

Synthesis and Modification of Carbon Nanomaterials utilizing Microwave Heating

Almut M. Schwenke, Stephanie Hoeppeener,* and Ulrich S. Schubert

Microwave-assisted synthesis and processing represents a growing field in materials research and successfully entered the field of carbon nanomaterials during the last decade. Due to the strong interaction of carbon materials with microwave radiation, fast heating rates and localized heating can be achieved. These features enable the acceleration of reaction processes, as well as the formation of nanostructures with special morphologies. A comprehensive overview is provided here on the possibilities and achievements in the field of carbon-nanomaterial research when using microwave-based heating approaches. This includes the synthesis and processing of carbon nanotubes and fibers, graphene materials, carbon nanoparticles, and capsules, as well as porous carbon materials. Additionally, the principles of microwave-heating, in particular of carbon materials, are introduced and important issues, i.e., safety and reproducibility, are discussed.

1. Introduction

By inducing temperatures of up to 1000 °C within just one minute^[1,2] microwave (MW) irradiation is a fascinating and promising tool for the preparation and modification of carbon materials. Microwave heating is based on the interaction of matter with electromagnetic radiation. It is independent of the thermal conductivity of the surrounding materials and allows an instantaneous on/off switching of the heating. Due to fast heating rates, shorter treatment times are possible, which result in time and energy saving processes and might even suppress undesired side-reactions and enable new reaction pathways.^[3] Since the 1980s, microwave equipment has been progressively entering chemical laboratories, thereby replacing conventional heating methods and broadening the toolbox of chemists, physicists and materials scientists. Starting their rise in the field of organic chemistry, microwave ovens are now gaining more

and more popularity for the synthesis of inorganic materials and in the field of nanotechnology.^[4,5]

In materials science, carbon nanomaterials play a major role in research and are thought to be an important component of future materials and devices.^[6,7] The first controlled synthesis of carbon nanotubes (CNTs) in 1991^[8,9] constituted the start for the research field of nanocarbon materials, further stimulated by the first preparation of graphene in 2004.^[10] CNTs and graphene possess a combination of outstanding properties which make them suitable for a wide range of applications; for example, e.g., their exceptional mechanical properties and their low density make them an interesting component

for reinforced composite materials. The high surface area and stability of carbon nanostructures is utilized for the fabrication of more-efficient devices for catalysis and sensing. Further potential applications are envisaged, among others in the areas of microelectronics, energy storage, and medicine.^[6,7] Besides CNTs and graphene, many other kinds of carbon materials are nowadays prepared and investigated including, for example, carbon dots (C-dots), carbon nanocapsules (CNCs), porous, activated carbons (ACs), and three-dimensional (3D) carbon composite materials.

During the last decade, microwave-based methods were rapidly emerging in carbon-research literature. Based on the high conductivity of many carbon nanostructures and the ferromagnetic nature of common catalysts for the synthesis of CNTs, strong interactions with microwave radiation occur. These interactions are due to effects that are less pronounced or even do not occur at all in common (organic) reactions performed using microwave heating. Consequently, microwave treatment can be a valuable tool for the synthesis and modification of carbon nanostructures.

The applied methods can be divided into top-down and bottom-up approaches. Top-down methods include the transformation of solid materials, e.g., polymers or graphite into carbon nanomaterials, the exfoliation of graphite oxide (GO) to graphene, the cleavage of graphene, or the unzipping of CNTs to obtain C-dots or graphene ribbons. Bottom-up methods refer to the preparation of CNTs, C-dots, and CNCs originating from liquid or gaseous carbonaceous precursors. The top-down processes are mainly derived from conventional methods as pyrolysis, thermal expansion, or classic acid-cutting processes.

A. M. Schwenke, Dr. S. Hoeppeener, Prof. U. S. Schubert
Laboratory of Organic and Macromolecular
Chemistry (IOMC)
Friedrich Schiller University Jena
Humboldtstrasse 10, D-07743 Jena, Germany
E-mail: s.hoeppeener@uni-jena.de



A. M. Schwenke, Dr. S. Hoeppeener, Prof. U. S. Schubert
Center for Energy and Environmental Chemistry (CEEC) Jena
Friedrich Schiller University Jena
Philosophenweg 7a, D-07743 Jena, Germany

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Bottom-up processes are, for example, inspired by chemical vapor deposition (CVD) or hydrothermal methods. Furthermore, methods for purification, functionalization, or annealing of carbon structures are available based on microwave-heating processes. Such methods are often derived from classical annealing and functionalization protocols, but benefit from the advantages of microwave-matter interactions.

In this review, a detailed overview is given on the possibilities and achievements in the field of carbon-materials research when using microwave-based heating approaches. Thereby, the focus is set on the microwave processes themselves, illuminating special features and advantages, as well as the comparison with conventional processes. In Section 2, a short introduction into microwave heating is provided, focusing especially on the interaction of microwaves with carbon materials. Furthermore, practical “tricks” reported in the literature to improve microwave-heating processes are summarized. Section 3 provides a detailed insight into different microwave-based processes, classified according to the type of carbon materials, starting with carbon nanotubes and fibers (CNFs), followed by graphene materials, carbon nanoparticles, and, finally, porous carbon materials. To sum up, remarks regarding safety and reproducibility are discussed, as well as future chances and challenges.

2. Fundamentals of Heating Carbon Materials Using Microwave Irradiation

2.1. Principles of Microwave Heating

Microwave heating is based on the principle that a material absorbs electromagnetic energy and converts it into heat. In commercial MW ovens, typically, electromagnetic radiation with a frequency of 2.45 GHz is applied. The energy of a photon of this frequency is much too low to actively break chemical bonds, and, thus, too low to “induce” chemical reactions by direct absorption of the microwave energy, as would be feasible with, for example, ultraviolet and visible radiation.^[3] Instead, microwave radiation just affects the rotation of dipoles and induces translational motion of free or bound charges within the reaction media. The commonly utilized microwave-heating mechanisms can be divided in dielectric, magnetic, and conduction losses. They are based on the rotation of dielectric or magnetic dipoles and the induction of Ohmic currents or ionic conduction. Since MW radiation produces an oscillating field, electric dipoles and charges continuously try to realign in the electric field. Thereby, kinetic energy is converted into heat due to molecular friction and random collisions.^[3,4] For magnetic materials and those with high electric conductivity, the magnetic loss provides an additional very strong heating effect.^[11,12] Its origin lies in the coupling of magnetic dipoles with the magnetic component of the electromagnetic field.^[13,14]

Major advantages of applying microwave-heating processes in materials science are the contactless heating, with a direct transfer of energy to the reactants instead of transferring heat, and the independence from heat convection. Furthermore, microwave heating enables very rapid heating rates with an instantaneous response to the starting and stopping



Almut M. Schwenke

studied Materials Science and Engineering at the Friedrich-Schiller-University Jena (Germany) and the Uppsala University (Sweden). Since 2012, she has been a Ph.D. student in the group of Prof. U. S. Schubert, focusing on the synthesis and processing of carbon and metal nanostructures utilizing microwave heating.



Stephanie Hoeppener

studied physics at the Westfälische Wilhelms-University Münster, Germany, where she earned her Ph.D. degree in 2001 under the supervision of Prof. H. Fuchs and Prof. L.F. Chi. After her Ph.D. studies she joined the group of Prof. J. Sagiv at the Weizmann Institute of Science (Israel), as a Minerva fellow. In 2003

she moved to the group of Prof. U. S. Schubert, Eindhoven University of Technology, The Netherlands. Since 2009, she has been the project leader for Nanolithography and Surface Functionalization and responsible for electron microscopy in the Jena Center for Soft Matter at the Friedrich Schiller University Jena, Germany.



Ulrich S. Schubert was born in Tübingen (Germany) in 1969. He studied chemistry at the Universities of Frankfurt and Bayreuth (both Germany) and Virginia Commonwealth University, Richmond (USA). His Ph.D. work was performed under the supervision of Prof. C. D. Eisenbach (Bayreuth, Germany) and Prof. G. R. Newkome (Florida,

USA). After a postdoctoral position with Prof. J.-M. Lehn at the Université Strasbourg (France), he moved to the Munich University of Technology (Germany) to obtain his habilitation in 1999 (with Prof. O. Nuyken). From 1999 to Spring 2000, he held a temporary position as a professor at the Center for NanoScience (CeNS) at the LMU Munich (Germany). From June 2000 to March 2007, he was Full-Professor at the Eindhoven University of Technology (Chair for Macromolecular Chemistry and Nanoscience), The Netherlands. Since April 2007, he has been Full-Professor at the Friedrich-Schiller-University Jena (Chair of Organic and Macromolecular Chemistry), Germany.

of the irradiation. Last but not least, it offers the possibility of obtaining volumetric, local, and material-selective heating.^[15]

Special MW ovens dedicated for use in laboratories are offered by various suppliers. Different output powers and working principles are available, as was described in detail by Kappe et al.^[3] One major way to classify MW ovens is to distinguish between multimode and single-mode reactors. Microwaves with a single-mode cavity usually have a maximum output power of 400 W and rather small reaction vessels intended for the development of new methods. Multimode ovens provide larger cavities, but the field distribution is not as homogeneous and the power density is lower compared to single-mode ovens. However, in total they can provide a higher output power. Besides the equipment dedicated for lab use, domestic MW ovens are applied frequently for organic syntheses and in materials science. Those devices generally are multimode ovens, exhibiting rather inhomogeneous field distributions and a pulsed output power of, commonly, 700 to 1000 W. Their most significant disadvantages are the lack of reaction control and safety precautions, as well as a poor reproducibility of the conducted reaction protocols.

2.2. Microwave Interactions with Carbon Materials and Local Heating

Considering carbon materials, the extended π -electron-system, and, thus, the electric conductivity of the materials, represents a very important feature for microwave heating, since it provides the requirement for effective Joule heating;^[2,15] for example, structurally “perfect” single-wall carbon nanotubes (SWCNTs) are ballistic conductors, and hence, no thermal loss would occur. However, as-synthesized CNTs possess imperfections, which leads to Ohmic conduction and enables the heating by MW irradiation.^[2] The fact that the MW absorption of CNTs rapidly increases when electric percolation is reached additionally underlines the dependence of microwave heating on the conductivity of CNTs.^[16] Since CNTs are diamagnetic, no significant magnetic-loss contribution can be expected.^[16] However, the ferromagnetic nature of common catalyst materials can be of eminent relevance for the transformation of microwave energy.

Hu et al.^[17] showed the importance of defects and the degree of oxidation on the microwave heatability of graphitic materials. Graphite and graphene oxide samples with different carbon-to-oxygen ratios were irradiated at a rather low average power of 160 W. The resulting temperature curves (Figure 1) clearly show a significant decrease of heating for materials with higher oxygen ratios, hence, for those samples with smaller π - π conjugated regions and lower electron mobility.^[17]

The penetration depth d_p is a vivid parameter to visualize the ability of a material to be heated by MW irradiation. The penetration depth is inversely proportional to the loss factor, and, consequently, is dependent on the permittivity of the material. It is defined as the depth where the microwave power drops to $1/e$; thus, 63% of the microwave radiation is already absorbed.^[18]

Materials with low loss factor have a very high penetration depth and are quasi-transparent to MW radiation.^[3]

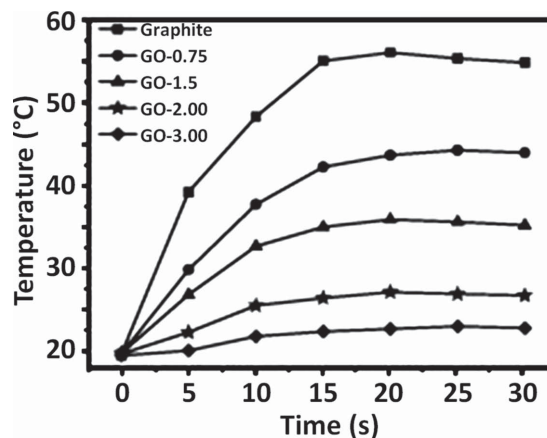


Figure 1. Influence of defects and, thus, the conductivity on the microwave heating properties of graphene displayed by the temperature profiles of graphite and graphene oxide samples with different carbon-to-oxygen ratios (from 24 wt% oxygen for GO-0.75 to 48 wt% for GO-3.00) exposed to MW irradiation at 160 W. Reproduced with permission.^[17] Copyright 2012, Elsevier.

Consequently, they are just heated by thermal transfer from components that do absorb the microwave radiation. This is, for example, the case for quartz glass or Teflon (see Table 1), which are thus very suitable materials for constructing reactions vessels and accessories.^[3,19]

Materials with a very high loss factor, on the contrary, exhibit a small penetration depth and, hence, only their surface is efficiently heated. Particularly in highly conductive materials, microwaves are absorbed very effectively due to strong interactions of the electric field of the waves with the nearly freely moving electrons of the material. However, the penetration depth in those materials is just some tens of nanometers or micrometers, and the major part of the incoming radiation is quasi-reflected.^[20] It is therefore common practice to describe the penetration depth of microwaves into conductive materials rather as a skin depth, which is dependent on the conductivity and the permeability of the material.^[21]

In Table 1, a collection of penetration depth data of some selected materials is displayed to provide a brief overview of their different orders of magnitudes. Unfortunately, microwave-absorption data reported in the literature are hardly comparable

Table 1. Penetration depth data of some materials and liquids for radiation at 2.45 GHz.

Material	Penetration depth [m]	Reference
Nickel	170×10^{-9}	[22]
Aluminum	1200×10^{-9}	[20]
Ethanol	80×10^{-6}	[23]
Graphite	38×10^{-6}	[24]
Silicon (1 Ω cm)	0.001	[25]
Water	0.014	[3]
Borosilicate glass	28	[23]
Teflon	92	[3]
Quartz glass	160	[3]

and exhibit a broad distribution. For nickel at 2.45 GHz, for example, penetration depths of 100 nm,^[25] 170 nm,^[22] and even 2.7 μm ^[26] are reported. A skin depth of 2.7 μm would imply a lower MW absorption for nickel than for aluminum. However, microwave-heating experiments with separation of the magnetic and the electric-field component unambiguously show the existence of a strong magnetic-heating effect, which results in a very short penetration depth of microwaves into magnetic nanomaterials.^[12] As a consequence, magnetic materials are only heated on their surface, much less than 1 μm in depth. However, regarding the synthesis of CNTs or the preparation of metal-core/carbon-shell nanoparticles, this very small skin depth of magnetic materials does not imply a limitation. Due to their nanoscale size, the particles are nonetheless heated over their complete volume.

Based on the material-specific absorption, MW irradiation can cause strong local heating and hot-spot formation. Amorphous carbon nanoparticles have been reported to reach 1283 °C within one minute of MW irradiation.^[2] Unpurified SWCNTs prepared by the high-pressure CO conversion (HiPco) process can be microwave-heated to temperatures of up to 1850 °C, whereas after purification and removal of the iron catalyst, only temperatures of 500 to 650 °C were measured.^[27] Additional to the strong heating, microwave treatment of CNTs results in intense light emission and outgassing.^[27,28] Light emission, perceived as electric-arc formation and sparking occurring upon MW irradiation of conductive materials, is a result of electron excitation leading to the ionization of the surrounding atmosphere.^[15] This generation of gas plasma is thought to be an additional potential source of the localized super-heating effects.^[2,15]

The local heating of certain components can be utilized for the preparation of materials and is in particular of importance for the microwave-induced growth and purification of carbon nanotubes. This efficient microwave heating of carbon materials can furthermore be used to improve the adhesion between CNTs and substrates,^[29] to manufacture and process CNT-polymer nanocomposites with lower power requirements,^[30] and to accelerate the curing of epoxy resins.^[31] Polymer-CNT composites can be obtained by microwave-assisted crosslinking,^[32] or CNT layers can be welded on polymer surfaces without changing the original CNT alignment or pattern.^[33–35] Further applications of the strong CNT-microwave-interactions include their use as susceptor material to promote sintering processes^[36] or to catalyze the cracking of crude oil,^[37] the area of broadband radar-absorbing materials for electromagnetic interface shielding,^[38,39] or even the field of water disinfection.^[40]

It is important to note that the loss factor for carbon materials was found to increase significantly with temperature. Thus, in practical applications, precautions have to be taken against a potential thermal run-away due to an increase in microwave absorption of the reactants in the course of a reaction.^[41]

One real drawback of the small penetration depth of some substances is that it limits the size of the reaction vial/sample, and simple upscaling is not always possible and, thus, simple upscaling by just using larger MW reactors is often not possible.^[2] Another major problem of microwave-heated reactions is that in situ measurements of the reaction conditions is difficult, since, especially, metallic instruments interfere with the electromagnetic field and can, thus, not be applied.^[3,4]

Commonly, the temperature of microwave reactions is measured by a fiber-optic probe or via an infrared (IR) sensor. However, these methods are not really suitable for carbon materials, where high temperatures and extremely fast heating occurs. Thermocouples would deliver more-reliable results, but have to be installed with care. Some profound considerations regarding the applications of thermocouples and optical pyrometers during the microwave treatment of active carbons were published by Menéndez et al. in 1999.^[1] A more-simple way is the ex situ introduction of a thermocouple, directly after the MW irradiation is switched off.^[17,42] An alternative, rather-indirect, method is the insertion of indicator materials into the cavity. The applied indicator should exhibit a known melting point and a low dielectric-loss factor, such that the results are not falsified by direct heating effects.^[43]

However, all of these methods just measure the average temperature in the synthesis reactor, and do not provide information about the temperature on the nanoscale or evidence for the occurrence of local hotspots. Druzhinina et al.^[44] provided at least a qualitative experimental proof for the existence of such local-heating effects. A self-assembled monolayer acted as a temperature-sensitive indicator layer on which iron nanoparticles were selectively deposited. Upon MW irradiation, the particles were heated. Subsequent ex situ atomic force microscopy (AFM) investigations revealed the partial degradation of the monolayer, which, however, just occurred in close vicinity around the iron nanoparticles (Figure 2).^[44]

2.3. Practical “Tricks” to Improve Microwave Heating

In order to further increase the heating rate and to induce demanding reaction conditions researchers have developed various methods and tricks. For example, specific substances, coatings, or triggers have been added to the reaction mixture to tune the reactions conditions.

Microwave-transparent substrates can be coated with a susceptor material to increase the heating efficiency and to decrease problems due to heat dissipation; for example, a metal layer,^[45] a coating of a conducting polymer,^[46] or an additional piece of silicon can be applied to enable CNT growth^[47] or the annealing of graphene^[48] on rather-microwave-transparent substrates; thus, without heating additives, the required elevated temperatures for the reaction could not be reached. Reaction vessels coated with silicon carbide^[49,50] or silicon carbide boards placed beneath a quartz vessel^[49] represent alternative approaches to increase the temperature rise of a microwave-heated system. To locally heat or trigger a reaction, graphite,^[51] graphene sheets,^[17] pieces of metal,^[52,53] or a single carbon fiber^[54] have been added as susceptors to reaction mixtures.

Several researchers have reported the influence of the sample mass on the outcome of a reaction, presumably based on heat accumulation, occurring when a larger amount of sample is irradiated. By applying a larger sample mass, more-demanding reactions could be conducted,^[55] less power is required to start a reaction,^[17,55] or a higher degree of functionalization^[56] is achieved. Furthermore, it was found that higher irradiation power is required to induce CNT growth on substrates with just micrometer-thick lines of catalyst compared to substrates that

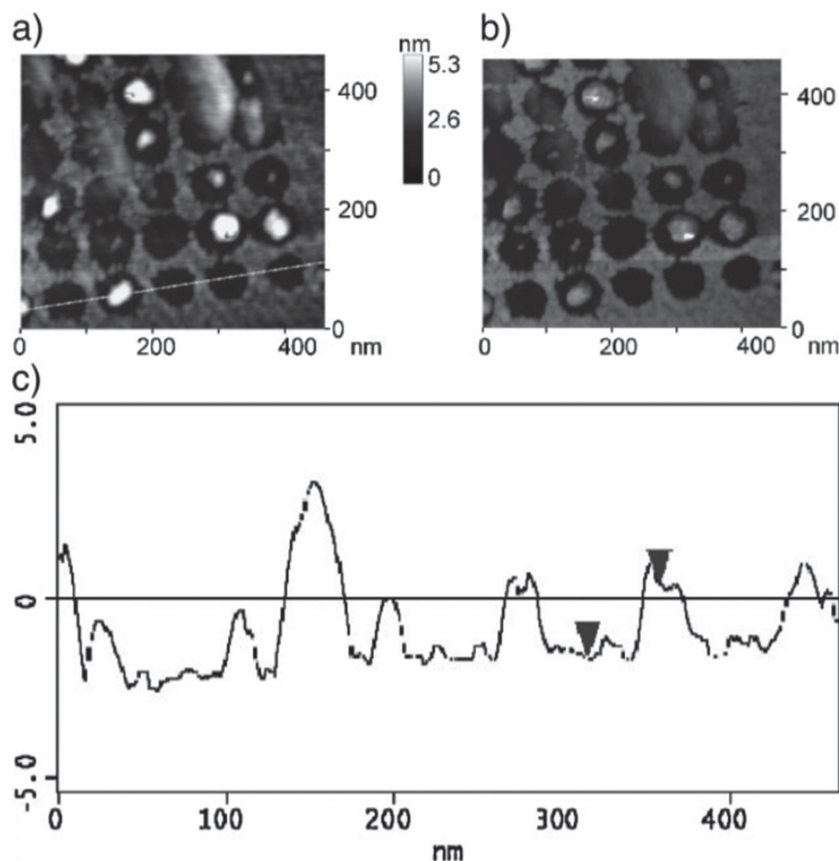


Figure 2. Scanning force microscopy images of an array of iron nanoparticles. After being exposed to MW radiation, a local degradation of the underlying OTS monolayer was observed. a) Height image, b) phase image and c) line profile of the height image. Reproduced with permission.^[44] Copyright 2009, Wiley.

are completely covered with a suitable catalyst.^[44] The heating efficiency can, as well, be improved by vacuum-drying of a carbon material. Due to the removal of absorbed water, microwaves can interact more effectively with the material itself, thus leading to a more-rapid heating and, consequently, a more efficient reaction.^[57]

For highly conductive materials, several other factors, besides the material specific loss factor have been identified to affect the microwave heating and the reaction efficiency.^[43,58] For example, arcing can be influenced by the morphology, particle size, particle density, and conductivity of the susceptor particles. Further influencing parameters are the boiling point, ionization energy, dielectric loss tangent, viscosity, and density of the solvent, as well as, additionally, the applied microwave power, rate of stirring and the reaction pressure.^[58] Moreover, for thin conductive plates, a specific overheating of the edge regions has been observed, resulting from the diffraction of electromagnetic waves.^[59]

2.4. Specific Microwave Effects

In the field of microwave chemistry, there is a debate about the existence of so-called specific or non-thermal microwave effects.

Supplementary to purely heating effects, these effects are thought to be responsible for potential microwave specific reaction rate enhancements.^[60] One developed concept is that of “molecular radiators”, which describes the direct coupling of microwave energy to specific reagents in a macroscopically homogenous reaction medium. This concept can be understood as the molecular analogue to the local heating of metal or carbon particles in an otherwise more-or-less microwave-transparent environment. For example, CH₂OH groups along a bio-macromolecule, such as cellulose, can act as molecular radiators. When irradiated with microwaves, these groups might be involved in localized rotations, and, consequently, initiate the cleavage of the polysaccharide chain.^[61] The existence of such specific microwave effects is, however, controversially discussed^[62–64] and, so far, considered mainly for the field of organic chemistry with macroscopically homogenous reaction mixtures. In the field of carbon materials, specific microwave effects are not (yet) a topic, and, in most cases, it can be assumed that purely thermal effects, even if just occurring on the nanoscale, are responsible for the extremely fast proceeding of reactions. The current state of the debate around microwave specific rate accelerations with a focus on inorganic nanomaterials prepared in the liquid phase can be found in a recent review from Zhu and Chen.^[5] After an intensive literature research the authors of that review came to the conclusion that, so

far, no evidence has been found that unambiguously proves the existence of specific microwave effects. Most of the reviewed reports on specific or nonthermal microwave effects have been found to be based on an inaccurate comparison of reaction conditions, and rate enhancements are observed due to the rapid heating when polarizable materials are irradiated.^[5] Dudley et al.^[60] provide a rather supporting view toward the existence of specific microwave effects, which they presented in a recent “Perspective” with a focus on microwave-heating of molecules in solution. From this article, a deep insight into the potential origin and nature of specific microwave effects and reaction-rate enhancements can be obtained.^[60]

The debate on microwave effects has already been ongoing for more than two decades,^[65] but it is still required that carefully planned and controlled experiments be developed^[19,66] in order to improve the understanding of microwave-assisted reactions, to avoid mis-interpretation of experimental results and to fully exploit the advantages of microwave irradiation in chemistry and materials science. Thus, when designing and interpreting an experiment, the potential specific effects of MW irradiation or the occurrence of local heating should always be kept in mind. We only briefly want to name four examples of how research is progressing to investigate potential specific microwave effects. For example, silicon carbide reactor vials

were designed to separate thermal and potential non-thermal microwave effects,^[67] a combination of temperature measurement by an internal fiber probe and an external IR sensor was applied to obtain more-reliable and reproducible heating profiles,^[66] and in situ Raman^[68] and NMR^[69] spectroscopy were used to investigate the molecular mechanisms associated with microwave-heating effects on chemical reactions.

3. Preparation of Materials

3.1. Synthesis of Carbon Nanotubes and Fibers

Since the first controlled synthesis of carbon nanotubes in 1991,^[8] several synthesis approaches for the controlled preparation of CNTs have been reported, including, for example, arc discharge, laser ablation, and chemical vapor deposition.^[70] Among these methods, there are also several microwave-assisted approaches. Some of them are derived from methods with conventional heating; others are making use of the specific features of microwave heating, e.g., the local heating of catalyst materials. In the following paragraph, the major microwave-based synthesis methods are discussed, subdivided in processes with liquid and gaseous carbon sources and those utilizing solid precursor materials.

3.1.1. Liquid and Gaseous Carbon Sources

Synthesis in the Gas Phase: One possible microwave-assisted approach to synthesize CNTs is to apply a synthesis route adapted from the common CVD process.^[71] In this process, a catalyst material is deposited on a substrate, which is then heated in the presence of a carbon source. When hydrocarbon vapor comes in contact with the hot catalyst particles, it will be catalytically decomposed, and the carbon dissolves into the particle. When the solubility limit of the catalyst at the particular temperature is reached, as-dissolved carbon precipitates and forms a crystalline tubular structure.^[71]

A wide range of different set-ups have been reported in the last decade, using either commercially available or specifically tailored self-made reactors. Two different main synthesis routes can be identified. On the one hand, long-time irradiation with high power is applied. In these approaches, the whole reaction chamber is heated to a high temperature, which results in a process very similar to the classical CVD process. The other route is based on the local heating of the catalyst material. Microwaves are irradiated for a rather short time span of minutes or even just seconds and the environment temperature in the reaction chamber remains rather low.

In 2002, Park and co-workers^[22,72] were the first to report a method for the synthesis of CNTs based on a microwave-heating mechanism. The authors utilized a commercial MW oven (800 W) and a mixture of acetylene and hydrogen was flowing through the reactor during the whole irradiation time of 0.5 to 30 min (**Figure 3A**). With this set-up, CNTs could be grown on carbon black as a substrate. However, no CNT growth was obtained on SiO₂ as a support. Contrary to carbon black, SiO₂ is a microwave insulator, and does not absorb microwave

energy, but, instead, dissipates the energy absorbed by the catalyst particles. Thus, with a SiO₂ support, the crucial temperature for CNTs growth could not be reached. This problem of energy dissipation by non-absorbing substrates could be overcome by utilizing sulfur as an additive for the synthesis, either in the catalyst (CoS_x) or as a component in the reactant gas (H₂S). Sulfur plays an important role by lowering the melting point and liquefying the catalyst in the CNT synthesis. As a consequence, the utilization of low-melting-point substrates was possible and CNTs could be directly grown also on polymer substrates. However, after the synthesis, the catalyst-loaded surface of the polymer substrates was partially damaged by melting and, when SiO₂ was used as substrate, cracks were observed. The authors concluded that this one-sided deformation of the substrate represents an indication of the local heating of catalyst particles.^[22,72]

Later on, Park and co-workers^[45] further improved their method and constructed a flexible field emitter array by growing CNTs on a Teflon substrate. This was achieved by applying a chromium interlayer between the polymer substrate and the cobalt catalyst layer. Irradiation of just 300 W (single-mode) for 5 s without any pretreatment was sufficient to grow 5 to 6 nm-thick CNTs from an acetylene precursor, while no damage to the substrate occurred.^[45]

The growth of carbon nanofilaments via methane decomposition over microwave-heated carbon-based materials was studied by Fidalgo et al.^[76] Activated carbon, containing some mineral content, and carbon microfibers impregnated with nickel or cobalt salt solutions were applied as substrates. The reaction chamber was flushed with nitrogen and the desired operating conditions were reached before the reactant gas (CH₄/N₂) was introduced. However, quite long irradiation times and high temperatures were required in order to grow CNFs (800 °C/130 min and 400 W/50 min for activated carbon and carbon microfibers, respectively), and only few and rather short filaments were obtained, in particular when carbon fibers were applied as substrate. As key parameters for the shape and size of the filaments the nature, the amount and dispersion of the catalyst metal were identified. The amount of nanofilaments seemed to be dependent on the composition of the inflow gases. The authors carried out control experiments using conventional heating with an electric furnace, but did not obtain any nanofilaments. Thus, it was concluded that, when microwave heating is applied, the formation of hot-spots and, consequently, electric arcing and the occurrence of N₂-microplasmas (micro in space and time) play decisive roles in the growth of the nanofilaments.^[76]

Fu et al.^[73] also utilized the decomposition of a methane-nitrogen mixture (1:4), but did not require any catalyst to obtain CNTs. A homemade microwave furnace with a power of 6 kW was equipped with carbon felt as microwave absorbing material (**Figure 3B**). The reaction was carried out at 1100 °C for 60 min under a flowing reactant gas, and resulted in a high amount of Y-shaped CNTs (**Figure 3C**). Since no catalyst was applied, it is impossible that this Y-shape was induced by the coalescence of catalyst particles. The authors instead suggested that fluctuations of the gas flow play a critical role for the branching, e.g., by the introduction of defects into the hexagonal network of the tubes. Due to the uniform, rapid, and volumetric heating

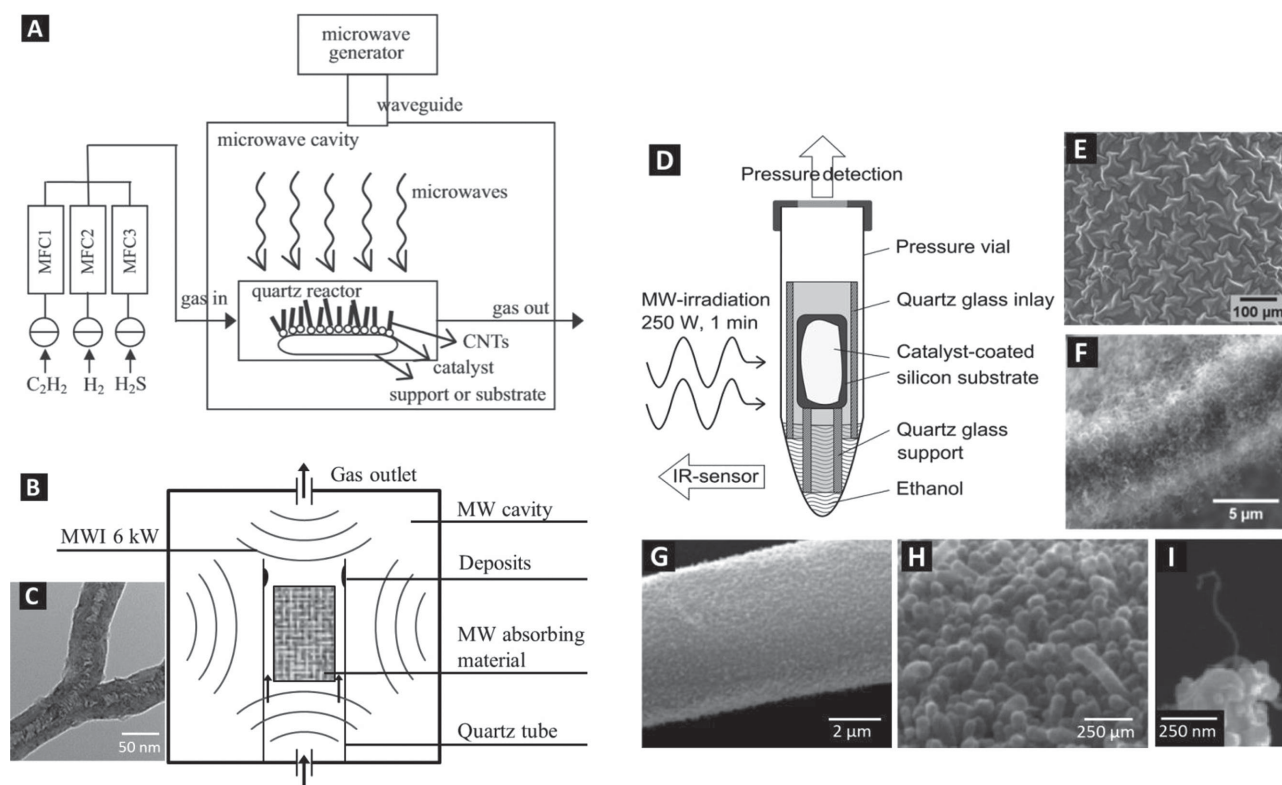


Figure 3. Schematic drawings and electron-microscopy images of the resulting products of three different experimental set-ups for the synthesis of CNTs from gaseous or liquid precursors. A) A domestic MW oven with a quartz reactor and a catalyst-coated substrate.^[22] B) A home-made microwave furnace including a MW-absorbing material to reach the reaction temperature. No catalyst was required to obtain Y-shaped CNTs (C).^[73] D) A set-up including a commercial single-mode microwave reactor and liquid carbon sources for the synthesis of CNTs on catalyst-coated substrates. E) Top-view of a CNF coating and F) cross-section of a striped-off CNF film.^[74] G, H) Patterned nanofiber assemblies with small structural size and good selectivity. I) Higher magnification image of the image in (G).^[44] A) Reproduced with permission.^[22] Copyright 2003, Wiley. B, C) Redrawn with permission.^[73] Copyright 2009, Elsevier. D–F) Adapted with permission.^[74] Copyright 2014, Wiley. G, H) Reproduced with permission.^[44] Copyright 2009, Wiley. I) Adapted with permission.^[75] Copyright 2010, American Chemical Society.

characteristics of microwave heating, the free radicals obtained by the decomposition of methane can rapidly form active carbon clusters, which then act as nuclei for the formation of CNTs. In this particular case, the formation of CNTs seems to be catalyzed by the MW field.^[73] By adjusting the synthesis conditions and by applying ferrocene as catalyst, it was possible to grow aligned CNTs (ACNTs) using a similar microwave reactor. Densely packed CNTs with a length of 60 μm were grown at 550 to 700 $^{\circ}C$ for 30 min with acetylene as the carbon source.^[77]

Druzhinina et al.^[47] utilized a commercial single-mode microwave reactor to grow multi-wall CNTs and CNFs on different substrates, e.g., silicon, quartz glass, and mica. A quartz-glass support was used to vertically place the catalyst-coated substrate above a reservoir of liquid carbon source (Figure 3D). The irradiation power was 300 W at a maximum, and not more than five minutes of irradiation was required. Different catalyst materials based on iron, nickel, and cobalt salts and various alcohols as carbon sources were screened. The best results, in terms of uniformity and size of the synthesized CNTs, were obtained utilizing ethanol as the carbon source and nickel-based catalyst materials. Additionally, the type of substrate plays an important role. For the microwave-transparent substrates, i.e., quartz glass and mica, it was observed that even

under high-power irradiation, no CNT growth was initiated. CNTs could only be grown on these substrates when a silicon wafer was placed behind, in order to enhance the absorption of microwaves and to compensate for the limited heating of the insulating substrates.^[47] Furthermore, micropatterned carbon-nanofiber films with a structure width of 6 μm could be grown by utilizing a TEM grid as a stamp for the catalyst deposition (Figure 3G, H).^[44] The authors observed that higher power values were required to induce the growth of carbon nanofibers on such patterned substrates, and concluded that, apparently, heat-dissipation effects played a crucial role.

With a similar set-up, the successful fabrication of CNT AFM probes was performed by growing CNTs localized on the apex of commercially available AFM tips (Figure 3I).^[75] For this purpose, several cantilevers were mounted on a piece of silicon wafer by means of conducting silver paste to overcome heat-dissipation effects and to allow the convenient handling of the tips. Irradiation of 200 W for 5 min was sufficient to induce CNT growth. Furthermore, utilizing this process, 10 μm -thick large-area carbon nanofibrous films were grown from a nickel acetate catalyst by MW irradiation at 250 W for only 1 min. The CNF coatings could be easily detached from the substrate due to the up-arching of the catalyst layer during its reduction and

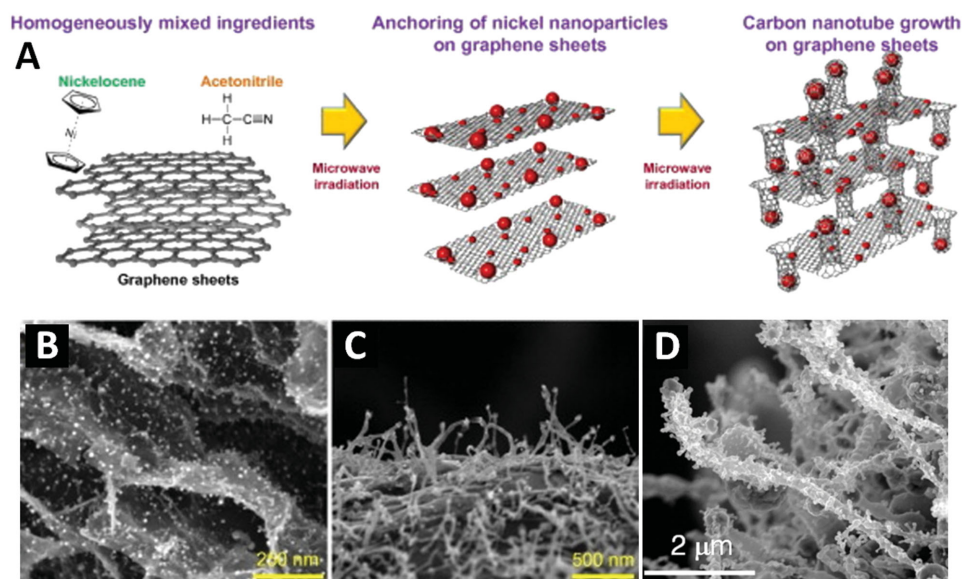


Figure 4. A) Schematic illustration of the microwave-assisted synthesis of a self-assembled 3D G-CNT-Ni nanostructure. B–D) SEM images of well-distributed nickel nanoparticles on the inner and outer surfaces of graphene, which catalyze the CNT growth between graphene layers (B), full-grown CNTs after completion of the MW irradiation (C),^[78] and hierarchical graphene-CNT-iron 3D nanostructure with small-branch CNTs grown on the first stem CNTs (D).^[79] A–C) Reproduced with permission.^[78] Copyright 2013, Elsevier. D) Reproduced with permission.^[79] Copyright 2013, American Chemical Society.

the subsequent growth of CNFs from both sides of the catalyst layer (Figure 3E,F).^[74]

Synthesis in the Liquid Phase: Oh and co-workers^[78] developed a method to grow CNTs directly on graphene sheets by utilizing thermally exfoliated reduced graphene oxide and nickelocene (Figure 4). After dispersing the powder in acetonitrile, the mixture was placed in a multimode MW oven and was irradiated at 700 W for 5 min, cooled for 5 min, and, thereafter, irradiated for a second time. During the microwave treatment, defects were formed on the graphene, which acted as nucleation sites for the formation of nickel nanoparticles. On these nanoparticles, CNTs could grow. Since the nickel catalyst remained in the tips of the CNTs, consequently, a 3D graphene-CNT-nickel nanostructure was formed. In this configuration, the CNTs play the role of spacers, which prevent the graphene layers from both re-stacking and agglomeration, and, consequently, ensure a high specific-surface area. Since CNTs are directly bonded to the graphene sheets, the contact resistance at the junctions is minimized, providing good electric conductivity, which is important for applications in the field of energy storage. Unfortunately, no detailed information was provided regarding the ratio of the educts, the type of reaction vessel, the obtained temperatures, and whether the reaction mixture was stirred during the microwave treatment.

Using a similar approach, Oh and co-workers^[79] prepared a hierarchical structure, growing a second generation of smaller CNTs (10 to 20 nm in diameter) on the previously grown CNTs (40 to 60 nm), which were still attached to the graphene sheets (Figure 4D).^[79] After the first synthesis step, during cooling, ferrocene vapor attaches to the just-grown first generation of CNTs. Thus, upon a second microwave treatment, thinner CNTs could grow directly on the stem CNTs. Multiple cycles of MW irradiation were performed subsequently, each time for

30 s at 700 W. However, just very short CNTs were obtained in the second growth step.

CNTs were furthermore grown on graphene with palladium acetate as catalyst and an ionic liquid (IL) as the carbon source, by mixing the reactants with graphene plates in a weight ratio of 1:1:1 (each 0.5 g).^[80] Mainly, rather-short CNTs of well below 1 μm were obtained. When the IL and palladium were heated in the absence of graphene, extensive formation of longer CNTs was observed. When graphene and palladium were heated in the absence of IL, no CNTs were grown, but a cutting of graphene sheets occurred. The authors concluded that carbonaceous by-products from the microwave-induced decomposition of the IL serve as the carbon source for the CNT growth.

3.1.2. Solid Precursor Materials

Besides the application of gaseous or liquid carbon sources, solid carbon materials can be used as precursor materials for the preparation of CNTs. Thereby, the precursor can be either directly transformed into a crystalline structure by a solid-state transformation, or CNT growth can occur by a solid-vapor-solid transformation. The latter case is typical when graphite or metalocenes are utilized as the precursor. Polymers can be utilized in both ways, either growing CNFs by vaporization of the polymer or by transforming conductive polymer structures into graphitized carbon, and thereby, retaining the original shape of the precursor material.

Solid-Vapor-Solid Transformation: Graphitic precursors can be applied in different ways to synthesize CNTs. Méndez et al.^[81] prepared CNTs by vaporization of powdered graphite or mixtures of graphite with either sucrose or boric acid under vacuum, without employing any catalyst material.

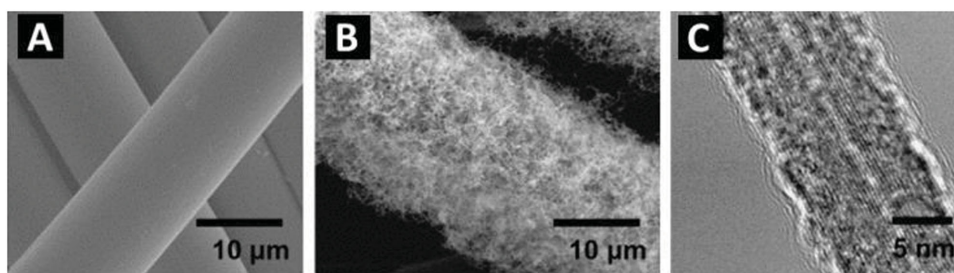


Figure 5. CNT growth from activated carbon fibers impregnated with iron chloride without additional carbon source. A,B) SEM images of the ACF specimen before MW irradiation (A) and after MW irradiation (B). C) HR-TEM image of a nanofiber.^[83] A–C) Reproduced with permission.^[83] Copyright 2006, Elsevier.

The synthesis was completed within 60 min (180 min for the boron compound) utilizing a domestic MW oven at 800 W. Reaching an estimated oven temperature of approximately 1200 °C, CNTs with diameters of 50 to 400 nm were obtained.^[81]

Vivas-Castro et al.^[82] synthesized multi-wall carbon nanotubes (MWCNTs) by mixing graphite with iron acetate in a quartz ampoule and heating it in a domestic MW oven with an irradiation power of 1000 W. The evacuated ampoules were either irradiated directly or were partial submerged in water. In the latter case, most of the microwave radiation was absorbed by the water and only attenuated irradiation reached the sample. Thus, the temperature increased more slowly and continuously. Furthermore, the ampoules were in a rocking motion due to the boiling water. After 120 min at 1000 W, all of the graphite had been converted into MWCNTs. On the other hand, without water, 7 min were sufficient for the appearance of MWCNTs and the almost complete reaction of the precursors. When the capsules were submerged in water, small iron particles were attached to the tips of the CNTs, and the CNTs were curled, whereas without water, the CNTs were completely filled with iron and well-oriented and aligned. However, direct MW irradiation led to a rapid temperature increase within just a few seconds. Thus, care has to be taken in this case to avoid accidents, as, for example, reactions can be so fast and violent that the explosion of the ampoules can occur.^[82]

Yoon et al.^[83] used activated carbon fibers (ACF) as a support and carbon source for the growth of CNTs (Figure 5). The ACFs were impregnated with an iron chloride solution and placed in a quartz-tube reactor. Microwave irradiation at 400 W was performed under flowing argon and after a treatment for 60 to

90 s, which appeared to be the optimal time frame; the ACF surface was covered with MWCNTs of 10 to 40 nm in diameter. In contrast, after just 30 s of irradiation, only particles of a few tens of nanometers were observed and, after 120 s, large carbon particles together with very thick, fibrous carbon appeared. Without catalyst impregnation, no CNTs were formed at the same reaction conditions.^[83]

Pentsak et al.^[84] investigated the CNT growth from graphite impregnated with nickel acetylacetonate when irradiated for 5 to 30 min in a domestic MW oven. The focus of this study was set on the influence of the surrounding atmosphere and was performed from the perspective of catalysis. In the field of catalysis, carbon materials are commonly utilized as supports for metal nanoparticles, which can be also prepared by microwave-heating approaches. In this study, CNT growth occurred when the impregnated graphite was irradiated under an inert atmosphere of argon or under vacuum conditions (Figure 6B). In contrast, if oxygen was present, no CNTs were observed; instead etching and pitting of the graphite substrate occurred, caused by the heated nickel nanoparticles (Figure 6C). The authors pointed out the strong correlation between the two research areas of carbon nanomaterials synthesis and the preparation of supported catalyst materials, which have been, however, so far studied more or less independently of one another, although stimulating effects from each other can be expected.^[84]

Takagi et al.^[50] developed a method for the preparation of CNTs utilizing polymeric precursors. The authors synthesized CNTs in gram-scale from polystyrene at 800 °C by utilizing a domestic MW oven remodeled with a thermocouple and a

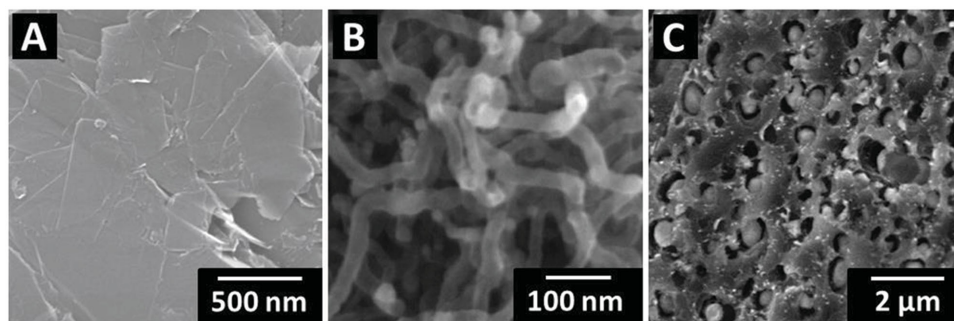


Figure 6. SEM images of nickel-acetylacetonate-impregnated graphite: A) Initial system, B) CNTs were grown after MW irradiation in vacuum conditions, and C) pitting and etching occurred after MW irradiation in air.^[84] A–C) Reproduced with permission.^[84] Copyright 2014, American Chemical Society.

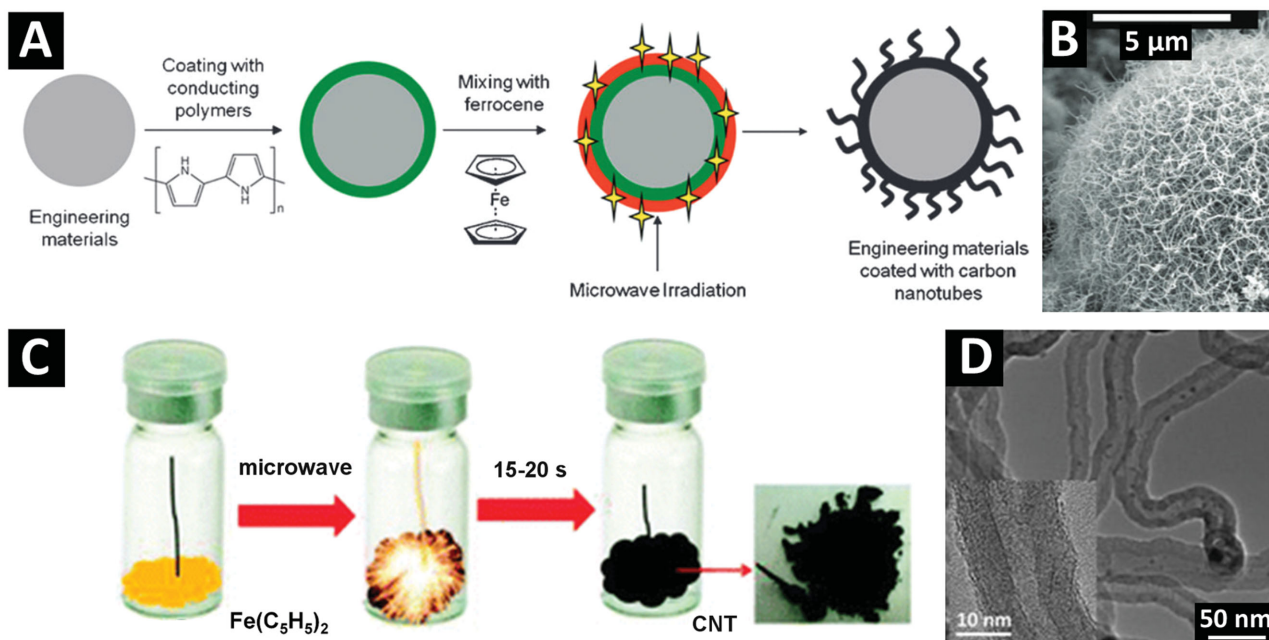


Figure 7. Schematic illustration of CNT-fabrication processes utilizing solid precursors and additional susceptor materials, as well as EM images of the resulting products. A) Pop-tube approach applying a conducting polymer as MW susceptor to grow CNTs on engineering materials (B).^[46] C) Microwave synthesis triggered by a single carbon fiber vertically placed to ferrocene precursor powder resulting in MWCNTs (D).^[54] A,B) Reproduced with permission.^[46] Copyright 2011, The Royal Society of Chemistry. C,D) Reproduced with permission.^[54] Copyright 2013, The Royal Society of Chemistry.

thermoregulator to control the temperature. A small furnace coated with silicon carbide was placed in the microwave cavity and a temperature of 800 °C was reached in the furnace within 5 min by applying 600 W; thus, far less energy is consumed compared to a conventional furnace. Commercial granulated polystyrene and nickel nanoparticles were mixed in a quartz-glass tube placed in the furnace and were calcined for 10 min under a nitrogen atmosphere. The resulting CNTs were 25 to 100 nm in diameter. A nickel ratio of 30 wt% was found to be optimal, and an increase of the amount of precursors resulted in a strong increase of the product-to-precursor ratio. According to the authors, this might be due to better contact between the reactants because of the limited space in the test tube. Other carbon sources were tested as well; sugars yielded no CNTs, poly(vinyl alcohol) resulted in a very small yield, and, with polyethylene, a fairly high amount of CNTs could be obtained. Polystyrene was chosen for the detailed study due to its higher weight percentage of carbon.^[50] Polystyrene was also utilized by Hojati-Talemi et al.,^[52] who prepared carbon nanofibers with a stacked-cup morphology. However, a rather different way of catalyst deposition was used. The polymer was placed in an evacuated quartz-glass tube together with a metal target from which catalyst particles were sputtered when MW irradiation was applied for a sufficient time (for instance, 90 s at 700 W with iron catalyst). For this process, a domestic MW oven was used, and the temperature reached more than 800 °C, as was measured utilizing an IR temperature sensor.^[52]

In the so-called PopTube approach,^[46,85] a catalyst powder, e.g., ferrocene, is physically mixed with a conductive material, which absorbs microwaves very efficiently (e.g., conducting polymers, indium tin oxide, graphite powder, or carbon fibers).

Upon MW irradiation, the conductive material will be rapidly heated to high temperatures. Thus, the ferrocene decomposes to iron, which serves as catalyst, and cyclopentadienyl, which can serve as carbon source. However, syntheses with additional hexane as a carbon source were performed as well to further increase the length and density of the CNTs. This microwave-initiated growth only takes 15 to 30 s and no inert-gas protection is required. Besides mixing precursors with conductive powders a slightly different approach was developed to grow CNTs, even on non-conductive, engineered substrates, by pre-coating them with a conductive material. For example, polypyrrole-Cl (PPy-Cl)-coated glass fibers or fly ash were used (Figure 7A,B). Thus, this approach is quite universal regarding the material and structure of the substrate. Unfortunately, no detailed information about the heating procedure and the specifications of the used microwave oven were provided. A synthesis temperature of above 1100 °C was stated, which is, however, not based on measurements, but only determined in comparison with results reported in the literature.^[46]

Hu et al.^[86] adopted the PopTube approach and synthesized micrometer-long CNTs on an ultralight graphene aerogel without an additional carbon source. The ferrocene coating was applied by impregnation and, after drying, the sample was heated with a MW oven at 800 W for 1 min in a quartz tube flushed with argon.^[86]

Nie et al.^[54] also synthesized CNTs by applying ferrocene as a catalyst material and carbon source. A single, vertically placed carbon fiber (3 to 4 cm long) was used as the trigger for the pyrolysis of the ferrocene in a sealed glass vial. Since graphitic material is a good microwave absorber, a large amount of heat is generated upon microwave irradiation, and arcing

occurred at the tips of the fiber. This leads to local temperature hot spots sufficient to decompose ferrocene and to carbonize cyclopentadienyl (Figure 7C). For a sample of 100 mg of ferrocene, an irradiation time of 20 s with a conventional domestic microwave with 1000 W power resulted in a yield of ca. 40% of MWCNTs (around 20 nm in diameter). No obvious changes were observed when the irradiation time was extended to 25 s. Replacing the carbon fiber with 1 mg of commercial CNTs as microwave absorber also resulted in the formation of a large amount of CNTs. On the other hand, no reaction was observed when CNTs were mixed with the ferrocene powder and only little product, consisting of carbon particles rather than CNTs, was obtained when a carbon fiber powder was applied as microwave receptor. This difference was furthermore recognizable by the intensity of the microwave plasma, which was far less intense than observed for one single carbon fiber. The growth rate and the yield, thus, depended significantly on the type and distribution of the susceptor material, and it seems that an accumulation of susceptor material is required to induce the reaction.^[54]

Bajpai and Wagner^[87] utilized a similar approach, with ferrocene as the carbon source and catalyst. The authors found the addition of both graphite and carbon fibers to be necessary to induce sufficient arcing and heat transfer. Utilizing both additives, a fast growth of MWCNTs was obtained after just 5 s of irradiation, using a domestic MW oven with an output power of 1800 W. Hence, the authors caught up the “speed record”, so far just obtained with a CVD-like approach by Park and co-workers.^[45] Additionally Bajpai and Wagner^[87] attempted to investigate the influence of different power levels on the synthesis speed and morphology of the obtained carbon nanofibers, but did not observe any significant differences. However, the authors disregarded the fact that domestic microwave ovens actually exhibit only one fixed radiation power and that the selectable power levels state the percentage of time that the magnetron operates with its full power.^[3] Thus, in the study of Bajpai and Wagner^[87] actually just the average irradiation power was adjusted, not the applied peak/maximum power.^[87,88]

Solid-State Transformation: Another approach with solid precursor materials is the direct transformation of electrically conductive polymer structures into graphitic carbon nanostructures, thereby retaining their original shapes.

Zhang and Liu firstly reported such an approach in 2006, and included their research in a review in 2011.^[89] The basic concept is that nanostructured conducting polymer precursors absorb microwaves very efficiently and, thus, when subjected to microwave radiation, are rapidly carbonized to nanocarbons within one reaction step.^[90] Accompanied by extensive sparking, a weight loss of more than 50% occurred for polypyrrole as precursor, and the carbon content of the remaining structure was above 90%. The bulk morphology of the polypyrrole remained similar, although some shrinkage occurred. High-resolution transmission electron microscopy (HR-TEM) imaging could prove the graphitization of the previously amorphous material with a layer spacing of 0.34 nm. The transformation was performed in air, utilizing a domestic MW oven and irradiation times of 3 to 5 min. According to the authors, however, no oxidation occurred during the heating in air, since, due to the rapid temperature increase, carbonization occurs before oxygen

can react with the backbone. Of course, this process is only successful for conductive polymers; otherwise no heating occurs. In optimal conditions, the conductivity of the polymer should be sufficiently high to absorb microwaves, but low enough to enable the radiation to reach the center of the structures and not to be limited to heating up the surface only.

3.1.3. MW-Assisted Purification and Modification of CNTs

Microwave radiation can not only be utilized for the preparation of carbon nanomaterials, but also for post-synthesis treatments and the modification of as-synthesized structures. Depending on the synthesis method, as-prepared CNTs are often far away from the theoretically predicted perfect structure, thus, of a quasi-infinite, hexagonal network of covalently, sp^2 -hybridized carbon atoms.^[91] Furthermore, during CNT synthesis various carbon by-products can form and, in most cases, metal-catalyst particles are included in the tips or roots of the CNTs. In order to improve the quality and purity of CNTs, post-synthesis processes are applied that increase the crystallinity and/or remove impurities. The microwave-assisted purification of CNTs can be divided into two main categories: reagent-free processes and acid-assisted processes. Both approaches were first reported in 2002.^[92,93] Profound details on the underlying theory and heating mechanisms of microwave-assisted CNT purification can be found in a review by MacKenzie et al.^[2]

Reagent-Free Modification Processes: The scope of solid-state microwave irradiation of CNTs is to locally heat the metal-catalyst particles incorporated in the tips or roots of the CNTs. Metals are excellent microwave absorbers; thus, they can be heated very fast and efficiently. Upon microwave irradiation the carbon passivation layer around the metal catalyst will be ruptured or decomposed and the metal will be oxidized. Simultaneously, amorphous carbon by-products are converted to CO_2 . Subsequently, the metal impurities can be easily removed, e.g., by a mild acid or another liquid without the requirement of prolonged refluxing or ultrasonication, which might degrade the quality of the CNTs. The major advantage of this method is that high temperatures are just reached locally, without causing significant damage to the overall structure of the CNTs.^[93,94]

Harutyunyan et al.^[93] developed a solid-state irradiation method where SWCNTs were irradiated for 20 min at a power with a maximum of 150 W in flowing air. Afterward, the sample was refluxed in 4 M HCl for 6 h, which resulted in a residual catalyst content of less than 0.2 wt%.^[93]

Vázquez et al.^[94] reduced the iron content of commercially available HiPco tubes (26 wt% iron) by microwave-heating under air in a domestic multimode MW oven at an average power of just 80 W for a total time of 5 min. After washing with concentrated HCl, an iron content of 16 wt% was obtained and was further reduced to 9 wt% after a second treatment. However, this process could not be applied for other kinds of CNTs with lower initial metal content.^[94]

Chajara et al.^[95] found a way to purify CNTs by dispersing them in dichloromethane or toluene, but without any additional acidic/oxidative reagents. Within a short microwave treatment a significant decrease of metal content (from 12 to 2 wt% for HiPco SWCNTs) and the removal of amorphous carbon (from

90 to 28 wt% for CVD SWCNTs) was obtained as concluded from thermogravimetric analysis (TGA). Thereby, considerably fewer purification-induced defects were observed, compared to that from other typical purification treatments involving oxidative and/or acidic reagents. The authors suggested that the thermal delamination of non-graphitized carbon from the CNTs is the key step of this process, but, additionally, the dissolution of the amorphous carbon into the solvent represents a critical issue in order to prevent re-aggregation. Nonpolar solvents were found to be superior to polar solvents, which is based on their ability to dissolve the relatively nonpolar impurities. Additionally, nonpolar solvents absorb less microwave energy, which is, instead, directly absorbed by the dispersed CNTs; thus, efficient heating can be obtained.^[95]

Not only metal-catalyst particles and amorphous carbon by-products can be removed by microwave treatment, but also defect annealing in the CNT walls can be induced. Upon microwave irradiation, defective sites reconstruct to form graphitic structures by outgassing of hydrogen and reduction of oxidized sites. Typically, annealing temperatures above 1200 °C are required to decrease the defect density of CNTs. This is, however, not compatible with, for example, commonly utilized substrate materials for the growth of vertically aligned CNTs. Moreover, such an annealing is time-consuming and costly. By MW treatment, annealing can be obtained within a few minutes, leading to an improvement in thermal stability, mechanical properties, and electrical conductivity of CNTs grown on a silicon substrate.^[96] Such rapid microwave treatment can of course also be applied for the annealing and hole-doping of graphene. However, utilization of a silicon substrate has been found to be crucial to rapidly reach the elevated temperatures required for the annealing.^[48]

Care has to be taken, since prolonged MW treatments can lead to degradation by introducing new defects. This was observed for CNTs by thermogravimetric analysis. Furthermore, microwave irradiation at a power of 700 W in ultra-high vacuum was found to fuse/weld neighboring HiPco SWCNTs; thus, they afterward formed junctions. This nanotube reconstruction was accompanied by intense light emission, strong heat release, and outgassing.^[28]

Similar solid-state annealing processes as for CNTs can be applied to improve the photoluminescence properties of carbon nanodots^[97] or to modify the surface chemistry and porosity of carbon fibers.^[98] Thermal treatment in a flow of N₂ gas has been reported to eliminate surface groups and to reduce the micropore volume and size of activated carbon fibers.^[98]

Modification Processes Utilizing Additives: Microwave-assisted acid purification is another approach to remove catalyst residues and amorphous carbons from as-synthesized CNTs.^[2] Typically, CNTs are dispersed in concentrated acids, e.g., HNO₃, H₂SO₄, or H₂O₂, and are heated to an average bulk temperature of 100 to 230 °C for 15 to 60 min, as can be found in the review by MacKenzie et al.^[2] Conventional acid-reflux purification is rather time-consuming. By applying microwave heating, the reaction times can be significantly shortened, e.g., from 16 h to 1 h for purification in 5 M HNO₃, thereby additionally reducing the risk of introducing defects into the sidewalls of the CNTs. Compared to solid-state irradiation and subsequent washing, an improved purification (>90% efficiency) can be obtained by microwave heating of the CNTs while dispersed in

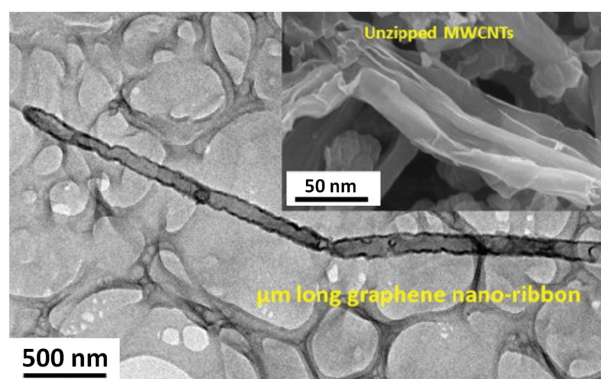


Figure 8. TEM image of a micrometer-long graphene nanoribbon prepared by ionic-liquid-assisted microwave unzipping of a CNT. The inset shows an SEM image of such unzipped MWCNTs.^[104] Reproduced with permission.^[104] Copyright 2013, Elsevier.

the acid. Microwave-assisted purification is, moreover, highly dependent on the structure of the pre-synthesized CNTs, e.g., the number of walls or the metal content. Small diameter tubes and defective tubes are more reactive than MWCNTs and well-graphitized CNTs. Furthermore, metallic SWCNTs have been found to burn more rapidly compared to semiconducting ones. This is due to the fact that metallic SWCNTs can be microwave-heated two orders of magnitudes faster than semiconducting ones, which is based on their much higher loss factor.^[99] For this reason, microwave treatment can be used to enrich the content of semiconducting CNTs in a mixture of SWCNTs and to narrow the size distribution of CNTs.^[100,101]

However, heating CNTs in concentrated acids does not only result in purification, but, simultaneously, often leads to the functionalization of the sidewalls with, for example, carboxylic and hydroxylic groups.^[2] If unintentionally occurring, this might be problematic for applications. Otherwise, however, many protocols have been developed for the controlled functionalization of CNTs, graphene, and fullerenes dispersed in a reaction media. Besides acidic treatments, cycloaddition reactions are most often applied to obtain controlled functionalization of the starting materials.^[102]

Additionally, MW radiation can be used to longitudinally unzip CNTs; thus, few-layer graphene nanoribbons are formed. For example, CNTs dispersed in water can be catalytically unzipped by palladium nanoparticles attached to the CNTs,^[103] and pristine MWCNTs were unzipped by mixing them with an ionic liquid, together with MW irradiation at 700 W for 4 min^[104] (Figure 8). In an acid-assisted approach with H₂SO₄/H₃PO₄ and KMnO₄, MWCNTs were split within a few minutes, and, depending on the irradiated power (150 to 250 W), the stepwise opening of the CNTs could be observed.^[105] In a similar way, like the unzipping of CNTs, carbon quantum dots can be prepared by acid-assisted cleavage of graphene, as will be described in Section 3.3.1.^[106]

3.2. Preparation of Graphene Materials

In the last few years, graphene research has developed into a strong field of research and application. Graphene is the first

2D atomic crystal that has been prepared, and it possesses a combination of outstanding properties, such as extreme mechanical strength, exceptionally high electronic and thermal conductivities, and impermeability to gases.^[6] The first preparation of graphene was conducted by mechanical exfoliation with repeated peeling of small pieces of highly oriented pyrolytic graphite.^[10] With this method, few-layer graphene of up to 10 μm in size could be prepared. Nowadays, there are several additional techniques to either prepare graphene by a top-down process, e.g., by exfoliation and reduction from graphite or graphite oxide, or by applying bottom-up processes, e.g., the synthesis of graphene sheets by chemical vapor deposition.^[6] Whereas hardly any microwave-assisted bottom-up approaches have been reported in literature, microwave heating is widely used for the exfoliation and reduction of graphitic precursor materials. With microwave treatments, the preparation of graphene can be performed by solid-state reduction of dry graphite oxide (GO), the reduction of GO in suspension, or by heating graphite intercalated compounds (GICs). Furthermore, the simultaneous reduction and doping of GO and the preparation of hybrid materials is also possible.

3.2.1. Microwave-Assisted Exfoliation and Reduction of Graphite Oxide

Graphite oxide represents an important precursor for the preparation of graphene. Due to its hydrophilic character, it can be easily dispersed in water, thereby being exfoliated into graphene oxide flakes. Such graphene oxide suspensions provide a convenient method for the processing and deposition of graphene materials. Subsequent to the film formation, a reduction step is required to transform the GO, at least partially, back to the parent graphene state and to obtain so-called reduced graphene oxide (r-GO).^[107] Commonly, the so-called Hummers method is applied to prepare graphite oxide by mixing graphite with sodium nitrate, sulfuric acid, and potassium permanganate.^[108]

For the reduction process, either reducing agents or high-temperature treatments can be used. However, reducing agents such as hydrazine and dimethylhydrazine are highly toxic and, furthermore, r-GO products suffer from a low carbon-to-oxygen atomic ratio (C/O). Additionally, reduction reactions are performed in aqueous suspensions; this entails agglomeration of the hydrophobic r-GO sheets. On the other hand, high-temperature annealing ($>1000\text{ }^{\circ}\text{C}$) results in modest C/O ratios and an efficient expansion of the layers due to the release of CO_x gases, but implies a large consumption of energy.^[109,110] Consequently, microwave-assisted heating of dry GO powder has been proposed as an efficient method for the solid-state expansion and reduction of precursors prepared by the (modified) Hummers method into microwave-exfoliated graphite oxide (MEGO).

To achieve this, Zhu et al.^[111] identified a minimum of 40% of the full power (700 W) of their domestic MW oven to be required. The radiation time thereby varied from 10 to 40 s depending on the microwave power and sample mass. Accompanied by “violent fuming”, few-layer thick graphitic sheets were obtained and the C/O ratio increased from 0.79 (GO) to 2.75 (MEGO). Prolonged microwave treatment induced sparking or even resulted in burning. The as-prepared MEGO

exhibited a “worm-like” morphology and a moderately high specific-surface area of $463\text{ m}^2\text{ g}^{-1}$.^[111] By applying a simple activation with KOH, Zhu et al.^[112] achieved specific-surface-area values up to $3100\text{ m}^2\text{ g}^{-1}$. This is well above the theoretical surface area of $2630\text{ m}^2\text{ g}^{-1}$, valid for the perfect structure of a single infinite graphene sheet.^[113] However, care has to be taken in choosing an appropriate amount of the GO sample and an appropriately sized container to minimize dangers during the expansion, which usually occurs in a violent, explosive manner. Containers with a pressure-release valve and utilization of a chemical hood are highly recommended to avoid the accidental inhalation of MEGO powder or released gas.^[111]

Li et al.^[109] applied MW radiation of 400 W for only two seconds to turn a free-standing GO film from brown to black and increase its conductivity from 0.07 S m^{-1} to 10^4 S m^{-1} , which is comparable with the conductivity of high-temperature ($1050\text{ }^{\circ}\text{C}$) exfoliated graphene. The maximum surface temperature recorded by an IR thermometer was $400\text{ }^{\circ}\text{C}$, whereby the temperature increase in the second half of the irradiation time was observed to be much faster than the temperature rise at the beginning. The change in heating characteristics is caused by the different response of GO and r-GO to MW irradiation. During the reduction, the number of polar groups decreases, but, on the other hand, the area of the conjugated π -structures increases, leading to improved microwave absorption. Thermogravimetric analysis revealed an increasing thermal stability of MEGO for increasing MW irradiation times. Raman spectroscopy, however, showed no change in frequency of the G-mode after microwave treatment, and the obtained MEGOs exhibited significantly different peak positions to graphite.^[109] The authors further investigated the heating and reduction mechanism to show that there is an optimal irradiation time to obtain reduced graphene. By heating and cooling a GO film in several cycles and, each time, recording the temperature rise, it was revealed that for the first 13 cycles the temperature rise gradually increased, which is caused by the recovery of the sp^2 structure. In the following cycles, however, the rate of temperature rise decreased again, back to the level of the second cycle. This result indicates that an extended exposure to MW radiation in air causes re-oxidation of the graphite structure, as was confirmed by XPS.^[109]

Shulga et al.^[114] investigated the microwave-assisted reduction process of GO in detail. The resulting MEGO contained 0.73 wt% hydrogen and 4.2 wt% of oxygen, but some sulfur was found too, probably remaining from the sulfuric acids used to prepare the GO. Furthermore, gaseous side-products occurred, consisting of mostly CO_2 , CO, H_2O , and, in some cases, SO_2 . IR spectroscopy revealed similar absorption properties as those of graphite. Surprisingly, Raman spectra of the initial GO and resulting MEGO indicated just small differences, with the D-band intensity rather increasing during the MW treatment. This suggests the defect concentration increases, despite the significant reduction of the oxygen content. The surface area increased from $20\text{ m}^2\text{ g}^{-1}$ for GO to approximately $600\text{ m}^2\text{ g}^{-1}$ for MEGO. However, upon prolonged storage in air, an increase of oxygen content and decrease of specific surface area were detected, which implies that MEGO is a metastable material at ambient conditions.^[114]

Hu et al.^[17] examined the influence of different amounts of graphene from thermal expansion (GT) on the heating properties of GO/GT mixtures. Graphene, which is a good microwave

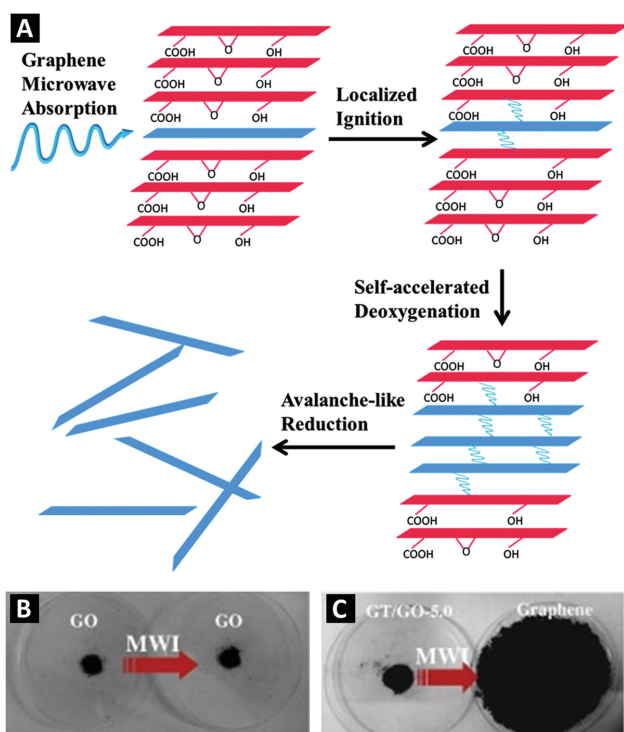


Figure 9. A) Illustration of the graphene-triggered reduction of GO to graphene.^[115] B,C) Photographs of GO (B) and a GO–graphene mixture (C) before and after MW irradiation, showing the negligible response of GO to MW irradiation and the strong influence of graphene on the reaction.^[17] A) Reproduced with permission.^[115] Copyright 2013, The Royal Society of Chemistry. B,C) Reproduced with permission.^[17] Copyright 2012, Elsevier.

susceptor, can be heated much faster than graphite oxide, which has a partially disconnected π -system. Consequently, pure GO exhibited little temperature variation and volume expansion, whereas the addition of 0.5% GT resulted in a temperature increase to 100 °C within 10 min of MW irradiation at 800 W. With an increasing amount of graphene, the heating was accelerated; thus, a mixture with 2.5% GT could be heated to about 1000 °C within 3 min and a mixture with 5% GT finally resulted in an avalanche-like reaction, which ignited within 10 s and resulted in a remarkable volume expansion (Figure 9C). This avalanche-like deoxygenation is based on the local heating of graphene stimulating the reduction of adjacent GO (Figure 9A). Once the resulting graphenic structures on the GO sheets are large enough, the Joule heating mechanism occurs, which further accelerates and spreads the deoxygenation and exfoliation of the surrounding GO. For pure GO the C/O mole ration was nearly unchanged even after 10 min, whereas, for the sample with 5% of graphene, only 2 min of MW irradiation resulted in a C/O ratio of 11.5, increasing to 17.0 after 10 min. However, the authors report that direct exfoliation of pure GO could be achieved as well when a large amount (>1.2 g) of oxidized graphite was irradiated for 1 min at 800 W. Even after the harsh oxidation treatment of the Hummers method, GO still contains some sp^2 -bonded regions. These graphitic “impurities” may act as the initiators of the deoxygenation reaction, if enough heat can be accumulated due to the large amount of precursor.^[17]

The microwave absorption and, consequently, the microwave reduction of GO can also be improved by vacuum-drying of as-prepared GO at different temperatures.^[57] Drying at 50 °C for one minute was sufficient to significantly enhance the exfoliation. This observation is attributed to the removal of absorbed water. As a result, microwaves can interact more effectively with labile oxygen containing functional groups, which leads to a faster heating. In this way, the exfoliation and reduction efficiency can be significantly improved.^[57]

Park et al.^[116] investigated the influence of the gas atmosphere on the solid-state reduction of GO. A hydrogen atmosphere is reported to play an important role during thermal reduction and exfoliation of GO, since it leads to the formation of H_2O instead of CO_2 . Thus, it prevents the loss of carbon and the emergence of vacancies and defects. The reactant mixture (GO with 10 wt% graphene nanosheets (GNS)) was placed in a quartz bottle filled with either Ar gas or a H_2 /Ar gas mixture (10:90 vol%) or kept under ambient atmosphere. The subsequent MW irradiation was performed at 1600 W. Intensive characterization studies revealed the superior properties of GO reduced under H_2 /Ar compared with those prepared at ambient atmosphere or hydrothermal reduction. For example, within 40 s reduction time, a G/O ratio of 18.5 was obtained under H_2 /Ar atmosphere compared with 11.45 (pure Ar), 3.6 (air), and 4.9 (hydrothermal without any reducing agent after 5 min). The r-GO that was prepared hydrothermally consisted of randomly agglomerated and wrinkled sheets. With the solid-state method a more-effective exfoliation and a higher specific-surface area of $586\text{ m}^2\text{ g}^{-1}$ was obtained.^[116]

Microwave hydrothermal reduction of GO within 2 to 10 min of MW irradiation at 800 W for a mixed solution of *N,N*-dimethylacetamide and water (DMAc/ H_2O) was also reported, leading to a conductivity of 200 S m^{-1} ^[117] and also in acidic aqueous solution upon MW irradiation of 80 W (single-mode) for 10 min leading to a C/O of 9.1.^[118]

3.2.2. Thermal Exfoliation of Graphite Intercalated Compounds

The basic principle behind the exfoliation of graphite-intercalated compounds (GICs) is to prepare intercalated or functionalized graphite, which is subsequently thermally expanded by the outgassing of the intercalated species. In contrast to GO, which comprises oxygen-containing functional groups, for GICs, the graphenic structure of the layers remains mainly intact and the guest substances are just located in between the layers. Consequently, efficient heating by MW irradiation is assured.

Luo et al.^[119] developed a modification of the Hummers method involving a pre-exfoliation of expandable graphite intercalated with organic, sulfuric and nitric acids. Solid-state microwave treatment of less than 2 s in a vial sealed under a nitrogen atmosphere resulted in single-layer graphite oxide membranes with a size of up to thousand square micrometers. Due to the rapid heating, fewer point defects were generated by oxidation of the intercalated compounds compared with thermal expansion by conventional heating methods. The graphite expanded to approximately 200 times of its original volume. Thin flakes were formed but the lateral dimensions remained unchanged. Subsequently, graphene oxide was prepared according to the

Hummers method. Due to the pre-exfoliation by microwave heating, milder conditions could be applied, e.g., no ultrasonication was required, and thus, larger flakes were obtained and less starting material had to be used.^[119]

An even more convenient approach was developed by Sridhar et al.^[120] The authors mixed natural graphite, hydrogen peroxide, and ammonium peroxydisulfate in a glass tube at a ratio of 2:1:0.1 and irradiated it at 500 W for 90 s in a domestic MW oven. Accompanied by flashing, the graphite was rapidly exfoliated to graphene worms of 150 times the original volume. This process presumably includes three steps: firstly an oxidation reaction by decomposition of ammonium peroxydisulfate releasing oxide radicals; secondly, the decomposition and intercalation of hydrogen peroxide; and, finally, the expansion of the graphene layers. Subsequently, ultrasonication created localized erosion, leading to ripping or shearing of the graphene platelets.^[120] Liu et al.^[121] slightly adjusted the method, increasing the yield from 5 to 30% by applying H₂O₂ as the re-intercalation source. However, care has to be taken when performing such reactions, since excessive microwave intensity, longer irradiation times, or large volumes of reacting mixtures can cause violent explosions.^[120]

Not only graphite, but also turbostratic PAN-based carbon fibers can be “unzipped” when immersed in hydrogen peroxide and hydrazine. Due to the lower degree of crystallinity, the carbon atoms are more accessible for oxidation, and exfoliation occurs at milder conditions than those needed for the exfoliation of perfectly graphitized carbon structures.^[122]

The common oxidation-based methods usually result in structural defects of the graphene sheets, which cannot be fixed subsequently. By avoiding oxidative reaction pathways during the synthesis, products with fewer defects can be obtained.^[123] Janowska et al.^[124] prepared few-layer graphene by immersing expanded graphene in an aqueous solution of ammonia. Upon MW irradiation, the infiltrated ammonia solution decomposes, thereby forming gaseous NH₃ and H₂O, which expanded the graphene layers.^[124] Fu et al.^[125] exfoliated iron chloride and nitromethane co-intercalated graphite immersed in water by heating the reaction mixture in a domestic MW oven at 700 W for 60 s. The authors state that by dispersing the GIC in deionized water, the reaction was performed at the boiling temperature of water. However, this temperature is well below the TGA decomposition temperature of the intercalated nitromethane. This led the authors to the conclusion that the decomposition temperature of the intercalated CH₃NO₂ decreases under MW irradiation, caused by the pressure built up by the rapid heating of the solvent trapped in the interstitial spaces of the partially exfoliated graphite layers. Two control experiments were performed; one by heating the reaction mixture in a tube furnace to 500 °C, and the second one suspending the sample in boiling water for 60 s. Neither of them resulted in the exfoliation of the graphite into thin graphene sheets.^[125] However, these experiments do not mandatorily prove the decomposition of nitromethane and the exfoliation of graphite at low temperatures, but rather are a good example for local and selective heating by MW irradiation, which cannot be monitored by conventional methods during a microwave experiment. Actually, no temperature measurement was reported for this exfoliation method.

Wang et al.^[123] prepared graphene sheets by microwave-assisted pre-expansion of acid-intercalated graphite and,

subsequently, applied a simple exfoliation in the aqueous phase with the assistance of the surfactant cetyltrimethylammonium bromide (CTAB) and ultrasonication. Graphene sheets with low defect density were obtained, and the number of layers could be adjusted by varying the amount of CTAB in the solution.^[123]

Exfoliation of graphite is also possible without any intercalating species, just utilizing thermal strain. Zheng et al.^[55] MW-irradiated natural flake graphite that was immersed in liquid nitrogen (LN). As a consequence of microwave heating, thermal expansion occurred. However, simultaneously, the graphene sheets on the surface of the graphite flakes were cooled by the LN, resulting in their shrinkage. Due to the emerging strain, exfoliated sheets rolled up to form high-quality carbon nanoscrolls (CNS), i.e., rolled up graphene nanosheets with helical structure (Figure 10). The CNSs were composed of 98.2% carbon and just 1.8% oxygen, probably due to the vigorous boiling of the LN which prevented any contact with oxygen during the synthesis. Furthermore, no doping or impurities were incorporated, since LN did not react with the carbon sheets, but is fully evaporated after the reaction. However, the formation of CNS only occurred when a large quantity of graphite (2 g in 100 mL of LN) was applied. It seems that heat accumulation was required to induce these processes. Small quantities of graphite were fully frozen, no sparks occurred, and, hence, no CNS were formed.^[55]

3.2.3. Simultaneous Reduction and Doping of Graphite Oxide

By microwave heating, graphite oxide can not only be reduced to graphene, but simultaneously even doping of the carbon sheets can also be obtained within very short time scales. In solid-state reactions, the addition of urea to a dry sample of GO leads to the formation of nitrogenated MEGO. For example, mixtures of GO and urea in a mass ratio of 2:1 resulted in MEGO with a nitrogen content of approximately 15 wt%.^[126] Another possibility for obtaining nitrogenated graphene is to microwave-heat r-GO under an atmosphere of flowing NH₃.^[127]

Simultaneous reduction and hydrogenation of GO to graphene can be obtained by irradiating GO under hydrogen atmosphere with a pressure of 1 mbar, which leads to the formation of a hydrogen plasma. Microwave treatment for 30 s with a power of 1000 W resulted in hydrogenated graphene with a C/O ratio of approximately 12 and a hydrogen content of 9 to 19 at%.^[128]

In suspension, nitrogen-doped graphene can be obtained by a microwave hydrothermal process utilizing an aqueous ammonia solution as oxygen reducing agent and chemical dopant. Reduced graphene with a nitrogen content of 6.1 at% was obtained after irradiating such a suspension for 8 min at 800 W in a sealed Teflon autoclave.^[129] Applying a single-mode MW oven, a power of just 100 W for 10 min was reported to result in nitrogen-doped reduced graphene oxide.^[130] Furthermore, sulfonated MEGO was prepared by MW treatment of GO dispersed in a mixture of nitric and sulfuric acid.^[131] Microwave heating a flask filled with expandable graphite and either liquid chlorine or bromine while being immersed in liquid nitrogen results in graphite chloride or bromide. Due to the

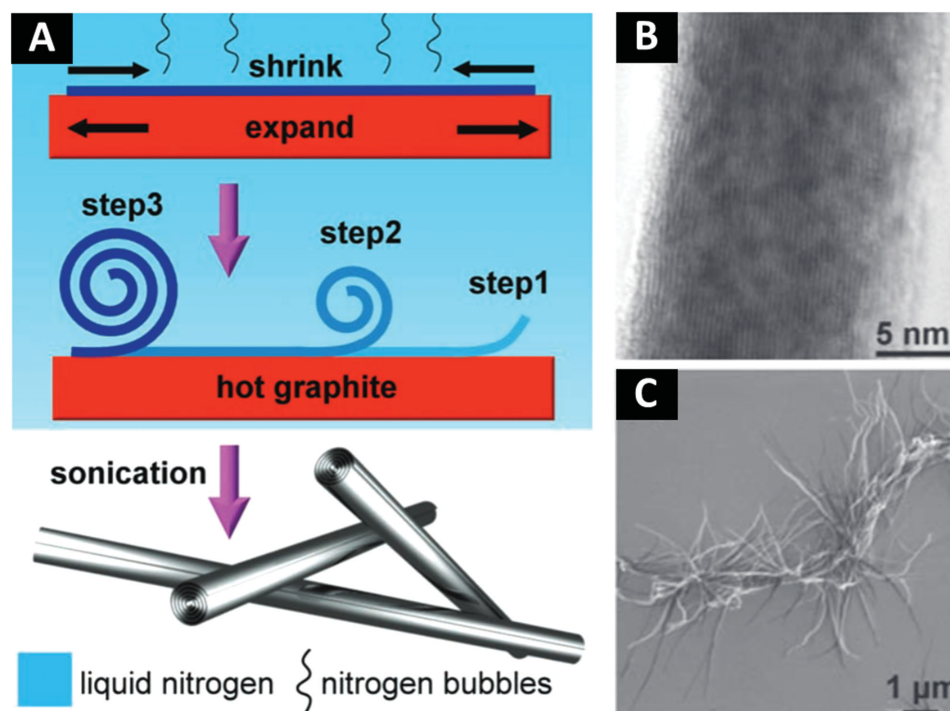


Figure 10. A) Schematic illustration of the exfoliation of carbon nanoscrolls from graphite by thermal stress. B,C) H-RTEM (B) and SEM (C) images of CNSs.^[55] Reproduced with permission.^[55] Copyright 2011, Wiley.

fast temperature increase of graphite under MW irradiation accompanied by luminous sparks, expanded graphite sheets can directly react with the halogen (700 W for 5 s). The halogenation efficiency was found to be higher when larger pieces of graphite were used and more-intense sparking occurred. In addition, liquid chlorine was more efficient than gaseous Cl_2 , due to the better intercalation behavior and its assistance to the rapid cooling of the reaction product.^[56]

Kim et al.^[132] reported a rapid IL-assisted microwave-reduction process. ILs are capable of efficiently absorbing microwave energy, and, thus, can induce a rapid reduction of GO. Only 15 s of MW irradiation were sufficient to reduce a mixture of GO and IL (1:1), whereas more than 60 s were required for the reduction of dry GO under the same conditions. Additionally, 1-ethyl-3-methyl imidazolium bis(tri-fluoromethylsulfonyle)imide (EMIM-NTf₂), used as a reaction medium, was retained in the porous structure of the resulting MEGO. This improved the electrochemical performance of supercapacitors made from this MEGO, compared to an electrode made from chemically reduced GO. However, care has to be taken when performing this synthesis, since MW irradiation for more than 30 s causes the decomposition of the IL and the evolution of a fuming gas.^[132]

3.2.4. Graphene Composite Hybrid Materials

Microwave approaches are not only used to reduce GO in a very short time, but it is also possible to simultaneously prepare graphene composite materials by adding a desired component to the microwave-treated mixture, e.g., carbon nanotubes or a metal salt.

Graphene–Metal Hybrids: By adding a metal salt to a GO suspension together with a reducing agent, the simultaneous reduction of GO and the formation of nanoparticles supported on the surface of MEGO sheets can be obtained. Metal-particle-decorated graphene has promising potential applications in the fields of catalysis, sensing, energy storage,^[133] and semiconductor crystals are of interest for optoelectronics or energy conversion.^[134] Furthermore, nanoparticles supported on graphene can act as a spacer, increasing the distance between the graphene sheets. In this way, re-stacking is prevented, the surface area is increased, and the remarkable properties of single- or few-layer graphene sheets can be preserved.^[133]

One obvious advantage of the microwave-assisted approaches for the decoration of graphene with nanoparticles is the very short reduction and synthesis time of only a few minutes. Furthermore, the uniform heating of the reaction mixture leads to high-quality, nearly monodisperse nanoparticles with no tendency for agglomeration.^[134] In contrast to just physically mixing rGO with a nanoparticle suspension, in situ synthesis results in well-dispersed NPs without significant aggregation (Figure 11). This is due to the oxygen functional groups of the GO starting material, which act as nucleation centers or anchoring sites, improving dispersion, limiting particle growth, and increasing the stability of the binding.^[135] Consequently, applying a simultaneous reduction of metal salt and GO does not only improve the wettability and dispersibility of GO compared to starting with graphene nanosheets, but it also improves the uniformity and dispersion of the nanoparticles formed in situ.

A variety of nanoparticle graphene composites can be prepared by applying such a suspension-based method, including

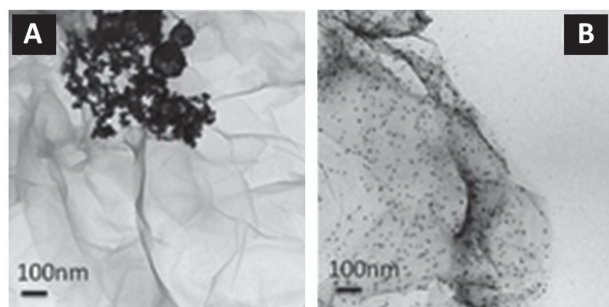


Figure 11. TEM images of graphene sheets containing Pd nanoparticles prepared by: A) mixing separately prepared Pd nanoparticles and graphene sheets, and B) simultaneous reduction of GO and Pd nitrate in water using hydrazine hydrate under MW irradiation.^[133] Reproduced with permission.^[133] Copyright 2009, The Royal Society of Chemistry.

the decoration of graphene with metal nanoparticles of, for example, palladium, copper, or bimetallic alloys,^[133] platinum,^[135,136] or silver,^[137,138] as well as nanocrystals of CdSe,^[134] Mn₃O₄,^[130,139] or SnO₂.^[140,141]

Such a simultaneous reduction of GO and the formation of metal nanoparticles can also be achieved by a solid-state decomposition of dry precursor materials without any liquid medium and reducing agent. Gollavelli et al.^[53] prepared magnetic graphene by microwave heating of GO and ferrocene, adding small pieces of silicon wafers as susceptors. Upon MW irradiation violent arcing occurred in the nitrogen-filled quartz tube, followed by the reduction of GO and the formation, as well as graphitization, of the iron nanoparticles. Pu et al.^[142] prepared MEGO–TiO₂ hybrids by a microwave-assisted combustion method, irradiating a gel-like precursor consisting of GO, titanyl nitrate, and additional urea and nitric acid.

However, care has to be taken when heating metal-nanoparticle-decorated carbon supports by MW irradiation. Depending on the kind of metal and the surrounding atmosphere, it has been shown that either carbon nanotubes can grow or etching and pitting can occur, induced by the heated metal nanoparticles.^[84]

A completely different kind of graphene–metal hybrid material was prepared by microwave-assisted reduction of GO coated on a nickel foam.^[143] After immersion of the foam in a GO suspension, the GO coating was reduced by MW irradiation at 1000 W for 2 min at ambient conditions. In this way, a direct contact between graphene and nickel without the need of conductive agents and polymer binders can be obtained, which decreases the resistance of electrodes and improves the cycle life, when applied in supercapacitors.^[143]

Graphene–Carbon Hybrids: For some applications, metal particles are not suitable to act as spacers for preventing the re-stacking of graphene sheets. Sridhar et al.^[144] developed a method to prepare 3D carbon nanostructures composed of “nanocup arrays” anchored on few-layer graphene (**Figure 12**). At first, carbon-coated titanium oxide particles were grown on graphene sheets in a one-pot microwave-assisted synthesis procedure using expandable graphite, titanium di-isopropoxide bis(acetylacetonate) as precursor, and an IL as the carbon source. Afterward, pure carbon structures were obtained by

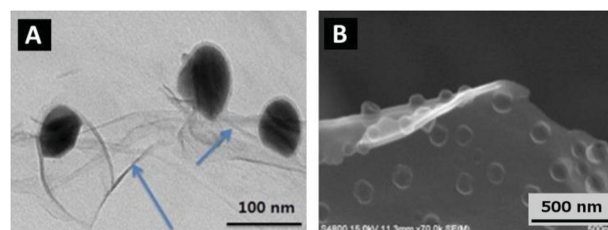


Figure 12. EM images of ionic-liquid-exfoliated graphene with graphene-shelled titania nanoparticles anchored on the surface. A) TEM image before and B) SEM image after etching with HCl.^[144] A,B) Reproduced with permission.^[144] Copyright 2013, Elsevier.

etching away the core of the graphene-coated titania nanoparticles. SEM and TEM investigations revealed the open and hollow structure of the multi-shell graphene nanocups being well-dispersed, anchored on the surface of the graphene sheets.^[144]

Pure carbon 3D structures can furthermore be obtained by adding CNTs as spacers between the graphene sheets, e.g., by simply mixing GO with CNTs before the reduction process.^[145,146] Chen et al.^[145] dispersed GO and functionalized CNTs (f-CNTs) in aqueous solution and, subsequently, microwave-heated the mixture to 150 °C at 80 W for 10 min. By reducing the GO, a composite was formed, consisting of crumpled and scrolled MEGO forming an open-pore system, while the CNTs built up an entangled network structure, connecting the individual MEGO sheets. Such a network, with fast electronic and ionic conducting channels, provides an ideal electrode material for application in, for example, lithium-ion batteries.^[145]

Lin et al.^[147] reported a 3D carbon structure consisting of multi-wall carbon nanotubes as the core with graphene oxide nanoribbons around them. This core/shell structure was prepared by the facile unzipping of MWCNTs via microwave heating of CNTs dispersed in concentrated acids.^[147]

Sponge-like 3D CNT–graphene composite electrodes were prepared by a different two-step microwave process, including the bottom-up synthesis and a subsequent carbonization process of cobalt phthalocyanine templated by acid-functionalized MWCNTs.^[148] In the first step, f-CNTs acted as the nucleation site for the formation of cobalt phthalocyanine and in the second step, assisted by the CNTs, carbonation occurred. Subsequent quenching in ice water supported the exfoliation of the formed graphite, resulting in a sponge-like graphene nano-architecture with a 3D macroporous structure.^[148]

Oh and co-workers^[78] prepared a 3D graphene–carbon–nanotube–nickel nanostructure by directly growing CNTs on graphene sheets. Nickelocene and GO were mixed in acetonitrile and, upon MW irradiation, first nickel nanoparticles were formed on the graphene, whereon, subsequently, CNTs were grown (**Figure 4**). Obviously, these structures do not consist purely of carbon, but the nickel-catalyst particles are incorporated in the tips of the grown CNTs.

Zeng et al.^[149] prepared a 3D hybrid material of CNTs and MEGO implanted into a Cu₂O matrix of micrometer spherical structures via electrostatic self-assembly and a microwave-assisted synthesis process. Cu₂O exhibits good photocatalytic properties, which can be utilized if being supported by a

network of CNTs assisting the transport of the light-generated charge carriers. This is of interest for applications, for example, in the field of water purification or optoelectronics. Unfortunately, CNTs generally tend to form agglomerates. However, GO shows strong π - π interactions with CNTs and provides nucleation sites for the formation of the copper oxide particles. In this way, a well-dispersed composite can be prepared by microwave-heating a mixture of acid-functionalized CNTs, GO, gelatin, glucose, and CuSO_4 . Simultaneously during the process, GO is reduced to MEGO; thus, a 3D electron-conducting network is formed.^[149]

3.2.5. Bottom-Up Synthesis of Graphene

Besides a broad variety of publications about exfoliation and reduction of graphitic structures into graphene sheets, there have also been a few methods reported regarding bottom-up microwave synthesis starting from hydrocarbon precursors. However, mostly, not just pure microwave heating is applied, but rather a microwave plasma is required to obtain graphene.^[150,151]

Hojati-Talemi and Simon^[152] developed a simple microwave-generated plasma process utilizing a solid carbon source without the need of a catalyst. A plasma, created in an evacuated quartz tube by using a conventional MW oven, was used to degrade and carbonize polyethylene powder to produce graphene nanosheets. The plasma was triggered by an aluminum foil and could be observed as an emission of bright, purple-colored light, turning yellow after a few seconds. The temperature, measured by an IR sensor at the outer walls of the quartz tube, reached approximately 250 °C after 10 s, 625 °C after 30 s, and then went up to 800–900 °C. Polystyrene precursors resulted in nano-onions, whereas polyethylene, which exhibits a higher H/C ratio, prevented the active edges from joining, and thus, resulted in nanosheets.^[152] Utilizing various catalyst materials, e.g., copper, nickel, aluminum, iron, and graphite, polystyrene could be transformed into nanoparticles with different morphologies. Applying transition metals instead of aluminum as the trigger resulted in sputtering of metal-catalyst nanoparticles that than could guide the process toward the formation of nanofibers.^[52]

Lin et al.^[49] directly grew flower-like graphene on hexagonal boron nitride (h-BN), by using poly(methyl methacrylate) (PMMA) as the carbon source without the need for a catalyst or other additives. A graphene coating can highly increase the interfacial thermal conductivity between h-BN crystals and furthermore improve the wettability by metal melts. Commonly, when preparing such graphene coatings by CVD processes, transition metals are used as catalyst, which is, however, undesired for later applications. For the reported microwave approach, PMMA-coated h-BN crystal flakes were placed in evacuated quartz tubes and were subsequently treated with MW radiation in a domestic oven. The silica tube was placed on a silicon carbide board, which served as a heat reservoir and provided the thermal energy for graphene growth. The graphene layer not only grew on the substrates, but even extended beyond, since freshly formed graphene has highly active edges that can easily incorporate nascent carbon atoms from the decomposition of PMMA. The amount of PMMA was found to be critical to

assure the complete coverage of the substrates while avoiding obtaining amorphous carbon as a side product. However, the resulting graphene sheets were rather small, being well below 1 μm in size.^[49]

Additionally, using microwave-assisted processes, graphitic precursors with high crystallinity can be prepared for the subsequent exfoliation to graphene.^[148,153] For this purpose, first, metal phthalocyanine was synthesized using a domestic MW oven and, thereafter, carbonization was performed at 450 °C by microwave heating. Followed by a rapid cooling, few-layer graphene with 1 to 8 layers, depending on the cooling medium, could be obtained.^[153]

3.3. Preparation of Carbon Nanoparticles

3.3.1. Carbon Dots

Carbon nanoparticles with sizes below 10 nm, so-called carbon quantum dots (C-dots), have attracted special attention due to their excellent fluorescence properties, which make them attractive, for example, as optical-imaging agents for life-science applications (Figure 13). Up to now, well-established quantum dots have been based on semiconductors, mainly CdSe and ZnS. A major issue, however, is their toxicity and the risk of their accumulation in organs and tissues. C-dots, firstly observed in 2004 during purification of CNTs,^[154] offer a promising alternative to such heavy-metal-based quantum dots, being competitive in their optical properties, but being biocompatible and having a low toxicity.^[155] Further areas of potential applications include optoelectronics, photocatalysis, energy and charge transfer for fuel cells or electrochemical energy storage, and sensor technology.^[156]

Top-Down Approach: Graphene quantum dots (GQDs) can be prepared by a top-down approach by splitting graphite oxide into smaller sheets. Thereby, the oxygen-containing functional groups serve as reactive sites for the acid-assisted cleavage process (Figure 13A). The aim is to prepare zero-dimensional GQDs with a lateral size of less than 10 nm, which results in strong quantum confinement and special photoluminescence (PL) phenomena, different from those observed in graphene or graphene nanoribbons.^[106] After the cleavage, a reduction step is traditionally required. With the hydrothermal cleavage route, such a top-down fabrication process can take up to three days.^[158] By applying microwave-assisted methods, the reaction time can be significantly shortened (Table 2).

Wang et al.^[159] applied three different top-down approaches to cleave graphite oxide and compared the obtained fluorescent GQDs: i) heating under reflux in nitric acid, ii) microwave-assisted heating under reflux, and iii) microwave-hydrothermal synthesis. The GQDs prepared by the microwave routes exhibited higher quantum yields and longer fluorescence lifetimes, and the process was furthermore faster than the synthesis performed by conventional heating under reflux. In particular, the particles prepared by the microwave-hydrothermal method showed superior properties and a significantly shorter synthesis time (Table 2). The position of the emission peak, however, was almost the same for all three reaction routes, which suggests that the same fluorochrome was produced by all three methods.

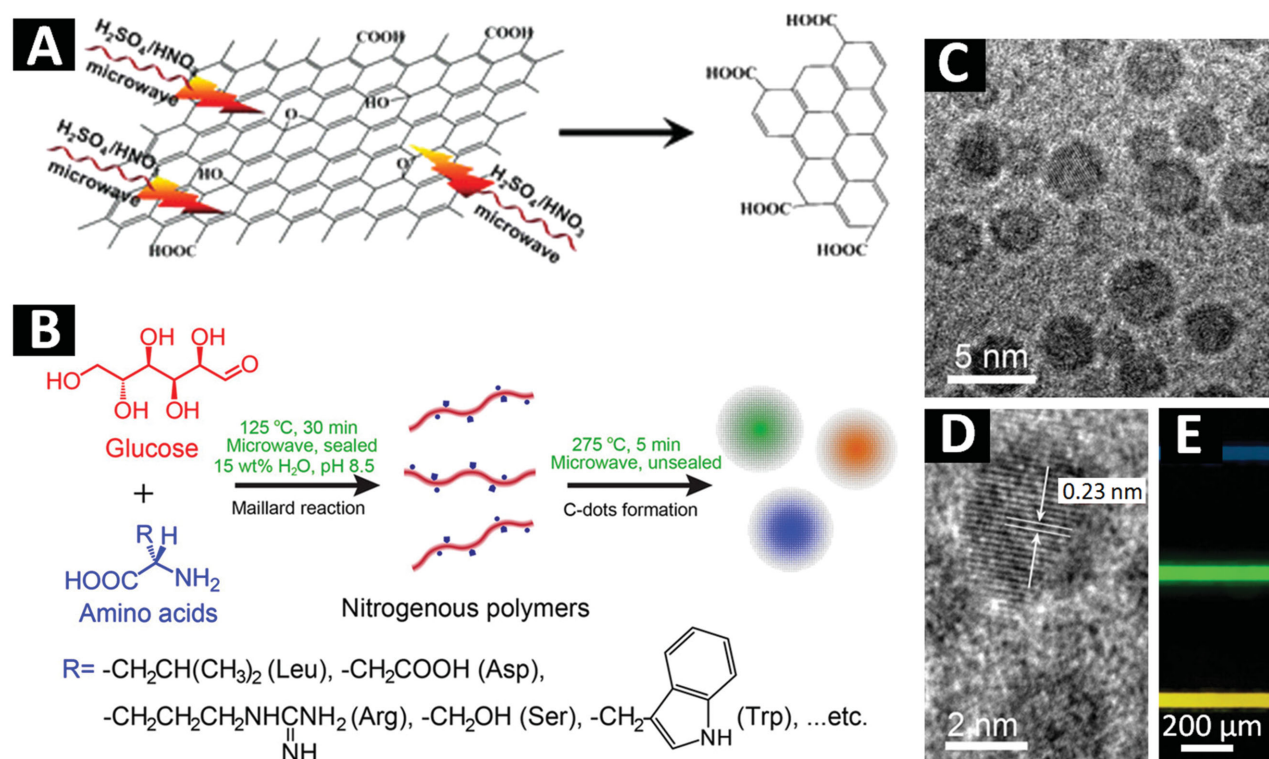


Figure 13. Carbon dots can be prepared by both top-down and bottom-up approaches. A) Schematic illustration of the oxidation cutting of graphene oxide into GQDs by $\text{H}_2\text{SO}_4/\text{HNO}_3$.^[106] B) Schematic illustration of the bottom-up synthesis of nitrogen-doped C-dots with tunable emission color by a two-step one-pot microwave synthesis. C, D) TEM images of Trp-C-dots prepared with the method in (B) under different magnifications. E) Fluorescence microscopy image of different-colored C-dots on a PDMS chip.^[157] A) Reproduced with permission.^[106] Copyright 2012, The Royal Society of Chemistry. B–E) Reproduced with permission.^[157] Copyright 2013, Nature Publishing Group.

The superior properties of the microwave-hydrothermally prepared GQDs can be explained by the combination of advantages arising from both the microwave-heating and the hydrothermal treatment. The rapid and direct heating, which eliminates effects of temperature gradients and, additionally, the possibility of obtaining temperatures above the boiling point by working at increased pressure, resulted in the fast preparation of monodisperse, small-sized and highly pure GQDs. When a prolonged reaction time was applied, the

quantum yield (QY) of the GQDs was found to be decreased, which might be caused by the decomposition of the particles. Furthermore, the particles from the microwave-assisted routes showed a tendency to aggregate.^[159]

Li et al.^[158] developed a facile method to prepare stabilizer-free greenish-yellow luminescent graphene quantum dots (gGQDs) under acidic conditions. A quantum yield of up to 11.7% was obtained applying MW irradiation under reflux conditions. Bright blue QDs (bGQDs) with a QY as high as 22.9%

Table 2. Overview of top-down fabrication methods for GQDs starting from GO or graphite.

Fabrication method	Reaction parameters	Particle size [nm]	Quantum yield/lifetime [%]/[ns]	Emission (excitation) wavelength [nm]	Reference
Conventional heating under reflux in HNO_3	12 h, 140 °C	3.3 ± 1.1	1.15/1.5	520 (460)	[159]
MW heating under reflux in HNO_3	8 h, 120 °C, 900 W	3.8 ± 1.4	1.91/2.34	520 (460)	[159]
MW-hydrothermal method with HNO_3	0.5–0.75 h, 800 W	4.0 ± 1.4	2.72/3.72	520 (460)	[159]
MW heating under reflux, with H_2SO_4 and HNO_3	1–5 h, 240 W	2–7 (4.5) Unchanged ^{a)}	11.7/–, 22.9/– ^{a)}	500 (260 and 340) 450 (260 and 340) ^{a)}	[158]
MW-heating under reflux with H_2SO_4 and KMnO_4 , starting from graphite	1 h, 600 W	2–8	9/–	420 (340)	[160]
MW-hydrothermal method with HNO_3	5 min, (10 min ^{b)}) 200 °C, 800 W	2–6	12.5/–	550 (490)	[161]

^{a)}After further reduction with NaBH_4 ; ^{b)}MW-hydrothermal method with HNO_3 , and functionalization with NH_3 .

were prepared in a second step by further reducing the gQDs with NaBH₄. The bQDs exhibited diameters in the range of 2 to 7 nm and heights of 0.5 to 2 nm, indicating a single- or double-layer structure of the QDs. The dimensions of the bQDs showed no perceptible difference, indicating that the blue shift is attributed to a structural change by the reduction process rather than due to a change in size.^[158]

Shin et al.^[160] simplified the top-down approach by preparing GQDs in a one-pot synthesis directly from natural graphite, thus omitting the need of preceding GO preparation. Graphite powder was mixed with H₂SO₄ and KMnO₄ and subsequently heated by MWI under reflux. An irradiation power of 300 W entailed rather-large-sized pieces of oxidized graphite, whereas 600 W resulted in small, mostly mono- or double-layer GQDs. With this straightforward method, a fairly high yield of approximately 70% was obtained, thus offering a simple approach for the production of GQDs in larger quantities.^[160]

By functionalizing GQDs, their emission wavelength can be further tuned. Chen et al.^[161] prepared GQDs of 2 to 6 nm in size, which, subsequent to the exfoliation process, were treated with a surface functionalization step in ammonia solution. This microwave-assisted treatment resulted in a redshift of the emission maximum to 550 nm. The emission was stable within a wide range of pH from 4 to 10 and was independent of the excitation wavelength.^[161]

Bottom-Up Approach: Another attempt for the preparation of carbon nanodots is to apply a bottom-up synthesis strategy, starting with liquid or solid carbonaceous precursor materials. Several methods have been reported, such as, for example, combustion, thermal, hydrothermal, or acidic treatment.^[156] However, there is the need for a fast, energy-efficient method without hazardous or expensive reactants to enable large-scale

synthesis of small and strong emitting C-dots for utilization in practical applications. This is addressed by developing microwave-assisted synthesis methods as summarized in Table 3.

In general, precursor solutions containing a carbon source and, if necessary, some additives or passivation agents are simply heated by MW irradiation, either in an open vessel or a hydrothermal setup. Most setups include multimode instruments or just a domestic MW oven, and irradiation is carried out usually for a few minutes mainly at 400 to 900 W. Thus, the required heating times are significantly shorter than for approaches that apply conventional heating. Typically, carbohydrates are used as the carbon source and, upon MW irradiation, a color change to yellowish-brown is observed, indicating the formation of C-dots.

The detailed mechanism for the formation of C-dots remains up to now unclear, but it is proposed that carbohydrates first experience hydrolysis, dehydration, and decomposition, which results in the formation of soluble compounds. Subsequently, polymerization and condensation produces different soluble polymeric products and C-dots are finally formed by aromatization and carbonization.^[173] It was found that, with prolonged processing times, more C-dots form and the PL intensity increases. However, if the irradiation time is too long, the PL is weakened and becomes slightly red shifted, probably due to the formation of larger particles.^[164,170]

Zhu et al.^[162] first reported a microwave-assisted pyrolysis approach for the preparation of C-dots using poly(ethylene glycol) (PEG) as a surfactant. The authors discovered a similar UV-vis absorption spectrum for both PEG-passivated and non-passivated particles, but the non-passivated particles expressed a poor luminescence with irregular spectra.^[162] Wang et al.^[163] improved this method with no need of further surface

Table 3. Overview of bottom-up fabrication methods for C-dots.

Reactants	Reaction parameters	Particle size [nm]	Quantum yield/lifetime [%]/[ns]	Emission (excitation) wavelength [nm]	Reference
<i>Carbon dots</i>					
Saccharides (glucose, fructose, ...) + PEG-200, aq.	2–10 min, 500 W	2–4	6.3/8.7	425 (330)	[162]
Carbohydrates (e.g., glycerol) + inorganic salt	14 min, 750 W	2.1 ± 0.76	9.5/8	430 (340)	[163]
Glycerol + 4,7,10-trioxa-1,13-tridecanediamine (TTDDA), open	10 min, 700 W	ca. 3.5, 1–5	12.0/8.71	450 (340)	[164]
Glucose, aq, closed vessel	1–9 min, 595 W	ca. 1.65 to ca. 21 (time dep.)	7–11/<6.3	303 (197)	[165]
Polysaccharides + acid + PEG, influence of solvents and cations, aq.	5–6 min, 450 W	1–10	–/<1.8	480 (370)	[166]
Citric acid + ethylenediamine, aq.	5 min, 700 W	2.5 ± 0.5	41.4/15.5	455 (360)	[167]
Triblock copolymers + phosphoric acid	4 min, 450 W	5–20	7/2.1	442 (380)	[168]
Flour, closed	20 min, 180 °C	1–4	5.4/–	442 (365)	[169]
<i>Carbon nitride dots</i>					
N,N-dimethylformamide + acid, open	0:40 min, 700 W	1–6	9/–	443 (360)	[170]
Amino acids (histidine) + acids or alkali, open	2:40 min, 700 W	2 ± 0.4	44.9/–	440 (360)	[171]
Formamide	30 min, 180 °C	2–15 (av. 7)	29/<38.9, Solvent dep.	404 (340)	[172]
Glucose + various amino acids (e.g., Tryptophane)	1. 30 min, 125 °C (closed); 2. 5 min, 275 °C (open)	2.9 (2–5)	69/22.7	e.g., 450 (430) (others: blue, green, yellow)	[157]

passivation steps, by just adding a tiny amount of an inorganic ion. The particles possessed a pH-independent PL within the pH range of 4.5–9.5 and could enter cells, thus, enabling PL-based cell-imaging applications.^[163]

Tang et al.^[165] reported a microwave-assisted hydrothermal method to prepare glucose-derived crystalline carbon dots with an average diameter as small as 1.65 nm. The particles exhibited an emission in the deep ultraviolet, which was size-independent, as was demonstrated even for particles with a diameter of 20 nm.^[165] Tuning of the PL properties of C-dots was obtained by the *in situ* addition of high-boiling-point organic solvents during the synthesis, as well as by applying different divalent cations.^[166]

By applying nitrogen-containing precursors, nitrogen-doped carbon dots can be prepared. Liu et al.^[174] reported the preparation of photoluminescent carbon nitride dots (CNDs) by microwave heating of organic amines in the presence of acids.^[174] The availability of acid or alkali was found to be of importance when utilizing amines or amino acids as precursors. Control experiments in the absence of these additives did not result in the formation of fluorescent CNDs, even if a prolonged reaction time was applied.^[170,171] However, graphitic CNDs with strong blue fluorescence and a QY of 29% were also obtained by microwave heating of pure formamide (HCONH₂) without any additives.^[172]

Wei et al.^[157] reported the synthesis of nitrogen-doped carbon dots with very high QYs of up to 69% and tunable multicolor luminescence, including blue, green, and orange (Figure 13E). The tailoring of the emission and the physicochemical properties was obtained by applying uniform reaction parameters and reacting glucose systematically with various natural amino acids in a MW one-pot, two-step reaction (Figure 13B). The special properties of microwave heating were beneficial for the homogeneous formation of uniform, nanosized C-dots. In a control experiment with a conventional hydrothermal set-up, only microscale particles were obtained. The different emission colors probably originate from the different sizes, shapes, and composition-related factors, based on the side-chain structure of the starting amino acid. C-dots with multiemission colors under the same excitation wavelength have drawn increasing interest for applications such as full-color displays or sensor arrays, and are desired components for optoelectronic devices, medical diagnosis, and biological imaging, such as real-time cellular imaging.^[157]

Microwave treatment can furthermore be utilized to anneal C-dots prepared by conventional heating methods; hence, improving their PL properties.^[97] A PL enhancement was obtained by microwave heating of an aqueous solution of C-dots prepared by conventional pyrolysis of plant leaves. In this way, the fluorescence intensity of the C-dots could be doubled without the introduction of any additional chemicals, which could be detrimental for further biological applications.

3.3.2. Fullerenes

Only very few reports are available on the synthesis of fullerenes using a microwave-assisted synthesis approach.^[175,176] Hetzel et al.^[176] utilized MW irradiation to vaporize graphite

powder as well as fluorinated graphite in order to prepare fullerenes, including C₆₀, C₇₀, and aza-fullerenes. The reaction was carried out in a borosilicate glass vessel using a single-mode microwave oven and an irradiation power of 200 to 300 W. Active cooling was applied during the synthesis; thus, the walls of the glass vial could be kept at a remarkably lower temperature compared to the internal temperature of the reaction mixture. The reaction temperature was approaching approximately 800 °C, which is the melting point of borosilicate glass, since deformation and failure of the borosilicate reaction vial were observed during some of the reactions. After extraction of the fullerenes from the soot or dust, the samples were analyzed by mass spectrometry, and peaks relating to fullerenes could be distinguished from the background noise. The authors, however, mention the problem of a quantitative assignment of the observed peaks due to the fact that, besides fullerenes, also nanotubes, onions, etc. can be potentially present and, moreover, aza-fullerenes can exhibit a large number of partially unstable isomeric forms. In general, the production of fullerenes seems to be mainly dependent on the input power, with increasing power leading to an increase in fullerene production, but independent of time and temperature. For higher yields, higher microwave power would be required, as well as a reactor with higher thermal stability, i.e., made from quartz instead of borosilicate.^[176]

3.3.3. Carbon Spheres

Besides carbon dots, larger nanoparticles, microspheres, and capsules can also be prepared by using microwave-heating methods.

One approach for the controlled preparation of carbon spheres is the solid-state transformation of pre-formed polymeric structures as already described in Section 3.1.2. Spherical precursors made from conductive polymers can be directly converted into carbon by treatment with MW radiation. For the preparation of nanoparticles from polypyrrole doped with chlorine (Ppy·Cl), the carbon content increased from 56% to more than 90%, and their original shape was retained, although the size of the structure was slightly reduced. The graphitization of the particles could be visualized by HR-TEM.^[90]

Other preparation methods are based on the microwave-hydrothermal treatment of carbon-containing precursor solutions. Harris et al.^[177] synthesized chains of graphitic carbon particles by microwave-hydrothermal treatment of a solution of PEG dissolved in a mixture of ethanol, water, and sodium hydroxide. Particles with sizes in the range of 340 to 620 nm were obtained at reaction conditions between 160 and 220 °C for 40 min, whereby the particle size increased with the applied temperature. TEM imaging suggested the graphitized structure of the core of each particle to be coated with some layers of amorphous carbon. According to the authors, these chains of nanoparticles are an intermediate product of the formation of CNTs, since for experiments with a synthesis time of 2 h at 220 °C, MWCNTs were formed at a yield of 17% within the reaction product.^[177]

Jung et al.^[178] prepared nitrogen-doped carbon microspheres with a uniform size distribution by microwave hydrothermal

carbonization of glucose solutions with the addition of urea. The synthesis was carried out within 15 min, much faster than conventional hydrothermal carbonization processes, which usually take 1 to 24 h. Non-agglomerated powder with a carbon content of 50% was obtained. The carbon content could be further increased to over 90% and the crystal structure could be improved by applying a second MW irradiation to the dried, solvent-free powder, placed into a quartz boat. Increasing the concentration of glucose resulted in larger spheres (200 to 650 nm), whereas an increase of the amount of urea led to a stronger nitrogen doping (0 to 10%). Furthermore, when urea was added, the spherical shape of the particles was degraded. Larger spheres with a rougher surface formed due to the high pH value of the solution.^[178]

Carbon microspheres covered with iron oxide nanoparticles can be obtained by utilizing a sugar–organometallic compound as a precursor.^[179] When aqueous NaNO_3 or ethylene glycol was applied as the solvent, the iron oxide nanocrystals formed on the surface of the carbon microspheres, where they were tightly studded. When pure water was used as the solvent, however, the carbon spheres and iron oxide nanoparticle agglomerates were found to be well-separated from each other and the carbon spheres were not studded with nanoparticles.

Krishnan et al.^[180] discovered that the addition of a small amount of graphene oxide to glucose significantly alters the morphology of the product obtained by hydrothermal carbonization and subsequent solid-state microwave treatment. Only 0.12 wt% of GO suppressed the formation of micrometer-sized spheres, and, instead, the formation of more-conductive carbon materials with a higher degree of carbonization was favored. At low GO concentration, dispersed carbon platelets were obtained, whereas higher amounts of GO resulted in the formation of free-standing carbon monoliths of r-GO foam. Control experiments with other carbon materials, e.g., graphite, CNTs, and r-GO, showed that only GO has a significant effect on the carbonization process. Due to its good water dispersibility and 2D structure, GO might act as a template for hydrothermal carbonization. Furthermore, upon MW irradiation, it serves as an in situ heating element to enable the rapid annealing of the carbon composite and to further increase graphitization and conductivity.^[180]

3.3.4. Core/Shell Metal/Carbon Particles and Carbon Nanocapsules

The term “carbon nanocapsules” (CNCs) refers to hollow carbon particles with well-graphitized structure.^[181] Due to their small size, CNCs can potentially serve as carriers that could be used for biomedical applications; for example, as magnetic-resonance-imaging (MRI) agents and drug-delivery carriers, or find application as catalyst supports or electrochemical capacitors.^[181,182] The main pathway for the preparation of CNCs is to synthesize core/shell particles and subsequently leach out the core of the structures.

Besides the preparation by applying electric arcing of graphite electrodes and chemical vapor deposition or thermal pyrolysis of organometallic compounds, there are a number of approaches utilizing microwave-based methods.^[181] The challenge is to produce CNCs with a well-graphitized shell at

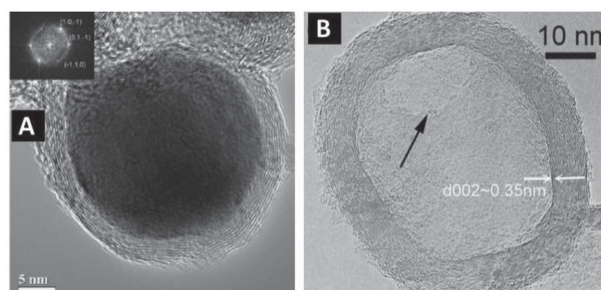


Figure 14. A) HR-TEM image of a core/shell iron/carbon nanoparticle prepared by microwave arcing of copper wires in a toluene solution containing 20 wt% $\text{Fe}(\text{CO})_5$ and 1 wt% $\text{C}_{60}/\text{C}_{70}$ after treatment with aqua regia. The inset is a Fourier transformed pattern at the center region of the iron core. B) HR-TEM image of a hollow carbon nanoparticle prepared by template growth after leaching out the cobalt core with aqua regia. A hole in the graphite shells can be seen at the location indicated by the arrow.^[183] A,B) Reproduced with permission.^[183] Copyright 2008, Wiley.

a high yield, and avoid them being mixed with CNTs or other byproducts.^[183]

Hsin et al.^[183] investigated microwave-arcing-induced formation of core/shell metal/carbon nanoparticles in organic solutions using metal carbonyl as the metal source, $\text{C}_{60}/\text{C}_{70}$ –toluene as the carbon sources, and copper wires to induce arcing. When metal wires or powders are added into organic solutions, MW irradiation will cause electric arcing between the tips of the metal wires (or sharp edges of the metal powders), leading to carbonization of the organic solvents and the formation of amorphous carbon. Such microwave-arcing phenomena have been found to be much more violent in nonpolar solvents than in polar solvents, and are easier to initiate in aromatic solvents than in alkyl ones.^[58] Metal-core nanoparticles have been generated by decomposition of organometallic complexes, subsequently forming iron–carbon alloys. Upon cooling, carbon is precipitated, forming a carbon shell around the metal particle. Applying irradiation cycles of “5 s on – 20 s off”, particles ranging from 10 to 30 nm with well-graphitized carbon shells of 5 to 10 layers were obtained without the co-formation of CNTs or a coating of amorphous carbon (Figure 14A). The presence of $\text{C}_{60}/\text{C}_{70}$ played a crucial role for the formation of well-graphitized carbon. Without fullerenes, only carbon nanoparticles with a poor graphite shell were obtained. Probably, fullerenes already serve as graphitized building blocks, which facilitates the formation of large-scale graphitized structures. Microwave thermal-annealing experiments have been performed, resulting in the disappearance of small iron/carbon nanoparticles and the formation of larger ones. To merge small particles into large ones, obviously, the carbon formation process has to be reversible. This means the previous shell has to be dissolved into the core before fusion. Upon cooling to room temperature, the formation of a new carbon shell occurs, which was found to consist of 15 to 30 well-graphitized layers.^[183]

In a second approach Hsin et al.^[183] used pre-formed cobalt nanoparticles as template in a toluene $\text{C}_{60}/\text{C}_{70}$ solution in order to be able to predetermine the composition and shape of the metal-core nanoparticles. However, it was observed that the graphitized carbon shells were covered with a layer of amorphous carbon, defects occurred (in particular around the smaller

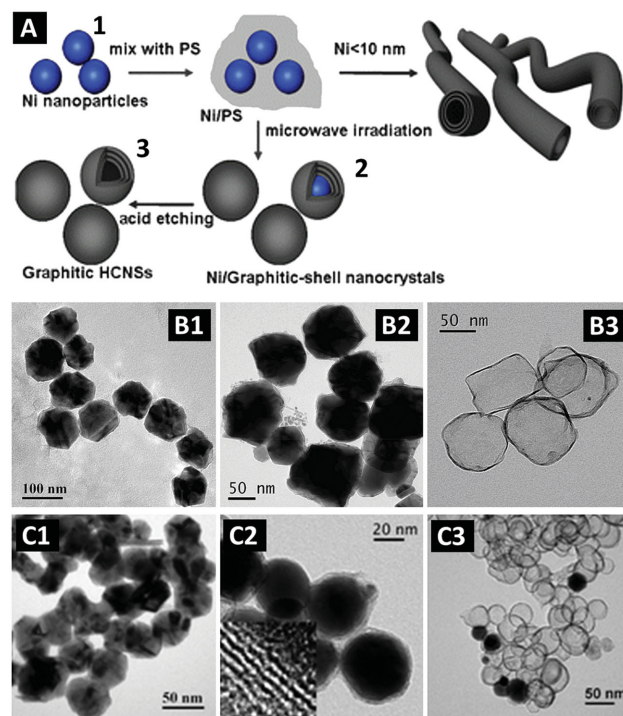


Figure 15. Microwave-induced synthesis of Ni/graphitic-shell nanocrystals and graphitic carbon nanocapsules. A) Schematic illustration of the process. B,C) Dependent on the size of the precursor particles, either capsules with the original shape of the precursor particles (B) or round-shaped capsules (C) are obtained. B1,C1) TEM images of Ni precursor particles of different sizes. B2,C2) Ni/graphitic-shell nanocrystals after the microwave reaction. B3,C3) Products from (B2,C2) after etching.^[182] A–C) Reproduced with permission.^[182] Copyright 2008, The Royal Society of Chemistry.

nanoparticles), and some carbon nanoparticles were fused together. Upon treatment with aqua regia at room temperature, the cobalt cores were leached out, leaving behind hollow graphene shells, in contrast to the shells prepared in the first approach, which were resistant to acid corrosion and protected the core nanoparticles (Figure 14).^[183]

A template approach was also developed by Chen et al.,^[182] who prepared highly graphitized CNCs by utilizing polymer precursors (Figure 15). Polystyrene and nickel nanoparticles were mixed and treated with MW radiation in the solid state under an inert gas atmosphere. After less than one minute of irradiation a graphitic shell with a rather-homogeneous thickness was formed around each Ni nanoparticle (inset in Figure 15C2). By acid treatment, most nickel cores were dissolved, leaving behind hollow graphitic CNCs with inner diameters resembling the size of the original Ni particles (Figure 15B,C). For medium-sized Ni particles, round-shaped CNCs were obtained (Figure 15C), whereas larger particles resulted in CNCs with the original-shape of the Ni particles (Figure 15B). Very small Ni particles (e.g., 8 nm), on the other hand, resulted not only in encapsulated particles, but also in the growth of CNTs. The reason for this might be the very short penetration depth of microwaves into metallic nickel. Therefore, even though the bulk material of larger particles remains relatively cool, the surface temperature rises high enough to

cause the pyrolysis of PS and to produce a graphitic shell with the original shape of the catalyst particle. Smaller particles (e.g., 40 nm NiNP), however, will be heated more homogeneously and will melt completely, thus becoming spherically shaped. The growth of CNTs from the very small NiNP is based on their higher curvature and the need to minimize the energy that is required for the nucleation of the graphene layer. Additionally, a control experiment using conventional furnace heating confirmed the advantages of microwave heating. Conventional heating of the precursor powder to 800 °C resulted in aggregated Ni/carbon structures with irregular sizes and shapes, particles, and CNTs.^[182]

As another type of carbon source, ionic liquids can be applied. Metal nanoparticles coated with an amorphous carbon layer were prepared by heating a metal salt together with an ionic liquid, e.g., copper or nickel nitrate and 1-butyl-3-methylimidazolium tetrafluoroborate (BMIBF₄). The decomposition of the IL results in the formation of carbon, which can act as reducing agent for the metal ions to form pure metal NPs covered with carbon.^[184]

Zheng et al.^[51] developed a completely different approach to prepare hollow carbon nanocapsules by reducing graphite oxide precursors. Upon MW irradiation, high-temperature spots and sparking were induced in a mixture containing GO, dioxane, and some graphite as heating additive. Due to the temperature rise, the annealed GO was reduced and rolled up. As a result, CNCs were formed, having diameters mostly in the range of 300 to 700 nm and wall thicknesses of 5 to 15 nm. The majority of the CNCs was adsorbed on the graphite flakes, but could be dissolved by sonication. In a control experiment without additional graphite flakes in the solution, no sparks and no changes of the GO sheets were observed.^[51]

Guo et al.^[185] developed a microwave-assisted carbonization strategy for the accurate deposition of a thin carbon coating on ZnO nanorods without the formation of agglomerates or byproducts. At first, the ZnO nanorods were functionalized with amino groups. Glucose was grafted on the nanorods and, subsequently, carbonization was induced by heating a dispersion of functionalized nanorods in glycerol in a MW oven. Thereby, the ZnO nanorods remained nicely dispersed and did not change in shape: only their surface became slightly rougher. The coating remarkably reduced the cytotoxicity of the ZnO nanorods when tested on mouse fibroblasts and exhibited excellent photocatalytic activity.^[185]

3.4. Preparation of Porous Carbon Materials

Carbon nanomaterials not only include nanoparticles and fibers, but also nanostructured bulk materials, such as, for example, porous materials. Porous carbon structures are of interest due to their high specific-surface area, which is, among others, desirable for applications in catalysis, sensing, energy storage, or waste-water treatment and solvent recovery. Porous carbons can, for example, be obtained by templating processes or self-assembly of particles.^[186,187] Another possible method of preparation is to heat-treat solid carbon materials to obtain so-called “activated carbons” (AC). Traditionally, activation is carried out by conventional heating mechanisms

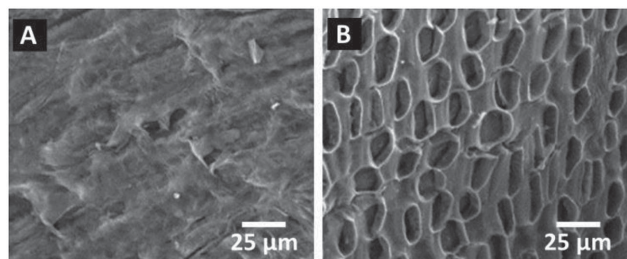


Figure 16. Activated carbon prepared from pineapple char. A,B) SEM images of the char (A) and the product (B) after impregnation with KOH and microwave treatment at 600 W for 6 min.^[192] A,B) Reproduced with permission.^[192] Copyright 2012, Elsevier.

with treatment temperatures of 400 to 950 °C and activation times of 0.5 to 5 h.^[188] In recent years, microwave heating emerged as an alternative activation method. Due to the volumetric heating characteristics of microwave irradiation, the processing time can be decreased significantly, which is furthermore most often accompanied by a decrease of the energy consumption.^[187]

Various carbonaceous materials can be used as precursors. Foo and Hameed intensively studied the preparation of activated, nanoporous carbons from biomass waste, utilizing precursors ranging from empty oil palm fruit bunches,^[189] over sunflower seed shells^[190] to orange peel.^[191] Basically, in the first stage, the carbonaceous material is pyrolyzed under an inert or reducing atmosphere in a furnace. Subsequently, the char is impregnated with an activation agent, e.g., KOH or K₂O₃, followed by a microwave-induced chemical activation under nitrogen for, e.g., 8 min at 600 W.^[190] The activation process is based on the diffusion of the potassium compound into the internal structure of the char matrix. This widens existing pores and creates new ones by oxidation reactions (Figure 16). The optimum amount of activation reagent induces a fast reaction without blocking, burning off, or widening of the pores.^[191] For example, the activation of orange peel resulted in activated carbon with a carbon content of 73%, and the specific-surface area (Brunauer–Emmett–Teller (BET)) rose from 7 m² g^{−1} for the char to 1400 m² g^{−1} for the final activated product. Typical pore sizes were between 2 and 5 nm, with an average of slightly above 2 nm, showing that the majority of the pores fall within the range of mesoporosity.^[191]

In a second category, carbon activation is performed without a preceding carbonization step in a furnace, but rather with a simple one-step microwave treatment of the chemically impregnated precursor.^[193] For example, cotton-stalk^[194] or pine-wood^[195] precursors impregnated with ZnCl₂, peanut shells impregnated with H₃PO₄,^[196] or pineapple peel impregnated with KOH^[192] were heated at 500–700 W for about 6 to 10 min under an inert atmosphere. The obtained specific-surface areas were 794, 1459, 950 and 1006 m² g^{−1}, respectively. Since the precursor materials for activated carbon are poor microwave absorbers, the activating agent plays an important role not only for the chemical reactions, but also as a microwave absorber and heating agent. Without impregnation, no significant heating and, thus, no activation of the precursor could be achieved.^[195]

Alslaibi et al.^[197] compared the preparation of AC from agricultural by-products by conventional heating processes and microwave treatment. Their study entailed optimum conditions in the range of 400 to 800 °C for 1 to 3 h for conventional heating, compared with 350 to 700 W for just 5 to 15 min in the case of microwave-based heating. Furthermore, microwave treatment resulted in higher surface areas than conventional heating for most of the tested precursors (i.e., 1400 m² g^{−1} for bamboo waste). The authors pointed out that, besides the reduction of energy consumption, microwave treatment can reduce the consumption of gases due to the shorter treatment time.^[197] In a pilot-scale upscaling reactor, Li et al.^[198] managed to activate 100 kg of coconut-shell char within one batch, utilizing a self-made reactor with a 60 kW microwave chamber.

Further details about the effects of various microwave heating parameters on the physical and chemical properties of activated carbons prepared from agricultural waste can be found in a recent review.^[199] Besides providing a systematic comparison of literature data, the authors concluded that there are optimum values for the major parameters, i.e., irradiation power, treatment time, impregnation ratio, and agent flow rate. These reaction parameters should neither fall below nor exceed the found optimum limits, since, in both cases, properties such as pore structure or carbon yield were found to deteriorate.^[199]

In a critical review, Zaini et al.^[193] pointed out that the recent developments in the field of MW preparation of AC are based mainly on empiric observations. However, besides the fact that microwave-based activation occurs faster than for conventional processes, the theoretical understanding of the processes has barely improved. More dielectric-property data of carbonaceous precursors, as well as chemical agents and reactant mixtures, dependent both on frequency and temperature, are required to increase understanding, to improve the experimental parameters, and to further proceed toward upscaling the processes. Furthermore, improved *in situ* temperature measurement and, consequently, on-line control of MW-radiation power is needed to prevent thermal runaway, overheating, and damage due to the increase in loss factor of carbon materials with rising temperature.^[193]

Another way of preparing activated carbons is the exfoliation of non-graphitic carbon doped with metallic potassium and tetrahydrofuran (THF). Upon microwave treatment under atmospheric conditions, a microporous compound is formed. This process is based on the exfoliation of graphene layers via the explosion of intercalated materials, and is thus similar to the process used for the preparation of graphene.^[200]

Xerogels are also a suitable precursor for the preparation of porous carbon structures. By applying MW irradiation, the required synthesis times can be significantly shortened, e.g., 5 h were found to be sufficient, compared with several days for conventional heating methods.^[201] Aqueous organic xerogels were synthesized by the polycondensation of resorcinol and formaldehyde. Subsequently, this precursor solution was kept at 85 °C for 3 h for gelation and curing and was afterward irradiated with a maximum power of 700 W, until the synthesis was completed. Since the xerogel itself does not absorb microwaves, the reaction is automatically stopped and the product is cooled down when all the solvent is evaporated. Afterward, the sample was pyrolyzed in a conventional furnace at 800 °C, resulting in samples with

a specific surface area of $600 \text{ m}^2 \text{ g}^{-1}$. The microwave approach was found to not only reduce the synthesis time significantly, but also resulted in products with improved textural development and smaller pores by being more tolerant regarding the pH value of the precursor solution. A further advantage of the microwave approach is that it allows the accurate determination of the point of gelation by observing the amount of energy consumed with time. The evaporation of solvent causes a decrease in temperature. Thus, at the beginning, more power is required to maintain the set temperature. After gelation, the solvent is trapped inside the polymeric structure and is, thus, less easily evaporated. Consequently, a lower power is required to maintain the temperature of the reaction mixture. Therefore, the point of gelation can be identified by the change in slope of the energy consumption.^[201] By mixing the prepared xerogel with a potassium hydroxide activating agent and applying a microwave treatment of 6 to 30 min under a nitrogen atmosphere, the specific-surface area could be increased to around $2200 \text{ m}^2 \text{ g}^{-1}$ by, as the authors call it, a one-step carbonization and activation process. Thereby, the mesoporosity of the xerogel precursor material was partially preserved and, in addition, a large volume of ultramicropores in the range of 0.4 to 0.7 nm was obtained.^[188]

4. Challenges: Reproducibility and Safety

Besides the microwave-assisted exfoliation of graphite, which is a widely established method at least in research, most microwave synthesis procedures have so far only been performed on the lab-scale. Upscaling these microwave methods at a reproducible, high-quality level while keeping the short synthesis times and the efficient heating still remains a challenge.

The two most-critical issues that have to be addressed in microwave-based carbon nanomaterial research are safety and reproducibility. Reproducibility requires a suitable system for comparing applied irradiation power or, even better, the actually absorbed microwave power, and, furthermore, a reliable method for measuring and controlling the reaction temperatures. However, reliable temperature control is, in general, a critical issue for microwave chemistry, even if no local heating or extremely good microwave susceptors are applied.^[202–204] Care has to be taken when designing and interpreting microwave experiments in order to avoid drawing the wrong conclusions regarding reaction temperature, yield, or efficiency, since local temperature hot spots have not been taken into consideration. The measured temperature for microwave-heated reactions is dependent on many factors, including the type of sensor (internal fiber optics or thermocouple versus external infrared sensor), the height where the sensor is mounted, whether stirring is applied, as well as whether and where special microwave susceptor materials are placed. A comprehensive review on how to measure reaction temperature in microwave-heated transformations was recently published by Kappe.^[66]

However, there is hardly any known way of measuring the temperature of microwave reactions, including selective, local heating. Often in carbon research literature, only temperature estimations are stated, which are based on the melting of a component included in the reaction chamber (e.g., container glass or substrate material). This is utilized as the only

indicator for the range of maximum temperatures that were reached at some point during the irradiation.^[90,176] However, this most often implies failure of the system and, thus, a significant safety risk. Temperatures of up to 1500°C have, for example, been reported based on the occurrence of deformed quartz tubes.^[52]

Besides the applied irradiation power and the occurrence of certain temperature and pressure values, the output of microwave reactions is dependent on various other parameters, for example, the used MW oven, which makes comparisons difficult. This is even valid if the same type of MW oven is used, not to mention ovens from other suppliers or even other operating principles. Such influential factors are, for example, the geometry of the reaction vessel, the type of radiation (single-/multimode, direction), and the age and condition of the magnetron.^[64]

Further important aspects are the applied sample mass^[17,55] and the size and material (i.e., absorption properties) of the substrate, as well as the application of any further heating additives.^[17] Since all these aspects can strongly influence the heating of the reactants, and consequently the output of the reaction, they ought to be carefully reported. Reproducibility is most problematic when domestic MW ovens are used without any additional specification. Such ovens exhibit a rather-inhomogeneous field distribution and, furthermore, the irradiation power is adjusted by delivering pulses of a fixed power level. Therefore, the maximum power of these domestic MW ovens significantly influences the outcome of the reaction, which is, however, often disregarded for the careful report of experimental conditions and the interpretation of results.

Generally, the utilization of domestic MW ovens cannot be recommended at all. This is derived not only from the problem of reproducibility, but also more so from the perspective of safety issues. Domestic MW ovens lack of any sensor system that can provide feedback on the progress of the reaction, and do not provide safety precautions, like explosion-proof cavities, the possibility for magnetic stirring, and reliable fast cooling after the reaction.^[3,66]

Even though much pioneering work has been performed with domestic microwave ovens, the challenge of increasing safety and reproducibility nowadays demands the application of dedicated laboratory microwave systems.

Safety represents a very important issue when highly microwave-absorbing materials are applied and strong local heating might occur. Since high (local) temperatures can be reached within just a few seconds, safety precautions have to be taken. If microwave susceptors and heating agents are “out of sight” of the applied temperature probe, local heating and high-temperature reactions are possible, even in laboratory microwave ovens that are equipped with a safety shutdown for the case that a certain temperature limit is exceeded. This involves a chance and a risk at the same time. In literature, occasional warnings are delivered and accidents have been reported. These include explosions due to fast and violently proceeding reactions^[82,120,205] and melting of glass vials due to the occurrence of high temperatures in close vicinity to non-thermally stable vessel materials, when too high a power or irradiation times that are too long are applied.^[90,183] For heating carbon and metal materials, borosilicate glass is generally not recommended since its melting/softening

temperature is too low, and quartz equipment is required. Nevertheless, metal and carbon materials should not be in direct contact with the walls of the reaction vessel, but rather should be covered with a solvent or any other protection.

Different tools and tricks have been reported to overcome these safety issues. The applied precautions range from submerging quartz ampoules in water to decrease the radiation that reaches the sample,^[82] over introducing a quartz-glass inlay within the borosilicate glass to prevent contact between highly absorbing samples and the glass wall of the vial,^[74] up to flattening the corners of highly microwave-absorbing substrates^[74] to avoid hot-spot formation. Additionally, MW irradiation can be applied in short intervals with an intermittent cooling time to prevent overheating and the breaking of the reaction vial,^[117,138,183,206] or active cooling^[176] can be used. By cooling the outside of the reaction vessel during MW irradiation, the reactants can be heated up while the vessel walls remain cold and reaction products are quenched when coming into contact with the glass walls, thereby preventing melting and failure.^[176]

Regardless of the number and kind of safety precautions, new reactions that involve materials with high or unknown microwave-absorption properties should always be tested carefully. This implies the application of just small amounts of material, low powers and short irradiation times, and the use of appropriately sized, thermally stable containers. If possible, containers with pressure-release valves should be applied, and it is recommended that the MW oven be operated in a fume hood in case of gas release, vial failure, or explosion.^[111,120]

5. Conclusions and Outlook

This review of the current literature clearly shows that there is not simply something like “the microwave-assisted method” to prepare carbon nanomaterials. Instead, microwave radiation can be applied in very different ways to synthesize or modify carbon materials, and there are various reasons to do so. Some of the synthesis routes reviewed herein represent, more or less, a copy of a conventional method, but improve the existing methods by accelerating the synthesis. Due to faster heating processes, the overall reaction time can be reduced, hence, decreasing the consumption of energy and inert gas. Furthermore, improved properties can be obtained. For the activation of carbon materials, for example, the synthesis time was reduced by approximately 90% compared to conventional heating^[197] and the synthesis time for xerogels could be reduced from several days to just 5 h.^[201] A similar acceleration of synthesis procedures was observed for the hydrothermal preparation of carbon microspheres,^[178] as well as for the acid-reflux purification of CNTs, where, additionally, the risk for introducing defects into the sidewalls was reduced when microwave heating was applied.^[2]

Other methods, on the contrary, are not simply derivations from conventional processes, but are based on special thermal microwave effects,^[62] meaning the selective and extremely fast heating of metals and graphitic carbon upon irradiation with microwaves. Examples for this category are the selective purification of SWCNTs, based on different chiralities and diameters,^[100,101] or the synthesis of CNTs by selective heating

of catalyst nanoparticles on substrates with little thermal stability.^[45]

A further major advantage of microwave-heated reactions is the simple monitoring of the reaction parameters. Due to automated power adjustment in temperature-controlled synthesis procedures, even the energy consumption during the course of a reaction can be tracked, thereby allowing conclusions on changes in the heatability of the reactants and products; consequently, conclusions on the point of transformation can be drawn.^[201]

There is, however, still plenty of room for improvement. One remaining problem of microwave chemistry is the fact that many processes are not yet sufficiently understood and, consequently, advantages cannot be fully exploited. A closer connection between theoretical studies and practical synthetic research would be beneficial to obtain more-systematic progress. Partially, it seems that a bit of audacity is necessary to move forward in this field of research, with its rapid synthesis processes and extremely fast heating rates. However, safety precautions should hereby not be neglected. This includes, amongst others, that domestic microwave ovens, with all the problems they entail, should be avoided, and instead, a shift toward the application of dedicated laboratory microwave ovens needs to be performed.

Another challenge is the topic of up-scaling. Since microwave reactors cannot be arbitrarily scaled up, new ways, such as, for example, continuous-flow processes, have to be developed for processing of larger batches at reasonable yields and for improving reproducibility. By putting more effort in these directions, a wider range of innovative carbon nanomaterials prepared via microwave heating processes will emerge, potentially fulfilling the requirements for industrial applications.

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- [1] J. Menéndez, E. Menéndez, A. García, J. Parra, J. Pis, *J. Microwave Power Electromagn. Energy* **1999**, 34, 137.
- [2] K. MacKenzie, O. Dunens, A. T. Harris, *Sep. Purif. Technol.* **2009**, 66, 209.
- [3] C. O. Kappe, D. Dallinger, S. S. Murphree, *Practical Microwave Synthesis for Organic Chemists: Strategies, Instruments, and Protocols*, Wiley-VCH, Weinheim, Germany **2009**.
- [4] I. Bilecka, M. Niederberger, *Nanoscale* **2010**, 2, 1358.
- [5] Y. J. Zhu, F. Chen, *Chem. Rev.* **2014**, 114, 6462.
- [6] K. S. Novoselov, V. I. Fal'ko, L. Colombo, P. R. Gellert, M. G. Schwab, K. Kim, *Nature* **2012**, 490, 192.
- [7] M. de Volder, S. Tawfik, R. Baughman, A. Hart, *Science* **2013**, 339, 535.

- [8] S. Iijima, *Nature* **1991**, 354, 56.
- [9] M. Monthieux, V. Kuznetsov, *Carbon* **2006**, 44, 1621.
- [10] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, *Science* **2004**, 306, 666.
- [11] K. I. Rybakov, V. E. Semenov, S. V. Egorov, a. G. Ereemeev, I. V. Plotnikov, Y. V. Bykov, *J. Appl. Phys.* **2006**, 99, 023506.
- [12] J. Cheng, R. Roy, D. Agrawal, *Mater. Res. Innovations* **2002**, 5, 170.
- [13] Z. Peng, J.-Y. Hwang, M. Andrieu, *Appl. Phys. Express* **2012**, 5, 0273041.
- [14] L. Lutsev, N. E. Kazantseva, I. A. Tchmutin, N. Ryvkina, Y. E. Kalinin, A. V. Sitnikoff, *J. Phys.: Condens. Matter* **2003**, 15, 3665.
- [15] J. A. Menéndez, A. Arenillas, B. Fidalgo, Y. Fernández, L. Zubizarreta, E. G. Calvo, J. M. Bermúdez, *Fuel Process. Technol.* **2010**, 91, 1.
- [16] K. R. Paton, A. H. Windle, *Carbon* **2008**, 46, 1935.
- [17] H. Hu, Z. Zhao, Q. Zhou, Y. Gogotsi, J. Qiu, *Carbon* **2012**, 50, 3267.
- [18] X. Zhang, D. O. Hayward, *Inorg. Chim. Acta* **2006**, 359, 3421.
- [19] J. Robinson, S. Kingman, D. Irvine, P. Licence, A. Smith, G. Dimitrakis, D. Obermayer, C. O. Kappe, *Phys. Chem. Chem. Phys.* **2010**, 12, 4750.
- [20] M. Vollmer, *Phys. Educ.* **2004**, 39, 74.
- [21] K. J. Rao, B. Vaidyanathan, M. Ganguli, P. A. Ramakrishnan, *Chem. Mater.* **1999**, 11, 882.
- [22] E. H. Hong, K.-H. Lee, S. H. Oh, C.-G. Park, *Adv. Funct. Mater.* **2003**, 13, 961.
- [23] Linn High Therm GmbH, Microwave Heating, **2006**.
- [24] National Research Council, *Microwave Processing of Materials*, The National Academic Press, Washington, DC, USA, **1994**.
- [25] A "calculator for Skin Effect Depth", 2014, <http://chemandy.com/calculators/skin-effect-calculator.htm>, accessed May 2015.
- [26] M. Gupta, E. W. W. Leong, *Microwaves and Metals*, John Wiley & Sons, Singapore **2008**.
- [27] A. Wadhawan, D. Garrett, J. M. Perez, *Appl. Phys. Lett.* **2003**, 83, 2683.
- [28] T. J. Imholt, C. A. Dyke, B. Hasslacher, J. M. Perez, D. W. Price, J. a. Roberts, J. B. Scott, A. Wadhawan, Z. Ye, J. M. Tour, *Chem. Mater.* **2003**, 15, 3969.
- [29] H.-C. Su, C.-H. Chen, Y.-C. Chen, D.-J. Yao, H. Chen, Y.-C. Chang, T.-R. Yew, *Carbon* **2010**, 48, 805.
- [30] R. Benítez, a. Fuentes, K. Lozano, *J. Mater. Process. Technol.* **2007**, 190, 324.
- [31] V. K. Rangari, M. S. Bhuyan, S. Jeelani, *Composites, Part A* **2011**, 42, 849.
- [32] M. N. Nadagouda, R. S. Varma, *Macromol. Rapid Commun.* **2007**, 28, 842.
- [33] R. Xie, J. Wang, Y. Yang, K. Jiang, Q. Li, S. Fan, *Compos. Sci. Technol.* **2011**, 72, 85.
- [34] J. Tark Han, D. Kim, J. Suk Kim, S. Kwon Seol, S. Yol Jeong, H. Jin Jeong, W. Suk Chang, G.-W. Lee, S. Jung, *Appl. Phys. Lett.* **2012**, 100, 163120.
- [35] C. Gau, H. T. Chen, H. S. Ko, *J. Micromech. Microeng.* **2010**, 20, 065009.
- [36] X. Zhou, L. Shen, L. Li, S. Zhou, T. Huang, C. Hu, W. Pan, X. Jing, J. Sun, L. Gao, Q. Huang, *J. Eur. Ceram. Soc.* **2013**, 33, 2119.
- [37] K. Li, B. Hou, L. Wang, Y. Cui, *Nano Lett.* **2014**, 14, 3002.
- [38] X. L. Liu, D. L. Zhao, *Adv. Mater. Res.* **2006**, 11–12, 559.
- [39] Y. Li, C. Chen, X. Pan, Y. Ni, S. Zhang, J. Huang, D. Chen, Y. Zhang, *Physica B* **2009**, 404, 1343.
- [40] S. M. Al-Hakami, A. B. Khalil, T. Laoui, M. A. Atieh, *Bioinorg. Chem. Appl.* **2013**, 2013, 458943.
- [41] J. E. Atwater, R. R. Wheeler Jr., *Appl. Phys. A: Mater. Sci. Process.* **2004**, 79, 125.
- [42] H. Yixin, L. Chunpeng, *Trans. Nonferrous Met. Soc. China* **1996**, 6, 35.
- [43] A. G. Whittaker, D. M. P. Mingos, *J. Chem. Soc., Dalton Trans.* **1995**, 2073.
- [44] T. Druzhinina, W. Weltjens, S. Hoeppener, U. S. Schubert, *Adv. Funct. Mater.* **2009**, 19, 1287.
- [45] B.-J. Yoon, E. H. Hong, S. E. Jee, D.-M. Yoon, D.-S. Shim, G.-Y. Son, Y. J. Lee, K.-H. Lee, H. S. Kim, C. G. Park, *J. Am. Chem. Soc.* **2005**, 127, 8234.
- [46] Z. Liu, J. Wang, V. Kushvaha, S. Poyraz, H. Tippur, S. Park, M. Kim, Y. Liu, J. Bar, H. Chen, X. Zhang, *Chem. Commun.* **2011**, 47, 9912.
- [47] T. Druzhinina, S. Hoeppener, U. S. Schubert, *Adv. Funct. Mater.* **2009**, 19, 2819.
- [48] Y. Kim, D.-H. Cho, S. Ryu, C. Lee, *Carbon* **2014**, 67, 673.
- [49] T. Lin, Z. Liu, M. Zhou, H. Bi, K. Zhang, F. Huang, D. Wan, Y. Zhong, *ACS Appl. Mater. Interfaces* **2014**, 6, 3088.
- [50] Y. Takagi, L. Tauchi, H.-D. Nguyen-Tran, T. Ohta, M. Shimizu, K. Ohta, *J. Mater. Chem.* **2011**, 21, 14569.
- [51] J. Zheng, H. Liu, B. Wu, Y. Guo, T. Wu, G. Yu, Y. Liu, D. Zhu, *Nano Res.* **2011**, 4, 705.
- [52] P. Hojati-Talemi, M. Asghari-Khiavi, G. Simon, *Mater. Chem. Phys.* **2011**, 127, 156.
- [53] G. Gollavelli, C.-C. Chang, Y.-C. Ling, *ACS Sustainable Chem. Eng.* **2013**, 1, 462.
- [54] H. Nie, M. Cui, T. P. Russell, *Chem. Commun.* **2013**, 49, 5159.
- [55] J. Zheng, H. Liu, B. Wu, Y. Guo, T. Wu, G. Yu, Y. Liu, D. Zhu, *Adv. Mater.* **2011**, 23, 2460.
- [56] J. Zheng, H.-T. Liu, B. Wu, C.-A. Di, Y.-L. Guo, T. Wu, G. Yu, Y.-Q. Liu, D.-B. Zhu, *Sci. Rep.* **2012**, 2, 662.
- [57] S. Liu, J. Wu, Z. Zhou, L. Gao, S. Luo, X. Xu, Z. M. Wang, *J. Mater. Sci. Mater. Electron.* **2012**, 24, 1298.
- [58] A. G. Whittaker, D. M. P. Mingos, *J. Chem. Soc., Dalton Trans.* **2000**, 1521.
- [59] S. V. Egorov, A. G. Ereemeev, I. V. Plotnikov, V. E. Semenov, A. A. Sorokin, N. A. Zharova, Y. V. Bykov, *J. Phys. D.: Appl. Phys.* **2006**, 39, 3036.
- [60] G. Dudley, R. Richert, A. Stiegman, *Chem. Sci.* **2015**, 6, 2144.
- [61] J. Fan, M. De Bruyn, V. L. Budarin, M. J. Gronnow, P. S. Shuttleworth, S. Breeden, D. J. Macquarrie, J. H. Clark, *J. Am. Chem. Soc.* **2013**, 135, 12728.
- [62] C. O. Kappe, B. Pieber, D. Dallinger, *Angew. Chem. Int. Ed.* **2013**, 52, 1088.
- [63] G. B. Dudley, A. E. Stiegman, M. R. Rosana, *Angew. Chem. Int. Ed.* **2013**, 52, 7918.
- [64] C. O. Kappe, *Angew. Chem. Int. Ed.* **2013**, 52, 7924.
- [65] J. Jacob, L. H. L. Chia, F. Y. C. Boey, *J. Mater. Sci.* **1995**, 30, 5321.
- [66] C. O. Kappe, *Chem. Soc. Rev.* **2013**, 42, 4977.
- [67] D. Obermayer, B. Gutmann, C. Oliver Kappe, *Angew. Chem. Int. Ed.* **2009**, 48, 8321.
- [68] J. R. Schmink, N. E. Leadbeater, *Org. Biomol. Chem.* **2009**, 7, 3842.
- [69] Y. Tasei, F. Tanigawa, I. Kawamura, T. Fujito, M. Sato, A. Naito, *Phys. Chem. Chem. Phys.* **2015**, 17, 9082.
- [70] J. Prasek, J. Drbohlavova, J. Chomoucka, J. Hubalek, O. Jasek, V. Adam, R. Kizek, *J. Mater. Chem.* **2011**, 21, 15872.
- [71] M. Kumar, Y. Ando, *J. Nanosci. Nanotechnol.* **2010**, 10, 3739.
- [72] E. H. Hong, K.-H. Lee, S. H. Oh, C.-G. Park, *Adv. Mater.* **2002**, 14, 676.
- [73] D. Fu, X. Zeng, J. Zou, H. Qian, X. Li, X. Xiong, *Mater. Chem. Phys.* **2009**, 118, 501.
- [74] A. M. Schwenke, S. Stumpf, S. Hoeppener, U. S. Schubert, *Adv. Funct. Mater.* **2014**, 24, 1602.
- [75] T. S. Druzhinina, S. Hoeppener, U. S. Schubert, *Nano Lett.* **2010**, 10, 4009.

- [76] B. Fidalgo, Y. Fernández, L. Zubizarreta, A. Arenillas, A. Domínguez, J. J. Pis, J. A. Menéndez, *Appl. Surf. Sci.* **2008**, 254, 3553.
- [77] D. Fu, Q. Ma, X. Zeng, J. Chen, W. Zhang, D. Li, *Phys. E: Low-Dimensional Syst. Nanostructures* **2013**, 54, 185.
- [78] S.-H. Bae, K. Karthikeyan, Y.-S. Lee, I.-K. Oh, *Carbon* **2013**, 64, 527.
- [79] S.-H. Lee, V. Sridhar, J.-H. Jung, K. Karthikeyan, Y.-S. Lee, R. Mukherjee, N. Koratkar, I.-K. Oh, *ACS Nano* **2013**, 7, 4242.
- [80] V. Sridhar, H. Kim, J. Jung, C. Lee, S. Park, I. Oh, *ACS Nano* **2012**, 6, 10562.
- [81] U. O. Méndez, O. V. Kharissova, M. Rodríguez, *Rev. Adv. Mater. Sci.* **2003**, 5, 398.
- [82] J. Vivas-Castro, G. Rueda-Morales, G. Ortega-Cervantez, J. Ortiz-López, L. Moreno-Ruiz, M. Ortega-Avilés, in *Carbon Nanotubes – Synthesis, Characterization, Applications*, (Ed.: S. Yellampalli), InTech, Rijeka, Croatia **2011**, pp. 47–60.
- [83] D.-M. Yoon, B.-J. Yoon, K.-H. Lee, H. S. Kim, C. G. Park, *Carbon* **2006**, 44, 1339.
- [84] E. O. Pentsak, E. G. Gordeev, V. P. Ananikov, *ACS Catal.* **2014**, 4, 3806.
- [85] Z. Liu, L. Zhang, S. Poyraz, J. Smith, V. Kushvaha, H. Tippur, X. Zhang, *RSC Adv.* **2014**, 4, 9308.
- [86] H. Hu, Z. Zhao, Y. Gogotsi, J. Qiu, *Environ. Sci. Technol. Lett.* **2014**, 1, 214.
- [87] R. Bajpai, H. D. Wagner, *Carbon* **2015**, 82, 327.
- [88] FAQ – ACP Inc. – Accelerated Cooking Products, <http://en.acpsolutions.com/faq/>, accessed: May 2015.
- [89] X. Zhang, Z. Liu, *Nanoscale* **2012**, 4, 707.
- [90] X. Zhang, S. K. Manohar, *Chem. Commun.* **2006**, 2477.
- [91] A. V. Melechko, V. I. Merkulov, T. E. McKnight, M. A. Guillorn, K. L. Klein, D. H. Lowndes, M. L. Simpson, *J. Appl. Phys.* **2005**, 97, 0413011.
- [92] M. T. Martínez, M. A. Callejas, A. M. Benito, W. K. Maser, M. Cochet, J. M. Andrés, J. Schreiber, O. Chauvet, J. L. G. Fierro, *Chem. Commun.* **2002**, 1000.
- [93] A. R. Harutyunyan, B. K. Pradhan, J. Chang, G. Chen, P. C. Eklund, *J. Phys. Chem. B* **2002**, 106, 8671.
- [94] E. Vázquez, V. Georgakilas, M. Prato, *Chem. Commun.* **2002**, 2308.
- [95] K. Chajara, C.-H. Andersson, J. Lu, E. Widenkvist, H. Grennberg, *New J. Chem.* **2010**, 34, 2275.
- [96] W. Lin, K. Moon, S. Zhang, Y. Ding, J. Shang, M. Chen, C. Wong, *ACS Nano* **2010**, 4, 17161722.
- [97] L. Zhu, Y. Yin, C.-F. Wang, S. Chen, *J. Mater. Chem. C* **2013**, 1, 4925.
- [98] P. Carrott, J. Nabais, M. Ribeiro-Carrot, J. Menéndez, *Microporous Mesoporous Mater.* **2001**, 47, 243.
- [99] J. W. Song, H. W. Seo, J. K. Park, J. E. Kim, D. G. Choi, C. S. Han, *Curr. Appl. Phys.* **2008**, 8, 725.
- [100] H. Qiu, Y. Maeda, T. Akasaka, J. Yang, *Sep. Purif. Technol.* **2012**, 96, 182.
- [101] H. Qiu, Y. Maeda, T. Akasaka, *J. Am. Chem. Soc.* **2009**, 131, 16529.
- [102] S. P. Economopoulos, N. Karousis, G. Rotas, G. Pagona, N. Tagmatarchis, *Curr. Org. Chem.* **2011**, 15, 1121.
- [103] I. Janowska, O. Ersen, T. Jacob, P. Vennégues, D. Bégin, M.-J. Ledoux, C. Pham-Huu, *Appl. Catal. A* **2009**, 371, 22.
- [104] S. Vadahanambi, J.-H. Jung, R. Kumar, H.-J. Kim, I.-K. Oh, *Carbon* **2013**, 53, 391.
- [105] C.-L. Sun, C.-T. Chang, H.-H. Lee, J. Zhou, J. Wang, T.-K. Sham, W.-F. Pong, *ACS Nano* **2011**, 5, 7788.
- [106] S. Chen, J.-W. Liu, M.-L. Chen, X.-W. Chen, J.-H. Wang, *Chem. Commun.* **2012**, 48, 7637.
- [107] D. R. Dreyer, R. S. Ruoff, C. W. Bielawski, *Angew. Chem. Int. Ed.* **2010**, 49, 9336.
- [108] W. J. Hummers, R. Offeman, *J. Am. Chem. Soc.* **1958**, 80, 1339.
- [109] Z. Li, Y. Yao, Z. Lin, K.-S. Moon, W. Lin, C. Wong, *J. Mater. Chem.* **2010**, 20, 4781.
- [110] W. Luo, B. Wang, X. Wang, W. F. Stickle, X. Ji, *Chem. Commun.* **2013**, 49, 10676.
- [111] Y. Zhu, S. Murali, M. D. Stoller, A. Velamakanni, R. D. Piner, R. S. Ruoff, *Carbon* **2010**, 48, 2118.
- [112] Y. Zhu, S. Murali, M. D. Stoller, K. J. Ganesh, W. Cai, P. J. Ferreira, A. Pirkle, R. M. Wallace, K. A. Cychosz, M. Thommes, D. Su, E. A. Stach, R. S. Ruoff, *Science* **2011**, 332, 1537.
- [113] N. Setoyama, T. Suzuki, K. Kaneko, *Carbon* **1998**, 36, 1459.
- [114] Y. M. Shulga, S. A. Baskakov, E. I. Knerelman, G. I. Davidova, E. R. Badamshina, N. Y. Shulga, E. A. Skryleva, A. L. Agapov, D. N. Voylov, A. P. Sokolov, V. M. Martynenko, *RSC Adv.* **2014**, 4, 587.
- [115] E. Vázquez, F. Giacalone, M. Prato, *Chem. Soc. Rev.* **2013**, 43, 58.
- [116] S.-H. Park, S.-M. Bak, K.-H. Kim, J.-P. Jegal, S.-I. Lee, J. Lee, K.-B. Kim, *J. Mater. Chem.* **2011**, 21, 680.
- [117] W. Chen, L. Yan, P. R. Bangal, *Carbon* **2010**, 48, 1146.
- [118] T. Lu, L. Pan, C. Nie, Z. Zhao, Z. Sun, *Phys. Status Solidi* **2011**, 208, 2325.
- [119] Z. Luo, Y. Lu, L. A. Somers, A. T. C. Johnson, *J. Am. Chem. Soc.* **2009**, 131, 898.
- [120] V. Sridhar, J.-H. Jeon, I.-K. Oh, *Carbon* **2010**, 48, 2953.
- [121] X. Liu, J. Liu, D. Zhan, J. Yan, J. Wang, D. Chao, L. Lai, M. Chen, J. Yin, Z. Shen, *RSC Adv.* **2013**, 3, 11601.
- [122] V. Sridhar, J.-H. Jeon, I.-K. Oh, *Carbon* **2011**, 49, 222.
- [123] Z. Wang, J. Liu, W. Wang, H. Chen, Z. Liu, Q. Yu, H. Zeng, L. Sun, *Chem. Commun.* **2013**, 49, 10835.
- [124] I. Janowska, K. Chizari, O. Ersen, S. Zafeiratos, D. Soubane, V. Da Costa, V. Speisser, C. Boeglin, M. Houllé, D. Bégin, D. Plee, M.-J. Ledoux, C. Pham-Huu, *Nano Res.* **2010**, 3, 126.
- [125] W. Fu, J. Kiggans, S. H. Overbury, V. Schwartz, C. Liang, *Chem. Commun.* **2011**, 47, 5265.
- [126] K. Gopalakrishnan, A. Govindaraj, C. N. R. Rao, *J. Mater. Chem. A* **2013**, 1, 7563.
- [127] Y. Xin, J. Liu, X. Jie, W. Liu, F. Liu, Y. Yin, J. Gu, Z. Zou, *Electrochim. Acta* **2012**, 60, 354.
- [128] A. Y. S. Eng, Z. Sofer, P. Simek, J. Kosina, M. Pumera, *Chemistry* **2013**, 19, 15583.
- [129] I. T. Kim, M. W. Shin, *Mater. Lett.* **2013**, 108, 33.
- [130] C.-L. Liu, K.-H. Chang, C.-C. Hu, W.-C. Wen, *J. Power Sources* **2012**, 217, 184.
- [131] B. G. Choi, H. Park, M. H. Yang, Y. M. Jung, S. Y. Lee, W. H. Hong, T. J. Park, *Nanoscale* **2010**, 2, 2692.
- [132] T. Kim, H. Chang Kang, T. Thanh Tung, J. Don Lee, H. Kim, W. Seok Yang, H. Gyu Yoon, K. S. Suh, *RSC Adv.* **2012**, 2, 8808.
- [133] H. M. A. Hassan, V. Abdelsayed, A. E. R. S. Khder, K. M. Abouzaid, J. Turner, M. S. El-Shall, S. I. Al-Resayes, A. A. El-Azhary, *J. Mater. Chem.* **2009**, 19, 3832.
- [134] A. F. Zedan, S. Sappal, S. Moussa, M. S. El-Shall, *J. Phys. Chem. C* **2010**, 114, 19920.
- [135] S. Sharma, A. Ganguly, P. Papakonstantinou, X. Miao, M. Li, J. L. Hutchison, M. Delichatsios, S. Ukleja, *J. Phys. Chem. C* **2010**, 114, 19459.
- [136] F. Zhang, F. Wang, Y. Zhang, *Int. J. Electrochem. Sci.* **2012**, 7, 1968.
- [137] Y. Han, Z. Luo, L. Yuwen, J. Tian, X. Zhu, L. Wang, *Appl. Surf. Sci.* **2013**, 266, 188.
- [138] A. M. Shanmugaraj, S. H. Ryu, *Electrochim. Acta* **2012**, 74, 207.
- [139] L. Li, Z. Guo, A. Du, H. Liu, *J. Mater. Chem.* **2012**, 22, 3600.
- [140] T. Chen, L. Pan, X. Liu, K. Yu, Z. Sun, *RSC Adv.* **2012**, 2, 11719.
- [141] C. Zhong, J. Wang, Z. Chen, H. Liu, *J. Phys. Chem. C* **2011**, 25115.
- [142] X. Pu, D. Zhang, Y. Gao, X. Shao, G. Ding, S. Li, S. Zhao, *J. Alloys Compd.* **2013**, 551, 382.

- [143] Z. Huang, H. Zhang, Y. Chen, W. Wang, Y. Chen, Y. Zhong, *Electrochim. Acta* **2013**, *108*, 421.
- [144] V. Sridhar, I. Lee, H.-S. Yoon, H.-H. Chun, H. Park, *Carbon* **2013**, *61*, 633.
- [145] T. Chen, L. Pan, K. Yu, Z. Sun, *Solid State Ionics* **2012**, *229*, 9.
- [146] C. Zhong, J.-Z. Wang, D. Wexler, H.-K. Liu, *Carbon* **2014**, *66*, 637.
- [147] L.-Y. Lin, M.-H. Yeh, J.-T. Tsai, Y.-H. Huang, C.-L. Sun, K.-C. Ho, *J. Mater. Chem. A* **2013**, *1*, 11237.
- [148] Z. Xu, Z. Li, C. M. B. Holt, X. Tan, H. Wang, B. S. Amirkhiz, T. Stephenson, D. Mitlin, *J. Phys. Chem. Lett.* **2012**, *3*, 2928.
- [149] B. Zeng, X. Chen, X. Ning, C. Chen, W. Deng, Q. Huang, W. Zhong, *Appl. Surf. Sci.* **2013**, *276*, 482.
- [150] A. Dato, M. Frenklach, *New J. Phys.* **2010**, *12*, 125013.
- [151] M. Tian, S. Batty, C. Shang, *Carbon* **2013**, *51*, 243.
- [152] P. Hojati-Talemi, G. P. Simon, *Carbon* **2010**, *48*, 3993.
- [153] Z. Xu, H. Li, W. Li, G. Cao, Q. Zhang, K. Li, Q. Fu, J. Wang, *Chem. Commun.* **2011**, *47*, 1166.
- [154] X. Xu, R. Ray, Y. Gu, H. J. Ploehn, L. Gearheart, K. Raker, W. A. Scrivens, *J. Am. Chem. Soc.* **2004**, *126*, 12736.
- [155] S.-T. Yang, X. Wang, H. Wang, F. Lu, P. G. Luo, L. Cao, M. J. Mezziani, J.-H. Liu, Y. Liu, M. Chen, Y. Huang, Y.-P. Sun, *J. Phys. Chem. C* **2009**, *113*, 18110.
- [156] H. Li, Z. Kang, Y. Liu, S.-T. Lee, *J. Mater. Chem.* **2012**, *22*, 24230.
- [157] W. Wei, C. Xu, L. Wu, J. Wang, J. Ren, X. Qu, *Sci. Rep.* **2014**, *4*, 3564.
- [158] L.-L. Li, J. Ji, R. Fei, C.-Z. Wang, Q. Lu, J.-R. Zhang, L.-P. Jiang, J.-J. Zhu, *Adv. Funct. Mater.* **2012**, *22*, 2971.
- [159] Q. Wang, H. Zheng, Y. Long, L. Zhang, M. Gao, W. Bai, *Carbon* **2011**, *49*, 3134.
- [160] Y. Shin, J. Lee, J. Yang, J. Park, K. Lee, S. Kim, Y. Park, H. Lee, *Small* **2014**, *10*, 866.
- [161] S. Chen, X. Hai, C. Xia, X.-W. Chen, J.-H. Wang, *Chemistry* **2013**, *19*, 15918.
- [162] H. Zhu, X. Wang, Y. Li, Z. Wang, F. Yang, X. Yang, *Chem. Commun.* **2009**, 5118.
- [163] X. Wang, K. Qu, B. Xu, J. Ren, X. Qu, *J. Mater. Chem.* **2011**, *21*, 2445.
- [164] C. Liu, P. Zhang, F. Tian, W. Li, F. Li, W. Liu, *J. Mater. Chem.* **2011**, *21*, 13163.
- [165] L. Tang, R. Ji, X. Cao, J. Lin, H. Jiang, X. Li, K. S. Teng, C. M. Luk, S. Zeng, J. Hao, S. P. Lau, *ACS Nano* **2012**, *6*, 5102.
- [166] S. Chandra, S. H. Pathan, S. Mitra, B. H. Modha, A. Goswami, P. Pramanik, *RSC Adv.* **2012**, *2*, 3602.
- [167] Y. Zhai, Z. Zhu, C. Zhu, J. Ren, E. Wang, S. Dong, *J. Mater. Chem. B* **2014**, *2*, 6995.
- [168] S. Mitra, S. Chandra, T. Kundu, R. Banerjee, P. Pramanik, A. Goswami, *RSC Adv.* **2012**, *2*, 12129.
- [169] X. Qin, W. Lu, A. M. Asiri, A. O. Al-Youbi, X. Sun, *Sens. Actuators, B* **2013**, *184*, 156.
- [170] S. Liu, L. Wang, J. Tian, J. Zhai, Y. Luo, W. Lu, X. Sun, *RSC Adv.* **2011**, *1*, 951.
- [171] J. Jiang, Y. He, S. Li, H. Cui, *Chem. Commun.* **2012**, *48*, 9634.
- [172] S. Barman, M. Sadhukhan, *J. Mater. Chem.* **2012**, *22*, 21832.
- [173] Y. Liu, N. Xiao, N. Gong, H. Wang, X. Shi, W. Gu, L. Ye, *Carbon* **2014**, *68*, 258.
- [174] S. Liu, J. Tian, L. Wang, Y. Luo, X. Sun, *RSC Adv.* **2012**, *2*, 411.
- [175] J. Martínez-Reyes, L. G. Díaz Barriga-Arceo, L. Rendón-Vazquez, R. Martínez-Guerrero, N. Romero-Parada, E. Palacios-González, V. Garibay-Febles, J. Ortiz-López, *ISRN Nanomater.* **2013**, *2013*, 524548.
- [176] R. Hetzel, T. Manning, D. Lovingood, G. Strouse, D. Phillips, *Fullerenes, Nanotubes, Carbon Nanostruct.* **2012**, *20*, 99.
- [177] A. T. Harris, S. Deshpande, X. Kefeng, *Mater. Lett.* **2009**, *63*, 1390.
- [178] A. Jung, S. Han, T. Kim, W. J. Cho, K.-H. Lee, *Carbon* **2013**, *60*, 307.
- [179] S. Zhao, D. C. Cooper, H. Xu, P. Zhu, J. W. Suggs, *Appl. Surf. Sci.* **2013**, *264*, 242.
- [180] D. Krishnan, K. Raidongia, J. Shao, J. Huang, *ACS Nano* **2014**, *8*, 449.
- [181] K. C. Hwang, *J. Phys. D: Appl. Phys.* **2010**, *43*, 374001.
- [182] K. Chen, C. Wang, D. Ma, W. Huang, X. Bao, *Chem. Commun.* **2008**, 2765.
- [183] Y. Hsin, C. Lin, Y. Liang, K. C. Hwang, J. Horng, J. A. Ho, C. Lin, J. R. Hwu, *Adv. Funct. Mater.* **2008**, *18*, 2048.
- [184] D. S. Jacob, I. Genish, L. Klein, A. Gedanken, *J. Phys. Chem. B* **2006**, *110*, 17711.
- [185] Y. Guo, H. Wang, C. He, L. Qiu, X. Cao, *Langmuir* **2009**, *25*, 4678.
- [186] J. Lee, J. Kim, T. Hyeon, *Adv. Mater.* **2006**, *18*, 2073.
- [187] F. K. Yuen, B. H. Hameed, *Adv. Colloid Interface Sci.* **2009**, *149*, 19.
- [188] E. G. Calvo, N. Ferrera-Lorenzo, J. A. Menéndez, A. Arenillas, *Microporous Mesoporous Mater.* **2013**, *168*, 206.
- [189] K. Y. Foo, B. H. Hameed, *Desalination* **2011**, *275*, 302.
- [190] K. Y. Foo, B. H. Hameed, *Bioresour. Technol.* **2011**, *102*, 9794.
- [191] K. Y. Foo, B. H. Hameed, *Bioresour. Technol.* **2012**, *104*, 679.
- [192] K. Y. Foo, B. H. Hameed, *Microporous Mesoporous Mater.* **2012**, *148*, 191.
- [193] M. A. A. Zaini, M. J. Kamaruddin, *J. Anal. Appl. Pyrolysis* **2013**, *101*, 238.
- [194] H. Deng, L. Yang, G. Tao, J. Dai, *J. Hazard. Mater.* **2009**, *166*, 1514.
- [195] T. Wang, S. Tan, C. Liang, *Carbon* **2009**, *47*, 1880.
- [196] Z.-Y. Zhong, Q. Yang, X.-M. Li, K. Luo, Y. Liu, G.-M. Zeng, *Ind. Crops Prod.* **2012**, *37*, 178.
- [197] T. M. Alslaiibi, I. Abustan, M. A. Ahmad, A. A. Foul, *J. Chem. Technol. Biotechnol.* **2013**, *88*, 1183.
- [198] W. Li, J. Peng, L. Zhang, K. Yang, H. Xia, S. Zhang, S. Guo, *Waste Manage. (Oxford, U.K.)* **2009**, *29*, 756.
- [199] R. Hoseinzadeh Hesas, M. A. W. Wan Daud, J. N. Sahu, A. Arami-Niya, *J. Anal. Appl. Pyrolysis* **2013**, *100*, 1.
- [200] S.-E. Chun, J. F. Whitacre, *J. Power Sources* **2013**, *240*, 306.
- [201] E. G. Calvo, E. J. Juárez-Pérez, J. Menéndez, A. Arenillas, *J. Colloid Interface Sci.* **2011**, *357*, 541.
- [202] R. Hoogenboom, T. F. A. Wilms, T. Erdmenger, U. S. Schubert, *Aust. J. Chem.* **2009**, *62*, 236.
- [203] T. Erdmenger, C. R. Becer, R. Hoogenboom, U. S. Schubert, *Aust. Dent. J.* **2009**, *62*, 58.
- [204] R. Hoogenboom, M. A. M. Leenen, F. Wiesbrock, U. S. Schubert, *Macromol. Rapid Commun.* **2005**, *26*, 1773.
- [205] A. M. Shanmugaraj, W. S. Choi, C. W. Lee, S. H. Ryu, *J. Power Sources* **2011**, *196*, 10249.
- [206] P. Hojati-Talemi, R. Cervini, G. P. Simon, *J. Nanoparticle Res.* **2009**, *12*, 393.