PREPARATION OF NON-FOULING COATINGS MADE BY CHEMICAL VAPOR DEPOSITION POLYMERIZATION

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Introduction

Future biomedical implant devices will use advanced surface engineering technologies to actively modulate tissue integration. Towards this goal, vapor-based polymer coatings have been interesting candidates for the coating of implant devices, because of their advanced processibility and their excellent intrinsic biocompatibility. For instance, a specific vapor-deposited polymer (parylene) is already used in FDA approved drug-eluting stents. The commercially available coatings lack however, anchor groups for further modification and therefore do not allow for immobilization of biomolecules or the implementation of protein-resistancy.

Experiments

[2.2]Paracyclophane synthesis: Chemicals were purchased from Aldrich and were used without further purification. Friedel-Crafts acylation of [2.2]paracyclophane with the corresponding acid anhydride, or acid chloride, using an excess of AlCl3 resulted in 4-acetyl [2.2]paracyclophanes in high yields.

CVD polymerization: 4-Benzoyl[2.2]paracyclophane was synthesized via a three-step synthesis.4 The starting material was sublimed under vacuum and converted by pyrolysis into reactive species, which polymerize upon condensation (Scheme 1). A constant argon flow of 20 sccm was used as carrier. Sublimation temperatures were kept at 110-130 °C followed by pyrolysis at 800 °C. Subsequently, polymerization occurred on a rotating, cooled sample holder placed inside a stainless steel chamber with a wall temperature of 130 °C. The coating pressure was 540 mbar. The exit of the chamber was connected via a cooling trap to a mechanical pump. X-ray photoelectron spectroscopy, (Perkin Elmer/PHI 5400), and FTIR spectroscopy (Nicolet 6700) were used for characterizing the resulting polymers. In addition to flat PDMS and PDMS microchannels, flat silicon and platinum-coated silicon were included as reference samples.3

Photopatterning of CVD coated microfluidic devices. After surface modification via CVD polymerization, the coated substrates were immersed in an aqueous solution of polyethylene glycol (PEO, 10.000 g/mol, 3 weight-%). In these studies, both star-PEO and linear chain PEO were compared. For patterning, a photomask was brought in close proximity to the outside surface of the device (the depth of the microchannel was 50 µm). Samples were then exposed to broad-range UV radiation of about 320 nm wavelength for 30-60 min. DI-water was used to separate excess PEO. For protein adsorption studies, samples were incubated with protein solutions for 5 min.

Results and Discussion

A conformal film of PPX-CO-Ph was deposited on the sample surfaces using CVD polymerization. The reaction follows the mechanism shown in Scheme 1. The chemical structure of the resulting polymer coatings was verified by grazing-angle FTIR spectroscopy and XPS spectroscopy. The FTIR spectrum was in accordance with previous findings and reveals characteristic bands of the C=O stretches at 1612 and 1665 cm⁻¹. X-ray photoelectron spectroscopy was used to confirm the results of the FTIR study. The XPS survey spectrum and the high-resolution spectra of oxygen and carbon indicate 95.5 atom-% carbon and 4.5 atom-% oxygen, as compared to the theoretical value of 95.8 atom-% carbon and 4.2 atom-% oxygen. The high-resolution C1s spectrum further reveals characteristic signals for aliphatic and aromatic carbon (C-C, C-H) normalized to 285 eV, C-C=O at 285.9 eV, C=O at 286.1 eV, and a signal indicating a Π-→Π* transition at 291.5 eV. The latter signal is characteristic for aromatic molecules and has been previously reported for similar poly-p-xylylenes.1

Table 1 compares the theoretical and experimental data obtained by XPS analysis of the PPX-CO-Ph coating with the theoretically obtained values. The excellent accordance between both data sets suggests that side-reactions, such as decomposition of functional groups, can be largely excluded under the conditions used for CVD polymerization. This is important for surface engineering applications, where CVD coatings form reactive interfaces for subsequent, often complex immobilization steps.

As with the flat PDMS, the PDMS microchannel were first coated with the photoactive coating via CVD polymerization followed by the incubation with an aqueous solution of PEO. For this purpose, the PEO solution was filled into the microchannel for 30 min. Next, the solution was removed, tried with a stream of argon and the photomask was placed on bottom side facing the luminal surface of the microchannel. After UV exposure, the non-bound PEO was removed and the entire channel was incubated with the protein solution. Fig. 1 shows fluorescence micrographs of a microchannel consisting of a deep and shallow area that was incubated with fluorescence-labeled fibrinogen. Fig. 1a is focused on the shallow part of the microchannel, while Fig. 1b shows the pattern on the deep surface of the microchannel. Although the pattern is clearly observable, the features are less sharp on the deeper luminal surface than on the shallow surface. The reduced contrast for the deeper channels is a result of the wider distance of the surface from the mask. Nevertheless, fibrinogen is adsorbed only to the PEO-free squares establishing a discontinuous protein pattern within the microchannel.

Table 1. Chemical Composition of PPX-CO-Ph Coating Determined by XPS

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Fig. 1. Spatially controlled non-fouling on a PDMS-based microfluidic channel. Two images are with different focus of (a) outside the channel (b) inside the channel.
Conclusions

We have demonstrated the feasibility of using these reactive polymers to control non-specific protein adsorption on different substrates of silicon and PDMS. More importantly, experiments have also been conducted with 3-D patterning in a PDMS-based microfluidic channel demonstrating the creation of spatially controlled non-fouling surfaces in 3-D geometries. In addition, the photopatterning method overcomes the continuous patterns in laminar flow patterning. This novel technique consists of two steps: (1) CVD polymerization of the photodefinable coating, and (2) photopatterning. This generic surface engineering protocol is widely applicable to a range of materials and even hybrid structures, because of the substrate independence of the CVD coating step. With the precise control of non-specific protein adsorption and the ease of photopatterning technique in three dimensions, we foresee the technology to be useful for cell-based screening and diagnostic bioassays.

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References