Assembly of Nanoparticles using Surface-Grafted Orthogonal Polymer Gradients

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Introduction

Polymer-coated surfaces are routinely used in industrially important applications including prevention of biofouling[1] (in fabrication of protein-resistant surfaces), improving stability of colloidal dispersions,[2] surface lubrication,[3] or enhancing wettability and adhesion[4]. Polymer chains chemically bound to the surface represent a special class of polymer coatings that has gained considerable attention in the past few years in nano- and biotechnology applications. This is primarily due to the ease of growing polymer chains on a variety of functional surfaces and the ability of grafted polymer chains to withstand harsh operational conditions of solvent and temperature. The chemical grafting approach also allows for manipulation of the length (or equivalently molecular weight, MW) and grafting density (σ, number of chains per unit area of grafted surface) of polymer chains attached to the surface. MW and σ determine the conformation of polymer chains, which in turn, governs the effectiveness of polymer coating for a given application. For example, it has been predicted that adsorption of small proteins (and the subsequent biofouling) on a surface can be minimized by using polymer brushes having high grafting density (high σ) whereas thicker brushes, i.e., large molecular weight, MW) are preferred to achieve similar repellency for larger proteins.[1] Polymer brushes are widely used to prevent coagulation of colloidal particles. This steric stabilization is best realized by using long grafted chains with relatively high surface density.[2] Adhesion promotion between a polymer melt and brush-coated surface is found to depend critically on σ.[5] Short chains with very high σ are suitable for enhancing the lubrication of a polymer coated surface with a sliding surface. Thus, it is desirable to be able to systematically manipulate the conformation by controlling MW and σ of the chains.

Our group has recently developed combinatorial methods for preparing surface-tethered polymers with smoothly
varying $\sigma$ and MW. A gradient in $\sigma$ so formed was utilized to study mushroom-to-brush crossover in surface-anchored polyacrylamide (PAAm). In another study, gradient in MW of anchored PAAm was exploited to control the loading of gold nanoparticles on brush surfaces. Such gradient surfaces offer combinatorial platforms for quick and inexpensive investigation of a multivariate phenomenon. Similar study by traditional methods typically requires preparation of numerous samples, ostensibly under similar experimental conditions. The combinatorial methods described in ref. [7,8] obviate such difficulties and enable unambiguous exploration of the large $\sigma$ and MW space, albeit requiring two different kinds of samples. In this work, we combine the above-mentioned methodologies and form an orthogonal gradient structure, wherein $\sigma$ and MW of anchored polymer chains vary continuously in two orthogonal directions on a single substrate. We utilize this structure to combinatorially study the effect of MW and $\sigma$ on the assembly of nanoparticles on grafted polymer surfaces.

Experimental Part

All chemicals were obtained from Aldrich and used as received. The silicon wafer and glass slide were cut into rectangular pieces (6 cm $\times$ 5 cm) and were exposed to ultraviolet/ozone (UVO) treatment (Jelight Company, Inc., model 42) for 30 min. A concentration gradient of octyltrichlorosilane (OTS) was formed along shorter edge (X-direction) of the specimens by using silane vapor diffusion technique proposed by Chaudhury and Whitesides. The samples were then kept immersed in the polymerization initiator solution maintained at $-10^\circ$C for about 12 h. The initiator, [11-(2-bromo-2-methylpropionyloxy)undecyl]trichlorosilane (BMPUS), was synthesized following the literature recipe.

Poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) was grown from the initiator layer by atom transfer radical polymerization (ATRP), following the recipe of Matyjaszewski et al. De-aerated polymerization reaction mixture was transferred to the reaction chamber built in a custom-made polymerization apparatus (see Figure 1). The apparatus comprises two concentric glass chambers; the inner one acts as a reactor and the outer chamber serves as a heating jacket. Silicon and glass specimens were held back-to-back and lowered into the polymerization mixture in a direction perpendicular to that of the initiator concentration gradient. To achieve the first step we use the organosilane vapor diffusion technique. Since the initiator BMPUS molecules have low vapor pressure at room temperature, their gradient formation is rendered difficult by the “classical” diffusion method. Hence, we use the so-called “back-filling” method, wherein we first form a molecular gradient of OTS and fill the remaining space on the substrate with initiator molecules, thus generating a gradient in initiator molecules in the reverse direction. Growing chains from such a concentration gradient of initiator would result in grafting density gradient of grown brushes along the direction of initiator gradient (X-direction).

After forming the concentration gradient of the initiator molecules, we proceed to form the gradient in MW of grafted chains. We grow PDMAEMA brushes by “grafting from” technique using atom transfer radical polymerization (ATRP). Among the available radical polymerization methods, ATRP has been the most widely used polymerization method to grow surface-bound polymer assemblies with low polydispersities. A number of factors contribute to the extensive use of surface-initiated ATRP in recent

Figure 1. Photograph of the polymerization apparatus used to create orthogonal gradient on an initiator-coated substrate.

Results and Discussion

Fabrication of surface grafted orthogonal gradient entails two steps: (1) formation of a molecular concentration gradient of initiator molecules and (2) growth of surface anchored chains with a molecular weight gradient in the direction perpendicular to that of the initiator concentration gradient. To achieve the first step we use the organosilane vapor diffusion technique. Since the initiator BMPUS molecules have low vapor pressure at room temperature, their gradient formation is rendered difficult by the “classical” diffusion method. Hence, we use the so-called “back-filling” method, wherein we first form a molecular gradient of OTS and fill the remaining space on the substrate with initiator molecules, thus generating a gradient in initiator molecules in the reverse direction. Growing chains from such a concentration gradient of initiator would result in grafting density gradient of grown brushes along the direction of initiator gradient (X-direction).

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Aqueous solution of gold nanoparticles (diameter of $16.9 \pm 1.8$ nm as measured by transmission electron microscopy) was prepared by citrate reduction of HAuCl$_4$. Gold nanoparticles were attached to PDMAEMA orthogonal gradient prepared on glass substrate by immersing the substrate in gold sol (pH $\approx 6.5$) for about 15 h. To characterize the loading of nanoparticles in the brushes, we measured visible light absorbance at various points on the glass slide using VASE in transmission mode.
years:[16] (1) ATRP is a controlled/“living” radical polymerization. Consequently, ATRP is remarkable in its simplicity and ability to grow polymers with low polydispersity.[16a] (2) Unlike ionic polymerization methods, ATRP has no stringent requirements on the experimental conditions with regards to purity of the chemicals used, presence of water etc. (3) A large variety of monomers are amenable to polymerization by ATRP. (4) High grafting density brushes can be synthesized with surface-initiated ATRP.[16b]

To achieve MW gradient in a direction perpendicular to that of $\sigma$, we rotated the sample by $90^\circ$ and immersed it in polymerization mixture (along $Y$-direction) placed in a deaerated reaction chamber. By continuously removing the polymerization medium from the chamber a MW gradient on the substrate was generated in the $Y$-direction.[8] The MW of grafted polymer chains at various points along $X$-direction for a given $Y$ should be approximately the same since all those points remain in the reaction media for the same period of time.[17] In Figure 2 we plot the dry thickness profile of grown PDMAEMA in $X$ ($\sigma$ gradient) and $Y$ (MW gradient) directions. Dry thickness of grafted polymer is given by $h = (\sigma M)/(\rho N_A)$, where $M$ is molecular weight of polymer, $\rho$ is polymer density, and $N_A$ is Avogadro’s number. Thus, $h$ depends on both MW and $\sigma$ of the grown polymer. For a given value of $Y$, $h$ on our sample increases continuously as one moves away from the OTS end along $X$ direction. Similar trend in thickness is observed along $Y$ direction for a given $X$ as one moves from a region that was in the reaction media for a shorter period to a region that stayed in the mixture for longer time. These measurements indicate that orthogonal gradient was successfully formed.

Formation of assemblies comprising nano-objects placed in chemically and structurally well-defined environments represents an important milestone on the pathway towards realization of the goal of nanotechnology. In this regard, nanoparticles attached to a solid, tangible substrate represent an area of great significance. In our previous work,[10] we have shown that utilizing surface-grafted polymers as an anchor between substrate and particles can tremendously increase loading of nanoparticles on a solid substrate. Specifically, we demonstrated that amino group containing polymers have affinity towards citrate-covered gold nanoparticles. This attraction is due to the electrostatic interaction between positively ionized amino group in slightly basic gold sol and negatively charged gold nanoparticles and possible hydrogen bonds formed between the amino groups of the polymer and the citrate groups on the surfaces of the particles.[10] The study of attachment of citrate-covered gold particles on orthogonal PDMAEMA substrate was carried out with two objectives: (1) to study how MW and $\sigma$ affect loading of particles in the brushes and (2) to visualize the orthogonal gradient. This visualization is made possible by the strong visible light absorbance associated with surface plasmon resonance of gold nanoparticles.[18,19] In Figure 3 we show a photograph of the...
orthogonal gradient upon particle uptake in the brush. Color of the slide changes gradually from light pink (region of low MW and low σ) to dark violet blue (region of high MW and high σ) as one moves along the directions of increasing MW and σ. This color variation is indicative of inter-particle plasmon coupling associated with increase in uptake of particles in the brush as MW (or σ) increases.[18,19] In Figure 4, we plot visible light absorbance spectra collected along σ (path A) and MW (path B) gradients. There are two points worth noting in these plots: (1) increase in intensity of the plasmon absorbance peak in the direction of increasing MW or σ and (2) concomitant red shift of the plasmon peak position. The first feature is due to the increasing number of particles attached to the polymer chains, whereas the second feature suggests intensified inter-particle plasmon coupling accompanying the nanoparticle crowding on the substrate.[18] Such a correlation between plasmon peak intensity and the number of adsorbed particles has been well documented in the literature.[10,19]

It is interesting to compare this experimental work with theory describing favorable interaction of particles with brushes. Currie et al. studied the formation of complex between grafted polymer chains and mesoscopic particles using an analytical self-consistent-field theory.[5,20] They predicted that grafting longer chains enhances adsorption of the particles. Longer chains offer more adsorption sites resulting in favorable polymer-particle interaction, which outweighs the increase in osmotic pressure in the brush upon particle attachment. The number of adsorbed particles also increases as grafting density is increased in the low grafting density regime. This is because of the increased attachment sites that become available as σ is increased. However, there is a maximum in the adsorption as a function of σ. At very high σ, the osmotic pressure caused by insertion of particles in the grafted layer overcomes the favorable polymer-particle binding energy. This results in expulsion of particles from the proximal (i.e., closer to the substrate) to the distal (i.e., away from the substrate) region of the brush. The maximum in particle adsorption is a manifestation of the balance between the increasing number of adsorption sites and increasing osmotic repulsion as σ is increased. Our gold nanoparticle adsorption results along MW gradient arm of the orthogonal gradient substrate are in line with the theory. However, we do not observe a maximum in number of adsorbed particles as a function of σ. Instead, adsorption increases monotonically as σ is increased. We suspect that this is due to the large size of particles (diameter ≈17 nm) used in our study compared to the average distance between the grafted polymer chains.

Conclusions

We have shown that orthogonal gradient in molecular weight and grafting density of surface-anchored polymers can be conveniently prepared by generating number density gradients of polymerization initiators on surface followed by surface-initiated atom transfer radical polymerization. These orthogonal gradients were used as functional combinatorial templates to direct the assembly of nanoparticles. We envisage that such orthogonal gradient substrates offer an expeditious and efficient multivariant platform that can be utilized in other scientifically and technologically important applications.

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References


[17] We note that here we assumed that the molecular weight of the polymer brushes did not depend on the density of the initiator. For further details on this topic, see ref.[7,9]

