

Soft Matter

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Hierarchical self-assembly of ‘hard-soft’ Janus particles into colloidal molecules and larger supracolloidal structures

Thomas S. Skelhon,[‡] Yunhua Chen[‡] and Stefan A.F. Bon*[‡]

Received (in XXX, XXX) XthXXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXXXX 20XX

DOI: 10.1039/b000000x

Here we report the self-assembly of ‘hard-soft’ micron-sized Janus particles into clusters in aqueous media. The assembly process is induced by the desorption of a polymeric stabiliser from particles, that is polyvinylpyrrolidone (PVP) polymer. Upon contact through collision and coalescence of the soft polymeric lobes, the newly formed clusters adopt a minimized surface area to volume ratio, thereby forming distinct microscopic supracolloidal analogues of simple molecular valence shell electron pair repulsion (VSEPR) spacefill structures. To explain this behaviour, colloidal stability of our particle suspensions were studied with and without an adsorbed steric surfactant. Simulations of expected cluster morphology, compared with those from cryo-SEM analysis support the mechanism of assembly driven by surface area minimization in the case of soft-soft interactions. Altering the soft lobe size with respect to the hard lobe indicates a moderate effect on number of primary particles per cluster. Additionally, higher order structures of clusters containing a number of primary particles exceeding what is possible for a ‘solid’ core cluster are observed. As such, we also investigated the formation of suprastructures using a high number of ‘hard-soft’ Janus particles and verify their effective stabilization of air bubbles.

Introduction

Colloidal molecules, a term coined by van Blaaderen and coworkers,¹ describes the formation of supracolloidal structures, through assembly of colloidal building blocks, that resemble the configuration of atoms in molecules both in angular arrangement and respective lobe size to that of valence shell electron pair repulsion (VSEPR) space-fill geometries. These intricate structures attract great interest in colloid science and soft matter physics, as they produce anisotropic or patchy objects (anisotropy referring to shape, size, chemical and physical characteristics). They may be used as further building blocks for hierarchical self-assembly and as model systems for mimicking molecular assembly in shape and directional interactions.^{2,3}

To control the formation of colloidal molecules and thus the assembly process the building blocks themselves often have anisotropic features, but not always as for example in the work of Pine and co-workers particle clusters were fabricated in an emulsion system.⁴ When anisotropy of a single particle is opposing in character one speaks of Janus particles. The vast majority studies of Janus particles focus on their amphiphilicity.⁵⁻¹¹ Generally, Janus particles can be made by a variety of routes, such as phase separation,¹²⁻¹⁸ surface nucleation,¹⁹⁻²¹ microfluidics,²²⁻²⁵ micro-contact^{26,27} and particle PRINT,^{28,29} etc. One easy accessible anisotropic shape and chemistry would be ‘dumbbell’ or ‘peanut’-type particles. For example, dumbbell particles with a magnetic ferrofluid lobe can assemble into clusters and chains whilst being subjected to a magnetic field.³⁰ The conformation of which is a competition between magnetic

attraction and steric hindrance. Anisotropic dumbbell particles featuring a ‘rough’ and ‘smooth’ phase were also reported to aggregate into clusters, whereby only the ‘smooth’ lobes of the particles interact, the ‘hard’ phases providing a sterically repulsive force against aggregation.³¹ Despite showing good control of selective interactions to form regular clusters, most of these techniques exploit reversible interactions, whereby application of sufficient shear or a change in ionic strength would cause disintegration of the cluster. Kraft *et al.* manufactured clusters which are permanently bonded together using a dumbbell type of morphology of which one lobe was liquid.³² These colloidal shapes were made in situ as a result of induced phase separation which led to the formation of the liquid lobe. The clusters formed upon collision at which point the liquid phase allowed for rearrangement of the clusters into an energetic favourable geometry. The shapes were locked-in by polymerization of the liquid phase.

Herein, we take a similar approach towards fabricating colloidal clusters. Instead of using liquids to arrange the colloidal building blocks, we use ‘hard-soft’ Janus particles (**Fig. 1**). The advantages are that we do not make use of a volatile phase and that we have no need for a post polymerization step. The soft section of the polymer particle acts as adhesive, which upon assembly ‘glues’ the building blocks in place, which makes locking the structure together by a post chemical reaction unneeded. Our particles are ‘dumbbell’ shaped with lobes of distinct glass transition temperature, that is -54 °C for the ‘soft’ poly(*n*-butyl acrylate) (PBA) lobe and 100 °C for the ‘hard’ poly(styrene) (PS) lobe. Polyvinylpyrrolidone(PVP) is used as

steric stabiliser in their synthesis to impart colloidal stability to these particles whilst dispersed in an aqueous phase. The aggregation and thus self-assembly of these 'hard-soft' Janus particles is triggered upon partial removal of the steric barrier by dilution of the dispersion and stirring.

Experimental section

Materials

Styrene (Reagent Plus, 99%), *n*-butyl acrylate (>99%), poly(vinyl pyrrolidone) (PVP-K90, 360,000 g/mol), all were supplied by Sigma-Aldrich, UK. Azobisisobutyronitrile (AIBN, 97%), ethanol (absolute AR) and methanol (AR) were purchased from VWR and used as received. Monomers were filtered through a basic alumina column to remove inhibitor before use. Deionised water was used in all experiments.

Synthesis of hard-soft Janus particles

Micron-sized polystyrene seed latexes with narrow particle size distribution were synthesized by dispersion polymerization. Briefly, styrene (25.0 g), AIBN (0.25 g), PVP (1.5 g) and methanol (70 g) were charged to a 250 mL round bottom flask and purged with nitrogen gas purge for 20 minutes, whilst stirring using a magnetic stirrer. Next, the mixture was heated to 70°C for 24 hours whilst stirring was maintained and the reaction was kept under a slight nitrogen over pressure. After this, the resulting polymer dispersion was cooled to room temperature, purified by centrifugation, decantation of the supernatant, and re-dispersion into methanol (repeat twice) before analysis by optical microscopy and laser scattering analysis.

To make the hard-soft Janus particles dispersion in methanol a second step was required. Typically PVP-K90 (0.03 g), *n*-butyl acrylate (1.5 g), AIBN (0.1 g), water (5.70 g) and methanol (17.3 g) were added to a 27.0 g methanol dispersion of polystyrene seeds particles (solids content of the seed latex = 11 wt%). The mixture was stirred and purged with nitrogen for 20 minutes. After this, the flask was heated to 70°C for 24 hours to carry out the seeded dispersion polymerization under a nitrogen atmosphere.

Particle cluster formation

Methanol dispersions of 'hard-soft' particles were sedimented by gravity before replacement of an equal volume of supernatant with deionised water. Settled particles were re-suspended in fresh media by gentle swirling. This process was repeated twice more before dilution to 0.1 wt% solids content in deionised water. After which agitation by hand-shaking for 30 seconds was applied to generate clusters.

Particle stabilised foams

10 mL of an aqueous suspension of purified hard-soft particles at 0.1 wt% (w/w) was hand-shaken in a 15 mL glass vial in the presence of air as to thoroughly aerate the suspension. The remaining foam layer was carefully resuspended in fresh deionised water prior to imaging.

Characterization

Laser diffraction measurements

Bulk particle sizing measurements were undertaken using a Mastersizer 2000 (Malvern Instruments, Malvern, UK). Dilute aqueous particle suspensions were introduced using the Hydro S dispersion unit. Time-lapse measurements of 400 min duration, sampling every 20 min were undertaken in a closed system using degassed tap water in ambient conditions stirring at 1750 rpm. Laser was aligned to optimum transmission intensity and a background spectrum collected to eliminate any contaminants presenting in the final data. Dilute suspensions of 1 wt% were introduced drop wise by submerged syringe to ensure no premature flocculation or bubble introduction until 5% laser obscuration was reached. A 30 sec ultrasonic cycle to remove any bubbles and break apart any flocculation was run before the measurement ensued. Concentration of particulate was fixed at 0.04 vol% with respect to total media volume, as determined by Mastersizer instrumentation.

Turbidity measurements

To determine the turbidity, 'hard-soft' particles of 1:1 PS/PBA ratio were first synthesized, and diluted in pure water or PVP-K90 solutions to 0.2 g/L of particulate content. 10 mL of these suspensions were sealed in a glass vial and mounted into a Model 777 Microarray Oven (SciGene, California, USA) before rotating at a set speed under ambient room temperature conditions. The radius from the centre of the vial to the rotor centre was fixed at 20 cm. Periodically, samples from the vials were measured for absorbance at 540 nm using a UV/Vis spectrophotometer. A calibration curve of known primary particle concentration was measured to back calculate primary particle concentration from absorbance (Fig. S1, ESI†). Absorbance measurements at 540 nm were taken for set concentrations of polystyrene particles (PS seed), poly(butyl acrylate) particles (BA seed) and 'hard-soft' Janus particles. Evidently, the PS seed absorbs and scatters more light than PBA beads, due to the higher refractive index of polystyrene compared with poly butyl acrylate (1.57 against 1.47 respectively). As expected, the Janus particle absorbance sits between these values, although biased towards the polystyrene value. This is due to the larger size and aspect ratio of the Janus particle as opposed to a sphere. A simple exponential function was fitted against these values, which was in turn used to calculate concentration of singular particles from absorbance. We apply the assumption that particles, irrespective of size, scatter light equally, and that we may measure flocculation by the decrease in initial particle number.

Optical and electron microscopy

Particles were imaged on a Leica DM2500 using a Nikon D5100 camera. Cryogenic Scanning Electron Microscopy analyses were carried out using a Zeiss Supra 55-VP Field Emission Gun Scanning Electron Microscope with a Gatan Alto 2500 cryo transfer system and a Gatan C1002 Liquid Nitrogen cold stage. Dilute aqueous suspensions of particles were drawn into a brass rivet and cooled in liquid nitrogen. Samples were heated to -90 °C under high vacuum for 10 minutes to remove contaminant ice through sublimation followed by platinum sputter target coating

in an argon atmosphere (20 seconds, 10 mA). Imaging was undertaken at $-120\text{ }^{\circ}\text{C}$ using a 3 kV accelerating voltage with a gold anti-contaminator at $-189\text{ }^{\circ}\text{C}$. Image analysis was conducted with ImageJ software.

5 Simulations of cluster formation

Surface Evolver (Ken Brakke) was used to graphically depict the lowest surface energy morphology of volume constrained Anisotropic particle clusters of $1 < n > 5$. Simulations were built on coarse Janus particles consisting of two separate domains. At the start of the simulation, the particles were in contact by a central domain. Depending on the number of primary particles and desired hard:soft lobe ratio, the separate lobes and central soft domain volume ratio was constrained to the desired parameter. The simulation was then iterated, refined and further iterated until the difference in interfacial energy between the last two iterations was negligible.

Cluster counting measurements

During the polymerisation, 8 mL aliquots of reaction mixture were withdrawn from the reaction flask at 95 min and 191 min into the seeded dispersion polymerisation and cooled on ice to quench polymerisation. The remainder of the reaction was heated for a total of 1425 min. All three samples were analysed by gravimetry and optical microscopy before diluting to 0.1 wt% (w/w) solids content with methanol before allowing suspensions to sediment by gravity. The supernatant was then replaced with an equivalent volume of 50/50 methanol/water (v/v) before gently swirling to redisperse particles. This process was repeated once more using fresh water instead. To induce cluster formation, each suspension was handshaken for 30 seconds and imaged under an optical microscope. Populations of clusters containing 2-5 primary particles were counted using ImageJ software, recording over 100 clusters for each sample over 3 micrographs per sample.

Results and discussion

Hard-soft Janus particles used in this study were synthesized by seeded dispersion polymerization. A series of hard-soft colloidal dumbbells were made from a PS spherical seed, with varying sizes of the PBA lobes. For example, **Fig. 1b** and **1c** display hard-soft Janus particles with PBA:PS volume lobe ratio of approximately 0.53:1. PVP-K90 was used as the steric stabiliser in both steps of the synthesis to impart colloidal stability to these particles when dispersed in an aqueous phase. Aggregation and thus self-assembly of these Janus particles can be triggered upon partial removal of physisorbed PVP in combination with shear. Adsorbed PVP is easily removed (rebalance partitioning of PVP between particles surface and the continuous aqueous phase) upon dilution of the dispersion.

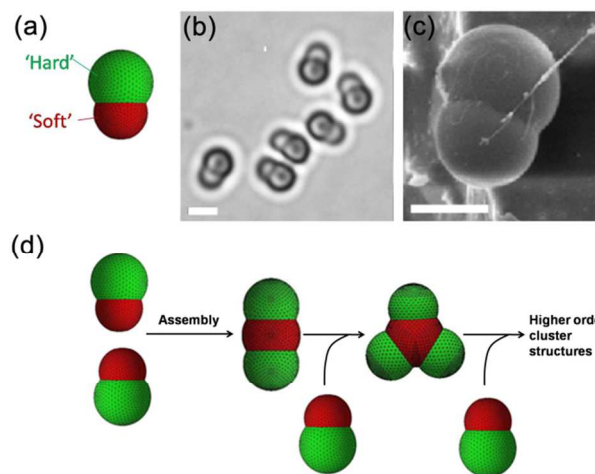


Fig. 1 (a) schematic illustration of polystyrene (PS, 'hard')-poly(*n*-butyl acrylate) (PBA, 'soft') Janus particles; (b) optical and (c) Cryo-SEM image of the 'hard-soft' particles; (d) 'hard-soft' particles assembled to colloidal molecules. Scale bars in (b) 2 μm and (c) 1 μm .

The method of dilution as means to trigger assembly was first tested with hard polystyrene microspheres (diameter of approximately 2 μm) synthesised using PVP as steric stabiliser to observe the effect of dilution on colloidal stability in stirred conditions. From time-lapse laser scattering measurements, it became clear that diluted particle dispersions (1 wt%) flocculated into clusters over time, whereas microsphere suspensions with added PVP stabiliser in the medium were stable against long term flocculation, despite the shear conditions experienced within the flow cell of the instrument (**Fig. s2, ESI†**). The desired loss of colloidal stability upon dilution is attributed to the partial desorption of PVP from the surface of the particles.

Based on the microsphere flocculation results, the rate of flocculation of the 'hard-soft' Janus particles was studied. The concentration of particles was measured by scattering data (turbidity) from UV/VIS measurements at 540 nm. We employed a technique to measure the singular Janus particle concentration as a function of time whilst under the influence of a constant mixing shear force using a rotary oven. The rate of flocculation appeared to be proportional to the applied shear force, and exhibits an exponential decay profile (**Fig. s3, ESI†**). In a similar series of experiments the contribution of PVP in the continuous phase towards restricting flocculation was studied. For this we measured turbidity of dilute suspensions of particles at fixed rotor speed of 32 rpm, with various concentrations of PVP dispersed into the aqueous phase. It clearly shows that without any added PVP to the solution, the particles flocculated rapidly as expected. However upon the addition of PVP to the suspension, flocculation rates slowed down, until at $3 \times 10^{-5}\text{ mol/dm}^3$, flocculation was completely prevented (**Fig. 2**). These results verify that indeed self-assembly can be induced upon dilution of a dispersion (leading to partial desorption of PVP from the surface of the particles), and thus can be used as strategy for the cluster formation of our hard-soft Janus particles.

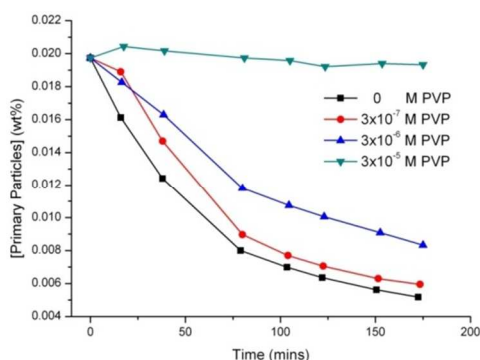


Fig. 2 Primary 'hard-soft' Janus particle concentration as a function of time for a range of PVP-K90 concentrations in the continuous phase (mixing speed at 32 rpm), as measured by turbidity.

The second part of this study involves the visualization of the particle clusters after partial flocculation of the Janus particles using dilution and shear (the latter to enhance impact velocity). The self-assembled cluster morphology can be governed by the orientation of particles upon collision resulting in four possible interaction regimes; hard-hard, hard-soft, soft-soft and simultaneous hard-soft (Fig. 3, note that the angle of collision can vary). We hypothesize that only a soft-soft collision can lead to adhesion of the soft lobes, as they are easily deformable and compatible (miscible) with one another. A hard-soft collision is less likely to lead to permanent locking as the 'hard' PS lobe is chemically incompatible with the 'soft' PBA lobe.

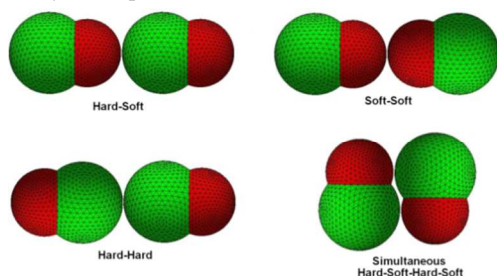


Fig. 3 Schematic of possible collision arrangements for two 'hard-soft' Janus particles.

Fig. 4a and 4b depicts clusters with the number of primary particles (N_p) incorporated from 1 to 5, as directly visualized under Cryo-SEM and optical microscope, also see an overview image of clusters in Fig. s4, ESI†. They confirm our hypothesis. A striking aspect of these images is that all of these structures bear a significant meso-scale resemblance to valence shell electron pair repulsion (VSEPR) space-fill models for simple molecules. We believe that the reduction of interfacial area for the cluster is the driving force behind rearrangement into these regular structures. Upon collisions of soft lobes, their temporary deformation leads to a higher surface area and a raised surface tension due to the lack of PVP presence. Accordingly, the soft component will deform to minimize interfacial energy, and therefore form the geometries as seen in the microscopy images. Surface energy minimization simulations were conducted to model the morphology of particle aggregates from 1 to 5 primary particles upon a soft-soft interaction by 'Surface evolver' (Fig. 4c). The simulation data obtained from the surface energy

minimisation show a consistent agreement with the morphologies from the Cryo-SEM and light microscopy images, indicating that surface energy minimisation is indeed the driving force behind the controlled geometry we observe experimentally.

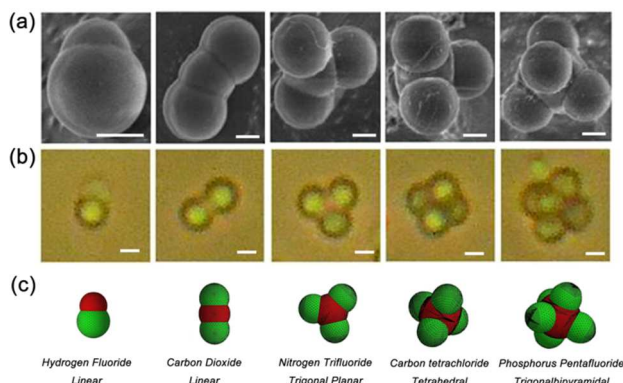


Fig. 4(a) high resolution Cryo-SEM and (b) optical images of clusters in suspension with primary particle number 1-5; (c) respective graphical surface energy minimization simulation from Surface Evolver, green indicates the 'hard' PS phase, red indicates the 'soft' PBA phase. Bottom row shows examples of simple molecules with analogous VSEPR spacefill geometries. All scale bars: 1 μm .

We also investigated the effect of increasing the soft PBA lobe size in relation to the PS seed particles to see if lobe size ratio affects the number distribution of primary particles found in clusters. Three different samples were prepared with PBA:PS volumetric lobe ratios of 0.13:1, 0.32:1, and 0.53:1 (Fig. 5). In all three samples clusters containing two primary particles, that is dimers, are the most prevalent followed by trimers, tetramers and pentamers. This is logical as once a dimer is formed there is reduced available soft surface area for further particles to adhere to the 'soft' part of the cluster. Interestingly, the size of the PBA lobe appears to have a small influence on the cluster size distribution. Upon increasing the size of the PBA lobe, larger clusters are formed. This effect is plausibly due to the magnitude of soft PBA surface area available for the primary particles to adhere to. As the surface area increases, more primary particles can contribute to the cluster, indicating a degree of geometric constraint arising from the hard PS seed particles (Fig. 6, also see the images of clusters in Fig.s5, ESI†).

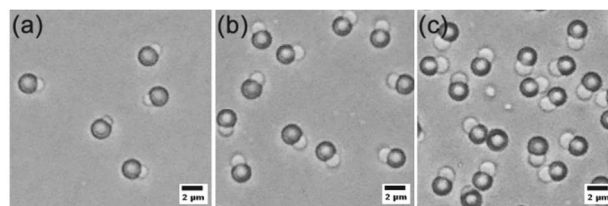


Fig. 5 Optical micrographs of 'hard-soft' Janus particles used in cluster counting study, with conversion value at time of sample extraction and PBA lobe volume ratio, (a) conversion: 26%, PBA:PS volume ratio: 0.13:1; (b) conversion: 50%, PBA:PS volume ratio: 0.32:1; (c) conversion: 91%, PBA:PS volume ratio: 0.53:1.

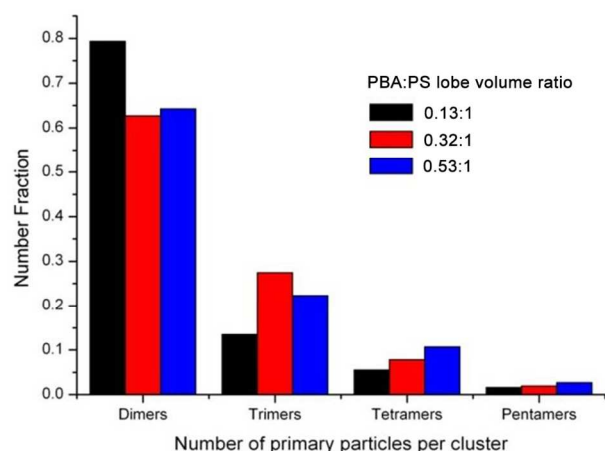


Fig. 6 Populations of clusters containing 2-5 primary 'hard-soft' Janus particles with three different soft lobe sizes.

In addition to colloidal molecule type clusters, much larger supracolloidal structures potentially in the form of colloidosomes were also observed, as seen in **Fig. 7a**. From the SEM images it is possible to see that the soft PBA phase of the Janus particles have coalesced, effectively embedding the hard PS particles in a soft elastic PBA matrix. In some cases the number of primary Janus particle constituents of the colloidosome shaped clusters exceeds the maximum number possible for a cluster possessing a central core and therefore it is plausible that the Janus particles coalesced in a 2D planar manner over a curved surface to form an actual colloidosome, that is a hollow supracolloidal structure (**Fig. 8c**). A plausible template is air bubbles present as result of the agitation process. Theoretically, chemically isotropic Janus dumbbell or peanut-shaped particles have been shown to preferentially lie tilted or 'flat' at an interface, therefore maximizing the displaced interfacial area.³³ This orientation allows the coalescence of the PBA lobes between the particles in a planar manner. Clusters not necessarily are hollow as there is a fine balance between the volume of the supracolloidal structure and the number of hard-soft Janus building blocks. For example, a quick calculation on the clusters displayed in **Fig. 7b** shows that they most likely do not have an internal cavity.

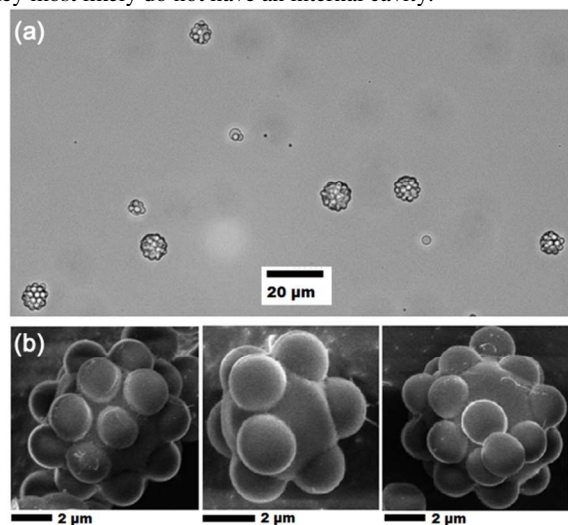


Fig. 7 (a) optical microscopy image of higher order particle clusters; (b) Cryo-SEM images of examples of individual higher order clusters.

To further investigate the self assembly of these 'hard-soft' particles at 2D curved interfaces, large hollow colloidosomes were made through the assembly of 'hard-soft' Janus particles at a bubble interface (**Fig. 8a**). Densely packed particle domains assembled into a hexagonal close pack configuration can be clearly seen on a large bubble (**Fig. 8b**). As stated before, in theory, hard-soft particles can lie horizontally across the interface and coalesce in a 2-D planar manner. In an ideal case of complete coverage, this allows the formation of microcapsule type colloidosomes, which are hermetically sealed by the coalescence of the soft component. This will negate the need for a mechanism to seal the interstitial areas between particles such as sintering,³⁴ required in other examples of microcapsule formation using Pickering stabilizers. The bubbles are stable for an extended period of time, and have attained complete surface coverage as seen in **Fig. 8c**. This is expected behaviour for Pickering stabilized bubbles which allow gas diffusion and shrinkage until the particles jam on the surface as a result of decreased interfacial area.

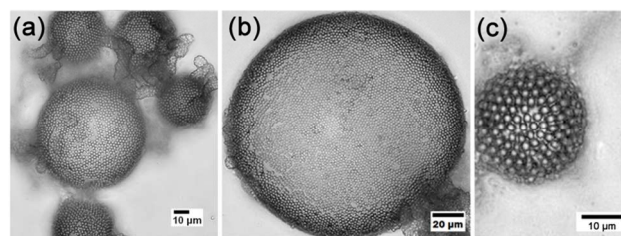


Fig. 8 (a) optical microscopy image of air bubbles of various sizes stabilised by 'hard-soft' particles; (b) a large bubble stabilised by Janus particles with clear hexagonal close pack domains; (c) colloidosomes one day after formation.

Conclusions

In conclusion, the formation of colloidal molecules and microcapsule type colloidosomes was reported using 'hard-soft' Janus particles. Cluster morphologies were governed by the deformation of the coalesced soft phase, energetically driven by surface energy minimisation and resembled the shape of simple molecules. The use of 'hard-soft' Janus particles allows for the preparation of non-permeable colloidosome-type microcapsules in a single step. We hope to have shown that Janus particles have more to offer than amphiphilicity, and that by using a different opposing characteristic interesting colloid science follows.

Acknowledgements

Part of the equipment used in this research was obtained through Birmingham Science City: Innovative Uses for Advanced Materials in the Modern World (West Midlands Centre for Advanced Materials Project 2), with support from Advantage West Midlands (AWM) and part funded by the European Regional Development Fund (ERDF).

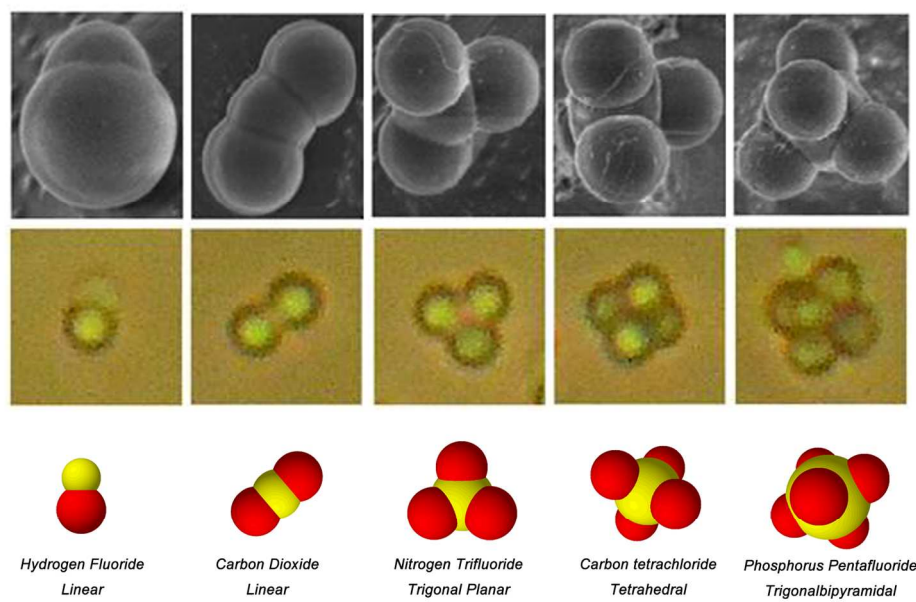
Notes and references

⁷⁰ Department of Chemistry, University of Warwick, Coventry CV4 7AL, UK. E-Mail: s.bon@warwick.ac.uk

† Electronic Supplementary Information (ESI) available: synthesis and characterisation of 'hard-soft' Janus particles and clusters. See DOI: 10.1039/b000000x/

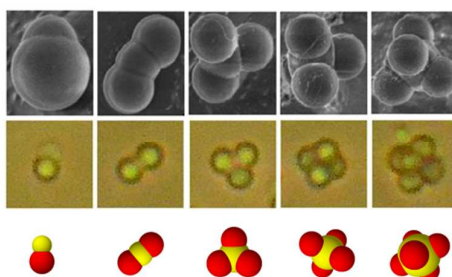
‡ These authors contributed equally.

- 5 1. A. van Blaaderen, *Science*, 2003, **301**, 470-471.
2. S. C. Glotzer, *Science*, 2004, **306**, 419-420.
3. Zhang, A. S. Keys, T. Chen and S. C. Glotzer, *Langmuir*, 2005, **21**, 11547-11551.
4. V. N. Manoharan, M. T. Elsesser and D. J. Pine, *Science*, 2003, **301**, 483-487.
- 10 5. D. L. Cheung and S. A. F. Bon, *Soft Matter*, 2009, **5**, 3969-3976.
6. B. J. Park, T. Brugarolas and D. Lee, *Soft Matter*, 2011, **7**, 6413-6417.
7. L. Hong, A. Cacciuto, E. Luijten and S. Granick, *Langmuir*, 2008, **24**, 621-625.
- 15 8. S. Sacanna, W. T. M. Irvine, P. M. Chaikin and D. J. Pine, *Nature*, 2010, **464**, 575-578.
9. S.-H. Kim, A. D. Hollingsworth, S. Sacanna, S.-J. Chang, G. Lee, D. J. Pine and G.-R. Yi, *J. Am. Chem. Soc.*, 2012, **134**, 16115-16118.
- 20 10. A. Kumar, B. J. Park, F. Tu and D. Lee, *Soft Matter*, 2013, **9**, 6604-6617.
11. R. Aveyard, *Soft Matter*, 2012, **8**, 5233-5240.
12. L. M. Liz-Marzan, M. Giersig and P. Mulvaney, *Chem. Commun.*, 1996, 731-732.
- 25 13. N. Saito, R. Nakatsuru, Y. Kagari and M. Okubo, *Langmuir*, 2007, **23**, 11506-11512.
14. J.-W. Kim, D. Lee, H. C. Shum and D. A. Weitz, *Adv. Mater.*, 2008, **20**, 3239-3243.
15. H. R. Sheu, M. S. El-Aasser and J. W. Vanderhoff, *J. Polym. Sci., Part A: Polym. Chem.*, 1990, **28**, 629-651.
- 30 16. B. Liu, H. Mohwald and D. Wang, *Chem. Commun.*, 2013, **49**, 9746-9748.
17. T. Yamagami, Y. Kitayama and M. Okubo, *Langmuir*, 2014, **30**, 7823-7832.
- 35 18. B. G. P. van Ravensteijn, M. Kamp, A. van Blaaderen and W. K. Kegel, *Chem. Mater.*, 2013, **25**, 4348-4353.
19. H. Yu, M. Chen, P. M. Rice, S. X. Wang, R. L. White and S. Sun, *Nano Lett.*, 2005, **5**, 379-382.
20. A. Perro, E. Duguet, O. Lambert, J.-C. Taveau, E. Bourgeat-Lami and S. Ravaine, *Angew. Chem. Int. Ed.*, 2009, **48**, 361-365.
- 40 21. M. Pan, L. Yang, B. Guan, M. Lu, G. Zhong and L. Zhu, *Soft Matter*, 2011, **7**, 11187-11193.
22. S. Lone, S. H. Kim, S. W. Nam, S. Park, J. Joo and I. W. Cheong, *Chem. Commun.*, 2011, **47**, 2634-2636.
- 45 23. Z. Nie, W. Li, M. Seo, S. Xu and E. Kumacheva, *J. Am. Chem. Soc.*, 2006, **128**, 9408-9412.
24. Y. Chen, G. Nurumbetov, R. Chen, N. Ballard and S. A. F. Bon, *Langmuir*, 2013, **29**, 12657-12662.
25. S. Yang, F. Guo, B. Kiraly, X. Mao, M. Lu, K. W. Leong and T. J. Huang, *Lab on a Chip*, 2012, **12**, 2097-2102.
- 50 26. T. Kaufmann, M. T. Gokmen, C. Wendeln, M. Schneiders, S. Rinnen, H. F. Arlinghaus, S. A. F. Bon, F. E. Du Prez and B. J. Ravoo, *Adv. Mater.*, 2011, **23**, 79-83.
27. T. Kaufmann, M. T. Gokmen, S. Rinnen, H. F. Arlinghaus, F. Du Prez and B. J. Ravoo, *J. Mater. Chem.*, 2012, **22**, 6190-6199.
- 55 28. T. J. Merkel, K. P. Herlihy, J. Nunes, R. M. Orgel, J. P. Rolland and J. M. DeSimone, *Langmuir*, 2009, **26**, 13086-13096.
29. H. Zhang, J. K. Nunes, S. E. A. Gratton, K. P. Herlihy, P. D. Pohlhaus and J. M. DeSimone, *New Journal of Physics*, 2009, **11**, 075018.
- 60 30. D. Zerrouki, J. Baudry, D. Pine, P. Chaikin and J. Bibette, *Nature*, 2008, **455**, 380-382.
31. D. J. Kraft, R. Ni, F. Smalenburg, M. Hermes, K. Yoon, D. A. Weitz, A. van Blaaderen, J. Groenewold, M. Dijkstra and W. K. Kegel, *Proc. Natl. Acad. Sci. U.S.A.*, 2012, **109**, 10787-10792.
- 65 32. D. J. Kraft, W. S. Vlug, C. M. van Kats, A. van Blaaderen, A. Imhof and W. K. Kegel, *J. Am. Chem. Soc.*, 2008, **131**, 1182-1186.
33. B. J. Park and D. Lee, *ACS Nano*, 2011, **6**, 782-790.
34. A. D. Dinsmore, M. F. Hsu, M. G. Nikolaides, M. Marquez, A. R. Bausch and D. A. Weitz, *Science*, 2002, **298**, 1006-1009.
- 70



152x96mm (300 x 300 DPI)

TOC graphic



We demonstrate the self-assembly of 'hard-soft' micron-sized Janus particles into clusters in aqueous media. Upon the coalescence of the soft polymeric lobes, the newly formed clusters adopt a minimized surface area to volume ratio forming distinct microscopic supracolloidal structures.