SYNTHESIS OF PURE AND NITROGEN DOPED NANOTUBES WITHIN CARBON FIBRE CLOTH MATRIX

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Abstract

Three-dimensional (3D) carbon nano-structures containg carbon nanotubes (CNTs) and less crystalline carbon nanofibres (CNFs), essential for development of many applications, are still challenging from the synthesis perspective. Well known engineering materials such as carbon, ceramic or glass fibres could be exploited as a support for the formation of 3D nano-structures. We have demonstrated use of non-woven carbon fibre cloth as a 3D scaffold for CNT synthesis with the nanotubes filling the spaces between carbon fibres.

Introduction

Carbon nanotube - carbon fibre composite materials and 3D carbon nano-structures are increasingly important for aerospace and automotive applications. Growth of CNTs and CNFs on the surface of carbon fibres was first reported to improve composite shear strength (Dawns and Baker, 1991; Dawns and Baker, 1995) and load transfer at the fibre/matrix interface (Thostensen et al., 2002). The high surface area of carbon and ceramic fibres coated with nanotubes and nanofibres is important for use in electrochemical applications (Sun et al., 2003; Wang et al., 2004, Marphy et al., 2003). Jo et al. (2004) reported excellent field emission properties of CNTs grown on the surface of carbon fibres in carbon cloth, which could potentially be used in flat panel displays. Boskovic et al. (2005) reported low temperature DC PECVD synthesis of carbon nanofibres on the surface of carbon fibres using Co colloid catalyst. However, growth of CNTs on the carbon fibre surface could only have limited impact on the bulk properties due to the relatively small thickness of the CNT layer. In order to more efficiently fill the empty space between carbon fibres in the cloth with CNTs we developed a simple floating catalyst method using thermal CVD that is suitable for scale-up. The carbon nanotubes were grown using a solution of ferrocene in toluene as a source of iron catalyst and carbon at 760 °C The carbon nanotubes were found not attached to the carbon fibre surface but rather grow in between them. Pyrazine ($C_4H_2N_2$) was added to the solution of ferrocene in toluene in order to introduce nitrogen into the system and grow nitrogen doped CNTs. Doping nanotubes with nitrogen is expected to particulary improve the electrical conductivity and provide different approaches of activating the surface of the nanotubes. The addition of pyrazine into the otherwise hydrocarbon feedstock was also found to produce mochiral multi-walled carbon nanotubes, where all of the grapheme layers within each CNT were either zigzag or armchair (Koziol et al., 2005).

Experimental

Carbon fibre bundles, woven and non-woven carbon fibre cloth can be used as a three-dimensional scaffold for carbon nanotube synthesis on surface of carbon fibres and in the empty space between them. A floating catalyst method, already optimised for CNT synthesis (Singh et al., 2003), has been used to create a dense 3D carbon structure within the volume of carbon fibre cloth. The nanotubes were grown at 760 ^{o}C and at feed rate of 1.2 ml/hour of a 9.6 wt% ferrocene in toluene solution. A mixture of Ar and 10% H_2 was used as the carrier gas and the total gas flow rate was maintained at 750 ml/min. The first stage furnace was pre-heated at 200 ^{o}C to ensure that ferrocene in toluene solution is vaporised as it was injected. The second stage furnace, where nanotubes were grown for 2 hours was at 760 ^{o}C. Pyrazine ($C_4H_2N_2$) was also added to the solution of ferrocene in toluene in order to introduce nitrogen into the system and grow nitrogen doped carbon nanotubes. The nitrogen-doped carbon nanotubes were grown at 760 °C using argon as a carrier gas.

Results and Discussion

The use a floating catalyst method with ferrocene in toluene solution resulted in CNT growth in an empty space between the carbon fibers in carbon fibre cloth (Fig. 1 and Fig. 2). The nanotubes are approximately 10 to 20 µm long, much longer than nanotubes that could be grown on the surface of carbon fibres, and with diameters ranging from 10 to 100 nm. The nitrogen-doped carbon nanotubes were grown between carbon fibres and when unsupported by the substrates they formed octopus-like structures where many nanotubes were grown from the same central catalyst particle (Fig. 2b). These nanotubes are not attached to the carbon fibre surface and can be preserved in the matrix by impregnation with polymers or other carbon materials. This will allow the formation of high CNT weight fractions polymer or carbon-carbon composites that could transfer excellent CNT properties to the macroscopic level. Alternatively, nanotubes could be blown away from the matrix using gas at a high flow rate.

It is also possible to synthesized CNTs and CNFs by using a process in which the catalyst is impregnated and dispersed within the carbon fibre cloth. Boskovic (2004) has found that when the catalyst is impregnated and dispersed within a fibrous matrix (carbon or ceramic fibre cloth or felt), rather than being left on the surface, a more efficient deposition of nanofibres and/or nanotubes results. A fine iron powder catalyst dispersed in iso-propanol was impregnated within carbon cloth (VCL N, Morgan Crucible Plc) using an ultrasonic bath. The samples were then dried producing a fibrous matrix with an impregnated finely dispersed metal powder. Carbon nanotubes and nanofibres were grown using an ethylene and hydrogen mixture at 650 ºC. The nanotubes/nanofibres are produced in clumps originating from the surface of the catalyst particles. The amount of carbon nanomaterials produced could be controlled using variation of catalyst loading.

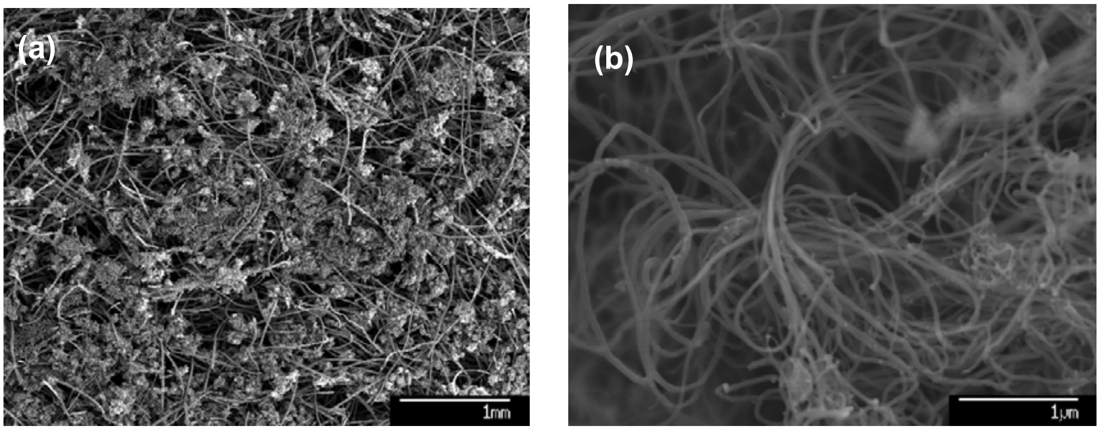

Figure 1. SEM images of carbon nanotubes grown on the carbon fibre cloth (VCL N, Morgan) using 9.6 wt% ferrocene in toluene in Ar flow: (a) CNT carpet between carbon fibres in the cloth, (b) enlarged surface of the CNT carpet showing individual carbon nanotubes.

Veedu et al. (2006) reported that well-aligned CNTs grown perpendicular to 2D woven fabric of SiC fibres improved significantly the mechanical and thermal properties. Interlaminar fracture-toughness of the resulting 3D composite has shown an improvement of 348% compared with the base composite without CNTs. The interlaminar shear sliding fracture toughness was improved by about 54%. It is also reported that addition of carbon nanotubes has significantly improved the dissipation of vibrational energy under cyclic loading. The coefficient of thermal expansion was reduced to 38% of the original value and thermal conductivity was improved by 51%.

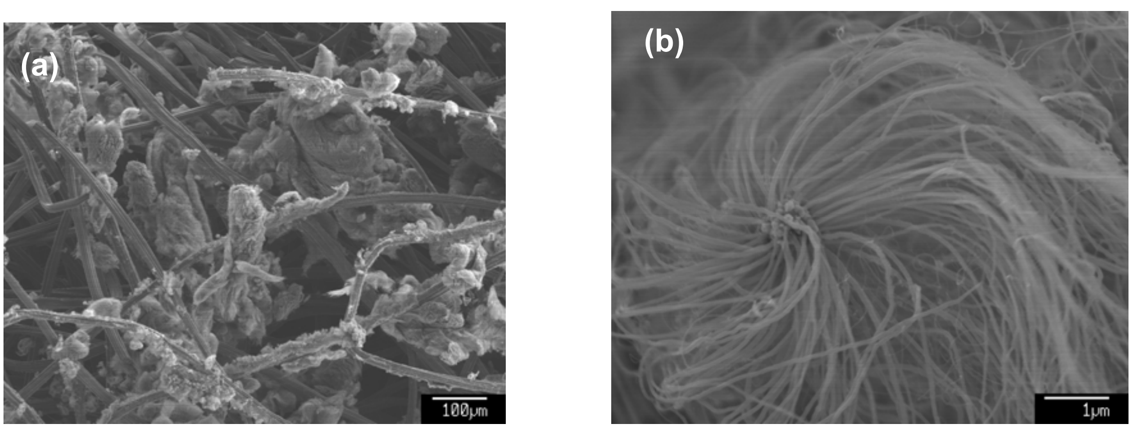

Figure 2. SEM images of carbon nanotubes grown on the carbon fibre cloth (VCL N, Morgan) using ferrocene with added pyrazine ($C_4H_2N_2$) in toluene in Ar flow: (a) nitrogen-doped carbon nanotubes grown between carbon fibres and, (b) when unsupported by the substrates they forming octopus-like structures where many nanotubes were grown from the same central catalyst particle.

Three-dimensional composite materials containing CNTs or CNFs and carbon fibres are good candidate for many potential applications. High thermal conductivity of these materials may be of use in automotive and aerospace applications and for heat distribution or hot spot control. The high electrical conductivity of these materials could be used for example in electronic components packaging, as gas diffusion layers in fuel cells or in electromagnetic shielding. The carbon fabric impregnated with carbon nanotubes could be used for lightweight structures and for armour.

Conclusions

We have demonstrated use of carbon fibres bundles and non-woven carbon fibre cloth as a 3D scaffold for carbon nanotube synthesis on surface of carbon fibres and in the empty space between them. A mixture of ferrocene and toluene were pyrolysed over the cloth at the same temperature in order to grow the nanotubes in between the fibres. Doping nanotubes with nitrogen is expected to particularly improve the electrical conductivity but also mechanical integrity due to the N-N interaction between the nanotubes. Growth of CNTs in the empty space between the carbon fibres could results in improvement of mechanical properties, thermal conductivity and electrical conductivity with potential for many applications especially in aerospace and electrochemical industry.

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