Rational construction of self-assembly azobenzene derivative monolayers with photoswitchable surface properties

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** Abstract **

Photo-responsive azobenzene (ABZ) derivatives with different end groups (R) as switchable molecules were employed to construct self-assembled monolayers (SAMs) on silicon substrate by using 3-glycidoxypropyltrimethoxysilane (GPTS) as the bridging molecules. The assembly process was optimized by changing various parameters, including the type and concentration of ABZ derivatives, reaction time, etc. The obtained SAMs were fully characterized and evaluated using UV spectroscopy, atomic force microscope (AFM), ellipsometer, static contact angle and X-ray photoelectron spectroscopy (XPS). It is found that the end group property of azobenzene derivatives is critical to the obtained SAMs’ photosensitive properties. Compared with hydrophobic compounds (4-(4′-aminophenylazo) benzoic acid, ABZ-CF\(_\text{3}\)), the hydrophilic compounds (4-(4′-aminophenylazo) benzoic acid, ABZ-COOH) show excellent reversible photoswitching performance with a large contact angle change of 35° under optimized process, and the SAMs are removable by thermal treatment at 240 °C in air for only 5 min. © 2018 Chinese Chemical Society and Institute of Materia Medica, Chinese Academy of Medical Sciences. Published by Elsevier B.V. All rights reserved.

Stimuli-sensitive materials have attracted considerable attention due to their special properties in response to particular stimuli including light [1–3], pH [4, 5], heat [6–8], enzyme [9–11], etc. Light can be used as a precise stimulus through choosing suitable wavelength, intensity and polarization direction, and the resulting photosensitive materials have a wide application in lithography, optical switches, data storage [12–15]. The reported photoswitchable surface was mainly achieved by photosensitive molecules, structure of which transform with light stimuli in a certain wavelength range. Azobenzene (denoted as ABZ), a typical chromophore with two phenyl rings linked through an azo (−N=N−) bond, is versatile to construct photoswitchable and intelligent surface, and have received much attention in both fundamental research and application exploration. Azobenzene chromophores undergo isomerization from trans (E) to cis (Z) upon exposure to UV irradiation [16], resulting in significant changes in both geometry, electric dipole moment and orientation of end groups. Azobenzene isomerization from Z to E occurs when exposure to heat. This reversible transformation property enables ABZ molecules potential active component in photoelectronics, information storage, and micro/nano surface patterning. Kramer et al. [17] reported light-activated ion channels as an alternative strategy for controlling neuronal activity which achieved rapid, remote and noninvasive regulation. Jiang and coworkers [18] designed an azobenzene functionalized gold surfaces throughgrafted arginine-glycin-aspartate (RGD) peptide on polyethylene glycol (PEG)-terminated self-assembled monolayers (denoted as SAMs) which can be used for controlling mammalian cell adhesion. Rampi and coworkers [19] fabricated a series of azobenzene derivative alkanethiol SAMs on Au surface and demonstrated the excellent electrochemical behavior of azobenzene chromophores modified films with good cycling stability.

It is believed that the sort of end groups (R-group) with different geometry and hydrophobicity in azobenzene derivatives greatly influence physical and chemical properties of surface. Terfort et al. [20], developed a divergent route to synthesize a series of azobenzenealkanethiol compounds with the structure p-R\(_2\)C\(_6\)H\(_4\)N

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The SAMs formed onto gold substrate exhibit various hydrophilic and hydrophobic properties owing to the different chemical behavior of the end groups. Also there are reports about the construction of SAMs containing azobenzene chromophores as photosensitive molecules onto silicon wafer substrate. Generally, SAMs were obtained by two-step process [21,22], in which the silicon wafer surface is modified first to generate active sites, followed by grafting of photoswitchable molecules with azobenzene groups. However, the systematic investigation about factors that have influence on the property of SAMs has not been reported yet, and the reported contact angle change observed under UV and visible irradiation is usually less than 10°.

In this report, we systematically investigated the influence of silicon substrate properties, the density of coupling agent and the functional end groups on the SAMs properties. We explored a series of SAMs containing azobenzene with different end groups, including trifluoromethyl, single carboxylic acid, and double carboxylic acid. A silicon wafer surface treatment procedure was optimized and grafted with GPTS to formed epoxy-ended surfaces, and afterwards, a monolayer of azobenzene derivatives were grafted (Scheme 1). The obtained SAMs were characterized and tested using UV, AFM and contact angle. The designed SAMs exhibit an enhanced hydrophilic-to-hydrophobic transition from the cis to trans form with a contact angle change of up to 40°.

Toluene, ethanol, 3-glycidoxypropyltrimethoxysilane (GPTS, Silane Coupling Agent KH-560), dimethylsulfoxide (DMSO) and acetone were purchased from Shanghai Chemical Corp without further purification. The photoswitchable compounds 4-(4'-aminophenylazo) benzoic acid (ABZ-COOH), 4-(4'-aminophenylazo) benzenetrifluoride (ABZ-CF3), 4-(4'-aminophenylazo) 3-phenyl glutaric acid (ABZ-(COOH)2) were purchased from Shanghai Run-Biotech Co., Ltd. Silicon wafer was purchased from Sotila and cut into 1.5 cm x 1.5 cm pieces. Deionized (DI) water was used in this study.

A silicon wafer substrate was first rinsed using acetone, ethanol and water sequentially to remove impurities. The following methods were then employed in the substrate treatment, respectively. Method 1 used a mixture of H2SO4:H2O2:H2O (SPM) as the treatment solution, heating at 80 °C for 15 min. Method 2 used hydrofluoric acid (HF, 10 wt%) to treatment and followed water rinsing for next activation step. NH4OH (7 wt%) was then used to treatment silicon wafer for 10 min. Method 3 also used HF to treat silicon wafer, then a mixture solution of NH4OH:H2O2: H2O = 1:1:5 was chosen to treat wafer at 80 °C for 15 min. Finally, the silicon wafer was rinsed again by DI water and dried by pure N2. The water contact angle in air is less than 3° after above treatments, which means the silicon wafer surface was activated by surface oxidation, and ready for GPTS modification. 3-Glycidoxypropyltrimethoxysilane (GPTS) was dissolved in toluene at different concentrations of 0.1-0.4 mol/L. The silicon wafer was immersed into above GPTS/toluene solutions for 20~120 min at 25 °C, and then removed from solution and washed by CH3Cl2 and ethanol to remove GPTS residuals. The epoxy-functionalized surfaces were dried under N2 atmosphere. The designed and synthesized azobenzene derivatives were dissolved in DMSO using different concentrations from 0.1 mol/L to 0.4 mol/L. The grafting time was set 24 h at room temperature. Afterwards, the SAMs were rinsed by ethanol to remove ungrafted azobenzene residuals. The self-assembly monolayer was dried using N2 gas.

Surface spectroscopy and microscopy systems were used to test XPS at 300 W Mg-Kα irradiation. An automatic contact angle goniometer equipped with a flash camera (JC2000D1, China) was employed to measure sample surfaces by a sessile drop method at room temperature. An ellipsometer (GES-5E, Germany) was used to measure the thickness of monolayers. The thickness was measured at a wavelength of 633 nm with an angle of incidence of 75°. The 366 nm light with a flux of 11 mW/cm² was used to test photoswitchability of SAMs. AFM images were obtained by Scanning Probe Microscope (Multimode 8, America) at contact mode. UV-vis spectra of azobenzene derivatives in THF solution were measured using a UV-vis recording spectrophotometer (Lambda 750, America).

For grafting the bridging molecule GPTS, silicon substrates need to be pretreated and cleaned to remove oxides and impurity and thus generating rich surface silanol groups for the following grafting process. Various surface pretreatment methods using various mixed etching or oxidative solutions of different volume ratios, including SPM (sulfuric acid-hydrogen peroxide mixture, H2SO4:H2O2:H2O) treatment method, DHF (diluted hydrofluoric acid, HF:H2O2:H2O) treatment method [23,24] have been reported for surface pretreatment prior to modification and grafting. The

![Scheme 1. Synthesis route and photoswitching chemistry of SAMs.](image)
silicon wafer surface treatment has been proved to be a significant factor in the success of the latter grafting step. Both methods mentioned above were investigated in this study, and the surface properties of the treated silicon substrates were studied using atomic force microscope (AFM) and static contact angle measurement.

When pretreated with SPM method, the silicon substrate has a rough surface as revealed by AFM observation (Fig. 1a), and the static contact angle measurement indicated the silicon substrates remain a hydrophobic surface with a large contact angle of 121° (Fig. 1b). It is believed the oxides and impurity were not removed completely through this method, probably due to the insolubility of surface oxides like silica in the solution. After cleaned with DHF method, a hydrophilic, but rough and inhomogeneous surface was generated, which is not favorable for construction of SAMs with good continuousness (Fig. S1 in Supporting Information). Compared with above mentioned method 2, the obtained substrates pretreated with method 3 exhibit a smooth and hydrophilic silicon surface. It indicates numerous siliconol groups were generated, which is highly desirable for building uniform SAMs (Figs. 1c and d). Therefore, in this study, the silicon wafer was treated using method 3 to remove impurities and generate a hydrophilic surface.

In the following steps, the self-assembled monolayers are constructed according to Scheme 1. Firstly, the silicon wafer was further grafted with the organosilane GPTS in dry toluene at room temperature at optimal soaking time and concentration to prepare epoxy-silane films. Secondly, different kinds of azobenzene derivatives dissolved in DMSO were added to react with the epoxy-silane modified silicon wafer for 24 h. Finally, the silicon wafers were washed by ethanol for several times to remove excess azobenzene derivatives, dried in N2 atmosphere. The obtained SAM-modified surfaces were tested by UV irradiation (wavelength, 366 nm) to evaluate photoswitching properties. Epoxy-silane is a typical coupling agent to react with functional groups such as $-\text{NH}_2$, $-\text{COOH}$, $-\text{SH}$, etc.

In this study, GPTS was used as a surface modification agent to react with hydroxyl groups on the silicon wafer surface, with an accessible epoxy end group on the surface for subsequent azobenzene derivatives grafting. The formation of a high quality GPTS monolayer on the silicon surface is critical for uniform azobenzene derivatives grafting, which is complicated because of competitive reaction of GPTS with water from the air and hydroxyl group on silicon wafer surface. In the presence of water, GPTS is hydrolyzed and form solid silica particles which results in undesirable multilayer structures. Previous report by Caykara [25] revealed the key factor for this competition reaction is controlling organosilane concentration. In this work, different GPTS concentrations ranging from 0.1 mol/L to 0.4 mol/L and grafting reaction time were investigated. Fig. 2a shows the water contact angle measurement results with different GPTS concentrations (0.1–0.4 mol/L) at the selected contact time 24 h, further grafted with a fixed ABZ-CF$_3$ solution (0.4 mol/L) for 24 h. The contact angle decreased from 54° to 49° along with the increasing concentration of GPTS. At ABZ-CF$_3$ concentration of 0.1 mol/L, the water contact angle of the substrates increased with a maximum of 54° at 60 min (Fig. 2b). It indicates the grafting density increases with longer soaking time at a certain concentration. After the silicon wafer was covered over by a monolayer of epoxy-silane molecules through the Si-O-Si chemical bond, no more epoxy-silane would grow on the surface and there obtained a constant contact angle with further increasing grafting time. As a result, the optimal condition for fabrication of epoxy-terminated layers is 0.1 mol/L concentration of GPTS and 100 min as soaking time for reaction.

Since the end groups derived from azobenzene derivatives can influence the SAMs surface hydrophobicity, three different photoswitchable monomers were used to investigate the photosensitive

![Fig. 1. AFM images of silicon wafer after treatment with different methods(a, c), the corresponding contact angle (CA) test results (b, d). (a) Silica wafer was treated by using method 1 (treatment solution, H$_2$SO$_4$/H$_2$O$_2$/H$_2$O). (c) Silica wafer was treated by using method 3 (treatment solution, NH$_4$OH: H$_2$O$_2$/H$_2$O).](image1)

![Fig. 2. Variation curve of contact angle of epoxy-terminated layers further treated with ABZ-CF$_3$ with (a) different GPTS concentration (soaking time: 24 h), (b) soaking time (GPTS: 0.1 mol/L).](image2)

![Fig. 3. The chemical structures of (a) ABZ-CF$_3$, (b) ABZ-COOH and (c) ABZ-(COOH)$_2$.](image3)
surface properties. ABZ-R was grafted on the substrate by forming C—N covalent bond with epoxy group of GPTS, as shown in Scheme 1. The chemical structures of azobenzene derivatives with hydrophilic end group —CF₃ and hydrophilic end groups —COOH and —(COOH)₂ are shown in Fig. 3. The reversible photoswitching performance of ABZ-R molecules were investigated by UV spectroscopy in THF (tetrahydrofuran), shown in Fig. S2 in Supporting information. To investigate the trend of surface hydrophobicity change during the light stimuli process, water contact angle of the three ABZ-R monolayers were measured with irradiation time of 180 min under 366 nm UV light, as shown in Table 1. The water contact angle for ABZ-CF₃ significantly increased from 42° to 68° after UV irradiation for 3 h, which indicated the surface hydrophobicity was enhanced with the UV stimuli due to the trans-to-cis transition of azobenzene derivatives. Compared with the hydrophilic end group modified SAM derived from ABZ-CF₃, the hydrophilic end group grafted ABZ-COOH SAMs showed better photoswitching performance, with the water contact angles of ABZ-COOH based SAMs increasing from 35° to 70° under UV irradiation for 3 h corresponding a maximum angular variation of 35° (Table 1, Fig. 4), which is much larger than the reported water contact angle change of SAMs [24]. Such a trend is mainly attributed to the large hydrophobic difference of hydrophilic —COOH moieties and the benzene ring of ABZ-COOH, since —COOH and the benzene ring were exposed on the surface due to the trans-to-cis transition before and after UV irradiation, respectively. The water contact angle recorded with the ABZ-COOH-based SAMs surface also showed a dramatic change in wettability with prolonged exposure time. However, the water contact angle with UV exposure of ABZ-(COOH)₂-based monolayers only changed from 50° to 74°, corresponding a maximum change of 24° which indicates a weak hydrophobic-to-hydrophobic photoswitching behavior. Such a relatively poor performance is reasonable because the ABZ-(COOH)₂ with two —COOH functional groups are easier to form intermolecular hydrogen bonds, which stabilizes the trans configuration, posing hindrance for the transformation from trans to cis state [26].

The surface morphology of silicon wafer after each grafting process was investigated using AFM. As shown in Fig. S3 (Supporting information), the obtained substrate after clean and pretreatment exhibits a smooth and flat surface. After grafting with GPTS and ABZ-R, the substrate shows a uniform surface morphology (Figs. 3c and d) which indicates a successful surface grafting of GPTS and ABZ-R layer. Ellipsometry was used to measure film thickness. In the trans state, the monolayer thickness is about 2.54 ± 0.16 nm, which was tested at wavelength 633 nm and the angle of incidence is 75°. According to

Table 1

<table>
<thead>
<tr>
<th>ABZ-derivatives</th>
<th>Contact angles after UV exposure for 0-180 min</th>
<th>Max Δθ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 min</td>
<td>60 min</td>
</tr>
<tr>
<td>ABZ-CF₃</td>
<td>42°</td>
<td>48°</td>
</tr>
<tr>
<td>ABZ-COOH</td>
<td>35°</td>
<td>46°</td>
</tr>
<tr>
<td>ABZ-(COOH)₂</td>
<td>50°</td>
<td>55°</td>
</tr>
</tbody>
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Fig. 4. The contact angle (CA) measurement results of the ABZ-COOH modified surface at different UV exposure time: (a) 0 min, (b) 60 min, (c) 180 min.

Fig. 5. The molecular thickness simulation of GPTS-ABZ-COOH monolayer (calculated by Chem 3D software) [26].

the theoretical calculation by Chem 3D software, the molecular size of the trans state GPTS based azobenzene derivatives is about 2.1 nm [25]. Experimental film thickness was in good agreement with simulation analysis (Fig. 5), which illustrates a monolayer of GPTS-ABZ-COOH was formed on the silicon wafer. To further confirm the surface composition of on the surface of SAMs film, X-ray photoelectron spectroscopy (XPS) was employed to monitor the composition variation on the silicon wafer before and after removed monolayers by rapidly calcining in air.

In conclusion, a series of surface treatment methods have been studied to achieve an effective surface treatment of silicon substrates for grafting functional organosilane molecules and construction of well-defined azobenzene-derivatives-based self-assembly films. By using different azobenzene-derivatives, several types of SAMs with both hydrophobic and hydrophilic moieties were fabricated on the obtained hydrophilic silicon wafers and fully characterized. Various parameters, including the functional end groups of azobenzene-derivatives, grafting agent concentrations, incubation time, have been systematically investigated to realize an optimal grafting procedure and method. Compared with hydrophobic compounds (ABZ-CF₃), the hydrophilic compounds (ABZ-COOH) show a large contact angle of 35° under optimized conditions and excellent reversible photoswitching performance. The outstanding performance of the hydrophilic photo-responsive molecules-based SAMs in controlling the surface wettability via molecular orientation makes them good candidates for various potential applications in high-density data storage, patterned printing, bio-adsorption and so on.

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