Hydrothermally synthesised Fe$_2$O$_3$ nanoparticles as catalyst precursors for the CVD production of graphitic nanofibres

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Abstract. Graphitic nanofibres (GNFs) have been grown by chemical vapour deposition at 500°C and 700°C, using 6 nm and 20 nm particles of Fe$_2$O$_3$ produced by supercritical water hydrothermal synthesis (scWHS). The morphologies of catalyst and GNFs have been examined using the combined techniques of conventional transmission electron microscopy, high resolution electron microscopy, selected area electron diffraction and powder X-ray diffraction. GNF production varied from well ordered nanofibres with an average diameter of 100 nm, to very large, disordered fibres with diameters ranging from 500 nm to ~2 μm. Larger fibres were found to have a compound structure composed of discreet domains of graphite and multiwall nanotubes. 20 nm particles produced by scWHS were associated with significant increases in the yield of GNFs as compared with traditional catalyst precipitation routes.

1. Introduction

In recent years nanostructured carbon has proved to be an intriguing materials system. Carbon nanotubes (CNTs) and graphite nanofibres (GNFs) have already been utilised as electrically conductive fillers in polymer composites and as lubricants, with other potential applications including use in field emission and nanometre scale electronic devices and as hydrogen storage materials [1]. However, as with any novel material, the practical employment of GNFs and CNTs in commercially viable technologies requires a high level of control over the material functional properties, morphology and yield. In the case of nanostructured carbon, this level of control may become attainable through improved knowledge of the catalyst mediated carbon nanostructure growth mechanism. Although much research has been carried out to determine the growth mechanisms of such materials, many aspects of the growth are not yet understood. One area requiring clarification is the process by which synthesis temperature and hydrocarbon/hydrogen concentration lead to a modification of the nanofibre morphology. This can result for example, in transitions from herringbone nanofibre morphology, with graphitic planes stacked as cones around a diamond shaped catalyst particle, to a platelet nanofibre morphology, with graphitic planes normal to the long axis of the nanofibre emanating from an oval catalyst particle. Alternatively, a multiwall nanotube structure may be produced, associated with either a rounded, encapsulated catalyst particle, or with a clean catalyst particle with exposed facets [2]. Other areas of contention concern the phase of the catalyst particle throughout nanofibre development and the driving forces that result in the absorption, diffusion and precipitation of the carbon leading to nanofibre propagation [3].

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Here, the use of nanoparticulate Fe$_2$O$_3$ catalyst precursors for the chemical vapour deposition (CVD) growth of graphitic nanofibres is presented. Although Fe$_2$O$_3$ has been used in the past as a convenient precursor for iron, through a novel production process using supercritical water hydrothermal synthesis (scWHS) [4], precise control of the nanoparticle size distribution is attainable, thereby providing a suitable catalyst on which to carry out the growth of nanostructured carbon. CVD growth is performed on two size distributions of scWHS Fe$_2$O$_3$ nanoparticles to appraise the effect on carbon morphology and further comparison made with the yield produced using precipitated Fe$_2$O$_3$.

2. Experimental

Fe$_2$O$_3$ nanoparticles were synthesized through the hydrothermal reaction of supercritical water and iron (III) nitrate nonahydrate using dehydration temperatures of 300°C and 100°C, respectively. Fe$_2$O$_3$ particles were also prepared according to a simple precipitation method, whereby iron nitrate was heated with an aqueous ammonia solution to 100°C, under magnetic stirring. Graphitic nanofibres were grown on the freeze-dried Fe$_2$O$_3$ particles by CVD, using a controlled environment horizontal tube furnace. Catalysts were heated under argon to the reaction temperature of 500°C or 700°C, and subsequently exposed to a synthesis gas mixture of 80% H$_2$/20% C$_2$H$_4$ for 1 hour, before natural cooling under argon. Nanoparticles and graphitic nanofibres were structurally characterized by powder x-ray diffraction (PXRD) using a Bruker D8 diffractometer. Nanoscale imaging and selected area electron diffraction (SAED) were carried out using a Jeol 2000fx transmission electron microscope (TEM) equipped with an ISIS energy dispersive x-ray (EDX) analysis system. HREM was carried out using a Jeol 4000fx equipped with a Gatan image filter. TEM samples were prepared by sonicating the powders in acetone for three minutes and then pipetting drops of the suspension on holey carbon film copper grids.

3. Results and Discussion

Figure 1 presents conventional bright field TEM images of the three varieties of catalyst precursor used for graphitic nanofibre synthesis. Figure 1a shows the morphology of catalyst particles prepared through the precipitation technique, whereas Figures 1b and 1c show particles synthesised by ScWHS at 300°C and 100°C, respectively. The larger particles (Fig.1b), were crystalline with a mean diameter of 20 nm and exhibited a faceted morphology, while the smaller particles (Fig.1c), with a mean diameter of 6 nm, exhibited less well defined morphology and extent of crystallinity. Particle comparison emphasizes that the supercritical synthesis process, as compared with simple precipitation, is capable of producing catalysts with smaller mean diameters and greater morphological and dimensional control.

Table 1 presents the GNF yields for the three catalyst size distributions at the two CVD reaction temperatures. The yields were calculated for one hour syntheses as the percentage mass increase due to GNF deposition relative to the starting mass of Fe catalyst, accounting for the decomposition of Fe$_2$O$_3$ to Fe during initial reaction. In particular, the 20 nm scWHS particles were responsible for a
large increase in nanofibre yield at both CVD temperatures. The details of each experiment are discussed below.

Figure 2a shows a bright field image of GNFs produced by CVD at 500°C using the 20 nm scWHS Fe₂O₃ nanoparticles. The nanofibres exhibited a well ordered graphitic structure and both platelet and herringbone morphologies were observed, associated with diamond and oval shaped single crystal catalyst particles, respectively. Figure 2b shows two herringbone fibres emanating from an Fe₃C catalyst particle. The Fe₃C is considered to be a reaction product arising from the initial reduction of Fe₂O₃ to Fe and final cool down of the Fe-C solid solution formed during GNF growth. The catalyst particles and nanofibres had a mean diameter of 100 nm whilst the yield of the nanofibres was greater than that obtained from the precipitated catalyst with 485% and 210% mass increases, respectively. The high level of graphitic ordering within these nanofibres suggests that carbon deposition in this instance occurred as part of a steady-state growth process.

Figure 3 shows bright field images of the fibres produced at a CVD growth temperature of 700°C using the 20 nm scWHS Fe₂O₃ nanoparticles. For these experimental conditions the yield of carbon deposited was much higher than that produced using conventional Fe₂O₃ catalyst synthesis, with a 1033% mass increase. However, the fibres produced were less well ordered and had a much broader diameter distribution, ranging from 500 nm to ~2 µm. In particular, it is noted that the large fibres exhibited a pseudo-platelet morphology with graphite planes normal to the fibre long axis. However, growth appeared to be emanating from a cluster of particles measuring 50 nm to 1 µm, rather than a single crystal catalyst particle normally associated with GNF growth. A striped texture was also associated with many of the larger fibres. At high magnification however, such nanofibres often appeared to consist of smaller graphitic domains with multiwall nanotubes observed at the nanofibre surface, constituting a ‘compound nanofibre’ (e.g. Figures 3c and 3d). The presence of multiwall nanotubes at the GNF edge (Fig. 3d) suggests that the smaller catalyst particles may be producing finer tubes and fibres that coalesce to form much larger compound GNFs. Additional material comprising globular clumps and strands of carbon with irregular morphology were also identified (e.g. arrowed in Figure 3a). The striped texture and disordered graphitic nature of the fibres produced suggests that the carbon deposition in this instance was symptomatic of a non-steady-state growth process.

No carbon deposition was observed under CVD growth conditions of 500°C using 6 nm scWHS nanoparticles of Fe₂O₃. PXRD investigations demonstrated that the Fe₂O₃ had reduced to Fe during this CVD process, but the resultant lack of carbide formation and absence of GNF growth proves to be an intriguing result. The nanoparticles simply agglomerated to form large single crystals (Figure 4). The implication is that carbon absorption is inhibited for these particles under these growth conditions, but this aspect requires further study.

Figures 5a and 5b illustrate the GNFs produced under CVD growth conditions of 700°C using 6 nm scWHS Fe₂O₃ particles. The resultant nanofibres were graphitically disordered, adopting herringbone and platelet morphologies, and a compound sub-structure. This is highlighted in the HREM image of Figure 5b, which shows distinct graphitic domains. Nanofibre dimensions were of the order of 500 nm, whilst nanofibre yield was found to be comparable to that of the precipitated catalyst with a 343% mass increase. As with the GNFs produced at 700°C using 20 nm scWHS Fe₂O₃ particles, it appears from this GNF morphology that a non-steady-state deposition process is associated with these experimental growth parameters.

**Table 1: GNF yields**

| Fe₂O₃ catalyst | Percentage GNF yield |
|----------------|----------------------|
| Precipitated   | 210                  |
| scWHS (6 nm)   | 0                    |
| scWHS (20 nm)  | 485                  |

| | 500°C | 700°C |
|---|-------|-------|
| Precipitated | 368   |       |
| scWHS (6 nm)   | 343   |       |
| scWHS (20 nm)  | 1033  |       |

Figure 2. (a) TEM image of GNFs produced by CVD at 500°C using the 20 nm scWHS Fe₂O₃ catalyst. (b) Fe₃C catalyst particle and the associated GNFs.
In summary, scWHS allows control over the size distribution and morphology of Fe₂O₃ nanoparticles, making them ideal catalyst precursors for the regulated production of GNFs through CVD. The processing relationships between GNFs and the catalyst particles employed in their growth have been examined. Variation in the starting particle size (6 nm and 20 nm) and synthesis temperature (500°C and 700°C) was found to have a substantial effect on the nanofibre morphology and the final catalyst particle shape. GNFs varied from well-ordered herringbone and platelet fibres to disordered compound nanofibres, comprising smaller graphitic domains and nanotubes. From these results it appears that CVD performed at 500°C using crystalline 20 nm Fe₂O₃ particles can be used to produce highly ordered GNFs at higher yields than those obtained using the precipitated catalyst, through a steady-state growth process. Even higher yields can be attained at 700°C using this catalyst albeit by means of a non-steady-state growth process and, at the expense of graphitic ordering and dimensional control.

4. References

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