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A new purification method for single-wall carbon nanotubes (SWNTs)

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Abstract. A new purification procedure is introduced, which uses the advantages of column chromatography and vacuum filtration. Potassium polyacrylate is used as stationary phase. This method is based on the idea that the size of the existing cavities in the polymer increases during a swelling process in distilled water. The cavities are big enough to entrap the nanoparticles, but allow for a free movement of nanotubes and bundles.

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Since their discovery in 1991 [1] the interest in carbon nanotubes has been steadily increasing. Various applications, such as electronic devices [2, 3], tools in nanotechnology [4], and hydrogen storage [5] have been proposed. In the optimized arc-discharge process for single-wall nanotubes (SWNTs) daily production reaches 2–3 g of raw material, containing approximately 70% SWNTs. [6, 7]. The laser ablation method [8] yields up to 20 g of raw material per day, containing up to 50% SWNTs [9].

However, these methods yield an inhomogeneous raw product, consisting of tubes which vary in diameter and length. In addition to that, carbon species such as fullerenes, polyhedra and other graphitized carbon structures, as well as amorphous carbon, are found. All these carbon allotropes are closely entangled. In the case of SWNTs, they build up ropes consisting of up to 100 tubes. In addition to that, impurities of metal clusters can stick on the tips of the ropes and interconnect the SWNTs. These clusters originate from the catalyst (usually Ni, Fe, Co and Y), required for the formation of the single-layer structures. Therefore, in order to explore the enormous potential of technical applications, effective purification methods are becoming increasingly important.

We describe here a new purification procedure which uses the advantages of column chromatography and vacuum filtration. Potassium polyacrylate was used as a stationary phase. Due to its swelling capacity as a result of absorbing large amounts of water and forming gels, it has been used for many technical applications as a "superabsorber". The absorbed water cannot be released at room temperature even under pressure [10]. The basic idea of this method is that the size of the existing cavities in the polymer increases during the swelling process. These cavities are supposed to be big enough to encapsulate nanoparticles but to allow the nanotubes and bundles to move.

This new purification procedure allows for the separation of SWNTs from carbon nanospheres, metal nanoparticles, polyaromatic carbons and fullerenes.

The process involves three steps: First, raw material is treated in 65% nitric acid for 3 h under reflux (typically 150 ml of acid per 100 mg of raw material). During this

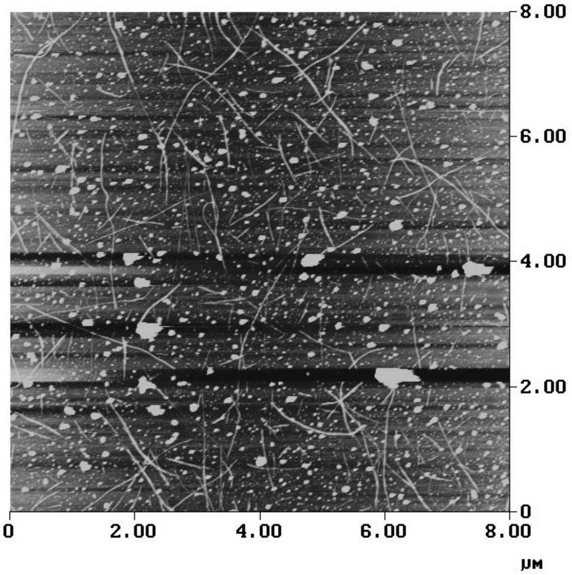

Fig. 1. AFM image of SWNTs after nitric acid and ultrasonic treatment. This image clearly shows a large amount of impurities and single SWNT bundles

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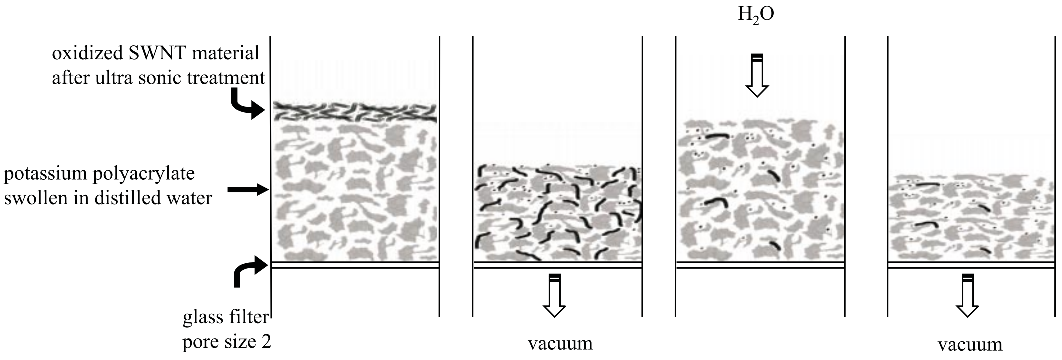

Fig. 2. Schematic representation of the chromatographic purification setup

time a weight loss of about 20% occurs. After the black solution is centrifuged, a black sediment remains at the bottom of the centrifuge jar. The clear brownish-yellow supernatant acid is decanted off. The sediment still contains substantial amounts of trapped acid, which is removed by repeated re-suspension of the sediment in distilled water, then centrifuging and decanting the supernatant liquid. After these successive washing/centrifugation cycles the liquid phase becomes somewhat less acidic. The supernatant liquid (following centrifugation) becomes first colorless and then increasingly dark. Although this solution is still acidic (about pH 1) it is combined with the following fractions because of the presence of SWNTs. The remaining sediment is dispersed in distilled water by treating it with between two and three short (0.5-s) ultrasonic pulses. This results in the formation of a weakly acidic (pH 3–4) suspension containing roughly 1 mg of only SWNTs and nanoparticles per milliliter of distilled water. After this step most of the metal catalyst is removed. For permanent storage the solution was brought to pH 8–9 by using potassium carbonate. This causes an increasing repulsive interaction between the resulting carboxylic groups of the oxidized SWNTs, which are discussed below. The next step is the treatment of the SWNTs with an ultrasonic tip for about 1 min. This treatment reduces the nanoparticles to smaller pieces, while tubes and bundles are also smashed. But finally the difference in size between SWNTs and degraded particles increases (Fig. 1).

The final and most important step is the elution of the suspension through a column filled with potassium polyacrylate swollen in distilled water. When dry 99% of the particles of the cross-linked polymer are smaller than 1 μm. The particle size increases by about 300 times during the swelling process. This creates small hollows which are big enough to entrap nanoparticles as well as SWNTs and bundles of comparable size. The height of this column is about 6–7 cm. It depends on the diameter how much material can be loaded. In general, 1 ml of a 1-g/l aqueous SWNT dispersion per 15 ml of swollen potassium polyacrylate was found to be the optimum ratio to obtain SWNTs of high purity. In Fig. 2, the principle of our method is outlined schematically. In contrast to normal chromatographic procedures, which often use high pressure for elution, vacuum is applied in order to sqeeze the swollen polymer particles like a sponge.

SWNTs that are so big that they cannot be entrapped within the cavities can move freely and elute in high quantities (more than 40 % mass) as the first fraction. The remaining material contains a large portion of SWNT fractions of lower quality which can be washed out again by swelling the gel with distilled water and pumping repeatedly. Most of the degraded material remains in the cavities.

To test the effectiveness of this procedure several runs were carried out and the products were characterized, especially with AFM. For this purpose, the various fractions were deposited on surface-modified silicon wafers. Figure 3 shows a representative AFM image of the first fraction collected.

After repeated swelling of the gel with distilled water and pumping, the higher fractions elute. They contain more nanoparticles and degradation products, as exemplified in Fig. 4 for fraction 2.

Raman spectra were recorded to further characterize the purification process in bulk [11]. Evidence of a possible chemical modification of the SWNTs via oxidation of the carbon framework can be expected [12]. The D-line at around 1340 cm^{-1} and the G-line, centered at 1560 cm^{-1}, are attributed to impurities and the SWNTs, respectively [11, 13]. Their relative intensities provide an indication of the purity.

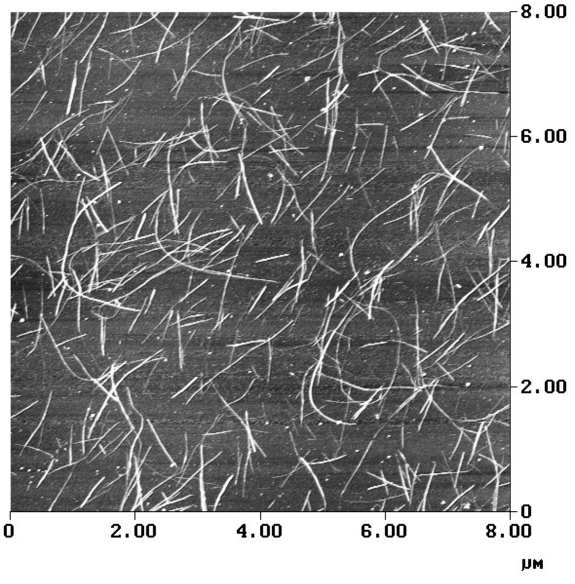

Fig. 3. AFM image of the first fraction. It shows a large number of SWNT bundles and only a very small amount of impurities (*single dots*). These impurities mostly consist of amorphous carbon, but there is also the possibility of catalyst particles still existing

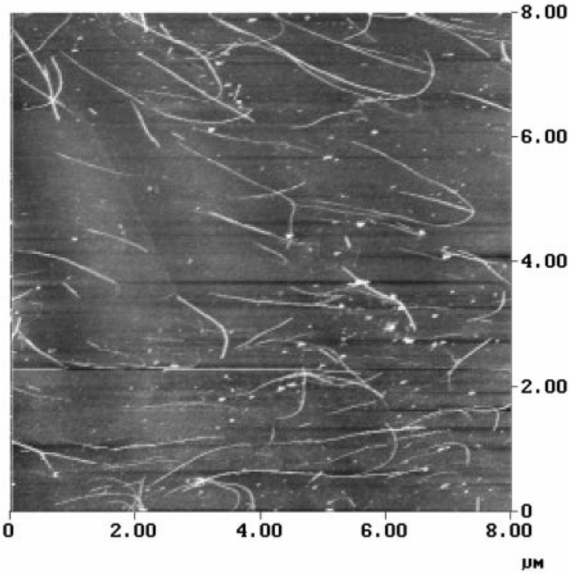

Fig. 4. AFM image of the second fraction

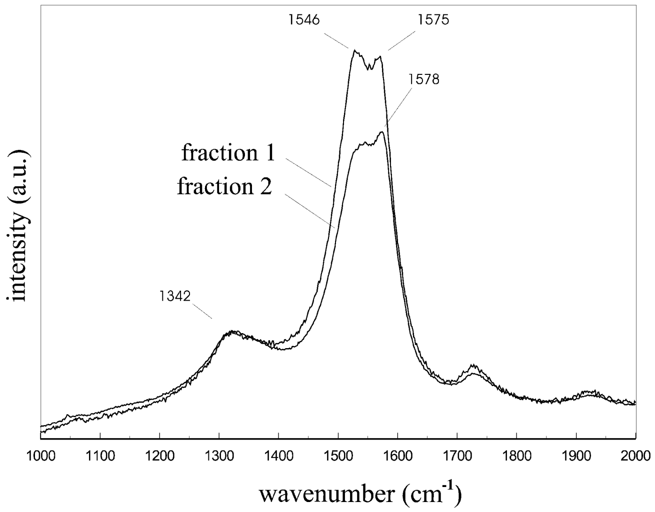

Fig. 5. Raman spectra of the two collected fractions. The different intensities of the G-line at about 1560 cm^{-1} compared to the similar intensities of the D-line at 1342 cm^{-1} indicate the purities of the collected fractions. Both peaks are also seen in the spectra of raw material (see Fig. 6) but in different ratios

However, it is not possible to use these results as an absolute value, because the intensities depend on many different factors, for example resonant enhancement effects [13]. Figure 5 shows the Raman spectra of the first two fractions, scaled to the intensity of the D-line. A lower SWNT content in the second fraction is apparent from the smaller intensity of the G-line.

Compared with the Raman spectrum of this purified SWNT, the raw material shows a more distinct splitting of the G-line as expected for pristine material (Fig. 6) [14]. According to Pimenta et al. [15] the pronounced modes at around 1540 cm^{-1} originate from metallic SWNTs, which are resonantly enhanced for excitation with an energy of ≈ 1.9 eV. However, in the spectrum of the oxidized fractions the low energy modes of the G-line around 1540 cm^{-1} are only barely visible and the other modes are upshifted. These changes upon oxidation indicate the loss of metallic character due to functionalization or a selective decomposition of metallic SWNTs. The additional contribution to the large broad peak of disordered carbon at around 1340 cm^{-1} (D-line) in the spectrum of the oxidized SWNTs, might originate from disordered or carboxylated carbon, which is formed on oxidation.

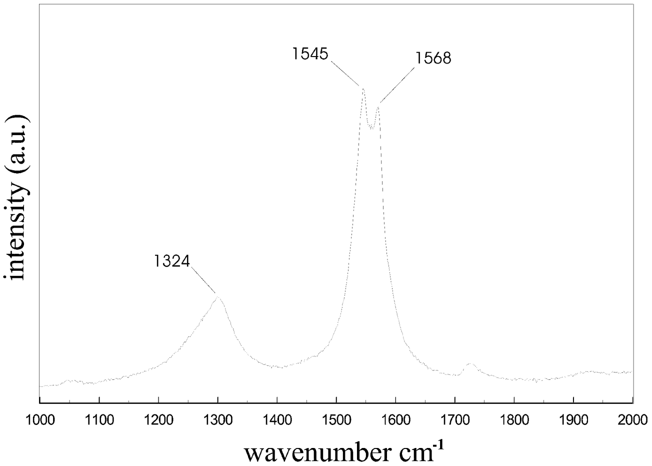

Fig. 6. Raman spectrum of raw material. The relatively high ratio between the D- and G-line intensity is attributed to the larger content of amorphous carbon as compared to the purified material

In conclusion, we have presented AFM and Raman spectroscopic measurements as evidence of SWNT separation from the different carbon species, as well as metal particles, using a new and simple purification procedure which takes advantage of both column chromatography and vacuum filtration. The complete procedure comprises three steps:

- Oxidation to remove catalyst particles, fullerenes and diminish amorphous carbon.
- Ultrasonic treatment to decompose nanoparticles, as well as SWNT ropes. In doing so, the difference in size between particles and SWNTs increases.
- Purification of the resulting material by vacuum filtration using potassium polyacrylate as a stationary phase.

This very simple procedure requires no expensive filter systems nor appliances and it enables the purification of large amounts of raw material within hours. This simple but effective procedure requires no expensive filter systems nor appliances, and it allows to purify large amounts of raw material within hours.

During purification, the SWNTs are provided with carboxylic groups which represent a suitable basis for further chemical derivatization.

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