Supplementary Online Material

Experimental Details:

The characterization was carried out with the following techniques:

SEM with a JSM-7500F at 5-20 kV, XRD with an Empyrean PANalytical and a Rigaku Smartlab powder X-ray diffractometers (Cu K-α, λ = 0.154 nm). A 200 kV American FEI Tecnai G2F20 was employed to obtain TEM, STEM and EDX analyses. Magnetic measurements were performed with a VSM (Quantum Design) at room temperature. XPS analyses were performed with an Escalab 250Xi.

Supplementary Figures:

Fig. Supp. 1A: Typical XRD diffractogram of a powder consisting of Fe₃C filled CNOs buckypaper flakes before the annealing stage showing the presence of a single phase of Fe₃C inside the CNOs.
Fig. Supp. 1B: Typical XRD diffractogram of filled CNOs (produced by pyrolysis of 0.5 g of ferrocene) after 1h of annealing showing the presence of Fe$_3$C and $\alpha$-Fe inside the CNOs. Note the presence of an intense $\alpha$-Fe peak in the region of 45 degrees 2$\theta$ which can be attributed to the foam nucleation process.

Fig. Supp. 1C: Photograph showing the large quantities and the morphology of the as grown Fe$_3$C filled CNOs buckypaper flakes obtained by pyrolysis of large quantities of ferrocene (see yellow arrow for example).
Fig.Supp. 2: SEM micrographs of the carbon foam obtained after the annealing stage (stage II) with an increasing level of detail. Note in B and in D the presence of small quantities of residual CNOs in the foam surface. In E and F the exceptionally high and continuous ferromagnetic filling rates (bright areas) of the carbon foam are shown with backscattered electrons.
Fig.Sup. 3: EDX analyses (area 1 in the micrograph in Fig.3) of the as grown carbon foam completely filled with $\alpha$-Fe obtained after the annealing stage (stage II).

Fig.Sup.4: XRD diffractogram of the carbon foam sample obtained after the annealing stage (stage II, after annealing Fe$_3$C filled CNOs obtained by pyrolysis of 0.5 g of ferrocene). A single phase of $\alpha$-Fe is found.
Fig.Supp. 5A: Typical XRD diffractogram of the filled CNOs obtained by pyrolysis of 0.8 g of ferrocene before stage II showing the presence of Fe$_3$C inside the CNOs.

Fig.Supp. 5B: Typical XRD diffractogram of filled CNOs (obtained by pyrolysis of 0.8 g of ferrocene) after 1h of annealing showing the presence of Fe$_3$C and $\alpha$-Fe together with a residual 002 reflection of the CNOs. Note the presence of an intense $\alpha$-Fe peak in the region of 45 degrees 2$\theta$ which can be attributed to the foam nucleation process.
Fig. Supp. 6: Typical SEM (in A,F) and backscattered electrons (in B-E) micrographs of the intermediate CNOs/carbon foam sample obtained after annealing (for 1 h) the filled CNOs produced by pyrolysis of 0.8 g of ferrocene. The magenta arrows indicate the obtained iron filled carbon foam while the cyan arrows indicate the residual filled CNOs not yet decomposed by the annealing process.
Fig.Supp. 7: Photograph showing the large quantities and the morphology of the iron filled carbon foam (see yellow arrow) obtained by annealing of the filled CNOs produced by pyrolysis of large quantities of ferrocene for a timescale of approximately 20 hours. Note the characteristic grey color of the amorphous carbon foam.

Fig.Supp. 8A: Photograph showing the large quantities and the morphology of the iron filled carbon foam obtained by annealing of the filled CNOs produced by pyrolysis of large quantities of ferrocene (10 g) for a timescale of approximately 35 hours. Note the characteristic grey color of the amorphous carbon foam.
Fig.Supp. 8B: Photograph showing the large quantities and the morphology of the iron filled carbon foam obtained by annealing of the filled CNOs produced by pyrolysis of large quantities of ferrocene (10g) for a timescale of approximately 35 hours. Note the characteristic grey color of the amorphous carbon foam.

Fig.Supp. 8C: SEM micrograph of the Fe-filled CFM sample obtained after annealing for a timescale of 35 hours.
Fig. Supp. 9: HRTEM image of an as grown Fe$_3$C filled CNO structure (before the annealing stage). Note the presence of concentrically arranged graphitic layers which confirm the presence of the carbon onion structure.

Fig. Supp. 10: TEM image showing another example of two as grown Fe$_3$C filled CNOs structures (before the annealing stage). Note the presence of concentrically arranged graphitic layers which confirm the presence of the carbon onion structures also in this case.
Fig. Supp. 11: HRTEM image showing another example of an as grown Fe$_3$C filled CNO structure (before the annealing stage). Note the presence of concentrically arranged graphitic layers which confirm the presence of the carbon onion structure.

Fig. Supp. 12: Low magnification TEM image showing another example of the diameter-variation of the as grown Fe$_3$C filled CNO structure (before the annealing stage).
Fig. Supp. 13: X-ray diffractogram (red line) and Rietveld refinement (green line) of the carbon foam sample obtained from pyrolysis of 10 g of ferrocene after annealing for 2 h. The following database cards were used: 1008725 for Fe₃C (Pnma), 1011060 for graphitic carbon (P6₃/mmc), 1100108 for α-Fe (Im-3m), 1534888 for γ-Fe (Fm-3m).

Fig. Supp. 14: X-ray diffractogram (red line) and Rietveld refinement (green line) of the carbon foam sample obtained from pyrolysis of 10 g of ferrocene after annealing for 23 h. The following database cards were used: 1011060 for graphitic carbon (P6₃/mmc), 1100108 for α-Fe (Im-3m), 1534888 for γ-Fe (Fm-3m).
Fig.Supp. 15: X-ray diffractogram (red line) and Rietveld refinement (green line) of the carbon foam sample obtained from pyrolysis of 10 g of ferrocene after annealing for 35 h. Note the disappearance of the 002 carbon reflection in the region of 26 degrees 2θ. Interestingly the presence of γ-Fe was still observed in the sample. Additionally small peaks of hematite Fe₂O₃ possibly due to oxidation of a small portion of residual CNOs after complete consumption of the carbon layers during annealing, were found. The following database cards were used: 1100108 for α-Fe (Im-3m), 1534888 for γ-Fe (Fm-3m) and PDF#33-0664 for hematite Fe₂O₃.

Fig.Supp. 16: XPS spectrum of as grown CNOs after annealing for 2 hours. Note the presence of a small peak ascribed to oxygen which can be attributed to adsorption of
oxygen in the outer layers of the CNOs-walls (as confirmed by XRD analyses above where no iron oxide phases were detected, Fig.Supp.13). Note that the penetration depth of the X-rays in this technique is below 10 nm (much lower than that of X-rays in the XRD measurements which is in the order of many micrometres, 8-10 micrometres). Considering that the thickness of the CNOs walls is in the order of 5 to 80 nm the signal of the Fe$_3$C crystal encapsulated inside the CNOs is expected to be low.

![XPS spectrum](image)

**Fig.Supp. 17:** XPS spectrum of the filled CNOs/CFM mixture after annealing for 20 hours. Note the presence of a peak ascribed to oxygen which can be attributed to adsorption of oxygen species in the outer layers of the CNOs-walls. This interpretation is in agreement with the XRD analyses shown above where no iron oxide phases are found after 20 hours of annealing (Fig.Supp.14). The strong C peak can be ascribed to the presence of a relatively large quantity of not yet converted CNOs in the surface of the CFM sample. Note the presence of a slight decrease in the C1s peak with respect to the case shown in Fig. Supp.16. As written above, it is important to notice that the penetration depth of the X-rays in this technique is below 10 nm (much lower than that of X-rays in the XRD measurements which is in the order of many micrometres, 8-10 micrometres). Therefore the signal of the Fe$_3$C/Fe crystals encapsulated inside the CNOs/CFM mixture is expected to be low.
Fig.Supp. 18: XPS spectrum of the filled CNOs/CFM mixture after annealing for 29 hours. Note the presence of KLL and 1s oxygen peaks which can be attributed to the possible formation of minor quantities iron oxide species byproducts (in agreement with the XRD analyses in Fig.Supp.15). A sharp drop in the intensity of the C1s peak is also found and can be ascribed to the conversion of the majority of the sample into CFM. Note in this case the increase in the intensity of the Fe2p peak and the appearance of other peak features (Fe LMM and Fe3s) which are also an indicator of 1) the formation of Fe-filled CFM in the sample and 2) the possible presence of iron oxide by-products, in agreement with XRD analyses above in Fig.Supp.15. As written above, it is important to notice that the penetration depth of the X-rays in this technique is below 10 nm (much lower than that of X-rays in the XRD measurements, which is in the order of many micrometres, 8-10 micrometres). Therefore the signal of the Fe crystals encapsulated inside the CFM mixture is expected to be low.