NANOENGINEERED SELF-ASSEMBLED TWO-DIMENSIONAL AND THREE-DIMENSIONAL MATERIALS

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ABSTRACT

This paper summarizes work in the molecular-level self-assembly of two-dimensional and three-dimensional materials. Synthesis processes are briefly discussed, and examples of multiple properties achievable in two-dimensional and three-dimensional self-assembled materials are given.

Keywords: self-assembly, layer-by-layer synthesis, multifunctional material, nanotechnology

1. INTRODUCTION

The ability of systems to self-organize, self-replicate or self-assemble themselves is of particular interest as system complexity increases to the point that the directed control of organization, fabrication or maintenance of all of the individual parts becomes cumbersome. Self-replicating materials and devices such as DNA and self-replicating 3D printers, self-evolving systems such as automatons in the Game of Life, and self-improving software are examples. Typically in such applications, an initial design is created and rules for development control organization and fabrication. Materials may be self-organized and self-assembled using the same approach; Langmuir-Blodgett films[1] are an early example of self-organizing two-dimensional molecular systems.

This paper is divided into three sections. The first section discusses two-dimensional materials that are self-assembled using layer-by-layer molecular deposition processes and an example of a material that is formed using this approach, the second section describes the general concept of a three-dimensionally self-assembled material and gives an example of a material motivated in part by the need to extend two-dimensional limits, and the final section summarizes possible applications and extensions.

2. TWO-DIMENSIONAL SELF-ASSEMBLED MATERIALS

Two-dimensional layer-by-layer self-assembly processes[2,3] may be used to form thin films on the surfaces of supporting substrates or free-standing films independent of a substrate. Multiple molecule-thick layers of polyelectrolytes or nanoparticles are gradually built up one monolayer at a time until a desired thickness is obtained. The net electrical surface charges on the molecules may be modeled as being responsible for alternating monolayer build up. An example of this well-known layer-by-layer (LbL) or electrostatic self-assembly (ESA) process is shown in Figure 1.

At the left, a substrate is suitably treated to effectively present a net negative charge immediately at its surface. Cationic polyelectrolytes in solution are then shown to be brought in contact with the substrate by dipping the substrate into the solution or spraying the substrate with the solution. Ionic bonding between the anionic substrate and the cationic molecules effectively creates a net positive outermost surface, and rinsing the surface with water removes any extra molecules that are attached by weak van der Waals bonds. The result is a nearly perfect monolayer of cationic molecules on the substrate. A subsequent similar monolayer of anionic nanoparticles can then be formed as shown on top of the cationic surface, by either dipping or spraying that surface with the solution of nanoparticles and again rinsing with water. A third layer may be similarly formed using the cationic polyelectrolyte solution, and a fourth with the anionic nanocluster solution, and so on.

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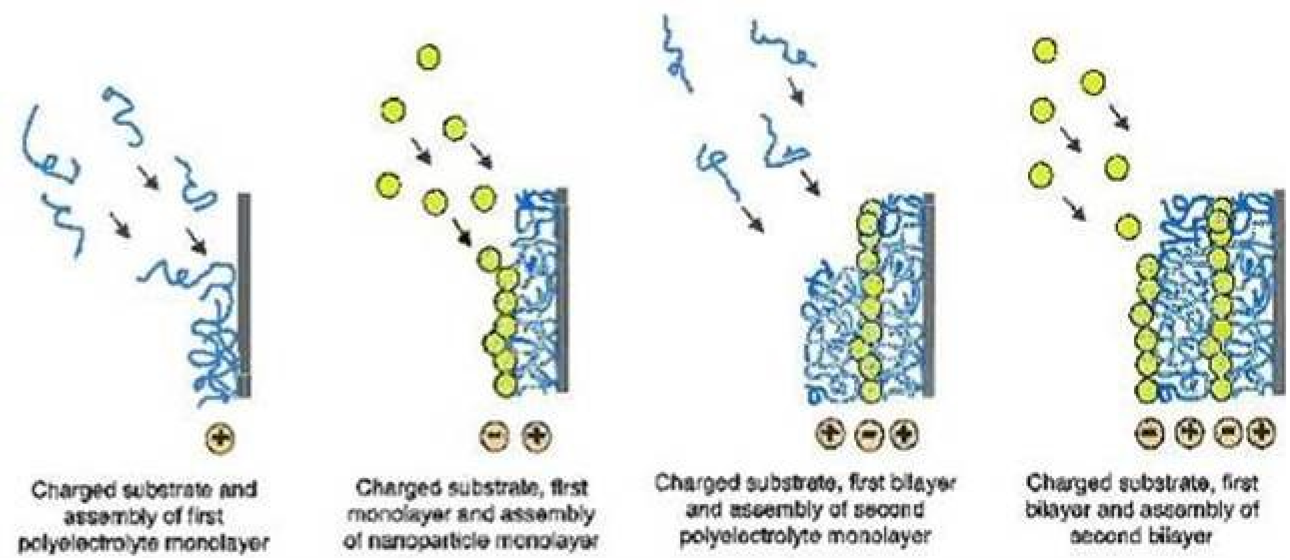
Thousands of molecular layers may be gradually built up in this way until a desired thickness is achieved. Figure 2 shows the increase in the thickness of the total thin film as a function of the number of bilayers deposited. The four lines shown correspond to different self-assembled molecules – zirconia nanoclusters, poly(sodium styrene sulfonate) (PSS), poly{1-[p-(3'-carboxy-4'-hydroxyphenylazo)benzenesulfonamido]-1,2-ethandiyl}(PCBS), poly(diallyldimethylammonium chloride) (PDDA), and PolyS-119, a polymer dye. Because these self-assembled materials are different, the thicknesses of each of the formed bi-layers are different, hence the different slopes.



Charged substrate and assembly of first polyelectrolyte monolayer

Charged substrate, first monolayer and assembly of nanoparticle monolayer

Charged substrate, first bilayer and assembly of second polyelectrolyte monolayer

Charged substrate, first bilayer and assembly of second bilayer

Figure 1. Layer-by-layer two-dimensional electrostatic self-assembly of multiple polyelectrolyte and nanocluster monolayers.

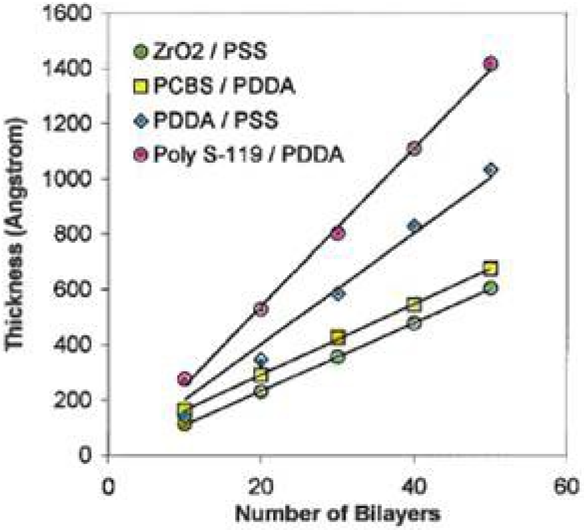


Figure 2. Increase in thickness of two-dimensional self-assembled multi-layer thin films as a function of the number of bilayers deposited. Thickness versus number of bilayers is plotted for four different material combinations.

The constitutive properties of the resulting thin films, so their electrical, optical, magnetic, mechanical, thermal, ion transport and other behaviors, are dependent upon the two molecules used to create the individual monolayers. Varying the molecules used to make the film changes these properties. For example, in relatively thick films, a segment of multiple layers of molecules A and B may be first formed, followed by a segment of multiple layers of different molecules C and D, followed by a segment of multiple layers of molecules A and B. If the segments containing molecules A and B are electrically conductive, and the middle segment containing molecules C and D is a non-conducting dielectric, this (AB)(CD)(AB) layer stack effectively forms an electrical capacitor. Similar electrical devices may be formed in much the same way. As another example, if A and B form a segment with a particular dielectric constant and C and D form a segment with a different dielectric constant, then a film of the form $[(AB)(CD)]_n$ may be created to act as a multilayer dielectric stack filter, where n is the number of ABCD periods of the filter. Because the thicknesses of single AB and CD bi-layers can be measured, and the dielectric constant or index of refraction of each of the segments can be controlled by modifying the molecules in each of them, a variety of filter functions can be designed and fabricated.

Many modifications are possible to this basic process[2,3]. To obtain a mechanically robust thin film coating on a substrate, an adhesion promoter may be introduced at the interface between the substrate and the first monolayer. If instead a free-standing film is desired, a chemically compatible release layer may be introduced at this interface and, after a sufficiently-thick material is formed, it may be removed by either acid or base etching. The substrate may then either be discarded or cleaned and reused.

2.1 Metal Rubber™ as an example of a free-standing two-dimensionally self-assembled material

Metal Rubber is an example of a two-dimensionally self-assembled material that demonstrates several of the above properties and examples. It is typically formed using electrically conductive metal nanoclusters and non-conducting polymers as a free-standing thin film sheet, although with modification can be fabricated in low areal density fabric and extrudable resin forms. The self-assembly process leads to well-controlled physical separation of the metal nanoclusters. This is evidenced by an electrical conductivity on the order of 10^7 S/m, or on the order of that of iron, for a metal nanocluster volume percentage at percolation of less than 0.01%. It is also evidenced by the semi-transparent bluish hue shown in Figure 3. Rayleigh scattering due to small particles such as the nanoclusters in Metal Rubber is proportional to (d^6/λ^4), where d is the size of the clusters and λ is wavelength. Since the metal cluster size is on the order of 10nm, the scattering is small as shown, and the wavelength term is responsible for the bluish hue. Of perhaps greater importance to other two-dimensionally self-assembled materials, and to the motivation of three-dimensionally self-assembled materials discussed below, these observations suggest very good physical dispersion of the metal clusters in the nanocomposite film. Dispersion is important to mechanical, thermal, transport and other properties, and here, if cluster agglomeration occurred, the film would exhibit significant white scattering. Figure 4 shows an atomic force microscope surface amplitude plot of the height of a gold nanocluster/polymer Metal Rubber surface and exhibits good spatial uniformity in the plane of the surface.

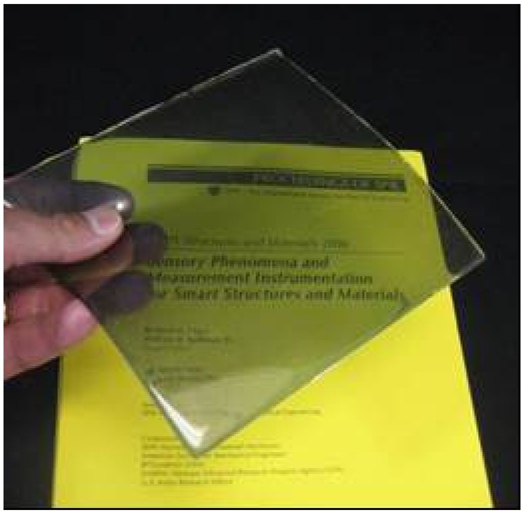


Figure 3. Two-dimensionally self-assembled free-standing Metal Rubber sheet material exhibits little scattering.

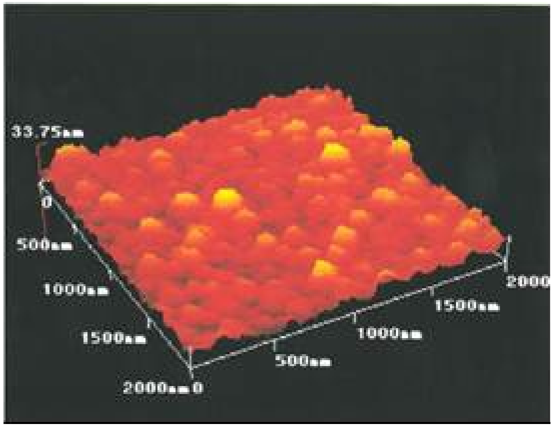


Figure 4. Atomic force micrograph showing the surface amplitude of Metal Rubber sheet material.

While the incorporation and dispersion of metal nanoclusters control the electrical conductivity of the material, the selection and design of the polymer molecules are largely responsible for the thermomechanical properties. Young's modulus may be controlled from less than 1 MPa to greater than 500 MPa, and elongation or strain as large as 1,000% prior to failure are possible. Unlike metal thin films formed by evaporation or sputtering processes, these materials remain electrically conductive after large physical deformation and subsequent relaxation.

3. EXTENSION TO THREE-DIMENSIONAL SELF-ASSEMBLY: HYBRIDSIL® ICEPHOBIC MATERIALS

Self-assembled two-dimensional thin film coatings and free-standing materials are limited by their thickness dimension. A number of authors have investigated means by which two-dimensional self-assembly design concepts may be transitioned to the creation of three-dimensional materials.[4,5,6] One design idea is to synthesize functional groups along the length of controlled molecular weight polymer chains in such a way that complexing with nanoclusters and other materials and crosslinking between multiple chains occurs in a managed way. Moreover, the motivation for this design is that it may lead to the control of multiple macroscopic constitutive properties of three-dimensional bulk materials rather than adhered or free-standing thin film or sheet materials.

HybridSil[7] is an example of such a material motivated by three-dimensional self-assembly design concepts. Originally developed as a coating that is blast-and fire-resistant[8], HybridSil can be modified through molecular-level design to accentuate other properties. As an example, HybridSil icephobic coating material mitigates the build-up of ice on substrates. It demonstrates an ice work of adhesion of approximately 60kPa at -10°C and a dynamic adhesion/accretion temperature as low as -8°C. ASTM D1003 Taber abrader measurements indicate negligible weight loss or damage after 500 cycles with a 500g load. Figure 5 shows a comparison of uncoated steel substrate and steel coated with HybridSil icephobic material.

4. SUMMARY

Materials may be formed using two-dimensional and three-dimensional synthesis processes. Design of material precursors prior to fabrication allows the materials to 'self-assemble' themselves and permits control over multiple engineering constitutive behaviors. Metal Rubber is an example of a two-dimensionally self-assembled material that may be formed as an electrically conductive, mechanically flexible coating on a substrate or as a free-standing sheet material. HybridSil icephobic and other related materials have been inspired in part by a desire to similarly control multiple properties in bulk rather than thin film and sheet materials. A wide range of properties is possible in both two- and three-dimensionally realized material systems, and applicable to numerous demanding applications.

Figure 5. HybridSil icephobic-coated steel substrate (left) and uncoated substrate (right) demonstrating mitigation of ice build-up on surfaces.

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[7] HybridSil® is a registered trademark of NanoSonic Inc. HybridSil icephobic and Metal Rubber are both classified as EAR99 by the U.S. Department of Commerce.

[8] http://www.onr.navy.mil/Media-Center/Press-Releases/2011/Protective-Coating-Spray-100-ONR.aspx