

The Selective Heating of Iron Nanoparticles in a Single-Mode Microwave for the Patterned Growths of Carbon Nanofibers and Nanotubes

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The fast and cheap synthesis of carbon nanotubes is addressed in a large number of recent publications. At the same time, microwave-assisted synthesis has also gained interest. Besides the fact that reaction kinetics can be positively influenced by the use of microwave irradiation and advanced reaction conditions can be applied, absorption of microwave radiation depends on the material properties, thus resulting in a selective heating mechanism. The selective heating process allows for locally created temperatures high enough to promote the growth of carbon nanofibers and nanotubes on patterned iron catalyst layers. The resulting fibers are micrometers long, and can be synthesized in short time scales of a few minutes, yielding dense films of carbon fibers with uniform height. Here, the selective heating of surface bound iron nanoparticles is investigated in more detail, and experimental evidence for this effect is provided by utilizing a self-assembled monolayer of *n*-octadecyltrichlorosilane, which acts as a sensitive indicator for locally elevated temperatures. Special emphasis is placed on the development of an improved and controllable experimental setup that permits the safe and fast fabrication of the desired carbon objects.

1. Introduction

The use of microwaves in organic and inorganic synthesis is a rapidly expanding field.^[1,2] It has been found that in many cases reaction times can be reduced, in contrast to classical synthetic approaches, and the formation of undesired byproducts can be suppressed.^[3,4] Advances in technology have permitted single-mode microwave instrumentation designed to generate homogeneous microwave radiation. Reactions are carried out in closed reaction vessels, which operate safely under high pressure conditions (up to 22 bar), and make it possible to monitor the

reaction conditions, such as the pressure and the temperature, during the irradiation process.

Besides the possibility to perform the synthesis under high pressure conditions, an important effect of microwaves is the fact that their absorption depends on the material properties of the compounds in the reaction vial. In particular, the permeability and conductivity of the material play an important role in the efficiency of absorption of microwaves. Therefore, a selective heating process can be used to locally generate high temperatures.

Such a selective heating mechanism is of special interest for the synthesis of carbon nanofibers and carbon nanotubes (CNTs) directly on surfaces. Such systems have recently been the focus of many research projects, as one-dimensional carbon structures are expected to provide extraordinary material characteristics. Potential applications for such objects are seen in nanoelectronic circuits,^[5–7] wherein they form electrical interconnections between different patterned layers.^[8–11] Commonly used techniques to synthesize such materials focus on chemical vapor deposition (CVD),^[12–14] which plays an important role in the growth of nanofibers and nanotubes on, in some cases even pre-patterned, catalyst layers.^[15] However, the conditions under which the synthesis takes place are generally very demanding in terms of the exposure of the substrate material to high temperatures. Typical temperatures required for the growth of carbon nanotubes on suitable metallic catalyst particles are well above 600 °C.^[16] This is regarded as a major restriction if low melting point substrates are used, or if temperature-sensitive device components are already pre-fabricated on to the substrates, i.e., if CNTs are to be embedded into integrated circuits. Therefore, there is a demand to develop fabrication methods that allow synthesis while reducing the temperature to which the substrates have to be exposed.

2. Investigation of the Selective Heating Process

The use of selective heating processes represents here a promising alternative to common techniques (such as chemical vapor

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deposition) as they can be obtained by the use of microwave irradiation. Hong et al. previously reported on the synthesis of carbon nanofibers and nanotubes on surfaces by using microwave radiation.^[17,18] They predicted the selectivity of the heating mechanism theoretically; however, experimental evidence for this explanation has, so far, not been reported. A major difficulty has been the temperature measurement, which is performed in conventional as well as synthetic single-mode microwave systems by an infrared sensor that measures only the average temperature of the reaction chamber or the vial. To investigate the selective heating process, we propose to use a self-assembled monolayer of *n*-octadecyltrichlorosilane (OTS) as a sensitive, qualitative indicator for the local temperature in different regions of a substrate, as the monolayer will degrade upon exposure to high temperatures.^[19] This approach is suitable to provide an indirect proof of the selective heating process and generates an ex situ mapping of the local temperatures generated in different parts of the substrate during the microwave irradiation.

The use of suitable patterning techniques for the OTS monolayer allows, moreover, defining of the position of individual catalyst particles, i.e., iron metal particles. Aside from making analysis of the temperature mapping easier, this process offers attractive possibilities to integrate (individual) carbon nanofibers or nanotubes on pre-defined positions on a surface or even within device frameworks.

The fabrication of such catalyst arrays on OTS monolayers has been previously reported (Fig. 1a–c).^[20] The key step here is the local application of a suitable bias voltage on the OTS monolayer via a conductive scanning force microscopy (SFM; NT-MDT, Solver Pro) tip (μ Mash, CSC37, Pt coating). This process results in a chemical conversion of the surface terminal $-\text{CH}_3$ groups of the OTS monolayer into acid groups by an electro-chemical oxidation process.^[21] Thus, a chemically active template is created that can be used for further physico-chemical modification.^[22–25] The patterned areas can be loaded with iron(II) acetate ions that develop into particles upon a chemical reduction by exposure to hydrazine vapor (Fig. 1c) and subsequent oxidation of the iron particles as they are kept under ambient condition. By this process, well defined nanoparticle arrays can be formed that can act as antennas for the absorption of microwave radiation. An irradiation experiment was performed on a substrate that was patterned with a 7×7 grid of iron nanoparticles, spaced 100 nm apart. This substrate was subjected to microwave irradiation, with special emphasis placed on the development of a safe

experimental process. To maintain the controllability of the heating process, the reaction vial contained several milliliters of ethanol underneath the substrate, which was placed on a quartz support above the liquid ethanol (Fig. 1d). The presence of the ethanol ensures the safe performance of the synthetic single-mode microwave setup and can, moreover, serve as a suitable carbon source in subsequent experiments to grow carbon nanofibers and nanotubes.^[26]

In a first experiment, the targeted overall temperature within the reaction vial was maintained on a level which is not yet sufficient to initiate the growth of one-dimensional carbon systems. The substrate was exposed to microwave radiation (10 min exposure time at a microwave power of 150 W in an Emrys Liberator single-mode microwave, Biotage) in a capped pressure vial. The maximum temperature within the reaction vial was restricted to an average temperature of 120 °C, as measured by the integrated IR sensor. The reaction was stopped by flushing the reaction chamber with nitrogen until room temperature was reached.

Subsequently, the nanoparticle array was investigated by tapping mode scanning force microscopy (Fig. 2). Characteristic, uniform hole structures were observed around the remaining particles and in the positions where particles were located within the original nanoparticle pattern. While OTS monolayers are generally stable, it was observed that degradation takes place if they are exposed to high temperatures. The degradation of the OTS monolayer at the positions of the particles is a clear indication that higher temperatures have been generated by the microwave irradiation due to the preferential absorption of the microwaves by the metallic nanoparticles. The size of the holes significantly exceeds the size of the particles, indicating that the vicinity of the particles is also heated due to heat dissipation effects. The analysis of the depth of these holes indicates a depletion of 2.1 nm, which is slightly less than the expected depth estimated for a well ordered OTS monolayer, suggesting a minor degradation of the OTS monolayer in regions without iron catalyst present. Nonetheless, the monolayer still exhibited hydrophobic surface properties, as indicated by a water contact angle of 90° to 100° (in contrast to 114° for the untreated OTS monolayer). It was observed that most of the iron particles were detached from the grid structure; however, the uniform diameter of the hole structures allows us to conclude that the particles were removed only after the heating process. It is not clear if the particles were removed during the cooling cycle of the microwave,

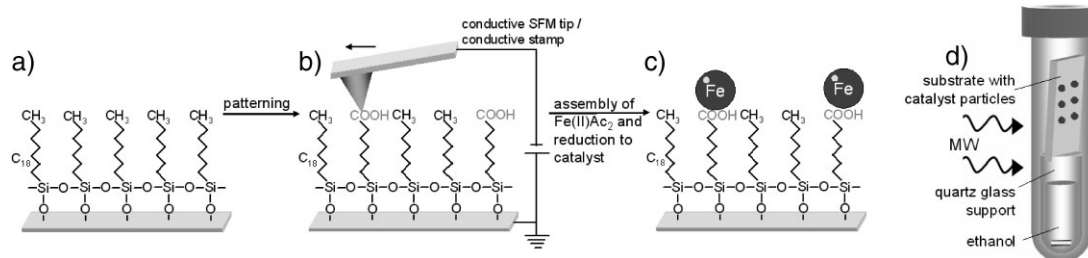


Figure 1. Schematic outline of the experiment. a) Electro-chemical patterning is performed on an *n*-octadecyltrichlorosilane monolayer. b) By the local application of bias voltage pulses, an electro-chemical oxidation takes place, converting the top methyl groups to carboxylic groups. c) The carboxylic acid groups serve as a template for the site-selective placement of iron(II) acetate, which can subsequently be reduced to yield magnetite nanoparticles. d) The substrate is placed in a capped pressure vial on a quartz support above a reservoir of liquid ethanol and irradiation takes place.

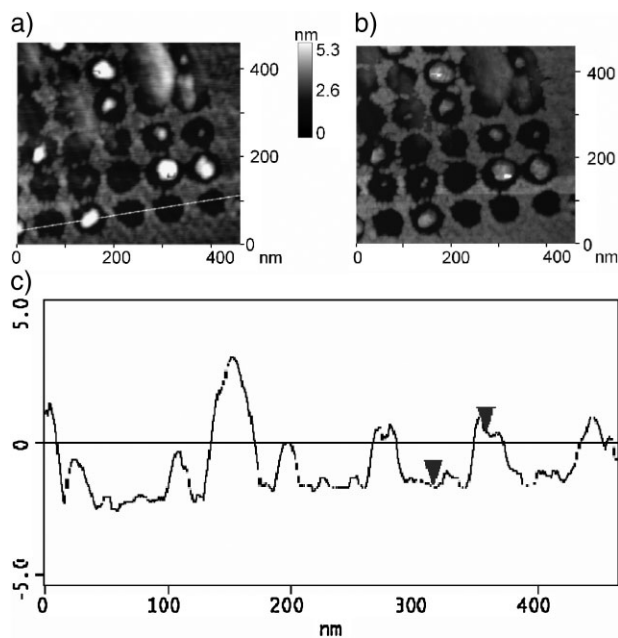


Figure 2. Scanning force microscopy images of the array of metallic nanoparticles that are formed on a regular grid of individual surface spots, inscribed with voltage pulses of -10V applied to the tip of the SFM. a) After microwave irradiation was applied to the particle array, a significant degradation of the underlying OTS monolayer was observed (height image). b) Phase image. c) Line profile of the corresponding height image, which provides evidence of a higher temperature at the positions of the nanoparticles due to the better absorption of the microwaves by the metallic particles.

which causes the condensation of ethanol vapor on the substrate, or during the SFM investigation due to the scanning tip, or during the cleaning process (with adhesive tape) to which the surface was subjected.

3. Microwave-Assisted Growth of Carbon Nanofibers and Carbon Nanotubes

Based on the previous results, which prove the efficiency of the selective heating process further experiments were performed to use the selective heating of catalyst particles for the growth of carbon nanostructures. Consequently, the experimental conditions required to grow such nanostructures were determined, and

the possibility to combine the process with the introduced patterning approach was addressed. In a first step, the experimental conditions leading to the formation of carbon nanofiber structures on non-patterned catalyst layers were investigated. Two different approaches can be used to form the catalyst material; the previously reported approach of directly forming iron nanoparticles on the surface by reduction of iron cations with hydrazine vapor, or by application of elevated temperatures to the iron(II) acetate, which causes the activation of the catalyst and triggers the formation of the particles.^[27]

Catalyst layers formed by the latter process were used for irradiation experiments, and reaction times of 3 minutes at a microwave power of 300 W resulted in the formation of dark, black coatings on the catalyst layers (Fig. 3a). However, the overall temperature within the reaction vial remained at a relatively low level of 130 to 150 °C as measured by the IR sensor system. Detailed investigation of this coating with different techniques was performed. Scanning electron microscopy (SEM; XL30 ESEM-FEG, Philips) revealed that the coating consisted of a densely packed assembly of fibers with diameter of typically 40–100 nm and a length of several micrometers (Fig. 3b). More disordered films, as shown in Figure 3c, demonstrate more clearly the diameter and structure of the synthesized objects. Further information on the nature of these fibers was provided by Raman spectroscopy (RamanStation HTS, Avalon). Characteristic peaks at 1 294 and 1 556 cm^{-1} were observed, corresponding to the D and G modes of carbon; these peaks are also observed for multiwall carbon nanotube systems.^[28]

The black coating of the substrates was partially removed from the surface to enable further characterization. The material was dissolved in dimethyl formamide or ethanol; however, dispersions were only stable for a few minutes before the material started to precipitate. This precipitation was attributed to the bundling of the material in solution, an effect that is also well known for CNTs. Droplets of these solutions were applied on silicon surfaces coated with aminopropyltrimethoxysilane (APTMS, Sigma–Aldrich) or carbon-coated transmission electron microscopy (TEM) grids by dropcasting. Despite the low solubility and the tendency to form bundles in solution, individual fibers could be visualized by means of SFM (Nanoscope IIIa, Multi-mode, Digital Instruments; Fig. 4a) and TEM (Fig. 4b and c; Tecnai G², FEI). Both methods clearly confirm the fiber-like structures of the material and show the presence of catalyst particles, which appear as dark spots in the TEM micrographs.

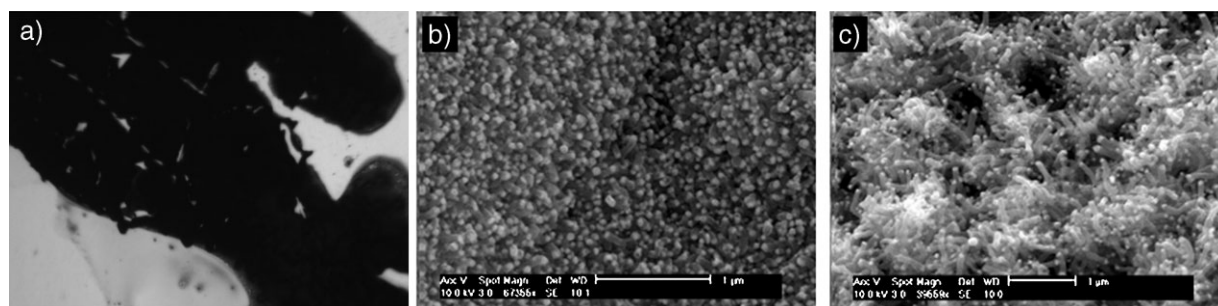


Figure 3. After microwave irradiation, a black coating is formed on the catalyst layers. a) Optical image of the black coating formed on a droplet of iron catalyst spotted on the surface. b) Dense film of nanofibers exhibiting uniform length of the nanofibers. c) Disordered film that shows the presence of individual fibers.

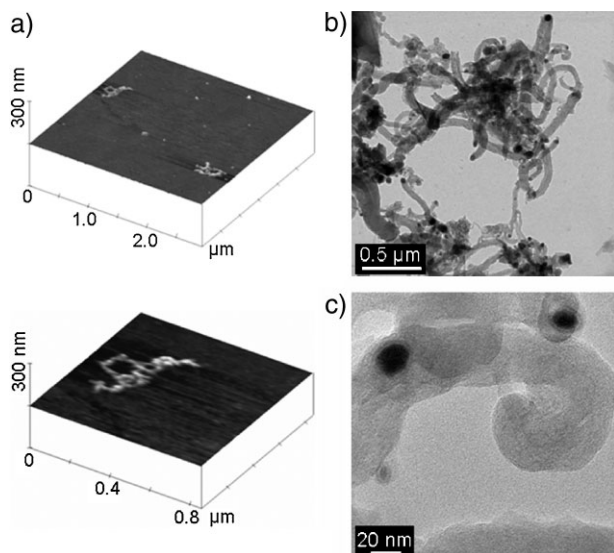


Figure 4. a) Scanning force microscopy images of individually dispersed nanofibers on an APTMS coated silicon wafer. b and c) Transmission electron microscopy images of a bundle of carbon nanofibers. Clear evidence for the presence of the metallic seed particles is found.

The formation of these fibers was observed on different substrates; silicon, glass, and Teflon. While with iron catalyst particles carbon fibers were mainly produced, and only occasional hollow nanotubes were generated, significant improvement of the tube quality in terms of smaller diameters could be obtained by using alternative catalysts. Nickel(II) acetate resulted in the formation of tubes with a mean diameter below 20 nm, which were also grown with an irradiation time of 5 min at 200 W microwave power (Fig. 5).

The short synthesis time required to produce these tubes is regarded as a major advantage of microwave synthesis. Despite the differences in the experimental conditions, which makes direct comparison difficult, our method exhibits certain advantages. For example, a closed reaction vial resulted in safer reaction conditions in contrast to a previously reported approach.^[12] The use of liquid ethanol helps to avoid highly reactive and flammable carbon sources, i.e., acetylene and hydrogen mixtures.^[13,14] Moreover, it seems that the high pressure conditions, which are generated due to the evaporation of the ethanol, are beneficial for the growth of the carbon fibers on the catalyst layers.

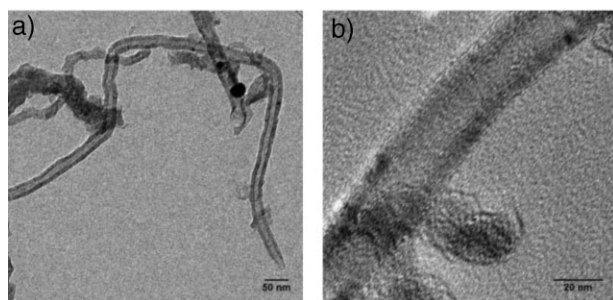


Figure 5. a) TEM microgram of thin carbon nanotubes formed on nickel catalyst layers. Tube diameters are 20 nm. b) High-resolution TEM of the hollow structures.

4. Patterned Growth of Carbon Nanotubes and Nanofibers

Interesting possibilities emerge from the use of patterned substrates, as they provide an easy means to localize the catalyst particles and thus to define the position of the fiber material. Additional experiments were performed to synthesize patterned structures. Patterned catalyst layers were fabricated according to the approach summarized in Figure 1a and b, however, a conductive TEM grid was used instead of a conductive SFM tip to initiate the electro-oxidation process,^[29] thus catalyst patterns with micrometer resolution were obtained.

Figure 6a depicts a relatively large structure, resembling a pattern that was generated by the electro-oxidation with a hexagonal TEM grid (Mesh 50, bar diameter 75 μm). The typical black coating is exclusively formed on the hexagonal structures after the catalyst deposition and the microwave treatment. However, thinner structures could also be produced by using a fine mesh TEM grid, which results in structures with a typical line width of 6 μm (Fig. 6b). Both structures were investigated by means of SEM and showed the presence of carbon structures, where most of the fibers appear to stand upright and have a diameter of 40 to 100 nm and a rather uniform length (Fig. 6c and d). It is readily observable that the nonstructured OTS substrate remains completely free of tube material, and the boundaries of the structures are sharply restricted to the imprinted structure, demonstrating the high selectivity of the process. It was observed that the growth of carbon nanofibers on such patterned substrates requires higher heating power values, as apparently heat dissipation effects play a crucial role.

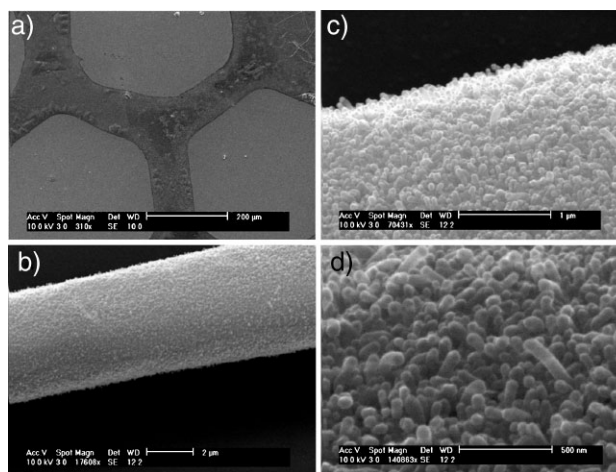


Figure 6. Towards the fabrication of patterned nanofiber assemblies. a) Patterned carbon nanofiber arrays on a hexagonal structure electro-oxidized with a TEM grid (Mesh 50, hexagonal grid). b) Smaller bar features (Mesh 400 fine bar grid) after the site-selective growth of nanofibers. Both structures show good selectivity of the grown structures and the presence of a black coating. c) Zoom-in of the structure in (b) with special focus on the border of the grown structures to emphasize the selectivity of the growth process. d) The zoom-in on the nanofiber films demonstrates the uniform length and diameter of the individual fibers.

5. Conclusions

It was demonstrated that small iron nanoparticles can be selectively heated by microwave radiation. The selective heating process has been used for the growth of carbon nanofibers on silicon, and other substrates, for example, glass and Teflon; however, synthesis conditions differ significantly. The selective heating of the catalyst particles opens attractive possibilities to implement a process that requires little experimental effort to obtain nanofibrous structures. Of special importance is the fast reaction time that is required to obtain the nanofiber material; irradiation times as short as three minutes were sufficient. A major advantage of this approach is the fact that the heat development is limited to the close vicinity of the nanoparticles itself, while the average overall temperature, as measured by an IR sensor, remains at low values of 130 to 150 °C. The carbon nanofiber synthesis approach was adapted to the special requirements of the microwave setup and was optimized in terms of safety and environmental aspects. By using ethanol as a carbon source, provided by a liquid reservoir which is located beneath the sample, a flux of highly flammable and explosive feeding gas mixtures was avoided.

Preliminary results on patterned OTS/silicon substrates suggest that smaller areas covered with a suitable catalyst layer can be obtained by this method, with important implications for the effective integration of carbon nanofibers into device frameworks. However, the tube growth conditions seem to be influenced by heat dissipation characteristics and additional studies addressing this issue have to be performed. Furthermore, the reaction conditions in terms of average temperature, applied power, catalyst material, and carbon source are important parameters that influence the growth process of the nanofibers and nanotubes. A detailed investigation of these effects is currently being performed.

The integration of (individual) carbon nanofibers and nanotubes into hybrid structures, consisting of other non-transition metal components, is another area that might profit from the characteristic, selective heating of different material by microwave irradiation. It is assumed that the heating efficiency of other structures, for example, transistor structures, is significantly lower compared to iron, nickel and cobalt particles, which are generally used as catalyst particles for the growth of carbon nanofibers and nanotubes.

6. Experimental

Silicon wafers were purchased from UniversityWafer and were used as a substrate for the self-assembly of *n*-octadecyltrichlorosilane (OTS, ABCR) monolayers (SAMs). Patterning of the substrates was performed either with a conductive SFM tip (μ Mash, CSC37, Pt coating, -10 V bias voltage, typical oxidation time of 20 ms dot^{-1}) or commercially available copper TEM grids (Mesh5 50, bar diameter $75 \mu\text{m}$, -30 V bias voltage with a patterning time of ~ 30 s). SFM patterning and imaging was performed on a Solver Pro SFM Microscope (NT-MDT).

Iron acetate purchased from STREM chemicals was used to prepare the ethanol solution (1 mmol). Oxidized substrates were immersed in this solution for 10 minutes. Subsequently, these ions developed into iron oxides upon the exposure to hydrazine vapor (ACROS Organics) and storage at ambient conditions. These substrates were exposed to microwave irradiation (10 min at microwave power of 150 W in an Emrys

Liberator single-mode microwave, Biotage) in the presence of an alternative carbon source (Ethanol, Biosolve) for the demonstration of the selective heating process and 300 W and 3 min irradiation time for the synthesis of carbon nanostructures.

Tube and fiber materials were characterized by scanning electron microscopy (XL30 ESEM-FEG, Philips), Raman spectroscopy (RamanStation HTS, Avalon), and TEM (Tecnai G^2 , FEI). For TEM investigations, the black coating of the substrates was removed and dispersed in dimethyl formamide (Biosolve) to enable further investigations. Droplets of this solution were applied on silicon surfaces coated with aminopropyltrimethoxysilane (APTMS, Sigma-Aldrich) by dropcasting. CNTs were also visualized by means of AFM (Nanoscope IIIa, Multimode, Digital Instruments).

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- [1] C. O. Kappe, *Angew. Chem.* **2004**, *116*, 6408. *Angew. Chem. Int. Ed.* **2004**, *43*, 6250.
- [2] F. Wiesbrock, R. Hoogenboom, U. S. Schubert, *Macromol. Rapid Commun.* **2004**, *25*, 1739.
- [3] M. Iannelli, V. Alupei, H. Ritter, *Tetrahedron* **2005**, *61*, 1509.
- [4] F. Wiesbrock, R. Hoogenboom, U. S. Schubert, *Macromol. Rapid Commun.* **2004**, *25*, 1739.
- [5] Y. Huang, X. Duan, Y. Cui, L. J. Lauhon, K.-H. Kim, C. M. Lieber, *Science* **2001**, *294*, 1313.
- [6] S. J. Tans, A. R. M. Verschueren, C. Dekker, *Nature* **1998**, *393*, 49.
- [7] R. Martel, T. Schmidt, H. R. Shea, T. Hertel, P. Avouris, *Appl. Phys. Lett.* **1998**, *73*, 2447.
- [8] A. P. Graham, G. S. Duesberg, W. Hoenlein, F. Kreupl, M. Liebau, R. Martin, B. Rajasekharan, W. Palmer, R. Seidel, W. Steinhoeft, E. Unger, *Appl. Phys. A* **2005**, *80*, 1141.
- [9] J. Kong, H. T. Soh, A. M. Cassell, C. F. Quate, H. Dai, *Nature* **1998**, *395*, 878.
- [10] N. R. Franklin, Y. Li, R. J. Chen, A. Javey, H. Dai, *Appl. Phys. Lett.* **2001**, *79*, 4571.
- [11] R. D. Bennett, A. J. Hart, A. C. Miller, P. T. Hammond, D. J. Irvine, R. E. Cohen, *Langmuir* **2006**, *22*, 8273.
- [12] M. S. Dresselhaus, G. Dresselhaus, P. Avouris, *Carbon Nanotubes: Synthesis, Structure, Properties and Applications*, Springer, Berlin, Germany **2001**.
- [13] S. Iijima, *Nature* **1991**, *354*, 56.
- [14] T. W. Ebbesen, P. M. Ajayan, *Nature* **1992**, *358*, 220.
- [15] H. Kind, J.-M. Bonard, C. Emmenegger, L.-O. Nilsson, K. Hernadi, E. Maillard-Schaller, L. Schlapbach, L. Forró, K. Kern, *Adv. Mater.* **1999**, *11*, 1285.
- [16] R. F. Wood, S. Pannala, J. C. Wells, A. A. Puzos, D. B. Geohegan, *Phys. Rev. B* **2007**, *75*, 2354661.
- [17] E. H. Hong, K.-H. Lee, S. H. Oh, C.-G. Park, *Adv. Funct. Mater.* **2003**, *13*, 961.
- [18] E. H. Hong, K.-H. Lee, S. H. Oh, C.-G. Park, *Adv. Mater.* **2002**, *14*, 676.
- [19] H. Shin, Y. Wang, U. Sampathkumaran, M. R. De Guire, A. H. Heuer, C. N. Sukenik, *J. Mater. Res.* **1999**, *14*, 2116.
- [20] S. Hoepfener, U. S. Schubert, *Small* **2005**, *1*, 628.
- [21] R. Maoz, E. Frydman, R. Sidney, R. Cohen, J. Sagiv, *Adv. Mater.* **2000**, *12*, 725.
- [22] D. Wouters, U. S. Schubert, *J. Mater. Chem.* **2005**, *15*, 2353.

- [23] S. Hoepfener, R. Maoz, R. Cohen, R. Sidney, L. Chi, H. Fuchs, J. Sagiv, *Adv. Mater.* **2002**, *14*, 1036.
- [24] C. R. Becer, C. Haensch, S. Hoepfener, U. S. Schubert, *Small* **2007**, *3*, 220.
- [25] S. Hoepfener, A. S. Susha, A. L. Rogach, J. Feldmann, U. S. Schubert, *Curr. Nanosci.* **2006**, *2*, 135.
- [26] S. Maruyama, R. Kojima, Y. Miyauchi, S. Chiashi, M. Kohno, *Chem. Phys. Lett.* **2002**, *360*, 229.
- [27] Z. F. Ren, Z. P. Huang, D. Z. Wang, J. G. Wen, J. W. Xu, J. H. Wang, L. E. Calvet, J. Chen, J. F. Klemic, M. A. Reed, *Appl. Phys. Lett.* **1999**, *75*, 1086.
- [28] A. K. M. Fazle Kibria, Y. H. Mo, K. S. Nahm, *Catal. Lett.* **2001**, *71*, 229.
- [29] S. Hoepfener, R. Maoz, J. Sagiv, *Nano Lett.* **2003**, *3*, 761.
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