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Synthesis and H_2 adsorption on graphitic nanofibres

M. Bououdina, D. Grant, G. Walker*

Advanced Materials, School of Mechanical, Materials, Manufacturing, Engineering and Management,
University of Nottingham, Nottingham NN7 2RD, UK

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Abstract

Graphitic nanofibers (GNFs) were successfully synthesised at low temperatures (500 °C) using NiO powder as the catalyst precursor and a H_2/C_2H_4 gas mixture with a high yield, around 60 g $g_{catalyst}^{-1}$ h^{-1}. XRD patterns confirm that during the formation of GNFs the NiO was reduced to form metallic Ni. TEM study confirmed the formation of a graphitic phase in the form of GNFs, where the diameter is controllable with synthesis temperature, from 500 to a few nm. Surface treatments have been carried out and these have been used to modify the GNF morphology and surface chemistry. H_2-uptake measurements using a Sievert's apparatus are reported and correlated with the GNF properties.

Keywords: Graphite nanofibers; TEM; XPS; H_2-uptake

1. Introduction

Many intermetallic materials such as ($LaNi_5$, $ZrMn_2$, TiFe, Mg, etc.) have shown a reversible H_2 absorption/desorption reactions [1]. However, most of these materials are too heavy to meet the DOE H_2 capacity target of 6.5 wt.% for on board transport storage systems. Mg-based hydrides such as MgH_2 and Mg_2NiH_4 have been rekindled recently, due to their large H-storage capacities, 7.6 and 3.8 wt.%, respectively, but their technical applications are limited by their slow hydriding/dehydriding kinetics and high decomposition temperatures, 275 and 255 °C (at 1 atm), respectively [2]. Graphitic nanofibers (GNFs) belong to carbon nanostructures based on that for graphite. The basic microstructure consists of stacked graphite layers, which can be arranged parallel/perpendicular to the fiber axis, or herringbone structure, often with an amorphous component. The angle between the graphitic planes and the fiber axis which determine the type of structure is determined by the shape of the catalyst particle, as reported by Boellard et al. [3]. The as-prepared GNF morphology and microstructure depend on catalyst composition, catalyst support, gas mixture, and reaction temperature. In addition, GNFs can be produced with different diameters, ranging from 10 to 200 nm. Recently, H_2 adsorption exhibited by GNFs, have attracted attention as potential candidate as a hydrogen storage materials (HSM). There are some H_2 storage capacities reported for GNFs from 1–2 wt.% up to 10 wt.% [4–7], but there is a lack of reproducibility in these measurements. Theoretically, H_2 can be adsorbed on the surface and then incorporated between graphitic sheets of GNFs. The space between the sheets which is ≥3.35 Å, acts like a slit-shaped pore hence enabling GNFs to physisorb large amounts of H_2, whose kinetic diameter is only 2.89 Å [4]. H_2 capacity of GNFs has been measured by volumetric [8], gravimetric (TG) [9], and thermal desorption spectroscopy (TDS) [10]. But, nevertheless, the reported H_2 capacities are disparate, and further studies are needed to better understand the factors that influence the values (as well as the measurements). The irreproducibility is partially due to poor characterisation, highly variable GNF samples, and other experimental parameters concerning the H_2-uptake measurements such as: low amounts of GNFs used (around 50 mg or even less), low H_2 purity and humidity of H_2 gas.

In this paper, we report the synthesis of graphitic nanofibers as well the formation of Ni carbide phase at low temperatures, and the effect of the synthesis temperature on the type of the graphitic structure formed. The GNF samples were characterised by XRD, TEM, XPS, BET and H_2-uptake measurements.

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* Corresponding author. Tel.: +44 115 951 3752; fax: +44 115 951 3800.
E-mail address: gavin.walker@nottingham.ac.uk (G. Walker).

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2. Experimental

GNFs were prepared using NiO powder as the catalyst precursor, the NiO powder was synthesised using Ni-nitrate [$Ni(NO_3)_2·6H_2O$] (Alfa Aesar) solution added to 2 M ammonia solution (Fisher Scientific) and dried at 120 °C. The catalyst precursor was loaded in an alumina crucible and placed in a tube furnace. The feedstock gas H_2/C_2H_4 at 80:20 sccm, was flowed for 2 h at a given temperature (500 and 700 °C). The reflux treatment was carried out using 30 mg of GNF powder in 100 ml of 2 M nitric acid (HNO_3) at 110 °C for 2 h. The samples were washed with deionised water and then dried at 80 °C. GNF samples were characterised using X-ray diffraction (Siemens D500 equipped with Kα Cu $\lambda = 1.5418$ Å), transmission electron microscopy (JEOL JEM-2000FX II), X-ray photoelectron spectroscopy (VG Scientific ESCA Lab X-ray photoelectron spectrometer fitted with a twin Mg/Al X-ray) and BET surface area analysis (Quantachrome Autosorb-1). The GNF samples were degassed at 200 °C for 2 h prior to multipoint (7 points) BET measurements. H_2-uptake measurements have been carried out using a Sievert's apparatus. The samples were degassed at 200 °C under high vacuum for 1 h.

3. Results

3.1. GNFs synthesis

The GNFs growth depended on the experimental conditions. It has been found that: (i) the efficiency of the synthesis procedure depends on the temperature [11]; (ii) the GNFs were synthesised at relatively low temperatures (350–400 °C) with an optimum yield of 57 $\mathrm{g\,g_{catalyst}^{-1}\,h^{-1}}$ within the temperatures range 500 °C $\leq T \leq$600 °C, but decreased drastically below this temperature range, 2.4 $\mathrm{g\,g_{catalyst}^{-1}\,h^{-1}}$ at 350 °C; (iii) the use of a low H_2/C_2H_4 gas ratio mixture, gave proportionally higher GNF growth rates, as the ratio of carbon carrying gas is increased. Furthermore, it is found that the presence of Ni_3C phase as catalyst favours the formation of more crystalline fibers at low temperatures, fine diffuse bands can be observed from SAD patterns.

3.2. XRD

Fig. 1 displays X-ray diffraction patterns of GNFs prepared at different 500 and 700 °C before and after reflux treatment. A very broad carbon diffraction line (0 0 2) can be observed with the presence of some additional diffraction peaks with low intensity, attributed to Ni metal.

3.3. BET analysis

Table 1 reports the values of surface area of the as-prepared GNFs and after reflux treatment. It can be noticed that the GNFs surface areas were influenced by the synthesis temperature, increasing with lower synthesis temperature, 51 $\mathrm{m^2\,g^{-1}}$ for the 700 °C sample compared to 170 $\mathrm{m^2\,g^{-1}}$ for the 500 °C sample. After reflux treatment, the surface area increases three times higher for GNFN7 and only 13% for GNFN3.

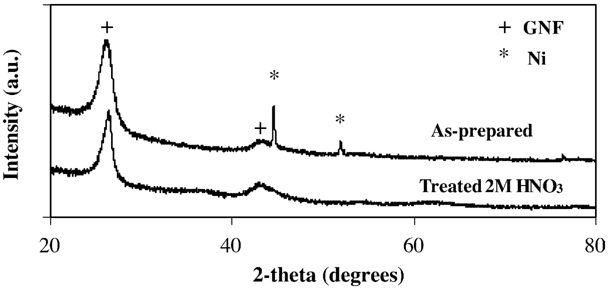

Fig. 1. XRD patterns of GNF3 as-prepared and after reflux treatment.

3.4. XPS analysis

XPS analysis was carried out on selected GNF sample prepared at 500 °C. From the C1s spectra, it is clear that the spectrum consists of a main binding energy peak with high intensity attributed to graphitic C–C species and another small peak with relatively low intensity attributed to C–O. This is in good agreement with values reported in literature, 284.7 eV [12]. Moreover, no additional binding energy peaks were detected, which could be attributed to the presence of impurities. After reflux treatment the C–C graphite peak keeps same position. However, additional binding energy peaks were detected, which could be attributed to the presence of impurities, such as $Ni(OH)_2$.

3.5. TEM analysis

TEM images of some selected as-prepared GNFs are displayed in Fig. 2. For the sample prepared at 500 °C (GNFN3), the fiber diameters could be grouped into three ranges (Fig. 2a): large (>100 nm), medium (30–100 nm) and small (<30 nm). Selected area diffraction (SAD) pattern gave two arcs in line with the fiber axis consistent with a platelet structure. The diffuse nature of the pattern indicates some level of amorphisation within the fiber, in agreement with the relative intensities area observations stated above.

TEM image of GNFs synthesised at 700 °C shows mainly two fiber diameters (Fig. 2b): large (>100 nm) and small (<30 nm). It was noticed that the fibers had a smaller length compared to those synthesised at 500 °C. SAD pattern of the 100 nm fiber shows well-defined arcs that indicates a platelet type microstructure, with a more defined crystallinity structure.

Table 1
Surface area of selected GNFs samples

Sample	As-prepared GNF	Treated GNF
GNFN3	170	192
GNFN7	51	132

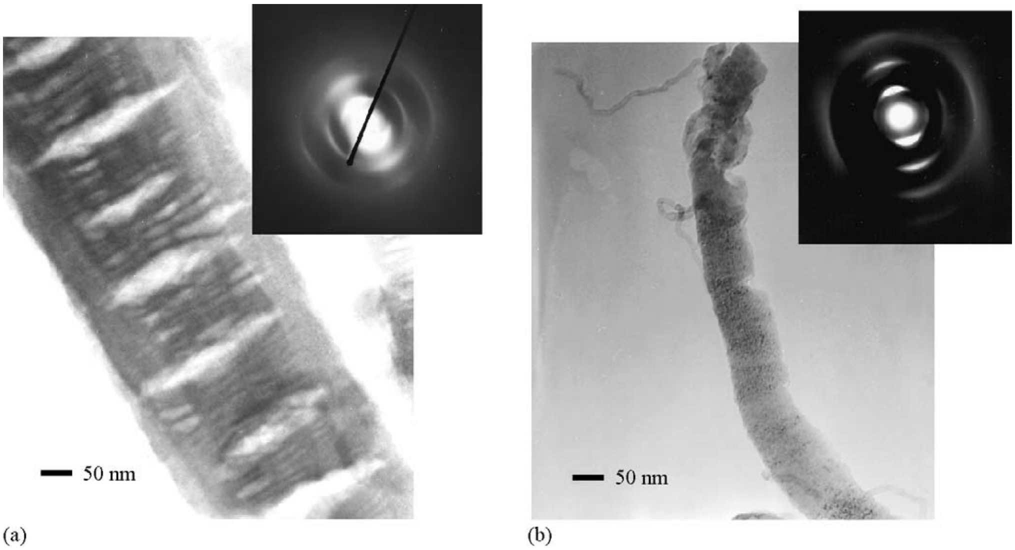

Fig. 2. TEM images of as-prepared GNFs: (a) at $T = 500\,^{\circ}\mathrm{C}$ and (b) at $T = 700\,^{\circ}\mathrm{C}$.

3.6. H_2-uptake measurements

After degassing, 100 bar of H_2 pressure were admitted into the sample chamber. After 20 h, no significant H_2-uptake was measured for either the as-prepared or the reflux treated samples (<0.2 wt.%).

4. Discussion

GNFs were synthesised in high yield using NiO as the catalyst precursor and achieved a yield of 60 g g_{catalyst}^{-1} h^{-1}. Both XRD and TEM analyses confirm the formation of GNF. NiO was used as the catalyst precursor. NiO diffraction peaks were not detected on XRD patterns of as-prepared GNFs. However, new peaks were observed and indexed as Ni metal. TEM images show that the diameter as well as the length vary with the preparation temperature, ranging from a few nanometres to 500 nm, and can be microns in length. BET measurements carried out on prepared GNFs showed an increase in surface area with lowering synthesis temperatures as well after nitric acid reflux treatment. No H_2-uptake has been observed for both as-prepared and treated samples. This may be due to the amorphous carbon film which remain on the surface of the fibers even after reflux treatment or to the remaining residual impurities that formed during the growth or surface treatment. No significant H_2-uptake has been detected so far, further surface treatments are underway in an attempt to improve the H_2 adsorption. Any adsorbed H_2 was merely due to physisorption to the external surface of the GNFs.

5. Conclusion

GNFs were successfully synthesised by thermal CVD method using unsupported NiO powder as a catalyst precursor and H_2/C_2H_4 mixture gas. XRD, XPS and TEM analysis confirmed the formation of GNFs. The surface area of as-prepared GNFs increased after reflux treatment, about three times higher than as-prepared sample. H_2-uptake measurements showed no significant uptake for these samples.

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