

## Low temperature synthesis of carbon nanofibres on carbon fibre matrices

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### Abstract

Carbon nanofibres are grown on a carbon fibre cloth using plasma enhanced chemical vapour deposition from a gas mixture of acetylene and ammonia. A cobalt colloid is used as a catalyst to achieve a good coverage of nanofibres on the surface of the carbon fibres in the cloth. The low temperature growth conditions that we used would allow growth on temperature sensitive polymers and fibres. The nanofibres grown by a tip growth mechanism have a bamboo-like structure. A significant increase of the bulk electrical conductivity of the carbon cloth was observed after the nanofibre growth indicating a good electrical contact between carbon nanofibres and carbon fibres. The as-grown composite material could be used as high surface area electrodes for electrochemical applications like fuel cells and super-capacitors.

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### 1. Introduction

The properties of carbon nanotubes (CNTs) and the less crystalline carbon nanofibres (CNFs) have attracted considerable interest for both scientific and technological issues [1,2]. Their impressive mechanical properties [3], high current carrying ability [4], and field emission performance [5] have opened the way to a number of applications such as field emission devices [6], interconnects [7], sensors [8,9], super-capacitors [10,11], fuel cells [12] and battery electrodes [13]. However, many potential applications are still hindered because of the high temperature conditions required during the CNT growth. There are four main CNTs growth methods:

arc discharge [14], laser ablation [15], chemical vapour deposition (CVD) [16] and plasma enhanced chemical vapour deposition (PECVD) [17–23]. In CVD, CNTs and CNFs are grown using the catalytic decomposition of hydrocarbons over transition metal catalysts such as iron, cobalt and nickel at temperatures ranging from 550 to 1000 °C [16]. Much lower growth temperatures can be reached when PECVD is used [20–23], opening the possibility to use temperature sensitive substrates like plastics [24].

Several research groups already synthesised CNFs and CNTs on the surface of carbon fibres using thermal CVD at temperatures between 600 and 660 °C. Downs and Baker [25,26] grew CNFs on the surface of carbon fibres in an ethylene–hydrogen environment using a copper–nickel (3:7) catalyst at 600 °C. The growth of carbon nanofilaments on the surface of carbon fibres improved the composite shear strength of the fibre by

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over 4.75 times, by forming interlocking networks and by increasing the surface area from  $1 \text{ m}^2/\text{g}$  up to  $300 \text{ m}^2/\text{g}$  [26]. Thostenson et al. [27] grew carbon nanotubes on carbon fibre surfaces at  $660^\circ\text{C}$  using sputtered stainless steel catalyst and an acetylene/nitrogen gas mixture. They concluded that selective reinforcement of the fibre/matrix interface by nanotubes would give an improved load transfer. Smiljanic et al. [28] grew CNTs on carbon paper using Co–Ni or Fe as catalyst. They reported good adhesion and electrical contact between CNTs and the carbon paper fibres. However, they did not observe any nanotube or nanofibre growth at temperatures below  $650^\circ\text{C}$ .

Here we report on the growth of CNFs on carbon fibre surfaces at lower substrate temperatures using PECVD. We have used a dc PECVD process that enables carbon nanotube growth at substrate temperatures as low as  $120^\circ\text{C}$  [21] and colloidal catalyst [29] in order to achieve a good carbon fibre surface coverage. The as-grown CNFs are attached with a good electrical contact to carbon cloth fibres. Such a material can potentially be used as high surface area electrodes for electrochemical applications like fuel cells, batteries and super-capacitors. Sun et al. [30] already demonstrated that carbon nanotubes grown on carbon paper could be used as an electrode in a fuel cell for electrocatalysis by depositing Pt nanoparticles on CNTs. Recently, Jo et al. [31] reported very low operating electric field for field emission from carbon nanotubes grown on carbon cloth that is important for efficient lamps, filed emission displays and vacuum electron sources. Our low temperature nanofibre synthesis on fibre matrix materials opens new opportunities for the use of temperature sensitive fibre matrix materials. We believe it can enable further advances in electrochemical and field emission applications by the introduction of temperature sensitive electrode materials coated with CNFs.

## 2. Experimental

Cobalt colloidal particles were synthesised following the inverse micelle method as described by Chen et al. [32]. A temperature control and a careful purification method were used as described in detail elsewhere [29]. Briefly, the Co colloid was purified by flocculation with only methanol in order to keep a high cobalt concentration. Additional purification by centrifugation narrows the particle size distribution but resulted in a lower colloid concentration. The amount of Co colloid deposited onto carbon fibres appeared crucial to achieve a dense and uniform CNF coverage. Typically, VCL N carbon cloth samples (Morgan Speciality Graphite,  $15 \times 15 \times 2.5 \text{ mm}$ ) were placed into a Schlenk tube under an Ar atmosphere and soaked with concentrated purified Co colloid (0.5 ml per sample). The solvent was

gently removed in vacuo. This colloid impregnation/solvent removal cycle was repeated up to three times to achieve an optimal coverage.

Impregnated carbon cloth samples were transferred into a dc PECVD vacuum chamber previously described [21]. They were heated up to the desired growth temperature (200 to  $400^\circ\text{C}$ ) for 15 min under a 1.2 mbar ammonia atmosphere. The temperature was measured using a thermocouple embedded in the cloth sample placed on the top of the graphite strip heater before striking the plasma. The heater current was then maintained throughout the experiment. Applying a voltage of 600 V between the heater stage (cathode) and the gas shower head (anode, 2 cm above heater) ignites a dc plasma discharge with average plasma current of 20 to 30 mA. Glow in the cathode region was not observed under these conditions. A gas mixture of  $\text{C}_2\text{H}_2$  (50 sccm) and  $\text{NH}_3$  (200 sccm) at a total pressure of 1.5 mbar was introduced during 20 min.

The morphology and the structure of the Co colloidal particles and CNFs were investigated using a field emission gun scanning electron microscope (FEGSEM, JEOL 6340 F), and a high-resolution transmission electron microscopy (HRTEM, JEOL JEM 3010, 300 kV). The CNFs were dispersed onto holey-carbon TEM grids for HRTEM analysis.

In order to investigate the electrical contact between the CNFs and the carbon fibres, the as-prepared samples were cut into  $4 \times 17 \text{ mm}$  strips and copper foils were wrapped around the ends of the strips to establish a good electrical contact between the electrodes and the carbon fibres. The electrical conductivity of the strips was measured using a Wentworth probe station inside a Faraday cage with an HP4140B dual voltage source. As-supplied and Co colloid-coated carbon fibre cloth strips of the same dimension were also used for comparison.

## 3. Results and discussion

SEM observation of the samples after PECVD revealed that CNFs had grown on the carbon fibre surface of the cloth (Fig. 1). A dense CNF coverage of the carbon fibres was obtained as a result of the uniform coating of the carbon fibre surface with the colloidal catalyst. Insufficient application of the colloidal catalyst onto the carbon fibre surface resulted in patchy CNF coverage. The CNF coverage throughout the volume of the cloth can be improved by directing the gas flow through the bulk of fibrous substrate. In order to optimise the flow pattern we drilled holes onto the heater stage. Nanofibres grown on the surface of the carbon fibres present a preferential orientation in the direction of the applied electric field. This is illustrated in Fig. 1b–d where the CNFs grown on the side facing the anode are

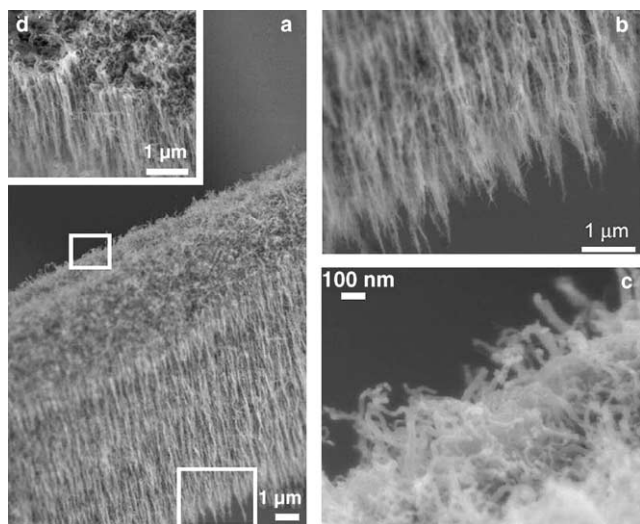


Fig. 1. (a) Carbon nanofiber coating of the surface of a carbon fibre grown using a  $C_2H_2:NH_3$  flow ratio of 50:200 sccm with heater temperature at 400 °C, (b) carbon nanofibres alignment (enlargement of the bottom selected area from Fig. 1a), (c) entangled carbon nanofibres grown on the opposite side of the carbon fibre (enlargement of the top selected area from Fig. 1a), and (d) enlargement of the border area between aligned and entangled growth from the middle of the fibre in Fig. 1a.

straight and aligned towards the anode whereas the CNFs grown on the opposite side of the fibre are entangled. No alignment effect was observed in control experiments using only thermal decomposition at 600 °C without plasma discharge. The typical length of the CNFs is between 1 and 5  $\mu m$  with diameters in the range 10–80 nm. A similar wide diameter distribution was also found by Boskovic et al. [20] for CNF synthesis using Ni powder catalyst at substrate held at room temperature. HRTEM analysis confirmed the presence of crystalline Co nanoparticles with diameters of 2–4 nm (Fig. 2). However, the diameters of the catalyst particles found

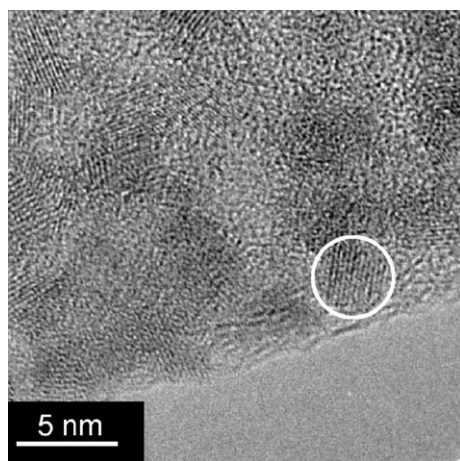


Fig. 2. HRTEM image of Co colloidal nanoparticles used as catalyst with an average diameter from 2 to 4 nm.

at the CNFs tips are much larger. This indicates sintering of the catalyst particles before and during the growth process.

A TEM image of CNFs synthesised at heater temperature of 250 °C on the carbon fibre surface is shown in Fig. 3a. Detailed HRTEM investigation of the CNF structure (Fig. 3b) showed a bamboo-like structure of the graphene layers with a characteristic interlayer spacing of 0.34 nm. The bamboo-like structure, reflecting higher degree of crystallinity, was observed for CNFs grown using Co colloidal catalyst on carbon fibre

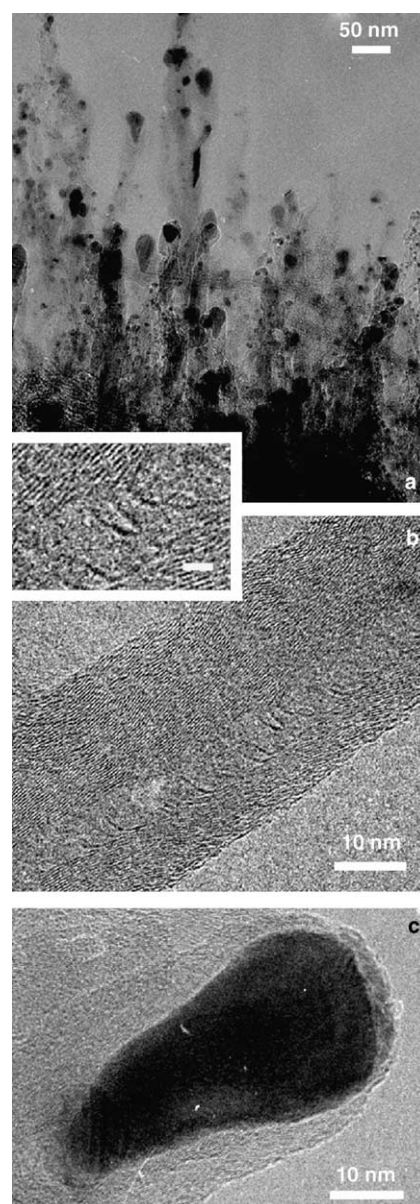


Fig. 3. (a) TEM image of CNFs grown on the surface of a carbon fibre at heater temperature of 250 °C, and  $C_2H_2:NH_3$  flow ratio of 50:200 sccm, (b) TEM image showing a bamboo-like structure of a CNF synthesised under the same conditions (insert image scale bar is 5 nm), and (c) TEM image of a Co catalyst particle at the tip of a CNF synthesised under the same conditions.



substrate at much lower heater temperature than 500 °C reported by Hofmann et al. [21] using the same growth conditions and apparatus setup and 6 nm thick Ni catalyst on silicon substrate. These findings suggested that crystallinity of CNFs synthesised using a low temperature PECVD might not be as strongly influenced by a heater temperature as in thermal CVD and that catalyst and substrate absorption of plasma energy can also influence CNF structural properties. Boskovic et al. [20] reported a cup-stacked CNF structure with a good crystalline quality using low temperature radio frequency PECVD suggesting also an important influence of the type of plasma source on the substrate and catalyst particle heating. Cobalt catalyst particles were observed on the CNF tips (Fig. 3c), confirming a tip growth model [33]. The catalyst particles observed at the CNF tips shows that a Co catalyst particle remains active and exposed to the carbon from the vapour phase during the growth process. Significant diffusion of the catalyst into bulk carbon from the substrate would stop the growth process. It is likely that the lower substrate temperature we have used slows down the catalyst particle diffusion into the substrate. It could also account for the tip growth mechanism. No CNF growth was observed when Co colloid-treated carbon cloth was simply annealed in the absence of a carbon containing feed gas. Thus, the carbon cloth does not act as a solid carbon source at the conditions we used. HRTEM observation showed also that only a very small amount of unwanted amorphous carbon formed on the CNFs sidewall during the plasma deposition (Fig. 3b). This confirms the etching effect of ammonia in mixture with hydrocarbon gas when used with the ratio found optimal for CNTs formation in our previous study [21]. The balance between deposition and etching strongly depends on the nature of the plasma, the etchant and the hydrocarbon gas and as previously demonstrated by Merkulov et al. [34] and Teo et al. [35].

The observed elongated shape of the catalyst particles (Fig. 3c) is consistent with the TEM observation of Helveg et al. [36]. These authors presented a time-resolved high-resolution in situ TEM observation of the formation of CNFs from methane decomposition over supported nickel catalyst. The lattice resolved images showed that graphitic nanofibres form with Ni nanoclusters located at the tips, and that the reshaping of the Ni particle into a highly elongated shape assists the alignment of the graphite sheets into a multi-layer CNF structure [36]. We believe that the formation of nanofibres in the conditions described here occurs via a surface diffusion growth mechanism similar to the one described by Helveg et al. [36]. Hofmann et al. [21] found that the activation energy for the growth rate of carbon nanotubes synthesised in dc PECVD is 0.23 eV, much less than for thermal CVD (1.2–1.5 eV), concluding that the growth occurs by surface diffusion

of carbon on the catalyst. The low temperature of the substrate was also confirmed by the growth of CNTs on plastic substrates that could not sustain higher temperatures using the same apparatus setup [24]. Although, the growth activation energy appears lower in PECVD than in thermal CVD, the actual growth temperature within the catalyst particles on cloth is very hard to determine. For high-frequency plasma excitation the small metal catalyst particle in the CNF tip could selectively acquire a higher temperature based on high-frequency plasma heating resulting in a higher carbon diffusion rate. High-frequency plasma heating of small metal particles has been demonstrated [37]. Teo et al. [38] reported that only by plasma heating substrate can reach temperatures as high as 700 °C in dc PECVD at 200 W plasma power using  $C_2H_2/NH_3$  mixture at 12 mbar. In our dc PECVD system at 20 W plasma power we have used  $C_2H_2/NH_3$  mixture at 1.5 mbar gas pressure. At low plasma power of 20 W and gas pressure of 5 mbar Teo et al. [38] reported that cathode reached temperatures of 200–250 °C. However, they did not mention that plasma heating might be also depended on the type of material and therefore have different effect on substrate and catalyst. Boskovic et al. [23] recently reported growth of CNFs when substrate was placed on a water-cooled sample holder and substrate was maintained at room temperature. As long as CNF growth occurs with catalyst particle at the tip high substrate temperature requirement might not be necessary [39].

In Fig. 4, the  $I$ - $V$  characteristics of the carbon cloth strips are shown. The effective bulk resistance is obtained as an average of the measurements on six different samples. The effective resistance of the carbon fibre clothes was not significantly changed after Co colloid catalyst coating. However, with CNF coverage the effective resistance dropped from an average value of around

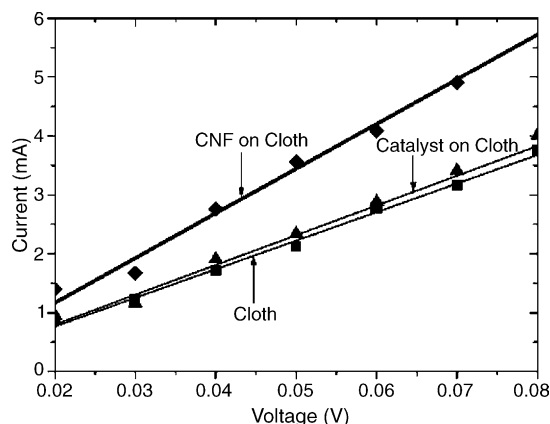


Fig. 4. Average  $I$ - $V$  characteristics of carbon cloth fibre strips with carbon nanofibre coated carbon fibres (CNF on cloth, 13  $\Omega$ ), with impregnated Co colloid catalyst (catalyst on cloth) and as supplied carbon cloth (cloth, 20  $\Omega$ ).

20  $\Omega$  to an average of about 13  $\Omega$ . The lowest measured effective resistance reached 12  $\Omega$ . This increased conductivity suggests that CNFs grown on the fibres create more electrically conductive paths from one end of the cloth strip to another, nearly doubling the cross-sectional conductive area of the carbon fibre cloth strip. This might also be interpreted as an evidence of the good electrical contact between CNFs and carbon fibres in the cloth. Direct conductivity measurement between individual CNF and carbon fibre is required for further investigation.

#### 4. Conclusions

Carbon nanofibres were grown on the carbon fibre surface in the cloth at substrate temperatures as low as 250 °C. When the acetylene and ammonia gas mixture was allowed to flow through the cloth sample carbon fibres at top and bottom surface of the cloth were covered with nanofibres. The use of Co colloid catalyst enabled an excellent coverage of the carbon fibre surface and opened a successful route for CNF growth on three-dimensional surfaces. The PECVD method allows a low temperature growth and the alignment of the nanofibres. It was successfully used for the first time for the growth of carbon nanofibres on carbon fibres. Electrical conductivity measurements confirmed a significant improvement of the electrical conductivity of the CNF coated carbon fibres, indicating that this could be an excellent electrode material for fuel cells and supercapacitors. We believe that the low temperature PECVD method we reported will open new possibilities for the production of CNF and CNT based nanocomposite materials using temperature sensitive polymer and organic fibre matrices. Such composite materials could be very important for electrochemical, field emission, sensing or reinforcement applications or smart textiles development.

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