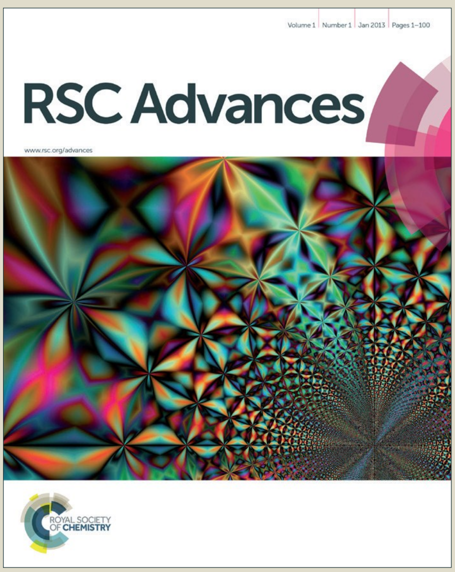
RSC Advances



Journal Name

ARTICLE

Colloidosome like structures: Self-assembly of silica microrods

P. Datskos,[a] G. Polizos,[a] M. Bhandari,[b] D. A. Cullen[c] and J. Sharma.[a*]

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Self-assembly of one-dimensional structures is attracting a great deal of interest because assembled structures can provide better properties compared to individual building blocks. In the present work, silica microrod self-assembly has been demonstrated by exploiting Pickering emulsion based strategy. Micron-sized silica rods were synthesized employing previously reported methods based on polyvinylpyrrolidone/pentanol emulsion droplets. Rods self-assembled to make structures in the range of ≈10-40 μm. Smooth rods assembled better than segmented rods. Assembled structures were bonded by weak van der Waals forces.

Introduction

Self-assembly of colloidal structures has seen an increasing interest in the last two decades because of their potential properties that are expected to be superior than those of the respective individual consituents.[1] Different approaches, for instance, DNA-self-assembly, Langmuir-Blodgett layers, hydrophobic-hydrophilic interactions, organic linkers, and Pickering emulsions have been employed to assemble the colloidal structures.[2] Many of these examples focused on assembling the isotropic (spherical) structures. The main focus on isotropic structures was due to their easy availability and well-understood properties. Not many efforts have been done to assemble anisotropic structures such as wires, rods, and tubes. Limited studies have been reported for assembling anisotropic nanostructures (e.g., nanorods),[3] nevertheless, there are not many efforts for assembling micron-sized rods (microrods). Similarly, most of the previously reported studies investigated assembly of materials of only one size and shape, that is, particles or nanorods of one type.

Recently, *Kuijk et al*. has demonstrated a nice strategy to synthesize nearly uniform silica microrods using emulsion droplet based anisotropic growth,[4] before that silica rods were not available and thus no self-assembly effort of such rods has been reported. Many reports followed to further improving the shape of these rods, making hybrid rods, and using the rods in composite materials.[5,6] Recently, *Bon et al.* employed the rod growth strategy to make completely a new type of structures 'the matchsticks'.[7] However, no work focused on the self- assembly of these rods. Taking the silica rod work to the next level, beyond the improvement of rod properties, in the present work, we demonstrate the self-assembly of these rods by using Pickering emulsion based approach, and also investigate the effect of rod shape on self-assembly behaviour.

Pickering emulsions are 'water in oil or oil in water emulsions' stabilized by colloidal particles.[8] When water in oil or oil in water is mixed, initially small droplets are formed, which eventually coalesce to make a continuous phase in order to decrease the energy of the system. The addition of solid particles results in attaching the particles at the water-oil interface and thus reducing the energy required to stabilize the system, and therefore avoiding the coalescing of the emulsion droplets. Pickering emulsion formation is more efficient if the particles can be wet by both oil and water phase. Therefore we selected a water-pentanol system, as pentanol is mildly non-polar and results in the phase separation of water. Additionally, pentanol's 'OH' groups can interact with the 'OH' groups on silica rods and thus can lead to enhanced stability of Pickering emulsions.

Experimental

Chemicals

Sodium citrate, absolute ethanol, tetraethylorthosilicate (TEOS), pentanol, and ammonium hydroxide (28–30 % NH_3 in H_2O) were bought from Fisher Scientific. Polyvinylpyrrolidone (PVP: MW= 40,000) was bought from Sigma Aldrich. The desired solutions were made by mixing appropriate quantities of these chemicals.

Synthesis and purification of silica rods

Silica rods were synthesized by using reported methods.[4] Briefly, 2.0 g of PVP was dissolved in 20 mL of pentanol in a glass vial. 560 μL water, 200 μL sodium citrate (0.18 M), 2.0 mL

[a.] Nanosystems, Separations, and Materials Research Group; Energy and Transportation Science Division; Oak Ridge National Laboratory, One Bethel Valley Road, Oak Ridge, TN 37831, USA.
Email: sharmajk@ornl.gov
[b.] Building Envelop Group, Oak Ridge National Laboratory, One Bethel Valley Road, Oak Ridge, TN 37831, USA
[c.] Material Science and Technology Division, Oak Ridge National Laboratory, One Bethel Valley Road, Oak Ridge, TN 37831, USA
† Electronic Supplementary Information (ESI) available: [particle synthesis and more SEM images]. See DOI: 10.1039/x0xx00000x

ethanol, and 400 µL NH_4OH solution were added to the PVP/pentanol solution and vortex for few minutes. 200 µL of tetraethyl orthosilicate (TEOS) was added to the above solution and vortex again. The mixture was incubated overnight at room temperature to obtain the silica rods. Before using for self-assembly, rods were washed by using ethanol three times and centrifuging at 2500 rpm for few minutes. The washing and centrifuging steps helped in removing the unreacted reagents and small nanoparticles that form as a side product during rod synthesis.

Segmented silica rods were synthesized by systematically changing the reaction temperature during the rod growth, while keeping the other conditions same as above.[6] Two types of segmented rods were synthesized by using the temperature and time conditions (a) rods grown by incubating at 20 ˚C (2 hrs.)–40 ˚C (40 min.)–20 ˚C (16 hrs.), and (b) by incubating at 40 ˚C (40 min.)–20 ˚C (2 hrs.)–40 ˚C (16 hrs.). Both types of rods are shown in Fig. 2 as (a) and (b).

Self-assembly of silica rods

To self-assemble silica rods, in a typical experiment, we added 90 µL aqueous solution of silica rods (≈15% by weight) in 910 µL of pentanol and vortex the sample for 30 minutes. Placed the sample for 5 hours to obtain silica rod stabilized Pickering emulsions. Because of the increased weight of silica rod stabilized emulsion droplets, the droplets settled down at the bottom of eppendorf vial (Fig. 1 a).

Characterization of silica rods and self-assembled structures

Silica rods and self-assembled structures were characterized by using scanning electron microscope (SEM). SEM studies were performed by using Merlin 200 microscope. SEM samples were prepared by depositing the washed silica rods on a silicon wafer. Silicon wafers were used to minimize the charging of the silica samples since silica is a bad conductor of charge. In order to image silica rod assemblies, 2 µL of solution was taken from the settled down self-assembled structures at the eppendorf bottom. Water and pentanol were allowed to evaporate and the dried self-assembled structures were imaged using SEM. Fig. 1 b shows (i) SEM images of unassembled silica rods, (ii) high magnification SEM image of self-assembled silica rod structures, and (iii) low-magnification SEM image of self-assembled structures.

Results and Discussion

Fig. 1a shows the schematic of self-assembly process and Fig. 1b shows the SEM images of as formed silica rods (i), a high magnification SEM image of silica rod assembled structure (ii), and a low magnification SEM image of silica

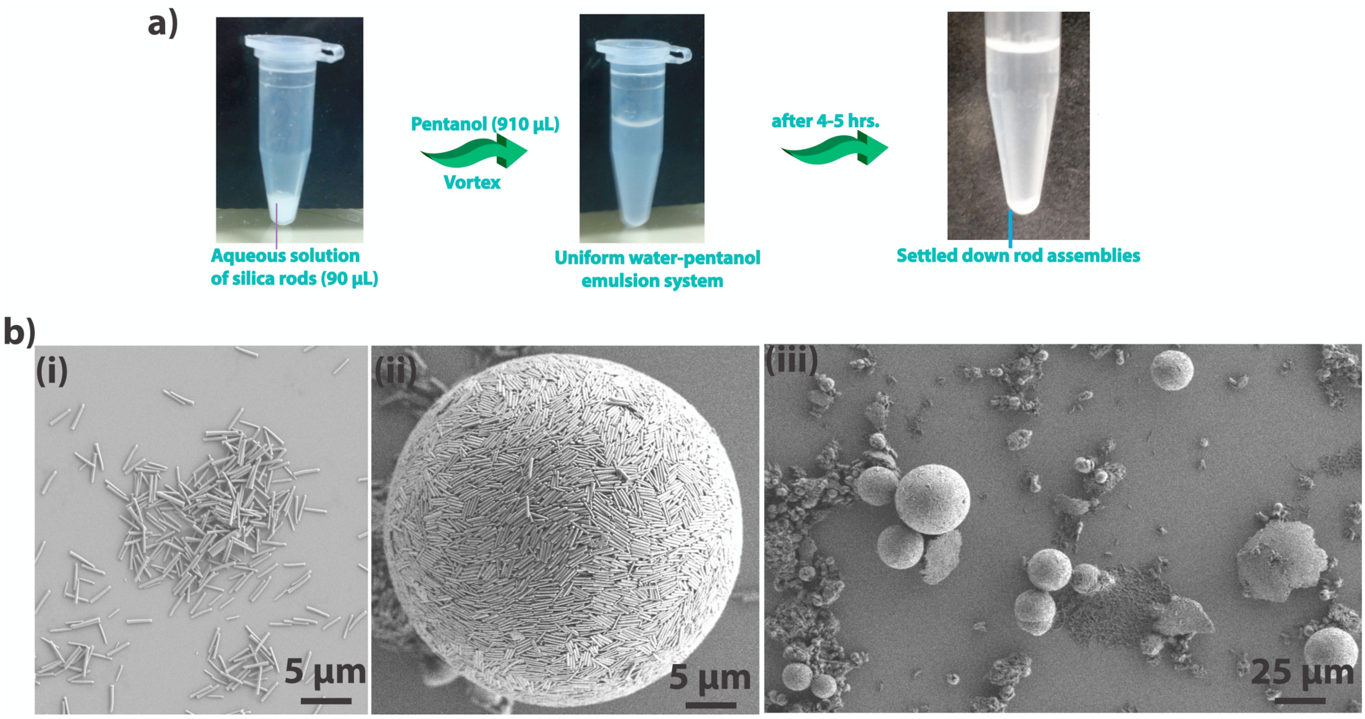


Fig 1. a) Schematic showing the self-assembly process, and b) (i) unassembled-smooth silica rods, (ii) self-assembled silica rod structures, and (iii) a low magnification SEM image showing intact self-assembled and broken self-assembled structures.

Journal Name

ARTICLE

rod assemblies (iii). Fig. 1b(ii) shows a colloidosome[9] like structures made from self-assembly of silica rods at the interface of water and pentanol. We call these structures as colloidosome like structures, as though the rods are not bonded by any covalent or ionic bonds, but they remained intact like colloidosomes even when dried. From low magnification SEM image (Fig. 1b(iii)) it becomes clear that though most of the rods remain assembled in colloidosome like structures, however some assemblies crumbled when dried. Additionally, we observed that when assemblies were washed with ethanol a few times, most of the structures disassembled, which proves that the binding forces in these structures are weak (van der Waals) in nature. To calculate the number of rods to make a self-assembled structure further theoretical calculations are required. Additionally, some broken structures in Fig. 1b(ii) reveal that rods assemble mainly at the surface and did not make the filled self-assembled structures. Fig. 1b(iii) shows that the assembled structures are of a wide size range (≈10-40 µm) that corresponds to the initial emulsion droplet size, which is stabilized by the rods. Since it is very difficult to make emulsion droplets of one size and therefore making of uniform self-assembled structures is almost impossible.

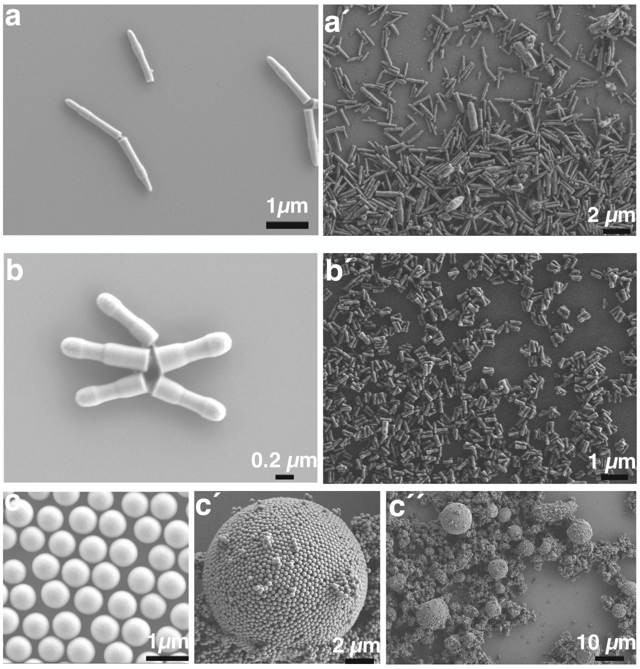


Fig. 2. (a and b) unassembled segmented silica rods, (a′ and b′) corresponding images showing failed self-assembly of rods shown in a and b, and (c) unassembled silica particles, (c′) high magnification SEM image showing self-assembled silica particles, and (c´´) a low magnification image showing self-assembled silica particles structures.

In order to further understand the effect of rod shape on self-assembly, we synthesized segmented silica rods by using a previously reported method (as explained in experimental section). To our surprise, no self-assembly of segmented rods occurred under the same conditions that were used for smooth rods. Fig. 2a and b show segmented rods before assembly and 2a´ and b´ show segmented rods after self-assembly process, respectively. From Fig. 2a´ and b´ it becomes clear that no self-assembled structures were visible after the assembly process. We assume, since segmented rods were having groves and crests, sufficient van der Waals interactions did not occur between the rods in order to make the self-assembled structures. This experiment proved that rod assembly depends upon the morphology of the building blocks and generally smooth building blocks are preferred over corrugated ones. Similarly, we synthesized silica particles and investigated particle self-assembly under same conditions used for the assembly of smooth rods. Particles self-assembled and made similar colloidosome like structures (Fig. 2c´ and c´´) to those were made by the smooth rods. Fig. 1b(iii) and Fig. 2c´´revealed that in addition to self-assembled structures a large fraction of unassembled particles or rods was present. Either some particles (rods) did not get incorporated into the assembled structures or these unassembled particles (rods) resulted from broken self-assemblies. Though, we did not perform the experiments, it appears that the polydispersity of the rods can negatively affect the rod assembly.

Conclusions

This work demonstrated self-assembly of silica rods by using Pickering emulsion based strategy. Additionally, We investigated self-assembly of rods of different morphologies (smooth and segmented), and found that smooth rods self-assembled easily while we did not see any self-assembly of segmented rods under same conditions. Similarly, spherical particles also made self-assembled structures. Therefore, in addition to self-assembly of silica rods, this work also demonstrates that under similar conditions the morphology of building blocks can also impact the self-assembly behaviour. We anticipate that this research will entice the broad research community for further investigating the self-assembly behaviour of micro-sized one-dimensional structures, effect of morphology on self-assembly behaviour, and self-assembly of hybrid systems (e.g., rods-particles). These studies will further help in making more reliable self-assembled structures mimicking nature.

Acknowledgements

J. Sharma is a Staff Scientist at the Oak Ridge National Laboratory managed by UT-Battelle, LLC, for the U.S. Department of Energy under Contract DE-AC05-00OR22725. This work is supported by DOE's Building Technology office award# 1027-1605 to J.S. A portion of this research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

Notes and references

1 Z. Nie, A. Petukhova, and E. Kumacheva, *Nat. Nanotechnol.*, 2010, **5**, 15.
2 Y. Tian, T. Wang, W. Liu, H. L. Xin, Y. Ke, W. M. Shih, and O. Gang, *Nat. Nanotechnol.*, 2015, **10**, 637; J. Sharma, R. Chhabra, A. Cheng, J. Brownell, Y. Liu, and H. Yan, *Science*, 2009, **323**, 112; T. Alejo, M. D. Merchan, M. M. Velazques, and J. A. Perez-Hernandez, *Mater. Chem Phys.*, 2013, **138**, 286; A. Sánchez-Iglesias, M. Grzelczak, T. Altantzis, B. Goris, J. Pérez-Juste, S. Bals, G. V. Tendeloo, S. H. Donaldson Jr., B. F. Chmelka, J. N. Israelachvili, and L. M. Liz-Marzán, *ACS Nano*, 2012, **6**, 11059; A. Abbas, R. Kattumenu, L. Tian, and S. Singamaneni, *Langmuir*, 2013, 29, 56; H. Liu, X. Gu, M. Hu, Y. Hu, and C. Wang, *RSC. Adv.*, 2014, **4**, 16751; P. V. Rjin, N. C. Mougin, D. Franke, H. Park, and A. Boker, *Chem. Comm.* 2011, **47**, 8376; C. Zhang, Y. Zhu, R. Zhang, Y. Xie, K. Wang, and X. Liu, *RSC. Adv.*, 2015, **5**, 90651; E. M. Walker, D. S. Frost, and L. L. Dai, *J. Coll. Interface Sci.* 2011, **363**, 307; J. Li, H. and D. H. Stover, *Langmuir*, 2010, **26**, 15554; L. Vigderman, B. P. Khanal, E. R. Zubarev, *Adv. Mater.,* 2012, **24**, 4811.
3 X. Lan, X. Lu, C. Shen, Y. Ke, W. Ni, and Q. Wang, *J. Am. Chem Soc.*, 2015, **137**, 457; B. nikoobakht, Z. L. Wang, and M. A. El-Sayed, *J. Phys. Chem. B*, 2000, **104**, 8635; S.-Y. Zhang, M. D. Regulacio, and M.-Y. Han, *Chem. Soc. Rev.*, 2014, **43**, 2301; N. R. Jana, *Chem. Comm.*, 2003, 1950.
4 A. Kuijk, A. V. Blaaderen, A. Imhof, *J. Am. Chem. Soc.*, 2011, **133**, 2346; J. Zhang, H. Liu, Z. Wang and N. Ming, *Chem. Euro. J.,* 2008, **14**, 4374; J. He, B. Yu, M. J. Hourwitz, Y. Liu, M. T. Perez, J. Yang, J. Nie, *Angew. Chem. Int. Ed*., 2012, **51**, 3628.
5 J. He, B. Yu, M. J. Hourwitz, Y. Liu, M. T. Perez, J. Yang, J. Nie, *Angew. Chem. Int. Ed*., 2012, **51**, 3628; W. Li, K. Lu, J. Y. Walz, and M. Anderson, *J. Am. Ceram. Soc.*, 2013, **96**, 298.
6 P. Datskos, J. Sharma,. *Angew. Chem. Int. Ed*., 2014, **53**, 451.
7 A. R. Morgan, A. B. Dawson, H. S. Mckenzie, T. S. Skelhon, R. Beanland, H. P. W. Franks, and S. A. F. Bon, *Mater. Horizons*, 2014, **1**, 65; B. W. Longbottom, L. A. Rochford, R. Beanland, and S. A. F. Bon, *Langmuir*, 2015, **31**, 9017.
8 S. U. Pickering, *J. Chem. Soc.* 1907, **91**, 2001; W. Ramsden, *Proc. R. Soc. London*, 1903, **72**, 156; A. D. Dinsmore, *Science*, 2002, **298**, 1006.
9 K. L. Thompson, M. Williams, S. P. Armes, *J. Colloid Interface Sci.*, 2015, **447**, 217.

Self-assembly of micron-sized silica rods is demonstrated using Pickering emulsion based strategy.