



Influence of microgel packing on raspberry-like heteroaggregate assembly



Shalini Saxena^{a,b}, L. Andrew Lyon^{b,c,d,*}

^a School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332, United States

^b Petit Institute for Biosciences and Bioengineering, Georgia Institute of Technology, Atlanta, GA 30332, United States

^c School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA 30332, United States

^d Schmid College of Science and Technology, Chapman University, One University Drive, Orange, CA 92866, United States

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ABSTRACT

We describe the influence of microgel packing on colloidal-phase mediated heteroaggregation using poly(*N*-isopropylacrylamide) and poly(*N*-isopropylmethacrylamide) microgels with 1% mol or 5% mol *N,N'*-methylenebis(acrylamide) cross-linker. This system is uniquely designed to interrogate the influence of microgel structure and stiffness on microgel deformation at a curved interface by eliminating the necessity of electrostatic charge pairing. Microgel monomer and cross-linker content is expected to influence deformation at a curved interface. Microgel deformation and swelling were characterized via atomic force microscopy (AFM) and viscometry. A systematic study of colloidal-phase mediated heteroaggregation was performed at varied effective volume fractions with all microgel compositions. Scanning electron microscopy (SEM) and qNano pore translocation experiments were used to assess the microgel coverage on the resultant raspberry-like particles (RLPs). Results reveal that microgel composition has a strong influence on the efficiency (as determined by microgel coverage) of RLP fabrication. The compositional effects appear to be related to the degree of microgel spreading/deformation at the interface, which is coupled to the influence of packing on assembly fidelity. These findings are widely applicable to systems where microgel deformation occurs at a curved interface. We also demonstrate that qNano pore translocation experiments can be used as a high-throughput method to analyze RLP microgel coverage.

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1. Introduction

Recently, architectural control of composite nano- and micro-particles has gained importance in the development of functional materials. The creation of multi-material colloidal particles (i.e. polymer/polymer [1], polymer/metal [2], polymer/mineral [3], mineral/metal [4], metal/metal [5], etc.) can lead to complex

properties that are not simple compositional averages of the individual materials, with those properties being tunable to meet specific needs of an application. Previous studies have investigated the use of hybrid colloids for a wide range of purposes such as drug delivery [6,7], sensing [8,9], photonics [10], optoelectronics [11], coatings [12], and stabilizers [13].

Hybrid colloids often involve two distinct materials arranged in a core-shell architecture. A variety of techniques have been explored for the development of such core-shell systems, one of which is heteroaggregation [14]. Heteroaggregates are caused by the aggregation of particles with different compositions and/or sizes in colloidal dispersions and have been investigated for use in manufacturing coatings, separations techniques, as well as pharmaceutical devices and biotechnology [15]. Previous methods to produce core-shell heteroaggregates often rely on ion-pairing to drive heteroaggregation or require covalent grafting of a shell onto a core particle [16–19]. Such methods result in a construct where the core particle is surrounded by a nanoparticle shell, which resembles a raspberry and is often termed a raspberry-like particle (RLP). Various parameters can be used to control the heteroaggre-

Abbreviations: AFM, atomic force microscopy; RLPs, raspberry-like particles; SEM, scanning electron microscopy; ϕ_{eff} , effective volume fraction; VPTT, volume phase transition temperature; NIPAm, *N*-isopropylacrylamide; pNIPAm, poly(*N*-isopropylacrylamide); NIPMAm, *N*-isopropylmethacrylamide; pNIPMAm, poly(*N*-isopropylmethacrylamide); BIS, *N,N'*-methylenebis(acrylamide); Aac, acrylic acid; SDS, sodium dodecyl sulfate; APS, ammonium persulfate; EDC, 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride; NHS, *N*-hydroxysuccinimide; AB, 4-aminobenzophenone; EtOH, ethanol; DMSO, dimethylsulfoxide; PS, polystyrene; PBS, phosphate buffer solution.

* Corresponding author at: Schmid College of Science and Technology, Chapman University, One University Drive, Orange, CA 92866, United States. Fax: +1 714 532 6048.

E-mail addresses: ssaxena30@gatech.edu (S. Saxena), lyon@chapman.edu (L.A. Lyon).

gation process. For instance, ion-pair driven heteroaggregation, which relies on electrostatic interactions between the core-particle and the shell particle, is sensitive to pH, ionic strength, and particle sizes. When stimuli-responsive components are used, this offers additional routes to control the rate of heteroaggregation including hydrogen bonding, temperature, or light [20,21]. Such parameters can even be used to produce reversible heteroaggregation.

Heteroaggregates have been constructed from a variety of materials, such as polystyrene/silicon dioxide [12], polystyrene/iron oxide [22], polystyrene/poly(2-vinylpyridine) [23], hydroxypropyl cellulose/silica [19], alginate/CaCO₃ [24], and many others. In addition, soft material components have been investigated for the development of RLPs. For example, microgels, which are nano- or micro-scale gel particles, have been investigated for use in heteroaggregation [23,25]. Using soft, deformable microgels to assemble atop hard sphere “cores” allows for increased contact area; the microgels are able to spread onto the hard spheres, which improves the mechanical stability of the complex [25]. This is beneficial because assembly of heteroaggregates is limited by both the strength of intraparticle bonds and the contact area between the particles. As an example of such soft/hard heteroaggregates, poly(*N*-isopropylacrylamide) (pNIPAM) microgels have been employed due to interest in their thermosensitivity [15]. PNIPAM exhibits a volume phase transition temperature (VPTT) at ~32 °C where it transitions from a swollen gel to a collapsed globular state [26]. PNIPAM microgels have been assembled atop SiO₂ core particles in a number of studies to produce RLPs [16]. Similarly, poly(*N*-isopropylmethacrylamide) (pNIPMAM) based microgels can be used for such systems, with these particles exhibiting a transition temperature at ~41 °C [26].

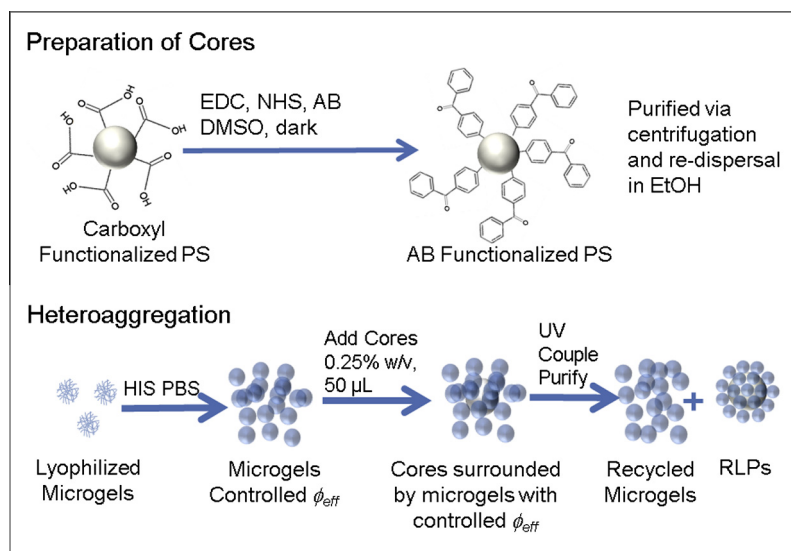
The Lyon group has previously reported the synthesis of raspberry-structured microgel heteroaggregates by immersing core particles into a densely packed colloidal (microgel) phase to apply a microgel coating [27]. It is hypothesized that this heteroaggregation occurs due to the amphiphilic nature of pNIPAM and pNIPMAM microgels, making interactions with the amphiphilic polystyrene core possible, even in the case where components possess charges of the same sign. Using this method, we have shown that ultra violet (UV) irradiation can be used to couple the microgels to carboxylated polystyrene (PS) core particles modified with 4-aminobenzophenone (AB). This covalent coupling via UV irradiation is not necessary for the formation of RLPs, but can be employed to enhance stability of the assembly. That study demonstrated the

assembly of RLPs using two different microgel compositions (neutral and anionic) and two different core particles (4.5 μm PS and “rough” PS with iron oxide grafted on the surface). Thus, the method allows for versatility in the composition of RLP components, lacking the constraints of ion-pair driven heteroaggregation such as sensitivity to pH and ionic strength. Moreover, since chemical compositional limitations have not yet been discovered for this system, it can be utilized to interrogate fundamental aspects of microgel deformation at a curved interface.

In the present contribution, we explore the sensitivity of the colloidal-phase mediated heteroaggregation process to the volume fraction of the microgel phase. We have modified the previously described method [27] to enable the creation of colloidal-phases of known volume fractions (Scheme 1), thereby obtaining greater control over the packing of microgels around the core particles. Volume fraction is the thermodynamic parameter of interest for colloidal phases [28]. For dispersions of spherical, repulsive hard spheres, the phase diagram predicts a disordered “fluid” phase at sphere volume fractions below 0.49, fluid/crystal coexistence, from 0.49 to 0.55, and an fcc crystalline phase above 0.55, with the maximal close packing occurring at 0.74. It is also typical to observe a kinetically trapped “glassy” phase with an approximate maximal packing of ~0.64; this glassy phase may coexist with a polycrystalline phase as well. Previous investigations of microgel phase behavior have indicated that microgels behave as hard spheres up to a volume fraction of 0.5 [29]. However, above this volume fraction, particle softness begins to influence the phase behavior, leading to a shift in the fluid/crystal phase boundary and a narrowing of the coexistence region [29]. Due to the unique softness of microgels, the parameter volume fraction is often replaced by the effective volume fraction (ϕ_{eff}) according to Eq. (1), where a represents the average distance between the center of two adjacent microgels, σ represents the microgel hydrodynamic diameter in dilute dispersions, and 0.740 corresponds to the volume fraction for hard sphere closest packing.

$$\phi_{\text{eff}} = 0.740(a/\sigma)^3 \quad (1)$$

We have also investigated how microgel network structure influences deformation at an interface based on microgel monomer and cross-linker content. Investigation of microgel deformation at planar interfaces has demonstrated the influence of microgel compositions on microgel rigidity and subsequent microgel spreading, leading to varied topographical features. Visual studies of several



Scheme 1. Colloidal-phase mediated heteroaggregation.

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