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Growth of aligned carbon nanofibres over large areas using colloidal catalysts at low temperatures

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Highly purified cobalt colloids have been employed as a catalyst to grow aligned carbon nanofibres at temperatures as low as 300 °C by dc plasma enhanced chemical vapour deposition over large areas.

Carbon nanotubes (CNTs) and less crystalline carbon nanofibres (CNFs) are nanoscale building blocks for an increasing number of applications.[1] For many applications, such as electron field emission,[2] fuel cells and supercapacitors,[3] it is desirable to grow CNTs and CNFs directly onto an appropriate surface. This implies deposition of a catalyst onto a surface prior to the CNT growth. Typically the catalyst (mostly Ni, Co or Fe) is deposited by either thermal evaporation or sputtering. An alternative is to deliver the catalyst from a colloidal solution, which can cover any surface, independent of size, shape or structure, easily and at low cost. This method is particularly useful for coating complex shapes such as foams, meshes or cloths.

Chemical vapour deposition (CVD) is a common method to grow CNTs and CNFs. It is known that the CNT diameter tends to depend on the size of the catalyst particle.[4–6] Complex metal-containing precursors such as ferritin[4] have been popular means to deliver nano-sized catalysts to a surface for the growth of CNTs. A Co colloidal catalyst was previously used by Ago *et al.*[7] to grow CNTs by thermal CVD.

However, CVD is typically performed above 500 °C. This is too high for the use of sensitive substrates such as plastic needed for many applications. On the other hand, plasma enhanced CVD (PECVD) enables CNT and CNF growth at much lower temperatures most likely because the plasma dissociates some of the gas species before they reach the catalyst surface. We were recently able to grow CNFs by PECVD directly onto plastic substrates, using sputtered nickel film as catalyst.[8,9] We believe that the combination of colloidal catalysts and PECVD will allow the growth of CNTs and CNFs on more complex, sensitive substrates needed for more unusual applications such as electrochemistry and sensors. We present here the first use of colloidal catalysts and PECVD for the low temperature growth of CNFs.

Here, the Co nanoparticles are synthesised following the inverse micelle method as reported by Chen *et al.*[10] In order to grow CNTs with a small diameter, we have selected an AOT (bis(2-ethylhexyl)sulfo succinate sodium salt) stabilised Co colloid with an estimated particle size of 3–4 nm previously reported.[10] We controlled the temperature during the exothermal reduction step of colloid synthesis using an ice–acetone bath, as higher temperatures may lead to a larger particle size.[11] Our high resolution transmission electron microscopy (HRTEM) studies confirmed the presence of crystalline Co nanoparticles with a particle size of about 2–4 nm.

The significant excess of surfactant present in the as-prepared solution must be removed prior to CNF growth. We developed extensive purification procedures, involving centrifugation and/or flocculation of the colloid by addition of a solvent.[12] Centrifugation is essential, not only to purify the colloid, but also to sharpen the size distribution of the colloid, and thus of the resulting nanofibres.[13] This technique is quite complicated as it is necessary to avoid the oxidative decomposition of the colloid in contact with air. In addition, the flocculated colloid obtained by centrifugation must then be redispersed by sonication. This may lead to the formation of agglomerates, which would be undesirable for CNF growth, or could damage the surfactant shell. Finally, it proved difficult to obtain solutions of purified colloid with a sufficient concentration of particles. Fortunately, flocculation of the colloid by addition of oxygen-free solvent can be performed in an inert atmosphere, further redispersion is performed under very mild conditions and purified colloid solutions can be obtained of the desired concentration. The size-selective centrifugation can be performed later in order to narrow particle size distribution and cut-off the fraction of larger particles. Thus, we were able to obtain solutions of the purified colloid with the required concentrations necessary for reproducible CNF growth.

Various methods were tested, including spin coating, dipping and blow-drying under the flow of an inert gas, to apply the Co colloid solution onto a Si wafer surface. The best results were achieved by simply covering the surface with colloid solution under inert atmosphere and allowing the solvent to evaporate. The amount of the colloid applied affects the CNF coverage of the Si wafer surface. The best coverage is obtained for samples with the highest Co precursor concentration. To achieve optimal surface coverage with CNFs, it was necessary to repeat the application/drying cycle several times. We found no significant gain in CNF coverage and quality due to surface modification by APTS and Ph_2P modified APTS.[14]

The CNTs were grown by dc PECVD.[8] Samples were heated up for 15 minutes in 1.5 mbar H_2 or NH_3 until the final deposition temperature between 300 °C and 450 °C was reached. The dc discharge was started by applying 600 V between the sample heater (cathode) and the gas inlet 2 cm above the heater (anode). Acetylene was let in as carbon feed gas just after the discharge was started. The pressure during deposition ranged from 1.5 to 3 mbar, depending on the gas mixture and temperature.

The size and structure of the nanofibres were analysed by scanning electron microscopy (SEM, JEOL 6340 FEGSEM) and high resolution transmission electron microscopy (HRTEM, JEOL JEM-3010, 300kV). For HRTEM analysis the CNFs were removed from the substrates and dispersed onto TEM grids.

Fig. 1 shows aligned CNFs grown from Co colloid, which was purified first by flocculation and then once by centrifugation. CNTs

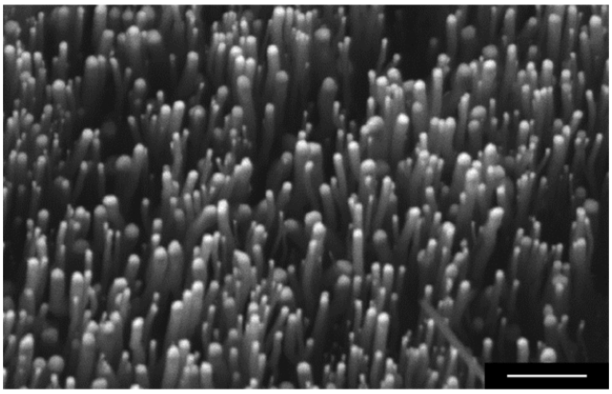

Fig. 1 SEM image of CNFs grown Co colloid, flocculated and centrifugated once. Cobalt catalyst particles are visible in the tips of the CNTs. 400 °C, $NH_3 : C_2H_2$ 200 : 50 sccm. Scale bar 500 nm.

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were deposited at a substrate temperature of 400 °C, using a mixture of $NH_3 : C_2H_2$ of 200 : 50 sccm. The Co catalyst particles are clearly visible in the tips of the CNFs, indicating tip growth. The presence of the Co catalyst in the tip could also be confirmed by energy dispersive X-ray analysis (EDX), and by TEM (see Fig. 3). In a control experiment a thermal deposition of the same substrates treated with the same Co colloidal solution under the same gas conditions but without the discharge led to very poor yields of curly nanofibres, confirming the key role of the plasma in their growth. The diameter distribution of the tubes ranges from 10 to 80 nm.

Fig. 2 shows a SEM image of CNFs from Co colloid which was purified twice by centrifugation after purification by flocculation. The CNTs were deposited at 300 °C and show a much smaller diameter distribution of 10–20 nm.

Fig. 3 shows a HRTEM image of an individual CNF from the sample shown in Fig. 2. The carbon nanofibre has a diameter of about the same size as the cobalt catalyst particle and a structure between bamboo-like and herringbone. The highly crystalline Co particle in the tip of the CNF is larger than the original colloidal particles, indicating that some sintering had taken place prior to the CNF growth process. At given conditions, a surface diffusion based growth mechanism can be assumed, as previously described for Ni thin film catalysts.[8,15]

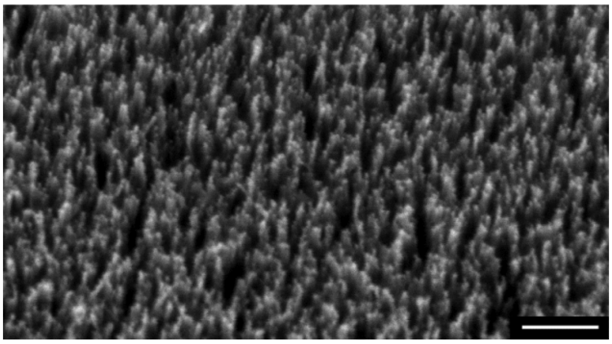

Fig. 2 SEM image of carbon nanofibres grown from Co colloid, flocculated and centrifugated twice. 300 °C, $NH_3 : H_2 : C_2H_2$ 200 : 200 : 100 sccm. Scale bar 250 nm.

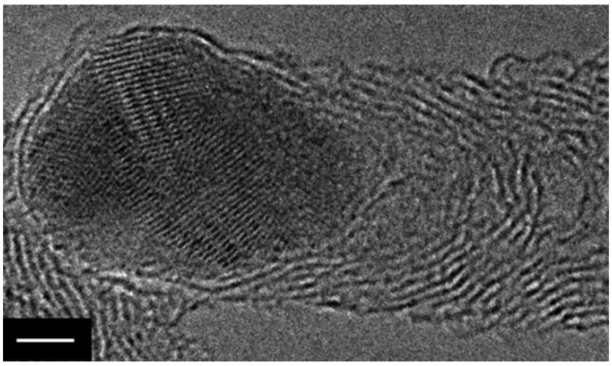

Fig. 3 HRTEM image of an individual CNF from the sample shown in Fig. 2. Scale bar is 2 nm.

The size distribution of the carbon nanofibres was directly related to the size distribution of the Co colloidal particles, and independent of other process parameters such as gas mixture and temperature. The growth rate varied with temperature similar to using a thin film of sputter deposited nickel as catalyst.[8] For 450 °C the growth rate is approximately 1.1 nm s^{-1} and decreases to 0.5 nm s^{-1} at 300 °C. The CNFs exhibited less bamboo like cross links at higher temperatures.

In conclusion we have shown that large surface areas can be covered easily with the described colloidal solutions. Uniform coverage of the substrate is achieved by repeated application of the colloidal solution onto the substrate. The size of the colloidal particles clearly defines the diameter of the growing CNFs. The diameter of the tubes was independent of the substrate temperature in the temperature range examined. We are currently investigating the growth of CNFs on three dimensional surfaces. The described Co catalyst provides an easy and cheap way of covering surfaces with a catalyst for the growth of CNFs.

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