Self-assembly of lobed particles into amorphous and crystalline porous structures

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<th>Journal:</th>
<th>Soft Matter</th>
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<tr>
<td>Manuscript ID</td>
<td>SM-COM-09-2019-001878.R1</td>
</tr>
<tr>
<td>Article Type:</td>
<td>Communication</td>
</tr>
<tr>
<td>Date Submitted by the Author:</td>
<td>28-Nov-2019</td>
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We report simulation studies on the self-assembly of hard-lobed particles (patchy particles where patches appear as lobes around a seed) of different shapes and show that various types of self-assembled morphologies can be achieved by tuning inter-lobe interactions. On self-assembly, the linear building blocks having two lobes around the seed formed rings, the trigonal planar building blocks formed cylindrical hollow tubes and two-dimensional sheets, and the square planar building blocks formed spherical clathrates. The tetrahedral, trigonal bipyramidal, and the octahedral-shaped particles formed compact porous crystalline structures which are constituted by either hexagonal close packed or face centered cubic lattices.

The pore size distributions revealed that linear, trigonal planar, and square planar building blocks create highly porous self-assembled structures. Our results suggest that these self-assembled morphologies will potentially find applications in tissue engineering, host-guest chemistry, adsorption, and catalysis.

Colloidal patchy particles have gained importance due to their ability to self-assemble into higher-order structures (colloidal molecules, colloidal polymers, and even colloidal crystals) dictated by their shapes and directional interactions. Based upon the structures and chemical functionalities, these self-assembled entities have potential applications as photonic band gap materials, catalysts, and biomaterials. Notwithstanding challenges in the controlled synthesis of patchy particles, several synthesis techniques have been devised and applied to demonstrate, for example, self-assembly of spherical triblock Janus particles into a two-dimensional kagome lattice. A staged self-assembly process in which different patches are sequentially activated was further shown to form porous structures as well as cubic diamond and body centered cubic lattices. Not only the spherical particles, non-spherical patchy particles (where patches appear as lobes around a central seed) have been shown to self-assemble into colloidal molecules and polymers. Moreover, soft patchy particles made up of terpolymers were shown to form long colloidal polymers by self-assembly or co-assembly between different types of building blocks.

Although non-spherical patchy particles of different shapes can be synthesized, detailed investigations on their self-assembled morphologies are yet to be carried out. A molecular simulation study on the self-assembly of spherical patchy particles revealed that structures like chains, sheets, tetrahedra, and icosahedra can be obtained depending on the number and location of patches on the spherical surface. We hypothesized that if patches appear as hard lobes and are positioned at specific locations to design specific particle-shapes, then the self-assembly of those particles may lead to higher-order structures. Moreover, directional interactions between the hard lobes will create more excluded volume around each particle because of their non-spherical shape that may lead to porous self-assembled structures.

In this work, we have studied the self-assembly of different types of hard-lobed particles into porous morphologies. Specifically, we have chosen lobed particles (SM, m denotes the shape and NL denotes the number of lobes present in the particle) as building blocks of seven different shapes (Fig. 1): snowman (S1SM), dumbbell (SDB), trigonal planar (S3P), square planar (S4P), tetrahedral (S4TH), trigonal bipyramidal (S5Bp), and octahedral (S6Oct). The shapes of lobed particles considered in this study are experimentally realizable. For example, Stefano et al. synthesized single to multi-lobed particles of different shapes by first nucleating oil droplets (3-methacryloxypropyl trimethoxysilane oligomers) around negatively charged polystyrene seeds and then solidifying the oil droplets using the radical polymerization technique. Meester et al. have also shown a way of producing lobed particles of defined shapes by reconfiguring the random aggregates of spherical colloids.
Fig. 1 Seven building blocks of different shapes are shown in space-filling representations. The central seed (C) and the lobes (L) are represented by red and yellow spheres, respectively.

For each building block, we have performed coarse-grained Langevin dynamics simulations using the GPU-accelerated software HOOMD-Blue. The non-bonded interactions between the lobes are attractive and have been modeled by the Lennard-Jones potential and the interactions between two central seeds (C) and also between a lobe (L) and a seed (C) are repulsive and have been modeled by the surface-shifted Lennard-Jones potential implemented in HOOMD-Blue (see supplemental methods, ESI†). For each building block, we have tuned the parameters (εLL/kBT; εLL is the depth of potential well for the L-L pair; kB is the Boltzmann constant, and T is the temperature), which we denote by εLL (reduced interactions between the lobes in kB T units), to observe its effect on the self-assembly. The εLL values employed in this work are 3.0, 3.8, 4.3, 5.0, 6.0, 7.5. We also carried out simulations with multiple initial configurations to test the robustness of self-assembled structures obtained, as has been done in previous studies. We further report the convergence of potential energy per particle vs. simulation time (Fig. S1, ESI†).

We have observed that the occurrence of self-assembly depends on the number of lobes (Nl) and the non-bonded interactions. In the case of S6CT, the lowest εLL value that shows self-assembly is 3.8, but the lowest εLL value showing self-assembly increases as the number of lobes decreases (Table S1, ESI†). The S1SM building blocks with one lobe do not show self-assembly for any εLL value. The S2DB building blocks exhibit self-assembly only at εLL = 7.5. Since the building blocks in all simulations have attractive interactions only through the lobes, a higher number of lobes around a seed creates a higher number of sites of attraction and thereby results in their self-assembly at a lower εLL value. For each system, we further estimated the change in AV−12 εLL−13 or reduced temperature, T* (Fig. S2, ESI†). In each case, we observed a sharp change in EP when the lobed particles undergo transitions from disordered states to self-assembled states, a feature of the first order transitions. Such transitions have also been observed in the self-assembly of spherical patchy particles with four patches at four equatorial positions or two ring patches near the poles that were found to undergo first order transitions from disordered phases to self-assembled two dimensional sheets.

Fig. 2 Self-assembly of S2DB building blocks: (A) Simulation domain showing the formation of self-assembled structures at εLL = 7.5, (B) Ring structures formed by the building blocks, (C) Radial distribution function for the C-C pair; (Inset) A snapshot of the first coordination shell of a building block, and (D) Trigonal prismatic geometry of the seeds in the first coordination shell.
Surrounded by three lobes from three different building blocks and hence the four lobes of the central tetrahedral building block is attached to each of the three lobes of \( S_{\text{TP}} \) building blocks as shown in the inset of Fig. 3C highlighting that each building block produces a sharp peak (except \( S_{\text{TP}} \)). For \( S_{\text{TP}} \) and \( S_{\text{TH}} \), the building blocks formed polyhedron-like structures at \( \varepsilon_{LL} = 5.0 \) (Fig. 3A and 3B). The square planar building blocks (\( S_{\text{SP}} \)), unlike their spherical analogues (spherical patchy particles having four surface patches at four equatorial \( \varepsilon \) positions that self-assemble into two-dimensional sheet-like \( \varepsilon_{LL} \) structures (Fig. 3D). In these structures, each of the three lobes is attached with two other lobes from different building blocks and thereby each building block is surrounded by 6 other building blocks in its first coordination shell and long range order is absent (Fig. 3E, F).

For \( S_{\text{TP}} \) and \( S_{\text{TH}} \), the building blocks formed polyhedron-like structures at \( \varepsilon_{LL} = 5.0 \) (Fig. 3A and 3B). The square planar building blocks (\( S_{\text{SP}} \)), unlike their spherical analogues (spherical patchy particles having four surface patches at four equatorial \( \varepsilon \) positions that self-assemble into two-dimensional sheet-like \( \varepsilon_{LL} \) structures (Fig. 3D). In these structures, each of the three lobes is attached with two other lobes from different building blocks and thereby each building block is surrounded by 6 other building blocks in its first coordination shell and long range order is absent (Fig. 3E, F).

Unlike \( S_{\text{TP}} \), the \( S_{\text{TH}} \) building blocks do not self-assemble into spherical clathrates but they are well-ordered inside the self-assembled structures as revealed by the RDF (Fig. 3B). The first coordination shell displayed in Fig. 3B (inset) shows that each of the four lobes of the central tetrahedral building block is attached to 12 other building blocks. Twelve seeds belonging to 12 building blocks present in the first coordination shell and the central seed with respect to which the first coordination shell is measured form hexagonal close packed structures constituted by two different kinds of planes (Fig. 5C). At higher \( \varepsilon_{LL} \), both \( S_{\text{TP}} \) and \( S_{\text{TH}} \) building blocks self-assemble to form porous wire-like structures (Fig. S5A and S5B, ESI†) and at very high \( \varepsilon_{LL} \) (\( \varepsilon_{LL} = 15.0 \)), \( S_{\text{SP}} \) building blocks formed two-dimensional sheet like structures (Fig. S6, ESI†).

The trigonal bipyramidal (\( S_{\text{TP}} \)) and the octahedral (\( S_{\text{OCT}} \)) building blocks formed compact polyhedron shaped self-assembled structures at \( \varepsilon_{LL} = 4.3 \) and 3.8, respectively (Fig. 5D, G). For both of these systems, multiple peaks present in the RDF (Fig. 5H) indicate that the building blocks are highly ordered and correlated in these self-assembled structures. The number of building blocks in the first coordination shell is 12 for both \( S_{\text{TP}} \) and \( S_{\text{OCT}} \). The first coordination shell for \( S_{\text{TP}} \) shows that the building blocks are tightly packed in these systems (Fig. 5D, H). For \( S_{\text{TP}} \), the seeds are arranged in hexagonal close packed structures comprised of two different planes similar to \( S_{\text{TH}} \) (Fig. 5C, F) but for \( S_{\text{OCT}} \), the seeds are organized as face centered cubes which are constituted by three different types of planes (Fig. 5D). With an increase in \( \varepsilon_{LL} \), the shapes of these self-assembled structures became gradually thinner and longer and at very high \( \varepsilon_{LL} \), they formed long extended structures (Fig. S5D and S6, ESI†).

We further characterized porous assemblies by computing the distributions of pore diameters (Fig. 4A) using the Zeo++ software by extracting the largest possible cuboids (Fig. S7, ESI†) from self-assembled structures. The pore-diameter distributions show that each building block produces a sharp peak (except \( S_{\text{DB}} \) and \( S_{\text{TP}} \)) showing uniform pore-sizes. However, the self-assembled structures obtained from \( S_{\text{DB}} \) have pores with larger...
Fig. 4 Self-assembly of S\textsuperscript{SP}\textsubscript{4} building blocks: (A) Simulation domain showing the formation of polyhedron shaped self-assembled structures at $\tilde{\epsilon}_{LL} = 5.0$. (B) Structures of spherical clathrates formed by the S\textsuperscript{SP}\textsubscript{4} building blocks, (C) Hexagonal close packing of self-assembled cuboctahedrons; the red spheres are the seeds of the lobed particles, (D) Radial distribution function for the C-C pair; the presence of multiple peaks indicates the formation of crystalline structures; (inset) the first coordination shell of a building block is shown with the lobes of the central building block highlighted in blue.

Fig. 5 Snapshots and data corresponding to self-assembly of S\textsuperscript{TH}\textsubscript{4} (panels A, B, C), S\textsuperscript{TBP}\textsubscript{5} (panels D, E, F), and S\textsuperscript{OCT}\textsubscript{6} (panels G, H, I) building blocks: (A, D, G) Simulation domains showing the formation of many polyhedron shaped clusters; (B, E, H) RDFs show the presence of multiple peaks indicating the formation of crystalline structures, and the first coordination shells (inset); the lobes of the central particles with respect to which the first coordination shell were measured are depicted in blue; (C and F) Hexagonal close packed structures comprised of two different planes a (green) and b (blue); and (I) Face centered cubic lattice comprised of three different planes a (cyan), b (blue) and c (green) formed by the seeds of 13 lobed particles (12 in the first coordination shell and 1 in the center).
Fig. 6 (A) Derivative distributions of the pore volume, and (B) the diameter ($D_f$) corresponding to the largest free sphere present in the self-assembled structures.

...diameters ranging between $4\sigma L$ to $8\sigma L$, due to the presence of...can self-assemble into higher order porous structures if the interlobe interactions are tuned. We show that not only the patch size, interactions between the patches (lobes) also determine the number of particles in the first coordination shell. At lower $\bar{v}_{LL}$, the dumbbell and the triangular planar ($S_3^{TP}$) shaped building blocks form highly porous amorphous structures. At lower $\bar{v}_{LL}$, the triangular building blocks are surrounded by 9 other building blocks and form cylindrical hollow tubes, but at higher $\bar{v}_{LL}$, they are surrounded by 6 building blocks to form two-dimensional sheets. Given these self-assembled morphologies, trigonal planar building blocks can be compared with the sp$^2$ hybridized carbon atoms which form carbon nanotubes and graphene sheets in two allotropic states. The square planar ($S_4^{SP}$) building blocks self-assembled into close packed spherical clathrates at lower $\bar{v}_{LL}$. Each spherical clathrate is constituted by 12 building blocks and the seeds of these 12 building blocks are located at the vertices of a cuboctahedron. The $S_4^{TP}$, $S_5^{TP}$ and $S_6^{OCT}$ building blocks self-assembled into very compact structures with smaller pore-sizes. The $S_5^{TD}$ and $S_6^{TP}$ building blocks were also observed to assemble in a hexagonal close packing arrangement, and the $S_6^{OCT}$ building blocks into face centered cubic lattices.

The self-assembly study carried out in this work is scale independent and therefore it is applicable to particles of sub-micrometer to micrometer sizes. Gong et al.\textsuperscript{22} have recently proposed a method called colloidal fusion to synthesize spherical patchy particles of different sizes. This method does not rely on the chemistry of particles but rather on a simple physico-chemical algorithm incorporating symmetry and composition information. Therefore, the method can produce patchy particles from nm to $\mu$m sizes. Pine and coworkers\textsuperscript{23} have also designed a method where the clusters of microspheres are first made using the emulsion-evaporation technique and then a two-stage swelling process followed by polymerization is performed to produce patchy lobed particles of different shapes. To our knowledge, the lobed particles synthesized so far are primarily designed with non-biodegradable polymers like polystyrene, which may...
not be suitable for biomedical applications, where biodegradable polymers are likely needed. Since the dumbbell-shaped particles generate larger and well-connected pores in self-assembled mor- phologies reported in this work, we surmise that these particles, if designed in the micron-size range and using biodegradable polymers, could be useful to mimic the extracellular matrix. The three lobed planar particles of nanometer size can also be used as building blocks to prepare synthetic channels for applications in molecular separations. If the interactions between the lobes are tuned, these particles can also self-assemble in two-dimensional sheets with likely applications in adsorption and catalysis. The four lobed planar particles are likely useful to study host-guest chemistry as they are capable of creating clathrate-like structures.

We suggest that findings from this work will inspire future experi- mental work aimed at exploring the self-assembly of lobed parti- cles of various sizes.

Acknowledgements

We are grateful for financial support provided by the National Science Foundation (award No. OIA-1757371; HV). We acknowledge computational support through the following resources: Premise, a central shared HPC cluster at UNH supported by the Research Computing Center; BioMade, a heterogeneous CPU/GPU cluster supported by the NSF EPSCoR award (OIA-1757371; HV); and the NSF-supported (ACI-1548562) Extreme Science and Engineering Discovery Environment (XSEDE). Comet resource at San Diego Supercomputer Center (SDSC) under grant TG-MCB160183 (HV). We also thank Dr. Maciej Haranczyk for discussions on pore-size distributions.

Conflicts of Interest

There are no conflicts to declare.

Notes and references
