

An Extremely Simple and Effective Strategy to Tailor the Surface Performance of Inorganic Substrates by Two New Photochemical Reactions

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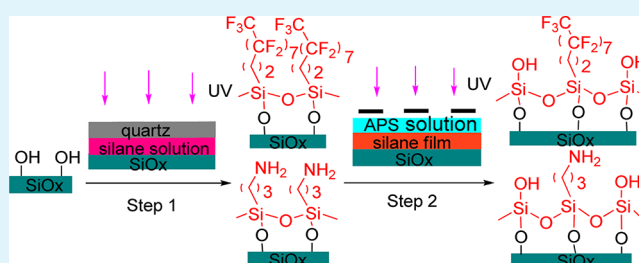
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S Supporting Information

ABSTRACT: This article reports on a new sequential strategy to fabricate monolayer functional organosilane films on inorganic substrate surfaces, and subsequently, to pattern them by two new photochemical reactions. (1) By using UV light (254 nm) plus dimethylformamide (DMF), a functional silane monolayer film could be fabricated quickly (within minutes) under ambient temperature. (2) The organic groups of the formed films became decomposed in a few minutes with UV irradiation coupled with a water solution of ammonium persulfate (APS). (3) When two photochemical reactions were sequentially combined, a high-quality patterned functional surface could be obtained thanks to the photomask.

KEYWORDS: SAMs, patterned surface, photochemical reaction, DMF, APS, UV



INTRODUCTION

Reactions of organosilane with hydroxyl-terminated substrate surfaces, such as glass, mica, SiO₂, Al₂O₃ and CuO, lead to the formation of self-assembled monolayers (SAMs) or multilayer films, which can be used in such fields as chromatography, electrochemistry, protective layers, surface catalysis, high-resolution imaging materials and functionalized surfaces with specific chemical, biological, adhesive or wetting properties.^{1–18} Various kinds of functional groups, including amino, thiol, epoxy, alkenyl and alkyl or fluoro-alkyl groups can be introduced to substrate surfaces for further surface modification.^{2–8} The general formation mechanism of the monomolecular film is believed to occur in two steps: First, in the presence of trace water, the ethoxy groups are hydrolyzed under acidulous or alkaline catalytic conditions; second, the hydrolyzed silanes react with the surface silanol groups and other silane molecules to obtain a polymerized network. This results in the formation of a two-dimensional, cross-linked network of Si–O–Si bonds. Two approaches, including chemical liquid and vapor deposition, have been mainly adopted to prepare a silane monolayer on flat surfaces.^{9–11}

Usually, silane monolayers can be produced by immersing inorganic substrates in a refluxing solution of 5-mM silane in toluene for several hours.¹ Halter reported on an impressed modified method where, by treatment of silica with the refluxing vapors of APTES, a strict monolayer film was fabricated on the surface with a few adherent polymer globules in dry toluene or xylene solution during 16 h.¹² Rönneberg et al.¹⁰ reported on a chemical vapor deposition at about 0.5–1

N m⁻² and 80–190 °C depending on the type of silane. Obviously, both methods required long times, high temperatures and elevated costs of reagents and organic solvents. Therefore, more facile and effective methods for preparing monomolecular organosilane films with few aggregations on the surface are expected to be developed.

In addition, the patterned chemical functional surface of these inorganic substrates can offer advanced properties such as selective adsorption and reactivity,^{13–18} as well as site-specific wettability,^{19–21} which have attracted extensive attention and become increasingly important in the research of molecular behavior on anisotropic surface. Proteins, DNA and cells can be immobilized onto patterned chemical surfaces to fabricate biochips, which are essential in the research of protein diagnostics, genomic hybridization and cell adhesion.^{13–18} Micropatterned wetted surfaces combined with micro- and nanostructure can be used to fabricate water-harvesting bioinspired materials.^{19–21} Patterned surface with oppositely charged functional groups can also be applied to control the rate of contact electrification.²²

Several techniques have been developed to produce these micropatterned surfaces. A brief review of existent patterning strategies is provided with some representative references: (1) Photoresists have been spin-coated onto a substrate surfaces, followed by exposure to UV irradiation through a photomask,

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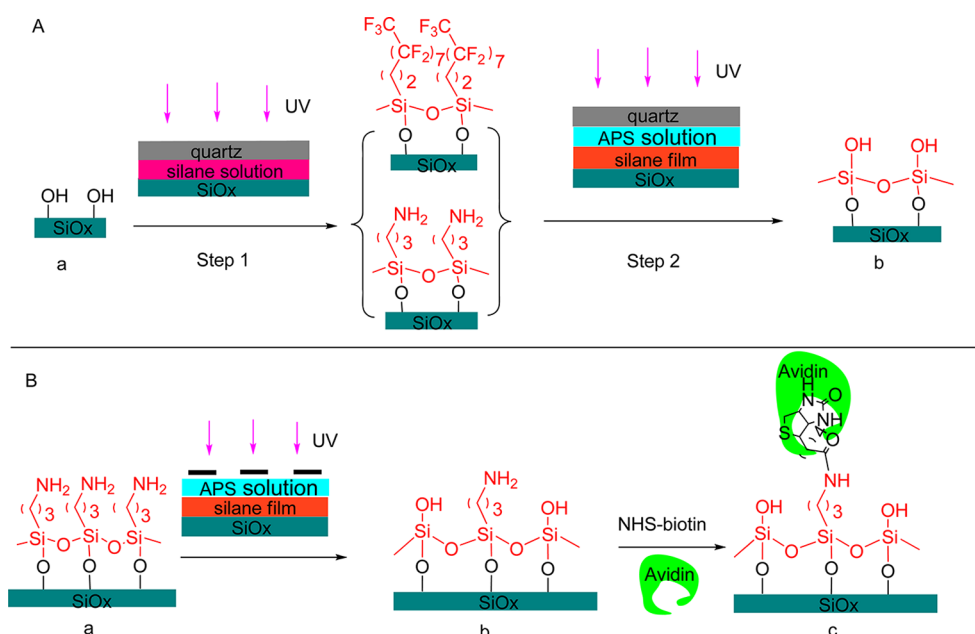


Figure 1. (A) Schematic formation and decomposition process of silane film on a glass slide surface by a photochemical reaction. (a) Glass surface after treatment with piranha solution; (b) resultant glass surface after silane film decomposition. (B) Schematic procedure of the patterned silane film by a photo-oxidation reaction: (a) APTES film formed by step 1; (b) APTES film micropatterned by step 2; (c) avidin immobilized on the patterned amino surface via NHS-biotin.

to prepare a patterned surface with hydroxy groups for silane deposition. After the photoresists have been striped, the remaining surface can be modified with another silane precursor. A major disadvantage of this technique for producing patterned films is that it requires many processing steps.^{17,23}

(2) Photosensitive silanes can be synthesized to modify a substrate surface. A patterned surface was obtained by deprotecting different protecting groups or activating photosensitive linkers to graft polymer layers at specific wavelengths, but the process usually involves a complicated synthesis of photosensitive silanes.²⁴ (3) Irradiation at very short wavelengths (193 nm, high-energy UV) can lead to the chemical degradation of the exposed silane film, creating a hydroxy terminal region differing from the original one. However, special silanes with aryl groups and long-time irradiation is crucial for this process.²⁵ (4) Patterned surfaces can also be achieved via microcontact printing (μ CP).^{26,27} However, the contact performance of a PDMS stamp with substrate and the transfer quality of adhesive molecules depends on numerous parameters that are difficult to control. Moreover, it is not convenient, and sometimes even impossible, to prepare patterned surfaces using μ CP. (5) Finally, near-field scanning optical microscopy (NSOM), X-ray, electron beam, ion bombardment, and STM or atomic force microscopy (AFM) techniques have been proven effective for the patterning of SAM.²⁸ However, specific and high-cost equipment has to be employed, and it is not easy to effectively fabricate large areas.

UV-light is a moderate medium that is extensively utilized to directly introduce lateral patterns onto the surfaces of organic substrates. A series of research studies on polymer surface modification by UV-induction in the presence of photosensitizers have been developed in our lab.^{29–32} Particularly, we have found that *N,N*-dimethylformamide (DMF) released $\text{HN}(\text{CH}_3)_2$ under UV light which could be used to fabricate on a poly(ethylene terephthalate) (PET) surface micro/nanoscale wells and channels with depths ranging from some nanometers

to several micrometers via a aminolysis reaction toward surface ester groups of PET. Ammonium persulfate (APS), on the other hand, displays an effective photooxidation capability that could be employed as a fast surface hydrophilic modification reagent for most commercial polymeric materials.

Against this background and taking into account the challenges involved in fabricating monolayer films and patterning for inorganic substrates, we attempted to explore novel approaches by a photochemical reaction, and achieved surprising but fantastic results. Indeed, using glass slides as a model for inorganic substrates and FAS-17 and APTES as typical representatives of functional silanes, we found that: (1) a silane monolayer could be formed quickly (within several minutes) under ambient temperature by UV irradiation and DMF; (2) the formed silane film could be decomposed by UV irradiation coupled with an APS water solution, thereby restoring the original hydroxyl-terminated surface; and (3) when the two photochemical reactions were sequentially combined, the high-quality patterned functional silane film could be obtained thanks to a photomask. As far as we know, not only have this strategy and the photochemical reactions it depends on never been reported but it is also a most simple, extremely fast and effective approach to fabricate patterned functional silane monolayers on the surfaces of flat inorganic substrates. It therefore has an extreme potential for numerous applications.

RESULTS AND DISCUSSION

We first investigated the preparation of a monolayer FAS-17 film as described in Figure 1A. Different from conventional methods, 4%(v/v) anhydrous DMF was added in a routine FAS-17 (7.5-mM) solution in anhydrous ethanol, which was used as the reactive agent. Then after wetting the surface of the glass slide treated by piranha solution, the setup with a quartz cover was UV irradiated for 4 min. After strictly washing and drying, the surface water-CA was 106.5°. The procedure above

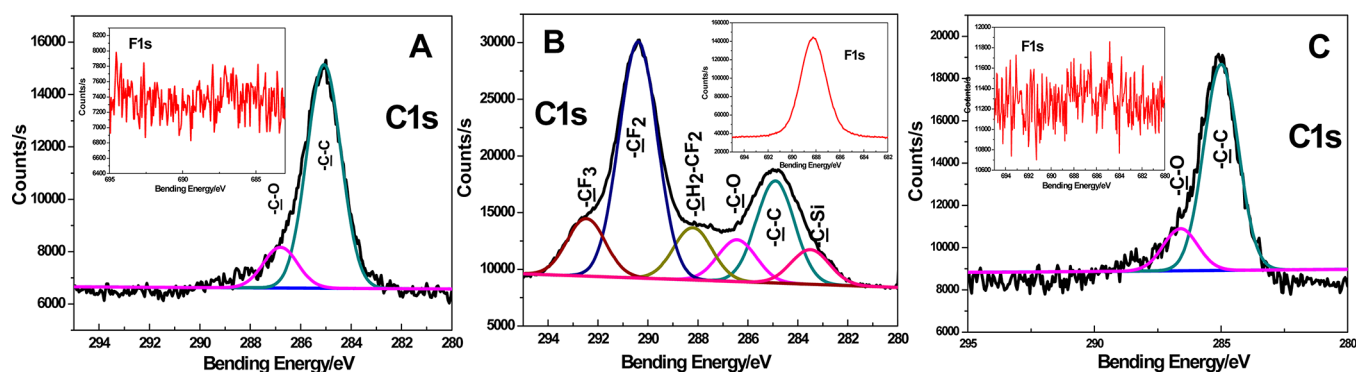


Figure 2. High-resolution C1s spectra of the glass surfaces with the insets showing the corresponding high-resolution F1s spectra. (A) Glass surface after treatment with piranha solution; (B) glass surface coated with FAS-17 film by photochemical reaction; (C) glass surface coated with FAS-17 film after treatment with photo-oxidation reaction.

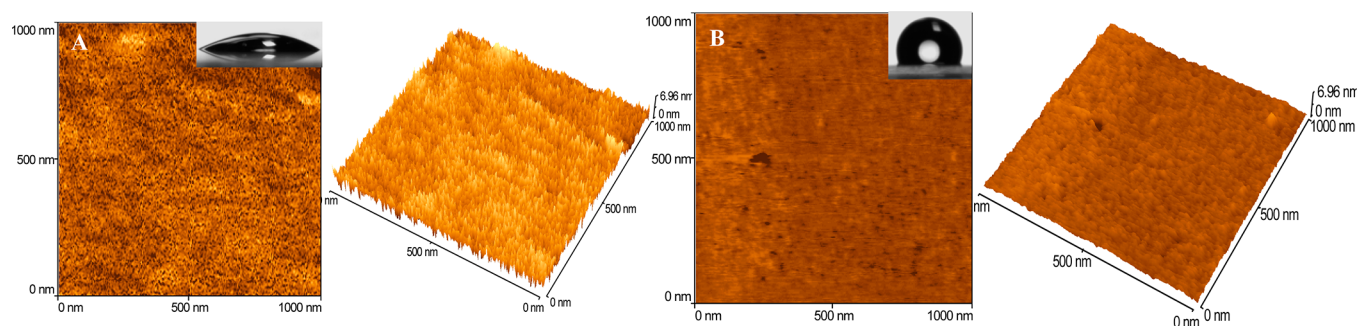


Figure 3. 2D and corresponding 3D AFM images of glass surfaces (the insets depict the wetting properties of the as-prepared surfaces). (A) Glass surface after treatment with piranha solution; (B) FAS-17 monolayer on glass surface by photochemical reaction.

was repeated, and the CA reached 114.3° . The CA maintained this value even after more repeats, which demonstrated that the glass slide had been completely covered by a FAS-17 film.

Compared with the bare glass surface with a CA of 31.2° (Figure 3A), the sample with the FAS-17 monolayer obtained through UV irradiation presented a significantly increased CA of 114.3° (Figure 3B), which definitely demonstrates the transformation of surface wetting ability from hydrophilic to hydrophobic owing to the formed FAS-17 film.

To investigate whether FAS-17 successfully conjugated to the substrate with little damage in molecular composition under UV irradiation, X-ray photoelectron spectroscopy (XPS) spectra (Figure 2A, B) were acquired from the cleaned and FAS-17-modified glass surfaces, respectively. The figures show the high-resolution C1s spectra with the corresponding F1s spectra in the inset obtained from the corresponding surface. Compared with the cleaned glass surface, the large peak at a bonding energy (BE) of 688.2 eV for F1s revealed the presence of F on the surface. This F concentration on the sample surface treated with FAS-17 increased markedly to 31.14% and the ratio of F/C was 1.35, which is in good agreement with a saturated coverage of FAS-17.⁶ Typical C1s XPS peaks recorded for the FAS-17 functionalized sample could be safely decomposed into six components, namely, $-\text{CF}_3$ (292.47 eV), $-\text{CF}_2$ (290.40 eV), $-\text{CH}_2-\text{CF}_2$ (288.21 eV), $-\text{C}-\text{O}$ (286.43 eV), $-\text{C}-\text{C}$ (284.89 eV) and $-\text{C}-\text{Si}$ (283.50 eV). These results demonstrate that FAS-17 was conjugated onto the glass surface without damage to the molecular structure during UV irradiation.

The surface morphology of the prepared film was observed by AFM. The morphologies of the cleaned and FAS-17-modified surfaces were shown in Figures 3A and B. The surface roughness value, R_{q} of the cleaned glass surface (Figure 3A) was 1.004 nm. This was rougher than silicon but still smooth enough for measuring the thin film described here. The roughness, R_{q} of the FAS-17 modified surface (Figure 3B) was 0.3504 nm, which was much less than the corresponding value of the cleaned glass surface, i.e., 1.004 nm.⁷ The estimated thickness of the FAS-17 film with incomplete coverage measured from randomly placed height profiles revealed a height of 1.454 nm (see Figure S1 in the Supporting Information), which was less than that of the FAS-17 monolayer, i.e., 1.6 nm from the ellipsometry results, but still close to the theoretic value of 1.43 nm.^{33,34} These results demonstrated that the FAS-17 monolayer had been formed on the glass surface with few aggregations occurring during the photochemical reaction, which was also in good accordance with the idea of a formed film with complete coverage as revealed by XPS.

The stability of the formed FAS-17 film by the approach described above was also evaluated by overnight incubation of slides in 0.1-M hydrochloric acid solution, phosphate and carbonate buffers. The pH values of these solutions was 1.0, 7.4, and 9.0, respectively.¹⁰ The CAs of the treated slides were 114.0, 113.2, and 113.6° ; in other words, the CA values had hardly changed compared with that of the untreated FAS-17-modified surface. These results indicated that the stability of the formed film was good enough for application under various conditions.

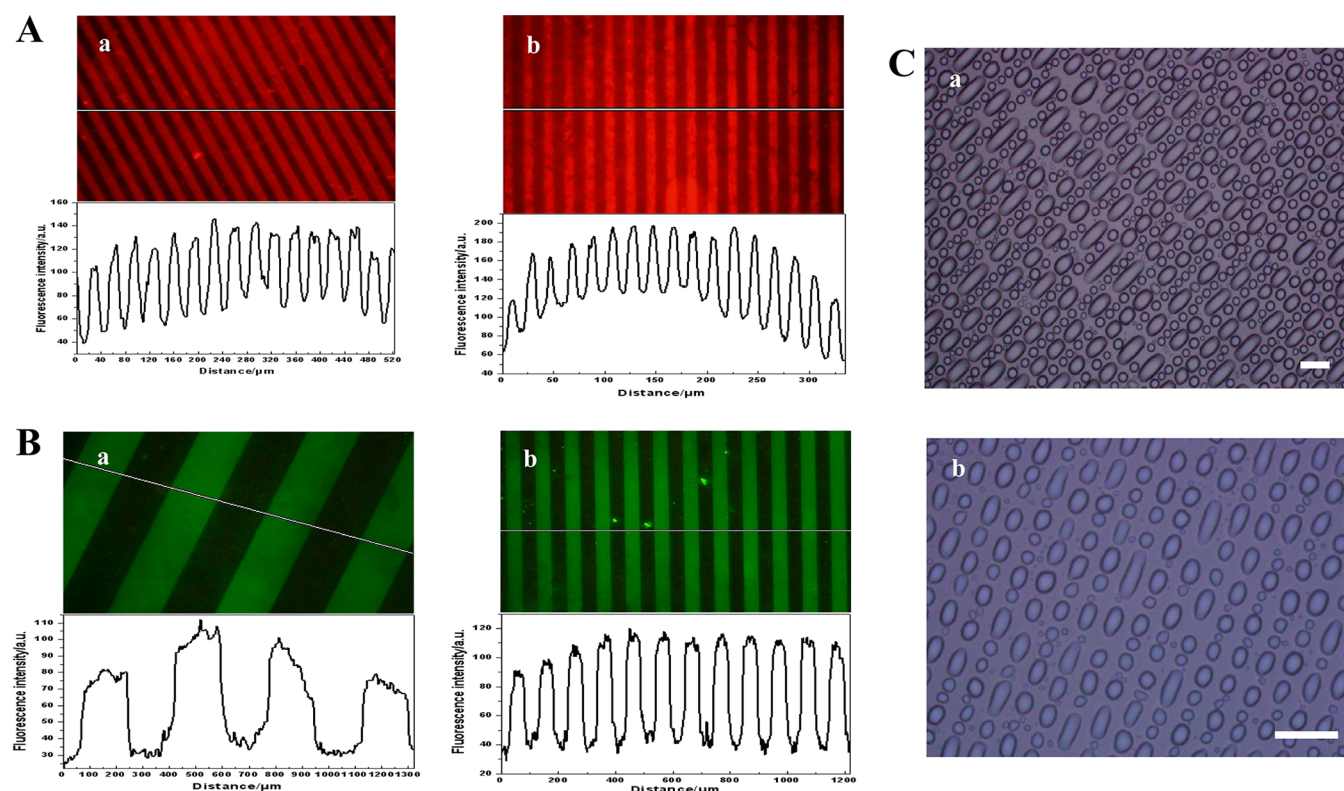


Figure 4. (A) Fluorescence images showing micropatterns formed by physical attachment of Rhodamine B dye to the FAS-17 molecular strips with widths of (a) 20 μm and (b) 10 μm . (B) Fluorescence images showing micropatterns formed by attachment of FITC-avidin to biotinylated amino functional strips with widths of (a) 200 μm and (b) 50 μm . (C) Optical images showing the different behavior of water vapor condensing on an anisotropic wetted surface with alternated hydrophobic and hydrophilic strips with widths of (a) 20 μm and (b) 10 μm . The scale bar corresponds to 50 μm .

Using the same procedure, we fabricated a monolayer film of APTES. The X-ray photoelectron spectroscopy (XPS) spectrum of the APTES-modified surface and the relevant analysis are reported in Figure S2 of the Supporting Information.

To determine possible reaction mechanisms of the process, we conducted two control experiments, i.e., DMF without UV radiation and UV radiation without DMF, and the results showed that no silane films were formed on the glass slide surface. Based on the references where XPS and ATR-FTIR gave direct evidence of the incorporation of tertiary amine on the PET-surface by “UV-induced surface aminolysis reaction” (USAR) at the presence of DMF,^{30,31} we propose a plausible mechanism as follows: Under UV irradiation the carbonyl group of DMF absorbs UV light, undertakes dissociation, producing a stronger base, $\text{HN}(\text{CH}_3)_2$, which promotes the hydrolysis of silane and sequential connection to the glass surface by a fast dehydration reaction. The more DMF that is used, the faster is the reaction, but 4% (v/v) is enough to fabricate a decent monolayer with the presented procedure and radiation time.

With the same reaction setup as described in Figure 1A, but with a thin APS solution (30 wt % in deionized water) deposited onto the silane-modified surface of the glass slide, and followed by irradiation of the assembly with a routine UV lamp ($120\text{W}/\text{m}^2$ at 254 nm), the slide surfaces returned to its original hydrophilicity, i.e., 31.9° , within 7 min for the FAS-17-modified surface or 3 min for the APTES-modified one. This value was almost the same as that of the bare glass surface (31.2°).

Figure 2C showed an X-ray photoelectron spectroscopy (XPS) spectrum after the photo-oxidation treatment of the FAS-17-modified glass surface. We could observe that the peak at a bonding energy (BE) of 688.2 eV for F1s disappeared and the peak of C1s returned to its original shape, which was similar to that of the cleaned surface (Figure 2A). For the APTES-modified surface, on the other hand, after the photo-oxidation treatment, the XPS spectrum showed the same result (see Figure S2 in the Supporting Information). The results revealed that the organic groups of these monolayers could be swept away completely by the photo-oxidation treatment.

When persulfate salt (a kind of moderate oxidant) was combined with a routine UV (254 nm) radiation, we obtained a significant etching with which organic groups of silane could be etched up in minutes in a manner similar to that of deep UV (193 nm),²⁵ which was unexpected and unusual. According to XPS results above and references where polymeric materials containing only C–H and C–C bonds on their surface and single-walled carbon nanotubes containing only C–C bonds were both modified at the presence of APS,^{32,35,36} it was believed that under UV radiation and with such a confined surface or interface reaction system, persulfate salt $\text{S}_2\text{O}_8^{2-}$ could directly decompose into two $\text{SO}_4^{\bullet-}$ radicals, which attacked the Si–C bond and formed reactive Si. Subsequently, through a reaction with water, Si–OH was formed as described in Figure 1B.

In principle, a simpler strategy to pattern glass surfaces with hydrophilic OH groups would be to directly introduce the FAS-17 monolayer by step 1 under a photomask. However, a high quality pattern could not be obtained as shown in Figure S3 in

the Supporting Information. The reason for this could possibly be the diffusion of the produced $\text{HN}(\text{CH}_3)_2$ by UV light to nonradiation areas. The red fluorescence came from Rhodamine B dye which was found to have a strong adsorption ability to the FAS-17 molecular regions (see Figure S4 in the Supporting Information).

Alternatively, when step 2 was used as photocleavage of the fully covering FAS-17 monolayer fabricated by step 1 under a photomask, a good pattern could be obtained as described in Figure 1B. From Figure 4A, a well-defined striped red fluorescence surface with a width of 20 and 10 μm could be observed after the attachment of Rhodamine B, thus confirming the formation of the patterned FAS-17 film on the surface. The red regions of the images referred to the unexposed regions where the FAS-17 molecular film remained, whereas the dark regions of the images corresponded to the irradiated regions where the FAS-17 molecular film was etched up, leaving behind a hydrophilic hydroxyl-terminated surface.

Currently, bioinspired water collection materials have been a subject of great interest because of their extraordinary capability to capture water from humid air. However, one of the challenges of these substrates is to fabricate patterned hydrophobic/hydrophilic surfaces. The strategy reported here provides a convenient and effective method to create anisotropic wetted surfaces. In our study, we observed the behavior of the water vapor condensing on anisotropic wetted surfaces on the basis of the strip-hydrophobic surface prepared by the approaches reported herein.

Figure 4C shows the obtained optical microscopy images for the water vapor condensing on the anisotropic wetted surface. On the striped wetted surface with the width of 20 μm , it can be observed that the water vapor condensed more easily into larger drops on the hydrophilic strips with lower CA, while transforming into small spherical drops on the hydrophobic strips with higher CA. When the same experiment was performed on the alternated strips with widths of 10 μm , a similar vapor condensation behavior was observed, but there were less spherical drops formed on the hydrophobic strips.

In the process water vapor condensing on hydrophobic and hydrophilic strips, first, water vapor condenses into seminal liquid drops on hydrophobic and hydrophilic strips; second, seminal liquid drops grow up with continuous vapor condensing. However, on the hydrophilic strips, seminal liquid drops are easier to form and sequentially tend to spread and gather into bigger water drops along the hydrophilic strips, while seminal liquid drops tend to grow up separately on the hydrophobic strips and the final drop size is depended on the width of the hydrophobic strips. In addition, we observed that (1) it is difficult for seminal liquid drops on hydrophobic strips to grow up because water drops tend to slip into hydrophilic strips when they are close to the boundary between hydrophobic and a hydrophilic strips; (2) seminal liquid drops is even not able to form on hydrophobic strips with too small width (Figure 4Cb). More quantitative conclusions are expected to be obtained in further study.

To further confirm that site-selective chemical reactions can proceed on the patterned functional glass surfaces, patterned amino-functional surfaces with 200 and 50 μm wide strips were prepared by photomasks of varying sizes. Here, APTES was employed to introduce amino groups to the glass surface by sequencing step 1 and step 2 (Figure 1B). By placing the strip-patterned amino-functional glass slides into a standard DMF solution of NHS-biotin for two hours, the biotin became

covalently attached to the slide surface. Afterward, avidin labeled with fluorescein isothiocyanate (FITC) was coupled via the specific biotin-avidin recognition interaction. The obtained samples were imaged by fluorescence microscopy and the results are shown in Figure 4B. A bright fluorescence was observed from the unexposed regions where the amino groups were intact, whereas the dark contrast corresponded to the areas where the organic amine molecule had been removed. The results proved that further reaction could be performed on the patterned functional surface. Moreover, this strategy provides a more convenient approach allowing us to fabricate biochips.

CONCLUSIONS

With glass slides as a model of inorganic substrates containing surface-hydroxyl groups and FAS-17 and APTES as typical representatives of functional silanes, it was found that: (1) a silane monolayer film could be formed quickly (within several minutes) under ambient temperature by UV irradiation coupled with DMF; (2) the formed silane film could be decomposed by UV coupled with a water solution of APS, thus restoring the original hydroxyl-terminated surface; and (3) when 1 and 2 were sequentially combined, a high-quality patterned functional silane film could be obtained with the aid of a photomask. The primary exploration showed that water vapor could condense and accumulate on the alternated hydrophobic and hydrophilic striped surface modified with FAS-17. Moreover, APTES was used to identify the capability of further reaction between the patterned functional surface and the active biomolecule. This study thus offers a new strategy for fabricating patterned functional surfaces, which has a promising application in preparing advanced interfacial materials such as bioinspired surfaces for water collection, protein, and DNA biochips and solar cells.

ASSOCIATED CONTENT

Supporting Information

Detailed experimental procedures and supporting figures. This material is free of charge and available at <http://pubs.acs.org>. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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The authors declare no competing financial interest.

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