Analytical ultracentrifugation – A versatile tool for the multidimensional characterization of nanoparticles

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Knowledge about the size, shape and optical properties of nanoparticles (NPs) is of high importance for many processes because product properties are directly influenced by these parameters. So far, combined analysis of size and shape or the determination of size and shape dependent optical properties has been a major challenge for nanoparticulate systems. Scattering or microscopic techniques are often limited by statistics, resolution and applicability to broad particle size distributions (PSDs). Ensemble based measurement devices such as the benchtop UV/Vis spectrophotometer fail to provide spectral information about individual species and require narrow size fractions instead.

These ubiquitous challenges provide the motivation and basis for the studies presented in this contribution. We have shown that analytical ultracentrifugation equipped with an UV-Vis multiwavelength detector (MWL-AUC) is a powerful tool for the simultaneous analysis of hydrodynamic and optical properties without the necessity of doing any purification step beforehand.1 AUC combines the fractionation of particles in a gravitational field with up to 280,000 g with UV-VIS spectroscopy. The distribution of particles in an optically accessible cell is measured in-situ using a CCD spectrometer, which captures full spectra ranging from 250 to 1000 nm at each radial position with very high temporal resolution during centrifugation.2

Sedimentation coefficients can be calculated for all species out of which PSDs can be derived. Our recent developments on the instrumentation, acquisition as well as the evaluation of MWL-AUC data allow us to significantly extend the possibilities of MWL-AUC.1, 3-4 Information on the size of all species in a mixture can be directly linked to their optical properties. Either extinction spectra can be determined or optical information can be used to deconvolute PSDs consisting of chemically heterogeneous NPs. For CdTe semiconductor quantum dots it is shown that the size dependent band-gap is derived in a single experiment.5 For plasmonic nanorods, a full 2D size and shape distribution is accessible using MWL-AUC.6 This is possible as hydrodynamic properties can be directly linked to the extinction spectra without any up-stream processing.

In case of non-plasmonic anisotropic particles, AUC can be coupled with analytics in the gas phase for mobility analysis using a scanning mobility particle sizer.7 This allows deriving the mean length and diameter of nanorods (e.g. ZnO). For mono-layered graphene oxide nanosheets, it will be shown that AUC is capable of resolving shape distributions with high accuracy, statistical confidence and experimental throughput, which makes it superior to the usually applied and very time consuming image analysis.8 For polydisperse PSDs, excellent statistics are obtained due to the evaluation at multiple wavelengths.4

In summary, our contribution will demonstrate that MWL-AUC is a powerful technique, which provides multidimensional access to an extensive range of particulate systems not accessible so far by any other technique. The direct correlation of size, shape and optical properties of NPs in the range between 1 nm and 1 µm is highly relevant for a variety of new applications because targeted product design becomes possible.

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