Surfactant Free, Solid Stabilized Emulsion as a Template to Synthesize Janus Colloidosomes.

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INTRODUCTION

The objective of this research is to synthesize Janus colloidosomes which can be controlled by external stimuli (electrical field, magnetic field, pH changes). Janus Collidosomes are structures with a core -shell morphology and having anisotropic surface properties on their hemispheres. Colloidosomes have potential applications in drug delivery. Colloidosomes that can be controlled by external forces will give an advantage in drug delivery applications for targeted drug delivery. The Janus colloidosomes may also be assembled via external forces to form scaffolds which can be helpful in tissue engineering. The objective here is to optimize an appropriate technique to synthesize a Janus colloidosome and lay the groundwork for further research in the field.

We report here the synthesis of Janus Colloidosomes with a poly(styrene) core and a outer shell of laponite particles. It is our hypothesis that the colloidal particles will have an anisotropic surface potential. It is expected that this anisotropic surface potential on the colloidosomes can cause them to respond to alternating electrical fields.

EXPERIMENTATION

Materials. Clay (Laponite RD, with a lateral diameter of ca. 25-35 nm and a thickness of 1 nm), with an ideal chemical formula of $[Si_8(Mg_{5.45}Li_{0.4})O_{20}(OH)_4]Na_{0.7}$, was donated by Rockwood Additives Ltd. 2,2-Azobis(2,4-dimethyl valeronitrile) initiator, styrene monomer, n-hexadecane hydrophobe, FeCl₃ and NaCl salt, dimethyl cyclohexane oil and ascorbic acid all of the reagent grade were obtained from Sigma Aldrich.

Procedure. The synthesis of Janus colloidosomes was conducted in two steps. The first step is preparing the colloidosome; and the second step is modifying the surface properties of the colloidosomes selectively. The laponite nanoparticles are dispersed in water by simple mixing. The styrene monomer with the hydrophobe and initiator is introduced in the above system and the system is emulsified using an ultrasonic homogenizer. Using the principle of pickering emulsions an emulsion of styrene monomer in water stabilized by the solid laponite nanoparticles is formed using a procedure described previously [1, 2]. This emulsion is heated to 51 °C for 4 hours to polymerize the styrene. Colloidal particles (colloidosomes) with a core of polystyrene and laponite armor are formed. These colloidosomes are then separated from the emulsion.

The colloidosomes are used as solid stabilizers for an emulsion of dimethyl cyclohexane in water by ultrasonic homogenization [3]. FeCl₃ solution is added to this emulsion. Ascorbic acid is used to maintain the pH. And the emulsion is allowed to stand for twenty four hours. The colloidosomes are then precipitated by evaporating the water at 100 $^{\circ}$ C and then the oil at 130 $^{\circ}$ C. The colloidosomes are washed thoroughly with deionized water to obtain Janus colloidosomes.

DISCUSSION

Colloidosomes having a core of polystyrene and a shell or an armor of laponite was synthesized in the first step using a procedure described previously [1,2]. The ion exchange capacity of the laponite is used to form the Janus colloidosomes in the second step. Laponite nanoparticle has Na⁺ ions adsorbed on their surfaces. These ions can be replaced by Fe³⁺ ions. Once the second Pickering emulsion is synthesized with the Janus colloidosomes themselves as the stabilizers [3] we then use this Pickering emulsion as a template to modify the surfaces of the colloidosomes. In the colloidosome

stabilized Pickering emulsion (of dimethyl cyclohexane in water); the colloidosomes are partially exposed to the cyclohexane on one hemisphere and water on the other. On adding FeCl₃ solution to the emulsion, it is dispersed in the aqueous phase

Ion exchange with the laponite armor occurs because of the Fe^{3+} ions present n the aqueous phase [4]. But this ion exchange is restricted to only the aqueous phase and the hemisphere in contact with the oil-phase (dimethyl cyclohexane) remains unmodified. On destabilizing the emulsion and separating the colloidosomes we obtain colloidosomes with Fe^{3+} ions on one hemisphere and the originally present Na⁺ ions on other hemisphere. This produces anisotropic surface potential on the colloidosome. We hypothesize that the application of AC electric fields in aqueous suspensions of these anisotropic colloidosomes can lead to electrophoretic motion [5].

REFERENCES

- 1. S. Cauvin, P. J. Colver, S. A. F. Bon, *Macromolecules* 2005, *38*, 7887
- 2. S. A. F. Bon, P. J. Colver, Langmuir 2007, 23, 8316
- 3. S. A. F. Bon, T. Chen, *Langmuir* **2007**, *23*, 9527
- N. Kozaia, K. Inadab, Y. Adachib, S. Kawamurab, Y. Kashimotob, T. Kozakib, S. Satob, T. Ohnukia, T. Sakaic, T. Satoc, M. Oikawac, F. Esakad, H. Mitamurad, *Journal of Solid State Chemistry*, **2007**, *180*, 2279
- 5. S. Gangwal, O. J. Cayre, M. Z. Bazant, and O. D. Velev, *Physical Review Letters*, **2008**, 100, 058302