

Nanolithography on responsive materials

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Received 18 Jul 2011; Accepted 10 Oct 2011; Available Online 10 Oct 2011

Abstract

Inspired by the fascinating working process of living systems, materials that can respond to external stimuli (mechanical, chemical, optical changes in environmental conditions, etc.) are of enormous interest owing to their applications in a wide range of fields including microfluidic devices, drug delivery, tissue engineering, sensors and actuators. This review, while being non-exhaustive in literature, emphasizes the promising applications of responsive materials as building blocks of biomimetic devices, together with the description of lithographic techniques used to pattern stimuli-responsive polymers at micro- and nanoscale. The goal of these endeavors is to mimic biological systems by capitalizing on the prominent properties of “smart” materials. Herein, we briefly describe the principles of responsive behaviors on various polymer materials to external stimuli such as temperature, pH and light. We also introduce current techniques employed in fabricating structures on responsive polymers, such as photolithography, soft lithography, and atomic force microscope nanolithography. Emphasis is placed on a specific approach that generates nanostructures on a polymer that swells under local protonation. Overall, the review highlights the importance of responsive materials allowing fundamental understanding of material properties and practical applications.

Keywords: Stimuli-responsive polymers; Nanolithography; Swelling; Protonation; Poly(4-vinylpyridine)

1. Introduction

Harnessing the fabrication of nanostructures has attracted considerable interests in the last decades. A number of lithographic techniques have been developed for patterning materials at micro- and nano-scales, aiming at manufacturing miniaturized devices that capitalize on their exceptional (different from the bulk) properties. Photolithography, electron beam and ion beam lithography, soft lithography, scanning probe lithography, to name a few, are examples of techniques that have been widely implemented in the production of semiconductor integrated circuits [1-4], sensors for detection of biological and chemical species [5-7], memory devices for high-density information storage, and microfluidic devices for chemical and medical analysis [8-10]. Table 1 lists several techniques that have been used in micro- and nanofabrication, which can be classified into two categories: parallel and serial implementation. Both approaches allow creating structures with at least one dimension in the nanoscale (sub-100 nm) regime. Parallel fabrication methods, such as photolithography, micro-contact printing and nano-imprinting, are efficient and suitable to form patterns over large areas in a single impression, but lack flexibility in generating

nanostructures of different geometries. In contrast, serial methods, such as electron lithography, ion beam lithography, and scanning probe lithography, allow fabricating complex patterns with flexible shapes at specific locations; however the most significant disadvantage of serial methods is that the speed is too slow to be used for mass production.

The above description indicates that the development of techniques able to create high-quality nanostructures in a faster and flexible fashion (ideally cheaper) represents a great challenge. As a potential alternative to satisfy the diversity of requirements involved in the fabrication of nanostructures, the inclusion of appropriate responsive materials (while still exploiting the advantage of current lithographic techniques) could provide promising routes to nanofabrication.

The concept of responsive materials or “smart” materials has been around for many years. They are materials able to change their properties (mechanical, chemical, electrical, structures or functions) in response to changes in environmental conditions. Research on responsive materials has dramatically increased owing to their capacity to be installed into a variety of applications ranging from the fabrication of electronic and mechanical components to the development of biological and

Table 1. Techniques for fabricating nanostructures.

Techniques	Mechanism	Properties	Patterning fashion
Photolithography	Photons	The resolution increases as the wavelength of the light source decreases. Diffraction limited resolution.	Parallel
Electron-/Ion-beam lithography	Particles	Nanometer resolution. Minimizes the diffraction limitation in photolithographic methods.	Serial
Soft lithography (μ CP, REM, MIMIC, and SAMIM)	Physical contact	Generate features with dimension ranging from micrometers to sub-100 nanometers. Pattern on nonplanar substrates and unusual materials.	Parallel
Scanning probe lithography (i.e., STM, AFM, and NSOM)	Mechanical, electrical, and optical modifications with scanning probes	The resolution approaches the atomic level; create structures with nearly arbitrary geometries.	Serial. Parallel when using arrays of tips
Dip-pen nanolithography	Tip-substrate molecular transport	The resolution is influenced by numerous parameters, including the composition of both the ink and the surface, writing speed, temperature and humidity.	Serial. Parallel when using arrays of tips

medical devices [11]. Among existing responsive materials, stimuli-responsive polymer materials are of a special interest due to their similarity to the biopolymers that form parts of the complex cell machinery in nature. The prominent feature of stimuli-responsive polymers is that they can undergo conformational and chemical transformations in response to physical and chemical variations in the surrounding environment, such as temperature, pH, light, chemical composition, ionic strength, mechanical stress, and electric potential [12-15]. Table 2 lists several representative stimuli-responsive polymers and corresponding stimuli used to trigger the response. Although the conformational changes of individual monomer units are small, they ultimately produce a large structural response in the bulk when summed over the entire polymer. Stimuli-responsive polymers can be used in solution, at surfaces or interfaces, even in 3D architectures. Their unique characteristic makes them adaptive to be engineered for uses in a broad range of fields, namely micro- and nanoactuation [16-18], sensing materials [19,20], microfluidic devices [21,22], information storage and regulation [23], molecular gates and switches [24-26], coatings with programmed structure and response [27,28], protein-ligand recognition [29], controlled drug-delivery and release systems [30-32].

Our aim in this review is to outline promising uses of stimuli-responsive materials (with an emphasis on polymer materials) and lithographic techniques in the area of micro- and nanostructure

fabrication. We have organized its content as follows: In Part 2, we briefly describe the principles of various polymer materials that respond to external stimuli, such as temperature, pH and light. Part 3 highlights the abilities of lithographic techniques to form patterns on stimuli-responsive materials. In Part 4, we report one specific approach to generate nanostructures on a polymer that swells under local protonation. Finally, we summarize the properties of responsive materials and lithographic methods in terms of their utility for gaining fundamental understanding of material properties and practical applications.

2. Stimuli-responsive polymer materials

2.1. Thermally-responsive polymers

Temperature is the most common stimulus used for triggering the environmentally responsive behavior of polymers. Thermally-responsive polymers have attracted enormous attention due to their ability to exhibit a phase transition caused by external temperature changes. A unique property of these polymers is the presence of a critical solution temperature at which the phase of polymer and solution is discontinuously changed. Some of them are characterized as having a lower critical solution temperature (LCST); such polymers undergo the transition from a soluble state to an insoluble state upon heating above the critical temperature. Conversely, others have an upper critical solution temperature (UCST) if the transition from a soluble

Table 2. Stimuli-responsive polymeric materials.

Type of stimulus	Polymer materials	Characteristics
Temperature	Poly(<i>N</i> -isopropylacrylamide) (PNIPAAm); poly(<i>N,N'</i> -diethylacrylamide) (PDEAAm); poly(<i>N</i> -vinylcaprolactam) (PVCL); poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) block copolymers.	Existence of low critical solution temperature (LCST); the inverse phase transition is mainly determined by the hydrophilic-hydrophobic balance of the polymer.
pH	Poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMAA) based polymer materials.	Incorporation of ionizable groups in the main or the side chains; phase transition occurs between protonation and de-protonation.
UV/visible light	Polymer containing chromophores in the polymer network	The discontinuous volume transition induced by UV light is caused by the osmotic pressure; the phase transition induced by visible light is due to the direct heating.
Electric signal	Polythiophene-based polymer gel; partially hydrolyzed polyacrylamide gels; electro-active polymers (EAPs).	Polyelectrolytes; EAPs convert electrical energy into mechanical energy.
Pressure	PNIPAAm and PDEAAm. Pressure sensitivity is a common feature of temperature-sensitive hydrogels.	Polymers show the pressure sensitivity near their LCST, probably due to an increase in their LCST with pressure.

state to an insoluble state takes place upon cooling below the critical temperature. Polymers are soluble in water through the hydrogen bonding formed between water molecules and the polymeric chains. In the case of thermally-responsive polymer solutions that exhibit LCST, an increase in temperature decreases their water solubility by contrast with the case in which the water solubility of most polymers increases with increase in temperature.

The unique property of thermally-responsive polymers showing an LCST is attributed to hydrophobic associations of polymer molecules and reduction in hydrogen bonding between polymers and water molecules. Below the LCST, hydrogen bonding between hydrophilic segments of the polymer chain and water molecules dominates, resulting in dissolution of the polymer in water. On the other hand, the hydrogen bonding interactions are weakened as temperature increases, and the hydrophobic interactions among hydrophobic segments become strengthened. Consequently, the polymer precipitates from the solution when the efficiency of hydrogen bonding becomes insufficient for the solubility of polymer molecules. The temperature-sensitive phase transition is completely reversible, and polymers are able to dissolve in water when the temperature decreases below the LCST. The reversible solubility governed by LCST arises from a drastic change in the hydrophobic-hydrophilic balance of the polymers as the temperature is raised past the transition temperature. The LCST of a given polymer is greatly dependent on the hydrogen-bonding capabilities of polymer monomer units, thus it can be altered as desired by adjusting the ratio of

J. Nanosci. Lett. 2012, 2: 23

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the hydrophilic and the hydrophobic segments of the polymer.

Thermally-responsive polymers have been studied extensively because of their practical applications. Among them, poly(*N*-isopropylacrylamide) (PNIPAAm) is one of the most investigated. It undergoes a conformational transition in pure water at around 32°C [33,34]. Polymer chains change from expanded coil configuration (a hydrophilic state) below this temperature to compact globule form (a hydrophobic state) above it (Figure. 1), accompanied by significant change in its adhesive properties. The fact that PNIPAAm's LCST lies close to the human body temperature makes it particularly suitable for drug delivery applications [33].

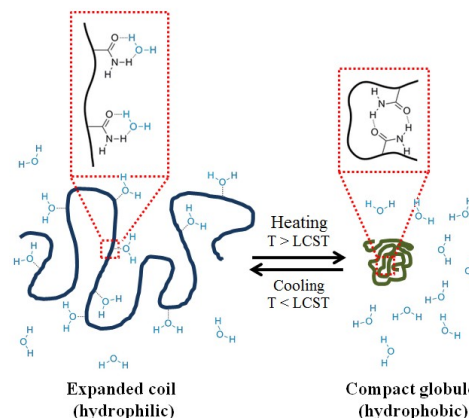


Figure 1. Schematic of PNIPAAm in response to temperature change.

Moreover, PNIPAAm can also be conjugated with a variety of natural or synthetic biomolecules, thus greatly extending its applications in more complex stimuli-responsive systems [35,36]. Other commonly studied thermally-responsive polymers are poly(*N,N*-diethylacrylamide) (PDEAAm), poly(*N*-vinylcaprolactam) (PVCL), block copolymers of poly(ethylene oxide) (PEO) and poly(propylene oxide)(PPO). PDEAAm also exhibits an LCST in a broader range of 25-32°C, still close to the human body temperature [37]. PVCL is water soluble at room temperature and gradually becomes insoluble in the range of 25-35°C [38]. A series of block copolymers made of PEO and PPO known as Pluronics, Poloxamers and Tetronics possess a reverse thermal gelation property. Solutions of PEO-PPO-PEO copolymers in water exhibit thermo-reversible sol-gel transition behavior, demonstrating phase transitions from sol to gel in the range of 5-30°C and gel to sol in the 35-50°C interval as the temperature monotonically increases [39].

2.2. pH-responsive polymers

Widespread studies have also been carried on polymers that respond to changes in pH. They typically contain pendant acidic or basic groups such as carboxylic and sulfonic acids, or basic amino groups that are capable of accepting or releasing protons in response to variations in the pH of surroundings. Polymers with a great number of ionizable groups are known as polyelectrolytes. Ionization of acidic or basic groups on polyelectrolytes occurs in a manner similar to monoacids or monobases. For the case of hydrogels made of such cross-linked polyelectrolytes, the pH-dependent transitions can be seen through big differences in swelling capabilities when the repeating monomer units undergo ionization. Consequently, the hydrodynamic volume of polymers increases as a result of the electrostatic repulsion among charges presented along the polymer backbones. The occurrence of pH-induced phase transitions usually requires a change in a narrow pH range close to the pK_a .

Poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMAA) based materials are typical examples of pH-responsive polymers. The combination of PAA and poly(allylamine hydrochloride) (PAH) was studied on flat substrates on account of its ability to change surface roughness and hydrophobicity, film morphology, as well as layer thickness in response to variations in pH [40-43]. Cross-linked PAH/PAA multilayers were utilized as ion-separation materials due to their ion permeability depending on the solution pH, which resulted from the pH-dependent swelling of the films [44]. pH-Sensitive bipolar ion-perm selective membranes were prepared by layer-by-layer (LbL) assembly and photo-crosslinking of benzophenone-modified PAA and PAH, showing pH-switchable

permselectivity for both cationic and anionic probe molecules in a single film at two pH conditions [45]. PAA and PHA (or, PMAA and PHA) were also used for the preparation of weak polyelectrolyte microcapsules. The pH-dependent stability of the resulting microcapsules provides opportunities for applications such as chemical reservoirs and controlled drug release [46,47]. In addition, hydrogen-bonded films made of PMAA and poly(*N*-vinylpyrrolidone) (PVPON) exhibited distinctive polyampholytic swelling as a function of pH. The produced surface-attached hydrogels, which were able to absorb and release dyes and macromolecules depending on pH variations, can be utilized for bio-separation and controlled delivery applications [48]. Other applications of pH-sensitive polymer films can be found in the fabrication of sensors and actuators by taking advantage of sharp transitions occurring in polymer materials that respond to external chemical and physical signals [20,49-54]. For example, a simple but highly sensitive nanosensor was demonstrated based on swelling (and shrinking) of pH-responsive ultrathin polymer brush [20]. The tuning of surface plasmon-resonance coupling between gold nanoparticles and a gold substrate (mediated by a swellable poly(2-vinylpyridine) (P2VP) brush layer) was monitored as a result of changing pH values. Localized surface plasmons are charge density oscillation confined to the metal nanoparticle boundary and triggered when illuminated by light with the proper frequency, which depend on the metal material, shape and, very important, the surrounding environment. When gold nanoparticles were adsorbed on the P2VP polymer brush, a 50 nm shift in the plasmon-resonance position occurred (as a result of the swelling and shrinking of the polymer brush) upon changing the pH from 5.0 to 2.0 and from 2.0 to 5.0, respectively (Figure 2). In another case, a bio-inspired system was successfully demonstrated for generating pH-responsive actuation [54]. In that system, a poly(acrylic acid-*co*-acrylamide) hydrogel that swelled and contracted in response to pH changes, acting as an analog to muscle, drove the movement of embedded microstructures.

2.3. Light-responsive polymers

The use of light as an external trigger is also considerably attractive because the optical excitation is essentially instantaneous and can be applied with high spatial and temporal accuracy. The benefits of using light as an external stimulus include scalable miniaturization, limited chemical contamination, ease of operation, and the potential of performing chemical reactions on a small scale without the need for channel confinement [55]. Moreover, the light activation possesses special advantages over other triggering mechanisms. For example, when using the thermal stimulus the reaction rate is limited by thermal diffusion through the bulk; in the cases based

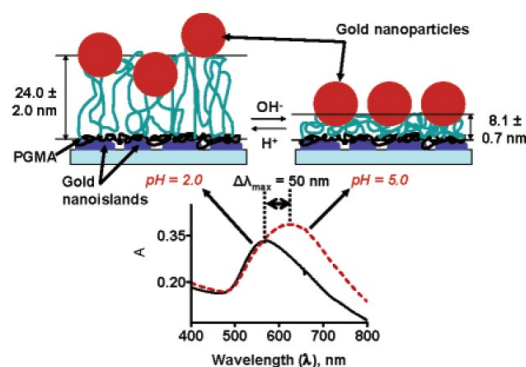


Figure 2. Top: Schematic diagram showing the reversible pH-induced swelling (and shrinking) of gold nanoparticle-attached P2VP brush layers. **Bottom:** The absorption spectra of the gold nanoparticle enhanced transmission surface plasmon resonance (T-SPR) spectroscopy at pH 2.0 and 5.0. Reprinted with permission from Ref. 20, copyright (2004) American Chemical Society.

on pH changes the process is limited by ion diffusion. Thermal and ion diffusion are more limiting than the diffraction limitation imposed by conventional optical tools.

Light-responsive polymers can be mainly classified into UV-sensitive polymers and visible light-sensitive polymers. The most studied light-responsive systems are polymers that react to UV light. Successful examples in response to UV irradiation have been reported [56,57]. The UV-sensitive polymers were synthesized by incorporating photosensitive molecules, such as leucocyanide and leucohydroxide, into the polymer network. These polymers exhibited a discontinuous volume transition upon UV irradiation. At a fixed temperature, the polymers discontinuously swelled on exposure to UV irradiation but shrank in the absence of UV light. The photo-induced transitions took place when the UV irradiation initiated an ionization reaction within the gels, creating osmotic pressure which induced swelling. Such polymers are of technological importance in developing optical devices such as optical switches, display units, and three-dimensional holograms. In addition, polymers containing cinnamic groups showed a shape-memory effect activated by UV light [58]. They can be deformed and fixed into pre-determined shapes by UV illumination and recover their original shapes when exposed to UV light of a different wavelength. In Figure 3, a plain film of such polymer was produced (Figure 3A, a). It was mechanically stretched, and exposure to UV light of $\lambda > 260$ nm further cross-linked polymer network in the elongated conformation (Figure 3A,b). Irradiating the elongated film with UV light of $\lambda < 260$ nm, the new crosslinks were cleaved and the polymer contracted (Figure 3A, c). The unique ability of these photo-responsive polymers opens up opportunities for medical and

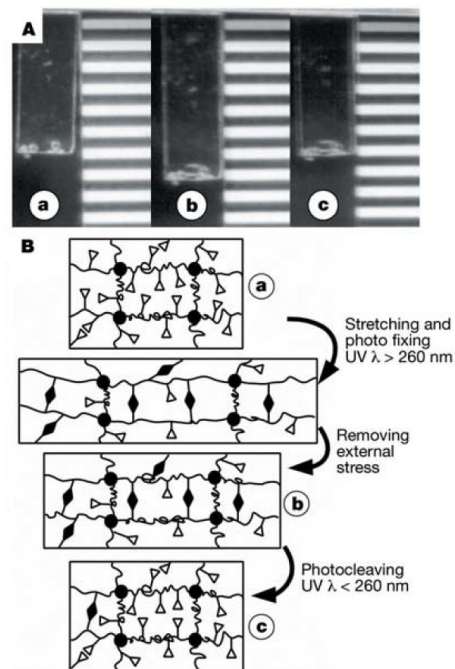


Figure 3. (A) A plain film of grafted polymer BHCA(10,2,1) (a copolymer of *n*-butylacrylate, hydroxyethyl methacrylate, and ethyleneglycol-1-acrylate-2-cinnamic acid with poly(propylene glycol)-dimethacrylate) shows the light-induced shape-memory effect: a) permanent shape (6 cm × 1.2 cm × 0.05 cm); b) temporary shape; and c) recovered permanent shape. **(B)** Molecular mechanism of shape-memory effect: the chromophores (∇) are covalently grafted onto the permanent polymer network (\bullet), forming photoreversible crosslinks (\blacklozenge); fixation and recovery of the temporary shape are realized by UV irradiation of appropriate wavelengths. Reprinted by permission from Ref. 58, copyright (2005) Macmillan Publishers Ltd: Nature.

other applications as they enable shape-recovery at ambient temperatures by using remote activation.

Compared to UV light, visible light is readily available and less harmful. Visible light-sensitive polymers were obtained by introducing a light-sensitive chromophore to *N*-isopropylacrylamide (NIPA)-based gels [59]. The mechanism of the phase transition induced by visible light was due to the direct heating of the polymer network, originating from the absorption of light by the chromophore which was then dissipated locally as heat. This is an extremely fast process [59], compared to phase transitions induced by UV exposure described above. Such polymers are potentially useful as artificial muscles, switches and memory devices [59]. Light-responsive polymers with near infrared (IR) sensitivity have also been reported [60]. By using the sensitizer (2,4,7-trinitro-9-fluorenylidene)malonitrile (TNFDM) in mixtures of poly(*N*-vinylcarbazole) (PVK) and *N*-ethylcarbazole (ECZ), the spectral response of the photosensitivity can be extended to the near IR. The

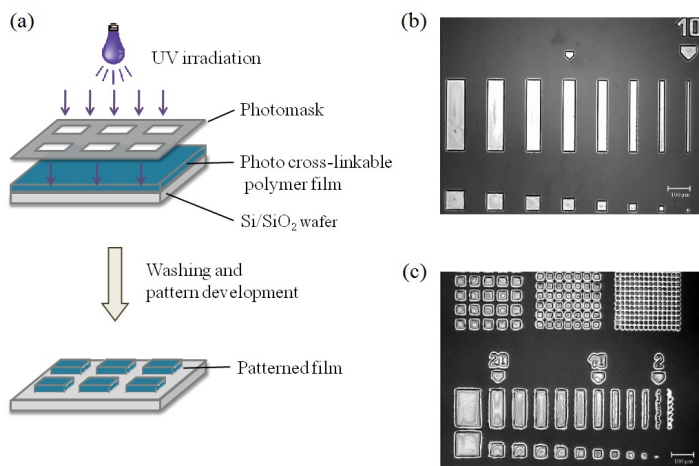


Figure 4. (a) Scheme showing the photolithographic fabrication of hydrogels. Optical images of generated features with 9.2 mol% DMIAAm on a HMDS pretreated Si wafer: (b) 10-80 μm patterns; (c) 1-30 μm patterns. Reprinted with permission: (b), (c), from Ref. 61, copyright (2003) Elsevier.

use of these near-IR sensitive polymers is particularly attractive in the application of biomedical imaging because most biological tissues are transparent to near IR [60]. Considering that tumors have a different refractive index from normal tissues, these near-IR responsive materials could be valuable for imaging tumors.

3. Nanolithography techniques

3.1. Photolithography

Photolithography is one of the most successful techniques used in the fabrication of patterns with resolution varying from micrometers to sub-100 nanometers. The generation of structures with smaller feature sizes can be realized by using illuminating sources with shorter wavelengths. In general, patterning is accomplished by selectively exposing a surface coated with a radiation-sensitive polymer film to photo-irradiation through a mask, and by subsequently removing selected regions of the film (pattern development step). The absorption of photons by the polymer layer induces chemical reactions in the exposed areas, resulting in a set of changes in the molecular structure of the film, and eventually modifies its solubility in an appropriate solvent. Changes in solubility of polymer films with light exposure can either increase the solubility of exposed portion (resulting in a positive image of the mask) or decrease the solubility (yielding a negative image of the mask). The mask can be placed in direct contact with, or in proximity to, the photosensitive material to spatially localize the radiation chemistry. The predominant photolithographic technique used today for fabricating microelectronic structures is based on optical projection systems, which overcomes problems such as contamination and damage of the masks, as well as substrates, associated to contact mode operation. In projection

mode, the image of the mask is reduced and projected onto a thin film of resist polymer through a complex alignment of lenses.

An attractive characteristic of photolithography is its high-throughput efficiency, capable of patterning large areas for manufacturing high-quality micro- and nanostructures. In addition to such traditional processes used by the semiconductor industry, photolithographic patterning of stimuli-responsive polymers is a growing field of research and a large number of applications are envisioned. Micropatterned structures of thermally-responsive PNIPAAm hydrogels were produced by using photolithographic patterning [61]. The films were irradiated with UV light through a mask where the

patterns were formed at exposed regions after development (Figure 4a). Features with lateral dimensions down to 4 μm at film thickness below 5 μm in the dry state could be obtained on this highly swelling material (Figure 4b and c). These micro-fabricated PNIPAAm hydrogels are promising candidates as working substances for micro-actuators because of their thermally-induced volume changes. Suitable applications include adjusting limbs in fluid microsystems such as tailor-made micro-pumps and micro-valves. For advanced applications, the adhesion of the swollen hydrogels, and thus, the resolution of particular patterns could be increased by the use of a specially designed adhesion promoter. The swelling properties of the resulting patterns could be adjusted either by the chromophore content of the polymer or by the UV irradiation time. Additionally, a novel strategy of chemical patterning making use of a mixed brush of P2VP and polyisoprene (PI) was reported [62]. The basic concept of this technique is the permanent storage of a pattern via photolithography on a brush surface, which is then reversibly developed and erased upon exposure to appropriate environments, such as solvent, pH and temperature. The mixed polymer brush was exposed to a selective solvent and irradiated by UV light through a photomask with the purpose to cross-link the chains selectively in the exposed areas. Therefore, in the illuminated areas the surface morphology was frozen, preventing phase segregation of the polymers. The nonirradiated areas were unaffected and retained their capability of switching conformation and wetting properties under appropriate stimulation. As illustrated in Figure 5, the difference in the surface composition of the exposed and dark areas of the top brush layer can be tuned by exposure to a solvent selective for one constitutive polymer (PI or P2VP), which resulted in the

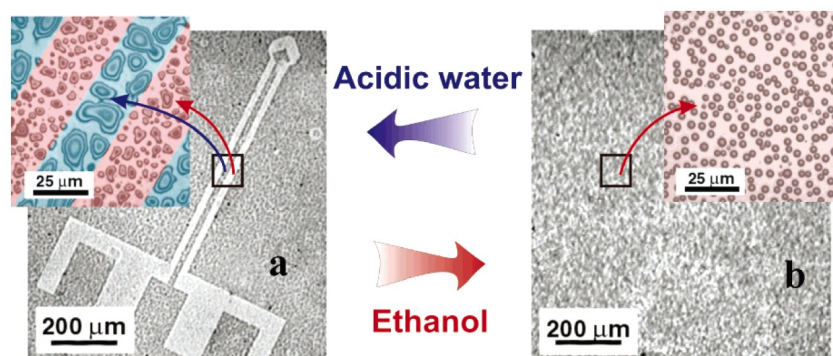


Figure 5. Optical microscopy images of the patterned brush treated with (a) acidic water and (b) ethanol. Insets demonstrate the hydrophilic (colored in blue) and hydrophobic (colored in red) regions, corresponding to the illuminated and dark areas respectively. Reprinted with permission from Ref. 62, copyright (2003) American Chemical Society.

visualization of designed patterns. Whenever the patterned brush was exposed to a nonselective solvent, the contrast in the film behavior disappeared and the drawn features were erased. This approach can be used for the design of smart sensors and the fabrication of switchable micro-channels upon external stimuli. In another example, switchable micro-patterned polymer surfaces consisting of P2VP and PAA were prepared using a combination of photolithography, “lift off”, and “grafting to” techniques [63]. Depending on the pH of the environment, these stimuli-responsive surfaces allow the switching of surface topography, wettability, and charge in an inverse manner. These surfaces have a large potential for microfluidic devices and microanalytical purposes (programmed protein adsorption).

3.2. Soft lithography

A variety of non-photolithographic techniques have been developed for fabricating micro- and nanostructures on surfaces that are not based on interactions with high-energy photon/electron particles. Among these methods, soft lithography is the collective name referring to a set of techniques that make use of a patterned elastomer, commonly made of poly(dimethylsiloxane) (PDMS), as the mold or stamp to transfer materials onto a substrate for generating patterns. The family of soft

lithographic techniques includes microcontact printing (μ CP) [64], replica molding (REM) [65], microtransfer molding (μ TM) [66], micromolding in capillaries (MIMIC) [67], and solvent-assisted micromolding (SAMIM) [68].

Microcontact printing is probably the best known example from which most concepts of soft lithographic techniques are derived. It is an efficient and inexpensive route to create patterns over large areas with spatial resolution down to the submicrometer range [64]. In the general procedure for carrying out μ CP (Figure 6a), an elastomeric PDMS stamp with a desired structure on its surface is used to transfer “ink” molecules to selected areas of a substrate. The molecular transfer occurs when the inked stamp is brought into conformal contact with the receiving surface. After removing the stamp from the surface, a pattern of monolayer is formed, and defined by the raised bas-relief structure of the stamp as a result of self-assembly process. In μ CP, alkanethiolates are widely used as inks on films of gold, silver and copper; similarly, alkylsiloxanes is chosen for printing silicon based substrates [64,69-71]. Microcontact printing offers advantages over conventional projection photolithography in applications involving surfaces that are nonplanar on the micrometer scale [72]. It is also applicable to produce microstructures on curved surfaces and inner

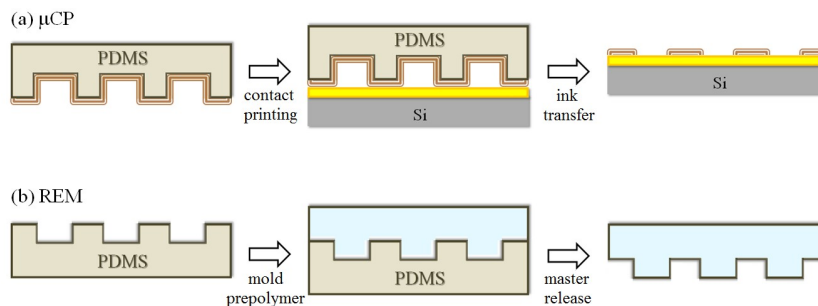


Figure 6. Scheme of (a) microcontact printing (μ CP) and (b) replica molding (REM).

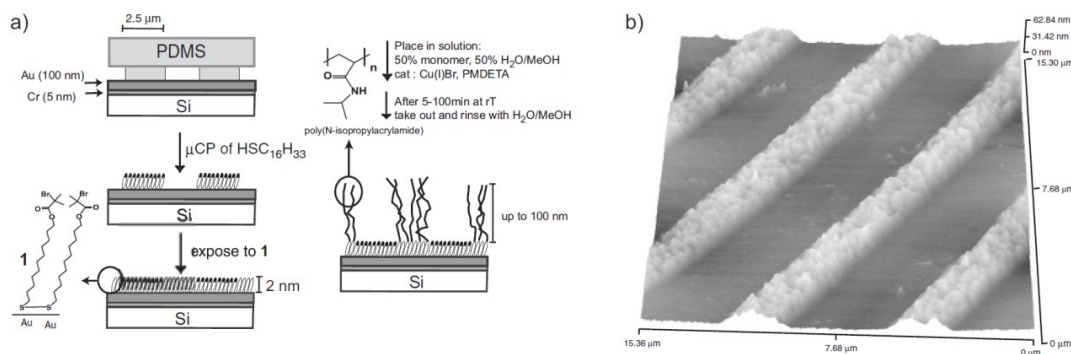


Figure 7. (a) Schematic procedure for micropatterning of PNIPAAm brushes on gold substrates. (b) AFM topographic image of discrete PNIPAAm brushes, obtained in water at 26 °C. Average polymer brush height is 46 ± 9 nm. Reprinted with permission from Ref. 76, copyright (2002) Wiley-VCH.

surfaces such as the inside of the hollow tubes and flasks [72,73]. In addition, this technique is remarkably suitable for large area fabrication (≥ 50 cm²) in a single impression because it is able to generate submicrometer-sized features over the entire area of a substrate in contact with the stamp at the same time [74].

To satisfy the requirements in the manufacturing of large numbers of nanostructures at low cost, other techniques such as replica molding have been developed. In REM (Figure 6b) an elastomer made of PDMS is cast against an original master whose surface has been patterned with nanostructures. The elastomeric replica is then used as a mold against which new relief nanostructures very similar to those on the surface of the original master are produced in organic polymers. Successful examples have demonstrated the capability of REM for generating duplicated structures within a few nanometers over a large area rapidly and economically [75]. Moreover, an extension of REM procedure offers the opportunity to modify the dimensions and shape of structures present on the mold by mechanical or thermal deformation: nanostructures with sizes smaller than those on the original master can be fabricated from REM against an PDMS mold while it is mechanically bent [75].

Micropatterned PNIPAAm brushes were attained on gold and oxidized silicon substrates through μ CP followed by surface-initiated polymerization [76,77]. Figure 7 shows a scheme of the patterning process (Figure 7a) as well as the resulting PNIPAAm structures on a gold surface (Figure 7b). First, the patterning of initiator-functionalized surfaces was carried out by microcontact-printing appropriate self-assembled monolayers as an inert background and backfilling surface initiators onto the unprinted regions interspersed with the inert layers. Secondly, the initiator surfaces were immersed in solutions of NIPAAm, allowing PNIPAAm chains to grow from the patterned, initiator-terminated substrates via surface-initiated polymerizations. In this procedure,

the patterning applied by μ CP allowed discrete areas of PNIPAAm brushes to be prepared on the surface, whilst the surface-initiated polymerization enabled a brush structure of controlled height to be generated. These patterned PNIPAAm brushes can be useful in areas including control of fluid flow, bioadhesion, molecular recognition and separation. Besides μ CP, utilization of REM has also been reported in the fabrication of actuators with size in micrometer range using responsive materials. Keller *et al.* succeeded in creating micron-sized thermoresponsive pillars made of side-on nematic liquid crystal elastomers by applying REM [78]. Briefly, a mixture containing liquid crystal monomers was heated to its isotropic phase and, a PDMS-made soft mold was then pressed down on the mixture. The melted sample filled the inner structure of the mold, forming an array of micron-sized pillars after a cooling process and UV irradiation. To produce thermo-responsive pillars, the alignment of the polymer backbone was realized by applying a suitably oriented magnetic field. Under the microscope, each pillar behaved as a small actuator that was able to contract and expand in response to small temperature changes around its isotropic transition temperature. The achievement of microscale actuators has potential applications in the fabrication of micro-pumps and micro-robots.

3.3. Scanning probe lithography

After the invention of scanning probe imaging instruments, such as the scanning tunneling microscope (STM) [79], the atomic force microscope (AFM) [80], and the near-field scanning optical microscope (NSOM) [81], their applications have been greatly extended from topographic imaging to surface modification [82]. Scanning probe lithography (SPL) comprises a set of relatively new techniques to alter surfaces of substrates making use of scanning probe microscopes. There have been many attempts for high-resolution patterning on a variety of surfaces. In a typical SPL performance, a sharp tip is brought into the close proximity of a sample for locally modifying the surface, while the

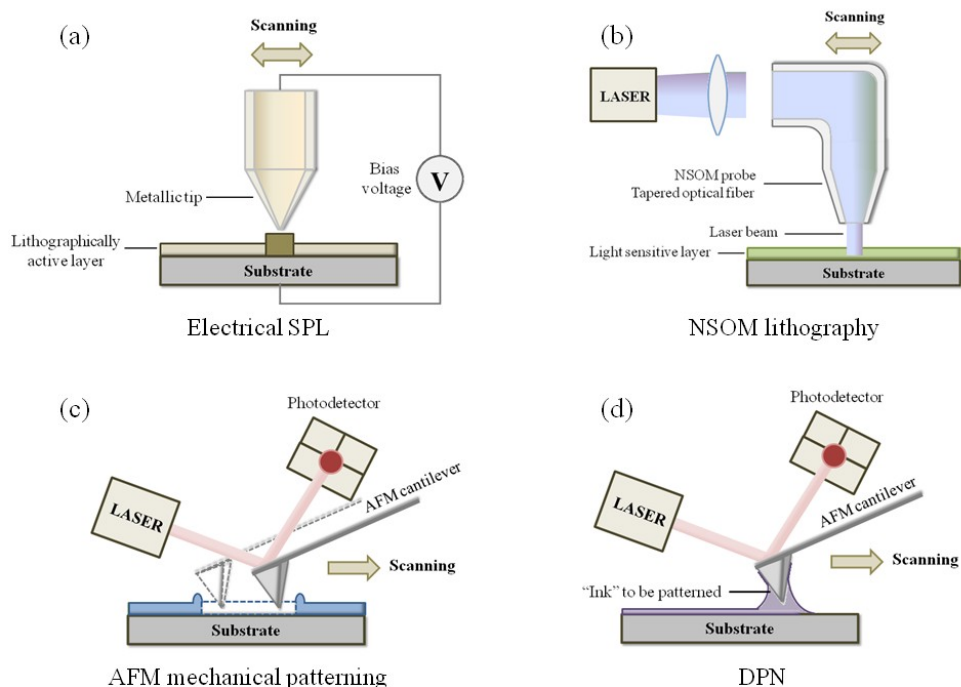


Figure 8. Schematic diagrams of (a) electrical surface modification, (b) NSOM lithography, (c) AFM mechanical patterning, and (d) DPN.

tip-sample distance is controlled via electronic feedback sensing. SPL techniques have unique advantages owing to their capability to both manipulate and image nanostructures. Because the transcription of patterns is defined by the scanning motion of the tip across the surface, SPL provides simplicity and flexibility in fabricating different geometries of nanostructures without photomasks or other master patterns.

SPL patterning can be accomplished by using different surface modification methods, such as electrical, optical, and mechanical modifications [83]. In the electrical approach (Figure 8a), upon the application of an electric field, the patterning material exposed to the electric field undergoes changes in its chemical or physical nature, resulting in a modification of the sample surface [84,85]. Optical modification of surfaces can be realized by coupling light to the sub-wavelength aperture of the NSOM probe [86,87]. In NSOM-based lithography (Figure 8b), a metallic aperture, fabricated at the apex of a tapered fiber probe, kept at ~ 10 nm distance from a surface of interest serves as a light source to permit near-field exposures of photosensitive layers. Light can be selectively delivered to regions under the probe, consequently triggering a reaction of the activated species on the sample. Because the sample is placed in the optical near-field regime, the diffraction effects that ultimately limit the resolution of the feature size in conventional “far-field” photolithography can be circumvented, and structures

down to ~ 100 nm are easily created. Additionally, the physical contact is frequently used in mechanical modification SPL schemes. In most cases, negative surface structures are generated by scratching mode in which the tip of a scanning force microscope is employed to remove the underlying substrate by applying mechanical force [88,89].

AFM nanolithography has attracted tremendous interest as a simple nanofabrication technique since the first papers on nanoshaving and dip-pen nanolithography (DPN) were published [90,91]. It allows for the production of nanostructures with dimensions ranging from a few nanometers to hundreds of nanometers. It has been successfully carried out in various environmental conditions, for example, under ambient conditions and in liquids [90,91]. The most straightforward way to apply AFM nanolithography may be mechanical scratching or nanoshaving (Figure 8c). In nanoshaving an AFM tip is used as a nanoshaver to plough a thiol monolayer on a gold substrate immersed in a solution containing another thiol molecules. Thus the portions previously occupied by the first thiol molecules are filled by the second one from the solution, leading to the reconstruction of a new monolayer [90]. Alternatively, AFM nanolithography can be used to directly deliver molecules or other materials to a nano-sized region of a substrate. DPN is a direct-write technique which has been one of the most popular AFM nanolithography methods (Figure 8d). It works in a way analogous to a conventional ink

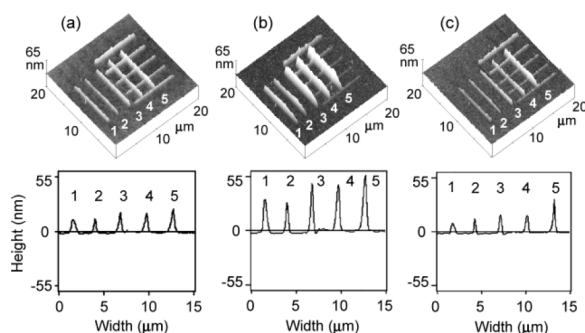


Figure 9. AFM topography images ($20\ \mu\text{m} \times 20\ \mu\text{m}$) and corresponding line profiles of a typical PNIPAAm brush line-pattern with line-widths ranging from 300 to 500 nm, imaged in (a) air, (b) water, and (c) a mixture of water/MeOH (1:1, v/v). Reprinted with permission from Ref. 105, copyright (2004) American Chemical Society.

pen. An AFM probe acts as a “pen”, which is coated with a substance of an “ink” to be patterned. When the probe is laterally scanned above a surface, the ink molecules are transferred from the tip to the underlying substrate through a liquid meniscus naturally formed across the tip-substrate gap [91,92]. Desired features are consequently generated as a result of chemical or physical adsorption of the ink to the surface. Ink and substrate combinations suitable for DPN rapidly expanded soon after the first demonstration of DPN on gold surface using thiol molecules. A diverse range of species such as small organic molecules, biological macromolecules, conducting polymers, metal ions and nanoparticles can be deposited onto appropriate surfaces via DPN technique [91,93-96]. Substrates used for DPN can be metals, insulators, semiconductors or other functional monolayers adsorbed on surfaces [97-99]. For a particular ink-substrate combination, the resolution of patterning is influenced by the experimental conditions, including the writing speed, the surface chemistry, the geometry and wettability of the tip, temperature and humidity [100-102]. The DPN method has proven capable of serial and parallel fabrication of nanostructures with precise control in terms of feature morphology and location [103,104].

Zauscher *et al.* demonstrated the fabrication of stimulus-responsive PNIPAAm brush nanopatterns on gold-coated silicon substrates by combining nanoshaving with surface-initiated polymerization [105]. In this approach a “thiol resist” was mechanically removed by an AFM tip using nanoshaving, and the resulting pattern was subsequently backfilled by self-assembly of a thiol initiator. Surface-confined PNIPAAm brush nanopatterns were formed on initiator-patterned surfaces at room temperature using controlled radical polymerization. A typical PNIPAAm brush line-pattern with line-widths of about 500 nm is shown in Figure 9, imaged in air, water and a mixture of water/MeOH (1:1 v/v). The conformation of nanopatterned polymer brushes depended not only on

the solvent conditions but also on the nanoshaving conditions such as tip force and shaving time [105]. Besides using nanoshaving associated with surface-initiated polymerization, the patterning of PNIPAAm nanostructures has succeeded by applying thermal dip-pen nanolithography (tDPN). Sheehan and coworkers demonstrated that surface-aligned PNIPAAm nanostructures can be directly and reproducibly patterned onto surfaces by tDPN [106]. In the procedure PNIPAAm ink was directly anchored from an AFM cantilever with an integrated heater to an epoxy-terminated silicon oxide substrate by heating the thermal probe close to the polymer melting temperature. The molten polymer was then covalently bonded to the functionalized surface by annealing. The heights and widths of PNIPAAm patterns could be controlled either by tip temperature, writing

speed, or both [106]. The surface-aligned PNIPAAm nanostructures enable reversible protein adsorption when driven through a thermally activated phase transition. Patterning by DPN has also been used in the fabrication of biomolecular switches. Elastin-like polypeptides (ELPs) are stimuli-responsive polypeptides that undergo a reversible hydrophilic-hydrophobic phase transition triggered by changes in temperature or ionic strength. ELPs were covalently grafted to carboxyl-terminated templates patterned by DPN on a gold surface [107]. As shown in Figure 10, the fabricated ELP nanoarrays have a lateral feature size of about 200 nm, which was governed by the feature size of the underlying templates. The ability of ELP nanostructures to reversibly capture an ELP fusion protein from solution makes it applicable in the fabrication of nanoscale biomolecular switches. In addition to nanoshaving and DPN, AFM is also employed for nanopatterning using electrostatic nanolithography. Valiyaveetil *et al.* reported the

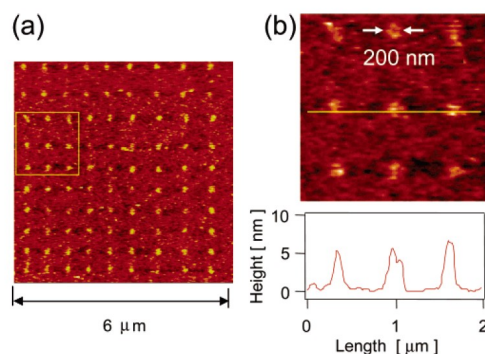


Figure 10. (a) AFM topography image of a 10×9 ELP dot array in PBS buffer at room temperature. (b) Zoomed-in view of region indicated in (a) and representative line profile, showing a typical feature height of 5 to 6 nm and a lateral feature size of about 200 nm. Reprinted with permission from Ref. 107, copyright (2004) American Chemical Society.

fabrication of arrays of nanolines and nanopits from a PMAA film on a Si substrate, using a negatively biased AFM tip [108]. The grooved and raised features generated by applying an appropriate bias between the tip and the substrate could be useful for applications such as data storage.

4. Electric field assisted DPN. Nanolithography on poly(4-vinylpyridine) (p4vp) thin films

Poly(4-vinylpyridine) (P4VP) can be prepared as polymer films simply by spin coating, which is immobilized onto solid substrates by subsequent UV irradiation [109]. A pH-dependent response of P4VP films gives rise to the changes in polymer structure and surface wettability [110]. Recently, due to its responsive characteristics, P4VP has been applied to polymer-brush-functionalized electrodes, which are designed for future “smart” bioelectronic devices [111,112]. Herein lithography is performed on the P4VP thin film to fabricate submicro- and nano-scale structures by taking advantage of its responsive property. As a common procedure, silicon wafers with a native oxide layer were cleaned either by sonication in isopropyl alcohol or by immersion into Piranha solution to remove contamination from surfaces. To further explore the influence of electric field applied between tip and substrate in the patterning process, the native oxide layer was then removed by dipping the pre-cleaned wafers into HF aqueous solution for this purpose. Polymer thin films were obtained by spin coating a solution of P4VP in n-butanol onto freshly prepared silicon substrates. To achieve the cross-linking of P4VP, the polymer-coated substrates were subsequently irradiated with a medium-pressure Hg lamp. Then crosslinked P4VP thin films remained after the removal of unbound polymers by soaking the irradiated films in n-butanol. To determine the thickness of the remaining films, a simple approach was to use ellipsometry, giving an average thickness of 40 nm by taking the value of 1.581 for the refractive index of P4VP.

The fabrication of structures on P4VP thin films is based on AFM nanolithography, where a sharp AFM tip is used for delivering molecules or ions into the polymer substrate in a manner similar to DPN. However, differing from the conventional feature creation via DPN, pattern formation on P4VP substrates relies on the polymer swelling response to the local protonation rather than the direct deposition of ink molecules. To trigger the protonation of polymer at desired locations, phosphate buffer solutions serve as the ink that contains an abundance of hydronium ions H_3O^+ . Solutions with different

pH values were prepared by dissolving sodium dihydrogen phosphate (NaH_2PO_4) and sodium hydrogen phosphate (Na_2HPO_4) in appropriate proportions in distilled water. For instance, 0.1 M acidic buffer solution of pH 4.0 was obtained via mixing 13.8 g/L and 0.036 g/L of the two phosphate salts, respectively. Prior to the patterning process, a conducting AFM tip with a relatively high spring constant was coated by dipping the probe into the acidic buffer solution for a short time (i.e., 1 minute). The inked tip was then used to transcribe the preprogrammed patterns under the control of a commercial AFM in contact mode. During each cycle of patterning operation, the tip was scanned across the sample surface at an invariable writing speed (i.e., 100 nm/s). Meanwhile, the contact force between tip and sample was held constant (i.e., 1 μN). To visualize the resulting patterns, topographic images were subsequently acquired by performing the non-contact mode AFM imaging with the same tip used for patterning. Both patterning and imaging processes were carried out in an ambient environment.

Swollen structures were created in the region where the acidic buffer ink was transported [113]. However, the process has suffered from a lack of consistency due to the potential factors intervening in the pattern formation. Sometimes clear patterns were generated, and in other occasions, no pattern was acquired under apparently similar conditions. To improve the consistency of the fabrication process, an electric field was introduced during the AFM lithography by applying a fixed bias voltage to the tip while the sample is grounded [114]. Typical voltages were up to +5 V (the voltages are quoted by referencing the polarity of the tip), which still left polymer films apparently undamaged. By positively biasing the tip, a raised pattern consisting of continuous lines was obtained, shown in Figure 11a (specifically, feature obtained using a contact force $\sim 1.0 \mu\text{N}$, whereas a bias of +5 V was applied in drawing process). Moreover, features with sub-100 nm line-width can be produced under appropriate patterning conditions, for example, using less contact

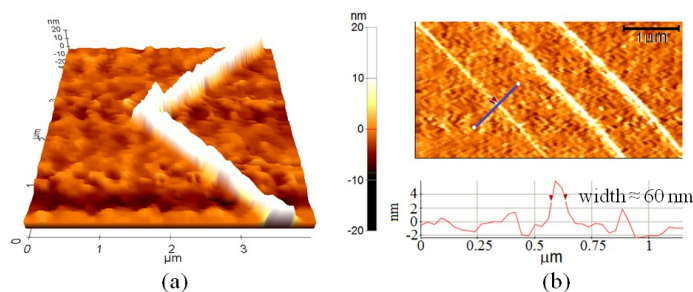


Figure 11. (a) Topographic image ($4 \mu\text{m} \times 4 \mu\text{m}$) of a feature drawn by applying a constant force of $1.0 \mu\text{N}$ and a bias voltage of +5 V. (b) Three line features created using (from left to right) contact forces of $0.6 \mu\text{N}$, $0.9 \mu\text{N}$, $1.0 \mu\text{N}$ and bias voltages of +5 V, +5 V, +4V, respectively. Line profile shows that the width of the line structure at the left is about 60 nm.

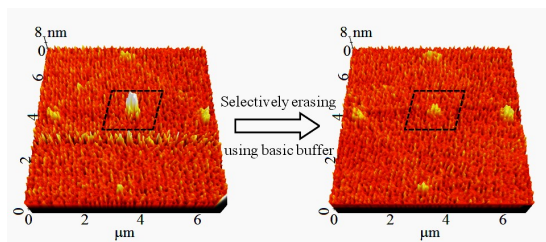


Figure 12. AFM topography images show (left) the initial patterned film, with five ‘dots’ pillars (the horizontal line beneath the central dot is an artifact of the imaging process) and (right) the final pattern after selective partial removal of the dot pattern at the center. The latter was obtained after applying twice the “erasing” operation using the tip inked with basic solution. The dot height decreased from 12 nm to 3 nm.

force. In Figure 11b, one line profile of thickness as small as ~ 60 nm is displayed.

In addition, the existing pillar pattern can be selectively erased because of the reversibility of P4VP swelling. In general, the “erasing” operation is carried out by keeping a tip, coated with basic phosphate buffer solutions, in contact and stationary on top of the swollen pattern. As shown in Figure 12, attenuation in the height of the “dot” feature at the center, from 12 nm to 3 nm is obtained.

Experimental results suggest that, when the inked tip is brought into contact with the polymer film, both *i*) a water meniscus which is naturally condensed between the tip and the substrate could act as a transport medium, and *ii*) concentration gradient of the ink solution could facilitate the diffusion of materials in the acidic ink into the polymer. As illustrated in Figure 13, the subsequent protonation of corresponding polymer region originates from the reaction of P4VP’s pyridyl groups with hydronium ions, thus resulting in a net electrostatic repulsion between positively charged nitrogen centers that

causes the polymer swelling. If the fixed pyridinium cations were the only ions present inside the polymer network, there would be an exceedingly large repulsion. However, the experimental observation suggests that such interaction is partially screened by the existence of counterions generated from the dissociation of phosphate salts in water.

The patterning process is likely to be influenced by numerous parameters, including tip-sample contact force, applied bias voltage, the composition of the ink, the writing speed, the temperature and humidity at which the experiment is performed. Herein our emphasis is on effects of the applied bias and contact force in controlling the properties of scribed patterns. The experimental results are summarized in Figure 14. A trend was observed that the pattern height increased when applying higher bias voltages, indicating that the role of electric field in the patterning process was to help drive the positive hydronium ions into the polymer network. Similar dependence of feature height on contact force was found: higher patterns arose from the use of stronger contact forces, which could be attributed to the wider tip-sample effective contact area where more hydronium ions could be delivered. This is different from the conventional DPN method in which the width of line feature is independent of the contact force [103]. In addition, no electrochemical reaction is needed for creating patterns on P4VP films, which is in contrast to the role of electric field played in electrochemical dipen nanolithography (E-DPN). The characteristic of this patterning approach can find applications in the area that requires feedback material response, such as micro- and nanofluidic devices (where controlled variable size compartments can be used to selectively sort out molecules according to their size). Furthermore, its reversible property offers an opportunity to utilize this material for proton-based memory devices.

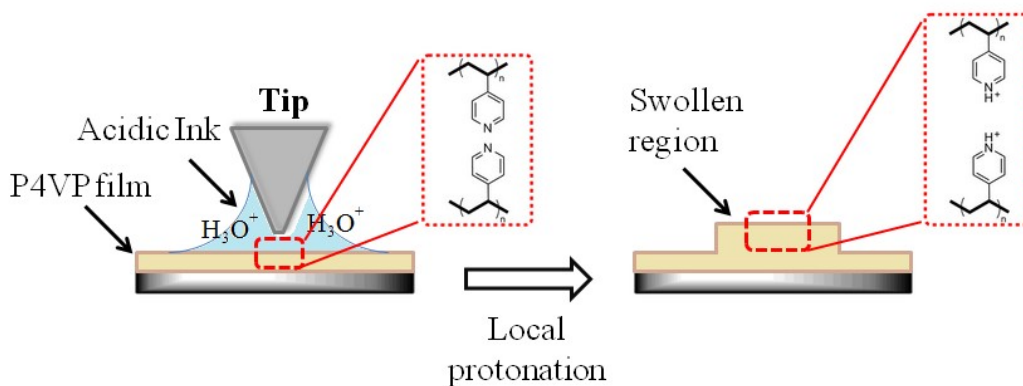


Figure 13. Schematic illustrating that the swollen pattern on P4VP thin films formed as a result of local protonation of the pyridine units.

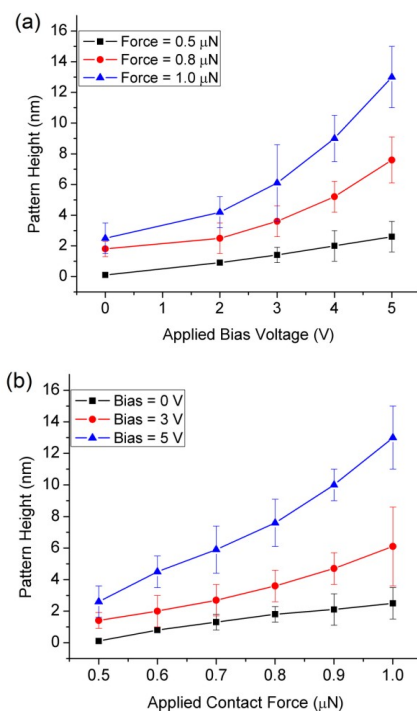


Figure 14. (a) Pattern height (nm) vs. applied bias voltage (V) at various fixed contact forces. (b) Pattern height (nm) vs. applied contact force (μN) under different constant bias voltages. Reprinted with permission from Ref. 114, copyright (2010) American Chemical Society.

5. Summary and conclusions

Nanotechnology has seen tremendous growth and is becoming an integrated part of our lives. This review has addressed three main aspects: (i) stimuli-responsive polymer materials and corresponding mechanism to produce such responses; (ii) representative lithographic techniques employed to fabricate nanostructures on responsive materials; (iii) a recent novel method used to generate patterns on P4VP substrates by taking advantage of local protonation process of this polymer. In parts 2 and 3, we briefly describe important techniques (photolithography, soft lithography and scanning probe lithography) currently being used for fabricating micrometer- and nanometer-scale patterning on materials that change their properties upon the application of external stimuli (i.e., temperature, pH, and optical). Besides being as powerful tools in laboratories for scientific research, these methods have also successfully demonstrated potentials in a number of practical applications, including design and fabrication of smart sensors, molecular switches and microscale actuators.

However, some critical issues remain in this field, such as fabrication of high-resolution structures is still challenging; quality of resulting patterns need to be further improved for specific applications;

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reliability and reproducibility of some process are not satisfied. Therefore, there is an urgent demand for effective patterning approaches which can be applied for a wide range of materials, allowing fabrication of well-defined nano-sized feature with optimal qualities and high repeatability. Any breakthrough of surface chemistry and development of lithographic methods would not only be beneficial to nanofabrication but also hold promise for the creation of new technologies.

In the last part, we described the capabilities of the electric-field-assisted DPN technique to fabricate nanostructures on P4VP thin films. By contrast with conventional DPN-based techniques, raised pillar patterns are formed as a result of local protonation and subsequent swelling of the substrate itself (a P4VP film). In order to trigger this process, hydronium ions were delivered through an inked AFM tip to the polymer film. Moreover, the protonation would become more effective due to the application of an electric field between the tip and the sample during the process. Particularly attractive is the feature that existing patterns can be erased using a tip coated with a basic ink. Such a reversible character of the fabrication process could be relevant to a wide range of potential applications. In nanoelectronics, for example, the swollen and non-swollen states could represent the ones and zeros in a memory device. In biotechnologies, these nanostructures can be used as variable size gates that open and close compartment in micro- and nanofluidic devices in applications involving separation of molecules or chemical reagents. Further, the control of pattern dimensions with nanometer precision, via an electric field, offers an opportunity to use these films as testbed for studying fundamental (thermodynamic and kinetic) physical properties of responsive materials at the nanoscale level.

Despite its current progress, the electric-field-assisted DPN technique would benefit from further efforts towards better understanding of the dynamics involved in the transportation of hydronium-ions from the tip to inside the polymer network. Why, for example, strong forces ($\sim\mu\text{N}$) are needed for a rapid pattern formation to occur? Apparently, the first monolayers of water (found naturally adsorbed on the polymer film) constitute a difficult barrier to overcome by the ions, in their way from the tip to the inside the polymer film. Functionalizing the responsive polymer film with, in turn, hydrophobic or hydrophilic layers would help to contrast this hypothesis. This strategy could allow finding the ultimate resolution of the technique.

With an application perspective for building memory devices (the reversibility of the electric-field-assisted DPN technique allowing the implementation of memory level changes), it would be worth to explore the use of solid state sources of protons. Such an application could benefit from

current efforts for developing solid acid materials as electrolytes in fuel cells. Also in that direction of technological applications, it would be worth to explore its implementation in a parallel fashion. For example, metallic (master) features can be fabricated on a flat (glass) substrate, all of them interconnected as to be able to apply a bias voltage. After spin-coating a layer of buffer solution on the metallic master features, the resulting wet stamp would be pressed against a P4VP film. By applying a bias voltage, the protonation would be more effective on the regions defined by the metallic features, hence the patterns from the master stamp will be replicated onto the polymer substrate by its swelling reaction. In addition, since different metallic regions on the master stamp could be electrically addressed at will, a given mask would be used for fabricating different patterns according to a programmable voltage pattern.

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Cite this article as:

Andres La Rosa *et al.*: **Nanolithography on responsive materials.** *J. Nanosci. Lett.* 2012, **2**: 23