c$-axis depletion observed in the graphitic CNO-shells, complementary ESR measurements were considered at the temperatures of 300 K, 150 K and 77 K. As shown in figure 5 a differential absorption peak (corresponding to the $\pi$-electron signal) could be detected at g-values of approximately 1.987–1.989 (at 300 K and 150 K respectively). A significant transition involving a differential absorption peak-shift towards larger g-values was then observed at 77 K together with an additional intense peak-feature which appears to be an indicator of intrinsic ferromagnetic ordering. A possible interpretation of such a transition may refer to existence of an $\alpha$-Fe to $\gamma$-Fe phase conversion [66] together with a possible anomalous thermal expansion effect of the latter ($\gamma$-Fe) phase, which was recently reported by Cambedouzou et al [67]. This observation indicates that volume enhancement may create an additional interfacial transition (and consequent $sp^3$-type and or vacancy-related stress-induced defects) in the carbon shells leading to the observed $\pi$-electron signal-shift.

An alternative interpretation of the intense differential absorption feature observed in the ESR spectrum at 150 K–77 K may refer to the formation of intrinsic randomly oriented ferromagnetic clusters into the (recrystallized) disclination-rich regions of the CNOs as a consequence of the recrystallization effect. This second interpretation is supported by the percolative theory of magnetism previously outlined by Kopelevich et al [54] and agrees with the Rietveld refinement analyses in ESI, where no significant changes in the intensities of the acquired $Fe_3C$ and $\alpha$-Fe peak-reflections was found (See ESI figure Supp. 4).

According to the percolation-theory [54], uncorrelated ferromagnetic clusters are formed below a certain temperature indicated as $T^*$, leading to finite values of $M_s(T, H)$, $M_{rem}(T, H)$, and $\Delta M(T, H)$ in zero field cooled
As the temperature decreases, ferromagnetic correlations develop on a larger scale, and a long-range ferromagnetic ordering emerges. In figure 5 it is possible to identify the $T \sim 150$ K as a transition temperature below which long range ferromagnetic cluster ordering appears to take place [24]. The origin of this phenomenon can be explained with the presence of recrystallized disclination-rich regions in the CNOs-shell [54].

Further investigation of the structural properties of the CNOs was then sought by Raman spectroscopy. Presence of defective sites in the CNOs in the form of mixed vacancy and sp$^3$ type (at 300 K) could be deduced by calculating the AD/AD$'$ ratio (yielded value of 9.77) as shown in figure 6. This observation is in agreement with the HRTEM analyses shown in figures 1, 2.
4. Conclusion

In conclusion we have reported the novel observation of low-temperature-driven recrystallization effects in multi-shells graphitic CNOs filled with Fe$_3$C/$\alpha$-Fe crystals from 298 K to 130 K. Appearance of additional 002 reflections as the temperature was decreased was reported, with two diffraction peaks arising in the region of 15° and 17° 2θ respectively (inter-shell distances of 0.513 nm and 0.592 nm respectively) and a broad feature in the region of 17° 2θ. The appearance of these three peaks was interpreted as a result of a partial recrystallization of the CNOs-layers at this temperature. This effect may possibly be related to a rearrangement of the disclination-rich regions of the CNO graphitic layers. A depletion in the graphitic c-axis of the CNOs was also extracted as the

![Figure 5. ESR measurements of the multishell graphitic Fe$_3$C/$\alpha$-Fe filled CNOs.](image-url)
temperature was decreased to 130 K. Complementary ESR measurements revealed a transition in the \( \pi \)-electron signal from 150 K to 77 K. This transition was interpreted as an indicator of the possible existence of localized ferromagnetic clusters, as suggested by the percolative theory of ferromagnetism, in the recrystallized disclination-rich regions of the sample [54].

Acknowledgments

We acknowledge NSFC Grant No 11750110413. We acknowledge Professor Anna Corrias for the help in the manuscript preparation and checking. We also acknowledge Dr Mark Baxendale.

ORCID iDs

Filippo S Boi https://orcid.org/0000-0002-1586-5141
Li Lei https://orcid.org/0000-0002-8649-2928

References

[1] Kroto H W, Heath J R, Brien S C O, Curl R F and Smalley R E 1985 C60: buckminsterfullerene Nature 318 162–3
[2] Ugarte D 1992 Curling and closure of graphitic networks under electron beam irradiation Nature 359 707–9
[3] Banhart F, Hernandez E and Terrones M 2003 Extreme superheating and supercooling of encapsulated metals in fullerene-like shells Phys. Rev. Lett. 90 185502
[4] Chhowalla M, Wang H, Sano N, Teo K B K, Lee S B and Amaratunga G A J 2003 (interstellar) Carbon onions: carriers of the 217.5 nm interstellar absorption feature Phys. Rev. Lett. 90 155504
[5] Sano N, Wang H, Chhowalla M, Alexandrou I and Amaratunga G A J 2001 Nanotechnology: synthesis of carbon ‘onions’ in water Nature 414 506–7
[6] Hultman L et al 2001 Cross-linked nano-‘onions’ of carbon nitride in the solid phase: existence of a novel \( C_{48} N_{12} \): Aza-fullerene. Phys. Rev. Lett. 87 225503
[7] Perez-Garrido A 2000 Giant multilayer fullerene structures with symmetrically arranged defects Phys. Rev. B 62 6979
[8] Ruoff R S, Lorents D C, Chan B, Malhotra R and Subramoney S 1993 Single crystal metals encapsulated in carbon nanoparticles Science 259 346–8
[9] Cabioch T, Thune E and Jouven M 2002 Mechanisms involved in the formation of onionlike carbon nanostructures synthesized by ion implantation at high temperature Phys. Rev. B 65 132103
[10] Qian X and Xiang Z 2012 Bucky-diamond versus onion-like carbon: end of graphitization Phys. Rev. B 86 155417

Figure 6. Raman Spectroscopy measurement of the Fe\(_3\)C/\(\alpha\)-Fe-filled multishell graphitic CNOs. The D/D' ratio was extracted in order to gain information on the type of defects present in the CNOs structure. A ratio of 9.77 could be extracted and ascribed to presence of mixed vacancy and sp\(^3\)-type defects [68].
Borgohain R, Yang J, Selegue J P and Kim D Y 2014 Controlled synthesis, efficient purification and electrochemical characterization of arc-discharge carbon nano-onions Carbon 66 272–84
Pech D et al 2010 Ultrahighpower micrometre-sized supercapacitors based on onion-like carbon Nat. Nanotechnology 5 651–4
Palkar A et al 2007 Reactivity differences between carbon nano onions (CNOs) prepared by different methods Chem. Asian J. 5 625–33
Elliott B R, Host J, Dravid V P, Teng M H and Hwang J H 1997 A descriptive model linking possible formation mechanisms for graphite-encapsulated nanocrystals to processing parameters J. Mat. Research 12 3328–44
Portet C, Yushima G and Gogotii Y 2007 Electrochemical performance of carbon onions, nanodiamonds, carbon black and multilayered nanodiamonds deposited in electrical double layer capacitors Carbon 45 2511–8
Joly-Pottuz L, Bucholz E W, Matsumoto N, Phillpot S R, Sinnott S B, Ohmac N and Martin J M 2010 Friction properties of carbon nano-onions from experiment and computer simulations Tribol. Lett. 37 75–81
Merijs-Meri R, Zicans J, Ivanova T, Bietenieks J, Puddabucksaya A, Kuzhir P, Maskimenko S, Macutkevich J, Kuznetsov V and Moseenkov S 2005 Carbon nanotubes and carbon onions for modification of styrene–acrylate copolymer nanocomposites Polym. Compos. 1048–54
Schwarz U S, Safran S A and Komura S 2001 Mechanical, adhesive and thermodynamic properties of hollow nanoparticles Mat. Res. Soc. Symp. Proc. 651 T3.1–3.6
Macutkevich J, Ransy J, Moseenkov S, Kuznetsov V, Nunn N and Shenderova O 2005 Dielectric properties of onion-like carbon and detonation nanodiamond/polydimethylsiloxane composites Polym. Compos. 36 2064–92
Pawlak R, Kawai S, Frensy S, Glotzel T and Meyer E 2011 Atomic-scale mechanical properties of orientated C60 molecules revealed by noncontact atomic force microscopy ACS Nano 5 6349–54
Zhang C et al 2011 The efficient synthesis of carbon nano-onions using chemical vapor deposition on an unsupported Ni–Fe alloy catalyst Carbon 49 1151–8
Wang M-S, Golberg D and Bando Y 2010 Carbon ‘onions’ as point electron sources ACS Nano 4 4396–402
Street K W, Marchetti M, Vander Wal R L and Tomasek J A 2004 Evaluation of tribological behaviour of nano-onions in Krytox 143 AB Tribol. Lett. 16 143–9
Yao Y L, Wang X M, Guo J J, Wang X W and Xu B S 2008 Tribological property of onion-like fullerenes as lubricant additive Mater. Lett. 62 2524–7
Boi F S et al 2017 Cm–size free-standing self-organized buckypaper of bucky-onions filled with ferromagnetic Fe3C, C, RSC Adv. 7 845
Boi F S, Du Y, Ivaturi S, He Y and Wang S 2017 New insights on the magnetic properties of ferromagnetic FePd3 single-crystals encapsulated inside carbon nanomaterials Mater. Res. Express 4 035021
Boi F S, Ivaturi S, Wang S and Zhang X 2017 Temperature driven structural transitions in the graphite–arrangement of carbon onions filled with FePd3 nano crystals Carbon 120 592–6
Wright E L 1988 The ultraviolet extinction from interstellar graphitic onions Nature (London) 336 227–8
de Heer W A and Ugarte D 1993 Carbon onions produced by heat treatment of carbon soot and their relation to the 217.5 nm interstellar absorption feature Chem. Phys. Lett. 207 480–6
Allamandola L J, Sandford S A, Tielens A G and Herbst T M 1993 Diamonds in dense molecular clouds: a challenge to the standard interstellar medium paradigm Science 260 64–6
Lucas A A, Henrard L and Lambin P 1994 Computation of the ultraviolet absorption and electron inelastic scattering cross section of multishell fullerene Phys. Rev. B 44 2888–96
Bernatowicz T J et al 1996 Constraints on stellar grain formation from presolar graphite in the murchison meteorite Astrophys. J. 472 760
Banhart F and Aijayan P M 1996 Carbon onions as nanoscopic pressure cells for diamond formation Nature (London) 382 433–5
Beege J W, Wilowiai T J, Robinson M S, Cronin J R, Mcgehee M D, Clemett S J and Gillette S J 1997 Experimental indication of a naphthalene-base molecular aggregate for the carrier of the 2175 Å interstellar extinction feature Astrophys. J. 487 976–82
Henrard L, Lambin P and Lucas A A 1997 Carbon onions as possible carriers of the 2175 Å interstellar absorption bump Astrophys. J. 487 719–27
Cabioch H, Th. C S, Henrard L and Lambin P 2000 Optical transmittance spectroscopy of concentric-shell fullerene layers produced by carbon ion implantation Eur. Phys. J. B 18 535
Tomita S, Hayashi S, Tsukuda Y and Fujii M 2002 Ultraviolet-visible absorption spectroscopy of carbon onions Phys. Solid State 44 450–3
Tomita S, Fujii M and Hayashi S 2002 Optical extinction properties of carbon onions prepared from diamond nanoparticles Phys. Rev. B 66 245424
Tomita S, Fujii M and Hayashi S 2004 Defective carbon onions in interstellar space as the origin of the optical extinction bump at 217.5 nanometers Astrophys. J. 609 220–4
Xiao J, Ouyang G, Liu P, Wang C X and Yang G W 2014 Reversible nanodiamond–carbon onion phase transformations Nano Lett. 14 3643–52
Palkar A, Kumbhar A, Athans A J and Echegoyen L 2008 Pyridyl-functionalized and water soluble carbon nano onions: first supramolecular complexes of carbon nano-onions Chem. Mater. 20 1665–7
Chen X H et al 2001 New method of carbon onion growth by radio-frequency plasma enhanced chemical vapour deposition Chem. Phys. Lett. 336 201–4
Rettenbacher A S, Elliott B, Hudson J S, Amirkhanian A and Echegoyen L 2006 Preparation and functionalization of multilayer fullerene (carbon nano-onions) Chem. Eur. J. 12 376–87
Davydov V et al 2014 Solid state synthesis of carbon-encapsulated iron carbide nanoparticles and their interaction with living cells J. Mater. Chem. B 2 4250–61
Hong S Y et al 2015 A new synthesis of carbon encapsulated Fe3C nanoparticles for high-temperature Fischer–Tropsch synthesis Nanoscale 7 16616–20
Li H, Li Y, Zhang Y, Liang C, Wang H, Li B, Adair D and Bakenov Z 2016 Fabrication and properties of carbon–encapsulated cobalt nanoparticles over NaCl by CVD Nanoscale Res. Lett. 11 432
Hayasaki Y, Hasumura T, Fukuda T, Nagaoka Y, Uki T, Iwai S, Uchida T and Maekawa T 2016 Synthesis of magnetic alloy-filling carbon nanoparticles in super-critical benzene irradiated with an ultraviolet laser Helv. Phys. Acta A 00171
Medranda D et al 2018 Ferromagnetically filled carbon nano-onions: the key role of sulfur in dimensional, structural and electric control R. Soc. Open Sci. 5 170981
Liu Q et al 2008 Synthesis of different magnetic carbon nanostructures by the pyrolysis of ferrocene at different sublimation temperatures Carbon 46 1892–902
