Combinatorial study of nanoparticle dispersion in surface-grafted macromolecular gradients

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Abstract

Surface-tethered assemblies of polymers with gradually varying molecular weight (MW) and/or grafting density are utilized to control the dispersion of nanosized particles. Using several case studies we show that these gradient polymer specimens represent ideal systems for combinatorial exploration of the parameters that control the distribution of the particles in surface-grafted layers. We demonstrate that the particle distribution is governed by the interplay between the particle size and the grafting density and molecular weight of the polymer brush.

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1. Introduction

Fabrication of nanoparticle/polymer composites represents one of the fastest growing fields of materials research. It has been widely recognized that the macroscopic properties of nanoparticle-based composites will reflect both the characteristics that are specific to nano-objects [1,2] as well as those which are characteristic of large-scale structure of nanopar-
ticles in the matrix [3–5]. The unusual optical, electronic, magnetic, adsorption, and other important materials characteristics of nanoparticle/matrix hybrids can be utilized in a large variety of applications, including high-density information storage media, sensors, magnetic fluids, medical diagnostics, membranes and catalysts, etc. [6]. Multiple papers reported the dispersion of nanoparticles in homopolymers and block copolymers in bulk and thin films [7–10]. Recent theoretical predictions [11–13] and early experimental studies [14,15] indicated that the distribution of nanoparticles in soft material matrices could be achieved by utilizing surface anchored polymer brushes. Theoretical studies of
brush/particle composite predict the distribution of the particles in the polymer brushes to depend on: (1) particle size; (2) polymer/particle interactions [14,16]; (3) polymer molecular weight (MW) [15,17,18]; and (4) the polymer grafting density [14,18]. Depending on the interplay among the aforementioned parameters, the particles can either be adsorbed on the tip of the brush or can penetrate inside the brush, thus forming two- or three-dimensional (2D or 3D) assemblies, respectively [12]. Although particle/polymer system has been the focus of a few experimental studies [14,15], a thorough and systematic exploration of this important class of materials is still lacking. In this letter, we report selected results from our lab that aim towards achieving complete understanding of this multivariate system.

In order to unambiguously analyze the effects of numerous system parameters involved in polymer brush/nanoparticle composite, we resorted to gradient polymer systems. Recently, several papers appeared that reported on the utilization of gradient assemblies of surface-tethered oligomers [19] and polymers for controlled and tailored adsorption of nanoparticles [17,18] and proteins [20]. Chemical gradients prepared on tangible substrates provide unique means of programmed material assembly [21–23]. Such gradient substrates can be utilized as combinatorial media facilitating systematic studies of adsorption on surfaces with variable (and adjustable) “sticking” properties. In this work, we report on systematic investigation of the interplay between the particle size and the conformation of the surface-tethered polymers by dispersing nanoparticles in surface-tethered macromolecules with a gradual variation of polymer grafting densities (σ) and/or polymer molecular weights. We will demonstrate that the continuous variation of the physico-chemical structure and property of the gradient substrates (σ or MW), not confounded by intervening gaps, eliminates the requirement of unconfirmed interpolation to determine the properties at a specific surface coordinate.

2. Experimental

All chemicals were obtained from Aldrich and used as received. Silicon wafers (Silicon Valley Microelectronics Ltd.) and glass slides (Fisher Scientific) were cut into pieces of desired sizes (1 cm × 6 cm for linear gradient and 5 cm × 6 cm for orthogonal gradient) and exposed to ultraviolet radiation/ozone (UVO) treatment (Jelight Inc., model 42) for 30 min. The polymer brushes utilized in this work were prepared by “grafting from” polymerization based on atom transfer radical polymerization (ATRP) on account of its ability to form polymers with low polydispersity [24]. This procedure involved the deposition of the ATRP initiator (11-(2-bromo-2-methyl) propionyloxy)-undecyl trichlorosilane, BMPUS) on the surface of either a silicon wafer or glass slide and subsequent polymerization initiated from the surface-bound BMPUS centers. In this work, we employed various macromolecules including poly(acryl amide) (PAAm), poly(N-isopropyl acrylamide) (PNIPAAm), and poly(dimethylaminoethyl methacrylate) (PDMAEMA) to control the attachment of gold nanoparticles. Linear gradient in MW of grafted PAAm was prepared using polymerization solution draining method [25–27]. Polymer brushes with gradually varying σ were prepared by decorating the substrates with molecular gradients of the polymerization initiators, followed by the surface initiated ATRP [28,29]. These two methodologies can be combined to form complex structures, in which σ and MW change independently in space; so called orthogonal gradients [18,20]. While synthesis of PAAm and PDMAEMA was carried out following the recipes in [17,18], respectively, PNIPAAm was grown using a polymerization mixture containing 6.3 g of NIPAAm, 4.86 g of methanol, 6.3 g of water, 0.56 g of N,N,N′,N′′-pentamethyldiethylenetriamine (PMDETA), 0.16 g of CuBr and 0.016 g of CuBr₂. The dry thickness profile of grown polymers at various points on the linear as well as on orthogonal gradient was measured by variable angle spectroscopic ellipsometry (VASE, J.A. Woollam, Co.).

Aqueous solutions of gold nanoparticles with two different sizes were prepared following literature recipes [30,31]. The diameter of particles prepared according to [30] was measured to be ≈16.9 ± 1.8 nm by transmission electron microscopy, whereas smaller particles were presumed to have diameters of ≈3.5 nm as reported in [31]. Gold nanoparticles were attached to surface-grown polymers by immersing the polymer-coated substrates in gold sol for more than 24 h.
3. Results and discussion

In our previous work, we demonstrated that the particle loading in surface-tethered polymer assemblies can be monitored using several experimental techniques, which include ultraviolet/visible (UV–vis) light absorbance spectroscopy [17,18], spectroscopic ellipsometry [17], scanning force microscopy (SFM) [17,19], X-ray photoelectron spectroscopy [17], and neutron or X-ray reflectivity [32]. We established that the particle loading and clustering inside the brush could be deduced from UV–vis experiments [17,18]. Specifically, the maximum intensity of the gold plasmon peak (\(A_{\text{max}}\)) in the UV–vis spectrum at wavelengths between 500 and 700 nm is a measure of concentration of gold particles present in the system, whereas the wavelength at which this maximum occurs (\(\lambda_{\text{max}}\)) is related to the distance between particles present in the system [1,33]. We monitored the kinetics of adsorption of gold nanoparticles in PNIPAAm brush using UV–vis spectroscopy. In Fig. 1, we plot \(A_{\text{max}}\) for PNIPAAm/gold nanoparticle system (particle diameter \(\approx 16\) nm) as a function of the deposition time from aqueous solution (pH 6.5). The PNIPAAm sample comprised polymers with a constant chain length (dry thickness \(\approx 15.5\) nm) and uniform grafting density (\(\sigma \approx 0.5\) chains/nm\(^2\)). The steady increase in \(A_{\text{max}}\) indicates that more particles get attached to PNIPAAm brush with increasing exposure of the PNIPAAm chains to the gold sol. The particle attachment to the polymers is facilitated by hydrogen bonding interaction between the citrate groups present on the surface of particles, and amide groups along the polymer backbone. After a deposition time of about 24 h, \(A_{\text{max}}\) reaches a steady level, which corresponds to the complete saturation of the brush with particles. In all our experiments we exposed the polymer brush-coated substrates to the gold sol for at least 24 h in order to assure an "equilibrium" particle loading. In Fig. 1, we also plot \(\lambda_{\text{max}}\) as a function of the particle deposition time. With increasing deposition time, \(\lambda_{\text{max}}\) increases (red shift), which is indicative of the reducing interparticle separation. It is worth noting that \(A_{\text{max}}\) and \(\lambda_{\text{max}}\) follow the same trend.

As mentioned previously, the particle partitioning in the surface-tethered polymer depends on the interplay between the particle size and the length and grafting density of the polymer on the surface. While smaller particles may be "allowed" to penetrate the brush, particles larger than the dimension of the surface-anchored chains are predicted to reside primarily on the tip of the brush [12]. We verified these theoretical predictions experimentally using various polymer/particle gradient systems. In bottom panel of Fig. 2, we plot the number density of gold nanoparticles (diameter \(\approx 16\) nm) adsorbing onto PAAm brushes with a constant grafting density (\(\sigma \approx 0.5\) chains/nm\(^2\)) and a variable length (expressed in terms of the dry PAAm thickness and the degree of polymerization of PAAm). The number densities of particles were obtained from scanning force microscopy scans performed at various positions on dry PAAm/particle gradient specimen. The data reveal that the number of particles attached to the polymer brush increase with increasing chain length or degree of polymerization. This observation is explained by the fact that the number of particles is proportional to the number of accessible charges along PAAm backbone, which increases with increasing PAAm MW. The bottom panel of Fig. 2 also illustrates the correlation between the particle number density and \(A_{\text{max}}\). Complementary experiments using angle-resolved x-ray photoelectron spectroscopy (see [17]).

Fig. 1. Intensity (\(A_{\text{max}}\)) and wavelength (\(\lambda_{\text{max}}\)) of the gold plasmon peak in the UV–vis spectrum (see inset) of 16 nm gold nanoparticle on poly(N-isopropyl acrylamide) (PNIPAAm) brushes as a function of the particle deposition time from aqueous solution at pH 6.5. Both \(A_{\text{max}}\) and \(\lambda_{\text{max}}\) were measured on dry samples. The dry thickness of the PNIPAAm brush was 15.5 nm, which corresponds to the PNIPAAm degree of polymerization of \(\approx 176\).
revealed that the gold nanoparticle resided primarily on the top of the PAAm brush (indicated schematically in the cartoon in Fig. 2).

Using the saturation $A_{\text{max}}$ values observed for the PNIPAAm- and PAAm-based nanoparticle hybrids we can make quantitative comparison between the numbers of particles adsorbed on each polymer. From Fig. 1, saturation value of $A_{\text{max}} \approx 0.65$ for PNIPAAm, with dry thickness ($h$) of 15.5 nm, which corresponds to the degree of polymerization of $N \approx 176$ [34]. From Fig. 2, the saturation $A_{\text{max}}$ value for a brush with a degree of polymerization equivalent to that of PNIPAAm is only about 0.14. This significantly smaller loading of the particles in the PAAm brush (relative to the PNIPAAm brush) is associated presumably with different strengths of the interaction between the particle surface and PAAm or PNIPAAm.

Using combinatorial techniques pioneered by our group, samples can be prepared that allow simultaneous and systematic study of the effects of the particle loading/polymer structure on a single sample. For example, we fabricated orthogonal polymer gradient substrates, in which the polymer molecular weight and grafting density vary independently in two orthogonal directions. The advantage of such orthogonal gradient structure is that one can simultaneously probe the effect of the molecular weight and grafting density on a single sample, thus improving the effectiveness and speed of adsorption screening. Fig. 3a shows a glass slide containing PDMAEMA orthogonal gradient on which 16 nm gold particles were adsorbed. At pH 6.5, the electrostatic interaction between the positively charged DMAEMA groups and...
citrate ions attached to the surface of the gold sol were responsible for binding the nanoparticles to the underlying brush. Color of the slide in Fig. 3a changes gradually from light pink (region of low MW and low \( \sigma \)) to dark violet blue (region of high MW and high \( \sigma \)) as one moves along the directions of increasing MW and \( \sigma \), indicating inter-particle plasmon coupling associated with increase in uptake of particles in the brush as MW (or \( \sigma \)) increases. In Fig. 3b, we plot visible light absorbance spectra collected along \( \sigma \) (path A) and MW (path B) gradients. The increase in intensity of the plasmon absorbance peak in the direction of increasing MW or \( \sigma \) are due to the increasing number of particles attached to the polymer chains. The concomitant red shift of the plasmon peak position suggests intensified inter-particle plasmon coupling accompanying the nanoparticle crowding on the substrate. Upon variation of \( \sigma \), the color variation is more pronounced for low MW (shorter) chains relative to longer chains, suggesting that the number of particles bound to the brush depends on the number of favorable sites that particles have access to.

In all the systems discussed so far, the particles were too big (diameter \( \approx 16 \) nm) to penetrate the brush. As a result, they always remained on the tip of the brush and formed a “quasi” 2D structure. In order to form 3D dispersions of nanoparticles inside the polymer brush, the particle size has to be reduced dramatically [17]. Accordingly, we prepared \( \approx 3.5 \) nm diameter gold particles [31] and allowed them to adsorb on top of PNIPAAm brushes with a gradient in \( \sigma \). The degree of polymerization (\( N \)) of PNIPAAm, estimated from the dry ellipsometry thickness, was about 205 [34]. The particle loading inside the PNIPAAm brush was determined using the UV–vis absorbance, following the procedures outlined earlier. In Fig. 4, we plot \( A_{\text{max}} \) as a function of the PNIPAAm \( \sigma \). The data shown in Fig. 4 reveal that the number of particles increases with increasing PNIPAAm grafting density, reaches a maximum at some intermediate grafting density (\( \sigma_{\text{max}} \)), and decreases with further increase of \( \sigma \). In contrast, the number of large particles partitioning in the brush was found to increase monotonically with increasing grafting density (cf. Fig. 3b). The behavior of the small particles can be explained as follows. For a given brush molecular weight, the number of adsorbed particles increases as grafting density is increased in the low grafting density regime. This behavior results from the increased attachment sites for the particles along the polymer backbone that become available as \( \sigma \) is increased. As predicted theoretically, particle loading inside the brush causes an increase in the osmotic pressure exerted by the grafted polymers [11,12]. At some grafting density (\( \sigma_{\text{max}} \)), a balance is achieved between the enthalpy gain associated with the particle attachment to the grafted polymers and entropy loss due to the osmotic swelling. Further increase in \( \sigma \) results in the expulsion of particles from the deeper areas inside the brush; the particles are only allowed to adsorb near the tip of the brush, resulting in reduction in total particle loading.

Our experimental results are in line with theoretical predictions of Wageningen group who predicted similar maxima in the number of attached particles as a function of grafting density [11,13]. Kim and O’Shaughnessy provided estimates for the 2D versus 3D assemblies of particles in polymer brushes. Specifically, they postulated that for systems exhibiting strong interactions between the particle and the polymer, which is the case of our system, particles smaller than \( b_{\text{max}} \approx a^{1/2}(N/\sigma)^{1/4} \), where \( a \) is the monomer size, could penetrate the brush. Using \( b_{\text{max}} \approx 3.5 \) nm, \( a = 0.5 \) nm and \( N = 205 \), we get \( \sigma \approx 0.34 \) chains/nm\(^2 \), which agrees well with the crossover value of 0.38 chains/nm\(^2 \) observed in our
study. Hence, our experimental findings for 3.5 nm sized particles seem to be in accord with the theoretical predictions. Thus, polymer gradients offer a simple yet powerful means to study the complex thermodynamic interactions present in polymer brush/colloidal particle system. More experimental and theoretical work is currently underway that aims at more detailed understanding of the various system parameters that govern the partitioning of nanoparticles inside surface-tethered polymers [35].

4. Summary

The dispersion of nanoparticles in surface-tethered polymer brushes was studied systematically using surface-grafted polymer assemblies with gradients in brush grafting density (σ) and/or molecular weight. Particles larger than dimension of the grafted polymer were found to reside primarily on the tip of the brush, the particle loading increased with increasing MW and σ. For particles much smaller than chain size, particle concentration in the brush initially increased with increasing σ, reached a maximum at an intermediate grafting density, and then decreased with further increase in σ. This behavior was attributed to the morphological transition from 3D to 2D like distribution of the particles inside the brush.

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References

[34]  was calculated from \( N = N_h/k_B T \), where \( k_B \) is the Boltzmann constant, \( T \) is the temperature, \( N_h \) is the number of particles at equilibrium, and \( \sigma \) is the monomer molecular weight. 