SFM Tips from the Microwave - Fast Microwave-assisted Synthesis of Carbon Nanotubes

Microwave supported synthesis has developed into a widely used tool in chemistry. We report on an approach that utilizes the different absorption capabilities of different materials for microwaves for the synthesis of carbon nanotubes (CNT) on different substrates. The growth mechanism and the applicability of the CNT growth for functional and structured surfaces, as well as for the fabrication of CNT functionalized SFM tips are summerized.

Microwave irradiation is a widely used tool in daily life. Besides being frequently utilized to rapidly heat food, in the past years microwave heating has found applications also in organic synthesis and could improve conventional synthetic protocols, resulting in fast reaction times, the formation of well-defined reaction products and high yields [1]. These improvements are mainly due to the fact that microwave reactions can be performed in closed pressure vials, permitting performance of reactions at high pressures and high temperatures. Moreover, the direct heating of reaction compounds results in the selective and homogeneous heating of the materials.

Up to now, the different absorption characteristics of materials for microwave radiation is an effect that was rarely utilized for synthesis [2,3], but on the other hand provides a very promising approach to synthesize nanomaterials, e.g. carbon nanotubes (CNT), at non-conventional reaction conditions.

Classical synthesis routes for the fabrication of CNTs on surfaces include mainly chemical vapor deposition approaches. Major drawbacks of this approach are the demanding reaction condition that have to be applied: Temperatures of several hundred degrees are required to decompose a carbon source at the catalyst sites to obtain CNTs. In particular, the high reaction temperatures strongly limit the choice of applicable substrate materials for solid supported films of CNTs. Alternative, synthesis conditions, which preferentially minimize the required temperatures, are very desirable, in particular with respect to polymeric substrates. In the following different aspects of the synthesis of carbon nanotubes by microwave irradiation are discussed.
Scanning Force Microscopy and Electron Microscopy have been utilized to investigate the CNT formation, and the impact of this alternative synthesis approach.

Selective Heating of the Catalyst -Material by Microwave Irradiation

In general, the synthetic approach to grow CNTs by microwave irradiation requires comparably low experimental efforts. Besides a synthetic microwave operating at 2.54 GHz and 200 to 300 W, which differs from conventional microwave ovens only in terms of the homogeneity of the microwave irradiation and the utilization of reaction vials that permit operation at 22 bar and temperatures of 200°C, no further experimental tools are required. A typical setup is depicted in figure 1a. The sample preparation involves only the deposition of the catalyst precursor, which is an aqueous solution of a metal salt, either iron, nickel, or cobalt, onto the substrate, which can be glass, silicon, or a polymer foil, e.g. PE. The catalyst loaded substrates are simply mounted on a quartz glass support within the reaction vial, and a liquid carbon source, i.e. ethanol, is added as a subphase. The vials are capped and are inserted into the microwave (fig. 1b). After an irradiation time of only 3 minutes, it is observed that on top of the substrates a black coating has formed, which shows, upon inspection with Scanning Electron Microscopy (SEM), the presence of a homogenous film of vertically aligned nanotube structures (fig. 2). This is, on the first glance, rather surprising, because the temperature control during the heating process never reached temperatures above 230°C, and hence, at this low temperatures, no CNT formation was expected.

However, as a special characteristic of microwave irradiation the absorption of the waves is governed by the material's properties. While conducting materials are very good microwave absorbers, i.e. the catalyst particles, insulators are transparent for microwave irradiation, e.g. the used substrates, and do not significantly absorb the
energy of the microwave irradiation. These differences in the microwave absorption capabilities result in a selective heating process of the catalyst material, while the overall reaction temperatures remain relatively low (approx. 200°C). To demonstrate this effect, Scanning Force Microscopy (SFM) investigations were performed utilizing a defined array of catalyst particles mounted onto a substrate that was coated with a self-assembled monolayer [4]. These thin layers exhibit a limited temperature stability, and thus, can serve as an indicator for the local temperature. For this experiment the overall exerted temperature was limited to 120°C and irradiation was performed for 10 minutes. Figure 3 depicts the result of the microwave irradiation. It can be seen that circular holes are formed in a grid-like fashion, that resembles the lithographically deposited catalyst particles prior to the irradiation process. The holes indicate that the temperature in close vicinity of the particles obviously is significantly higher compared to the temperature that is exerted on the rest of the substrates. This experiment is regarded as a good qualitative evidence for the selective heating mechanism of different materials by microwave irradiation [5].

Moreover, other important parameters could be identified influencing the nanotube formation. Besides the choice of the catalyst material, which influences the diameter of the formed tubes, the pressure has been determined as a governing parameter for the formation of the CNTs. Pressure values above 12 bar were required to allow the synthesis of carbon nanotubes [6].

**Applications of Microwave Generated CNTs**

Substrates, which are functionalized with carbon nanotubes, have attracted considerable interest in applied research and material science [7]. They can be used, e.g., as conductive or superhydrophobic surface coatings. The good control over the CNT formation motivates also the use of the microwave assisted synthesis for more specialized applications that involve e.g. the growth of individual CNTs in predefined locations. These applications might include the fabrication of field-emitter arrays, but can also simplify be the fabrication of carbon nanotube functionalized SFM tips. Such tips promise a great potential in terms of improved imaging capabilities, tip life-time, and for customized measurement modes. While, different suppliers commercially offer CNT functionalized tips, the commonly applied processes do not permit a cheap fabrication process, and thus, these tips are rarely used for routine measurements due to their high costs. Thus, the advantages of the microwave-assisted synthesis would be potentially interesting and could be beneficial for the development of an improved fabrication approach for carbon nanotube functionalized SFM tips.
A key issue, which had to be solved for such a fabrication process, was the placement of the catalyst material on the SFM tip [8]. It turned out that different approaches could be followed, including the picking of individual catalyst particles. Since this step is rather time consuming and is not compatible with high-throughput fabrication schemes, alternatively a force spectroscopy cycle or simple scanning of the tip on a layer of dried acetate solution turned out to be sufficient to deposit a limited amount of catalyst precursor material onto the SFM tip, which is during the microwave process converted into a catalyst particle upon thermal activation [9]. The next experimental challenge was the fact, that the heat dissipation had to be controlled. In contrast to CNT films, which exhibit a rather dense arrangement of catalyst particles, the heat dissipation in the vicinity of an individual particle turned out to be too high to generate reaction conditions suitable to synthesize carbon nanotubes. Mounting the individual SFM tips onto a weakly absorbing silicon substrate was sufficient to balance the energy losses and allowed moreover the convenient handling and parallel functionalization of several SFM tips. Figure 4a depicts an example for a SFM tip that has been functionalized by an individual CNT, which was grown by the microwave-assisted process. Since a large number of tips can be produced in parallel in a process that consumes just a few minutes, a potential decrease of the fabrication costs is expected. Preliminary results of experiments performed with CNT functionalized tips already demonstrated their reasonable stability, as well as their conductive properties (fig. 4b). Further adaptations in the experimental process will be pursued, and better control of the length of the CNTs grown on the SFM tip, as well as their growth direction, will be developed.

Conclusion

The development and optimization of a microwave-assisted fabrication process of carbon nanotubes opens several new possibilities for the functionalization of surfaces with carbon nanotubes, even if they are not compatible with general fabrication processes, e.g. concerning their temperature stability. The selective heating mechanism of metal particles by microwave irradiation could be demonstrated and identified as a key feature of the carbon were nanotube synthesis mechanism, which provides important advantages compared to conventional approaches. These include in particular the low synthesis temperatures, short reaction times of < 5 minutes, as well as the cheap and easy to handle reaction compounds (e.g. ethanol).

Based on the presented investigations other applications of the microwave assisted synthesis mechanism are envisioned which include e.g. the implementation of CNTs into integrated electronic circuits.
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References

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