The structure of core-shell microgels: A light, X-ray and neutron scattering study

Déborah Feller [a], Gerardo Campos-Villalobos [b], Sylvain Prévost [c], Emanuela Zaccarelli [b], Julian Oberdisse [d] and Matthias Karg [a]

[a] *Physikalische Chemie funktionaler Polymere, Martin-Luther-Universität Halle-Wittenberg, Halle (Saale), Deutschland*
[b] *CNR-ISC and Department of Physics, Sapienza University of Rome, Rome, Italy*
[c] *Large Scale Structures, Institute Laue-Langevin, Grenoble, France*
[d] *Laboratoire Charles Coulomb (L2C), Université de Montpellier, CNRS, Montpellier, France*

deborah.feller@chemie.uni-halle.de

Hybrid colloids that combine polymers and plasmonic nanoparticles, e.g. gold or silver, gained increasing interest over the last years. [1] Gold-poly- *N* -isopropylacrylamide (Au-PNIPAM) core-shell microgels were used for periodic coatings due to the localized surface plasmon resonance (LSPR) of the cores leading to surface lattice resonance (SLR), which position strongly depends on the core size. [2],[3] Compared to other core-shell microgels, Au cores can be precisely overgrown in the shell *in situ* . [2] Although cores grow in size, the overall hydrodynamic diameter of the microgels does not change. It is unknown how the internal structure of the shell changes during the overgrowth.
Here, we are analyzing Au-PNIPAM microgels with two different crosslinker densities (8 mol% and 16.5 mol%). The cores are overgrown from 14 nm in diameter to nearly 100 nm (see Figure 1a and 1b). We perform different scattering methods, namely light scattering (LS) and small-angle X-ray and neutron scattering (SAXS/SANS) to study the respective form factors. SAXS provides information about the gold cores (Figure 1c), LS about the shell and the cores in dependence of core size and SANS about the shell (Figure 1d). We also investigate the microgels at different temperatures, below, at and above the volume phase transition temperature (VPTT) of the thermoresponsive PNIPAM shell. Thus, we can compare swollen and collapsed state of each microgel batch. Additionally, temperature dependent extinction spectra are recorded to study the optical properties. We also perform reverse Monte Carlo and coarse-grained molecular dynamics simulations of the different microgels. The simulations provide further insights into the internal structure of the shell and the radial polymer density distribution before and after the overgrowth of the core.

Keywords:
core-shell microgels, Au-PNIPAM, thermoresponsive system, internal structure, small-angle scattering, form factors

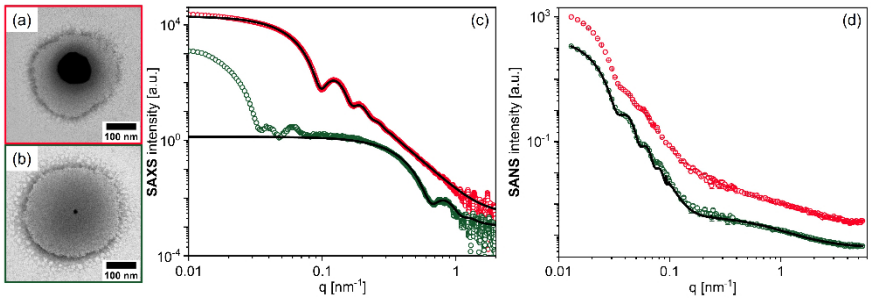

Figure 1. TEM images of Au-PNIPAM microgels with core sizes of 100 nm (a) and 14 nm (b) in diameter. Corresponding SAXS (c) and SANS (d) curves of the Au-PNIPAM microgels. Fits are shown in black.

References:

[1] M. Karg, T. Hellweg, J. Mater. Chem., 19 (2009), 8714-8727
[2] E. Ponomareva, K. Volk, P. Mulvaney, M. Karg, Langmuir, 36, 45 (2020), 13601-13612
[3] T. Honold, K. Volk, A. Rauh, J.P.S. Fitzgerald, M. Karg, J. Mater. Chem. C, 3 (2015), 11449-11457