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Design of Stimuli-responsive Surface for Reversible Wettability Switching by Vapor-Phase Assisted Photo-polymerization

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ABSTRACT

In exploring the development of stimuli-responsive surfaces capable of reversible wettability switching, our study delved into the efficacy of vapor-phase-assisted surface photo-polymerization (photo-VASP). This innovative approach modulated Si-wafer and cotton surfaces' chemical and physical attributes. The method involved strategically using a blend of hydrophobic and hydrophilic vinyl monomers, enabling fine-tuning surface properties. By carefully selecting monomer combinations, we achieved seamless copolymerization, effectively grafting the polymers onto the surfaces. The efficacy of this grafting process was validated through contact angle measurements post-solvent extraction of unattached polymers. Crucially, the surfaces engineered through this process demonstrated a remarkable capacity for reversible wettability switching, a feature dynamically controlled by the application and removal of external stimuli. This capability underscores the potential of our approach in creating advanced functional surfaces with tunable properties.

Keywords: Hydrophilic-hydrophobic property, photo-polymerization, stimuli-responsive, vapor-phase assisted surface polymerization (VASP)

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INTRODUCTION

The burgeoning field of surface functionalization on substrates is experiencing a surge in interest, underscored by the critical role of precise surface modifications in diverse areas such as printing, coating, and the utilization of fibers, membranes, and biomedical materials (Xi et al., 2023). The development of advanced materials with responsive surfaces capable

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of reversible switching between distinct states has garnered significant attention. Such precise control over the functionalities at the interface can be achieved through reversible chemical reactions involving both covalent and non-covalent bonds. This enables the tuning of properties in two-dimensional or three-dimensional structures with spatial and temporal accuracy. These sophisticated techniques for reversible manipulation of surfaces have become a focal point of research, holding immense potential for applications in controlled drug release, chromatographic separations, enhanced oil recovery, and optical switching (Chenglong et al., 2023; Guan et al., 2020; Mostafavi et al., 2023; Nagase et al., 2009; Onome et al., 2023; Thang et al., 2023). Researchers have successfully created "adaptive" or "active" surfaces that exhibit dual hydrophobic-hydrophilic behavior in response to stimuli like pH, temperature, or both, utilizing polymer brushes (Lin et al., 2022). These "stimuli-responsive" polymers undergo an abrupt change in properties, such as conformation or solubility, upon exposure to external stimuli like solvent, temperature, or pH. This dynamic alteration of interfacial properties like wettability in response to stimuli such as electrical potentials represents a leap forward in material science, robotics, and electronics (Brotherton et al., 2023).

The functional groups or radicals already present are employed in the following procedure to covalently link polymer chains to enhance substrate surfaces without altering the content. Immobilization of polymer chains onto a solid surface is mainly achieved through two methods: (1) the "grafting to" approach, which attaches pre-existing chains to surface-active groups via chemical reactions, as detailed by researchers such as Maity and Dawn (2020) and Wang et al. (2020); (2) the "grafting from" strategy that initiates the polymerization of monomers directly from the surface, noted by Gouget-Laemmel et al. (2023) and Higaki et al. (2018). Nevertheless, controlled functionalization of polymer surfaces poses a significant challenge, with these surface modification techniques often facing drawbacks like limited control over the chemical composition or mechanical discrepancies in the top layer leading to potential delamination, as observed by Hester et al. (1999).

A unique approach, the vapor-phase-assisted surface polymerization (VASP) technique, has been recognized as an effective method for generating microarchitectures on solid substrate surfaces. Highlighted by its solvent-free nature and precision (Andou et al., 2006, 2007; Chan & Gleason, 2005; Fu et al., 2002; Gu et al., 2003; Lau & Gleason, 2006; Wang & Chang, 2003; Yasutake et al., 2003), VASP offers additional advantages conducive to creating intricately structured composites (Nishida et al., 2005) and coatings (Gupta et al., 2008; Lau et al., 2003). This is achieved through the diffusion and adsorption of vaporized monomers onto the substrate's interstitial surfaces, where they polymerize in a "pseudo-grafting from" fashion. This process fosters the growth of polymer chains that fill in the gaps, ensuring a robust anchoring effect and exceptional binding strength at the polymer/

substrate boundary. Moreover, integrating physically controlled VASP with photo-induced polymerization has been a focus, leading to the generation of block copolymers through the covalent attachment of azo-type free-radical initiators to Si-wafers.

In this study, we describe the preparation of stimuli-responsive surfaces that contain both hydrophilic and hydrophobic segments on the surface, utilizing the vapor-phase assisted photo-polymerization (Photo-VASP) technique.

MATERIALS AND METHODS

Reagents

(3-Aminopropyl) trimethoxysilane (purchased from DAIKIN FINECHEMICAL LABORATORY, LTD. in Japan) and 2,2,2,3,3-pentafluoropropylmethacrylate (FMA) (also from DAIKIN FINECHEMICAL LABORATORY, LTD., Japan) were purified by distillation immediately before use. Acrylic acid (AA) (obtained from Wako Fujifilm, Japan) underwent the same purification process. 4-*tert*-butylprocatechol (Tokyo Kasei Kogyo Co. Ltd., Japan) was used as received without further purification. Ethylene glycol dimethacrylate (EGDMA), 2-Hydroxyethyl methacrylate (HEMA), and benzoin isobutyl ether (BIBE) (all purchased from Sigma-Aldrich) were purified by distillation before use. All other solvents were commercially available and underwent purification by distillation prior to use.

Typical Polymerization Method

The homopolymerization of FMA was conducted using an H-shaped glass reactor with a vacuum cock, a quartz cap for sealing, and a glass filter separator (pore size 20–30 µm) at the bridge. Photopolymerization was carried out through a 5320 W high-pressure mercury lamp (MORITEX Co., MUV-202-U).

An immobilized azo-type initiator on a 30 mm x 30 mm Si wafer was placed at the bottom of the H-shaped glass tube. FMA (2.0 ml) and 4-*tert*-butylcatechol (20 mg), as a polymerization inhibitor, were introduced via a syringe through the bottom-mounted glass cock under an Ar gas flow. The FMA within the tube underwent three additional freeze-pump-thaw cycles and was then sealed with a quartz cap under vacuum. The reaction proceeded with saturated FMA vapor (94.0 x 10^3 Pa) at 40°C, with UV irradiation directed at the Si-wafer surface through the quartz cap from 10 cm (illumination intensity on the surface was 3.2×10^3 lux through the saturated FMA vapor). After a predetermined reaction time, the product formed on the Si-wafer surface was dried under reduced pressure for 24 hours to remove adsorbed or absorbed monomers. Subsequently, the static contact angle of a water droplet on the product was measured, and the product was dissolved in chloroform for chemical structure analysis using SEM.

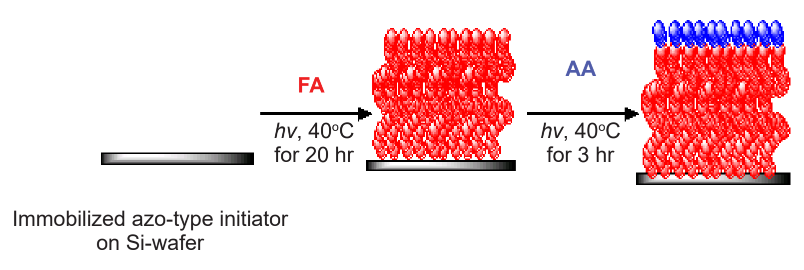
Characterization Methods

Fourier transform infrared (FT-IR) spectroscopy was analyzed using a JASCO FTIR 460 Plus spectrometer. The examination of polymers deposited on cotton fabric via scanning electron microscopy (SEM) was executed using a HITACHI S3000N scanning electron microscope, employing an accelerating voltage of 25.0 kV. The static contact angle measurement for water on the samples was conducted using a Drop Master 500 instrument by Kyowa Interface Science Co., Ltd. The contact angle of a water drop (2.0 µl, Milli-Q) was measured at five random points on each sample's surface.

RESULTS AND DISCUSSIONS

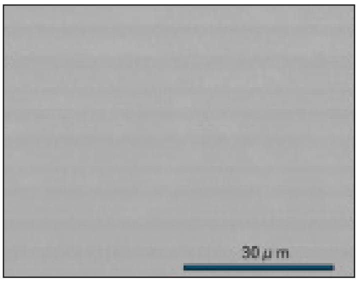
In this study, we described the fabrication of stimuli-responsive surfaces with both hydrophilic and hydrophobic segments on the surface using the (Photo-VASP) technique. The development of these stimuli-responsive surfaces was achieved through two approaches: Firstly, a component consisting of 2,2,3,3,3-pentafluoropropylacrylate (FA) as the hydrophobic segment and acrylic acid (AA) as the hydrophilic segment was used to prepare a pH-responsive surface with a block copolymer in several steps (Scheme 1). The preparation of a diblock copolymer on the surface by Photo-VASP, utilizing an azo-type free-radical initiator immobilized on a Si-wafer, has been previously reported and was successfully implemented (Andou et al., 2006). Microscopic reflection absorption FTIR and AFM characterized the block copolymers to evaluate the structure and determine the chemical composition. Secondly, the immobilization of cross-linked copolymer on fabric was achieved using Photo-VASP, a mixture of EGDMA and HEMA with BIBE as a photoinitiator.

To fully leverage the living radical-active species of the VASP method (Yasutake et al., 2003), we attempted the construction of a stimuli-responsive surface through block copolymerization by consecutively applying VASP. In this process, the monomer vapors of FA and AA were sequentially introduced onto the azo-functionalized Si-wafer surface. The photo-VASP of FA with AA was carried out through UV irradiation. Scheme 1

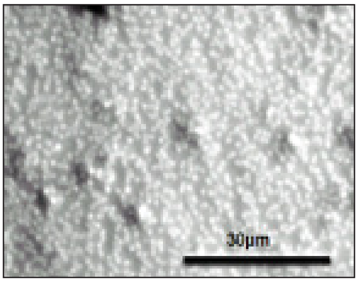


Scheme 1. Poly (FA-*b*-AA) is prepared on a Si surface and immobilized with an azo-type free radical initiator using the consecutive photo-VASP method

outlines constructing a grafted copolymer through this consecutive method. Initially, FA was polymerized on the surface within the reactor tube, after which the FA vapor was evacuated under argon flow. Subsequently, AA was introduced to commence the second stage of photo-VASP. Following photo-VASP, the polymer deposit on the surface was analyzed by SEM with a Backscattered Electron (BSE) detector. As depicted in Figure 1, the photo-VASP resulted in micro-separation composed of poly(FA-*b*-AA) grafted from the Si-wafer surface. Subsequently, free polymer deposits were eliminated through dissolution and washing with a suitable solvent. Compositional SEM analysis with a BSE detector revealed that covalently grafted polymer chains were present. The SEM images showed that the micro-separation structure on the surface disappeared after washing, resulting in a homogeneous surface appearance. This indicates that the micro-separation structure consisted of adsorbed monomers and deposited oligomers, which exhibited different wettability properties.



(a)



(b)

Figure 1. SEM images of Si-wafer before (a) and after (b) consecutive photo-VASP of FA/AA. Bar 30 μm

To verify the formation of a block copolymer on the surface, the modified Si-wafer surface was assessed by measuring the static contact angle with a water droplet, performed randomly at five points on the surface. The grafted poly (FA-*b*-AA) demonstrated water contact angles of 51° without the need for any external stimuli such as pH changes, suggesting the presence of poly (AA) segments due to the continuous Vapor-phase Assisted Surface Polymerization (VASP) process. In contrast, surfaces with poly (FA) typically exhibited water contact angles 102°.

To alter the surface property to a hydrophilic state, samples were immersed in 0.1M NaOH aqueous solution for several minutes to ionize the carboxyl groups of the AA units. Then, the sample was heated at 100°C under vacuum to transition the surface to a hydrophobic state, during which the carboxyl groups could aggregate and become buried under the flexible PFA chains. These treatments were repeated, with the surface property monitored via static contact angle measurement. The results, presented in Figure 2, illustrate the typical hydrophilic and hydrophobic properties achieved in the first cycle of the process, demonstrating the reversible wettability of the surface. However, the change in surface property was less pronounced after the second cycle. It is believed that the poly (FA) units may gradually hydrolyze in the presence of 0.1 M NaOH aqueous solution, leading to a transition to a completely hydrophilic surface. Thus, selecting more appropriate conditions for external stimulation is necessary to achieve repeatable functionality on the surface.

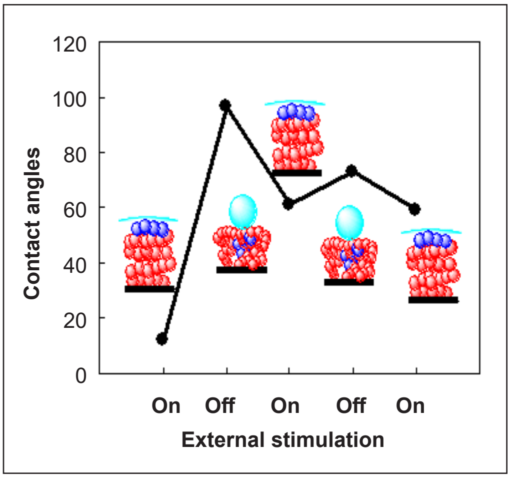


Figure 2. Reversible hydrophobic-hydrophilic conversion of the grafted poly (FA-*b*-AA) on Si-wafer under the cycle of external stimuli. Conditions of external stimuli are as follows: On means that the sample is dipped into 0.1M NaOH aq. Off means that the sample is heated at 100°C in vacuo

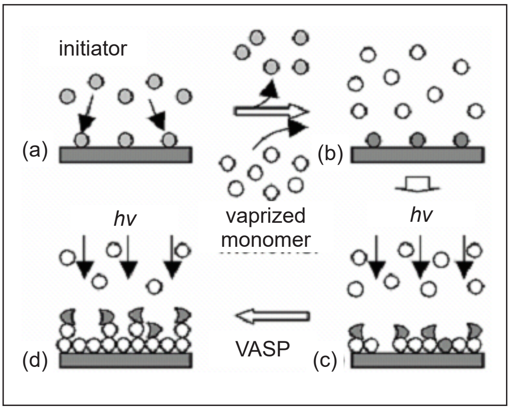
Several strategies for achieving reversible wettability switching surfaces have been developed. Depending on the approach, linear and cross-linked amphiphilic polymer layers can be obtained. The architecture of polymer grafts significantly impacts the wettability of a modified surface due to the dynamic motion of the grafted polymer chains with varying architectures (Yakushiji et al., 1998). Liang et al. (2000) reported that cross-linked polymer surfaces exhibit temperature-sensitive characteristics. However, the range of temperature changes is broad, indicating that the surface's sensitivity to temperature is relatively weak.

The second approach introduces a novel method for generating a cross-linked polymer layer on the surface to develop a surface capable of reversible wettability switching. This new method offers two main advantages: it allows for modifying the grafting layer's morphology. It ensures covalently strong bonding with the surface, enabling the substrate to be changed from a Si-wafer to fabric during the VASP process. Cotton fabric, known for its artificial and delicate surface morphology, demonstrates typical surface properties such as wettability, characterized by the smooth absorption of water droplets. It is well-documented that surface roughness significantly influences apparent hydrophobicity through the lotus effect (Jung et al., 2002). Furthermore, Ogiwara et al. (1974) demonstrated that the graft copolymerization of methyl methacrylate on cellulose occurs under UV irradiation. Consequently, surface modification of cotton fabrics by photo-VASP is anticipated to create durable surfaces resistant to external stimuli.

Utilizing BIBE as a photoinitiator, the photo-VASP process of EGDMA, a bifunctional monomer employed for creating cross-linked polymer networks, was performed. Scheme 2 presents a detailed, step-by-step illustration of the anticipated mechanism governing the VASP process under UV irradiation. The procedure initiates with step (a), which involves the distribution and subsequent adsorption of the vaporized initiator on the textile surface. This is followed by step (b), wherein the vapor phase is substituted with monomer molecules. Step (c) comprises the photolysis of the initiator upon UV exposure, leading to steps (c) to (d), during which the active species produced commence the polymerization of the monomer that has been adsorbed on the surfaces. Initially, cotton fabrics of dimensions 35 × 55 mm undergo pre-coating with BIBE via vapor phase adsorption for 1 hour at a temperature of 60°C. Post vapor phase adsorption, these fabrics are exposed to photo-irradiation for 24 hours at 40°C, as delineated in Table 1.

The treated cotton fabrics were subsequently dried in vacuo for 24 hours, and the contact angle with water droplets was measured. The modified cotton surface exhibited high contact angle values of 120° to water droplets, maintaining its hydrophobicity for over 10 minutes. The cotton surface treated with VASP of EGDMA and FMA demonstrated the same high value as those treated solely with VASP of FMA. Thus, EGDMA serves not only as a crosslinker but also as a hydrophobic monomer.

To fabricate a cross-linked copolymer hydrogel on fabric surfaces, photo-VASP of 2-hydroxyethyl methacrylate (HEMA, 1ml) as a hydrophilic monomer and ethylene glycol dimethacrylate (EGDMA, 1ml), with benzoin isobutyl ether (BIBE) as a photoinitiator, was performed. The cotton fabrics, measuring 35 × 55 mm, were initially pre-coated with BIBE via vapor phase adsorption for 1 hour at 80°C, followed by photo-VASP with the monomers for 2 hours at 40°C (Table 1). Subsequently, the cotton fabrics were dried in vacuo for 24 hours. Their contact angles (CA) with water droplets were measured under two conditions: “dry” condition,



Scheme 2. Mechanism of Photo-VASP process

Table 1
Results of VASP of vinyl monomers on cotton fabric surfaces under UV-irradiation[a]

	1st Step[b]			2nd Step				C.A.[b]	External stimuli	
	BIBE	Time	Temp.			Time	Temp.		Dry[c]	Wet[d]
No.	(ml)	(h)	(˚C)	Monomers	(ml)	(h)	(˚C)	(˚)	C.A.[b] (˚)	C.A.[b] (˚)
1	1	1	80	EGDMA	2	2	40	131	123	126
2	1	1	80	HEMA	2	2	40	0	0	0
3	1	1	80	EGDMA/ HEMA	1/1	2	40	127	134	0

[a] Reaction conditions: initiator adsorption, at 80 °C for 1 hr (BIBE); polymerization of vinyl monomers, at 40 °C under UV irradiation. The distance from the UV lamp to the substrate surface was 10cm. [b] Measured 5 s after setting a water droplet of 2.0 μL on the surface at 25°C. [c] Dry condition indicates heating at 110ºC for 30 min in a drying oven. [d] wet condition indicates exposing to steam at 100ºC for 10 min

where the surface was dried at 110°C for 30 minutes in a drying oven before measuring the CA, and "wet" condition, where the surface was equilibrated under steam at 100°C for 10 minutes before measuring the CA. The CA was recorded after 2 minutes under "dry" conditions and after 10 seconds under "wet" conditions. Interestingly, the CA values significantly varied based on the conditions, attributed to changes in the surface morphology of cotton due to thermal stimuli.

The cotton surface modified by poly(HEMA-*r*-EGDMA) exhibited reversible wettability behavior, responding to external stimuli. This wettability-switching phenomenon was reproducible, demonstrating a clear alteration in surface properties (Figure 3), indicative of the functionality's repeatability. The observed phenomena are attributed to the hydroxyl groups of poly(HEMA) on the modified cotton surface forming hydrogen bonds under "dry" conditions. Conversely, under "wet" conditions, these hydrogen bonds are disrupted by steam, resulting in a transition to a hydrophilic surface. The alternation in surface properties is believed to be governed by the balance between the hydrogen bonding among the hydroxyl groups of the HEMA units and the cross-linking density introduced by the EGDMA units.

This study illustrates that the photo-VASP techniques reported here offer straightforward methods for reversible wettability switching surfaces through two distinct approaches. The poly(FA-*b*-AA) grafted onto Si-wafers exhibited reversible wettability in response to external stimuli, although some defects were observed. The reversibility of the grafted linear polymer surfaces is limited by repeated application of stimuli, as the water contact angles progressively transition towards hydrophilic properties. It is clear that the poly(FA-*b*-AA) on the Si surface, covalently bonded to the substrate through the self-assembly monolayer technique, gradually deteriorates the chemical structure of the thin film under external stimuli. The current limitations of grafted poly(FA-*b*-AA) on Si-wafers include the need for continuous multiple reaction steps and the maintenance of surface structure. These could potentially be addressed by employing simultaneous photo-VASP of a bifunctional monomer on fabrics. From the second approach, the simultaneous photo-VASP technique applied to fabrics produced cross-linked poly(HEMA-*r*-EGDMA) on fabrics immobilized on the substrate, demonstrating the versatility and potential of photo-VASP techniques in surface modification applications.

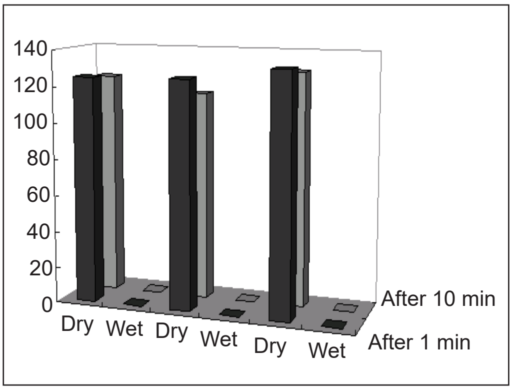


Figure 3. Effect of external stimuli on static contact angles of cotton surfaces modified by cross-linked poly(HEMA-*r*-EGDMA) layers

CONCLUSION

The products obtained demonstrated reversible wettability in response to external stimuli, underscoring the repeatability of this intelligent function. Two critical factors—the surface morphology and the chain transfer reaction to fabric surfaces under photo-irradiation—are essential for achieving distinct switching of reversible wettability properties, effectively overcoming damage from external stimuli.

The immobilization of the polymer layer on fabric through photo-irradiation proved highly reproducible and scalable. The resulting coatings were exceptionally robust, with the cross-linked poly(HEMA-*r*-EGDMA) surfaces maintaining their switching behavior even after being exposed to heat for 30 minutes at 110°C or steam for 10 minutes at 100°C. We believe this method endows surfaces/materials with unique properties suitable for fabric applications. Its significant advantages—solvent-free, allowing easy control of reaction parameters, maintaining constant monomer concentration, and requiring low energy consumption—offer an alternative approach for synthesizing various copolymer thin films.

These findings enable us to control and achieve numerous combinations using various monomers. The concepts introduced in this study are not confined to hydrogels alone but are applicable and should be extended to other categories of copolymers.

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