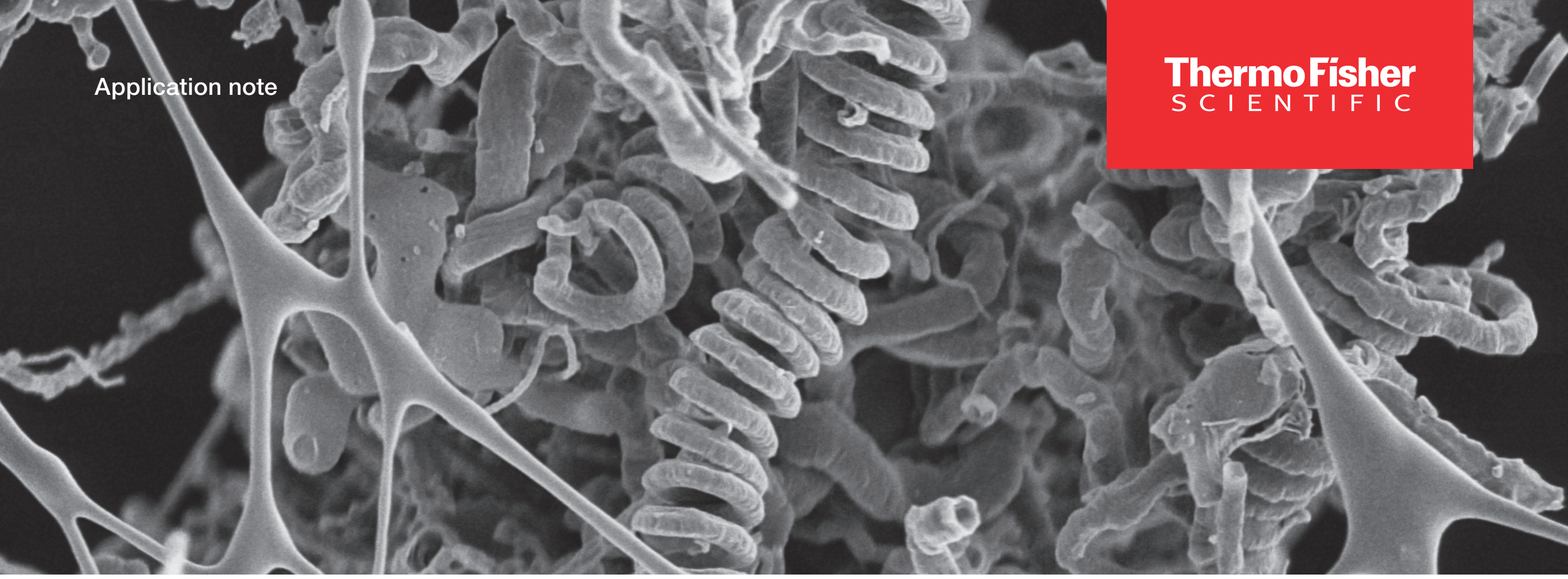

Apreo 2 SEM comprehensive characterization of bamboo-like carbon nanotubes

Morphological analysis of nanostructural information

Introduction

Due to the singular properties and potential applications in nanotechnology of carbon nanotubes (CNTs) and carbon nanofibers (CNFs), their growth mechanisms and different catalysts have been extensively studied. Catalyst materials that assist in nanotube formation, along with the shape, have a strong effect on parameters (e.g., the structure and morphology of the resulting nanotubes).

Iron and nickel are the most widely used catalysts for the growth of CNTs and CNFs, and the main method for producing CNTs and CNFs is catalytic vapor deposition (CCVD).[1] However, the literature reports that pure metallic Fe as well as Fe-C compounds (e.g., Fe_3C) have been found to catalyze carbon nanotube growth. As explained by Schaper et al., the carbide phase showed a clear role as an intermediate in the catalyst-mediated graphite formation, promoting the successive segregation of well-ordered new graphene layers on its surface, which can lead to the formation of a different type of CNTs.[2] These CNTs are generally referred to as “bamboo-like” for their internal structure, which differs from conventional CNTs.

While bamboo-like CNTs are members of the carbon nanotube family, their morphology and properties make them unique. They are a promising absorbent for the removal of organic pollutants due to their large surface area. Bamboo-like CNTs are increasingly used for lithium-ion battery electrodes, offering excellent hydrogen and lithium storage capacity. In this application note, we used the Thermo Scientific™ Apreo 2 SEM with Thermo Scientific ChemiSEM™ Technology to look at how these bamboo-like structures are made up of separated hollow compartments and bamboo knots which grow straight along the axis.

Materials and method

Formation of compartments in each bamboo-like carbon nanotube has been shown to be linked to the movement of the metal particle catalyst along the growth direction: often each joint’s shape is similar in shape to the metal particles at the tip.[3] The production of the typical structure of carbon nanotubes, made of compartments and knots, is the result of a particular and repetitive process of elongation and contraction involving the metal particle catalyst during the growth of carbon nanotubes.[4]

Completely characterizing bamboo-like carbon nanotubes is critical to determine whether synthesis has been successful and for which applications they are suited. In this investigation, detailed analyses were performed of several components, identifying the carbon nanotubes’ compartment structures, their size, and their metal catalysts’ size distribution and shape. To present a comprehensive view of features (e.g., morphology, topography, size, particle distribution and composition), bamboo-like carbon nanotubes were investigated using different techniques in a SEM platform. Transmission electron microscopy (TEM) is typically used to characterize the distribution of catalysts and the carbon nanotubes’ internal structures. However, in this case all characterization was conducted using an Apreo 2 SEM under different conditions, depending on the analysis type. The investigators acquired both scanning electron microscope (SEM) and scanning transmission electron microscope (STEM) images. All analyses were conducted in the same imaging session without switching tools or opening the SEM chamber multiple times.

The specimen was prepared from carbon nanotube powder that had been dissolved in ethanol and sonicated for 5 minutes. The resulting solution was used in sample preparations for SEM and STEM: 3 µl of the solution was drop-casted on a clean silicon wafer and 3 µl of the solution was drop-casted on a lacey carbon grid, then left to air dry.

Initially, SEM analyses were performed using the in-column Thermo Scientific Trinity™ Detection System, which has two in-lens detectors and one in-column detector. Images had been acquired both at low keV, to characterize the morphology and external surface of the CNTs, and at higher keV, for chemical analyses of the different materials, using Thermo Scientific ChemiSEM Technology, our integrated EDS solution. With ChemiSEM Technology, real-time compositional information was available while running the SEM characterization. With SEM and EDS integrated in a single interface, there was no need to switch to other software, since all the data interpretation tools were in one place.

Then, the Thermo Scientific STEM 3+ detector was used to perform STEM analyses. The STEM 3+ detector is retractable, with 11 individually addressable components with flexible segmentation that can be combined to retrieve enhanced levels of information. Using the detector, the samples could be imaged without breaking the vacuum between the STEM and the SEM imaging session. Additionally, no TEM grid manipulation was required, as the STEM 3+ detector could be inserted with a simple click in the SEM user interface. Due to its design, the STEM 3+ detector was able to provide bright field (BF) and high angle annular dark field (HAADF) imaging.

Next, Thermo Scientific Avizo2D Software's Analyzer function was used to conduct further statistical analyses by processing and analyzing features in a single 2D image or a set of 2D images. In this investigation, the Avizo2D Software was used to extract information on the size distribution of the iron particles, employing HAADF STEM imaging, with clear compositional contrast of catalyst particles that easily highlighted the iron in comparison to the lower atomic number composition of carbon nanotubes.

SEM analysis at low accelerating voltages

SEM characterization of the sample was conducted using two sets of imaging parameters. The first characterization was performed with an accelerating voltage of 1 keV and a relatively low beam current (6.3 pA) since carbon nanotubes become transparent to the primary electron beam with higher accelerating voltages. The Apreo 2 SEM provided high-quality performance at low keV to easily characterize the morphology of the carbon nanotubes (Figure 1).

Figure 1 shows two overview images acquired with the T2 detector, an in-lens secondary electron detector, part of the Trinity Detection System, which can provide different levels of detailed information, including sample composition, morphology, and surface features. Figure 1 shows the external topography and roughness of the carbon nanotubes.

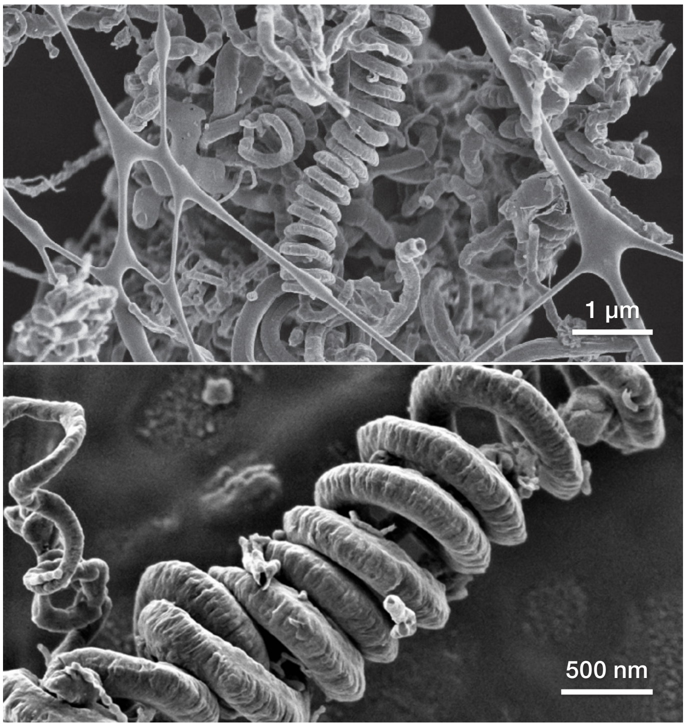

Figure 1. Overview of the different carbon nanotubes. Both (top and bottom) images show the tubes' morphology and surface roughness. Acc voltage 1 keV, beam current 6.3 pA.

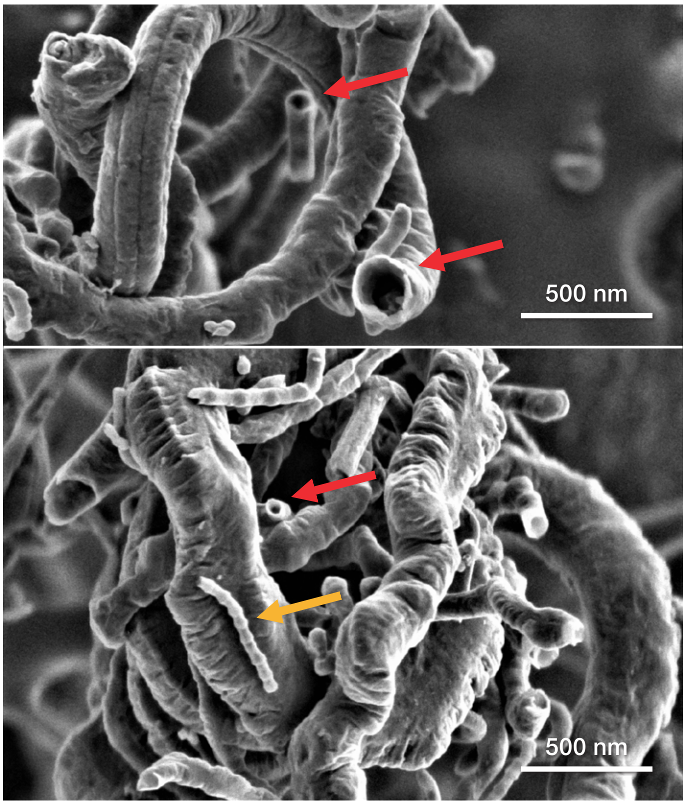

Figure 2. Higher magnification images of carbon nanotubes. Acc voltage 1 keV, beam current 6.3 pA. Red arrows in images show the inner part of the carbon nanotubes. The yellow arrow points to the characteristic shape of a bamboo-like carbon nanotube.

Higher magnification images were acquired for more detailed characterization (Figure 2), showing two images of carbon nanotubes aligned properly so that the inner structure is visible, through secondary electrons imaging. The nanotubes' round-shaped morphology is visible and, in the top image, the thickness of the wall of the nanotube in the center is about 15–17 nm. The characteristic shape of the bamboo-like nanotubes is also visible in the bottom image (see yellow arrow). A clearer view of this specific characteristic, together with the inner joint between the different compartments of the tube, would be more visible with STEM characterization. Secondary electrons imaging, however, does not clarify the presence or distribution of any catalyst particles that would be expected to assist with nanotube growth. To detect the catalyst particles, an EDS characterization of the sample was performed.

SEM-EDS analysis with ChemiSEM Technology

A higher accelerating voltage (15 keV) was applied when conducting a chemical analysis of the sample. As the nature of the catalyst was unknown, this accelerating voltage was chosen because it is high enough to excite the elements of many of the materials most used as catalysts in the formation of carbon nanotubes (e.g., Ni, Fe, Co). In addition, a higher beam current (0.2 nA) was used to ensure enough X-ray counts.

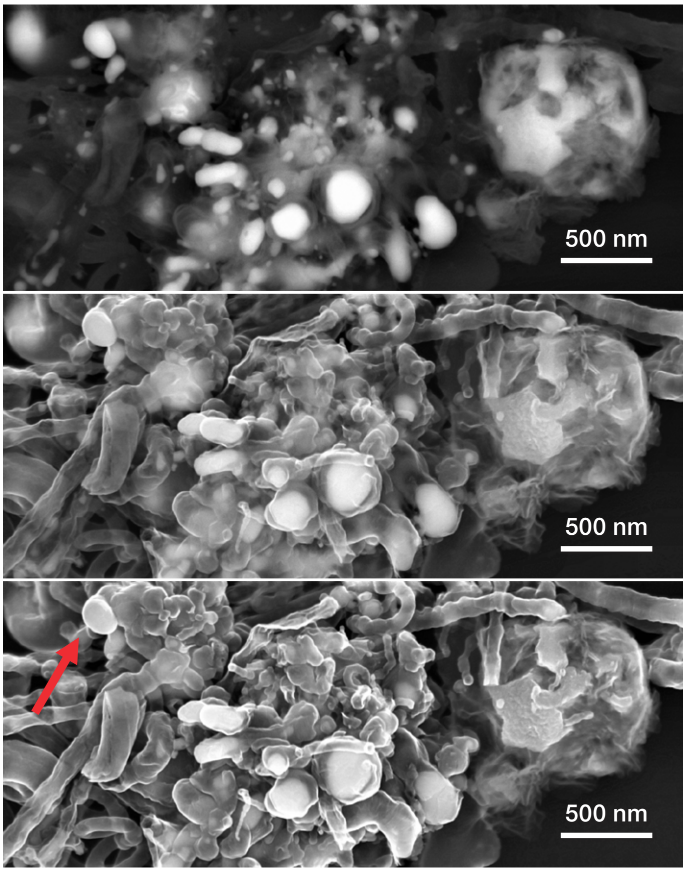

Figure 3. Set of three images simultaneously acquired using the Apreo 2 SEM and in-column Trinity Detection System. Using an accelerating voltage of 15 keV and a beam current of 0.2 nA, top image was acquired with a T1 detector, middle image was acquired with a T2 detector, and bottom image was acquired with a T3 detector.

The Trinity Detection System obtained all the needed information in one acquisition (Figure 3). The simultaneous acquisition by T1, T2, and T3 highlights a clear compositional contrast of the particles over the carbon nanotubes, and it also provides clear details on the carbon nanotubes' topography. Note: The tubes' roughness and morphological information were drastically reduced at 15 keV with respect to the analysis conducted at low keV because carbon nanotubes, like other light element materials, are transparent to the electron beam. Hence, even when imaging is performed with a secondary electron detector, the presence and distribution of the metallic catalyst particles (with a higher atomic number) are highlighted over that of the nanotubes. Finally, the T3 image mostly contains surface information, and the higher contrast of the catalyst particles has disappeared (see red arrow in Figure 3).

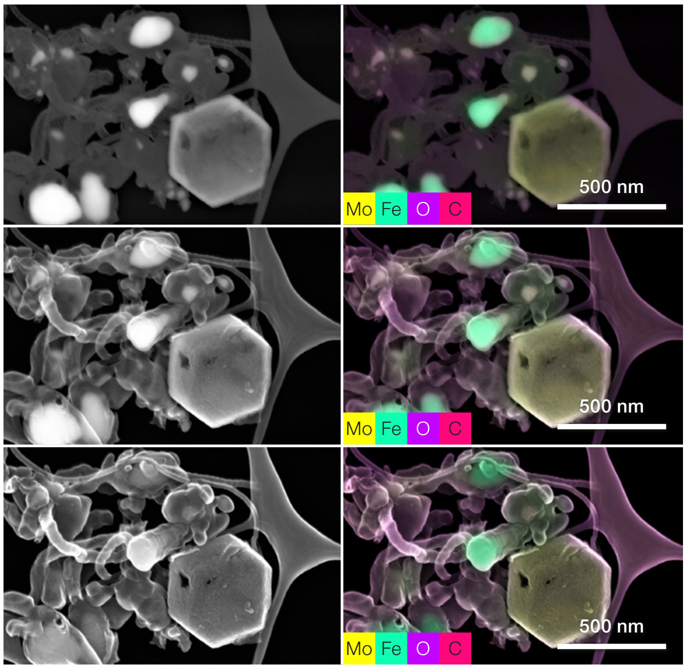

Figure 4. T1, T2, T3 images of a group of nanotubes with particles of different contrast. (left) Grayscale images. (right) Related ChemiSEM Technology images show iron-rich presence of the catalyst particles and an unexpected material rich in molybdenum and oxygen.

The main benefit of high accelerating voltage imaging is the ability to also collect the EDS signal in the same image acquisition. ChemiSEM Technology provides an always-on EDS detector that is continuously collecting and processing X-rays in the background during the acquisition of the grayscale images (Figure 4, left). The quantitative elemental information obtained differed from the raw signal usually acquired in a traditional EDS gross counts mapping analysis. ChemiSEM Technology images are shown, in which the present catalyst particles were easily seen in any of the available detectors (Figure 4, right).

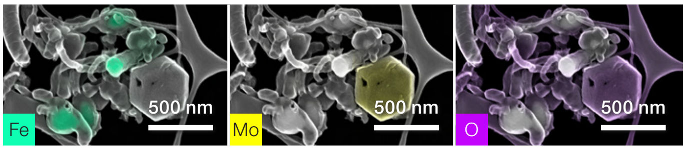

Figure 5. ChemiSEM Technology images showing distributions of elements of interest. From left to right, images show respectively the distribution of iron, molybdenum and oxygen.

To obtain a better view only of the distribution of the elements of interest, we generated a complete set of images in which only one element at a time was left active, as shown in Figure 5, with the T3 images used as a reference. Using ChemiSEM Technology, the catalyst employed to produce the bamboo-like carbon nanotubes was discovered to be iron rich. The oxygen image revealed that the catalyst was not oxidized, while hexagonally shaped particles, several of which were found on both the grid and the silicon wafer, appeared to be made of molybdenum oxide. The origin of the hexagonally shaped particles, however, is unknown.

STEM Analysis

The STEM 3+ detector was used to characterize the bamboo-like structure better. Thanks to flexible segmentation, the detector obtained different information from each segment. Specifically, the bright field (BF) mode helped to investigate the inner part the CNTs and the distribution of the different hollow compartments. The high angle annular dark field (HAADF) mode was used to highlight the presence and position of the iron catalyst particles inside or outside the carbon nanotubes.

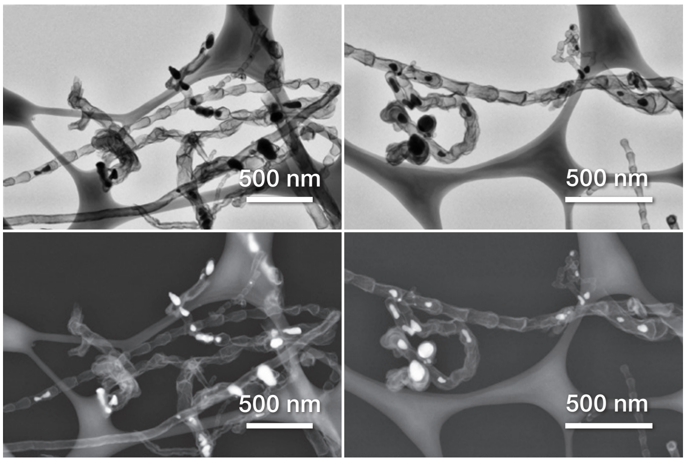

Figure 6. Bright field and high angle annular dark field images. Using an accelerating voltage of 30 keV and a beam current of 6.3 pA, (top row) BF images and (bottom row) HAADF images show the bamboo-like structure, distribution, and shape of the catalyst particles.

Figure 6 shows two sets of BF and HAADF images, in which the hollow interiors of the CNTs are easily visible, especially in the bright field images. They are divided into different compartments connected one to the other and separated from cylinder-shaped graphite layers by about double the measured diameter of each tube. Several catalyst particles show elongated tear-drop shapes along the tube's axis, which are commonly observed in nanoparticles that have tube growth performed by chemical vapor deposition.

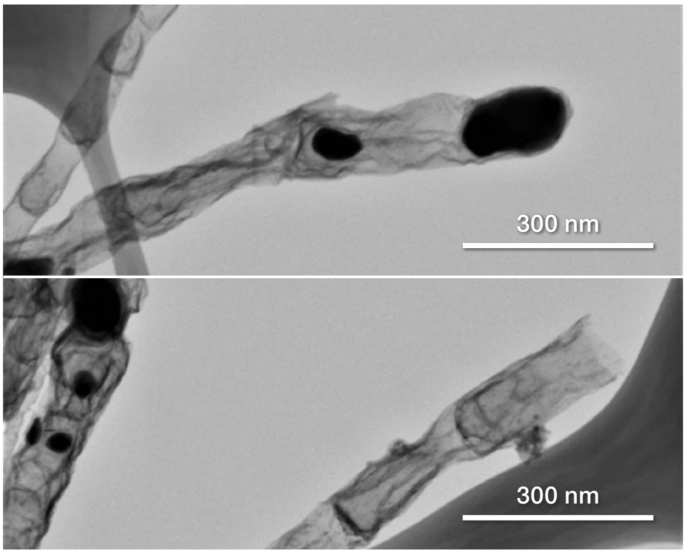

Figure 7. Bright field images of characterized bamboo-like carbon nanotube ends. Top image shows a closed end with an ≈5 nm layer on an elongated catalyst particle. Bottom image shows an open end.

BF higher magnification images in Figure 7 highlight the presence of two possible ends for the characterized bamboo-like nanotubes. The top image shows the presence of an iron-rich particle trapped in the closed end of a graphite layer with a thickness variable between 4 nm up to 9–10 nm. However, some of the nanotubes did not show the presence of a particle and an open end (bottom image, Figure 7).

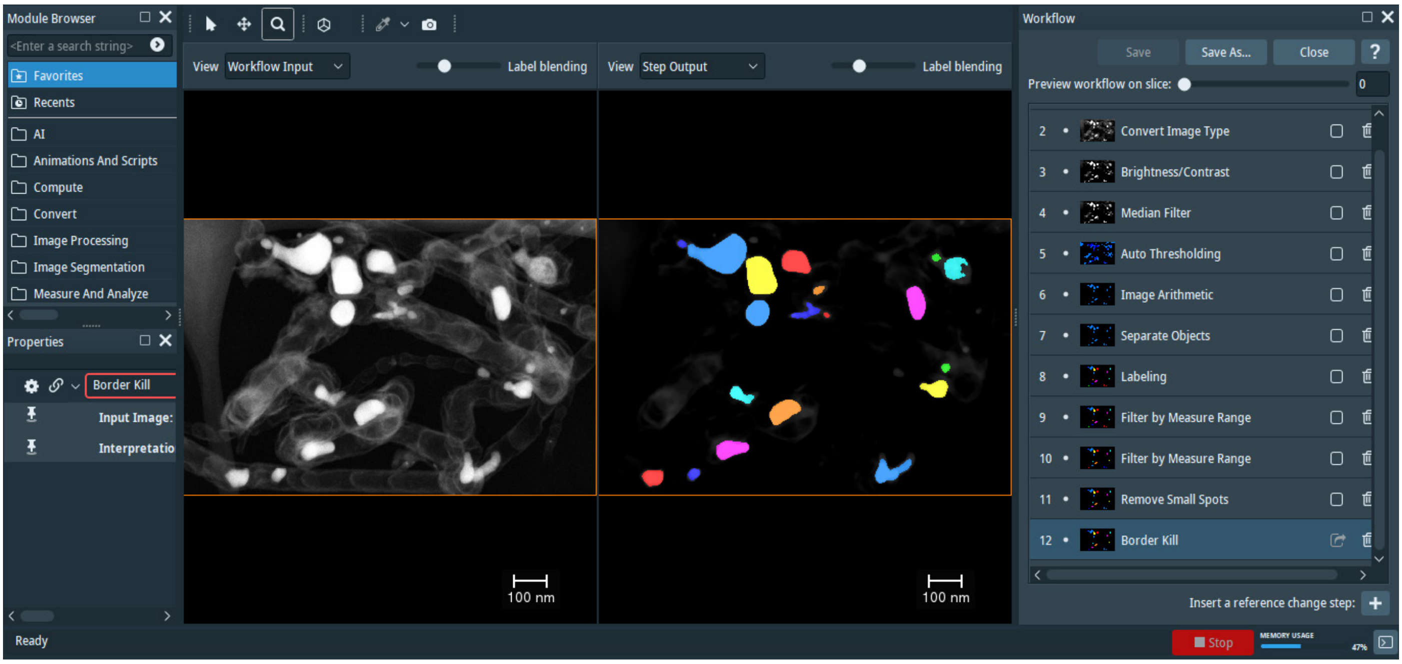

Figure 8. Overview of the Avizo2D Software user interface. A list of available operations is on the left, with steps in the developed recipe on the right.

Avizo2D Software Analysis

Avizo2D Software offers advanced image processing and segmentation techniques, for performing complex feature classification and statistics extraction on 2D images. For this investigation, Avizo2D Software (Figure 8) was used to process a batch of HAADF STEM images with similar magnification (Figures 9).

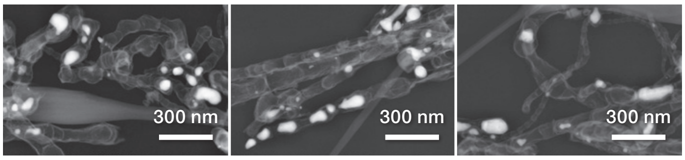

Figure 9. High angle annular dark field images with magnification comparable to that used in developing and testing the recipe to detect the catalyst particles.

With its workflow-driven approach, the Avizo2D Software facilitated building and running a short, easy-to-adjust, image analysis “recipe”. The main target of the developed recipe was to identify the catalyst particles based on the high material contrast provided by the HAADF STEM imaging in comparison to the lower contrast of the CNTs (Figure 9). The particles were then isolated from the rest of the STEM image and the size distribution (e.g., area or equivalent diameter) was extracted (Figure 10).

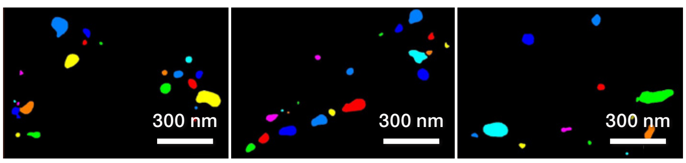

Figure 10. Catalyst particles were extracted from the images presented in Figure 9.

Located on the edge of the field of view, particles that might not be completely visible were removed to avoid alterations of the evaluation of size distribution. With advanced statistics extraction capabilities, several parameters were characterized, such as area (nm²), equivalent diameter (nm), and shape factor.

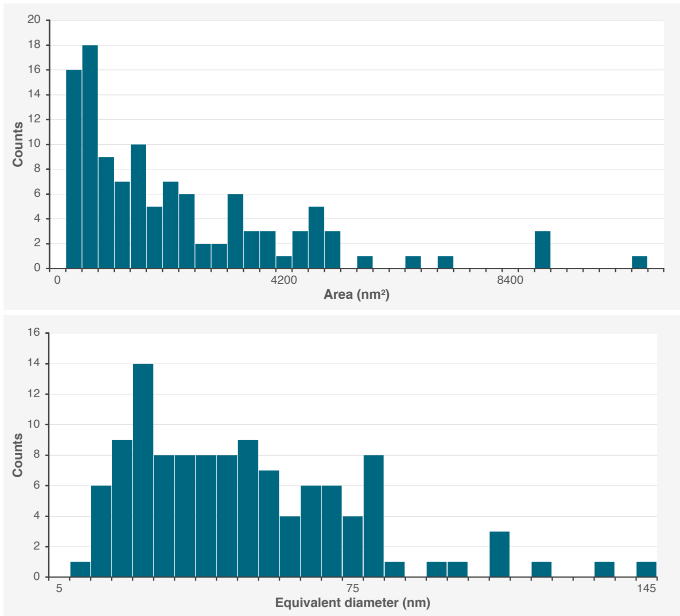

Figure 11. Area distribution of particles and equivalent diameter. (top image) Histogram shows the area distribution of the particles (nm²) and (bottom image) histogram shows the equivalent diameter distribution (nm).

The distribution of the area of the analyzed population of particles shows that most of the particles are in a range within 4,000 nm². The average area extracted was 2,500 nm² (top image, Figure 11). The equivalent diameter (bottom image of Figure 11) is the diameter of a disk of the same area of the considered particle. Equivalent diameter appears to be a better measurement than conventional diameter, as most of the objects of interest are not perfectly circular. The average diameter is around 40 nm and, as visible from the histogram, most of the particles have an equivalent diameter in the range between 10 nm and 80 nm.

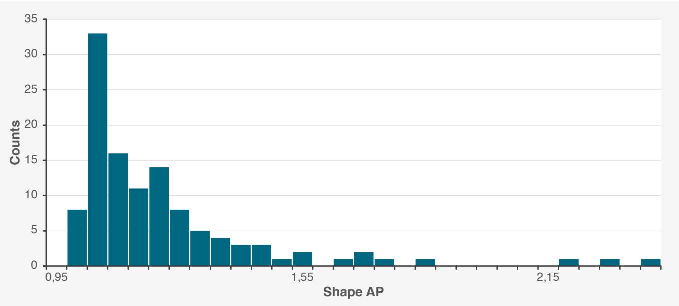

Figure 12. Shape factor distribution. Most particles showed a shape factor close to one, although outliers showed higher shape factors.

The shape factor is another parameter that was extracted from the particles in Figure 10. If a particle is a perfect disk, its shape factor value is almost one, whereas larger values indicate objects that are less compact. The shape factor distribution of the analyzed population (Figure 12) reveals that most of the particles have a value close to one, since most are round-shaped, but not perfect, disks. However, part of the population shows higher shape factor values, which indicates the presence of elongated particles.

Summary

Carbon nanotubes play an important role in materials research, with unique physical and chemical properties that show great potential for many applications in nanotechnology.

The Apreo 2 SEM, with ChemiSEM Technology and Avizo2D Software, showed the capability to provide a complete characterization of bamboo-like carbon nanotubes without a separate TEM instrument. Both SEM sample and TEM grid were characterized at the same time, with a wide variety of information at different accelerating voltages provided by the in-column Trinity Detection System. ChemiSEM Technology showed the catalyst particles' nature, identifying the presence of unknown materials (e.g., possible contaminants), while a complementary analysis of the bamboo-like structure and the localization of the catalyst particles was performed with HAADF STEM and conventional BF TEM images.

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