

Supplementary information:

Iron catalysts for the growth of carbon nanofibers: Fe, Fe₃C or both?

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Table S1. Types of catalysts and products at different growth temperatures

Temperature	575 °C	600 °C	650 °C	725 °C
Catalyst type	Fe ₃ C	Fe ₃ C	Fe ₃ C and Fe	Fe ₃ C and Fe
Product	CNFs	CNFs	CNFs	CNFs + CNTs

GROWTH:

Our optimised growth conditions correspond to 69% H, 18% C and 13% O (in atoms %), so that reducing elements are the major constituents of the plasma. Actually, we find little oxygen in the catalyst particles after growth, as shown in figures S1-3 below, which represent some electron energy-loss spectroscopy (EELS) mapping analysis on various carbon fibers after growth, with either Fe (figs. S1 & 2) or Fe₃C catalyst (fig. S3). Our understanding is that the role of water, as a weak oxidiser (as well as alcohol to a lesser extent), is essentially to remove amorphous carbon from the catalyst surface and avoid poisoning it during growth.^[1]

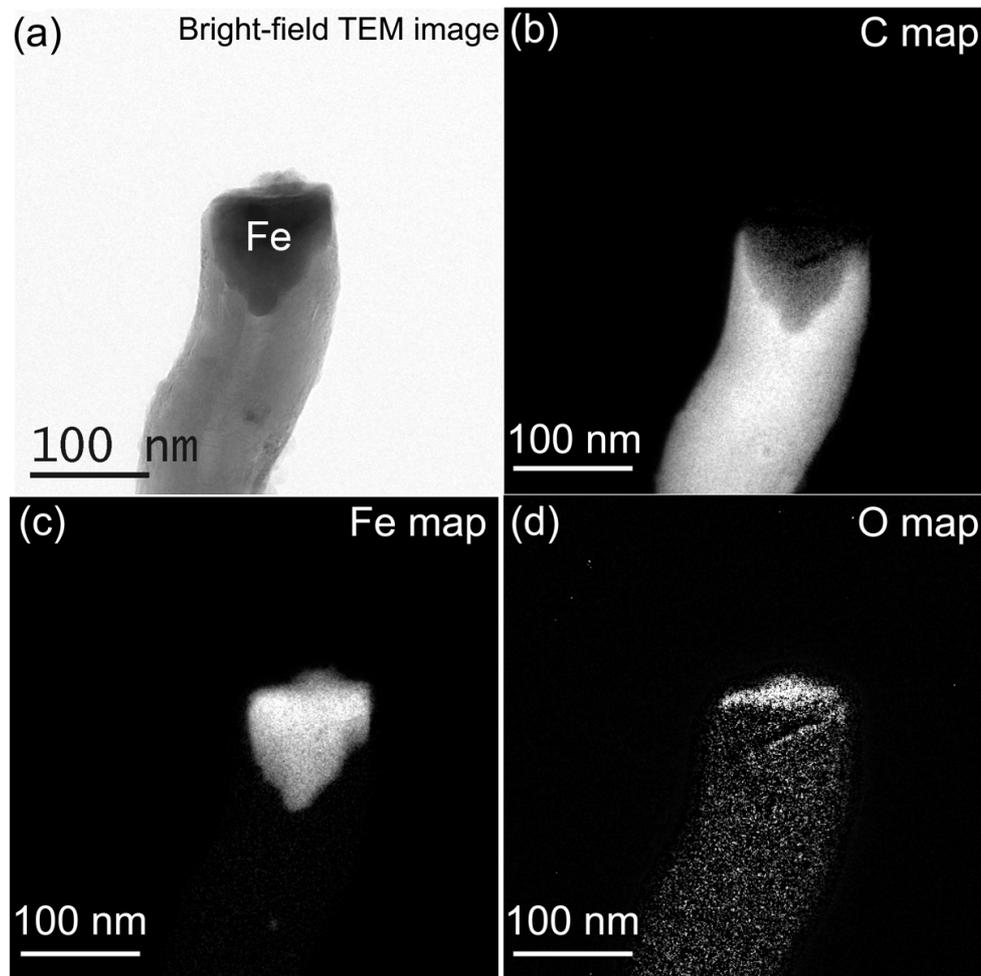


FIGURE S1: Element mapping of carbon (b), iron (c), and oxygen (c) of a CNF with Fe as catalyst.

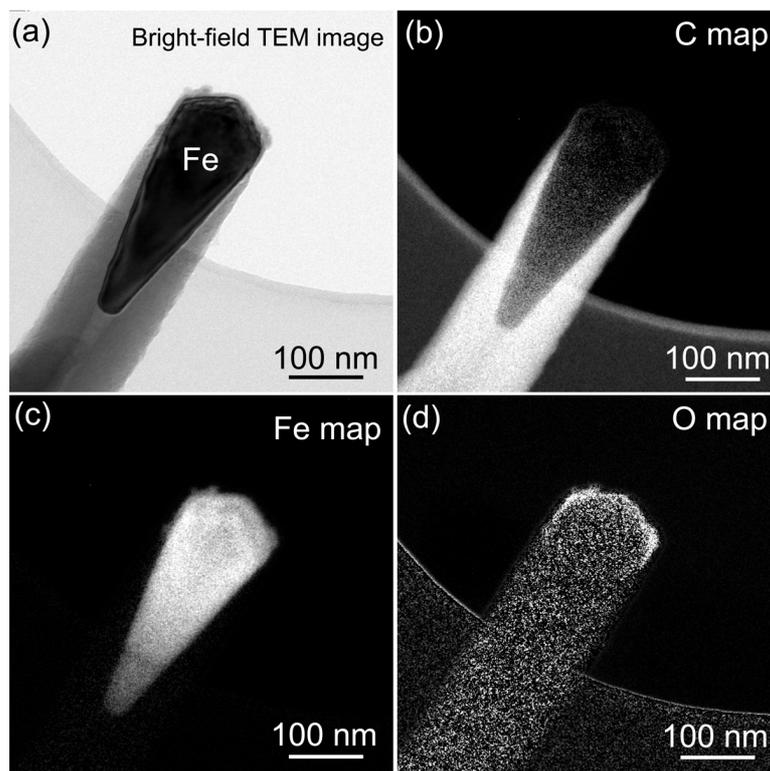


FIGURE S2: Element mapping of carbon (b), iron (c), and oxygen (c) of another CNF with Fe as catalyst.

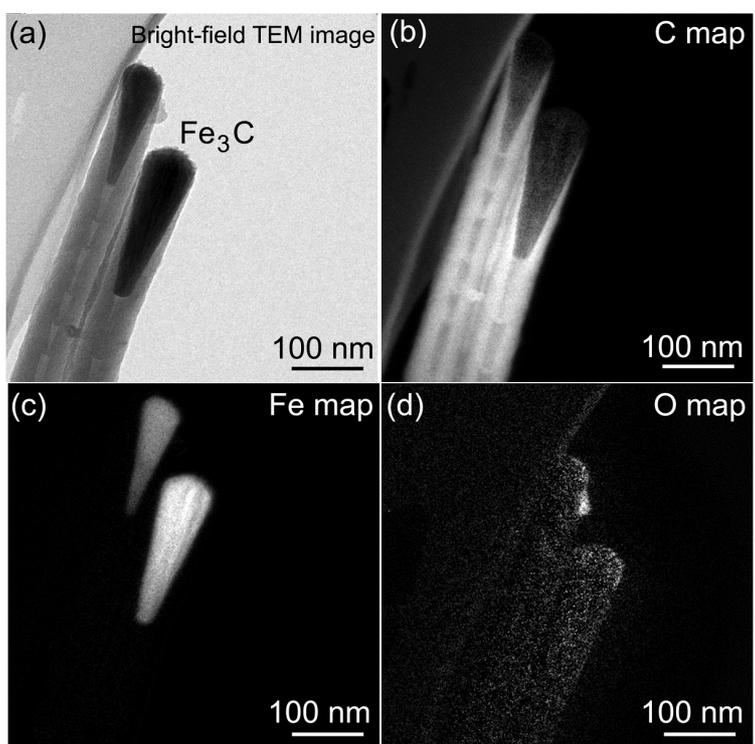


FIGURE S3: Element mapping of carbon (b), iron (c), and oxygen (c) of a CNF with Fe₃C as catalyst.

Indeed, the exposed surface of the catalyst particles seems to be slightly oxidised. However, there are at least three sources likely to contribute to the surface oxidation of catalyst particles: (i) oxide formation during the growth of CNFs; (ii) iron oxidation (native oxide) during the storage in air and at room temperature for some time; (iii), iron oxidation under the electron beam irradiation during the TEM experiments.^[2] We believe that the two latter reasons are likely to be the most important because the oxygen was found only at the bare surfaces of catalysts. Actually, the catalyst surface of CNTs/CNFs grown by PECVD is usually passivated by a carbon film after growth^[3], which prevents the formation of native oxide during storage; since we use water during growth, this carbon film is suppressed, which will tend to favour the formation of a native oxide, during storage (*i.e.*, before TEM analysis) and after growth.

ADDITIONAL CATALYST CHARACTERISATIONS

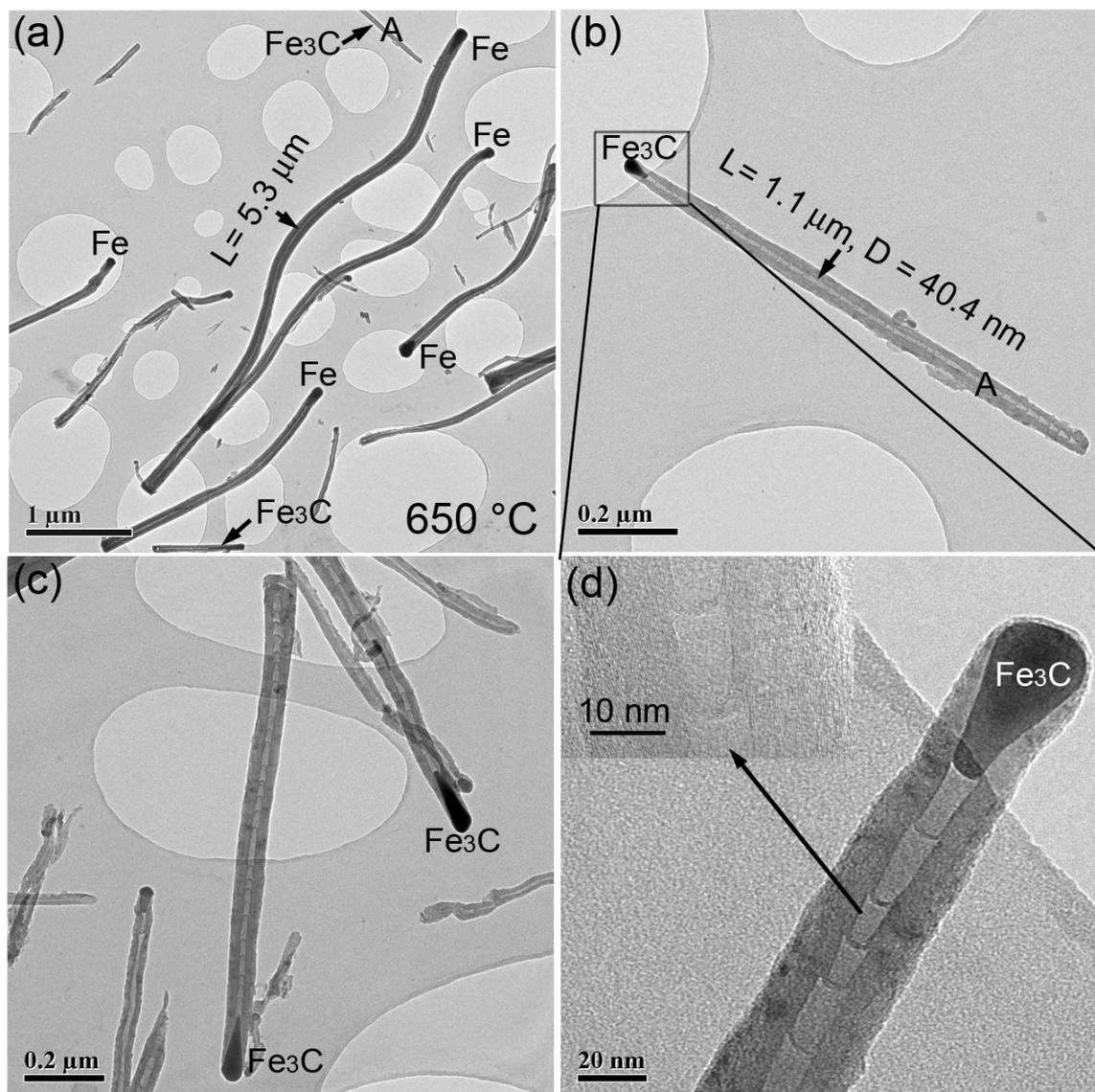


FIGURE S4. (a) TEM images of CNFs grown at 650 °C. CNFs catalyzed by Fe are longer and thicker than those catalysed by Fe₃C. (b-d) CNFs catalyzed by Fe₃C have always bamboo-like morphology with quasi-periodically arranged internal graphene membranes forming separated compartments inside the CNFs.

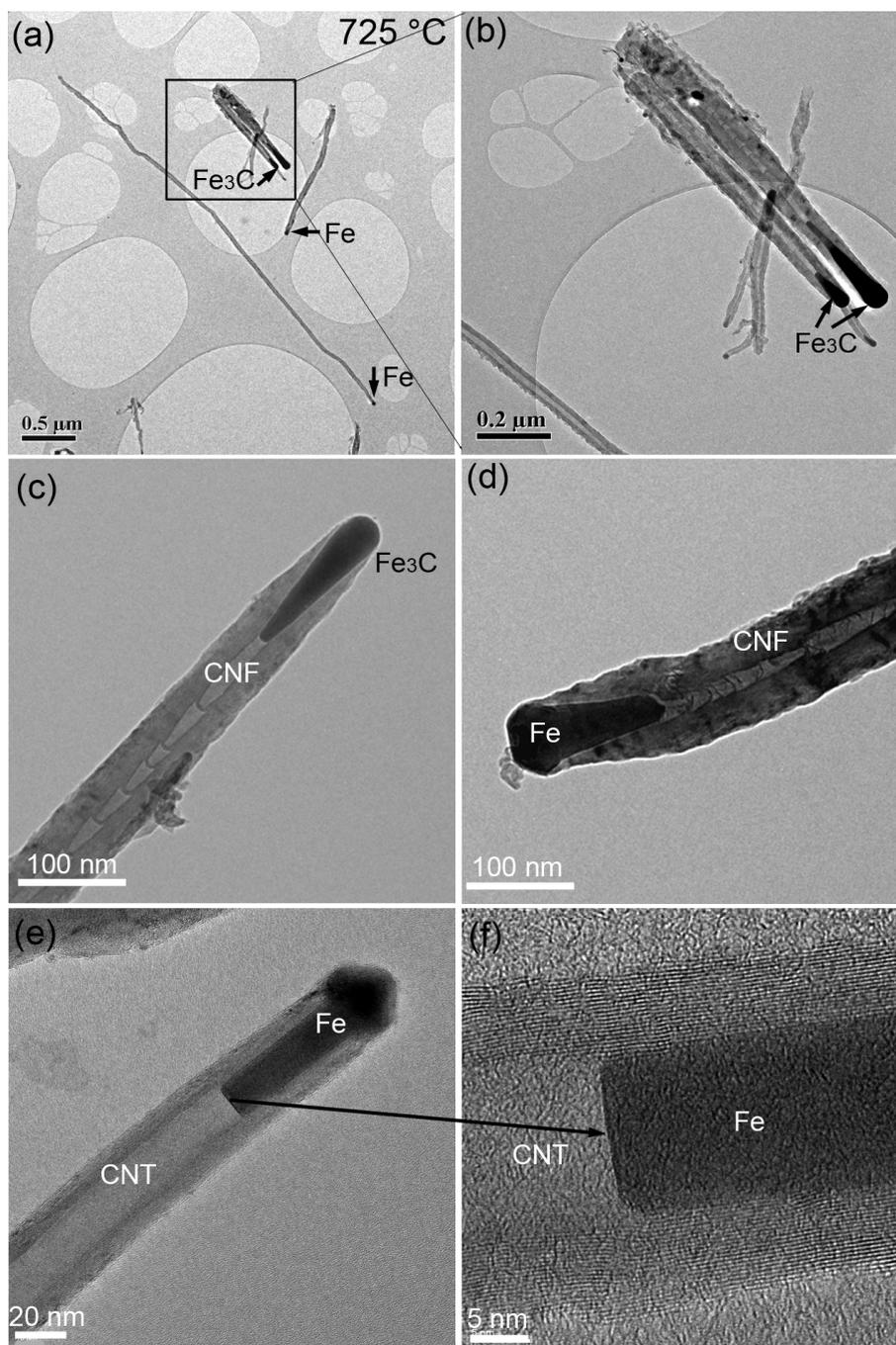


FIGURE S5. TEM images of CNFs grown at 725 °C. (a) CNFs catalyzed by Fe are longer than those catalysed by Fe₃C, but their diameter is reduced compared to what it was at 650 °C. (b,c) CNFs catalyzed by Fe₃C always exhibit a bamboo-like morphology with quasi-periodically arranged internal graphene membranes forming separated compartments in the inner part of CNFs. (e,f) CNTs are often observed at 725 °C, with Fe nanoparticles acting as the catalysts for their growth.

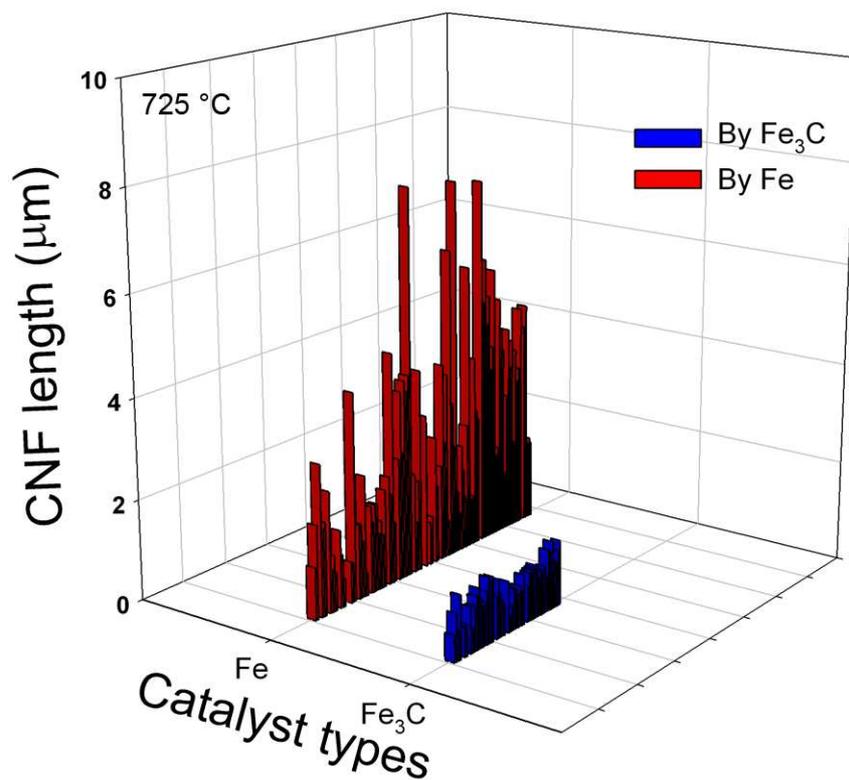


FIGURE S6. Plots of the length of CNFs catalyzed by Fe and Fe₃C at 750 °C. The length is measured by TEM. The average length of Fe-catalysed CNFs is nearly 3 times that of Fe₃C-catalysed CNFs.

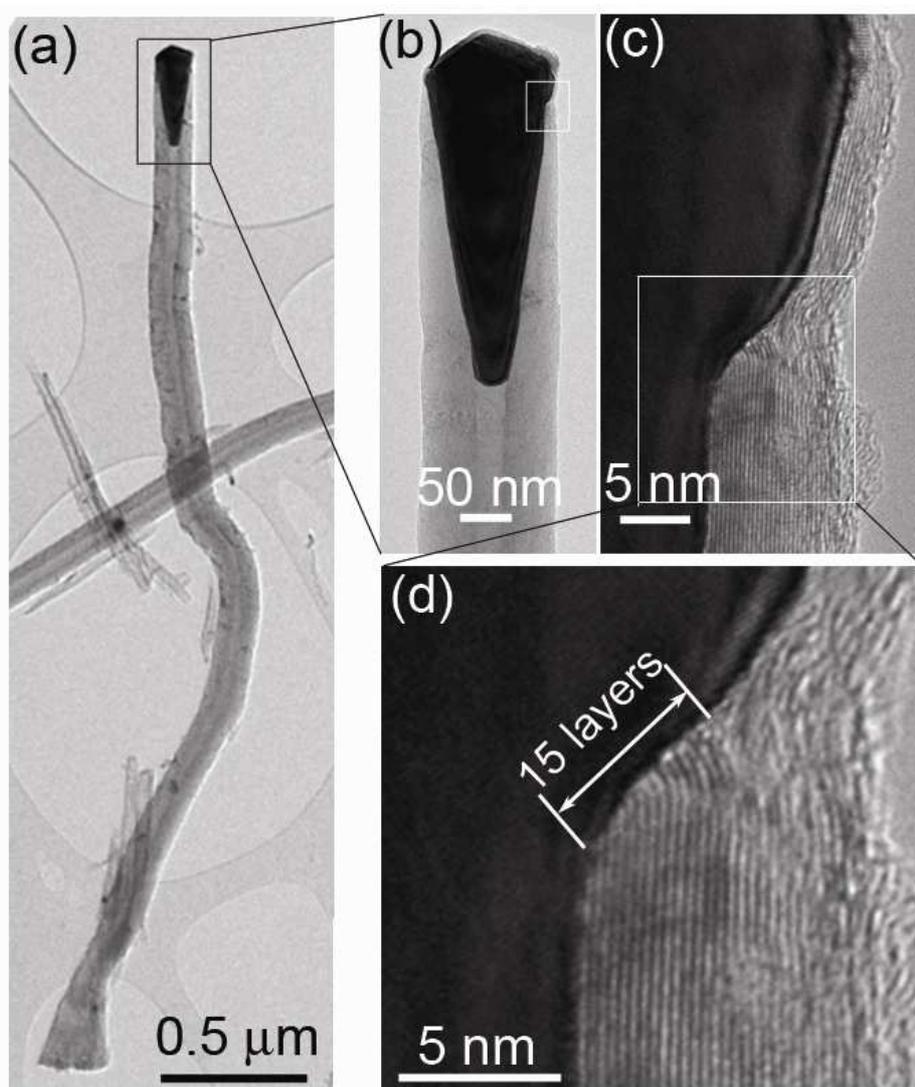


FIGURE S7. One CNF catalyzed by Fe. (a) low-magnification morphology of Fe and the corresponding CNF. (b,c) magnified image of the Fe catalyst. (d) HREM image showing the junction between Fe and the CNF. A group of 15 graphene layers nucleated under the Fe leading edge, where the step density is large is clearly shown.

REFERENCES:

- (1) See *e.g.*, Hata, K.; Futaba, D. N.; Mizuno, K.; Namai, T.; Yumura, M.; Iijima, S. *Science*, **2004**, *306*, 1362.
- (2) He, Z. B.; Maurice, J.-L.; Lee, C. S.; Gohier, A.; Pribat, D.; Legagneux, P.; Cojocaru, C. S. *Carbon*, **2011**, *49*, 435.

(3) Minoux, E. ; Groening, O. ; Teo, K. B. K.; Dalal, S. H.; Gangloff, L.; Schnell, J. -P.; Hudanski, L.; Bu, Y. Y.; Vincent, P.; Legagneux, P.; Amaratunga, G. A. J.; Milne, W. I. *Nano Lett.*, **2005**, 5, 2135.