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Two Component Particle Arrays on Patterned Polyelectrolyte Multilayer Templates**

By Haipeng Zheng, Ilsoon Lee, Michael F. Rubner, and Paula T. Hammond*

The assembly and fabrication of two- or three-dimensional (2D/3D) micro- and nanoscale colloidal structures are very promising techniques for the creation of novel materials and devices.^[1–4] These colloidal arrays have many potential applications such as photonic bandgap (PBG) crystals,^[5,6] optical switches and filters,^[7,8] chemical and biochemical sensors,^[9–11] optoelectronic devices,^[12,13] and templates for ordered microporous materials.^[14–17] A primary requirement for the success of these applications is the ability to direct particle assembly to form ordered arrays over large domains. A number of methods of colloidal assembly have been extensively studied, including gravity sedimentation,^[18,19] electrophoretic deposition,^[20,21] electrostatically induced crystallization,^[22,23] colloidal epitaxy,^[24] convective self-assembly,^[25,26] physical confinement,^[27–29] and self-assembly of particles at the air–liquid interface.^[30]

One challenge in the creation of these arrays is the introduction of two or more different elements within the matrix. Here, we present an approach to assemble a bicomponent array consisting of two different particles that are directed to corresponding regions of a surface. The Hammond research group has demonstrated the patterning of polyelectrolyte

multilayers using strong and weak polyions with high selectivity^[31–35] onto micro-contact printed surfaces.^[36,37] Colloidal particles can then be templated selectively on these patterned multilayer surfaces using electrostatic and hydrogen bonding interactions.^[38] Layer-by-layer polyelectrolyte thin films^[39,40] can provide functionality,^[41–43] as well as opportunities to increase adhesion between the multilayer surface and the colloid. For example, electroluminescent materials can be incorporated^[44,45] and patterned into multilayers on surfaces.^[34] The deposition of colloidal particles has also been successfully demonstrated on patterned self-assembled monolayers (SAMs) formed with alkanethiols on gold.^[46] An important difference between traditional SAMs and the multilayer surfaces described in this work is that polyelectrolyte multilayers can be tuned during the layer-by-layer assembly process to vary surface charge density, density of functional groups at the surface, film thickness, and wetting properties,^[47–50] the polymer thin film also imparts a conformal nature that enhances adhesion. Here, we direct two different sets of colloidal particles onto a patterned polyelectrolyte multilayer surface. The first set of negatively charged particles deposit on the multilayer surface primarily through electrostatic interactions, whereas the second set of colloidal particles adsorb onto a neutral SAM surface via secondary interactions. This principle, utilizing differences in the affinity of materials to various surface sites, has been demonstrated successfully in earlier work with polyelectrolyte multilayer films.^[51] Here, we expand this concept to include the positioning of two different particles on a defined array using two different approaches: ionic attractions coupled with hydrophobic and with hydrogen bonding interactions, respectively. This capability is relevant to the development of microphotonic arrays, biosensor devices, and templated microporous films.

Three sizes of polystyrene sulfate (PSS) latex spheres were used, with diameters of 0.53 ± 0.027 , 1.0 ± 0.024 , and 1.9 ± 0.073 μm (referred to hereafter as 0.5, 1.0, and 1.9 μm), corresponding to $N = 2.1 \times 10^5$, 1.5×10^6 , and 6.2×10^6 charges/particle with negative surface charge densities of 3.9, 7.6, and 8.8 $\mu\text{C}/\text{cm}^2$, respectively. Two kinds of amidine-terminated polystyrene (APS) spheres were also used, with diameters of 1.0 and 2.1 μm , corresponding to $N = 3.1 \times 10^6$ and 2.6×10^7 charges/particle and positive surface charge densities of 15.6 and 30.2 $\mu\text{C}/\text{cm}^2$, respectively. All micro-spheres were diluted to 1 g/100ml suspension. A cationic surfactant, dodecyltrimethylammonium bromide (DTAB) in aqueous solution at different concentrations ranging from 10^{-6} to 10^{-3} M (in all cases below the critical micelle concentration of DTAB, which is 16 mM), was used to shield the surface charges of the PSS spheres. The percent of charge shielding is the ratio of the number of charged DTAB molecules to the number of surface charge groups on the PSS spheres in the colloidal suspension.

The experimental procedure is outlined in the schematic in Figure 1. Microcontact printed gold surfaces were obtained by stamping stripes of $\text{HS}(\text{CH}_2)_{15}\text{COOH}$, and adsorbing a second neutral alkanethiolate onto the remaining bare gold regions, $\text{HS}(\text{CH}_2)_{11}(\text{OCH}_2\text{CH}_2)_3\text{OH}$ (EG), which resists

[*] Prof. P. T. Hammond, Dr. H. Zheng, Dr. I. Lee
Department of Chemical Engineering
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139 (USA)
E-mail: hammond@mit.edu

Prof. M. F. Rubner
Department of Materials Science and Engineering
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139 (USA)

[**] We gratefully acknowledge the MIT Microphotonics Research Center, the Charles F. Reed Fund, and the MIT Center for Materials Science and Engineering MRSEC program of the National Science Foundation, DMR-9400334 for funding this work.

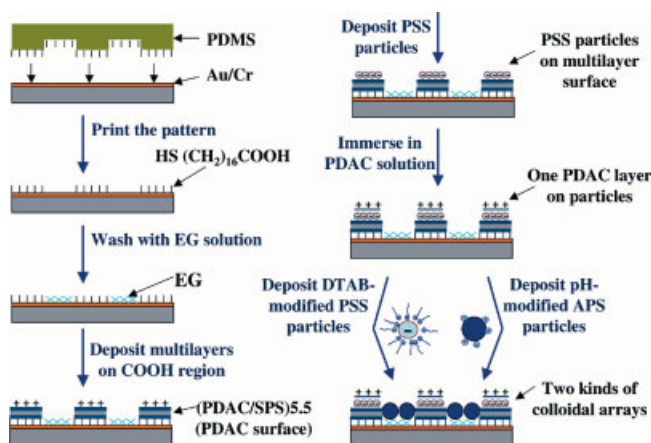


Fig. 1. Procedural schematic for deposition of two kinds of particle arrays on patterned templates.

polyelectrolyte deposition in solutions.^[52] Using the layer-by-layer alternating adsorption process, 5.5 bilayers of poly(dialldimethylammonium chloride) (PDAC) and sulfonated polystyrene (SPS) were adsorbed on the COOH SAM surface with high selectivity.^[31–33] When the resulting patterned multilayer with an outermost PDAC layer was immersed into a negatively charged PSS colloidal suspension for 20 min, particles adsorbed selectively on the multilayer surface based on electrostatic attraction. The EG SAM acted as a resist to colloid deposition, as reported previously.^[38] The surfaces of the deposited PSS particles were negatively charged; to prevent the deposition of positively charged particles on the multilayer region in the next step, the substrate was immersed into a PDAC aqueous solution for 20 min to obtain a uniform positive charge on the PSS particle surface.^[53,54] After modification with a single layer of PDAC, the particles remained stable and well-adhered on the multilayer surface, consistent with the alternating assembly processes of charged colloidal particles with linear polyions reported by others.^[55–58] The substrate was then placed in a DTAB-modified PSS latex sphere suspension or a pH-modified positively charged APS latex suspension for 1 h to allow the adsorption of a second set of colloidal particles directed toward the EG SAM surface through secondary interactions.

The scanning electron microscopy (SEM) and optical microscopy (OM) images of PSS colloidal arrays are shown in Figure 2. Without the addition of DTAB, deposition of all PSS particles occurred selectively on the PDAC multilayer surface through electrostatic interactions. Hydration and steric forces from the EG SAM effectively prevent deposition of charged PSS particles onto the EG surface. Figure 2a illustrates electron micrographs of 0.5 μm PSS particles on the patterned PDAC surface. It has been demonstrated in a previous paper that when low concentrations of DTAB are added to the colloidal suspension (10^{-6} – 10^{-5} M), the PSS particles deposit primarily on the multilayer surface with small changes in their packing density.^[38] As more DTAB (10^{-4} – 10^{-3} M) is added, the surfaces of the particles become increasingly hydrophobic as the negative charge density is reduced, and alkyl chains are

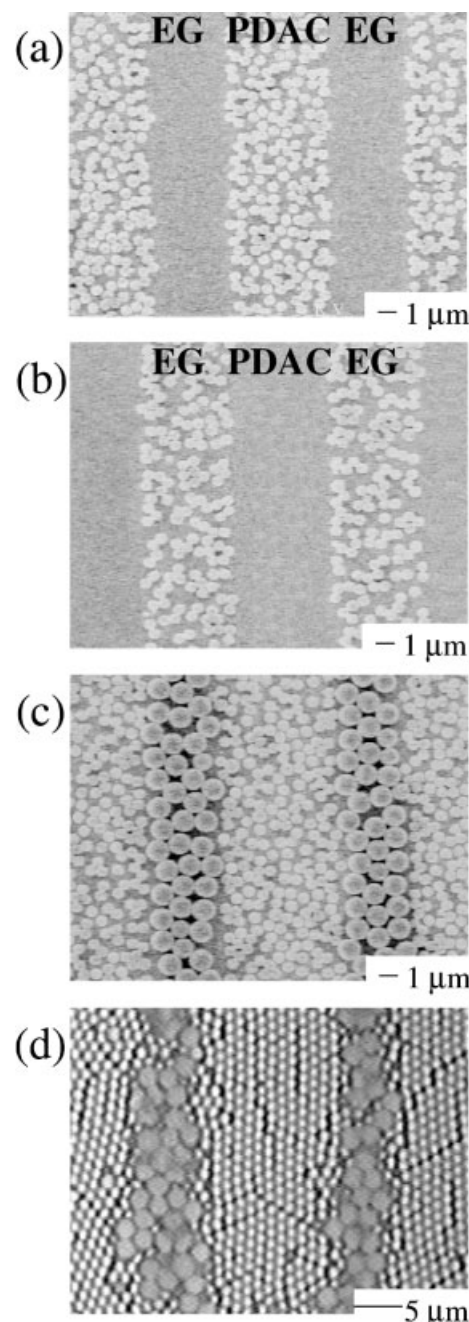


Fig. 2. a–c) SEM and d) OM images of PSS particles on patterned (PDAC/SPS)_{5.5}/EG surfaces: a) 0.5 μm particles on the PDAC surface; b) DTAB modified 0.5 μm particles on the EG surface (charge shielding is 460 %) and c) 0.5 μm particles on the PDAC surface and 1.0 μm particles on the EG surface; d) 1.9 μm particles on the PDAC surface and 1.0 μm particles on the EG surface.

introduced. The selectivity of the particles for the PDAC surface decreases sharply at a given degree of surfactant shielding, resulting in little or no selectivity, as reported earlier.^[38] Finally, at high degrees of shielding, the selectivity is reversed, and deposition occurs preferentially on the EG surface. To our knowledge, this is the first demonstration of the use of surfactant molecules as a means of tuning colloid packing density and selective deposition on surfaces. It was proposed that hy-

drophobicity is the main driving force in directing spheres to the EG surface (shown in Fig. 2b) when the degree of shielding with DTAB for 0.5 μm spheres reaches about 460 % (based on the latex particle surface charge provided by manufacturer) due to favorable interactions between hydrophobic ethylene groups in the EG SAM repeat units.^[35] It is possible that this interaction is further facilitated by direct interactions between the surfactant molecules and the EG surface as well. At high surfactant concentrations, it is likely that a double layer of surfactant exists around each particle, thus imparting a net positive charge on the particle. For this reason, deposition does not occur on the PDAC surface at high surfactant concentrations due to electrostatic repulsion with the positively charged surface. This phenomenon was discussed in detail in a previous paper.^[38] The sharp transition from the EG SAM as a resist to a region for deposition occurs at about 190 % and 95 % charge shielding for the 1.0 and 1.9 μm PSS spheres, respectively. By taking advantage of the resulting difference in selectivity, we can fabricate two component colloidal arrays on a single patterned surface.

Figures 2c,d demonstrate the capability of the procedure to generate highly selective particle deposition using different sizes of PSS particles. 0.5 μm (in Fig. 2c) or 1.9 μm (in Fig. 2d) spheres were first deposited on the PDAC surface, and 1.0 μm spheres were then close packed on the EG surface. Close packing on the PDAC surface is limited by kinetic effects due to the fact that there is strong adhesion between the negatively charged particles and the positively charged PDAC surface, which inhibits rearrangement and close-packing of the particles during the drying process. Greater packing densities have been obtained on multilayer surfaces utilizing particles with hydrophilic surfaces such as carboxylamide-modified spheres, when capillary forces can more effectively facilitate close packing.^[38] On the other hand, the packing density of the second colloidal array can be controlled easily by varying the extent of charge shielding of the particles. When charge shielding of the 1.0 μm spheres reached 190–240 %, the spheres became hexagonally close packed on the neutral EG SAM surface because of the physical confinement of the first colloidal array, and the mobility of the spheres on the neutral surface in the presence of strong capillary forces. When the concentration of DTAB was increased to 1.2×10^{-4} M and charge shielding of the spheres exceeded 260 %, the modified 1.0 μm spheres adsorbed more loosely on the surface, apparently due to repulsion between particles. This repulsion is presumably due to charge reversal of the particles induced by a surfactant multilayer. Upon drying, the particles were arranged randomly in loosely packed clusters (not shown here).

We have found that APS spheres will selectively deposit onto the EG SAM surface through hydrogen bonding interactions between the four hydrogen bond acceptor groups in each EG molecule in the form of lone pair oxygens,^[35] and the two hydrogen bond donor groups (=NH and $-\text{NH}_2$, $\approx\text{p}K_a$ of 9–10) in each amidine group on the APS particle surface. Because the APS colloidal particles are positively charged, APS spheres were repelled from the charged PDAC surface of an

SPS/PDAC multilayer, and tended to deposit on the outermost negatively charged SPS layer of the multilayer surface. When the pH of the colloidal suspension was 3.6–5.5, the APS spheres deposited onto the EG surface with high selectivity and good adhesion. On the other hand, if the pH was either 7.0 or lower than 3.6, most of the spheres were easily removed from the EG surface when the samples were rinsed with water. This result implies that there is an optimal number of charged amidine groups required for strong interactions with the oligoethyleneglycol functional group. Figure 3 shows composite colloidal structures on the PDAC/EG surface using sets of PSS

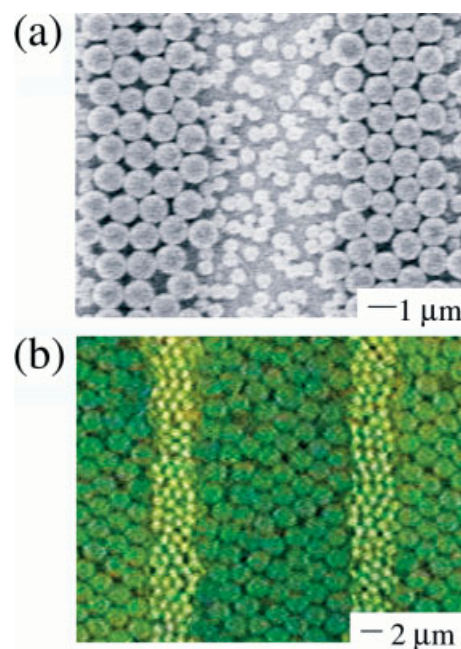


Fig. 3. Deposition of PSS and APS particles on patterned (PDAC/SPS)_{5,5}/EG surfaces: a) an SEM image, 0.5 μm PSS particles on the PDAC surface and 1.0 μm APS particles on the EG surface; b) an OM image, 1.0 μm PSS particles on the PDAC surface and 2.1 μm APS particles on the EG surface.

and APS spheres. After deposition of 0.5 μm negatively charged PSS particles on the PDAC surface and modification of the PSS colloid top surface with PDAC, the 1.0 μm APS particles were adsorbed onto the EG surface to form ordered hexagonally close-packed arrays, as shown in Figure 3a, when the pH of the APS colloidal suspension was 4.8–5.5. Charge repulsion between particles at these pH ranges may be modulated by hydrogen bond interactions or proton transfer not only between the EG functional group and the particle, but between amine and amidine groups on neighboring particles. In this pH range the surface of the APS spheres has some ratio of charged or uncharged groups, which provide strong adhesion between the spheres and the EG surface, and achieve a balance between repulsive and attractive interactions between spheres. By operating at or near optimal conditions for PSS particle deposition, it is possible to get close-packed 1.0 μm PSS particles on the patterned PDAC surface.^[59] Figure 3b shows the fabrication of two close-packed colloidal arrays with 1.0 μm PSS particles and 2.1 μm APS particles.

In summary, we have demonstrated that the concept of selective deposition can be applied not only to polyelectrolyte adsorption, but also to the deposition of charged particles on surfaces. By manipulating adsorption conditions, it is possible to direct two different sets of particles to different surface regions based on the manipulation of secondary interactions such as hydrophobicity and hydrogen bonding. This approach requires a balance between the use of interactions that can prevent deposition, such as steric and hydration forces or electrostatic repulsion, and those that encourage it. This effective method provides a flexible and versatile route to the fabrication of composite colloidal structures; the technique can be adapted utilizing different shaped patterned surfaces and other monodisperse colloidal particles such as silica, core-shell and metal-doped particles of varying size and surface functionality, and using functionalized spheres modified with polyelectrolyte multilayers to obtain electroluminescent, conducting, and other properties. The resulting composite colloidal structures will present interesting technological applications in photonics, electronics, and sensors.

Received: September 4, 2001
Final version: January 25, 2002

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Controlled Cluster Size in Patterned Particle Arrays via Directed Adsorption on Confined Surfaces**

By Ilsoon Lee, Haipeng Zheng, Michael F. Rubner, and Paula T. Hammond*

The precise positioning of colloidal particles in complex two- and three-dimensional (2D/3D) structures has attracted a great deal of attention for potential applications, such as optoelectronic devices,^[1] photonic bandgap materials,^[2] and biochip devices and sensors.^[3] A number of methods have been successfully used to direct the assembly of colloidal particles onto patterned surfaces, including flow-induced packing into cavities of controlled dimensions and shape^[4] to create highly

[*] Prof. P. T. Hammond, Dr. I. Lee, Dr. H. Zheng
Department of Chemical Engineering
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139 (USA)
E-mail: hammond@mit.edu

Prof. M. F. Rubner
Department of Materials Science and Engineering
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139 (USA)

** The authors acknowledge Felice Frankel at MIT for the optical micrograph image of colloidal assembly (Fig. 3a) and general discussion on capturing meaningful images for science. Thanks also go to Dr. Insung Choi and Dr. Yongwoo Lee for the synthesis of EG-thiol and helpful discussions on alkanethiolate SAMs, and to Dr. Gyoou yul Jung for micro-filtration of the colloidal solutions and for invaluable discussions on the potential application of patterned arrays to biological application. Funding for this work is provided by the Microphotonics Research Center and the Center for Materials Science and Engineering at MIT.