Traceable measurement of nanoparticle size using transmission scanning electron microscopy (TSEM)

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We developed a method which uses a scanning electron microscope operated in transmission mode to enable nanoparticle size measurements that are traceable to the SI unit 'metre'. Nanoparticles of three different material classes with sizes ranging from about 7 nm to 200 nm have been measured with expanded uncertainties (95% confidence interval) of about 1.5 nm to 5 nm.

1 Introduction

Nanoparticles are increasingly used in science and technology due to their size-dependent features which enable new and improved applications. Possible associated risks and regulatory demands emphasize the need for versatile and traceable methods for nanoparticle characterization, especially for size determination. Microscopic techniques are beneficially employed for this purpose because they directly yield information about the size distribution and morphology of the nanoparticles under test.

Scanning electron microscopy (SEM) is commonly applied for nanoparticle sizing due to its high spatial resolution. SEM in transmission mode (TSEM, [1]) offers highly accurate and traceable measurements [2], and at the same time allows for an automated analysis of a sufficiently large number of particles thus overcoming the drawback of deficient statistics often associated with electron microscopy [3].

2 Measurement procedure

The experimental setup has been described in detail in [2]. In short, particle samples are analysed using a standard SEM (Zeiss Supra 35 VP) equipped with a transmission detector placed underneath the sample. The detector records electrons which pass through the specimen without appreciable deflection. To speed up image acquisition and to minimize operator bias an automatic image acquisition has been developed. Fig. 1 shows, as an example, a TSEM image of gold nanoparticles. Also, image analysis has been automated to enable the evaluation of a series of TSEM images containing thousands of particles to attain particle size distributions.

2.1 Traceability

Traceable size measurements demand a calibration of the instrument, i.e. the determination of the pixel size in the recorded TSEM images. For this purpose we used a 2D grating with a nominal grating pitch of 144 nm consisting of aluminium bumps on silicon. The actual pitch of the grating in x and y direction was calibrated in our lab using a deep UV laser diffractometer which yields traceable values for the mean grating pitch [4]. For accurate nanoparticle measurements, possible spatial variations of pixel size within a TSEM image, e.g. caused by the so-called leading edge distortion, need to be considered [1].

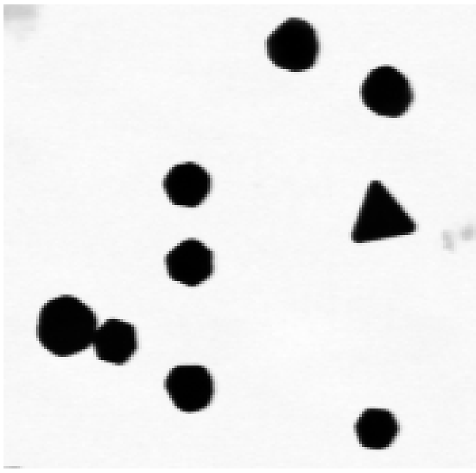

Fig. 1 *TSEM image of gold nanoparticles with sizes of about 80 nm to 120 nm.*

2.2 TSEM image modelling

For accurate size measurements a precise determination of the particle boundary is essential. A convenient and often used method to determine the particle boundary in images is the application of a grey value threshold level. However, conventional thresholding algorithms using global threshold levels are often based on practical issues and neglect the particular physical effects involved in image formation. Particle boundary detection and thus particle size analysis is considerably improved if the physical process of image formation is considered. In SEM and TSEM, the image formation process can be conveniently modelled using Monte Carlo simulations where the electron scattering processes in solid state and the electron detection are considered appropriately [5].

As an example, Fig. 2 shows a simulated and an experimental TSEM signal profile across a polystyrene sphere located on a carbon film. As can be seen, the signal level at the boundary position is not necessarily at the 50% level. Moreover, the threshold level depends on both particle size and material [3]. Consequently, an evaluation on per-particle level is needed which may be done by an automated image analysis. The dependence on material is due to different scattering properties, e.g. gold particles with high atomic number scatter electrons much stronger than less dense polystyrene particles.

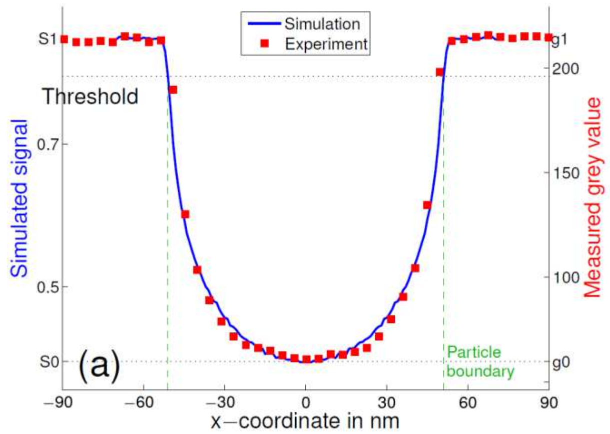

Fig. 2 *Experimental and simulated TSEM signal profile across a polystyrene nanoparticle.*

3 Measurement results

Fig. 3 shows, as examples, size distributions measured for two commonly used reference nanoparticles, i.e. gold [6] and silica nanoparticles [7]. The silica particles show a distinct asymmetric size distribution which is difficult to uncover when using so-called ensemble techniques like small-angle X-ray scattering (SAXS) or dynamic light scattering (DLS). From these size distributions, statistical size parameters like mean diameter or the distribution width can be determined.

The measurement uncertainty associated with the mean diameter depends on several influencing parameters. The most important ones are the uncertainty of the threshold level used for the evaluation, together with the settings of the image analysis parameters used to distinguish real particles from artefacts like dirt. In contrast, the uncertainty attributed to the calibration of the pixel size, or due to the particle statistics is of minor importance. The resulting measurement uncertainty (95% confidence interval) depends, among others, on particle size and particle type. It ranges between about 1.5 nm for small (10 nm to 30 nm) gold particles and about 4 nm to 5 nm for large (100 nm to 200 nm) polystyrene particles.

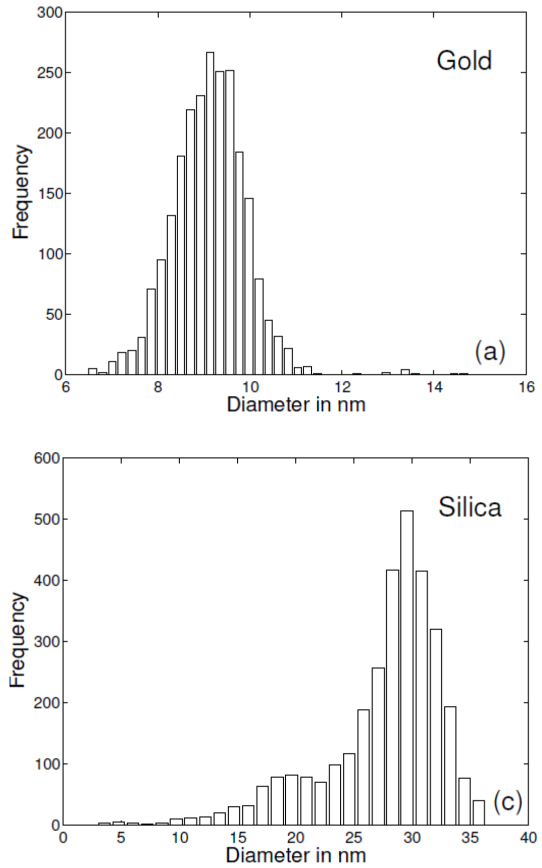

Fig. 3 *Size distribution of reference nanoparticles measured using the TSEM technique.*

4 References

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