POLYELECTROLYTE AND PARTICLE ADSORPTION TO NANOPATTERNED SURFACES

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Abstract: The adsorption of polyelectrolytes and nanoparticles onto patterned and curved surfaces is investigated (by fluorescence and electron microscopy) and exploited to produce anisotropic patchy particles. Various anisotropic properties are necessary for the self-assembly of complex structures. In this work, particles were bound temporarily to a substrate, so that part of their surfaces is occluded during subsequent surface modification by the adsorption of polyelectrolyte. The substrate surface charge has a significant effect on the adsorption of particles, which provided several advantages in comparison to bare glass substrates. These include much reduced deposition time, a high degree of coverage, and the ability to accommodate both negatively and positively charged particles. Moreover, patch production yield is consistently 99 % ± 1 %. Rapid coating methods transferable to roll-to-roll processing were tested, and step-by-step characterization methods to evaluate yield were developed. High-yield site-specific binding of complementary spheres to the lithographic region of patchy particles and surfaces was demonstrated, including binding to positive and negative patches.

Keywords: 5–10 keywords, polyelectrolyte adsorption, nanoparticle adsorption, patchy particles, roll-to-roll processing, site-specific binding

1. INTRODUCTION

There has recently been growing interest in using nanoparticles as tailored building blocks for self-assembly into new materials (van Blaaderen 2006; Glotzer and Solomon 2007). Anisotropic building blocks are necessary for the self assembly of complex structures. A method for preparing asymmetric particles is to chemically modify them. This approach can be used easily to modify very small building blocks (e.g., several nanometers), which are difficult to manufacture by top down approaches. The method, sometimes referred to as particle lithography, fundamentally consists of partially coating particles, which are called patchy particles. A great deal of interest in patchy particles has emerged, in part because they can resemble the inhomogeneous surface properties of globular proteins (Glotzer 2004; Zhang and Glotzer 2004; Snyder et al. 2005; Bianchi et al. 2006; Hong et al. 2006).

A limitation associated with previous experimental work has been the difficulty to produce large numbers of coated particles. A primary challenge to increasing yield is to create unaggregated particle monolayers with high coverage, for subsequent use in coating. Deposition of particles onto a bare glass substrate results in a low degree of coverage (which causes slow production rates). This paper explores the use of a polyelectrolyte-coated substrate to improve this initial step, and it characterizes the particle lithography process structurally, and in terms of throughput and yield. It also reports site-specific binding of complementary particles with these patchy particles.

2. EXPERIMENTAL

All chemicals were used as received: anionic polyelectrolyte poly(sodium 4-styrene sulfonate) (PSS, number-average relative molar mass $M_n \approx 70000$ g/mol, 30 % by mass in water, from Aldrich, note: equipment and instruments or materials are identified in the paper in order to adequately specify the experimental details. Such identification does not imply recommendation by the National Institute of Standards and Technology, nor does it

imply the materials are necessarily the best available for the purpose), cationic polyelectrolyte poly(allylamine hydrochloride) (PAH, $M_n \approx 70000$ g/mol, Aldrich), potassium hydroxide (KOH, Aldrich); pure ethanol (Warner-Graham Co.); and sodium chloride (NaCl, J.T. Baker). The radii of gyration for the two polyelectrolytes are approximately 31 nm (PSS in 0.5 mol/L NaCl)(Prabhu et al. 2003) and 22 nm (PAH in 0.05 mol/L NaCl).(Burchard et al. 1996) These radii decrease somewhat at elevated salt concentration. The following polymer concentrations were prepared and used: a.) 4.1 mg/mL PSS and b.) 1.87 mg/mL PAH, each in 2.0 mol/L NaCl. The polyelectrolyte concentrations are near the overlap concentration.

Polystyrene (PS) spheres ranging from 40 nm to 4690 nm in diameter were purchased from Invitrogen and from Polysciences. Additional polystyrene particles (600 nm diameter) were prepared using a previously reported emulsion polymerization method.(Schroden et al. 2002; Wang et al. 2005) Distilled and deionized (DI) water (Millipore, specific resistance = 18 MΩ.cm) was used for all experiments and washing steps. In this report, we employ a systematic nomenclature for particles and their surface coating. For example, PS600s$^-$ denotes a polystyrene particle, diameter 600 nm, sulfate surface chemistry, with negative surface charge. PS600s$^{(-)+}$ and PS600s$^{-)+}$ denote the same particle coated with the cationic polyelectrolyte, either completely or on only part of its surface, respectively.

Patchy particles were prepared by particle lithography, involving the following sequential steps: substrate preparation, particle adsorption, surface treatment and particle detachment. Briefly, a glass slide was cleaned in a base bath with 1 % mass KOH in a mixture of water/ethanol (3:7), and dried under N_2(g). Multilayer polyelectrolyte assemblies were prepared by consecutive alternating adsorption of cationic and anionic polyelectrolyte layers from 2.0 mol/L NaCl solutions, as noted above.

Traditional polyelectrolyte coating procedure is dipping successively into polyelectrolyte solutions and in water rinse baths (Decher et al. 1992; Decher 1997), and typically several minutes is required for equilibrium coating at each step (Bertrand et al. 2000). A much faster spraying process has also been developed (Schlenoff et al. 2000; Izquierdo et al. 2005). In this process the substrate is sprayed repeatedly with polyelectrolyte solutions and water rinse, which drain over the surface (held vertically). Hydrodynamic effects associated with this drainage have been suggested to increase mass transfer and adsorption rates. The polyelectrolyte layer reaches its final saturated state asymptotically after approximately 6 spray applications of solution and rinse. At approximately 12 s /cycle of solution and rinse, saturated layers may be produced in approximately 1 min.

Here we use a different rapid coating technique, with comparable speed, that uses polyelectrolyte solution much more efficiently and mimics an efficient roll to roll process. (Since the vast majority of the solution drains away during spray coating, it is either wasted or must be collected.) In our technique, the substrate to be coated is placed briefly (1 s) in contact with the polyelectrolyte solution, it is then held upright (vertical), with its edge touching the solution, so that surface tension removes the excess bead of solution that would otherwise hang from the substrate (holding again approximately 1 s). By switching alternately between these two positions, ten cycles is accomplished in 20 s. Washing is done likewise, by contacting the face and edge of the substrate onto clean water, to remove excess polyelectrolyte. In this way, multilayers can be built up rapidly (e.g., 80 s/bilayer). We have not carried out ellipsometry or reflectivity on these multilayer films to evaluate their structure, but they behave similarly in particle adsorption experiments to those films prepared by standard slow dip-coating procedures.

Typically, 3 or 3.5 bilayers were deposited onto clean glass, so that the outer-most layer was either PSS or PAH, respectively. These dried films were then exposed to a particle suspension for 1 min to 5 min to prepare an unaggregated particle monolayer (Serizawa et al. 1998). Substrates were selected so to have a charge opposite to the particles. The monolayer of particles was washed thoroughly with DI water.

Without drying, this assembly was then coated with a polyelectrolyte film, under standard and rapid dipping conditions as described above. The polyelectrolyte may adsorb everywhere (on substrate and particle) except where the two surfaces (particle and substrate) occlude one another and the polyelectrolyte is size-excluded. After such adsorption, the sample was washed repeatedly with DI water to remove any excess polyelectrolyte, and placed in 10 mL of a NaCl solution (0.1 mol/L to 5.0 mol/L, aq), and sonicated to detach adsorbed PS particles from the glass slide. The resulting particles were concentrated by removing salt solution with a Millipore stirring cell (0.2 μm to 0.6 μm pore size) until the final volume was approximately 2.0 mL.

Assemblies of particles were prepared by mixing the patchy PS particle solutions with a drop of appropriately charged particles and stirring for at least 10 h. When assembling large patchy particles with small uniform particles, the solution was filtered using an ultrafiltration Millipore stirred cell with appropriate pore size to remove the small particles that had not attached to the patchy particles. The solution was washed repeatedly with a NaCl solution (0.1 mol/L to 0.3 mol/L) to further remove non-absorbed particles.

The steps just described were monitored *in situ* by optical microscopy in bright field, using an Olympus IX71 inverted optical microscope, with either a 20x (NA = 0.4) or a 60X water-immersion (NA = 1.2) objective lens and with a charge-coupled device (CCD) camera. These observations were used to determine if any of the process steps (and variations of them) caused particles to move or detach prematurely. Fiducial marks and shadow evaporation (discussed below) facilitated these measurements. In addition, particle and aggregate suspensions were also examined by optical microscopy.

Slight variations of the preparatory methods described above were used to characterize these processes. The following is the method used to characterize the size-excluded polyelectrolyte adsorption process, whereby either the particles or the substrate may be patterned, i.e., partially coated with polyelectrolyte. A dry particle monolayer (touching spheres ok) was first coated with chromium by vacuum evaporation, so that each particle casts a shadow nearly vertically towards the substrate, thus marking its position. The sample was then rapidly dip coated in polyelectrolyte solution and then washed in DI water. To produce a charged pattern on the substrate, the polyelectrolyte here was of the same sign as the surface charge of the particle. When a thicker film was desired to enable mass thickness contrast examination by transmission electron microscopy (TEM), polyelectrolyte multilayers were deposited. Nearly all of the particles remained in position, as verified by optical microscopy. The particles were then removed by sonication and washing. To demarcate the resulting surface charge pattern on the substrate, this substrate was exposed to a suspension of charged fluorescent polystyrene nanoparticles for 10 min, washed with DI water, and dried with N_2(g). (Various sizes nanoparticles were used depending on requirements for fluorescence brightness and size relative to patch.) In some instances, this surface was also shadowed with Pt/C by vacuum evaporation to enhance contrast of topography. Finally, the surface was coated with evaporated carbon. The accumulated coatings (schematically shown in Fig. 1a) were then removed from the substrate using poly(acrylic acid) (PAA). An aqueous solution of PAA was cast on the surface in contact with the top layer of carbon and allowed to dry. The resulting glassy polymer chip was removed, bringing the underlying coatings with it. Floating this chip (coating side up) onto the surface of distilled water, the PAA was washed away and the coatings retrieved on copper grids. The specimens were then examined by bright-field TEM, using a Philips EM 400T, operated at 120 kV. Particles and their assemblies were also analyzed by scanning electron microscopy (SEM) using a Hitachi S 4700. Samples were prepared by depositing particles onto polyelectrolyte coated glass slides, and sputtering thin layers of gold at 13.3 Pa, 45 mA, and 90 s.

3. RESULTS AND DISCUSSION

As noted above, surface charge patterns on either the substrate (Fig. 1) or the particles (Fig. 2) result from coating the particle monolayer with a polyelectrolyte that has either the same or opposite charge as the particles, respectively. This polyelectrolyte is excluded from the contact region, as determined by the blob size of the polyelectrolyte (Verma et al. 1998) (diameter d_b) and the curvature of the spherical particle (radius a). The radius of the excluded (lithographic) region is calculated geometrically to be approximately $r_{patch} = (a\ d_b)^{1/2}$ (Snyder et al. 2005).

After adsorption of the polyelectrolyte, the masking spheres are removed from the substrate by sonication. The time of sonication required to remove the particles increases with decreasing particle size and increasing waiting time, as expected (Hubbe 1984; Yiantsios and Karabelas 1995; Janex et al. 1997). Particle lithography was carried out for a variety of masking particle sizes, ranging from 4690 nm to 100 nm (Fig. 1). Correspondingly, sonication time was varied from several seconds to a minute or two. (100 nm diameter was the smallest masking size attempted (Fig. 1e).) It is not known whether any polyelectrolyte is transferred from the substrate to the masking particle during its removal. We have no evidence of such transfer, and in any case, the contact area is much smaller than the patch size, so that site-specific binding of complementary particles is observed on the patchy surfaces (Fig. 1) and particles (Fig. 2). Fig. 1 illustrates surface-charge patterns on the substrate, made manifest by shadowing, fluorescent particle labeling, and direct mass-thickness contrast, as described above. Figure 1b is a combined fluorescence and bright-

field optical micrograph, which shows the location of the masking particles (marked by dark Cr evaporation) and of the surface-charge patches (labeled by small bright fluorescent particles). The masking particle here is PS4690s⁻ and the fluorescent label is PS100s⁻. The location of the fluorescent label relative to the positively charged patch is visible by TEM examination (Fig. 1c). For this image, the label particle was chosen to be larger for improved contrast.
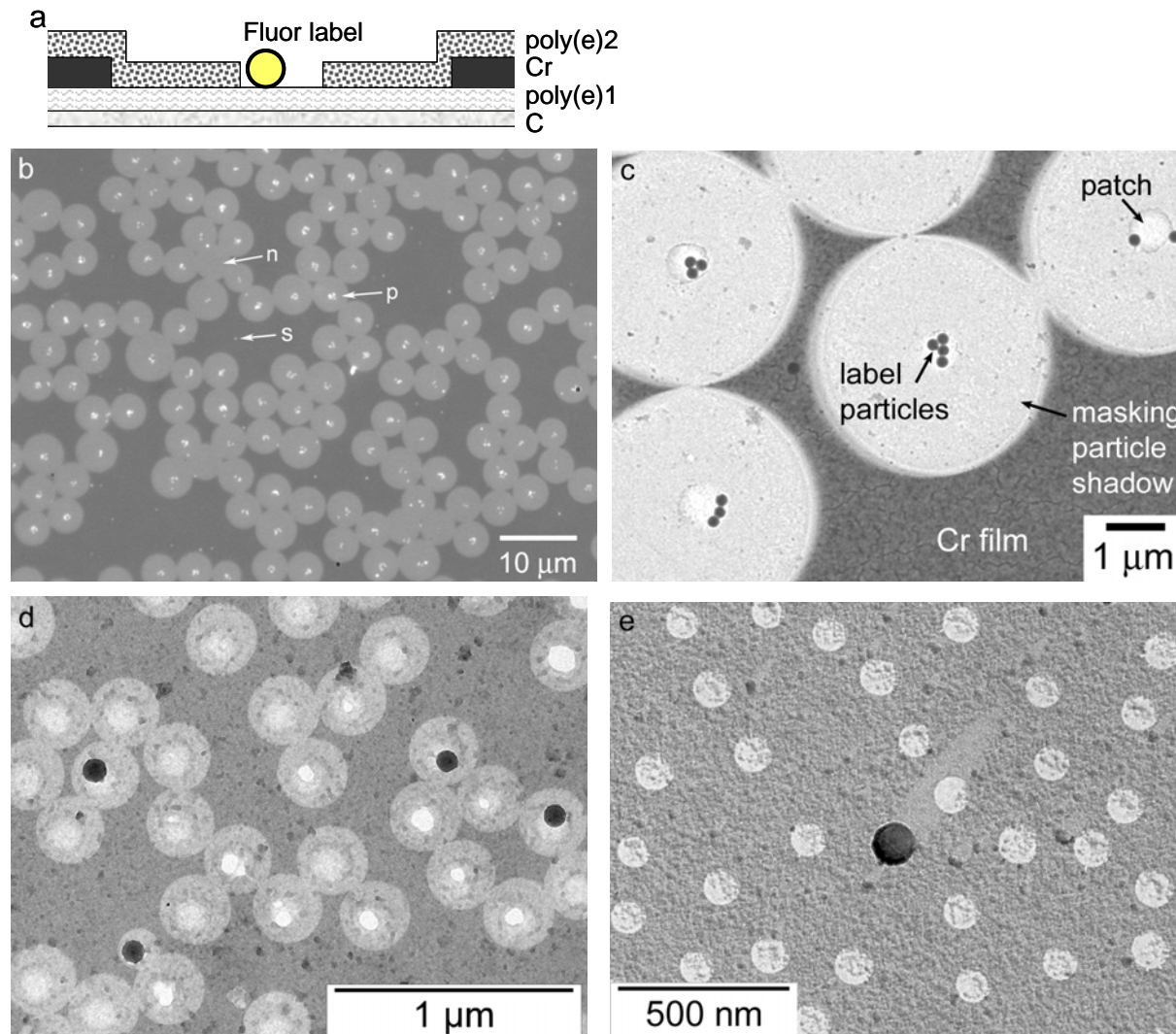

Fig. 1. Images of accumulated layers, following processes to produce and reveal surface charge patterns on the substrate. a.) Schematic of accumulated layers. b.) Fluorescence microscopy (with bright-field backlight). The dark background is an evaporated Cr layer that marks out the location of the PS4690s⁻ masking spheres (gray). Patch sites (e.g., labeled "p") are labeled with bright fluorescent PS100s⁻ particles. A stray fluorescent particle is labeled "s". The location labeled "n" is one of two types of sites (see text) without PS100s⁻ particles. c.) TEM image of a sample, as in (b), yet with PS200s⁻ spheres adsorbed to positively charged patches, visible by mass-thickness contrast. d.) TEM image with PS300c⁻ as the masking spheres. Four PS100s⁻ particles (dark) are adsorbed to different positively charged patch sites. e.) TEM image with PS100s⁻ as the masking spheres. Circular patches within the light gray circles are barely visible by mass-thickness contrast.

These experiments illustrate the yields of both particle lithography and of subsequent binding of particles to the surface patches, which are very high (e.g., Fig. 1b, "p"). There are three types of failures: a.) a masking sphere may fail to produce a surface charge patch (e.g., Fig. 1b, "n"), b.) the surface charge patch may remain unlabeled, or c.) the label particles may bind outside of the defined patch (e.g., Fig. 1b, "s"). While the stray particles "s" are obvious, distinction between the first two failures is more subtle. In the example "n" in Fig. 1 b, the shadow in the

Cr film overlaps its neighbors indicating that it was cast from a sphere that was not in contact with the substrate, so that polyelectrolyte was not size excluded there, and no patch can be created on either particle or underlying substrate. TEM mass-thickness observations are consistent, which show no patches under particles with overlapping shadows and do show patches in every case that the Cr shadows are distinct. Therefore, the yields can be determined by optical microscopy (Fig. 1b). From 10 independent samples of approximately 300 sites each, the failure rate for "n" is approximately 1% $\pm$ 1%; the failure rate of unlabeled sites is approximately 1% $\pm$ 1%; and the fraction of stray particles is approximately 3% $\pm$ 1%. While the patch production yield remains high regardless of masking particle size, the labeling yields depend on the sizes of both masking and labeling spheres, and on processing conditions. For example, the fraction of labeled sites in Fig. 1 d is small, even though the surface was bathed with a 2 % mass fraction suspension of PS100s⁻ for approximately 0.5 h, indicating that longer time or perhaps increased ionic strength may be desirable. The interaction of charged particles with patchy surfaces exhibits interesting subtleties, which depend on the relative sizes of particles, patches and Debye length, as explored for example in recent reports (Santore and Kozlova 2007; Huang et al. 2008).

Next we consider the rate of production of patchy particles, 300 nm diameter, as an example. This size particle may be adsorbed onto a surface at a density of 6 x 10^8 particles/cm². To review, the process involves coating the substrate with polyelectrolyte, then with particles, again with polyelectrolyte, and removal of particles from the surface by ultrasound. Given a 6 minute cycle to complete these steps, the production rate of patchy particles is of the order of 10^8 particles /min /cm². A roll to roll process can be more efficient. For example, if the speed of the substrate is 0.5 cm/s, a production rate of 2 x 10^{10} particles /min /(cm substrate width) is feasible. For comparison, 7 mL of 2 % mass fraction suspension contains approximately 10^{13} such particles.

Patchy particles can potentially form a variety of assemblies either in homogeneous or mixed solutions of particles, and the resultant assembly can be directed through mixing of appropriate particles. When a solution of patchy particles is mixed with a solution of uniform particles whose surface charge is complementary to the lithographic region, the particles (of different type) bind to each other (Fig. 2).
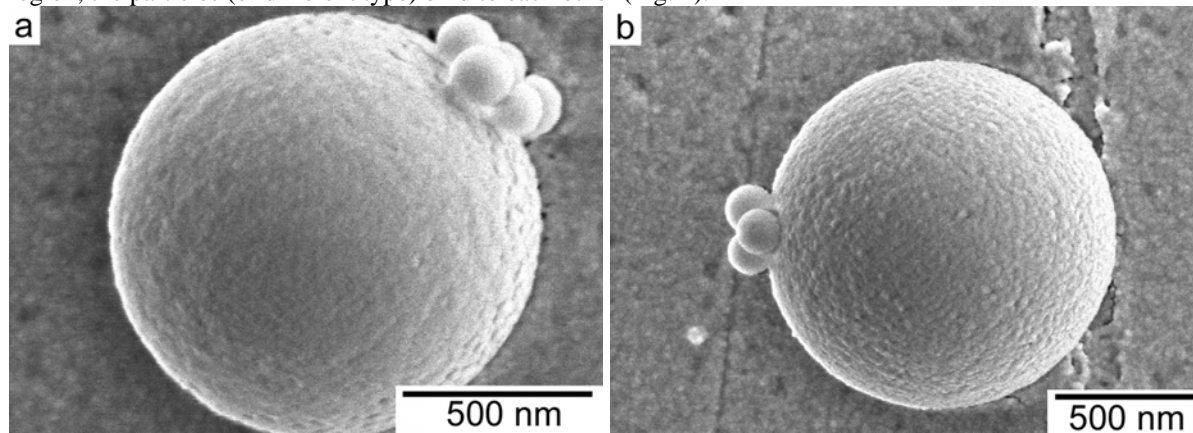

Fig. 2. SEM images showing PS160c⁻ particles attached to the patchy region of PS1100a⁺⁾⁻ particles.

CONCLUSIONS

The surface charge of polystyrene particles is modified by adsorption of polyelectrolyte to their surfaces. When the particles are in suspension their entire surface is coated, but if these particles are adsorbed first to a surface, a circular region of the surface is inaccessible, and a patchy particle or surface is produced.

The substrate surface charge has a significant effect on the adsorption of particles, which provided several advantages in comparison to bare glass substrates. These include much reduced deposition time, a high degree of coverage, and the ability to accommodate both negatively and positively charged particles. This strategy for depositing polystyrene particles onto a polyelectrolyte film may be compatible with roll-to-roll processing, providing a suitable route to producing large numbers of particles. Considering 300 nm particles, 10^8 particles/min/cm² can be produced in batch, or approximately 2 x 10^{10} particles/min/(cm roll width) in continuous roll processing.

Particle aggregation and assembly was also investigated. Site-specific binding of complementary spheres to the lithographic region of patchy particles was demonstrated, including binding to positive and negative patches. When the complementary particles are small, they serve well to detect the location of a patch and to measure its size. Since the net charge of these patchy particles is substantial, self-aggregation between patchy particles was observed only at high ionic strength, and did not yield unusual structure.

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