Simple and Fast Method for the Fabrication of Switchable Bicomponent Micropatterned Polymer Surfaces

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Received December 13, 2006. In Final Form: February 8, 2007

We report on the fabrication of micropatterned polymer surfaces that allow the reversible inversion of surface topography, charge, and wettability. Micropatterned surfaces were prepared by grafting two oppositely charged polyelectrolytes (poly(acrylic acid) and poly(2-vinylpyridine)) using a combination of photolithography, “lift off”, and “grafting to” techniques. The switchable surfaces are of interest in microprinting and for the design of microfluidic devices and programmed protein adsorption.

Introduction

Micropatterned surfaces are of considerable importance for microelectronics, printing technology, microfluidic and microanalytical devices, information storage, biosensors, etc.[1−5] Topographical relief and/or a contrast of physicochemical properties—such as wettability, charge, and fluorescence—are generated via a number of techniques including photolithography, microcontact printing, and dip-pen technology.[1,4,6] However, once a pattern is generated, it cannot be easily changed on the fly. This limits the usability of a patterned surface to a single specific application, and new microstructures have to be fabricated for new applications. Therefore, it is desirable to develop methods for the fabrication of structured surfaces with switchable and rewritable patterns.[7−9] One approach toward this goal is based on the site-selective deposition of stimuli-responsive materials forming self-assembled monolayers (SAM) or polymer brushes. On such surfaces, the topographical and physicochemical properties can be locally triggered by external control over the environmental conditions. For example, one-component structured layers of temperature sensitive polymers or weak polyelectrolytes have been used for site-selective swelling as a result of changing temperature or pH, respectively.[10−13] Novel surface properties are expected when two or more kinds of polymer chains[14−19] are grafted onto the same substrate. Along these lines, we recently demonstrated the fabrication of biocomponent polymer surfaces where hydrophobic/hydrophilic patterns appeared or disappeared depending on the environmental conditions.[17] However, the fabrication of patterned two- and multicomponent switchable surfaces is still not a trivial task.[20] Commonly, for the fabrication of patterned surfaces, researchers use surface initiated polymerization,[14−20] which requires high purification of the monomers and special conditions for polymerization procedures.

Here, we report on a simple and fast method for the fabrication of bicomponent micropatterned polymer surfaces with switchable properties using a combination of photolithography, “lift off”, and “grafting to” techniques. We demonstrate the unique behavior of bicomponent micropatterned surfaces that allow the switching of surface topography, wettability, and charge in an inverse manner. The basis of these stimuli-responsive surfaces is the site-selective grafting of two oppositely charged polyelectrolytes (Figure 1). Depending on the pH of the surroundings, one kind of the polymer chains is swollen (charged and hydrophilic), while the other is collapsed (uncharged and hydrophobic). The main advantage of such surfaces is their capability of inverse switching, for example, hydrophilic patterns can be reversibly converted into hydrophobic ones and vice versa, via external stimuli.

Experimental Procedures

Carboxyl-terminated poly(*tert*-butyl acrylate) (PBA-COOH, $M_n = 42\,000$ g/mol, $M_w = 47\,000$ g/mol) and carboxyl-terminated poly(2-vinylpyridine) (P2VP-COOH, $M_n = 39\,200$ g/mol, $M_w = 41\,500$ g/mol), synthesized by anionic polymerization, were purchased from Polymer Source, Inc. Polyglycidyl methacrylate

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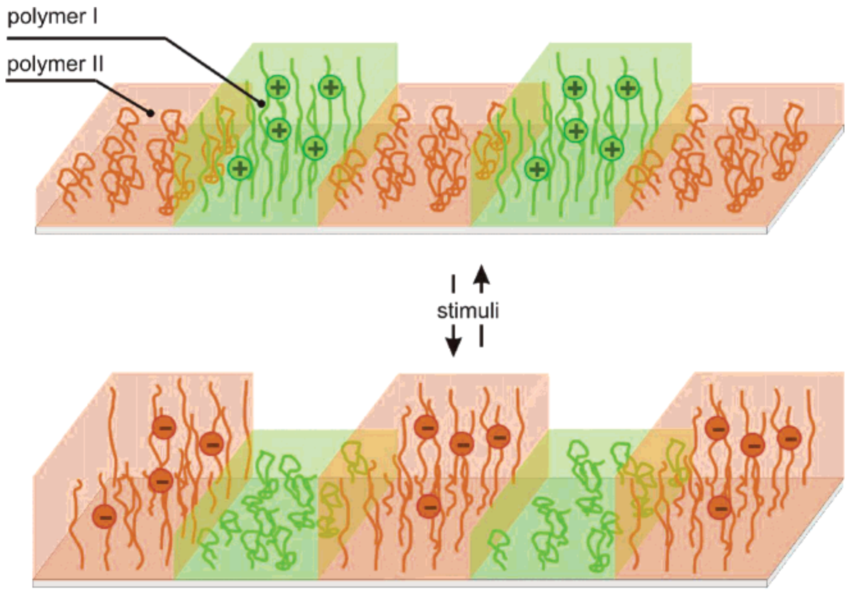

Figure 1. Concept of inversely and reversibly switchable micropatterned surfaces consisting of two oppositely charged polyelectrolytes. Depending on the surrounding conditions, one polymer is swollen (charged and hydrophilic), while the other is collapsed (uncharged and hydrophobic), thereby demonstrating the inverse switching of topography, wettability, and charge.

Table 1. Dissociation Constants (p*K*),[24−26] IEP, and Advancing Water Contact Angles of P2VP and PAA[a]

			advancing water contact angle (deg)	
polymer	p*K*	IEP	pH = 2	pH = 10
PAA	5.5	3.2	70	20
P2VP	2.3	6.7	25	75

[a] Dissociation constants are given for polymer chains in solution. Values of the advanced water contact angles were determined on monocomponent polymer films (thickness 8−10 nm in the dry state) grafted onto silicon wafers coated with a PGMA anchoring layer (see Experimental Procedures).

(PGMA) (M_n = 84 000 g/mol) was synthesized by free radical polymerization of glycidyl methacrylate (Aldrich). Methanesulfonic acid (Fluka) was used without additional purification. Casein fluorescein isothiocyanate (FITC-Casein) was purchased from Sigma. A photoresist (Clariant PL 177) and developer (AZ developer) were purchased from Microchemicals.

Highly polished single-crystal silicon wafers of {100} orientation (Semiconductor Processing Co.) were used as a substrate. The wafers were first cleaned in an ultrasonic bath for 30 min, placed in a hot piranha solution (3:1 concentrated sulfuric acid and 30% hydrogen peroxide; the mixture reacts violently with organic solvents and should be handled with care) for 1 h, and then rinsed several times with MilliQ water.

PBA/P2VP micropatterning was achieved using the following procedure: first, the surface of a Si wafer was coated with a thin film (1.5 nm) of PGMA from an 0.01% solution in chloroform. Next, a thick layer (several micrometers) of the photoresistor was spin-coated onto the PGMA-coated wafer. UV illumination through a mask and development resulted in the formation of topographical patterns of photoresist on the PGMA surface. Afterward, a thin (25 nm) film of PBA-COOH was spin-coated from a 0.5% solution in toluene. The remaining photoresist was decomposed by a second UV illumination and removed together with the covering PBA film by rinsing in the developer ("lift off"). As a result, patches of the PBA-COOH film were left on top of the PGMA layer. Annealing at 150 °C for 2 h led to a chemical reaction between the terminal carboxylic groups of PBA-COOH and the epoxy groups of PGMA, resulting in the formation of a grafted PBA layer. Ungrafted polymer was washed out by multiple rinses in chloroform. Next, a thick film (200 nm) of P2VP-COOH was spin-coated from a 1% solution in chloroform on the top of the PBA patterned surface. Annealing at 150 °C led to grafting of P2VP-COOH to the areas unoccupied by grafted PBA. Finally, PBA was hydrolyzed with methanesulfonic acid for 5 min, yielding poly(acrylic acid) (PAA).[21] The typical thicknesses of the PBA and P2VP grafted layers were found to be 11 and 5 nm, respectively, as measured by ellipsometry. The thickness of the PBA layer was reduced after hydrolysis to PAA by about 40% to 7 nm.

The thickness of the polymer layers was measured at $\lambda = 633$ nm and an angle of incidence of 70° with a SENTECH SE-402 microfocus ellipsometer as described elsewhere.[22,23] Advancing contact angles of water were measured using DSA-10 Krüss equipment. The mixed brush was exposed to an aqueous solution (of specified pH) for 2 min, dried, and used for contact angle experiments. AFM studies were performed with a Dimension 3100 (Digital Instruments, Inc.) microscope. The tapping mode was used to map the film morphology at ambient conditions. Optical microscopy was performed using an Axiovert 200 M microscope (Zeiss). For fluorescence measurments, a standard FITC filterset (excitation: HQ 480/40; dichroic: Q 505 LP; emission: HQ 535/75, Chroma Technology) was used.

Results and Discussion

To fabricate micropatterned polymer surfaces that are switchable in aqueous environments, we used poly-(2-vinylpyridine) (P2VP) and poly(acrylic acid) (PAA). These polymers reversibly change their conformation and charge depending on the pH. The PAA chains are negatively charged and extended at pH > 5.5, while the P2VP chains are positively charged and extended at pH < 2.3 (see p*K* and IEP values in Table 1). Both polymers are uncharged and collapsed for all other pH values. Surface grafted films of PAA and P2VP demonstrate reversible switching from moderately hydrophobic to hydrophilic behavior after treatment with alkali and acidic water, respectively (see values of advancing contact angle in Table 1).

Micropatterning was performed by a combination of photolithography, "lift off", and "grafting to" techniques (Figure 2 and Experimental Procedures). In brief, silicon wafers were coated

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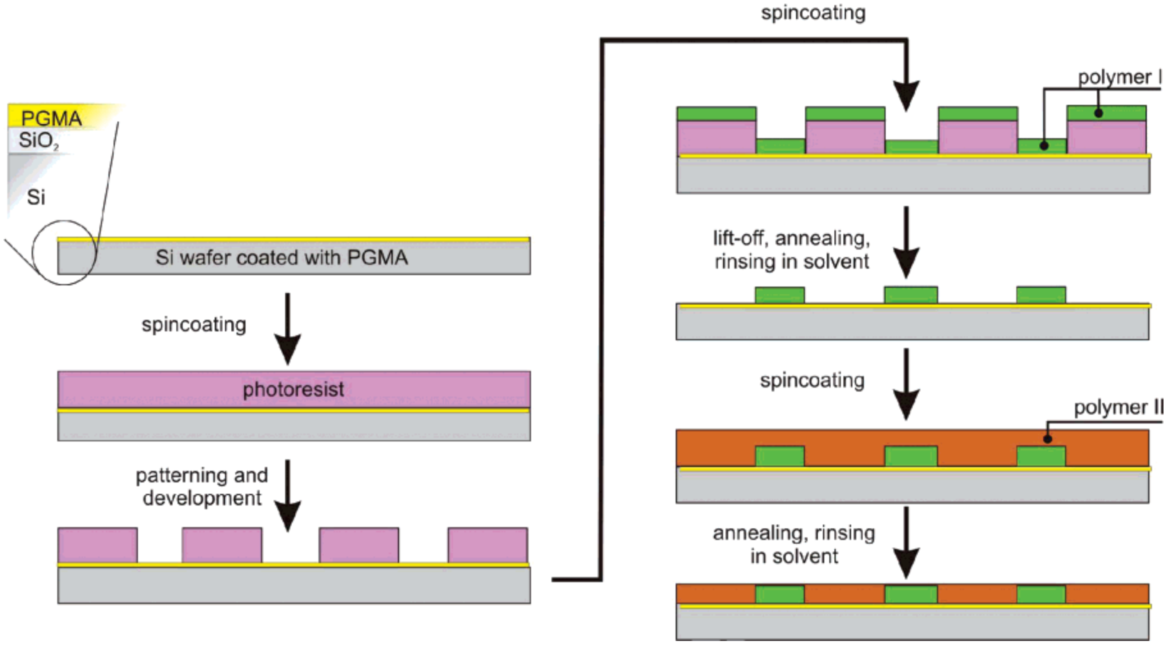

Figure 2. Preparation of micropatterned bicomponent polymer grafted layers using a combination of photolithography, "lift off", and "grafting to" techniques. Polymer I: PBA and polymer II: P2VP. After the micropatterned PBA/P2VP surfaces had been fabricated, PBA was hydrolyzed yielding PAA (not shown in the scheme).

with a 1.5 nm thick film of PGMA, which served as a coupling agent for carboxyl-terminated polymers.[27] Next, the photoresist was spin-coated, illuminated through a mask, and developed. Afterward, a 25 nm thick film of PBA-COOH was spin-coated, and the left over photoresistor and covering PBA film were removed after additional UV exposure by rinsing in the developer. The resulting patches of the PBA-COOH film on the top of the PGMA layer were annealed at elevated temperatures. This leads to a chemical reaction between epoxy groups on the surface and carboxylic groups at the tail of the polymer chains, resulting in formation of the grafted PBA pattern. The thickness of the grafted polymer film was essentially determined by the diffusion of the polymer chains through the layer of already grafted polymer chains and can be controlled by the time and temperature of annealing.[28] Next, P2VP-COOH was spin-coated on the top of the PBA patterned surface and grafted at elevated temperature. Finally, PBA was hydrolyzed yielding PAA.[21] The typical thicknesses of the PAA and P2VP grafted layers were found to be about 7 and 5 nm, respectively. Generally, the advantage of our technique is the combination of (i) high chemical stability of the obtained polymer layer (polymer chains are chemically anchored to the substrate), (ii) easy control over the molecular weight as well as the grafting density of the polymer, and (iii) simplicity of the fabrication procedure.

We investigated the topography of the patterned surfaces using atomic force microscopy (AFM). After treating the surfaces with pure water (pH = 6.7) and drying with nitrogen (Figure 3a,b, cross-section 1), we found the PAA features to be elevated above the P2VP area. However, exposure of the surface to HCl vapor inverted the surface topography: the collapsed PAA features were lower than the now elevated P2VP structures (Figure 3b−d, cross-section 3). This inverse switching resulted from electrostatic interactions within the polymer layer. Repulsion between the charged groups (carboxyl groups in alkalic medium and protonated pyridine rings in acidic medium) caused the swelling of the respective polymer, incorporating water molecules from the moderately humid air atmosphere (Figure 3d). Interestingly, the degree of switching could be controlled by the extent of exposure to the HCl vapor. The pattern was incompletely switched after a single 2−3 s exposure to HCl, when the heights of the PAA and P2VP features were approximately identical (cross-section 2). Full switching was achieved after a second exposure to HCl vapor (cross-section 3). We note that the patterned PAA/P2VP surface could be switched back to the initial state by rinsing in alkalic or pure water. We observed that such reversible switching between opposite states could be repeated more than 10 times (data not shown). Because the polymer layer was dried by nitrogen flux at room temperature, the polymers still contained water molecules. Therefore, we expect that the observed morphological behavior measured in air is qualitatively similar to one in solvent.[29,30]

Intriguingly, the switching of the surface topography was accompanied by the switching of the surface properties with regard to hydrophobicity. Local condensation of water droplets revealed a distinct contrast between P2VP and PAA areas (Figure 4a). After exposure to pure water (pH = 6.7), very small water droplets wetted the hydrophobic P2VP area, whereas larger drops occurred on the hydrophilic PAA area. The inverse scenario was observed after exposure of the patterned surface to acidic water (pH = 2). The observed switching between hydrophobic and hydrophilic surface properties was applied to the generation of various liquid patterns (Figure 4b). Using the PAA/P2VP pattern shown in Figure 3, where PAA formed nearly square-shaped

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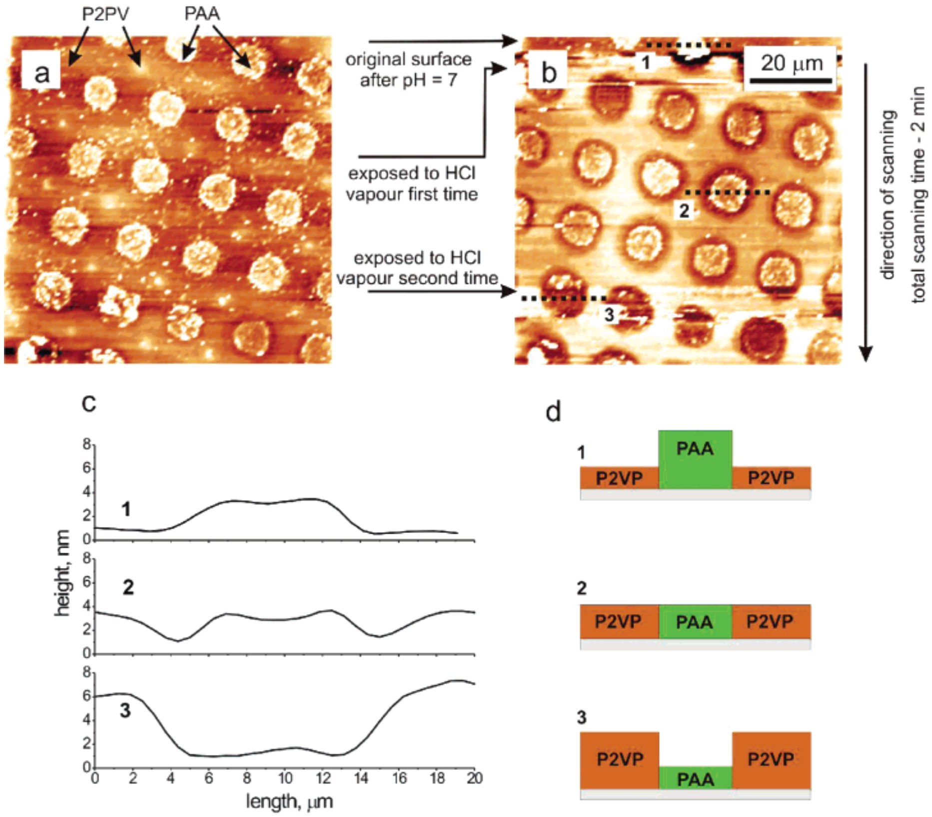

Figure 3. Surface topography of patterned PAA/P2VP under various conditions. (a) AFM image after exposure to pure water (pH = 6.7). (b) In situ observation of topography switching upon exposure to HCl vapor. First, the surface was treated with pure water (pH = 6.7, cross-section 1) and then exposed to HCl vapor twice (cross-sections 2 and 3). (c) Quantification of the topographical profiles from panel b. (d) Schematic diagram of the switching. The PAA features are swollen after exposure to pure water (cross-section 1). Exposure to HCl vapor leads to the depression of PAA, while P2VP becomes protonated and swollen (cross-sections 2 and 3). AFM scanning was performed in air at room temperature. The heights at the edges of the polymer pattern appear to be slightly elevated due to 1-D horizontal second-order flattening of the AFM image during scanning.

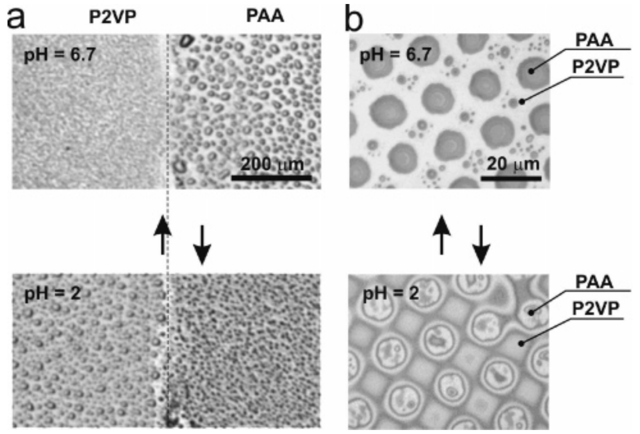

Figure 4. Adsorption of water droplets on structured PAA and P2VP surfaces. Optical bright-field microscopy of water droplets on a PAA/P2VP boundary (a) and microstructure (b) at different pH values. Water selectively wetted the P2VP or PAA areas at low or high pH, respectively.

patches between P2VP stripes, we generated either arrays of individual water droplets (Figure 4b, upper panel) or networks of checkered water channels (Figure 4b, lower panel) depending on the surrounding pH. Water selectively wetted the hydrophilic areas and did not spread over the hydrophobic ones. Notably, we observed the formation of smaller water droplets in the center of hydrophobic areas (PAA at pH = 2 and P2VP at pH = 6.7) probably caused by the dewetting of thin water films on the hydrophobic surface. Importantly, the shape of the liquid pattern was switched by merely changing the environmental conditions.

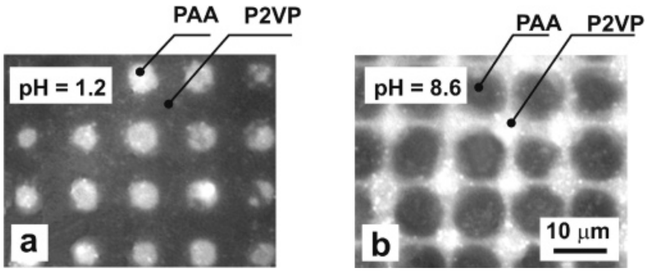

Figure 5. Fluorescence micrographs of FITC-casein adsorbed onto PAA/P2VP micropatterned surfaces. Adsorption of FITC-casein was performed at pH = 1.2 (a) and pH = 8.6 (b) from a 0.4 mg/mL solution in 10 mM phosphate buffer.

To test the usability of the inversely switchable surface for programmed protein adsorption, we applied fluorescently labeled proteins (FITC-casein) to the micropatterned PAA/P2VP surfaces. We observed that FITC-casein selectively adsorbed onto the PAA features at pH = 1.2 and to the P2VP features at pH = 8.6 (Figure 5). The selective adsorption of FITC-casein onto areas occupied by one of the polymers can be readily explained by considering electrostatic interactions. As stated earlier, P2VP is charged positively at pH $<$ 2.3, and PAA is negatively charged at pH $>$ 5.5 (Table 1). FITC-casein has an IEP of 7.63,[31] thus being charged negatively above this point and positively below. Therefore repelled from the P2VP features at low pH and from the PAA features at high pH can adsorb on polymer surfaces due to hydrophobic interactions or hydrogen bonds in the absence of electrostatic repulsion.

In summary, we have developed a straightforward method for the preparation of switchable micropatterned polymer surfaces based on bicomponent polyelectrolyte layers. This method utilizes a “grafting to” approach instead of the widely used surface initiated polymerization. This makes the preparation of bicomponent patterned polymer grafted layers simple and quick. We demonstrated that our approach allows the inverse and reversible switching of surface topography, wettability, and charge. This approach can be easily extended for the fabrication of multicomponent ($n > 2$) micropatterned polymer surfaces by repeating the structuring cycle multiple times. We foresee a large potential of inversely switchable micropatterned surfaces for (i) microprinting where the topographical features of the polymer layer can be used as a master that is switchable via external stimuli, (ii) microfluidic devices where liquid movement (direction, speed, etc.) can be easily manipulated by pH, and (iii) microanalytical purposes where chemicals and proteins can be deposited in a switchable site-selective manner (programmed protein adsorption).

Acknowledgment. The authors are grateful to Robert Tucker for helpful comments on the manuscript. This work was supported by the DFG (Grant SPP 1164), the BMBF (Grant 03N8712), and the Volkswagen Foundation.

LA063601Y