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Florian Nitze; Edy Abou-Hamad and Thomas Wågberg

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Carbon nanotubes and helical carbon nanofibers grown by chemical vapour deposition on C₆₀
fullerene supported Pd nanoparticles

Florian Nitze¹, Edy Abou-Hamad^{1,2} and Thomas Wågberg^{1,*}

1. Department of Physics, Umeå University, 901 87 Umeå, Sweden

2. Laboratoire Colloïdes Verres et Nanomatériaux, Centre National de la Recherche
Scientifique, Université Sud de France, Montpellier, France

Abstract

Chemical vapour deposition (CVD) represents a cheap and versatile method to produce carbon nanostructures. Here we present how we by using a standard CVD setup together with Pd nano particles as a catalyst can produce helical fibers with very periodic pitch, helicity, and narrow diameter distribution. The C₆₀ supported Pd catalyst particles are produced by a wet chemistry process and applied to silicon substrates. By raising the growth temperature from 550° C to 800° C we can tune the growth products from helical carbon fibers to straight hollow carbon fibers and finally to carbon nanotubes at the highest temperatures. In the intermediate temperature region of 650° C a mixture of all three components appears. At 550° C the efficiency of the process is optimised by the amount of water during the growth.

* Corresponding author, email: Thomas.wagberg@physics.umu.se, Fax: +46-90-7866673

20 Different from most previous studies we can detect most of the catalyst particles embedded in
21 the grown structures. In all fibers the catalyst particles are situated exactly in the middle of the
22 fibers suggesting a two-directional growth. From the shape of the catalyst particles and by
23 adopting a simple model we conclude that the fibers coil due to blocked carbon diffusion
24 pathways on or through the catalyst particles.

25

26 1. Introduction

27 Carbon nanotubes represent one of the key materials in the fast developing nanotechnology
28 research. Their electronic, mechanical and optical properties have made them to ideal
29 candidates for applications in such wide areas as field emission displays [1, 2], actuators[3]
30 and transistors[4]. A recent report by Gong, et al.[5] shows that vertically aligned nitrogen
31 doped multi walled carbon nanotubes possess excellent properties as metal-free electrodes for
32 oxygen reduction in alkaline fuel cells. Helical or coiled carbon nanotubes (HCNT) and fibers
33 (HCNF) represent a special class of nanostructured carbon. Due to their unique shape they
34 could potentially be applied in composites [6] or as very sensitive mass sensors enabling
35 measurements in the attogram (10^{-15} g) region[7]. Also, theory predicts that at least for the
36 single walled type, helical nanotubes should possess a very sharp electronic density of state
37 (DOS) at the Fermi level which might lead to superconductivity [8]. Ihara et. al. studied
38 helical CNTs in 1995 [8, 9] but even earlier studies of helical structures can be found [10, 11].
39 A number of different methods have been used to synthesize HCNTs or HCNFs. Most of
40 them are based on different varieties of chemical vapor deposition (CVD). At room-
41 temperature helical single walled carbon nanotubes were grown on a graphite substrate by
42 decomposition of fullerenes in the presence of Ni particles [12]. HCNTs could be synthesized
43 on patterned aligned CNT templates in combination with Fe catalyst [13]. Reducing pressure

44 and gas flow enables the growth of helical multi walled carbon nanotubes on silica supported
45 Co particles [14]. Also the co-pyrolysis of pyridine and $\text{Fe}(\text{CO})_5$ as floating catalyst showed
46 excellent result [15] and could even lead to vertically aligned helical carbon nanotubes (VA-
47 HCNs) [16]. Sulfur has been shown to play a key role in enabling different catalyst, that
48 under normal conditions are used for the growth of straight structures, to grow helical
49 structures [11, 17]. Motojima et. al synthesized coiled CNFs with additives like thiophene and
50 H_2S and suggested a growth mechanism for coiled carbon fibers based on the anisotropic
51 extrusion of carbon over a catalyst particle [18, 19]. It has been shown that it is possible to
52 synthesize HCNs and HCNFs on Fe nano particles at temperatures below 500°C [20, 21].
53 By using a mixture of ethylene and oxygen it was possible to synthesize HCNFs and CNFs on
54 Pd at 550°C [22].

55 In this report we use fullerene supported nano Pd particles to synthesize carbon
56 nanostructures. Nano sized Pd particles have been used for both the growth of YCNT [23],
57 HCNs [24], and HCNFs [22, 25] It has also been used as co catalyst together with Co to
58 lower the growth temperature of MWCNT [26]. The combination of Pd and CNT has also
59 large potential in a variety of research fields. Pd nano particle decorated bamboo-like CNTs
60 enable catalytic active materials in pH ranges where the nano particles usually would be
61 oxidized and inactivated [27]. Fuel cells require highly active catalysts and Pd decorated
62 CNTs show excellent ability as oxygen reduction agent [28, 29] at a reduced cost compared to
63 Pt-based techniques. The ferromagnetic free synthesis is also of interest for experiments of
64 magnetic character such like NMR measurements [30]. In our study we show that depending
65 on how we tune growth conditions different types of nano structures, from helical over
66 straight CNFs to MWCNTs can be produced in a single step using a standard CVD setup with
67 acetylene as precursor. Different from most approaches for helical structures we do not need

any addition of catalyst poisoning material such as sulfur to achieve the growth of helical CNFs. Additionally we produce nanostructures without the use of any ferromagnetic catalyst material. The nano catalyst particles are produced in a simple wet chemistry process and applied to silicon substrates.

2. Experimental Details

The Pd_2C_{60} complex was synthesized by a reaction of C_{60} with dipalladium-tribenzylideneacetone (Pd_2TBA) in a toluene solution. The reagents were dissolved in toluene in 1:1 molar ratio and stirred at 112°C (just at the boiling point of toluene) for three days under nitrogen flow [31]. The black precipitate was washed and decanted with toluene 4 times. Initially the decanted solutions were coloured indicating unreacted components, probably both C_{60} and rest products of TBA, but after the second round the solution was colourless. Before characterisation the fine black powder was dried under vacuum at 50°C for two days.

The CVD system [32] contains a 30 mm quartz tube in a horizontal furnace (ETF 30/12 H-V from Entech). The prepared catalyst material is dispersed in ethanol assisted by short ultrasonication (1 min). The resulting black dispersion was applied by drop coating onto small pieces of silicon wafers. Before transferring the coated silicon wafers into the CVD setup the samples were dried or calcinated in air. The exact specifications are described later and differ depending on the experiment design. The 5 nm Pd thin films were grown by e-beam deposition on oxidized silicon wafers and transferred into the CVD setup. During the 20-30 minutes heating ramp to reach the desired process temperature (550°C - 800°C) the substrates were purged in an Ar flow (100 ml/min). We used three different growth procedures. (i) *With ammonia* as support gas the samples were first pretreated with 25 ml/min ammonia, 75 ml/min Ar and 75 ml/min Varigon (95 % Ar + 5 % H_2) for 30 min followed by a growth

92 phase of 30 min when 10 ml/min of acetylene was added to the gas mixture. (ii) *Without*
93 *ammonia*, the process parameters were changed so that ammonia was replaced with Ar and
94 the growth was started directly (when reaching the correct temperature) without any
95 pretreatment phase. All other conditions were kept constant. For both (i) and (ii) 0.1 ml of
96 water was injected every 5 min during the growth phase. The injected water was evaporated
97 in a glass flask heated on a hot plate at 100° C and thereby saturating the Varigon gas which
98 was passing through the flask before entering the CVD system. By mixing the saturated
99 Varigon gas with the second gas flow just after the flask and due to the elevated temperatures
100 in the hot zone, no condensation between the flask and hot zone was observed. For method i)
101 and ii) 5 mg of catalyst material was dispersed in 0.5 ml of ethanol and drop casted and air
102 dried on twelve Si pieces (2 x 0.5 cm), six on the oxidized six on the non-oxidized side. For
103 the growth on calcinated catalyst the substrate where heated at 400° C until no black C₆₀ was
104 visible anymore. Method ii) was used for both the calcinated substrate and the Pd thin film.
105 (iii) *With ammonia but with controlled water injection to optimize growth conditions*. For this
106 set of samples the conditions used for (i) were further optimized by varying both acetylene
107 flow between 10 and 30 ml/min and the amount of injected water during the growth. This was
108 achieved by a direct injection system containing a precision syringe pump and a glass needle
109 passing directly into the hot zone. The temperature at the end of the glass needle was far from
110 the boiling point of water so that a direct evaporation of any injected water was assured.
111 Injection rates between 0 and 30 µl/min were tested. For sample set (iii) typically 10-30 mg of
112 catalyst was tested by dispersing it in 0.5-1.5 ml (ratio, 10 mg catalyst: 0.5 ml ethanol) of
113 ethanol by ultrasonication. The dispersion was drop casted on 2.5 x 2.5 cm sized oxidized Si
114 wafers. Tests showed that heating of 50° C resulted in a relatively homogenous catalyst film
115 on the substrate. Prior to CVD the catalyst was calcinated at 550° C for 2.5 h. Growth time
116 was varied between 30 to 600 min. In all experiments (i)-(iii), the samples were cooled for 30

117 min in 75 ml/min Ar and 75 ml/min Varigon (95 % Ar + 5 % H₂) followed by a cooling in
118 100 ml/min Ar flow.

119 For TEM (JEOL 1230) measurements the samples were dispatched from the substrates and
120 dispersed in water assisted by sodium dodecyl sulfate (SDS) by ultrasonication. The
121 dispersion was applied to the grids by dip coating and air drying.

122 3. Results

123 3. 1 Growth on fullerene supported Pd nano catalyst particles

125 Figure 1: Typical TEM pictures of the three main growth products. HCNFs (left), straight
126 hollow CNFs (middle) and thin (right) MWNTs.

127 The results section is outlined as follows; first we start by discussing the synthesis process,
128 the obtained products and its optimization. Thereafter we continue with discussing and
129 explaining the growth mechanism. We start by evaluating the set of samples produced by the
130 synthesis parameters described in (i) and (ii). In figure 1, we show typical TEM pictures of
131 the three major kinds of structures grown on C₆₀ fullerene supported Pd nano particles.
132 Helical carbon nanofibers (HCNFs), hollow CNFs and multi-walled carbon nanotubes
133 (MWCNTs) are present in different contributions in the synthesized samples. Beside these

main components, small amounts of different side products are produced, mainly amorphous carbon and graphitic nanoparticles.

Figure 2: (a) High percentage of HCNFs at 550° C, produced at conditions (i). (b) Appearance of all three components at intermediate temperatures (650 °C), produced at conditions (i), and c) HCNFs produced at optimized conditions of (iii).

Growth temperature is an important parameter in order to tune the type of grown nanostructures. To facilitate the reading of the manuscript we define the temperature regions used in our experiments as; 550 to 600° C *low temperature region*, 650 to 700° C *intermediate* and 750 to 800° C is defined as *high temperature region*. At low temperatures, especially at 550 °C, up to 99% of the grown wire-like structures are helical (figure 2a, and c). The amount of other side products is not taken into account but as seen in figure 2c the amount of amorphous carbon is relatively low. The growth at high temperatures changes so that a higher fraction of small MWCNTs and no or only very few helical components are synthesized at these conditions. At 800 ° C the growth of the investigated main components stops completely. In the intermediate temperature range the growth is characterized by a mix of all three components (figure 2b.) The average length of HCNFs is rather short (below 10 μm) at 550° C and increases to about 20 μm at 600 °C. Besides temperature, both substrate and ammonia treatment also have an effect on the growth products. We could see weak

signs that the pretreatment with ammonia and the presence of ammonia during the growth enables the growth of HCNFs to higher temperatures (figure 2b). This was only observed on pure silicon. Using oxidized silicon at 650° C without the presence of ammonia resulted in a growth with no HCNFs. Regarding substrate properties we observed that MWCNTs grow already at 650° C on oxidized but not on pure silicon. In general the catalyst particles in the HCNFs are much bigger than in the MWCNTs (this is further discussed later in the manuscript). The smaller particle size on the oxidized side of the silicon wafer could possibly be explained by the rougher surface compared to the non oxidized side which might lead to a lower degree of agglomeration of catalyst particles. The inverse argumentation can then be used to explain why a higher ratio of HCNFs can be found on pure silicon at this temperature.

In order to optimize the growth process we choose the parameters from (i) and (ii) that seemed to best promote HCNF growth and then tried to optimize these further. This was the set of samples described in (iii). It is generally believed that trace amounts of water in the ppm region can evoke super growth [33]. In our case the level of water injected by evaporation was far higher. Assuming a saturation of the carrier gas gives a water amount in the range corresponding to the maximum humidity at room temperature which is on the order of 25000 ppm. Injecting water using a syringe pump allowed us to precisely control the water level inside the reaction chamber. For ethylene, it has been shown that a high level of oxygen is essential for any fast growth of carbon structures [22, 25]. We believe that water plays a similar role here. The morphology of the grown structures is the same for any water level but the catalyst efficiency and the precursor conversion factor is highly affected. The exact impact of water, precursor flow rate and growth time needs to be further investigated and will be presented elsewhere. So far however, the optimum conditions within method (iii) were found

180 to be: 20 ml/min acetylene and 5 μ l/min of water over 80 min. At this set of parameters we
181 have a ratio of 3:1 acetylene to water molecules. These conditions give highly reproducible
182 results (figure 2c) with a yield of 130 mg out of 20 mg Pd₂C₆₀ catalyst. This corresponds to a
183 catalyst efficiency of the pure Pd of 2840 %.

184 We now proceed by discussing the growth mechanism of particularly the HCNFs. For a large
185 number of hollow CNFs or HCNFs the catalyst particles could be observed by TEM. For all
186 of these we could identify three consistent facts (Figure 4).

187 1) For straight CNFs, the catalyst particle sizes are identical with the outer diameter of the
188 grown structures and in general, HCNFs have smaller diameters than straight CNFs. 2) The
189 shape of the catalyst particle in 2D is rhombic for straight hollow CNFs (figure 3a, and b) and
190 triangular, slightly rounded for HCNFs (figure 3 c and d). Assuming that these are projected
191 symmetrically into 2D we conclude that the 3D shape for straight fibers is a double cone. For
192 helical structures, the interpretation is more difficult but from our observations the shape of
193 the particles appears to be a somewhat edged half sphere. 3) In none of the samples, we could
194 find more than one catalyst particle within one tube. Furthermore, if the fiber is split in half at
195 the catalyst particle, the length of the whole fiber, the helical parts or the straight parts are the
196 same, indicating a very symmetric growth in both directions away from the catalyst particle.

197

198 Figure 3: a-d): TEM pictures showing the catalyst particle shapes. For hollow CNFs (a, and

199 b) the particles are always rhombic and for HCNFs (c, and d) somewhat edged half sphere.

200 (The scale bars are only averages as the sections concentrates on the shape, less than actual

201 size.) e) schematic and simplified growth model in 2D with representations g_0 and g_1 for the

202 inhomogeneous growth speed and r_0 and r_1 for the inner and outer radius of the coil. $\Delta\Theta$, Δr

203 and Δt are defined in the figure.

204 There is a close relation between hollow CNFs and HCNFs. In the intermediate temperature

205 region, we often found a transformation from HCNFs to hollow CNFs. This change occurred

206 within several tens of nanometers as seen in Fig. 4a.

207

Figure 4: Three fibers at different growth states (a) Bend at the transition point from helical to straight. (b) Bend and catalyst shape of a different fiber just after transition. (The image is strongly digitally zoomed and should just show the symmetry in growth behavior and the bend at the transition point) (c) Almost perfect periodicity with representation r_0 and r_1 for the inner and outer radius of the coil as used in figure 3.

In all HCNFs, the periodicity built up directly without a significant transition range. From figure 4b it is clear that the transition occurs from helical to straight growth. This is true for all our observed transitions grown on Pd nanoparticles. Also in all HCNFs the structure was bent at the exact position of the particle as seen in figure 3 c and d. As shown in figure 3 the particle reaches the outer region of the fiber. For helical fibers, only one edge of the catalyst reaches the outer parts of the fiber (figure 3 c and d), whereas it reaches both sides for straight ones (figure 3 a and b). Assuming that the carbon feedstock diffuses through or on the particle, we suggest a 2-directional growth mechanism and a simple explanation why the fibers curl. Even though it is irrelevant for the following model we want to mention that surface diffusion is the most probable pathway since at these low temperatures the solubility of carbon in Pd is almost negligible [34, 35]. Teschner et. al. has reported a surface Pd-C

phase which might be applicable at the conditions present in our study [36]. All following considerations additionally assume that diffusion rate and growth rate are within the same range. We start with growth mechanism for CNFs suggested by Motojima et al. based on the idea of an anisotropic extrusion of carbon over a catalyst surface [18, 19]. Here we do not consider different extrusion rates due to different crystal faces or rotation of the catalyst particle but rather due to different diffusion pathways. Adopting and combining this model with a diffusion model for tip growth as suggested by Pannala et al. [37] and Wen et al. [38] but allowing a growth into two directions would easily explain our observed results. In figure 3 we present a schematic model for the growth process. If there would be blocked carbon diffusion pathways on the particle (or within), one part of each fiber is able to grow faster than the other. Since the front of the fiber is firm the resulting structure must curl. We believe that a constant gradient on the particles builds up due to equilibrium between feed and loss of carbon over the particle. This can equally be considered as equilibrium between growth rate and diffusion rate. We can then calculate the approximate gradient of fiber formation φ in an easy model.

$$\varphi = \frac{\Delta g}{\Delta r} \quad \text{with } \Delta g = g_1 - g_0 \text{ and } \Delta r = r_1 - r_0 \quad (1)$$

and other representations as shown in figure 3 and 4. We can then conclude the following. We assume that the outer shell grows with a constant maximum speed g_1 . We think it is reasonable to consider g_1 as the maximum speed of fiber formation. We now get the growth rate of the fiber by multiplying with time Δt . This results in a change in angle $\Delta\theta$ which curls the fiber. We can then conclude that r_0 only depends on the quotient of growth speed g_0 and the gradient.

$$\Delta\theta = \frac{g_1\Delta t}{(r_0 + \Delta r)} \quad (2) \quad \text{and} \quad r_0 = \frac{g_0}{\varphi} \quad (3)$$

The gradient will directly depend on the diffusion coefficient and the shape of the particle. This means that the inner radius r_0 of the coil depends on the equilibrium between growth and diffusion rate. Additionally for all growth speeds below g_1 the limiting factor is the diffusion rate and since r_0 is not zero the diffusion rate must be slightly higher than the growth rate. The equilibrium of growth and diffusion rate gives us direct information about the diffusion coefficient D .

$$D = \Delta g \Delta r = \varphi \Delta r^2 \quad (4)$$

In 3D we would of course need to replace distance with area. An improved 3D model in combination with precise timeline experiments to gain information about g_0 and g_1 would allow estimating the surface diffusion on the particle by measuring the inner and outer radius of the coil.

The discussed mechanisms also make it possible to explain the observed transitions from helical to straight fibers. As already mentioned we observe that all fibers start by a helical growth. Since all observed transitions go from helical to straight and the fibers curl preferentially at low temperature conditions it seems plausible that at low temperature there is a higher possibility of a partly inactivated catalyst since the lower temperature makes the ammonia and water less efficient in keeping the catalyst homogeneously active. If a partly blocked catalyst particle is “cleaned” during the growth process the diffusion pathways will become isotropic and the fibers will start to grow straight in agreement with our observations. The most probable reason is that the anisotropy of the catalyst is connected to some initial conditions of the catalyst such as coverage of the nano particle by carbon. Our

growth model is strongly supported by the form of the catalyst particles. In straight fibers, the diffusion of carbon on the catalyst drags the initial spherical catalyst particle into a perfectly symmetrical double cone as shown in figure 3. When the carbon feed is anisotropic the form of the resulting nano particle becomes strongly asymmetric. In figure 4b where the fiber has recently transformed from helical growth to straight it is clear that the catalyst particle does not yet look completely like for longer straight fibers but that it has already started to shape into a double cone. Additionally the bending of the fiber at the particle disappeared instantly. At the transition point the structure is strongly bent to about 90 degree (figure 4). This suggests that the transition occurs within a very short time and is triggered by rather a sudden opening of the blocked diffusion channels.

3. 2 Influence of C₆₀ support and growth on Pd films

To test if the C₆₀ support has a major influence of the growth products we performed two additional experiments to evaluate this. By evaluating the effect of calcinations that practically destroyed the C₆₀ but left the Pd nanoparticles we could see that the main benefit of the C₆₀ molecules is to provide support for separating the Pd into nanoparticles. This is further supported by the results from a second experiment where carbon nanofibers were grown directly on an e-beam deposited Pd film. The growth on Pd films is characterized by similar HCNFs but with a larger spread in diameters and larger amounts of amorphous carbon and other carbon nano particles. Furthermore we see that for HCNFs grown on Pd films we can find fibers with several transitions, from helical to straight and back to helical again, in contrast to the fibers grown on the C₆₀ supported Pd nanoparticles where only single transitions could be found (helical to straight). The reason is probably an over amount of catalytically produced carbon which can then again block the diffusion site.

293 4. Conclusion

294 We have shown that the by using a combination of C₆₀ supported Pd nano particles we can
295 efficiently grow very high amounts of HCNFs. The growth of HCNFs is possible also without
296 the support from C₆₀ but the later has a clear influence on both growth mechanism and purity
297 of the synthesis. Although our process is not especially cheap it provides a method that apart
298 from most others is both efficient and give homogeneous HCNFs with very periodic pitch and
299 diameter. Different from the assisted super growth observed for SWNTs by water in the ppm
300 region we see that water levels on the order of thousands of ppm are required to boost the
301 growth of HCNFs. From the shape of the catalyst particles and by a adopting a simple model
302 we conclude that the nanofibers curl due to blocked carbon diffusion pathways on the catalyst
303 particles. The structure of HCNFs could make them appropriate as composite material in
304 polymers to grow strong and flexible materials and their periodic pitch could also make them
305 suitable for functionalisation. We also plan a more detailed theoretical investigation in 3D in
306 combination with precise time dependent growth experiments to fully estimate the growth
307 mechanism of HCNFs and the diffusion rate of carbon on Pd.

308

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314

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