Morphology of Nanoparticles

A Characterization Using High-Resolution SEM

Potential candidates of reference nano-materials are manufactured and systematically characterized in particular with respect to their morphology (shape, size and size distribution) in the frame of the running large European project NanoValid. By exploiting the transmission operation mode in a SEM, known as T-SEM, it is demonstrated by means of three representative examples of nanoparticles how a quick morphological inspection up to a complete, metrological characterization is feasible.

Background

The characterization of the morphology of nanoparticles is becoming a task to be performed not only at a transmission electron microscope (TEM) but also more and more at modern, high-resolution scanning electron microscopes (SEM). A SEM is probably the most widespread analytical instrument available in analytical laboratories destined to characterize physical properties such as morphology, shape, size or size distribution of materials at the micro and nanoscale. The performance of a modern, high-resolution SEM, in particular its spatial resolution, can reach to enable identification and even morphology characterization of nanoparticles down to below 10 nm.

High-priority industrial nano-materials are being selected for manifold characterization with reliable analytical methods on a systematic basis under the frame of an EU FP7 research project entitled NanoValid [1]. The development of nanoparticle certified reference materials is an accompanying activity to be closely linked with. One inherent nano-morphological characterization technique is represented by the electron microscopy. In the following some significant results obtained by electron microscopy during the first year (of the four year project) are highlighted. One particular analytical option which was exploited successfully for the experiments of characterization of the nanoparticles in this project is the application of the transmission mode at a SEM - an older approach [2, 3] applied on modern materials such as nanoparticles. Recently [4, 5], traceable measurement of nanoparticle size and size distribution has been demonstrated with the so-called T-SEM (Transmission SEM).
Results

Three examples of materials from *NanoValid* have been selected to be highlighted as representative as far as their accurate morphological characterization by electron microscopy is concerned.

The first material consists of SiO$_2$ particles with diameters ranging from the micrometer down to below 100 nm (fig. 1). In order to enable the combination of two sensitive microscopy techniques (i) high-resolution SEM, to be performed with an electron detector of e.g. In-Lens type (correspondingly available at a Zeiss Supra40 SEM), and (ii) high-resolution T-SEM, the particulate material has been carefully deposited on a conventional carbon TEM grid. There are two versions of collecting the transmitted electrons: (i) by placing a semiconductor electron STEM detector directly under the TEM grid with the sample, and (ii) by incorporating the TEM grid with the sample into a special transmission setup, which "guides" the transmitted electrons via an electron multiplier onto the conventional Everhart-Thornley (E-T) detector [3]. The latter version was used in the present work. The attention of the reader shall be drawn in figures 1 onto the sensitivity of the "top" observation by the In-Lens detection as far as details in nanometer-range on the sample surface are concerned and in-depth details provided by the transmission "channel", respectively. Moreover, as systematically described in [4, 5], accurate and traceable dimensional results, i.e. of the nanoparticles diameter down to below 10 nm, can be gained by T-SEM.

The second example illustrates the practical performance of a modern SEM able to operate with both high-resolution SEM and T-SEM working modes on a SiO$_2$ nanoparticle material just in development at BAM as a feasible candidate as a certified reference nano-material. Even in a qualitative way it can be definitely stated from the T-SEM micrograph in figure 2a that the material consists of quite spherical shaped nanoparticles, is rather monodisperse, i.e. having a narrow
monomodal size distribution, and the size of the nanoparticles is close to 10 nm. All these findings could be confirmed by the inspection with the conventional TEM (fig. 2b). A further systematic data reduction involving the accurate determination of the size distribution of the SiO$_2$ nanoparticles on a metrological basis is in progress. The traceability of the size distribution "back" to SI units, i.e. length in this case, as measured with an electron microscope, is carefully taken into consideration. Thus, the two main sources generating significant measurement uncertainties are evaluated: (i) the calibration of the image magnification of the electron microscope and (ii) the calibration of the processing software, including the setup of the threshold necessary to delimitate the nanoparticles. In the addressed size range of about 10 nm these particular aspects are more challenging than for nanoparticles of several tens of nm or consisting of materials with a higher atomic number (producing higher contrast).

Finally, a third example of accompanying morphological characterization of engineered nanoparticles distributed in the frame of the NanoValid project by electron microscopy is represented by silver nanoparticles. After a proper preparation of the solution on a carbon TEM grid it could be unambiguously observed by means of T-SEM (fig. 3) that the nano-material consists of particles having a size ranging from below 10 nm up to about 50 nm and are of non-spherical shape. The example was selected in order to demonstrate how effective such a "quick" T-SEM characterization measurement can be for the manufacturers of the nanoparticles.

**Conclusion**

By means of three examples of nanoparticles selected as representative from the running large European project NanoValid it was demonstrated that a modern SEM is capable to provide a reliable characterization of the morphology of nanoparticles both (i) as a screening method for accompanying characterization "close" to the nanoparticles manufacturer and (ii) as a metrological tool for the evaluation of the shape and size distribution. The exploitation of the rather rarely used option of the transmission mode at a SEM (T-SEM) confers a significant enhancement of the quality of the results.

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References

Authors
Dr. Vasile-Dan Hodoroaba (corresponding author)
Dr. Steffi Rades
Natte Kishore
Dr. Guillermo Orts-Gil
Dr. Wolfgang E.S. Unger
BAM Federal Institute for Materials Research & Testing
Surface Analysis and Interfacial Chemistry
Berlin, Germany
http://www.bam.de/en

Contact

Bundesanstalt für Materialforschung und -prüfung (BAM)
Unter den Eichen 87
12205 Berlin
Germany
Phone: +49 30 8104 0
Telefax: +49 30 8112029