Multivariable reentrant condensation of microgel-polyelectrolyte complexes

Simona Sennato [a], Domenico Truzzolillo [b], Chiara Bazzoni [c], Stefano Sarti [c], Federico Bordi [a,c]

[a] Institute for Complex Systems (ISC), CNR, 00185 Rome, Italy
[b] Laboratoire Charles Coulomb (L2C), CNRS-Université de Montpellier, F-34095 Montpellier, France
[c] Physics Dept. La Sapienza University 00185 Rome, Italy

e-mail: simona.sennato@roma1.infn.it

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Recently, “smart" or “environmentally-sensitive” polymeric microgels have rapidly gained importance in materials science owing to their versatile applications, ranging from drug delivery to sensing and fabrication of advanced materials for photonics [1].
These nm- or micron-sized hydrogel particles are able to respond to external stimuli such as temperature, pH, or ionic strength by undergoing a rapid transition, at a critical value, from a swollen hydrophilic state to a collapsed hydrophobic state (volume phase transition, VPT). Depending on the external conditions, their behaviour falls between that of hard-sphere and ultra-soft colloids, making them very attractive in soft matter science, and giving rise to applications in several fields. The most widely studied material of this kind is based on the polymer poly(N-isopropylacrylamide) (pNIPAM) [1]. It can be cross-linked during synthesis to obtain microgel particles with a VPT of approximately 33 °C in water.
Indeed, the amount of applicative work on microgels is overwhelming with respect to attempts to grasp the fundamental understanding of the physical mechanisms behind the functional properties of multiresponsive microgels. In particular, it is well known that electrostatic interactions play a crucial role in the colloidal stabilization and phase behavior of charged microgel systems, as well as in the control of the uptake of small charged drugs to use microgel as stimuli-responsive drug delivery vectors. To fully control these processes understanding the electrostatics of microgels is essential.
Despite of that only a few investigations focus attention on electrostatic aspects [2].
Within this panorama, we investigated the multivariable controlled aggregation of pNIPAM microgels in the presence of the ε-polylysine, a small biocompatible polycation by means of Dynamic and Dielectrophoretic Light Scattering, Dielectric Spectroscopy and TEM Microscopy. We showed that increasing temperature above the VPT, polycation adsorption is promoted by the accumulating negative charge of collapsed microgel, giving rise to charge inversion and overcharging phenomena, accompanied by the formation of stable clusters with size and charge controlled by polycation/microgel molar ratio at the isoelectrical point. This peculiar electrostatically-driven controlled aggregation, known as reentrant condensation and deeply investigated in other class of soft colloids [3], is here primarily tuned by the VPT-transition of pNIPAM and opens new intriguing scenarios for the controlled self-assembly of soft colloids.

[1] R. Pelton, Temperature-sensitive aqueous microgels, Advances in Colloid and Interface Science 85 (2000) 1-33
[2] M. Quesada-Pérez and A. Martín-Molina, Monte Carlo simulation of thermo-responsive charged nanogels in salt-free solutions, Soft Matter 9 (2013)7086-7094
[3] S. Sennato et al. Salt-induced reentrant stability of polyion-decorated particles with tunable surface charge density, Colloids and Surfaces B: Biointerfaces 137 (2016) 109-120.
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