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Structural and adhesion properties of surfaces functionalized with polyelectrolytes and polystyrene particles

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Abstract

Surfaces functionalized with polystyrene particles and polyelectrolytes were used to investigate the morphological and adhesion properties of composite substrates. Atomic force microscopy (AFM) studies showed that surfaces with non-homogeneous topography have non-homogeneous adhesion properties. In addition, the homogeneity of the adhesion properties is dependent upon the chemical species used to functionalize the surface. Force volume (FV) imaging was utilized to map the adhesion of the fabricated substrates with high-resolution. The FV studies revealed that the hydrophobicity of the surface is not uniform despite the fact that the surface was functionalized with the same polyelectrolyte. The analysis methodology we report here opens the possibility to design better surfaces for future tissue engineering applications.

Keywords: AFM; Adhesion; Polyelectrolytes

1. Introduction

Recent publications have highlighted the usefulness of surfaces containing colloidal particles for the purpose of studying cell adhesion, attachment, proliferation and migration [1,2]. To increase the utility of such substrates a number of groups have utilized polyelectrolytes in order to accomplish sufficient assembly of particles on surfaces as well as to introduce variability in terms of chemical functionality and distribution of surface charge on a chosen substrate [3,4]. Despite the number of different fabrication approaches that have been reported, there is still a need to understand the fundamental mechanical and structural properties of such surfaces. The increased knowledge with regard to such properties can help researchers arrive at improved analytical methods for their adaptation in future tissue engineering and biomimetic applications [5]. In this work, we investigated the adhesion and morphological characteristics of a multilayer system composed of polymer particles and polyelectrolytes. Polystyrene (PS) particles are of particular interest due to the great potential they offer in surface functionalization routes and the possibilities they present for targeted drug delivery strategies. Combining PS particles with polyelectrolytes requires control over several parameters. Such parameters play a role in the formation of the multilayers and include the degree of charge, the strength of ionization, and the underlying surface properties [6]. To increase the understanding of these parameters we fabricated composite surfaces by using two kinds of polyelectrolytes and PS particles and investigated their adhesion and topography by atomic force microscopy (AFM) techniques.

2. Experimental

2.1. Materials and surface preparation

Prior to the patterning procedure surfaces were prepared in the following fashion: 1 cm × 1 cm silicon pieces were cut from a 4″ SiO_x wafer (Wafer Net, CA) using a diamond scribe. Every piece was cleaned with piranha solution (H_2SO_4:H_2O_2; 3:1, v/v) for 20 min, rinsed with deionized (DI) water and dried with a stream of nitrogen. This treatment

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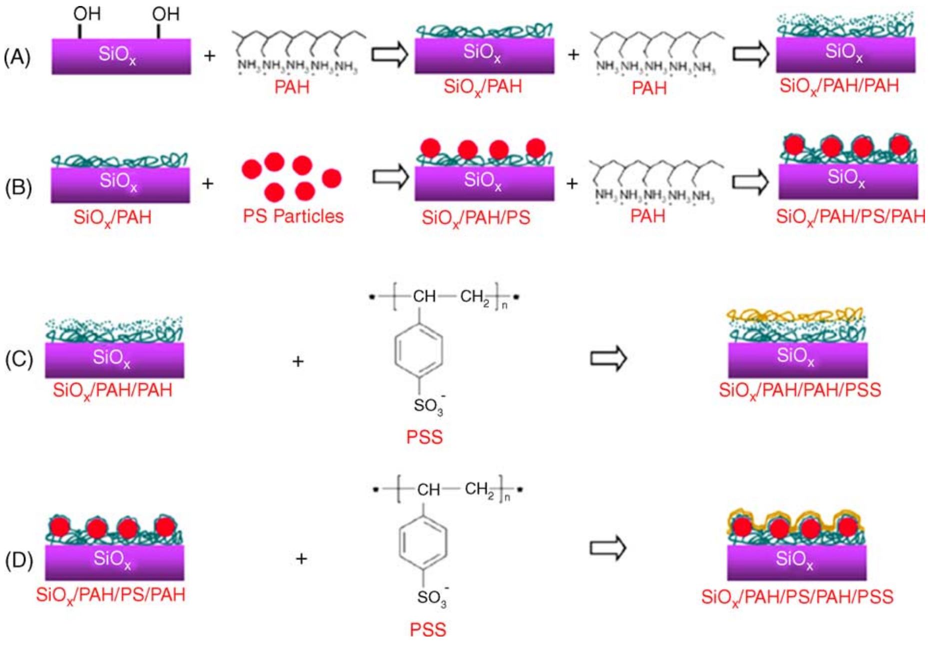

Fig. 1. Schematic representation of the composite surface preparation.

results in a negatively charged hard surface. Two different polyelectrolytes, positively charged poly(allylamine hydrochloride) (PAH), MW = 70,000 (Aldrich) and negatively charged poly(sodium-4-styrenesulfonate) (PSS), MW = 70,000 (Aldrich) were used. A literature procedure was used to perform the surface modification, Fig. 1 [7]. Briefly, we immersed a clean silicon substrate into 10 mg/mL PAH solution (0.5 M NaCl water solution was the solvent), for 20 min at room temperature followed by rinsing with DI water three times and drying with nitrogen. We performed contact angle measurement using a Tantec Inc. contact angle meter (Model CAM-PLUS MICRO) and utilizing the Half-Angle^{TM} Method. The static contact angles were measured within 30 s of depositing a drop of water. The contact angles were 20° for clean SiO_x and 22° for PAH terminated surface, and are consistent with similar experiments in the literature [6]. The surface was also modified with PSS using a similar protocol, Fig. 1A. We verified the deposition of the polyelectrolytes through X-ray photoelectron spectroscopy experiments. PS particles were utilized as described in the text in order to increase the utility of the surfaces. The particles were obtained from Aldrich.

2.2. *Atomic force microscopy and force volume imaging*

FV imaging is a mode where two operations of the AFM are incorporated. In this mode force curves are collected at each pixel of the image simultaneously with the height image. First, the height information of a certain pixel is obtained using the cantilever deflection or the oscillation amplitude, tapping mode AFM (TMAFM). Subsequently, the tip is withdrawn away from the sample surface and a force curve is obtained at that pixel. By combining all the force curves collected over the scanning area one can create a 3D map, or force volume map. Although, this is not an actual adhesion map one can derive information with respect to the adhesion between the tip and the sample from the numerous force curves collected. An advantage of this mode is that the height and adhesion properties of the sample surface can be correlated since they are collected simultaneously. The MultiMode^{TM} SPM (Veeco. Inc.) was used in the AFM experiments. The instrument allows the user to choose a distance which the tip travels and the amount of force applied to the surface. The latter is important since one always wants to keep the applied force consistent throughout the scanning area.

3. Results and discussion

Colloidal solution of polystyrene particles (Aldrich) with a manufacturer determined diameter of 100 nm and concentration of 12.5×10^{12} (5% by weight in water) particles/cm^3 was used. The PS particles were suspended in sodium azide (0.02% by weight in water) giving each particle a net charge of $1.5 \times 10^5\ e^-$ with a surface charge density of $-20\ \mu C/cm^2$. The PAH coated silicon oxide substrates prepared as described in Fig. 1 were exposed to a solution containing PS particles for 5 min. The substrates were subsequently rinsed with DI water for 20 s and dried under a stream of nitrogen. In the process, negatively charged PS particles were adsorbed onto the positively charged PAH surface via electrostatic interactions. The attractive forces between the surface and the PS particle compete with the repulsion among

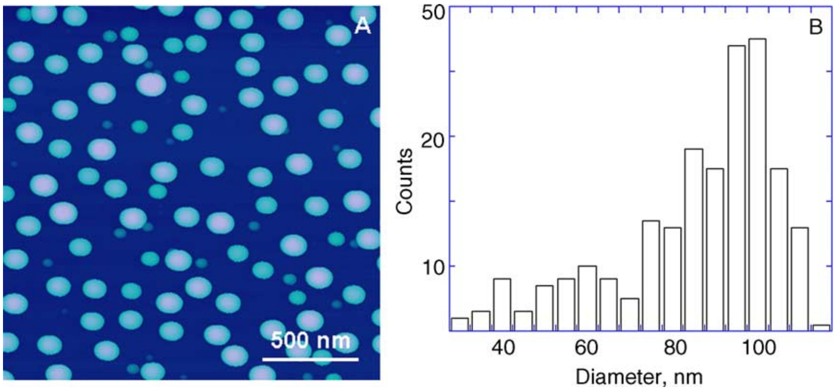

Fig. 2. (A) TMAFM height images, showing PS particles adsorbed onto a PAH thin film adsorbed onto a SiO_x surface; (B) The size distribution of the PS particles was measured from the TMAFM images.

the particles in order for the PS particles to be ordered on the surface. In addition, one assumes that there are no dipole to dipole interactions for the above to be true. However, the ordering of the particles is more complex and different forces besides electrostatic ones are known to make contributions [8]. In our initial studies we specifically fabricated surfaces with dispersed particles on the substrates rather than packed monolayers or multilayers. By experimenting with different dilutions it was found that the 1:100 dilution of the original particle mixture resulted in ∼20 PS particles in 1 μm^2 area. Furthermore, the size of PS particles was estimated from height measurements of ∼300 particles attached to the surface. The height was chosen as a measure, rather than the lateral dimension because of the possibility of convolution effects. The size distribution of the PS particles adsorbed onto PAH-coated SiO_x surface is shown in Fig. 2.

TMAFM was used to image the particles and subsequently collect the force volume images. Although contact mode tips are far more flexible than tapping mode tips the surface structures are disturbed if contact mode AFM is used. Initially force curves were collected on each sample. From the collected force curves the correlation coefficient, $s^* = 1/\text{slope}$, was found to be ∼75 nm/V. Force volume (FV) images were collected at a z travel distance of 100 nm with a sample number of 32 per curve, and 128 sample points per line. A trigger threshold of 0.03 V was used to eliminate the system's drift. The z-distance that corresponds to a threshold of 0.03 V (repulsive regime) can be calculated and was found to be 2.25 nm. The applied force that corresponds to the same threshold value differs from one tip to another. A threshold of 0.03 V usually corresponds to tens of nN force when a OTESPA tapping mode tip ($k \approx 40$ nN/nm) is used. In order to keep the experiments self consistent the same tip was used for all the force images obtained from each surface type. The simultaneous topography images were collected at 256 sample points per line. A typical force volume image is shown in Fig. 3. The individual force curves were extracted from force volume images and the adhesion forces were calculated. The adhesion force between the Si tip and PS particles was found to be (26.71 ± 7.71) nN whereas the adhesion force between the tip and PAH film was measured to be (16.61 ± 5.06) nN.

After collecting the force volume images the substrates were exposed to a PAH solution for 20 min. The solution was the same as the one used to prepare the SiO_x/PAH initial sub-

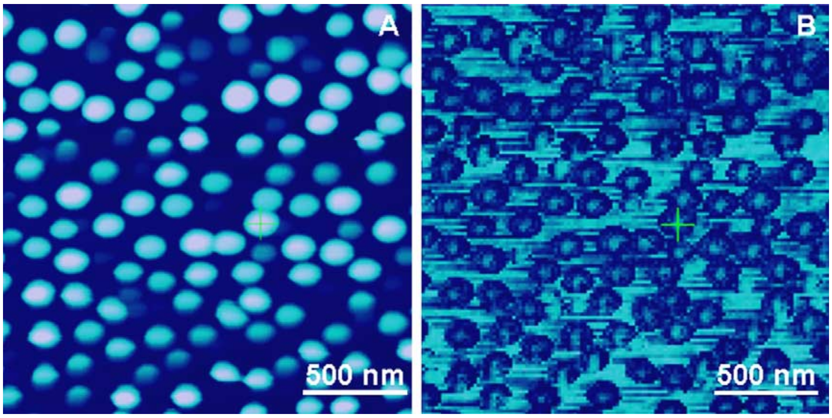

Fig. 3. (A) Topography and (B) FV image of PS particles adsorbed onto PAH coated SiO_x surface. The two images were collected simultaneously. The scales are 300 nm (A), and 250 mV for FV (B).

Table 1
Adhesion forces calculated from the FV images

Layers of polyelectrolytes	Composition	Adhesion forces (nN)
1	SiO_x/PAH	16.61 ± 5.06
	SiO_x/PAH/PS	26.71 ± 7.71
2	SiO_x/PAH/PAH	24.75 ± 8.04
	SiO_x/PAH/PS/PAH	40.02 ± 13.07
3	SiO_x/PAH/PAH/PSS	34.98 ± 9.83
	SiO_x/PAH/PS/PAH/PSS	53.82 ± 22.81

The ± values represent the standard deviation of the data.

strate. The samples were rinsed thoroughly with DI water for 20 s, dried with nitrogen, and characterized immediately. Since the PS particles and PAH are oppositely charged, a thin film of PAH should coat the PS particles and lock them onto the underlying surface. The FV imaging was done in the same fashion as before using a trigger threshold of 0.03 V. The adhesion force on the PS particles was estimated to be (40.02 ± 18.07) nN. Also, the adhesion force on the PAH film after the second adsorption, SiO_x/PAH/PAH, changed to (24.75 ± 8.05) nN. This change can be contributed to a conformational change of the PAH polyelectrolytes and the additional PAH deposited on the surface.

A layer of PSS polyelectrolyte was deposited onto the substrates following the characterization of the above samples. At this stage the PSS should coat the entire surface due to electrostatic interactions. From the FV images, the pull-off force between the tip and the PAH/PSS-coated PS particles was estimated to be (53.82 ± 22.81) nN. The results from the FV images on each type of surface are given in Table 1. The data shows that the adhesion force is different on the thin films on the hard surfaces versus on PS particles. In both cases the same functional groups were present and the adhesion force increased after each additional layer was deposited. The result is not surprising since the underlying surfaces beneath the polyelectrolyte films, SiO_x and PS particles, respectively, are expected to have different elastic properties.

4. Conclusion

In conclusion, we implemented the FV imaging method to investigate the adhesion properties of the system composed of PS particles and polyelectrolyte multilayer thin films. The results show that the composite substrate offers different adhesion properties throughout the surface terminated with the same functional groups. The methodology we describe can be utilized in other applications, such as design and evaluation of non-planar architectures for micron and nano-scale directed assemblies [9] and tissue engineering scaffolds [1,2].

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