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Free-Standing Carbon Nanofibrous Films Prepared by a Fast Microwave-Assisted Synthesis Process

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Carbon nanofibrous (CNF) films are of great interest for various applications, e.g., as substrates for electrodes, sensors, or catalysts. Here, a fast microwave-assisted synthesis is reported to fabricate square-centimeter large free-standing carbon nanofibrous films of approximately 10 μm thickness utilizing nickel-based catalysts and ethanol as carbon source. The obtained CNF coatings exhibit a good stability and partial self-delamination from the substrate is observed, which enables their easy detachment from the substrate without the need for further treatment. Scanning electron microscopy is applied to investigate the morphology of the films and to develop a growth model.

1. Introduction

Carbon nanofibers (CNFs) attract enormous research attention as they feature a combination of outstanding properties which are unrivalled by any other materials.[1] CNFs can be defined as cylindrical or conical structures with diameters ranging from a few to around 100 nm and lengths from some hundred nanometers to millimeters formed by different arrangements of graphene sheets. In line with this definition, carbon nanotubes (CNTs) are a special case of CNFs where the graphene sheets are 'rolled' into cylinders.[2] This arrangement with its semi-infinite, hexagonal network of covalently, sp^2-hybridized carbon atoms thereby forms the basis for the high stiffness, their special electronic properties as well as the chemical stability of carbon nanotubes.[2]

Like all nanostructured materials, carbon nanofibers possess a very high specific surface area which makes them, for example, suitable to serve as substrates for the deposition of active materials in order to prepare small devices. This high surface area, combined with the high mechanical, thermal and chemical stability of carbon nanostructures can, for example, be utilized to construct efficient devices for catalysis, sensing and filtration.[3–5] Their high electric and thermal conductivities make them furthermore attractive as substrate or additive materials for supercapacitors[6] or lightweight and flexible battery electrodes with enhanced energy conversion and storage capacities.[7–9]

Many of these applications require the preparation of stable CNF films or membranes. Often it would be desirable to transfer the as-synthesized films onto a substrate other than the ones they were grown on or even to obtain free-standing CNF films by directly peeling the coating off the substrate without disturbing their structure.[9–11] The most common way to grow carbon nanofibers is by utilizing chemical vapor deposition (CVD), which is a substrate-based synthesis method.[1,12] However, CNF coatings grown this way can usually not be easily detached from the substrate without destroying the structure of the carbon film owing to only weak van der Waals forces between the CNFs.[10] Thus, post-synthesis processes were developed to prepare free-standing CNF films. For example, the CNF ends can be oxidized with Ar/H$_2$ after their growth to induce the self-release of the film from the substrate.[10] Infiltration of acid[4] or short laser pulses[13] were applied to separate carbon nanofibrous films from glass substrates.

Apart from that, paper-like materials were prepared from CNF dispersions using drop-drying, vacuum-filtering and similar methods[9,13,14] or by 'domino-pushing' an array of aligned CNTs and afterwards peeling it of the substrate.[15] For the preparation of such 'bucky paper' materials CNTs are required to be dispersible and, thus, further additives are required. However, chemical processing and additives tend to contaminate the carbon films and the contact with liquids often entails the formation of foam-like structures.[10] Additionally, buckypapers are usually not aligned and not as thin as as-grown films, since they can only be handled as a free-standing film without a supporting nylon membrane when the film thickness is above 50 μm.[13,16]

2. Free-Standing CNF Films via Microwave-Assisted Synthesis

Here we report a one-step synthesis to obtain free-standing carbon nanofibrous films grown from various nickel-based catalysts utilizing a microwave-assisted synthesis approach. Thereby, very thin coatings with good stability were obtained, which could be detached from the substrate and no further treatment is required to obtain thin, free-standing carbon nanostructured films.

The microwave-assisted synthesis represents a very simple and fast way to grow carbon nanofibers.[17] This method is based on the material-specific absorption of microwave

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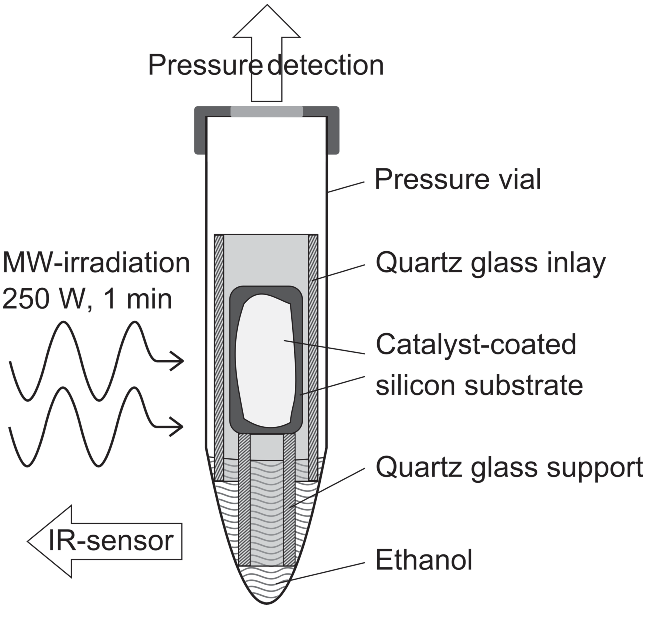

Figure 1. Sectional drawing of the experimental set-up for the microwave-assisted synthesis of carbon nanostructures.

irradiation.[18,19] Metallic, and in particular magnetic materials are very strong microwave absorbers compared to common solvents and non-conducting solids. The origin for their strong absorption lies in the movement of nearly free electrons and the rotation of the magnetic dipoles when exposed to an oscillating electromagnetic field.[20,21] As a consequence, magnetic materials can be heated very fast and efficiently and a strong, local temperature increase can be obtained when nickel, cobalt or iron catalyst particles are irradiated with microwaves.[22] The heated metal surfaces then enable the catalytic decomposition of the applied carbon source, the dissolution of carbon into the metal particles and the growth of carbon nanofibers,[1,12] whereas the overall temperature in the reaction chamber remains at a rather low level of less than 250 °C compared to much higher temperatures involved in the commonly applied chemical vapor deposition processes. Further major advantages of this microwave-assisted synthesis are the simple set-up without hazardous reactants, the use of a liquid carbon source (e.g., ethanol), no need of an inert gas atmosphere and very short reaction times of just minutes to seconds. Silicon wafers are utilized as substrates on which the CNF films are grown. Different catalysts are applied onto these substrates which are subsequently exposed to microwave irradiation in the presence of ethanol as a carbon source. A sectional drawing of the synthesis set-up is displayed in **Figure 1**. The pressure and temperature data measured during a typical synthesis process are shown in **Figure 2**. However, it has to be noted that the temperature is measured by an IR-sensor mounted outside the vial. Thus, it does not provide any information about the local temperature of the catalyst on the surface of the substrate.[22]

After the synthesis the substrates were covered with a black coating, which generally shows a very hydrophobic behavior. Those films could be easily detached from the substrate by using tweezers (**Figure 3**A). The typical weight of the obtained films was in the range of 1 mg per 1.5 cm^2. To reveal the morphology of the surface the films were investigated by means of scanning electron microscopy (SEM). Top-view images, showing the micro- and nanostructure of a representative CNF film, are displayed in Figure 3B and C. Additionally, transmission electron microscopy (TEM) was used to disclose the hollow structure of the fibers (Figure 3D).

Thermogravimetric analysis (TGA) was performed under airflow to evaluate the quality of the obtained CNFs.[23] Nearly no weight loss occurred below 500 °C (**Figure 4**), which indicates the presence of a high degree of crystalline carbon in the CNF films, since amorphous carbon already oxidizes at a lower temperature. Furthermore, the residual weight, which was assigned to nickel oxide, implies a low nickel content of the films.

Different nickel acetate based catalysts were prepared and applied for the synthesis of carbon nanofibrous coatings: A) ethanolic nickel acetate solution, B) flake-like precipitate obtained by aging of A), C) cuboid precipitate obtained by microwave heating of solution A) and D) nanosheets obtained by microwave heating of a 1:1 water/ethanol solution of nickel acetate (**Figure 5**A1–D1).

Stable and smooth CNF films only could be obtained when a certain amount of catalyst was applied. To quantify the required amount of catalyst the theoretical thickness of the nickel catalyst layer was calculated. For this purpose, a dense and homogenous metallic layer was assumed to be formed on the whole surface of the substrate by decomposition/reduction of the applied nickel compound and the nickel content of the catalyst

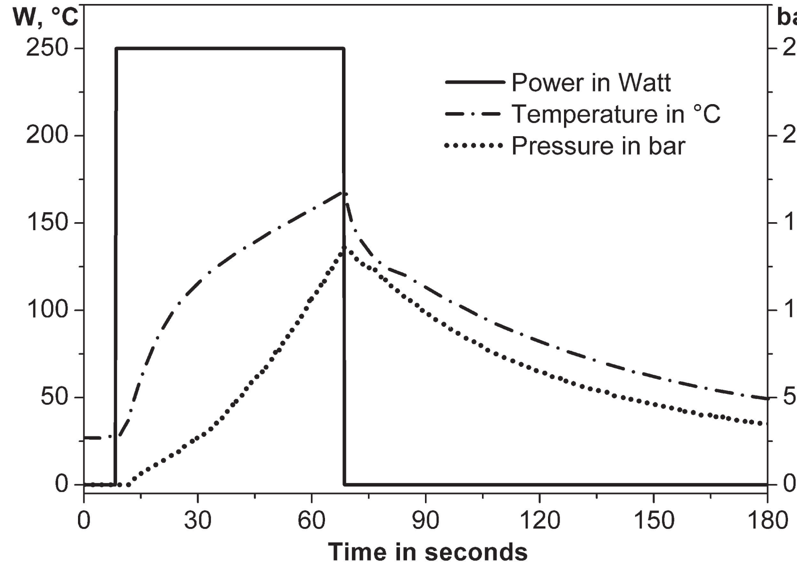

Figure 2. Power, temperature, and pressure curves of a typical synthesis. Microwave radiation of 250 W was applied for 1 min.

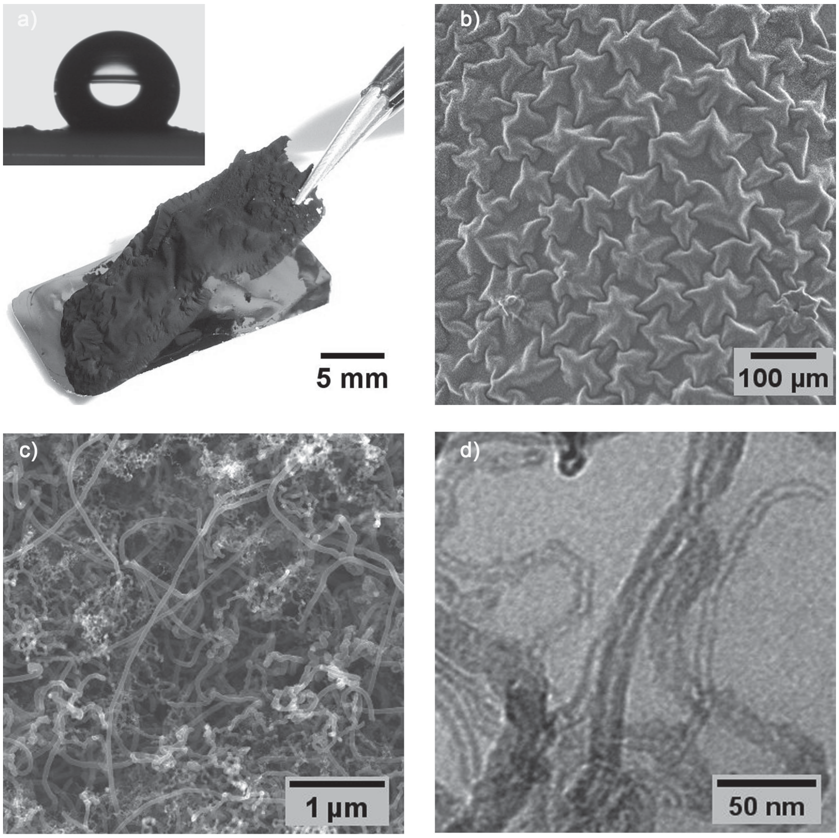

Figure 3. Micro- to nanostructure of the morphology of the CNF films: a) Photograph of a detached CNF film and image of a water droplet on a CNF film's surface showing the hydrophobic behavior. b,c) Representative top-view SEM images of a CNF film. d) TEM image showing the hollow internal structure of CNFs obtained by dispersing parts of a CNF film.

dispersions was determined by atomic absorption spectroscopy (AAS). For the nickel acetate solution and the flake-like catalyst particles an optimal synthesis result was achieved when the amount of nickel in the catalyst compound corresponded to a metallic nickel layer with a calculated thickness in the range of 40 nm. For the cuboid precipitate, however, this amount of nickel was not sufficient, but rather an amount corresponding to a nickel layer of 60 nm in thickness was required.

3. Morphologic Investigations

SEM imaging was applied to investigate the structure of the catalyst layers and the morphology of the free-standing films (Figure 5A2,3–D2,3). The focus of the SEM study was placed on the investigation of the cross-sectional areas of the films to obtain information on their structure and to draw conclusions on the film formation process.

The thickness of the surveyed cross-sections was in the range of 7 to 10 µm and often the films showed a characteristic microstructure, as can be seen in Figure 3B. Within the films the CNFs were randomly oriented and entangled and the morphology of the cross-sections appeared similar throughout different samples (Figure 5A3–C3).

Imaging with backscattered electrons was used to show the material contrast of a CNF film (Figure 5B3) in comparison with an image with pure topography contrast for which just secondary electrons were detected (Figure 5B2). By detecting the backscattered electrons from the sample nickel appears brighter than carbon due to its higher atomic number, thus, the catalyst particles are nicely visible and their distribution throughout the cross-section further confirms that the CNFs are not well-aligned, but randomly orientated. Additionally, the occurrence of 'tip-growth' during this microwave-assisted synthesis of CNFs[12] could be demonstrated.

CNF films grown from the nanosheet catalyst appeared more dense, but at the same time also thicker and much more brittle (Figure 5D3). The CNFs in those films seemed to be more oriented and less entangled as in the ones discussed above, which might be a consequence of their shorter length (compare the top-view images Figure 5D2 with Figure 3C). Furthermore, the films grown from the nanosheets exhibited a more homogenous CNF diameter distribution. This differences could be based on the fact that the nanosheet catalyst was prepared at a higher temperature compared to the other catalysts and, thus, consisted of nickel hydroxide.[24] As a result, a different heating and/or decomposition and, consequently, a different nucleation behavior

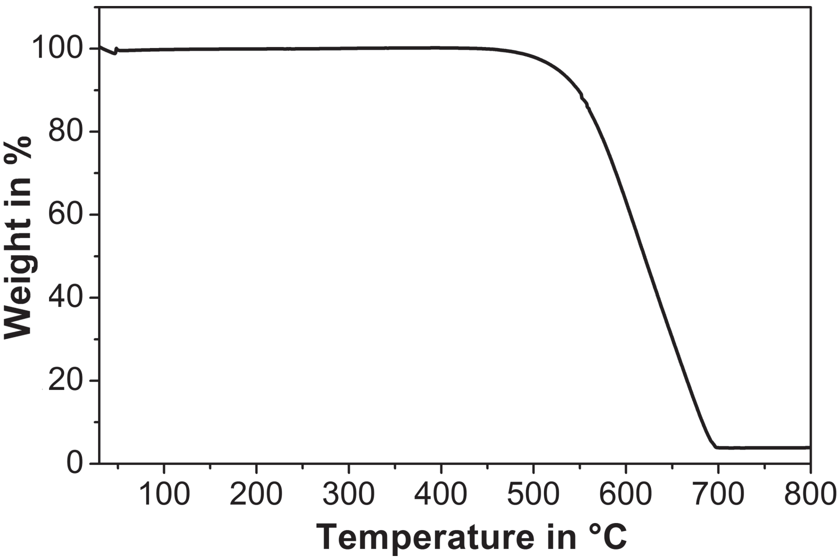

Figure 4. Thermogravimetric curve of CNF films heated under airflow.

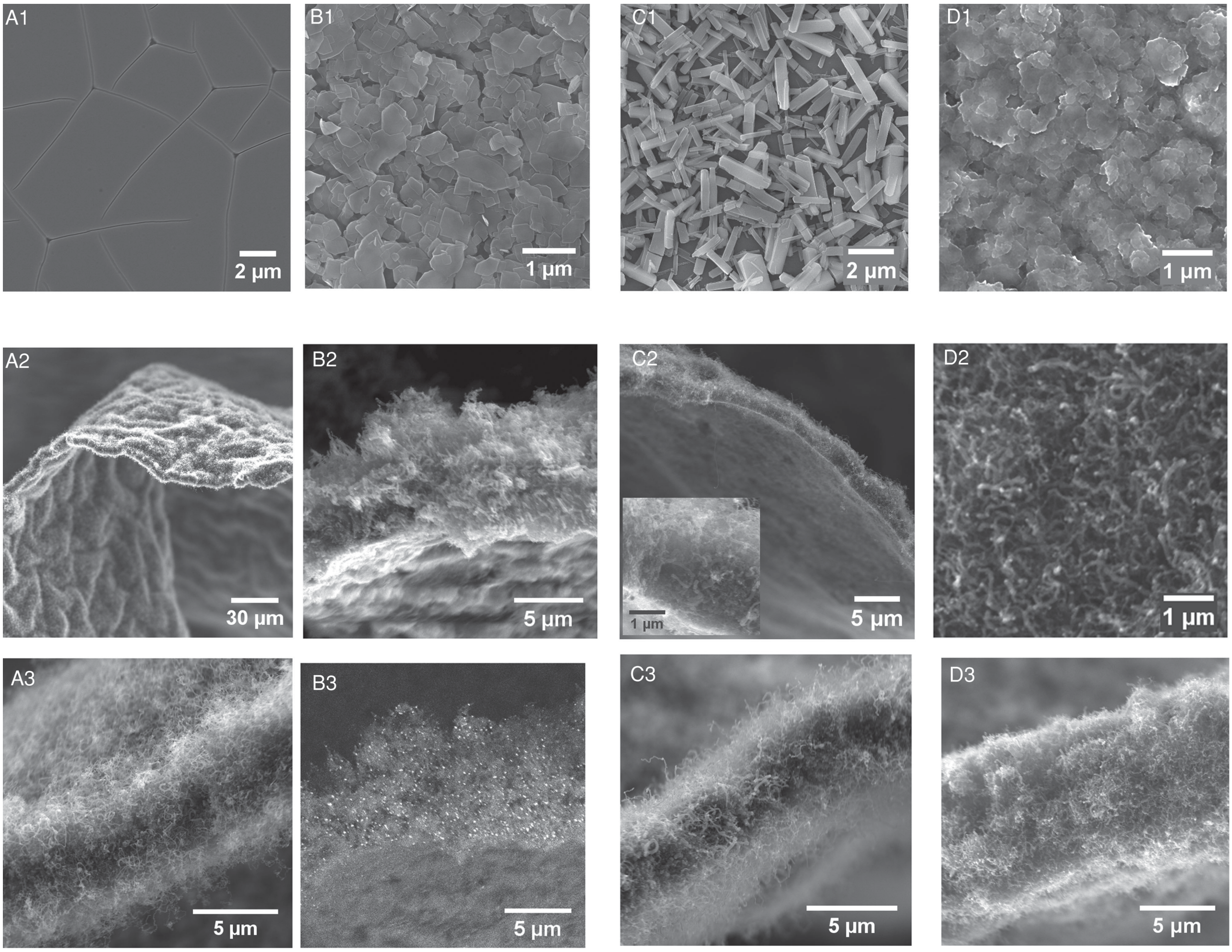

Figure 5. SEM images of catalyst layers and CNF films grown from these: nickel acetate catalyst (A1) and film prepared with this catalyst (A1,A2); flake-like precipitate (B1) and an obtained film displayed in topography contrast (B2) and material contrast (B3); cuboid precipitate (C1) and films prepared with a small amount (C2) and a larger amount of this catalyst (C3); nanosheets (D1) and a CNF film prepared from these in top-view (D2) and the cross-section (D3).

might have occurred. Not even when a larger amount of catalyst was applied, a mechanically more stable film could be obtained in this case.

In general, a homogenous catalyst layer with an optimized amount of nickel turned out to be an important prerequisite to obtain stable and smooth CNF films. When too much catalyst was applied the micro-roughness of the films was increased and blisters were formed in the film, but even in this case the thickness of the cross-section remained comparable. On the other hand, if not enough catalyst was applied no dense catalyst layer and, thus, no dense CNF film could be formed. A slight decrease of the commonly applied amount of catalyst still resulted in the formation of CNF films, which, however, where hardly detachable from the surface. A SEM image of such a film is displayed in Figure 5C2. In this case, no continuous CNF film was formed, but a smooth backside of the film is visible which probably contains unreacted residues from the catalyst which is the reason for its higher adhesion to the substrate and as well the smooth appearance of this film.

4. Development of a Growth Model

Concluding the SEM investigations, we propose the following processes to occur during the synthesis: Firstly, when the reaction is started, the nickel compound catalyst is decomposed to nickel oxide and is later reduced to metallic nickel.[25,26] During this transformation, the catalyst layer partly delaminates from the substrate and arches upwards. This process enables the nucleation and growth of CNFs from both sides of the catalyst layer. Starting from the middle, the CNFs then grow randomly oriented. Thereby, the CNF coating further takes off from the substrate and partly self-delaminates, which finally facilitates the easy detachment of the CNF films.

It was assumed that the arching and self-detachment just occurs when particles are used as catalyst, which exhibit a low adhesion to the substrate. However, it turned out that also ethanolic nickel acetate layers, which exhibited a much higher adhesion to the substrate than the randomly oriented catalyst particles, entailed self-detaching CNF films when enough catalyst was applied.

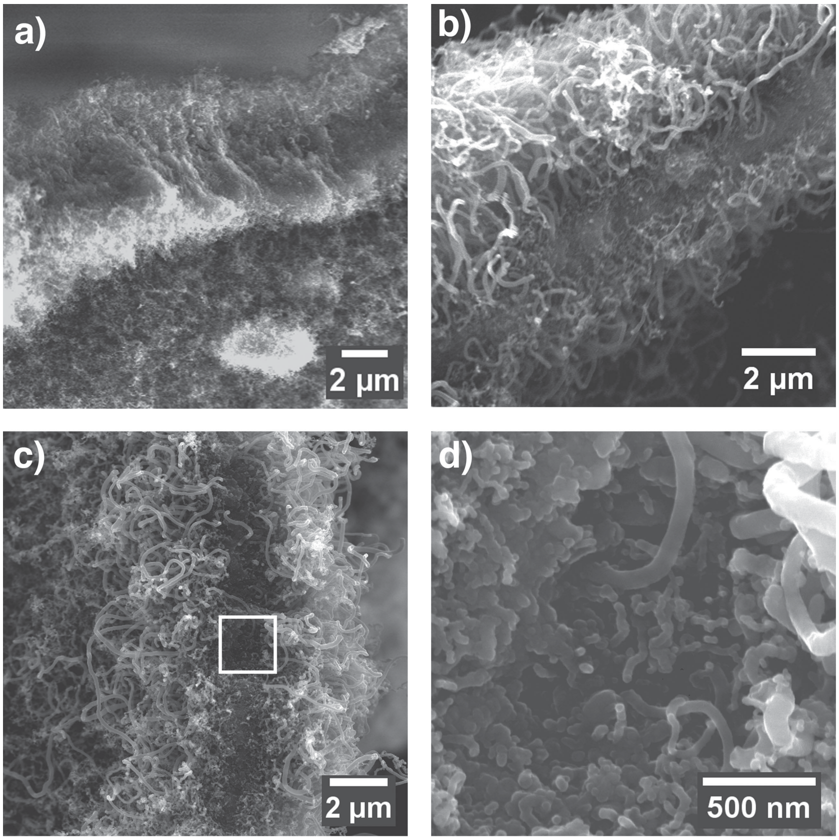

Figure 6. SEM images of atypically formed cross-sections of CNF films supporting the hypothesis that the films formed by CNF growth from both sides of the catalyst layer. The film displayed in A) was prepared utilizing the flake-like catalyst and the film shown in B-D) with the cuboidal precipitate. Image D shows the magnification of the area marked in C.

Thicker catalyst layers result on the other hand in general in large CNF diameter distributions. With spin-coated ethanolic nickel acetate layers thinner CNFs with smaller diameter distribution can be obtained,[17] but in return those CNF layers cannot be easily disassembled to free-standing films. Moreover, it was observed that if no arching occurs, CNFs can just grow on top of the catalyst layer. As a result, a smooth and thin film can be obtained, but detachment is hardly possible, as e.g. observed for the sample shown in Figure 5C2.

The assumption of CNF growth starting from both sides of the catalyst layer can be proven by the fact that occasionally during SEM investigation atypical or imperfectly shaped film edges appeared (**Figure 6**). For example, an area was observed where the CNFs were vertically aligned and the starting point for the growth is clearly located in the middle of the film (Figure 6A). In other samples, residues from the catalyst particles were found (Figure 6B) or, on the contrary, a lower CNF density in the middle of the film was observed (Figure 6C). These defects are probably the result of an agglomeration of catalyst particles and show the drawback of utilizing catalyst particles instead of depositing a soluble catalyst. Although in general films could be synthesized with different kinds of catalysts, a dissolved catalyst yields more continuous catalyst layers with a more homogeneous thickness than dispersed particles do. Furthermore, the inhomogeneous distribution of the particles explains why a higher amount of catalyst was required for the cuboid precipitate than for the nickel acetate solution and the flake-like precipitate, as described above.

The magnified SEM image of the partly hollow core (Figure 6D) moreover shows that the CNFs inside the film have smaller diameters than those on the outer area of the film. This finding suggests that the CNF growth occurs in several stages until all catalyst material is depleted and, thus, a film of entangled CNFs is formed. A similar observation of such a bimodal size distribution and the formation of entangled mats was reported by Luhrs et al. for the growth of carbon filaments on carbon microfibers when more catalyst metal salt was applied than the 'saturation loading'.[27] The authors, however, related the bimodal diameter distribution to the saturation of active sites on the surface of the microfibers with small catalyst particles and subsequent formation of larger, 'free' metal agglomerates. These catalyst particles, according to their size, then entailed the differently thick carbon filaments.

The fact that the lift-off from the substrate already occurs during the reduction step and is not caused by the growing CNFs pushing the film upwards, was tested by performing a synthesis where 250 W were irradiated for just 20 s. SEM images of this film, thus, provide information about an intermediate state of the film growth (**Figure 7**). The

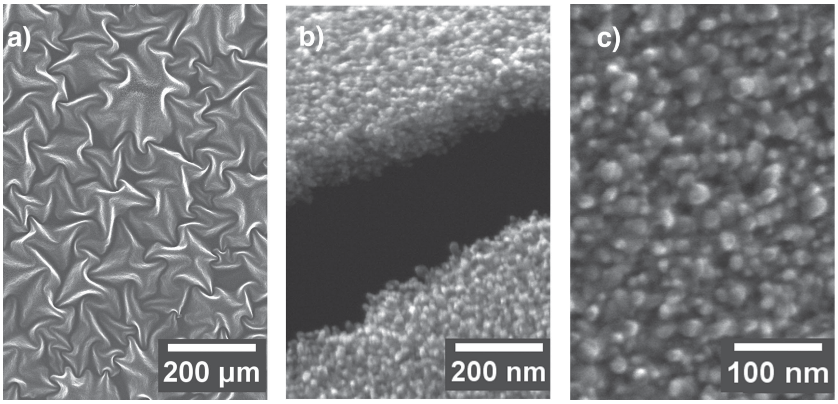

Figure 7. SEM images showing an intermediate state of the synthesis. After just 20 s of microwave irradiation the nickel acetate catalyst layer exhibits a rough microstructure (A). The film is partly detached from the substrate and has a thickness of around 100 nm as becomes apparent by a zoom-in into a crack in the film where an edge is visible (B). The surface features a grainy structure with structure sizes smaller than 30 nm but no CNFs were grown yet (C).

short irradiation time of 20 s was not sufficient to induce the growth of CNFs, but the surface exhibited a particulate structure (Figure 7C) and the catalyst film started to slightly arch upwards, forming a microstructure similar to those found for the CNF films as well (compare Figure 7A with Figure 3B). Across a crack in the film an edge with a thickness of around 100 nm could be imaged (Figure 7B). This image nicely proofs that the microstructure arose by arching and is not based on solid material.

5. Conclusions

The low experimental afford, the small number of processing steps and the extremely short synthesis time are regarded as the striking advantages of the introduced method to grow thin and entangled carbon nanofibrous coatings. The fact that these coatings can be directly peeled off the substrate as free-standing CNF films allows an easy handling of otherwise rather difficult to process CNF powders. The homogeneity of the films was found to depend highly on the amount of catalyst and the homogeneity of the catalyst layer. Catalyst layers casted from nickel acetate solution resulted in more homogeneous films than layers formed by dispersed nickel-compound particles. Further investigations are currently in focus of research as well as critical points regarding the up-scaling in terms of obtainable film sizes. Since in particular the deposition and structure of the catalyst films is assumed to play a major role evenly deposition of the catalyst solution will be tested by means of, e.g., applying spin-coating,[28] inkjet-printing,[29] or adding surfactants[30] to the catalyst solution.

6. Experimental Section

Film Synthesis: As substrate for the synthesis silicon wafers (p-doped, 1–10 ohm cm, 500 µm thickness, <100>, double side polished) were cut into rectangular pieces. The corners of the substrates were flattened to avoid the formation of hot spots during the microwave irradiation and the substrates were cleaned with isopropanol and ultrasound to eliminate splinters. Furthermore, an argon plasma treatment (300 W, Plasma system Nano, Diener Electronic) was applied to remove organic residues and to render the surface hydrophilic. In a typical synthesis procedure some microliters of an ultrasonicated catalyst solution/dispersion were drop-casted onto a piece of silicon of ca. 1.5 cm^2 in size (please note that the dimensions are only limited by the size of the microwave vials). The catalyst-coated substrate was subsequently placed in a microwave vial (size 0.5 to 2 mL), which contained half a milliliter of ethanol. A quartz glass support was used to keep the substrate above the liquid ethanol level and a quartz glass inlay was utilized to prevent contact between the substrate and the borosilicate glass of the vial (see Figure 1). The vial was then capped and exposed to microwave irradiation (Biotage Initiator) at 250 W for one minute.

Preparation of Catalysts: Different nickel acetate based catalysts were prepared and applied for the synthesis of carbon nanofibrous coatings: A) 0.1 M ethanolic nickel acetate solution, B) flake-like precipitate obtained by aging of a 0.1 M ethanolic nickel acetate solution, C) cuboid precipitate obtained by microwave heating 0.5 mL of a 0.1 M ethanolic nickel acetate solution for 3 h at 100 °C under stirring of 600 rpm and D) nanosheets obtained by microwave heating 0.5 mL of a 0.1 M nickel acetate solution (1:1 water and ethanol) for 1 h at 190 °C.[24]

Characterization: Scanning electron microscopy imaging was performed with a LEO 1530 Gemini, Zeiss with InLense detector. For SEM imaging of the catalyst layers, an equal amount of catalyst as applied for the syntheses was drop-casted onto a piece of silicon and subsequently sputter-coated with 3 nm of platinum. For the investigation of film morphologies, pieces of the films were detached from the substrate and glued onto a SEM-sample holder by means of a conductive tape.

For transmission electron microscopy a CM 120, Philips with 120 kV acceleration voltage was applied. The sample was dispersed in ethanol by applying ultrasound for a few seconds and was subsequently dropped onto a carbon coated copper grid.

Thermogravimetric analysis was performed under airflow with a heating rate of 20 K min^{-1} (Netzsch TG 209 F1). The sample contained several CNF films synthesized with catalyst A) and had a total mass of 4 mg. The image of the water droplet was taken with an OCA30 (Dataphysics).

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