

Pickering Emulsion as a Template to Synthesize Janus Colloids with Anisotropy in the Surface Potential

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A versatile new concept is presented for the synthesis of Janus colloids composed of Laponite nanoclay armored poly(divinylbenzene) with an anisotropic surface potential via a double Pickering emulsion template. First, polystyrene or poly(divinylbenzene) colloids stabilized with Laponite nanoclay are synthesized via a Pickering miniemulsion approach. These nanoparticle-stabilized colloids were then templated at a wax–water interface in a second Pickering emulsion in order to chemically modify one hemisphere of the colloids. Janus modification of the colloids was accomplished by cation exchange of sodium ions, originally present on the surface of the Laponite with various salts of modifying ions (Ca^{2+} , Fe^{2+} , and Fe^{3+}) in the suspension. The zeta potential of the chemically modified and unmodified colloids was compared. The maximum change in the zeta potential was given by the calcium ions, Ca^{2+} -adsorbed modified colloids as compared to unmodified sodium ions, Na^{+} -adsorbed colloids. The distribution of charges on the Janus colloids results in a nonuniform zeta potential. XPS and optical microscopy were used to verify the successful chemical modification by the cation exchange of Na^{+} for Ca^{2+} ions on one hemisphere of the Janus colloids.

Introduction

Particles having anisotropic properties are called Janus particles.¹ Particles may be anisotropic in shape and/or surface chemistry. Particles with chemical rather than shape anisotropy have potential importance and can play a role in recognizing specific molecules,^{2–4} self-assembling colloids,^{5,6} and stabilizing bubbles.⁷ It is important to develop methods for fine tuning both the geometry and chemical compositions of anisotropic particles. Moreover, to make these particles practical, they should be produced in bulk rather than on a particle-by-particle basis.⁸

High volumes of anisotropic colloids with precisely controlled surface potential and functionality cannot currently be produced. The synthesis of Janus colloids with differential surface potentials in large quantities with a bulk processing method has not yet been successfully accomplished. Although methods such as one-sided gold evaporation,⁹ colloidal crystallization,¹⁰ microcontact printing,¹¹ and electrified jetting¹² have been studied for the fabrication of various Janus particles, difficulties in scaling up the fabrication preclude the widespread use of these techniques. The first difficulty with these approaches is that an adhesion layer must be applied between the particle and the substrate,¹¹ which greatly limits the size and the geometry of the Janus particles that can be synthesized. A second limitation is that a cleaning step is needed,

after printing, to remove the adhesion layer. Furthermore, a reliance on printing surfactant molecules limits the possible chemical makeup.¹¹ Recently, other methods of fabricating Janus particles in large quantities have been developed more successfully. These, however, are not colloids with anisotropic surface potential but rather the simplest possible form of the anisotropic chemical makeup, the Janus particle, whose surface is divided into two different chemical compositions.¹³

A great need exists to develop anisotropic colloids via a bulk approach that is a scalable, highly parallel synthesis strategy and permits the formation of colloids with fine control over the surface potential and surface chemistry.

A number of methods of synthesizing Janus particles have been explored.¹⁴ These methods of producing Janus particles broadly employ shielding a part of a homogeneous particle and then modifying the unshielded part with chemical or physical modifying agents or joining two different materials to form a particle that is anisotropic in surface as well as bulk properties. The partial shielding method involves variants in which particles are laid in a tightly bound monolayer on a substrate or are partially embedded in a matrix. Thus, only one side of the particle is exposed to the modifying agents, giving us Janus particles. The tightly bound monolayer is formed by spin coating or drag coating¹⁵ homogeneous particles over smooth surfaces; subsequently, Janus particles are obtained by knocking these particles off of their substrate after the monolayer is modified either by sputtering,¹⁶ stamp coating,¹¹ or Langmuir–Blodgett-based methods.¹⁷ The tight monolayer shields one side of the particles from being exposed to the modifying agents. Partial shielding of the homogeneous particles can also be brought about by partially embedding a monolayer of

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particles on a substrate¹⁸ or on a Pickering emulsion^{13,19,20} and then chemically modifying these particles in an aqueous phase or vapor phase.²¹ The procedure for synthesizing Janus particles by the partial shielding of particles using a Pickering emulsion followed by modification in the aqueous phase is the method that we employ.

Pickering emulsions are emulsions stabilized by particles instead of surfactants.^{22,23} About a century ago, Ramsden²³ discovered that fine solid particles can be used as stabilizers in emulsions instead of surfactants. The supracolloidal structures obtained using Pickering stabilization are also referred to as colloidosomes.^{19,24,25} Pickering emulsions have potential applications in controlled drug delivery and cosmetics, arising from the controllable permeability of the particle shell.^{26,27} The first reported technique was for the preparation of hollow spheres by the assembly of micrometer-sized sulfate latex particles at octanol-in-water emulsion interfaces.¹⁹ Weitz and co-workers first coined the term colloidosome and performed systematic work to prepare these capsules with controlled size, permeability, and mechanical strength.²⁸ Recent innovations in Pickering emulsion synthesis include magnetic colloidosomes²⁹ and templated supracolloidal structures.³⁰

In this article, we report the synthesis of novel Janus colloids with an anisotropic surface potential using a previously documented Pickering miniemulsion approach to form colloids with a polymer core and a nanoparticle shell.^{31–33} These colloids are further templated onto a second Pickering emulsion for chemical modification. After breaking this emulsion, we obtain Janus colloids with anisotropic surface potentials using different salts to modify the particle surface chemically. The proposed strategies will allow us precise control over surface potential and surface chemistry.

To our knowledge, the synthesis of large quantities of Janus colloids with an anisotropic surface potential, allowing a response to external stimuli, with a bulk processing method has not yet been accomplished. We use a two-stage approach to synthesize these colloids. The concept of immobilizing silica particles in a wax was previously reported by Granick et al.^{13,21} and is based on the preparation of a large number of wax colloids coated with native inorganic silica particles and the sequential modification of both sides of the silica particles with different silanes. In this work, the synthesized Janus silica particles had an amino group attached on one side and the other side was an unmodified silica surface. These Janus particles were dipolar in nature because of amine groups on one side that are positively charged in DI water and the native silanol groups of the silica on the other side that are negatively

charged in DI water. Because of opposite charges, these particles formed particle chains.

On the contrary, in our work the Janus nature of the colloids is attributed to anisotropy in the surface potential rather than the surface charge. The screening of surface charge by different ions on each hemisphere of the Janus colloids leads to anisotropic Debye lengths, which results in anisotropy in surface potentials. The latter anisotropy manifests itself in the colloids' nonuniform zeta potential. The Janus colloids in this work are observed to cluster rather than chain in water with a certain conductivity.

The novelty of our approach lies both in the use of the nanoparticle-stabilized colloids as a particulate stabilizer for the second-stage Pickering emulsion (wax-in-water) and in the use of cation exchange for anisotropic modification of the nanoparticles adsorbed on the surfaces of the colloids.

Results and Discussion

A solid-stabilized emulsion approach^{22,23} was used to synthesize colloids as well as to modify them to form Janus particles. Initially, a Pickering miniemulsion of styrene or divinylbenzene monomer in water was prepared using Laponite nanoparticles as solid stabilizers. The emulsion was polymerized to obtain polystyrene or poly(divinylbenzene) colloids stabilized by Laponite nanoclay particles. These colloids were subsequently used as particles-of-a-kind to stabilize an emulsion of molten paraffin wax in water, referred to as stage II emulsion. The emulsion was then allowed to cool to fix the colloids at the interface of the wax particles and water. The colloids were modified chemically from the aqueous phase using suitable salts as described later. After modification, the salts were removed by filtration from the emulsion and the wax was removed by washing with a solvent to release the Janus colloids. This simple technique is a modification of the toposselective approach recently demonstrated by Granick et al.^{13,21}

Stage I Pickering Emulsion: Synthesis of Colloids

Laponite RD is a synthetic trioctahedral hectorite mineral clay composed of a central octahedral magnesium sheet sandwiched between two tetrahedral silica sheets all bound by oxygen atoms. It has a chemical formula of $[\text{Si}_8(\text{Mg}_{5.45}\text{Li}_{0.4})\text{O}_{20}(\text{OH})_4]\text{Na}_{0.7}$. The clay platelets are circular and 25–35 nm in diameter with a thickness of approximately 1 nm and a density of 2570 kg/m³.³⁴ The clay has an overall negative charge on the surface with positively charged edges. The negative charge on the surface of the clay is stabilized by positively charged sodium (Na^+) ions adsorbed on the surface of the clay as indicated by the chemical structure. These electrostatically bound ions can be substituted by other positively charged ions in cation exchange reactions.^{35,36} Exchanging the bound ions will change the surface charge potential of the clays depending on the type of ions exchanged (i.e., the valence and the size of the ions being exchanged). This property of clay makes it possible for the Janus colloids to have anisotropic surface potentials on their hemispheres.

The clay gets dispersed in water spontaneously because of the like charges on the clay particles, which stabilizes the dispersion. Varying concentrations (0.025–0.2 M) of sodium salt (Na^+) were added to the dispersion to flocculate the clay platelets and enhance the ability of the clay platelets to form a Pickering emulsion. On addition of salt, in this case $\text{NaCl}(\text{aq})$, the charges on the platelets get screened. The screening lowers the zeta potential,

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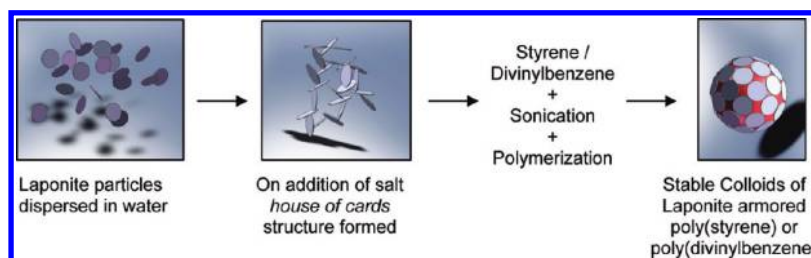


Figure 1. Schematic of the synthesis of Laponite nanoclay armored polystyrene or poly(divinylbenzene) colloids by a Pickering emulsion approach.

Table 1. Compositions of Pickering Emulsions Used to Study the Variation in Colloid Particle Size

experiment series no.	sample name	diameter (nm)	monomer mix (g)	NaCl concentration (M)
A	A1	258.30	3.00	0.000
	A2	177.03	1.01	0.000
	A3	274.03	5.09	0.000
	A4	305.00	9.00	0.000
B	B1	289.63	3.01	0.100
	B2	149.33	1.18	0.100
	B3	518.26	5.13	0.100
	B4	800.00	8.16	0.100
C	C1	274.03	5.09	0.000
	C2	461.40	5.11	0.050
	C3	296.30	5.13	0.025
	C4	518.26	5.13	0.100
	C5	540.00	5.13	0.200

thereby reducing the electrostatic repulsion and inducing the agglomeration of the Laponite platelets. Agglomerates of Laponite form a “house of cards” configuration that causes the media to form a viscous gel because of the positively charged edges and the negatively charged surfaces. In doing so, the salt helps to improve the partitioning of the platelets to the monomer–water interface, allowing it to act as a stabilizer for the emulsion.

Pickering miniemulsions were formed by dispersing the nanoclay in water, adding salt to the dispersion, adding the monomer mixture, and then sonicating to form the emulsion. The monomer mixture consisted of styrene or divinylbenzene monomer, azobisisobutyronitrile (AIBN) as the oil-soluble initiator, and hexadecane as the hydrophobe to prevent the ripening of the emulsion droplets.^{37,38} A schematic for the synthesis of the Laponite armored colloids or stage I emulsion is summarized in Figure 1. The emulsion was polymerized by heating in water at 60 °C for 48 h to obtain either polystyrene or poly(divinylbenzene) colloids stabilized by Laponite nanoclay platelets, which lay flat on the oil–water interface.³³

Effect of NaCl(aq) Salt Concentration on the Colloids

Three series of emulsions were prepared to determine the effect of the salt (NaCl) concentration on the particle size of the colloids. The compositions are shown in Table 1.

The monomer mixture for the synthesis of colloids contained styrene or divinylbenzene monomers, 8 wt % of hexadecane as the hydrophobe,^{37,38} and 3 wt % AIBN as the oil-soluble initiator. The first series of experiments (A) was conducted without NaCl(aq) and with varying concentrations of the monomer mixture. The second series (B) was conducted with 0.1 M NaCl(aq) and varying concentrations of the monomer mixture. The third

series (C) used varying concentrations of NaCl(aq) and a fixed monomer concentration. All three series used 100 g of water and 0.25 g of Laponite platelets. After sonication to form the emulsions, the emulsions were polymerized and then washed by filtration using a nitrocellulose membrane filter with a 200 nm pore size to remove the excess salt in the aqueous phase. Because the Laponite platelets are ~20 nm, they were removed while the colloids were left behind on the filter. The particle sizes of the emulsions were measured using a Malvern Zetasizer via a dynamic light scattering method. It was observed that all of the samples gave a unimodal particle size distribution. The histogram for sample A1 is shown in Supporting Information Figure S1.

From the particle size measurements, the excess number of Laponite platelets can be calculated by the equation³²

$$C_{\text{excess}} = C_0 - \frac{3\pi}{2} \left(\frac{\rho_{\text{part}}}{\rho_{\text{oil}}} \right) \left(\frac{h}{d_{\text{oil}}} \right) C_{\text{oil}} \quad (1)$$

where C_0 is the weight of Laponite platelets added to the emulsion, ρ_{part} is the density of the Laponite platelets, ρ_{oil} is the density of the monomer mix, d_{oil} is the diameter of the colloids, h is the height of the Laponite platelets, C_{oil} is the weight of the monomer mix, and C_{excess} is the weight of the excess amount of Laponite that remained in the aqueous phase and did not take part in the emulsion.

The second term in eq 1 expresses the weight of Laponite platelets that did take part in stabilizing the emulsion. The weight of excess Laponite particles was calculated to be in the range of 45–60% of the total amount of Laponite added to the emulsion. Therefore, it was necessary to separate the excess Laponite from the colloids formed so that it did not interfere with the Janus modification of the colloids. This was accomplished during the salt filtration step mentioned previously.

Effect of Monomer and NaCl(aq) Concentrations on Colloids

In Figure 2a, the effect of monomer concentration on the zeta potential at a fixed NaCl(aq) concentration (0.1 M) is seen. The principal reason for determining the zeta potential of the colloidal dispersions was to obtain an indication of the magnitude of the beginning of the diffuse double layer around the colloids. This can then be used to determine the effect of colloidal surface charge on such things as aggregation behavior and stability. The zeta potential increases up to ~5 g/100 mL of monomer, after which it becomes constant at ~60 mV. This indicates that the presence of NaCl(aq) contributes to the stability of the Laponite armored colloids at higher monomer concentrations.

The variation in the colloid particle size as a function of monomer concentration without and with 0.1 M NaCl(aq) is shown in Figure 2b.

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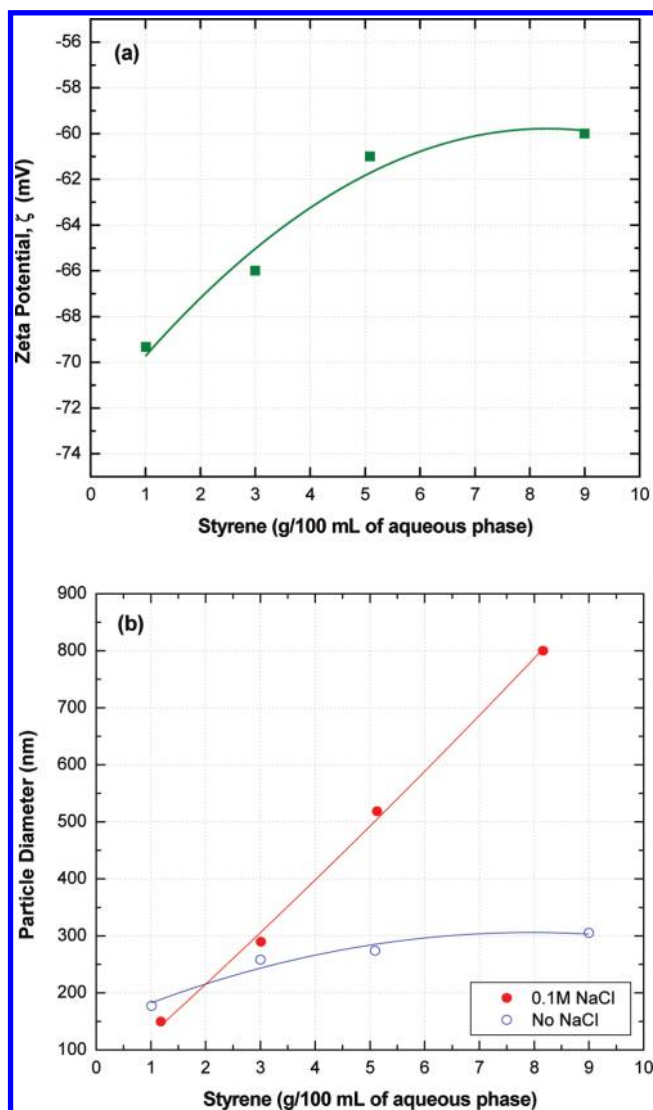


Figure 2. Variation in the (a) (■) zeta potential at 0.1 M NaCl(aq) and (b) particle size as a function of monomer concentration at (red ●) 0.1 M and (○) 0 M NaCl(aq) concentrations.

The colloid size increased with increasing monomer concentration. Specifically, at 0.1 M salt concentration, the colloid particle size increased linearly with increasing monomer concentration. A similar trend was observed when divinylbenzene was used in the monomer mix instead of the styrene. This is because the surface area of the stabilized interface remained constant because the number of Laponite nanoparticles in the aqueous phase remained the same while the volume of the oil phase (monomer) added to the emulsion varied. Thus, the surface area to volume ratio decreased with increasing monomer content, leading to the growth of colloid particle size as illustrated in Figure 2b. This behavior, however, is not observed with the series of emulsions prepared without NaCl(aq). In the latter case, the colloid particle size increased up to a critical monomer concentration (3 g/100 g water) and remained constant despite further increases in monomer volume.

It is speculated that this behavior is due to the fact that the Laponite particles cannot approach each other in a flat configuration if their surface charges are not screened because the edges of Laponite are positively charged and the faces are negatively charged. Subsequently, as the droplet diameter increased, the curvature of the interface decreased. Repulsion of the platelets

prevented them from adsorbing at the interface to lie flat adjacent to each other, thereby hindering their ability to stabilize large emulsion droplets. In this case, the platelets stabilize smaller droplets having a greater interface curvature where they could adsorb at an angle to each other (< 300 nm) as illustrated in Figure 3. In the absence of salt, there was no phase separation of any monomer with increasing monomer concentration. At higher monomer concentration, the interfacial area of the droplets increases. Therefore, to obtain the maximum droplet size that formed a stable emulsion, it was assumed that the amount of Laponite partitioned to the oil–water interface increases to compensate. This is the most plausible mechanism of stabilization in the absence of salt. When salt (0.1M NaCl) is used, the repulsion between the clay platelets is screened so that they can lie flat adjacent each other in order to stabilize larger droplets having a lower interfacial curvature.

In Table 1, it can be seen that the largest droplet sizes are obtained in the presence of NaCl(aq) and increase as a function of NaCl(aq) concentration. The aim of the third series of experiments was to determine the minimum NaCl(aq) concentration required to screen the charges between the Laponite platelets. This is done to optimize the colloid particle size with increasing monomer concentration. From Figure 4, it can be observed that a minimum concentration of 0.055 M NaCl is necessary for 0.25 g of Laponite to form colloids above 500 nm.

In Figure 5, the SEM image of the colloids depicts their relatively broad particle size distribution. A better understanding of the mechanisms governing the stability of these solid-stabilized emulsions requires the use of model systems with a monodisperse particle size distribution, and these studies will be published at a later date.

Modification of Colloids by Cation Exchange

Our hypothesis is that the cation exchange of sodium ions, Na^+ , for calcium ions, Ca^{2+} , on the surface of the nanoparticle-stabilized emulsion after polymerization will result in a colloidal particle that has a net negative charge, but with a heterogeneous distribution of charges with monovalent ions on one hemisphere and divalent ions on the other.

Colloids with a particle size of ~ 520 nm as indicated by samples C4/B3 were chosen for chemical modification. The modification of the colloids involved the exchanging of sodium (Na^+) ions on the Laponite nanoclay platelets with calcium (Ca^{2+}), ferrous (Fe^{2+}), and ferric (Fe^{3+}) ions. Initially, the colloids were modified completely to determine which ion gave the maximum difference in the electrical surface potential. The electrical surface potential is proportional to the surface charge density. The surface charge is related to the surface potential by the following equation³⁹

$$\sigma_o = \epsilon_r \epsilon_o \kappa \phi_o \quad (2)$$

where σ_o is the surface charge density, $\epsilon_r \epsilon_o$ is the product of the permittivity of the related media and vacuum, respectively, κ is the inverse of the Debye length, and ϕ_o is the potential at the surface.

Because the surface charge of all of the Laponite nanoparticles can be assumed to be the same, the surface charge of the ion-exchanged Laponite nanoparticles (on the colloids) is equivalent to that of the originally obtained Laponite nanoparticles with sodium ions on the surface. The surface charge depends upon the cation exchange capacity of the Laponite, and it is assumed that the surface charge remains the same throughout the course of the experiments. Thus, from eq 2 we can equate the surface charges of

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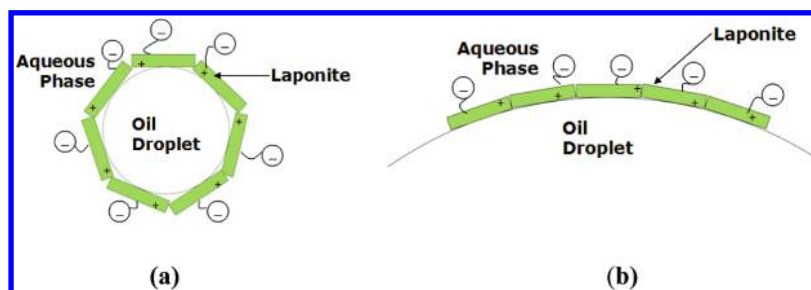


Figure 3. (a) The colloid without salt has a maximum limiting diameter because the charges between the Laponite particles are not screened, so they cannot lie flat in close proximity to each other. (b) On adding NaCl(aq), this becomes possible, allowing the particles to lie flat adjacent to each other, and thus the diameter of the particle can be controlled by adjusting the ratio of oil and Laponite.

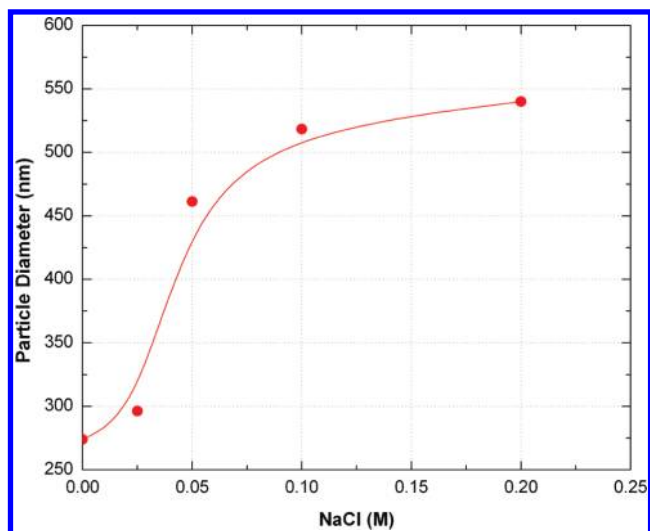


Figure 4. NaCl(aq) concentration plays a significant role in the particle size variation of colloids. At a fixed monomer, Laponite, and water concentration, the particle size increased up to a critical value (~ 520 nm) as the NaCl(aq) concentration increased.

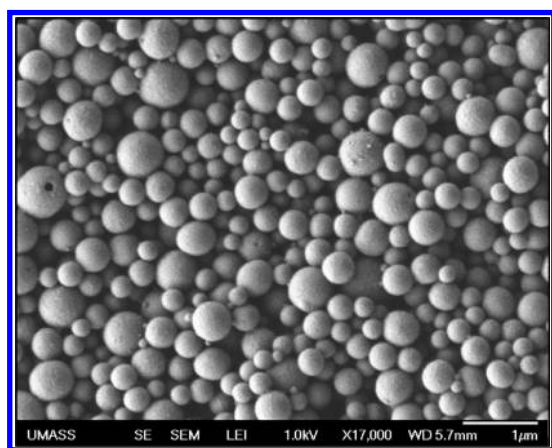


Figure 5. SEM image of the colloids illustrating their relatively broad particle size distribution.

the sodium-adsorbed Laponite particles and the ion-exchanged Laponite particles. Because the medium (water) will have the same dielectric permittivity, we obtain

$$\frac{1/\kappa_N}{1/\kappa_C} = \frac{\phi_{oN}}{\phi_{oC}} \quad (3)$$

where subscripts C and N are for exchanged ions and the initial sodium ions, respectively.

The Debye length is given by the equation

$$\frac{1}{\kappa} = \left[\frac{\epsilon_r \epsilon_0 k T}{1000 e^2 N_{AV} \sum_i Z_i^2 c_{io}} \right]^{1/2} \quad (4)$$

where $\epsilon_r \epsilon_0$ is the product of the permittivity of the related medium and vacuum, respectively, k is the Boltzmann constant, T is the temperature in Kelvin, e is the charge on an electron, N_{AV} is Avogadro's number, Z_i is the valence of ion i , and c_{io} is the concentration of the ions in moles per liter.

For our colloids, the Laponite nanoparticles (modified or unmodified) are dispersed in the same medium (i.e., water). Thus, it is assumed that they possess the same thermal energy kT . The only differences lie in the valence and the concentration of the cations adsorbed onto the surfaces of the Laponite nanoparticles. As stated earlier, because the surface charge density remains constant, the negative charges on the surface of the Laponite will remain constant and hence a monovalent ion will be replaced by only half the number of divalent ions and so on. That is, every available Na^+ ion on the surface of Laponite needs only half the corresponding number of Ca^{2+} ions to be replaced. Therefore, the ratio of the electrical surface potentials can be written as shown in eq 5. If we consider the Na^+ ions to be completely exchanged by Ca^{2+} ions, then the following change in surface potential is obtained:

$$\frac{1/\kappa_N}{1/\kappa_C} = \left[\frac{\sum_i Z_{iC}^2 c_{iC}}{\sum_i Z_{iN}^2 c_{iN}} \right]^{1/2} = \left[\frac{2^2 \times 1}{1^2 \times 2} \right]^{1/2} \quad (5)$$

$$1/\kappa_N = 1.411/\kappa_C$$

Thus, it can be hypothesized that the Debye length of the colloids with the original Na^+ ions adsorbed on Laponite will be 1.411 times longer than that on the colloids with Ca^{2+} ions exchanged. The exact values of the Debye length cannot be predicted because the exact concentrations of calcium and sodium cannot be determined and only relativistic concentration values can be calculated as shown above.

Moreover, the Debye length cannot be measured. The Debye length arises naturally in considering the screening of a source of electrical potential by a cloud of charged particles in the double layer whose density is determined by their energy in the electrical potential. As such, the zeta potential will be measured instead. The zeta potential is widely used for the quantification of the magnitude of the electrical charge at the double layer. The zeta potential, however, is not equal to the electrical surface potential in the double layer but is an approximation that can be applied using

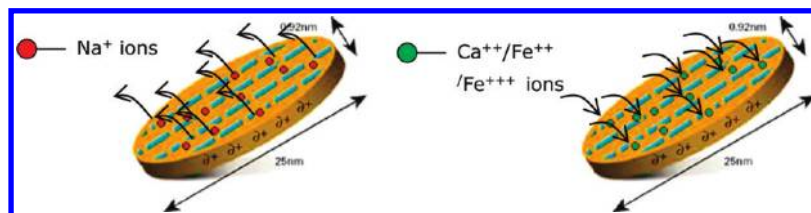


Figure 6. Schematic representation of the mechanism of chemically modifying a Laponite platelet by the cation exchange of Na^+ ions on the surface: (left) unmodified and (right) modified Laponite.

Smoluchowski's theory⁴⁰ under certain limitations.⁴¹ Given these limitations, the zeta potential is defined mathematically by Henry's equation³⁹ as

$$\mu_e = \frac{\varepsilon_r \varepsilon_0 \zeta}{\eta} f(\kappa R, \zeta) \quad (6)$$

where μ_e is the electrophoretic mobility, $\varepsilon_r \varepsilon_0$ is the product of the permittivity of the related media and vacuum, respectively, ζ is the zeta potential, η is the viscosity of the medium, R is the radius of the particle, and κ is the inverse of the Debye length. Thus, the mobility of a particle varies in direct proportion to the zeta potential.

Colloid modification was performed by conducting ion-exchange reactions as stated in the literature.^{35,36} Ion-exchange reactions require a high concentration of exchangeable cations under weakly acidic conditions. The ion-exchange procedure involved the removal of excess sodium chloride from the colloids, which was used to screen the repulsion between the Laponite nanoclay particles by filtering through a porous nitrocellulose membrane with average pore size of 200 nm. The complete removal of excess salt was ensured by measuring the conductivity of the colloid solution, which was found to be near that of deionized water. The colloids were maintained at an acidic pH of 2.5 by adding ascorbic acid. The colloids were then ion exchanged with chloride salts in 1 M solutions. Calcium(II) chloride, ferrous(II) chloride, and ferric(III) chloride were used as modifying salts for different batches of colloids. The colloids were stirred in solution with the salts for 24 h to ensure complete ion exchange with the Na^+ ions on the Laponite. The excess salt was removed by filtration using a nitrocellulose membrane. The cation-exchange mechanism for modifying Laponite platelets on the colloids is illustrated in Figure 6.

The zeta potentials of the different modified colloids were measured at varying colloid concentration with the Malvern Zetasizer using the Helmholtz–Smoluchowski equation.³⁹ The Helmholtz–Smoluchowski equation is a simplified form of Henry's equation that uses a constant of 1 in place of the complex function $f(\kappa R, \zeta)$. The zeta potentials of the different modified colloids are indistinguishable as shown in the Supporting Information (Figure S2). It was not possible to resolve the difference between the zeta potentials of the various modified colloids. This may be due to the lack of charge screening on the Laponite armored colloids. The Debye length at low salt concentrations is calculated from eq 6 to be approximately $1 \mu\text{m}$ in the absence of CO_2 in the air in contact with the salt solutions. A minor change in Debye length due to exchanged cations would not cause a significant difference in the zeta potentials of the different modified

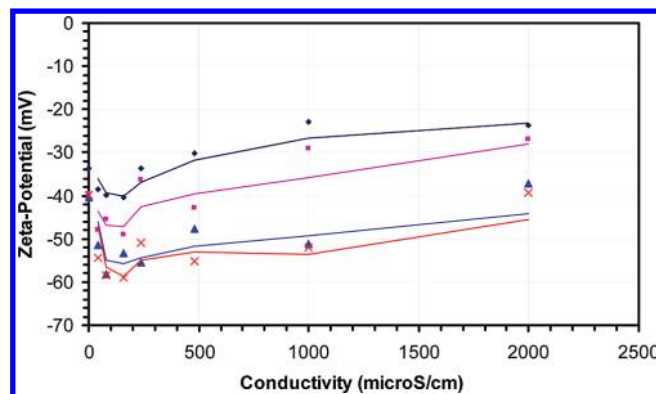


Figure 7. Zeta potential of modified colloids at a fixed concentration and at varying salt (NaCl(aq)) concentration: (◆) $\text{CaCl}_2(\text{aq})$ -modified, (pink ■) $\text{FeCl}_3(\text{aq})$ -modified, (blue ▲) $\text{FeCl}_2(\text{aq})$ -modified, and (red ×) unmodified. The zeta potential increased as the salt concentration increased for the different completely modified colloids. $\text{CaCl}_2(\text{aq})$ -modified colloids give the maximum change in the zeta potential as compared to the unmodified colloids (with Na^+ ions on the surface of Laponite). (The lines represent a two-point moving average to visualize the trend in the zeta potential better.)

colloids given by eq 5. If, however, the Debye length was reduced to nanometers, then a change in the Debye length would be reflected in the zeta potential.

Effect of Cation Exchange on the Zeta Potential

This hypothesis was tested in the next series of experiments. The reduction of the overall Debye length was accomplished by changing the conductivity by the addition of NaCl(aq) to the modified colloids, thereby screening the repulsions between them. NaCl(aq) was added in very low concentrations, and the zeta potential measurements were taken immediately to ensure that the Na^+ ions were not re-exchanged with the Ca^{2+} , Fe^{2+} , or Fe^{3+} ions. The zeta potential as a function of conductivity is shown in Figure 7. The measurements were made at a fixed concentration of colloids of 0.015% by weight, and the conductivity was varied by changing the NaCl(aq) concentration. It was observed that replicate readings were reproducible within a day of measurement and no flocculation of colloids was observed. It is important to note here that it was not possible to measure the minimum and maximum values of the zeta potential for the unmodified Laponite nanoparticles because upon the addition of salt (NaCl(aq)) a gel is formed (house of cards structure as shown in Figure 1). The standard deviations over all of the zeta potential readings were $\pm 2 \text{ mV}$.

The unmodified colloids gave the maximum negative zeta potential as expected. They are followed by Fe^{2+} -modified, Fe^{3+} -modified, and Ca^{2+} -modified colloids. This order is expected because the Fe^{2+} and the Fe^{3+} ions tend to be oxidized and their effective charges will be reduced. On the contrary, Ca^{2+} ions will not be easily oxidized, resulting in the maximum amount of

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(41) Detailed theoretical analysis proved that Smoluchowski's theory is valid only for a sufficiently thin double layer, when the Debye length, $1/\kappa$, is much smaller than the particle radius. Also, Smoluchowski's theory neglects the contribution of surface conductivity. This is expressed in modern theories as the condition of a small Dukhin number. See Dukhin, S. S.; Semnikhin, N. M. *Koll. Zhur.* **1970**, 32, 366.

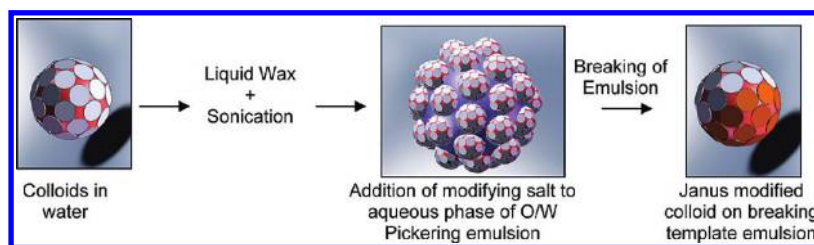


Figure 8. Schematic for the formation of Janus colloids using a Pickering (stage II) emulsion as a template. The poly(divinylbenzene) colloids are used as solid stabilizers for the purpose of Janus modification. First, the colloids stabilize a wax-in-water emulsion. Second, a modifying salt ($\text{CaCl}_2(\text{aq})$) is added to the emulsion. The Laponite disks on the aqueous side are ion exchanged, and upon breaking this emulsion, Janus colloids are obtained.

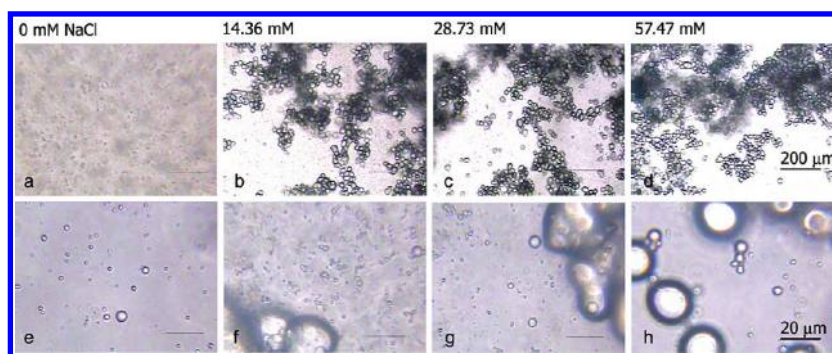


Figure 9. Optical micrographs illustrating the effect of $\text{NaCl}(\text{aq})$ concentration on the particle size of the templating (stage II) emulsion. As the $\text{NaCl}(\text{aq})$ concentration increased, the turbidity of the aqueous phase of the emulsion vanished and more droplets with a larger particle size were observed.

charge screening. (Evidence for this oxidation lies in the fact that the zeta potential and the conductivity of Fe^{2+} -modified colloids changed with time.)

Initially, the zeta potential measurements give a more negative value that slowly becomes positive with increasing salt concentration. This contradicted the expected result because a higher salt concentration will screen the charges and reduce the zeta potential/electrical surface charge potential even further. It is speculated that this is an artifact of the complex dependence of the $f(\kappa, R, \zeta)$ relationship in Henry's equation for which we assume a value of 1. This can be explained given the fact that as salt is added the hydrodynamic radius of the particle will initially decrease because of a reduction in the Debye length and the colloid will be able to travel at a higher velocity through the aqueous phase toward the oppositely charged electrode. As more salt is added to the aqueous phase, however, the charges on the colloid will be screened and their surface potential will decrease, resulting in a decrease in the attraction toward the oppositely charged electrode, hence slowing it down. This behavior was observed with clay suspensions by other researchers.³⁶ Because the calcium ions gave the maximum screening and are not affected by oxidation, calcium(II) chloride was used in all subsequent preparations of Janus colloids.

Stage II Pickering Emulsion: Janus Modification of Colloids by CaCl_2

To prepare Janus colloids, it is first necessary to prepare the stage II Pickering emulsion with the colloids as solid stabilizers. The schematic for the preparation of Janus colloids is shown in Figure 8.

To prepare stable stage II wax-in-water Pickering emulsions using the unmodified colloids as solid stabilizers, it was first necessary to determine whether NaCl (used to screen the charges

between Laponite while forming the colloids) needed to be removed. Colloids with a particle size of 250 nm were synthesized without NaCl . Stage II Pickering emulsions were then prepared using the colloids as solid stabilizers. A concentration of 10 g of a 25 wt % colloid suspension in 60 g of water along with 5 g of purified coconut oil (a mixture of low-molecular-weight hydrocarbons) was used to prepare these stage II Pickering emulsions.

The effect of increasing $\text{NaCl}(\text{aq})$ concentration on the particle size was determined to optimize the stage II wax colloid particle size. Four batches were prepared by sonication to form Pickering emulsions. It was expected that the colloids would stabilize the coconut-oil-in-water emulsion. The batches were cooled to 5°C to solidify the oil phase and then were observed under the microscope. Optical images (Figure 9) show large emulsion droplets and very small colloids floating in the water (continuous phase).

From the optical micrographs in Figure 9, we observed that at a relatively high $\text{NaCl}(\text{aq})$ concentration (d, h) of 57.47 mM there are a greater number of large spherical drops that appear to be flocculated. At moderate $\text{NaCl}(\text{aq})$ concentrations of 14.4 and 28.7 mM (b, c, f, g), there are fewer large flocculated droplets and a greater number of small droplets. Without $\text{NaCl}(\text{aq})$, there are very few large droplets present (a, e). The large droplets are attributed to stabilized oil-in-water emulsions, and the smaller droplets are attributed to colloids and excess Laponite, which is still present and is used to stabilize the oil phase. Thus, we can conclude from Figure 9 that a minimum of 0.058 M salt is needed to form a stable emulsion with the colloids stabilizing the droplets. The sodium chloride aids in screening the charges between the colloids, allowing them to approach each other to form the Pickering emulsion, just as in the case where the Laponite charges needed to be screened to form the stage I colloids. It was also observed that upon removal of sodium chloride by dialysis the emulsion did not break.

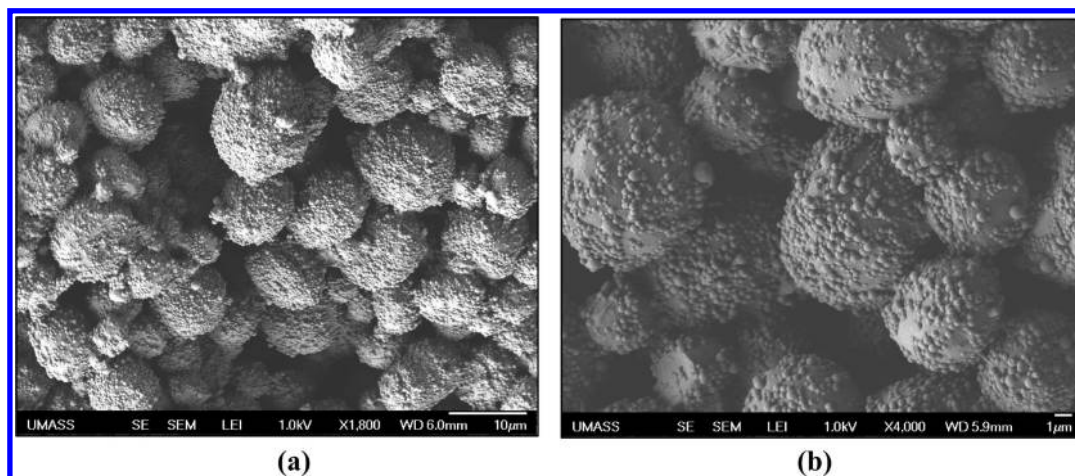


Figure 10. SEM images of colloid-stabilized wax particles: (a) dried wax-in-water stabilized by 450 nm colloids as solid stabilizers; (b) incomplete colloid coverage on wax due to imperfect washing or detachment of colloids during SEM sample preparation. Surface modification was performed at room temperature using wax whose melting point (Experimental Section) was 60 °C.

The large droplets in the stage II emulsion were used as a template to synthesize the Janus colloids. The colloids used to form Janus particles were composed of Laponite armored poly(divinylbenzene) colloids approximately 520 nm in diameter. The change in material from polystyrene to poly(divinylbenzene) is justified later in this article. The same recipe was used to synthesize the ~520 nm poly(divinylbenzene) colloids and the ~520 nm polystyrene colloids. Wax was used as the oil phase for the stage II emulsion. The colloids acted as particulate stabilizers to form a wax-in-water emulsion. Coconut-oil–wax (6 g) was melted by heating to 60 °C and was added to a 70 g aqueous phase containing 1.5% colloids with an ~520 nm particle size and 0.1 M sodium chloride. The emulsion was sonicated to obtain a Pickering emulsion of wax-in-water stabilized by the colloids. The emulsion was then allowed to cool to obtain dried wax-in-water colloids as shown in Figure 10.

Sodium chloride was necessary to form the emulsion as stated earlier. The size of the emulsion droplets was observed on a dynamic light scattering instrument as well as on an SEM instrument, as shown in Figure 10.

The emulsion droplets shown in the Supporting Information (Figure S3) were observed to vary in size from 10 to 60 μm with a mean peak size of ~14 μm . The shoulder observed was that of excess colloids in the aqueous phase that did not take part in the formation of the emulsion. The emulsion droplets creamed because of their large droplet size and density difference between wax and water. A clear aqueous phase was observed beneath the cream. The sodium chloride was removed by dialysis for 48 h so that the modifying salt could be introduced into the emulsion. After dialysis, the emulsion cream at the top was still present but the aqueous phase beneath became turbid. On analysis, this turbid phase was found to contain particles of ~520 nm in diameter. These particles were excess colloids that did not participate in stabilizing the emulsion. These excess colloids in the aqueous phase were removed by first filtering through a 2 μm Whatmann filter paper. The emulsion was then allowed to stand for 1 h and was separated. Calcium(II) chloride (1 M) was added to the emulsion along with 0.05 M ascorbic acid to maintain an acidic pH of 2.5 for cation exchange. The stage II emulsion containing our colloids was stirred to facilitate the cation exchange of Na^+ ions with Ca^{2+} ions on the Laponite surface. The water along with the modifying salt was removed after 24 h via a filtration membrane in order to retain only the organic phase and wax

from the emulsion. Next, the wax was dissolved in chloroform to leave only free colloids. For this purpose, the polystyrene colloids were replaced with poly(divinylbenzene) colloids for the formation of Janus colloids. This was done because polystyrene dissolves in chloroform and poly(divinylbenzene) does not because of its cross-linked network. Divinylbenzene was not used as just a cross-linking agent with polystyrene during the removal of wax with chloroform because the swelling of the cross-linked polystyrene colloids would have led to the desorption of the Laponite nanoparticles from the surface of the colloids. Colloids synthesized with 100% divinylbenzene would not dissolve or swell in chloroform and as such were used instead of styrene. The colloids were then filtered from the chloroform–wax solution using a filtration membrane as described before. These colloids adsorb on the wax–water interface during chemical modification. As a result of this partitioning, the colloids were shielded by the wax phase on one hemisphere, leaving the other hemisphere exposed to the aqueous phase. The cation exchange was then conducted from the aqueous phase on one hemisphere of the colloid. On subsequent destabilization of this stage II emulsion, the Laponite armored poly(divinylbenzene) colloids obtained had anisotropic surface charges of Na^+ ions on one hemisphere and Ca^{2+} ions on the other hemisphere, resulting in Janus colloids as shown in Figure 8.

Evidence of Janus Modification: 1. Zeta Potential Study

The zeta potentials of the Janus CaCl_2 -modified colloids were compared with the zeta potentials of the colloids completely modified by $\text{CaCl}_2(\text{aq})$ and the original unmodified colloids (with Na^+ on the surface of Laponite). The synthesis procedure for preparing completely modified and unmodified colloids is described in the Experimental Section.

The zeta potential of 0.015 wt % colloids as a function of conductivity is shown in Figure 11. The conductivity was varied by changing the $\text{NaCl}(\text{aq})$ concentration. The completely CaCl_2 - (aq) -modified colloids had a smaller negative zeta potential as compared to that of the unmodified colloids (i.e., those having Na^+ ions adsorbed on them). This result was expected as reasoned earlier with the poly(divinylbenzene) colloids. The ratio of the zeta potential of the unmodified and the completely modified colloids, $\zeta_{\text{Na}^+}/\zeta_{\text{Ca}^{2+}}$, varies from 1 to 1.41 as the conductivity is increased. At higher conductivity values, the zeta potential ratio

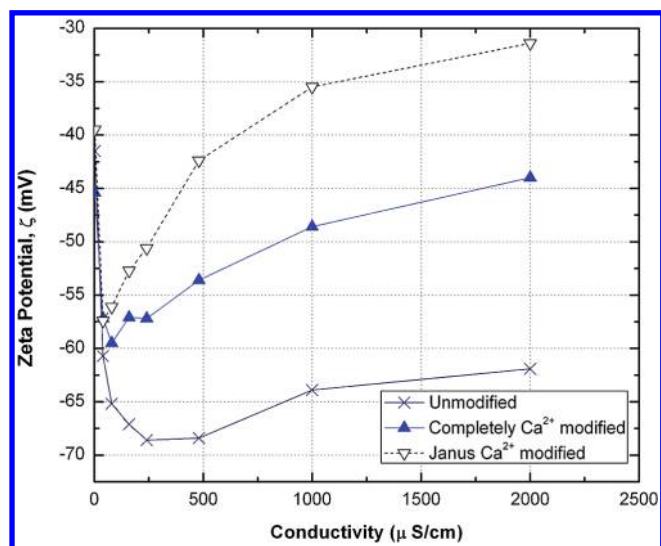


Figure 11. Effect of surface charge modification on the zeta potential of colloids. Modification was conducted using $\text{CaCl}_2(\text{aq})$ salt. (Blue \times) Unmodified, (blue \blacktriangle) $\text{CaCl}_2(\text{aq})$ -modified, and (∇) Janus $\text{CaCl}_2(\text{aq})$ -modified colloids. Note that the $\zeta_{\text{Na}^+}/\zeta_{\text{Ca}^{2+}}$ ratio is ~ 1.41 as predicted in eqs 3 and 5.

matches the value of 1.411 estimated from eqs 3 and 5. The Janus colloids, however, unexpectedly gave the smallest negative zeta potential among the three systems. Repeated measurements confirmed these results. This behavior for the Janus colloids is puzzling. It was expected that the values of the zeta potential of the Janus colloids would be between those of the completely modified and unmodified colloids, but the above trend was observed. One plausible explanation is that this may be an artifact of how the zeta potential is measured using the Malvern Zetasizer. The Malvern Zetasizer uses a fast field-reversal technique to suppress the flow of media due to electroosmosis at the walls of the measuring cuvette. Fast field reversal essentially reverses the electrical field to which the colloid is exposed a number of times per second. This does not significantly affect the unmodified and completely modified colloidosomes. In the Janus colloids, however, if there are anisotropic surface potentials, then this will result in an anisotropic Debye length that in turn leads them to exhibit a lower electrophoretic mobility and hence to display lower negative values of the zeta potential as predicted by eq 6. This anisotropic or nonuniform zeta potential is affected by the field reversal as studied by Anderson et al.⁴² for colloidal doublets with dipolar charges. They observed that when a colloid has anisotropic surface potentials it tends to get oriented in the direction of the direct current electrical field where the side with higher potential orients toward the oppositely charged electrode. When the direction of the field is changed, the anisotropic colloid will rotate and align its orientation to match the electrical field. The timescale for this rotation is a few seconds as noted by Anderson et al.⁴²

It is tempting to think of the electrophoretic mobility of a heterogeneous, anisotropic particle as a measure of its average charge when in fact it has a nontrivial dependence on the spatial distribution of surface charge.^{43–47} This is clearly demonstrated by a counter example of Long and Ajdari, motivated by chainlike

polyelectrolytes such as DNA molecules.⁴⁷ In linear electrophoresis, a spherical particle of nonuniform surface charge (or zeta potential) can move perpendicular to the field but only for certain orientations; it can also rotate but only transiently to align its dipole with the field axis.⁴³ Hence, we speculate that the fast field reversal in the Malvern Zetasizer causes our Janus colloid to rotate in response to the switching in the field. Because the colloids possess a net positive charge, they will continue to travel toward the electrode but the net result is slower electrophoretic mobility than what is predicted using Smoluchowski's equation.⁴⁰ Smoluchowski's theory⁴⁰ considers homogeneous particles, which are uniformly charged, so when this theory is applied in the Malvern Zetasizer to measure the electrophoretic mobility for colloids with anisotropy in surface potentials, the complexity of the nonuniform, heterogeneous zeta potential must be taken into account to obtain the true value. Subsequently, the true value of the zeta potential cannot be obtained unless the asymmetry of the surface potential is taken into account.

From an experimental point of view, much remains to be done to characterize the motion of these Janus colloids with heterogeneous anisotropic surface potentials in electrical fields, and this is the subject of ongoing research.

Evidence of Janus Modification: 2. Clustering Behavior of Janus Colloids

In the absence of direct zeta potential measurements, alternate experiments were performed to characterize the anisotropy in surface potential. From Figure 12, it is observed that the Janus-modified colloids aggregate into clusters whereas the unmodified colloids do not when suspended in an aqueous solution with a conductivity of 1000 $\mu\text{S}/\text{cm}$ adjusted with $\text{NaCl}(\text{aq})$. This phenomenon was observed in the aqueous phase and was observed through optical microscopy. The completely modified colloids formed flocs upon standing for 48 h, which was not observed for the Janus-modified and unmodified colloids. It is speculated that this is an example of repulsion among the like-charged spheres with long-range attraction due to the screening of the charges on one side. In so doing, this provides evidence of Janus modification by the cation exchange of Na^+ ions for Ca^{2+} ions.

In both water and oil, the range of electrostatic forces is on the order of the Debye length,

$$l_D = \left[\frac{\epsilon_0 \epsilon k_B T}{(2e^2 c)} \right]^{1/2} \quad (7)$$

where ϵ_0 is the permittivity of free space, ϵ is the zero-frequency dielectric constant of the medium, and c is the number density of ions.

It is speculated that replacing monovalent Na^+ with divalent Ca^{2+} ions resulted in the shrinkage of the Debye length only on the ion-exchanged side, as shown in Figure 13. This would occur because the surface potential would remain the same irrespective of the type of ions adsorbed on the colloids because the anionic charge on the Laponite platelets does not vary and the bound cations would act only to screen the charges of these negative charges depending on their valency, thus varying the Debye length. This anisotropic Debye length allows the colloids to approach each other only from that side where the charges are screened better by the Ca^{2+} ions (exchanged on Laponite for the Na^+ ions). This clustering occurs at longer-ranged distances than could reasonably be expected from van der Waals forces, which dominate at very short range.⁴⁸ Although this concentration of

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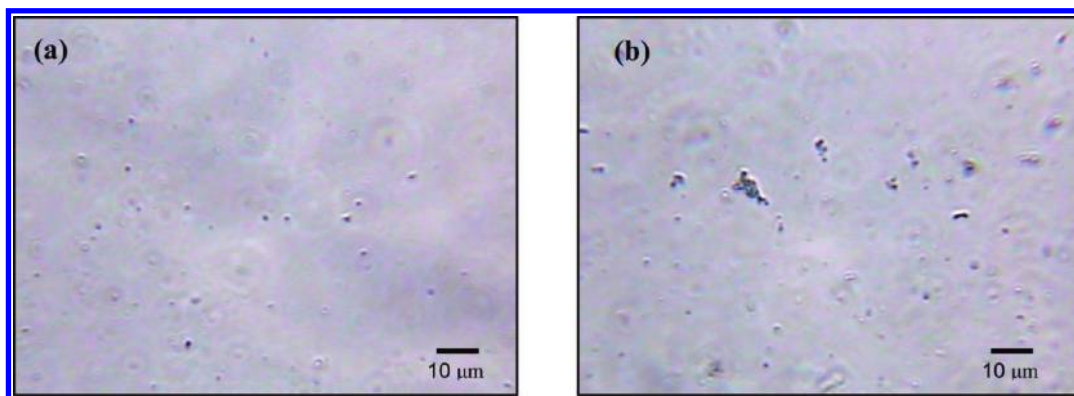


Figure 12. (a) Unmodified colloids showing the absence of clustering and (b) Janus colloids showing clustering. It is important to note that the completely modified colloids flocculated upon standing and so no images were obtained.

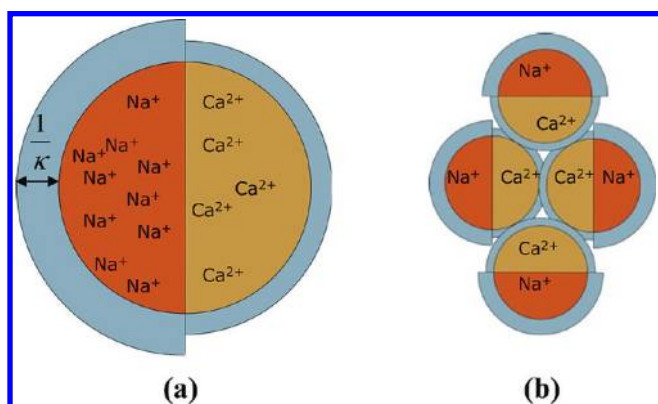


Figure 13. Schematic illustration of the clustering behavior of Janus colloids. (a) Exchanging Na^+ ions for Ca^{2+} ions results in a differential surface potential that in turn leads to an asymmetric Debye length ($1/\kappa$) allowing the Janus colloids to approach each other and (b) aggregate into clusters (idealized four-particle cluster shown).

NaCl(aq) is not enough to screen the charges from the unexchanged side with Na^+ ions, a partial repulsion exists that inhibits the flocculation of all of the particles.^{48–52}

Evidence of Janus Modification: 3. Elemental Analysis of Colloids by XPS

Initially, energy-dispersive X-ray spectroscopy (EDS) coupled with scanning electron microscopy (SEM) was used to determine the chemical composition of colloids, but it was not sensitive enough to detect the presence of the adsorbed ions on the Laponite nanoparticles. Instead, X-ray photoelectron spectroscopy (XPS) was used to verify the successful modification of colloids with Ca^{2+} ions. The XPS spectrum is shown in Figure 14, and the data for the sodium atom percent compared to the magnesium atom percent is illustrated in Table 2. The unmodified colloids gave the highest sodium ion content; the completely modified colloids gave the lowest and the Janus colloids gave an intermediate Na^+ ion content as measured by atom wt %. It was not possible to observe the intensity of any of the calcium peaks because they were overlapped by magnesium auger peaks. These results were expected and provided further evidence that Janus

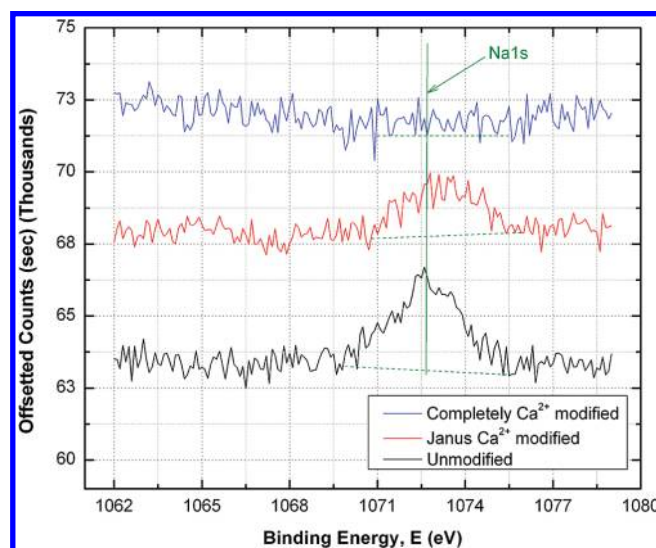


Figure 14. XPS analysis of colloids: unmodified, completely modified, and Janus, obtained from wax (stage II emulsion) were compared with each other for the Na^+ atom wt % with respect to magnesium (Mg^{2+}). It was observed that the atom wt % of the Na 1s peak decreased as the Ca^{2+} modification increased, with the unmodified colloid showing the highest, the completely modified showing the lowest, and the Janus Ca^{2+} -modified showing an atom wt % intermediate between both.

Table 2. Relative Atom Weight Percentages of Magnesium and Sodium in Different Colloids from XPS Peaks

element	unmodified (%)	Janus (%)	completely modified (%)
Mg	82.41	92.51	98.62
Na	17.59	7.49	1.38

colloids were synthesized with anisotropic surface charges because of the exchange of Na^+ for Ca^{2+} cations.

Conclusions

A versatile new concept for the synthesis of Janus colloids composed of Laponite clay armored poly(divinylbenzene) with anisotropic surface potentials has been demonstrated. To synthesize the Janus colloids, a surfactant-free, solid-stabilized Pickering emulsion as a template was utilized. Our hypothesis is that the cation exchange of sodium ions, Na^+ , for calcium ions, Ca^{2+} on the surface of the nanoparticle-stabilized emulsion after polymerization will result in a colloidal particle that has a net positive charge but a heterogeneous distribution of charges with

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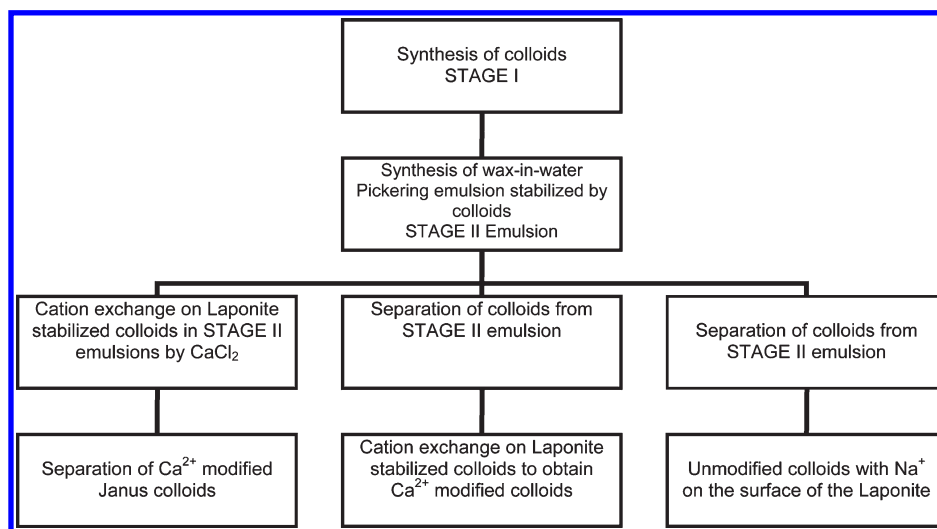


Figure 15. Schematic showing the steps involved in the synthesis of the Janus, completely modified, and unmodified colloids.

monovalent ions on one hemisphere and divalent ions on the other. Theoretical calculations show that the Debye length of the colloids with the original Na^+ ions adsorbed on Laponite will be 1.411 times longer than that on the colloids with Ca^{2+} ions exchanged. Thus, this anisotropic Debye length is expected to manifest itself in anisotropic, nonuniform zeta potentials.

It was initially expected that the zeta potential of the Janus colloids would be intermediate between the completely modified and unmodified colloids, but zeta potential measurements gave an unexpectedly lower value than for the completely modified colloids. A possible explanation lies in the way that the zeta potential is measured using the Malvern Zetasizer. It reverses the direction of the electrical field a number of times per second. The heterogeneous surface potential causes the Janus colloid to respond by rotating to align in the direction of the field; however, it was found by Anderson and others that this rotation occurs once per second, which is not fast enough to be completely aligned in the electrical field before the Malvern Zetasizer fast field reversal switches the direction of the field. As such, the colloids will not be able to attain their maximum electrophoretic mobility resulting in the lowest relative value of the zeta potential as compared to the completely modified and unmodified colloids.

Chemical composition analysis by XPS provided quantitative evidence of the exchange of Na^+ for Ca^{2+} ions on one hemisphere of the Janus colloids. Ultimately, using a technique that does not rely on electrophoretic mobility to characterize the heterogeneous surface potential will provide better evidence than zeta potential measurements. To this end, surface force microscopy (SFM) is being used to measure the interaction forces between the charged hemispheres and a charged atomic force microscopy tip. Indeed, the clustering behavior observed does provide qualitative evidence and also supports the XPS data indicating that the Janus colloids have anisotropic surface potentials.

From an experimental point of view, much remains to be done to characterize the motion of these Janus colloids with anisotropic surface potentials under electrical fields, and this is the subject of ongoing research.

Experimental Section

Materials. Styrene and divinylbenzene monomers were purchased from Sigma-Aldrich at 99% purity and were washed with 10% $\text{NaOH}(\text{aq})$ to remove the inhibitor. Hexadecane was bought from Fluka at 98% purity. The chloride salts iron(II) chloride,

iron(III) chloride, calcium chloride, and sodium chloride were purchased from Aldrich at 99% purity. ACS reagent grade chloroform was purchased from Aldrich at 99% purity. Ammonium hydroxide with 30% ammonia was purchased from Sigma-Aldrich. Laponite RD was kindly donated by Southern Clay Products Inc. Azobisisobutyronitrile (AIBN) oil-soluble initiator was purchased from Sigma at 98% purity. Distilled deionized (DDI) water was obtained using a Millipore Elix-3 reagent water system.

Methods. Sonication to prepare miniemulsions was performed using the 400 W Branson 450D sonifier. The miniemulsion was prepared by sonication for 6 min at 70% sonication amplitude with a break for 45 s after every minute. Zeta potential and particle size measurements of up to $1\ \mu\text{m}$ were performed using dynamic light scattering equipment by Malvern Zetasizer Nano-ZS. The Zetasizer is equipped with a 633 nm laser, a 173° scattering angle, and noninvasive backscatter (NIBS) technology for increasing particle size sensitivity. Before and after each measurement, the electrophoretic cell was washed with distilled, deionized water to prevent cross contamination. The temperature of the laboratory was kept at $22 \pm 2.5^\circ\text{C}$ during all experiments. Particle size measurements above $1\ \mu\text{m}$ were performed with a Beckman and Coulter LS13320 laser diffraction particle size analyzer. Filtration was performed using nitrocellulose membranes with a pore size of 200 nm. Scanning electron microscopy (SEM) images were obtained with a JEOL JSM-7401 field emission electron microscope. X-ray photoelectron spectroscopy (XPS) data was obtained on a VG Scientific Ltd. instrument. Conductivity was measured on a Mettler and Toledo SevenMulti conductivity measurement module.

Synthesis of Colloids. Initially, the synthesis procedure was optimized using styrene. Once optimized, divinylbenzene was used in all subsequent experiments. The monomer used for the synthesis of colloids contained styrene or divinylbenzene monomers, 8 wt % hexadecane as a hydrophobe,^{37,38} and 3 wt % AIBN as the oil-soluble initiator. Laponite (0.25 wt %) was dispersed in water by sonication at 80% power for 2 min, followed by the dissolution of $\text{NaCl}(\text{aq})$ in the Laponite suspension again by sonication for 2 min at 80% power. The required amount of monomer was introduced into this aqueous suspension, and this was sonicated for 2 min at 80% power to obtain a Laponite-stabilized emulsion of the monomer mixture in water. The emulsion was heated to 60°C in the water bath for 48 h for the monomer to polymerize. Laponite armored polystyrene or poly(divinylbenzene) colloids were thus obtained as shown in the schematic in Figure 15.

Synthesis of Janus, Completely Modified, and Unmodified Colloids. This procedure was modified from earlier work done by

Granick et al.^{13,21} Briefly, a 1.5 wt % suspension of ~520-nm-diameter poly(divinylbenzene) colloids with 0.1 M NaCl(aq) was prepared. Coconut oil–wax (6 g) was melted into this suspension by heating in an oven to 60 °C. This suspension was sonicated for 2 min while hot to form a Pickering emulsion of molten wax-in-water stabilized by the colloids. The wax was allowed to cool for 1 h to room temperature. NaCl was removed from the suspension by dialysis for 96 h in water at pH 10, adjusted by using ammonium hydroxide. After dialysis, the excess colloids (which did not take part in the Pickering emulsion) formed a hazy aqueous phase below a cream of wax droplets because of the density difference. The excess colloids were removed through a separating funnel, ensuring that no creamed wax droplets were lost. The wax droplets were diluted with water and were allowed to cream once again. The particle size of the aqueous phase below the cream was determined to ensure that particle sizes below 1 μm were not observed and that there were no excess colloids left. The synthesized colloids were all below 1 μm , so any of the excess colloids, if present, would be detected below that size limit. If excess colloids were observed, the aqueous phase was again separated and the wax particles were again diluted and allowed to cream. This procedure was followed until no excess colloids were obtained in the aqueous phase, determined via particle size measurements. This separated emulsion is designated the stage II emulsion.

$\text{CaCl}_2(\text{aq})$ (1 M) was added to the stage II emulsion. The emulsion was maintained at pH 2 using an ascorbic acid buffer. The above emulsion was stirred for 24 h to allow cation exchange to take place. Water was then removed from the emulsion and wax, and the colloids stabilizing it were washed with water to

remove all of the excess $\text{CaCl}_2(\text{aq})$. The wax was subsequently dissolved in chloroform to leave behind Janus colloids that were removed using a 200 nm pore size filter membrane.

To obtain the unmodified colloids, the stage II emulsion was first washed with water to remove any excess NaCl left over from the synthesis of the emulsion. The wax was then dissolved in chloroform to leave behind the colloids, which were then filtered out as before using a 200 nm pore size filter membrane.

To obtain completely modified colloids, the stage II emulsion was added to water containing 1 M $\text{CaCl}_2(\text{aq})$ and maintained at pH 2 by an ascorbic acid buffer for 24 h. Subsequently, the excess CaCl_2 was washed by filtering off the aqueous phase using the 200 nm pore size filter membrane.

All three types of colloids were dispersed in the desired concentration in water for further study.

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Supporting Information Available: Particle size histogram for the stage II colloids synthesized in sample AI. Zeta potential measurements of completely modified colloids at different concentrations in water and the droplet size distribution of stage II emulsions at a fixed NaCl(aq) salt concentration. This material is available free of charge via the Internet at <http://pubs.acs.org>.