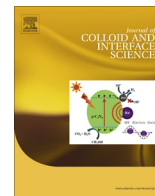




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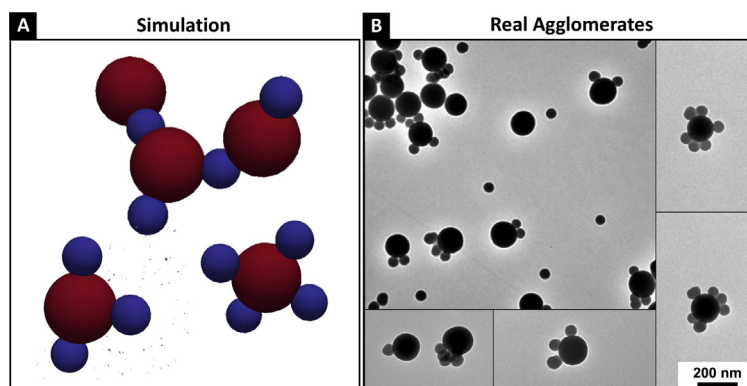
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## Regular Article

## Electrostatic assembly of zwitterionic and amphiphilic supraparticles

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## GRAPHICAL ABSTRACT



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## ABSTRACT

We demonstrate the electrostatic assembly of oppositely charged silica particles into an ensemble of well-defined core-satellite supraparticles, which are a type of patchy particle. To achieve controlled heteroaggregation, we used oppositely charged silica particles with different sizes ranging from 5 nm to 150 nm at several concentrations. The assembly works best with larger particles, resulting in a fairly low polydispersity and a low amount of bridging between the individual clusters. Using 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 adsorbed to the central particle. This behavior is not predicted by simple pairwise DLVO potentials which would anticipate an even spacing of the satellite particles on the core. We explain these 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 diameter of 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, instead forming small agglomerates during adsorption.

Finally, both the assembled zwitterionic clusters and clusters that were partially hydrophobized were tested for their capabilities as Pickering emulsifiers. The zwitterionic clusters showed a strongly increased surface activity compared to the individual particles, while the hydrophobized particles changed the emulsion type from w/o to o/w. Interfacial dilatational rheological tests supported the

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observations from the emulsion tests. With this, we demonstrate that a relatively unordered ensemble of supraparticles is able to show well-defined functionality at a higher hierarchical level as Pickering emulsifiers.

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## 1. Introduction

The colloidal assembly of individually dispersed nanoparticles into well-defined clusters consisting of only a few nanoparticles promises the scalable synthesis of advanced multifunctional supraparticles with well-defined surface moieties, also known as patchy particles. A facile and scalable synthesis route of patchy supraparticles would enable the fabrication of complex and functional colloidal assemblies, giving rise to non-hexagonal colloidal crystals [1], tailorable metamaterials [2] and eventually to complex nanomachines [3]. However, electrostatic heteroaggregation, which uses oppositely charged particles, and which is one of the simplest approaches to colloidal assembly, usually results in the uncontrolled precipitation of large clusters of particles. This general observation is opposed to a number of computational studies which predict that the controlled assembly of patchy particles via electrostatic assembly should be possible [4,5].

Next to the above mentioned visionary applications for particles that feature directional bonding, controlled surface anisotropy of heteroaggregate particles could give rise to particles with increased surface activity due to intermediate wetting properties of the particle surface, which should lead to an improved ability to stabilize Pickering emulsions [6,7]. In this respect, nanoscale heteroaggregates are reminiscent of the complex charge distribution in proteins, especially on the surfaces of virus capsids [8]. Hence, nanoparticles with localized surface regions of varying charge (or further properties like hydrophilicity) could prove to be a powerful addition to the portfolio of biofunctional colloids [9].

The term heteroaggregation is used to describe the instability of colloidal dispersions that consist of more than one type of particle [10]. The particles may differ in a variety of properties, including composition, shape, size, surface potential and charge. Here, we only address electrostatic heteroaggregation, i.e. the aggregation between oppositely charged nanoparticles as a result of Coulomb interactions. Heteroaggregates can be stable or unstable, depending on whether the aggregates remain as regular and well-dispersed units or whether they exist in large irregular masses that will eventually precipitate [5,12]. This behavior is also dependent on the relative particle sizes: particles similar in size tend to form large percolating agglomerates, giving rise to irregular clusters of particles. If there is a large difference in particle size, the smaller particles may adsorb onto the surface of the larger species creating a cohesive surface coating of the smaller particles on a central template particle [11,13,14]. Additionally, particle concentrations [15], surface functionalization [16] and solvent composition [17] also play a role in determining the final outcome of the aggregation process.

The interactions between colloidal particles with identical properties, called homoaggregation, can be appropriated by the DLVO theory [18]. The central assumption of the DLVO theory is the separation of the total interaction potential between two particles into attractive and repulsive contributions:

$$V_{DLVO} = V_A + V_R \quad (1)$$

The repulsive interactions are usually electrostatic in nature and arise due to the electrical double layer surrounding the spheres, originating from ionizable groups on the particle surface. When the particles are the same, the resultant force is repulsive;

when the particles differ in charge, as in heteroaggregation, the electrostatic forces are attractive. The electrical double layer can be quantified by the Debye-Hückel theory. It describes the thickness of the ion cloud surrounding a particle with the characteristic Debye-Hückel length  $\kappa^{-1}$  which is the distance from the particle surface at which the surface potential is merely 1/e of its initial value.

The electrostatic surface potential  $\psi$  of a particle with radius  $a$  as a function of the distance  $r$  from its surface can be approximated as

$$\psi(r) = \psi_0 \frac{a}{r} \exp(-\kappa(r-a)) \quad (2)$$

with the Debye-Hückel length  $\kappa^{-1}$  defined as

$$\kappa^{-1} = \sqrt{\frac{\epsilon \cdot k_B \cdot T}{2 \cdot N_A \cdot e^2 \cdot I}} \quad (3)$$

Based on the Poisson-Boltzmann equation, the gradient of the ion concentration  $c$  in the ionic cloud can be written as

$$c = c_0 \cdot \exp\left(\frac{e\psi(r)}{k_B T}\right) \quad (4)$$

where  $c_0$  is the ion concentration in the bulk phase and  $e$  is the elementary charge [19,20].

The attractive forces between colloidal particles usually consist of van der Waals forces which are a result of temporary dipoles and depend on the Hamaker constant  $A$  and the particle geometry. When expressed in terms of interaction energy, the DLVO potential can be written as

$$W_{DLVO} = W_{vdW} + V_{Coulomb} \quad (5)$$

with

$$W_{vdW}(r) = -A \frac{a}{12r} \quad (6)$$

and

$$W_{Coulomb}(r) = \frac{64\pi \cdot k_b T \cdot a \cdot I \cdot \gamma^2}{\kappa^2} e^{-\kappa r} \quad (7)$$

with  $\gamma = \tanh(\Psi/4)$ ,  $\Psi = ve\psi/kT$ , the ionic strength  $I$ , the Boltzmann constant  $k_b$  and the temperature  $T$  [21].

However, the DLVO theory only provides a basic framework to assess particle interactions in real-life systems. It has especially limited accuracy for systems with high ionic strength, submicron particles and interactions with more than two particles at one time.

There are a few notable exceptions to the otherwise suspicious lack of publications on stable heteroaggregates. For example, Dušak et al. studied the adsorption of small carboxylated maghemite nanoparticles to amino-functionalized silica particles and found that electrostatic heteroaggregation results in an uneven coating on the silica particles while covalent attachment gave rise to fairly well-defined structures [22]. Wagner et al. achieved a very regular coating of aminated polystyrene particles 154 nm in diameter with negatively charged gold or magnetite particles with diameters around 20 nm. Here, all particles showed notably high zeta-potentials above  $\pm 70$  mV which might explain the even spacing of the smaller particles on the bigger ones [23]. Alternative

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