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Quantitative crystallographic analysis of individual carbon nanofibers using high resolution transmission electron microscopy and electron diffraction

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ABSTRACT

High resolution transmission electron microscopy (HRTEM) and electron diffraction allow for a thorough crystallographic characterization of the herringbone structure of carbon nanofibers (CNF). A newly developed method for an extended quantitative structural evaluation of single carbon nanofibers is applied. The method is based on quantitative analysis of radial and azimuthal profiles extracted from selected area electron diffraction (SAED) patterns, nano beam electron diffraction (NBED) patterns or power spectra obtained by Fourier transformation of HRTEM images. Precise quantification of structural parameters, in particular cone apex angle, interlayer spacing and undulation of graphene layers is carried out. For the first time a profound interpretation of CNF diffraction patterns is given, proving the rotational disorder of the turbostratic structure and suggesting a random rotation between successive graphene cones. A series of crystallographic analyses along the axis of a single CNF reveal a continuous increase of the interlayer spacing during CNF growth. Additionally, the different techniques HRTEM, SAED, and NBED are evaluated in terms of attainable structural information, precision and applicability to different diameters of CNFs.

1. Introduction

Compared to carbon nanotubes (CNT), carbon nanofibers (CNF) are subject to lower manufacturing costs while maintaining large aspect ratio, high specific surface, exceptional mechanical strength, electrical conductivity, and chemical and thermal stability [1–3]. Thus, CNFs are promising candidates for industrial bulk production for a wide range of practical applications such as filler material to reinforce polymers [4,5], as catalyst support [6,7] or as anode material for lithium ion batteries [8,9]. Based on their high specific surface and the possibility of functionalization they are attributed a promising potential for catalysts [10], sensors [11,12] and membranes [13]. To further optimize CNF performance within these various applications, a more profound understanding of growth conditions and the resulting fiber structure is indispensable, but requesting a more detailed analysis of the fiber structure. Transmission electron microscopy (TEM) is the standard method to characterize the structure of CNTs and CNFs at the individual level, in particular to visualize the stacked graphene layers by high-resolution transmission electron microscopy (HRTEM) [14–16]. Besides HRTEM, also electron diffraction in the TEM in the form of selected area electron diffraction (SAED) and nano beam electron diffraction (NBED) provide fundamental information about the structure of single fibers [17–19]. Compared to numerous works in the literature about quantitative determination of various CNT structures there are only a few publications that go beyond a qualitative structure characterization of CNFs by means of HRTEM [15,20,21] and electron diffraction [18,22,23]. A reason might be the more complex structure of CNFs as compared to CNTs, yielding a much wider range of nanostructural variability. Up to present, the crystallographic interpretation of the CNF structures in the literature is limited to the discussion of orientation and shape of the (0 0 2) reflections in TEM diffraction patterns. The appearance of higher order reflections is not interpreted, and consequently specific structural features of CNFs like their turbostratic character are not yet characterized in detail. Although the shape of the reflections

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provides valuable and quantitative information about the CNF structure, it has so far not been exploited. In this light, a specific method for the evaluation of diffraction patterns of single CNFs will provide the opportunity for a detailed and quantitative structural characterization of CNFs.

In the present study, an extended investigation on the structure of CNFs by HRTEM and electron diffraction has been performed. In particular, a newly developed method for quantitative structural evaluation of single CNFs is applied. The method is based on analyzing reciprocal space images of single CNFs obtained from SAED and NBED patterns as well as power spectra computed by Fourier transformation of HRTEM images. The performance and reliability of the method is demonstrated by detailed characterization of the herringbone structure of CNFs. A series of crystallographic analyses is performed along the axis of a single CNF enabling new insights into structural variations during CNF growth and their relationship to processing parameters. Furthermore, the application of the different techniques HRTEM, SAED, and NBED is discussed in terms of attainable structural information and precision.

2. Experimental

2.1. CNF synthesis

The CNFs examined in this study were grown on the inner surface of porous ceramic alumina or zirconia substrates in a single channel geometry by chemical vapor deposition. Methane was used as carbon source and palladium as catalyst at a synthesis temperature of 750 °C. A more detailed description of the CNF synthesis is given in Ref. [24].

2.2. TEM characterization

TEM specimens were prepared by scraping the CNFs from the substrate and dispersing them in ethanol in an ultrasonic bath. A drop of the suspension was placed onto a holey carbon copper grid. The structural features of CNFs were studied by HRTEM, SAED, and NBED in a JEOL JEM 3010HT operating at 300 kV that is equipped with a LaB_6 filament and a 1k x 1k GATAN multi scan CCD-camera. The HRTEM studies were performed at a magnification of 300 k. SAED was conducted with field limiting apertures of 5 or 10 μm in diameter, resulting in an analyzed circular area of a diameter of about 100 nm and 250 nm, respectively. NBED is a type of convergent beam electron diffraction generating diffraction patterns from areas down to 1 nm in diameter [19,25,26]. A beam convergence angle about 1 mrad was applied here, resulting in a beam diameter (full width at half intensity) on the specimen of 50 nm. All specimens appeared to be stable during high resolution imaging and diffraction analysis. HRTEM images and diffraction patterns were analyzed within the software package Digital Micrograph (Gatan) using DiffTools [27], PASAD plug-in [28], and in-house written scripts.

3. TEM on single CNFs and principles of their crystallographic evaluation

A representative HRTEM image, SAED and NBED patterns of a single herringbone CNF are displayed in Fig. 1. In the HRTEM image, individual graphene layers are represented by lattice fringes visualizing the fiber structure on a nearly the atomic level (Fig. 1a). However, quantitative interpretation based on a direct evaluation of such HRTEM images requires extended and complex image processing [21,29]. The corresponding diffraction patterns obtained by SAED (Fig. 1c) and NBED (Fig. 1d), and the Fourier transform power spectrum of the HRTEM image (Fig. 1b) represent the structural information of the single fiber in reciprocal space. The power spectrum is the square of the amplitude of a Fourier transform [30].

Considering that the power spectrum of a HRTEM image is the numerical equivalent to the diffraction pattern [31], both the power spectrum and the diffraction pattern can be interpreted and evaluated in the same manner. Hereafter, the term diffraction pattern also includes the power spectrum, if not specified otherwise. It is emphasized that lattice fringes in the HRTEM image and electron diffraction only occur, if the lattice planes in the graphitic structure, i.e. the graphene layers, are approximately parallel to the incident electron beam. Thus, the HRTEM image along with the diffraction pattern only represents a 2-dimensional projection or section of the 3-dimensional fiber structure in both the real and reciprocal space [17,18]. However, the 2-dimensional diffraction patterns provide structural parameters concerning orientation, spacing, and curvature of the graphene layers, allowing a detailed crystallographic interpretation of a single CNF [18,23]. Each Bragg spot in the pattern represents a set of lattice planes in the graphitic structure with a specific interlayer spacing and a specific orientation. The distance of each spot to the center corresponds to the reciprocal interlayer spacing d_{hkl}, its direction is perpendicular to the corresponding layers [32] (Fig. 2a). Crucial for a detailed crystallographic evaluation of the pattern is the clear allocation of the fiber axis orientation relative to the diffraction pattern. Since the power spectrum is generated by a Fourier transform of the HRTEM image, the fiber axis directly corresponds to the fiber orientation displayed in the HRTEM image. Due to the helical path of the electrons through the magnetic lenses of the TEM, the diffraction pattern shows a certain rotation against the corresponding image of the fiber. The rotation angle can be determined by rotation calibration as described in Ref. [33]. For modern TEMs this rotation is negligible and the fiber orientation can be deduced from the bright field images. Another way to determine the fiber orientation is by defocusing the diffraction pattern as shown by the insets in Fig. 1c and d. The transmitted beam becomes a disc that displays a distorted image of the probed area [33,34]. The defocused NBED pattern exhibits a distinct discrepancy of fiber orientation that is, according to a different ray path, resulting in a focus sensitive pattern orientation compared to SAED [33]. Nevertheless the defocused NBED pattern helps to estimate the fiber orientation, since the diffraction pattern of a CNF displays a certain symmetry. Additionally, the streaking of the central spot in the power spectrum allows a direct determination of fiber orientation without comparison to the HRTEM image (inset Fig. 1b).

All the diffraction patterns consist of pairs of arched reflections located on concentric rings. These arched reflections show mirror symmetry along the fiber direction, indicating the axis symmetric fiber structure. According to Friedel's law, each reflection possesses an opposite anti-reflection forming a pair [33], and thus also the pattern is centrosymmetric. The reflections closest to the center correspond to the (0 0 2) lattice planes of graphite according to the stacking of graphene layers in the fiber structure. Owing to the conical layer structure in herringbone CNFs, the (0 0 2) reflections are inclined to the fiber axis (Fig. 1c). The schematic representations in Fig. 2 summarize the quantitative evaluation of diffraction patterns of a single CNF and how its real space structure and the reciprocal space representation are connected. Each set of parallel lattice planes is represented by a pair of anti-parallel reflections with diffraction vectors perpendicular to the planes (red and green Fig. 2a, respectively). According to this orthogonal relationship, the apex angle of the cones, 2θ, spanned by the (0 0 2) diffraction vectors is rotated by 90° to the fiber axis (Fig. 2a). It should be emphasized that the fiber axes of most CNFs are not exactly