Towards a method for quantitative evaluation of nanoparticles in suspension via Microprinting and SEM analysis

Francesca Bennet[1], Loïc Burr[2], David Schmid[2], Vasile-Dan Hodoroaba[1]

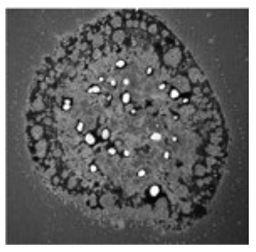
BAM
Bundesanstalt für Materialforschung und -prüfung

Background: Physico-chemical propeties of NMs

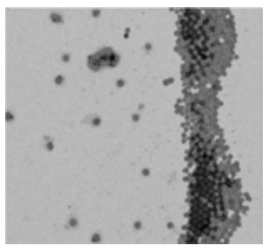
- Nanomaterials (NMs) come into increasing use, requiring understanding of which **structural aspects** (size, shape, aspect ratio, surface chemistry) influence their **physico-chemical and toxicological properties**
- Development of a library of analytical methods is necessary, which can provide **reliable, reproducible, accurate and validated data**
- Method implementation is enabled by an increase in **efficiency** as well as trend towards miniaturisation and **automation**

Goal: NP PSD and Concentration

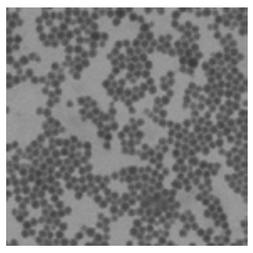
- Nanoparticles (NPs) in suspension need accurate methods for determination of their **concentration / size distribution**[1-4]
- Printing droplets of the suspension and imaging with scanning electron microscopy (SEM) enables simultaneous evaluation of particle size distribution and concentration
- Image evaluation with software (Fiji/ImageJ)
- Requirements:
  - **homogeneously** dispersed
  - **isolated** (not aggregated) particles
  - in a **monolayer**,
  - sufficient concentrations for **statistically significant** evaluation
- **Elimination of coffee ring effect**



☒ **Agglomerates & aggregates**



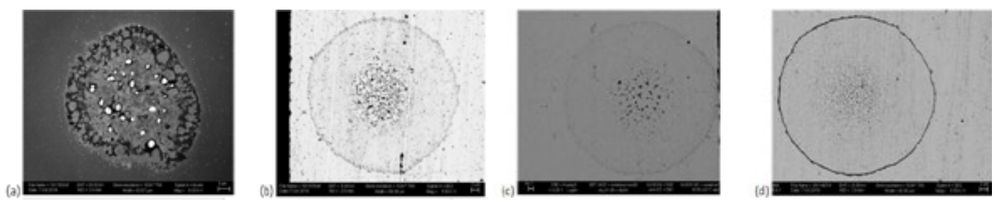
☒ **Agglomerate, coffee-ring effect**



☑ **Concentrated, no overlap**

Results

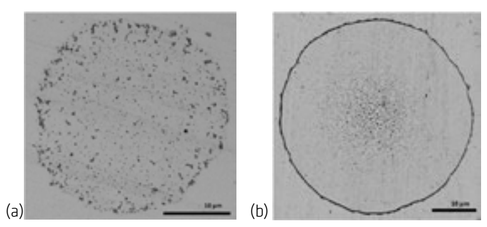
- Droplet behaviour is very material-dependent



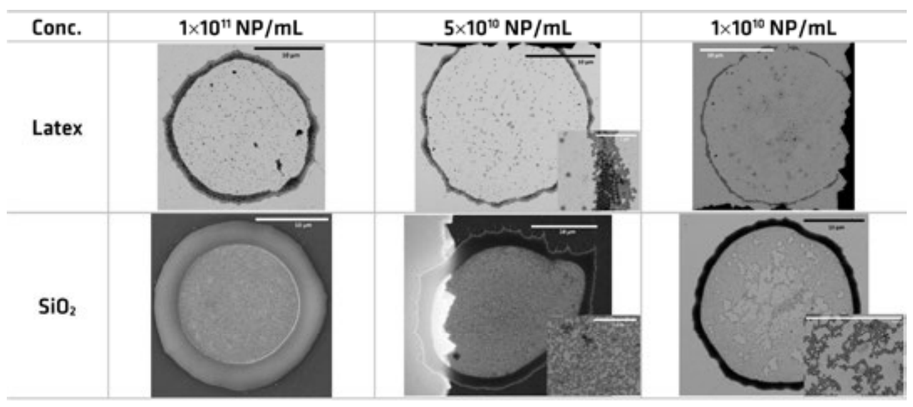
TSEM/SEM images of NPs printed at 40 °C and 30% R.H. (a) Au100 (b) Au20 (c) PS (d) SiO_2

- Lower temperature and higher relative humidity decreases coffee-ring effect

TSEM images of 1 x 10^9 NP/mL SiO_2 NPs printed at: (a) 21 °C / 80 % R.H. (b) 40 °C / 30 % R.H.

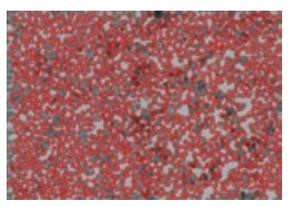


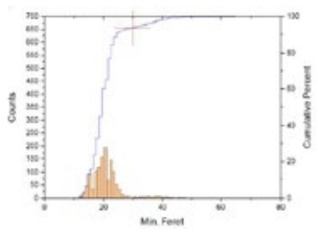
- Latex and SiO_2 NPs show improved coverage at higher concentrations and less coffee-ring effect at lower concentrations.
- Latex NPs have a much higher affinity for the substrate than each other. They form overlapping layers rather than single layers. Their low contrast makes digital image evaluation difficult.
- SiO_2 NPs shows a very strong coffee-ring effect, but also readily forms monolayers. These two effects compete.



SEM / TSEM images PS (Latex) and SiO_2 NPs printed at 21 °C and 80 % R.H. at varying concentrations

- Maximum estimated concentration to form a monolayer calculated for 20 nm SiO_2 NPs (3 x 10^{12} NP/mL): higher than concentration at which coffee rings were found



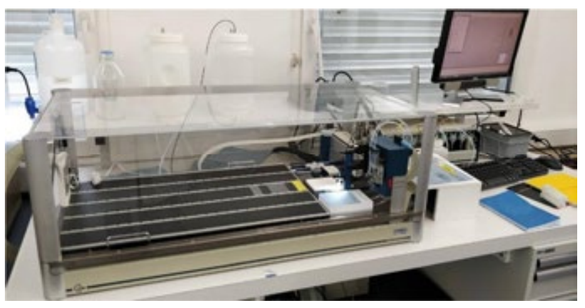


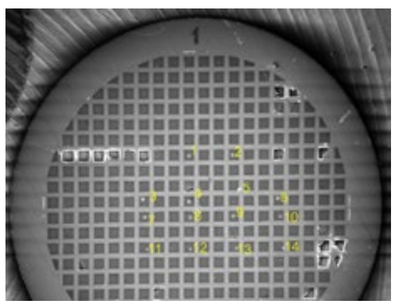
Estimate of particle concentration in monolayer using ImageJ software; the software is unable to distinguish between single particles and groups

- Both types of Au NPs show large amounts of agglomerates/ aggregates and impurities, and are therefore not suitable for this method.

Method

- Cu TEM grids coated with carbon film are printed with NP suspensions using a NanoPlotter (GeSim GmbH) piezo-electric printer
- Printing parameters (droplet volume, droplet speed, drop casting rate, printout drying) are optimised for each NP solution
- Different materials and sizes tested: Gold (Au) NPs (20 nm and 100 nm); Polystyrene NPs (100 nm) and SiO_2 (20 nm)
- Drops printed with a volume of 400 pL in a 4 x 4 array, with each suspension printed in 4 spots and grids repeated in triplicate





- Experimental parameters varied:
  - **Temperature** (21-40 °C)
  - **Relative humidity (R.H.)** (50-80 %)
  - NP **concentration** (10^9-10^{11} NP/mL)
- Imaged via SEM/TSEM

Summary & further work

- Options for reducing coffee-ring effect strongly limited by conditions available for printing
- Process must be optimised for each material type
- Further work with optimised substrates
- Au impurities/agglomeration may be due to ageing and salts from synthesis – these are not suitable for further work

[1] K. Kumagai and A. Kurokawa, Metrologia **56** (2019) (4), p044001.
[2] B. Michen, C. Geers, D. Vanhecke, C. Endes, B. Rothen-Rutishauser, S. Balog and A. Petri-Fink, Scientific Reports **5** (2015) (1), p9793.
[3] J. Mielke, P. Dohányosová, P. Müller, S. López-Vidal and V.-D. Hodoroaba, Microscopy and Microanalysis **23** (2017) (1), pp°163-172.
[4] R. Tannenberg, H. Eickhoff and W. Weigel, G.I.T. Imaging & Microscopy (2016), pp 33–35.
The authors thank Sigrid Benemann for SEM measurements and Dr. Christoph Hörenz for assistance with image processing

[1]Federal Institute for Materials Research and Testing (BAM), Division 6.1 Surface Analysis and Interfacial Chemistry, Berlin, Germany
[2]Swiss Center for Electronics and Microtechnology (CSEM), Landquart, Switzerland

Sicherheit in Technik und Chemie

ACEnano
Analytical and Characterisation Excellence

This project has received funding from the European Union Horizon 2020 Programme (H2020) under grant agreement no. 720952

www.bam.de