

Eco-Effective Materials by Self-Assembly

Sungrok Wang, Sungkwon Yoon, William T. Nichols*

Abstract—In this paper we discuss self-assembly as a powerful technique for the synthesis of eco-effective materials. We give three examples that exhibit increasing complexity in the building blocks undergoing self-assembly. In the first case, specific interactions are designed between nanoscale components that assemble up to centimeter scale. This technique however is limited to relatively few components because each component must be controlled separately. To address this issue the second example designs the functionality directly into building blocks that then assemble. This is the design principle used in biological cells. In the basic cell motif: a biological membrane is functionalized for each cell type but all cells assemble under similar conditions. In human engineering, we can't match nature's complexity in cellular building blocks. Accepting this limitation, the third technique uses biological cells directly in the assembly. Here the fully complex biological machinery creates intricate building blocks that can be used in self-assembly. Here we show an example of marine diatoms that are composed of intricate silica shells that assemble into macroscale patterns.

Keywords—Self-assembly, Eco-effective, Proteins, Diatoms

I. Introduction

Eco-effective materials synthesis is an emerging concept in materials science. Eco-effective materials are designed specifically to be both ecological and economic [1]. These materials are ecological because they are created from widely available materials, they are non-toxic and the synthesis requires low-energy and produces little-to-no waste. Importantly, they can be economic for same reasons because low-energy and low-waste synthesis greatly reduces the costs of manufacturing. A key point to recognize is that the ecological and economic value is created in the material through appropriate design. Nature provides the primary inspiration for eco-effective design where biological organisms must use materials available in their environment, and can not afford to invest valuable energy for inefficient growth of materials. A further point that can be taken from nature is that everything is hierarchically assembled from nanostructured macromolecules to micron scale cells all the way up to centimeter scale tissues and organs. New properties emerge at each level of organization creating the complexity and functionality of biological materials. For human engineered materials it is critical to begin to learn how to effectively use these design principles.

II. Hierarchical Self-Assembly

Fig. 1 shows the basic scheme of hierarchical self-assembly. As in all self-assembly the ordering is driven by a balance of forces where each force acts on a specific scale [2]. For example van der Waals forces act on molecular scales whereas surface tension can act effectively on micrometer and millimeter scale objects. As forces balance the equilibrium structure is built up from the nanoscale into microstructures and further up to macroscale objects.

Force balance will tend to create disordered, semi-close-packed materials if there no constraints on the assembly. In order to create specific ordered materials it is necessary to design the constraints on the assembling system of components. In this paper we will demonstrate how forces and constraints can be designed to create materials with one, two and three dimensional organization. When interactions are via linear forces the components are driven together making wires or threads in one-dimension. Commonly, the 1D wires may interact with each other along their sides where they have a large surface area. This causes the wires to line up side by side to create extended 1D objects such as fibers. When the self-assembling objects are confined in 2D, sheets are naturally formed. Because the objects are more free to move within the plane it is critical to consider two points. First, is that the forces should be reversible so that they can find their equilibrium configuration rather than a glass-like disordered state [3]. Second, the assembly must occur slow enough to give the objects time to find their equilibrium. These two points are especially critical for the case of no confinement. The objects are free to move in any direction. Typical self-assembly in three-dimensions produces close-packed structures. Colloidal crystals are prime examples of this case. However, if there are more specific interactions the assembly can be quite intricate. This is very commonly the situation in nature where the assembling objects are brought together through specific protein-protein interactions.

In the following three sections we will demonstrate the control of hierarchical assembly from the nanoscale to the macroscale using constraints as shown in Fig. 1. We will begin with the direct assembly of simple nanomaterials through chemical interactions. In subsequent sections the complexity of the building blocks in the assembly increases. First through nano-functionalization of hollow, microscale protein spheres that assemble into macroscopic materials. Second through the assembly of actual biological cells into engineered materials.

Sungrok Wang, Sungkwon Yoon, William T. Nichols
Division of Materials Science and Engineering, Hanyang University
Seoul, South Korea

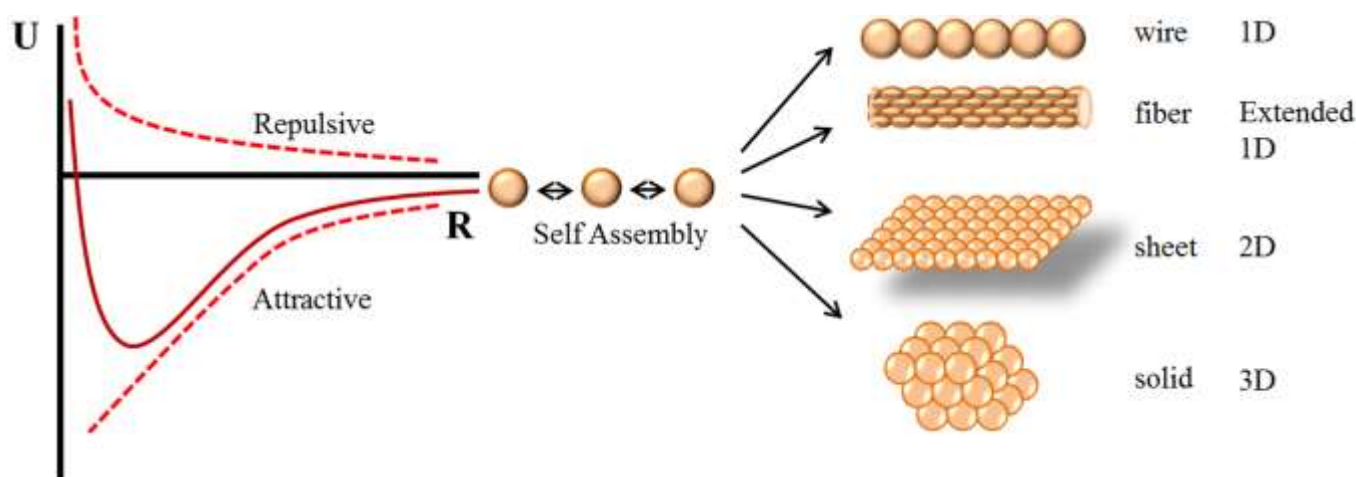


Figure 1. Concept of self-assembly with constraints.

III. Self-Assembly of Simple Nanomaterials

The essence of self-assembly is a balance of forces that drive nanomaterials or macromolecules to their stable thermodynamic equilibrium. When the driving forces act at different size scales there will be a hierarchical assembly. In principle any number of different objects can be assembled, however each component must be acted on by specific forces at the appropriate size scale.

Fig. 2 shows an example of the self-assembly of nanoscale

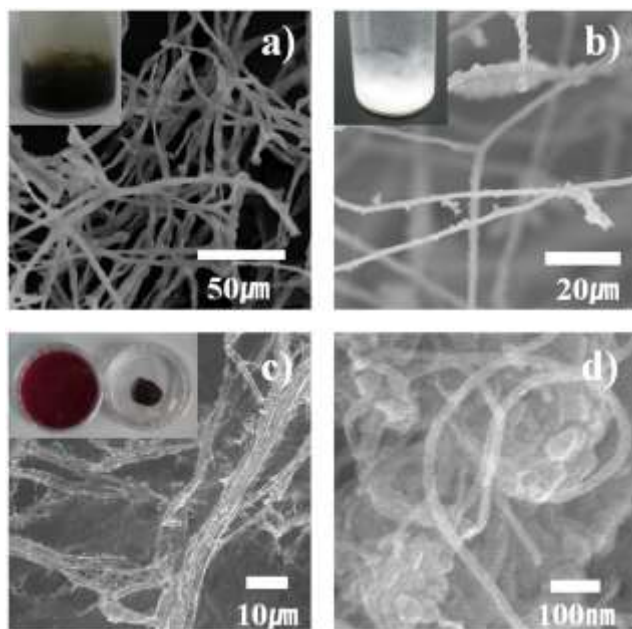


Figure 2. FE-SEM images of direct self-assembly of nanomaterials with the cyclodextrin molecule. (a) all cyclodextrin network; (b) cyclodextrin-TiO₂ composite network; (c) cyclodextrin-gold nanoparticle network and (d) cyclodextrin-TiO₂-carbon nanotube network.

units under driving forces at both the nanoscale and the microscale. The beta-cyclodextrin (CD) molecule consists of seven glucose molecules linked together to form a cone with hydrophilic ends and hydrophobic walls and interior cavity. Normally the ends of the CD molecule are hydrated shielding the hydrophobic region. In this state there is no force to drive an ordered assembly and the molecules stay dispersed in water. However, exposing an aqueous solution of CD to sunlight in the presence of a TiO₂ nanoparticle photocatalyst induces a ring breaking of the CD cone and subsequent dehydration [4]. The hydrophobic region of the modified CD molecule is now exposed to water, which drives the molecules together end-to-end forming chains of CD molecules. The key factor is that the shape of the cone and location of the hydrophobic regions that is responsible for the orientation along a specific direction forming 1D chains. As the chains form, their outer surfaces are also hydrophobic which in turn leads to bundling of the chains forming an extended thickness fiber as discussed in Fig 1. The force of assembly of the fiber is balanced by surface tension that limits the radius of the fibers. A surprising result from this work is that the microscale fibers can further assemble into macroscale networks through the interconnection of fibers. It is instabilities of surface tension that promote branching of the fibers into different directions that builds up self-supporting networks of CD molecules as shown in Fig 2(a).

During exposure to sunlight the CD molecules are modified and dehydrated through the TiO₂ photocatalyst nanoparticles. Many of the CD molecules separate from the surface, however a fraction stay on the surface forming a weak complex [5]. The CD molecules in the CD-TiO₂ complex will feel similar hydrophobic forces assembling them into fibers. This carries the attached TiO₂ nanoparticles into the network (Fig 2(b)). Overall the forces are similar so the structure of the fibers and the morphology of the networks are similar.

Because of the balance of forces the system based on CD molecules can be extended to any material that can be complexed with CD. For instance, gold nanoparticles also catalyze dehydration of CD molecules and can thus form Au-CD complexes. The result is a network of fibers with Au nano-

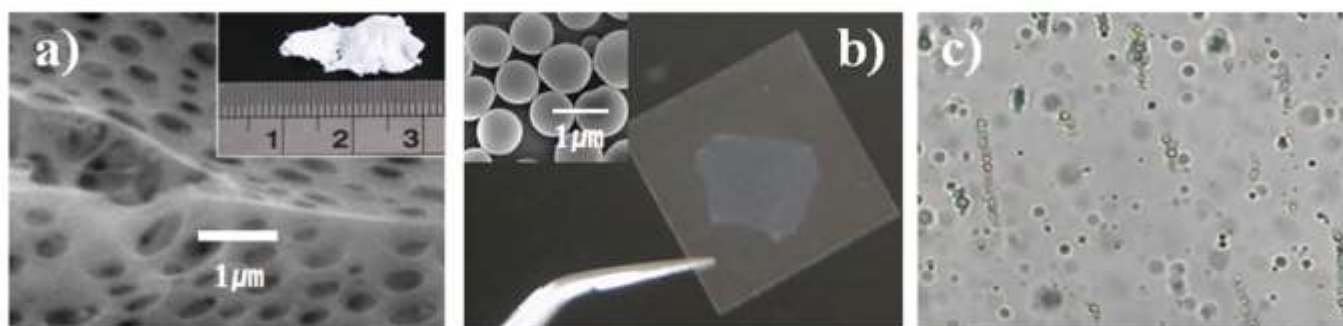


Figure 3. Self-assembly of protein microspheres. (a) 3D assembly of microspheres after freeze-drying; (b) 2D assembly of microspheres; (c) 1D fibers of magnetic functionalized microspheres created using an external magnet.

particles incorporated as shown in Fig 2(c). The inset of the figure shows that the optical properties change dramatically due to the presence of the small gold nanoparticles with a surface plasmon resonance in the visible range. Similarly CNT complexes with CD resulting in an intricate assembly at the nanoscale as shown in Fig. 2(d).

These self-supporting networks are promising for a number of eco-materials applications such as sensors, photocatalysts and solar cells. Furthermore, it is important to note that the networks are composed of low-cost materials and synthesized in water powered by sunlight making this a highly eco-effective process.

iv. Self-Assembly of Functional Building Blocks

Attachment of nanoscale materials to a molecule that induces assembly is a very useful platform, but it will be limited in how many components can be assembled. In addition, those assemblies are random composites because the forces are not specific to each component. Further, assembling up to the centimeter scale directly from nanoscale components is inefficient. A better design principle is to create building blocks at the microscale, then add nanoscale functionality to them. In principle almost any nanofunction can be added onto the microscale building block, then they are assembled up to the macroscale using the same set of forces. The prime examples of this concept are biological cells. In the biological design motif the cells are hollow spheroids that are functionalize on the molecular and nanoscale in both the interior and at the exterior surface. These cells then assemble hierarchically building up the tissues, organs and organ systems.

Hollow protein microspheres offer an opportunity to mimic this biological design motif. The protein microspheres are a hollow shell of cross-linked protein molecules encapsulating a interior oil phase [6]. The shell can be composed of a wide variety of proteins and the microsphere size and surface morphology can be varied. Moreover, like biological cells, the microspheres can be functionalized both inside and outside through electrostatic or covalent interactions. The major advantage is that the chemistry at the nanoscale is separate from the self-assembly occurring at the microscale. This allows

much more complex functionalities to be integrated into the final assembled material.

The microspheres contain a low density oil phase, therefore they float in aqueous solution. This buoyancy supplies a uniform force that drives the microspheres to the surface where they assemble into close packed arrangements. Fig. 3(a) shows this ordered three-dimensional assembly of microspheres after freeze drying to remove both the aqueous and oil phases leaving only the protein shells. It is also straightforward to use the design principle shown in Fig. 1 to control the self-assembled geometry through constraints. When the microspheres are constrained tightly to the interface a two-dimension sheet is formed Fig. 3(b). The inset shows the regular hexagonal close-packed structure of the sheet. To achieve a one-dimensional assembly another constraint must be added. By adding magnetic nanoparticles to the interior of the microspheres, linear interactions can be imposed by alignment of the magnetic dipoles to the direction of an applied magnetic field. The resulting one-dimensional assembly of aligned microspheres into chains is shown in Fig. 3(c).

These materials have numerous potential applications. For instance the protein scaffold is promising for tissue engineering applications. It may also be used to immobilize enzymes to create a biocatalytic support. Of particular interest are the 1D magnetic fibers, which might be used as artificial cilia for microfluidics. Again this platform uses low-cost widely available materials, protein and lipids, and uses a low-energy sonochemical method to synthesize the microspheres in water making it a very eco-effective process.

v. Self-Assembly of Biological Building Blocks

There is a great opportunity to expand the protein building blocks platform, but it is currently very far away from the complexity of actual biological cells. To assemble truly complex building blocks it is possible to use actual biological building blocks. Marine diatoms present an example that are easy to work with in the laboratory. Diatoms are single cell algae with an intricate silica exoskeleton shell called the frustule. These shells have evolved over millions of years to provide complex, highly multifunctional properties. Among



Figure 4. Schematic of the self-assembly of diatom frustules in a Langmuir trough.

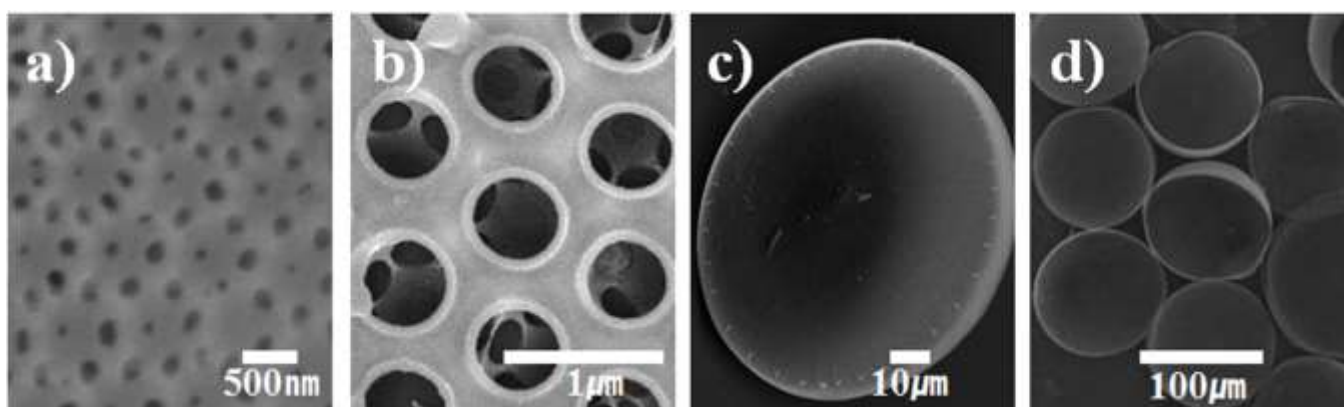


Figure 5. FE-SEM images of the assembly of marine diatoms showing their self-similarity at multiple size scales. (a) cribellum (outer) layer; (b) areola (inner) layer; (c) full diatom; (d) self-assembled diatoms.

the optimized properties are: high mechanical strength to protect the cell; ordered silica crystal patterns to focus sunlight energy onto the chloroplasts; and a hierarchical system of pores that sort and filter nutrient particles coming into the cell [7]. Growth of a surface as intricate and optimized as the diatom frustule is currently beyond the ability of engineering so it is advantages to simply use the bio-silica frustule directly in designed materials. One problem that arises however is that many engineering applications require patterns over centimeter scales while diatoms are on the order of only 100 micrometers. This requires that the diatom frustules be assembled.

Because the diatoms are buoyant we can again use this force to self-assemble them like in the case of the protein microspheres. However, unlike the protein microspheres, the diatom frustules are thin and disk shaped causing significant disorder due to stacking. Therefore, an additional force must be included. By using a Langmuir trough an ordered assembly can be achieved. The diatoms are first floated on a water surface at low number density. A surfactant is added to the surface providing a surface pressure driving the diatom frustules into a close packed structure as shown in Fig. 4.

When transferred to a substrate, the intricate diatom pattern extends up to the centimeter scale. Interestingly, the diatom

patterns are self-similar across the full size range from nanoscale to centimeter scale as shown in Fig. 5. At the smallest scale the pores of 200 nm diameter are hexagonally arranged Fig. 5(a). Within the shell further pores are 500 nm and 1 micron again with hexagonal symmetry Fig. 5 (b, c). The diatom frustules themselves maintain this hexagonal symmetry within the larger assembly.

VI. Conclusions

In this paper we demonstrated self-assembly as a means of synthesizing eco-effective materials. Three examples were given that exhibited increasing complexity of the building blocks. First, nanoscale building blocks were assembled directly through forces at the nanoscale. This technique, however is limited to relatively few components because each component must be controlled separately. To address this issue the second example designed the functionality directly into building blocks prior to their assembly. The third technique increased the complexity significantly by using actual biological cells directly. We showed an example of self-assembly of marine diatoms frustules into macroscale patterns. In all three cases the syntheses procedures are low-cost, and low-energy using widely available materials. These characteristics along with their ability to self-assemble into

functional materials makes them highly eco-effective processes.

Acknowledgment

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korean government (MSIP) (No. 2011-0013704) and the research fund of Hanyang University (HY-2010-N).

References

- [1] W. McDonough and M. Braungart, *Cradle to Cradle: Remaking the Way We Make Things*, North Point Press, New York, 2002
- [2] G.M. Whitesides and B.A. Grzybowski, "Self-assembly at all scales," *Science*, vol. 295, pp. 2418-2421, 2002
- [3] B.A. Grzybowski, C.E. Wilmer, J. Kim, K.P. Browne and K.J.M. Bishop, "Self-assembly: from crystals to cells," *Soft Matter*, vol. 5, pp. 1110-1128, 2009
- [4] S. Han, S. Yoon and W.T. Nichols, "Sunlight-initiated self-assembly of cyclodextrin networks," *Appl. Surf. Sci.*, vol. 261, pp. 730-734, 2012
- [5] M. Du, J. Feng, and S.B. Zhang, "Photo-oxidation of polyhydroxyl molecules on TiO₂ surfaces: from hole scavenging to light-induced self-assembly of TiO₂-cyclodextrin wires," *Phys. Rev. Lett.*, vol. 98, pp. 066102, 2007
- [6] K.S. Suslick, and M.W. Grinstaff, "Protein microencapsulation of nonaqueous liquids," *J. Am. Chem. Soc.*, vol. 112, pp. 7807-7809, 1990
- [7] D. Losic, J.G. Mitchell and N.H. Voelcker, "Diatomaceous lessons in nanotechnology and advanced materials," *Adv. Mater.*, vol. 21, pp. 2947-2958, 2009