

Physicochemical characterisation of nanomaterial

Possible stress factors for substances during sample preparation and analysis

- Stress factors for both BET and EM are (i) temperature, (ii) vacuum, (iii) holding time or duration of measurement, (iv) unsuitable solvents
- Additional stress factor for EM is the voltage of the electron beam (e.g. normal vs. gentle beam)
- So far, a lot of data was compiled on how to properly assess inorganic molecules, such as SiO_2 or TiO_2
- Overall, organic substances tend to be less stable during sample preparation and analysis compared to inorganic molecules whilst there is less experience on proper nano assessment

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So which sample preparation and analysis conditions should be used in case of organic materials?

- Sample preparation and analysis needs to assure that organic molecules are not (partially) destroyed which would lead to artefacts and thus, false analytical results
- Additionally, organic material often exists in hydrate forms which are integral part of the crystal lattice
- Crystal water is likely to be released during sample preparation and analysis by BET/EM due to too harsh treatment (vacuum, temperature, solvents, electron beam)
- This may destroy the crystal lattice and thus lead to artefacts, i.e. too high surface area in BET analysis or de-novo nano structures in EM assessment
- No clear defined conditions available yet which take special material properties into account
- Varying results from different external laboratories

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VSSA screening together with shape definition according to Wohlleben et al (2017);

$$\text{VSSA cutoff} = 60 \frac{\text{m}^2}{\text{cm}^3} \times \frac{D}{3}$$

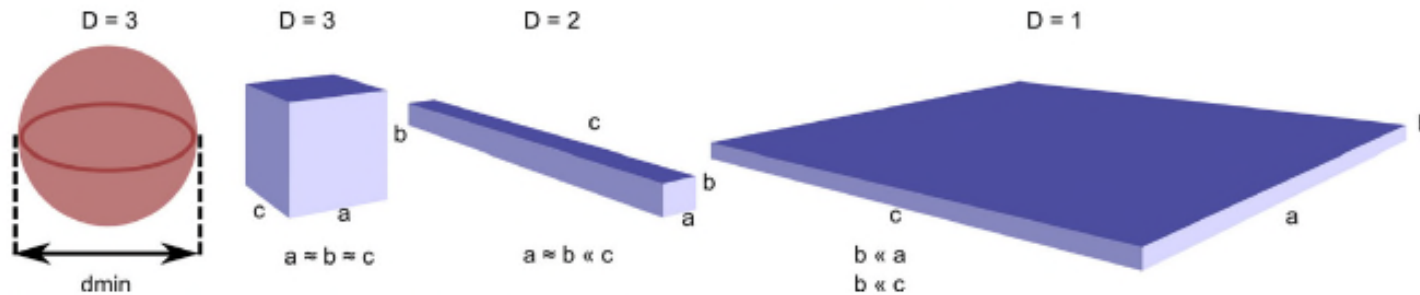


Fig. 1 Scheme of prototypical particle shapes, having $D =$ three, two, and one small dimensions

- In an ideal world, a defined substance can be properly categorized by EM into one category and thus, VSSA cut-off scheme can be applied
- But how to use VSSA cut-off if the dimension of the material cannot be clearly defined (e.g. complex mixture of 1 and 3 dimensional particles)?

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Current issues with EM for routine analysis

- Limited knowledge of how EU nano assessment can be applied
- Limited (TEM) or no (EM) automated assessment of particle size, particularly for one-dimensional particles
- Manual assessment of 100-1000 particles takes several hours and is thus very expensive (1000-5000€ per sample)
- Sample size (few μg) not representative for products which are produced in mt scale
- Thus, EM measurement is currently neither an objective, validated nor robust analytical assessment of nano status

Some questions

- Are there automated EM measurements available for nano classification of 1, 2 and 3-dimensional particles and mixtures thereof?
- How many particles have to be counted for a statistical correct evaluation, e.g. in case of a non-homogenous particle size distribution and polymorph materials?