Electrostatic Assembly of Zwitterionic and Amphiphilic Nanoparticles

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The colloidal assembly of individually dispersed nanoparticles into well-defined clusters consisting of only a few nanoparticles promises the scalable synthesis of advanced multifunctional nanoparticles with welldefined surface moieties, also known as patchy particles. However, electrostatic heteroaggregation, which is one of the simplest approaches to colloidal assembly, usually results in the uncontrolled precipitation of large particle clusters. In this work, we demonstrate the assembly of oppositely charged silica particles into well-defined core-satellite arrangements via electrostatic aggregation. To achieve controlled heteroaggregation, we studied the assembly of oppositely charged silica particles using particles with different sizes ranging from 5 nm to 150 nm at various concentrations. To obtain a positive charge on the otherwise negatively charged silica particles, we functionalized the core particles with APTES (aminopropyltriethoxysilane). It was concluded that the assembly works best with bigger particles, resulting in a fairly low polydispersity and a low amount of bridging between the individual clusters. The assembly of smaller particles produces high polydispersity, large clusters and uncontrolled aggregation and bridging. Furthermore, even with controlled aggregation into well-defined clusters in the case of bigger particles, we observe an uneven covering of the central particles with around 1-6 satellite particles absorbed to the central particle. This behavior is not predicted by simple DLVO theory which would anticipate an even spacing of the satellite particles on the core. We explain our observations by taking into account the interactions of the adsorbing particles within the ionic cloud of the central particle. We hypothesize that when the adsorbing satellite particles are small compared to the ion cloud of the core particle, they aggregate within the ion cloud and therefore do not create a well-defined monolayer on the surface of the core particle, but form small agglomerates during adsorption. The experiments were supported by modeling DLVO interactions with models of differing complexity which confirmed our hypothesis.

Finally, the most well-defined clusters consisting of APTES-coated silica particles with diameters of 150 nm and negatively charged silica particles with diameters of 80 nm at a ratio of around 1 to 4 big particles to small particles were tested for their capabilities as Pickering emulsifiers. To this end, a part of the clusters was functionalized with OTMS (octadecyltrimethoxysilane) to render the 80 nm particles hydrophobic while keeping the APTES-coated cores unaltered. This results in either zwitterionic or amphiphilic core-satellite particles which showed strongly increased surface activity compared to the individual particles as could be demonstrated by studying emulsion stability. Here, the hydrophobic functionalization changed the emulsion type from w/o to o/w. Interfacial dilatational rheological tests supported the observations from the emulsion tests.



Figure 1 Electrostatic heteroaggregation for the production of defined zwitterionic clusters. A) simple model based on DLVO interactions. B) Big particles: SiO_2 coated with APTES, d = 150 nm, small particles SiO_2 , d= 30 nm. C) Big particles: same as (B), small particles SiO_2 , d= 80 nm.

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