Fast Photo-Switched Wettability and Color of Surfaces Coated with Polymer Brushes Containing Spiropyran

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Received 18 January 2010; accepted 20 September 2011
DOI 10.1002/app.36254
Published online 28 December 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: An intelligent photo-responsive spiropyran (SP)-contained surface that combines reversible wettability conversion with photochromic behavior was prepared on etched silicon substrates by atom transfer radical polymerization. The heterocyclic ring cleavage of SP moieties under UV irradiation leads to the change of the surface wettability and color. Water contact angle (CA) of the prepared surfaces change from 138.8° ± 1.3° to 42.7° ± 1.7° after 5 min under 365 nm UV irradiation and recover to its original state after 20 min of visible light irradiation, accompanied by the color change between yellowish and purple. To our knowledge, this result is the highest and fastest CA variation reported for surfaces containing SPs.
 J Appl Polym Sci 125: 870–875, 2012

Key words: atom transfer radical polymerization; photo-responsive; morphology; spiropyran; wettability

INTRODUCTION

The wettability of solid surfaces is a very important property depending on the chemical composition and the geometric structures of the surfaces.[1–8] Recently, great attention has been paid to the surfaces with reversibly controlled wettability in various fields, such as drug-delivery systems, sensors, actuators, and microfluidic devices.[9–11] Photo-responsive materials ranging from inorganic nanomaterials to small organic molecules have been widely studied. For example, some semiconductor oxides, such as TiO_2, ZnO, SnO_2, and WO_3, exhibit photoinduced reversible wettability conversions.[12–16] This phenomenon is due to the mechanism that involves photogenerated electrons and holes as well as absorbed water.[17] In addition, several kinds of organic compounds and their derivates, such as azobenzenes, spiropyrans (SPs), and cinhamates,[18–24] have a photoinduced transformation between two chemical configurations. This may lead to the changes of molecular polar and surface-free energy that result in a transition of surface wettability accordingly. However, the reported photoresponsive surfaces consist of either inorganic or organic compounds that have some disadvantages to some extent. The main problem for inorganic-oxide-based surfaces is their low response speed to light stimulus. For inorganic oxides, the response time to UV irradiation range from several tens minutes to 2 or 3 days. And the reversible process usually takes much longer time from several days to several weeks. As to the organic-compound-based surfaces, the changes of contact angle (CA) induced by UV irradiation are narrow, which are inadequate to be put into a practical use. Lim et al.[25] fabricated a photoswitchable nanoporous multilayer film with wettability reversibly switched between superhydrophobicity and superhydrophilicity response to the UV–vis irradiation, but the photoresponsive moiety of the film is fluoro-contained. Therefore, it is still a challenge to fabricate a surface with large CA change and high-response speed induced by light stimulus.

In this work, we fabricated an intelligent photo-responsive SP-contained surface that combines reversible wettability conversion with photochromic behavior. The change of CA was amplified by increasing the roughness of the substrates with hierarchical micro/nanostructures. The water CA on the prepared film changed from 138.8° ± 1.3° to 42.7° ± 1.7° when exposed to UV-irradiation for only 5 min. The wettability recovered to its original state by

Additional Supporting Information may be found in the online version of this article.

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Contract grant sponsor: National Nature Science Foundation of China; contract grant number: 51173099.

Contract grant sponsor: National Key Basic Research and Development Program of China; contract grant numbers: 2009CB930602, 2011CB935700.

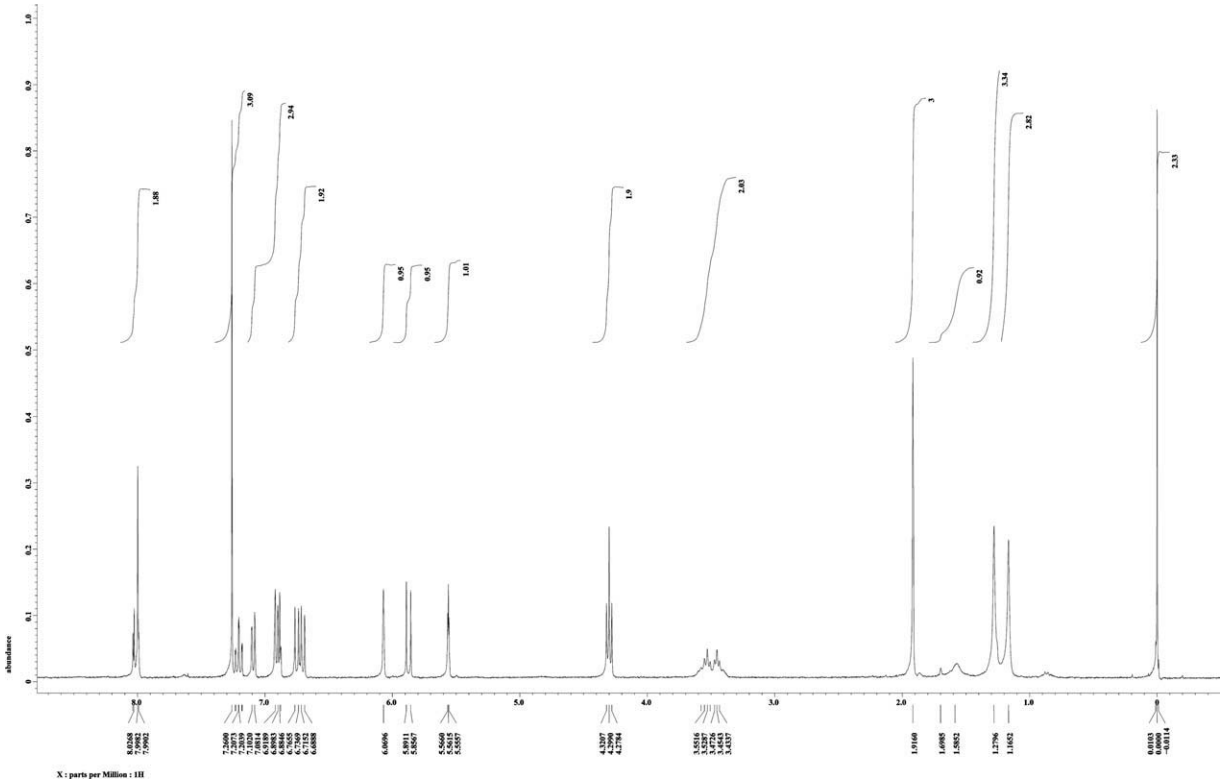


Figure 1 ^{1}H-NMR ($CDCl_3$, 300 MHz) spectra of spyropiran monomer. δ = 1.17(s, 3H), 1.28(s, 3H), 1.92(s, 3H), 3.45–3.55(m, 2H), 4.30(t, 2H), 5.56(d, 1H), 5.87(d, 1H), 6.07(s, 1H), 6.73(q, 2H), 6.89(q, 2H), 7.09(d, 1H), 7.18–7.28(m, 1H), and 7.99–8.03 ppm(m, 2H).

visible irradiation for about 20 min or being kept in the darkness for hours. At the same time, the SP-contained thin film shows color change between yellowish and purple.

EXPERIMENTAL

Chemicals

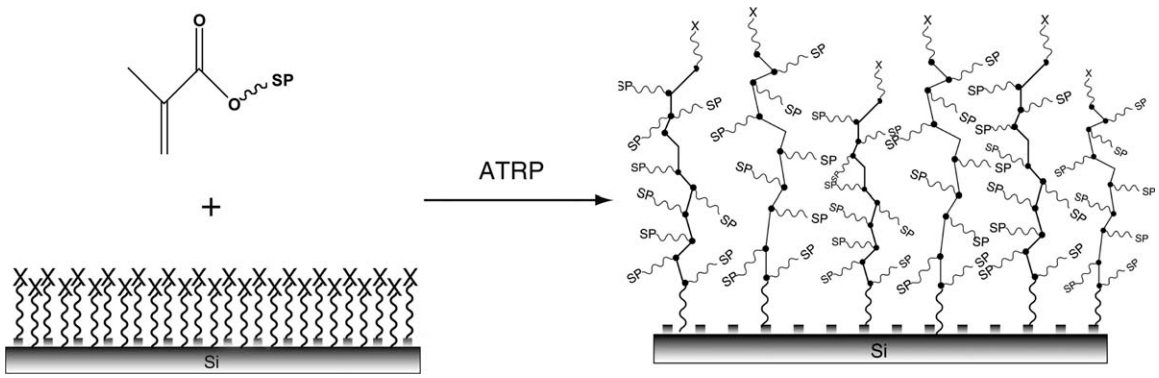
3-Aminopropyl-trimethoxysilane and α-bromoisobutyryl bromide were purchased from ACROS and Fluka, respectively. CuBr and *N,N,N′,N′,N′′*-pentamethyl diethylenetriamine were purchased from Aldrich. 1′-(2-Hydroxyethyl)-3′,3′-dimethyl-6-nitrospiro (2H-1-benzopyran-2,2′-indoline; SP alcohol) was purchased from the Nankai University Fine Chemical Laboratories. Other reagents and solvents were purchased commercially as analytical grade quality.

Synthesize of the SP monomer

The monomer 1′-(2-methacryloxyethyl)-3′,3′-dimethyl-6-nitrospiro-(2*H*-1-benzopyran-2,2′-indoline) (SP) containing functional C═C bond was synthesized by an esterification between methacryloyl chloride and 1′-(2-hydroxyethyl)-3′,3′-dimethyl-6-nitrospiro-(2H-1-benzopyran-2,2′-indoline) (SP alcohol) catalyzed by triethylamine. The SP alcohol was mixed in dichloromethane with triethylamine. The mixture was stirred and cooled to 0°. The methacryloyl chloride was added dropwise to the mixture within 1 h at this temperature. Then, after being stirred for 12 h at room temperature, the mixture was dried with a rotary evaporator. The products were separated by passing through a silica gel column to get the yellowish SP monomer with mobile phase of petroleum ether/ethyl acetate (21 : 1). Finally, the crude product was recrystallized from acetone and petroleum ether. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 1.17 (s, 3H), 1.28 (s, 3H), 1.92 (s, 3H), 3.45–3.55 (m, 2H), 4.30 (t, 2H), 5.56 (d, 1H), 5.87 (d, 1H), 6.07 (s, 1H), 6.73 (q, 2H), 6.89 (q, 2H), 7.09 (d, 1H), 7.18–7.28 (m, 1H), 7.99–8.03 ppm (m, 2H) (Fig. 1). MS: m/z = 421.

Graft of the poly (SP) thin films via ATRP

The poly (SP) thin films were grafted from flat silicon substrates, roughly etched silicon substrates and quartz slices via atom transfer radical polymerization (ATRP; see Scheme 1). The synthesis was operated through the following steps: first, immersed clean substrates in NaOH solution (0.1*M*) and then in HNO_3 (0.1*M*) to generate hydroxyl groups on the surface. Second, after being washed thoroughly with



Scheme 1 Atom transfer radical polymerization from silicon substrate with initiator grafed on the surface. The scheme shows polymerization of the SP monomer from the silicon substrate with initiator grafted on the surface in THF containing pentamethyldiethylenetriamine and Cu Br.

abundant distilled water and dried under a nitrogen flow, the substrates were immersed in a methanol solution that contained 5 wt % aminopropyl trimethoxysilane (ATMS) for at least 10 h to obtain chemically bonded-NH_2 groups on the surface. Third, after removing the residue ATMS on the surface by rinsing the substrates with methanol and dichloromethane, the substrates were immersed in dry dichloromethane that contained pyridine (2% v/v). The polymerization initiator α-bromoisobutyryl bromide was added dropwise to the solvent containing the substrates at 0°C, and the mixture was left for 1 h at this temperature then at room temperature for 12 h. Finally, the substrates were cleaned with dichloromethane, and the polymerization was accomplished by immersing the substrate with initiator grafted on the surface in a degassed solution of SP in THF containing CuBr and pentamethyldiethylenetriamine for 6 h at 65°C.

Characterizations

The surface morphology of the film was characterized by FE-SEM (JSM-6700F, JOEL). The photos of the quartz slice were taken by digital camera. Water CAs were measured with an optical CA meter (OCA20, Dataphysics) at room temperature. X-ray photoelectron spectra were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300-W Mg Kα radiation. The NMR measurements were carried out on an NMR spectrometer (Bruker DMX-30, Bruker Spectrospin) using $CDCl_3$ as the solvent and TMS as the interior label. Mass spectrometry was recorded on a Bruker ESQUIRE-LC electro-spray mass spectrometry.

RESULTS AND DISCUSSION

SPs, as typical photo-responsive organic materials, have been widely studied for their potential applications to sensors, optical switchings, memories, three-dimensional data storage, microfabrications, etc.,[22,23,26,27] but few reports concerning the wettability of films composed of or containing SP. For most previous studies of surfaces containing SP or its derivates, the CAs changed slightly and in hydrophobic state.[28–30] Moreover, dual photoresponsive surfaces altering both wettability and color have rarely been discussed. However, it is very important in many applications, such as smart windows, microfluidic devices, and bioanalysis.

Surface-initiated atom-transfer radical polymerization was used to fabricate photo-responsive poly (SP) thin films on flat silicon substrates, roughly etched silicon substrates and quartz slices. Through a grafting-from approach, the number of functional groups present on the surface can be greatly enhanced by connecting large polymer molecules with functional groups of each monomer repeat unit to the surface. It can be used to amplify the stimuli-responsive nature of the polymer coating at the surface.[31]

Morphology of the surface is another important factor that affects the surface wettability. The rough surface of silicon substrate was obtained by a facile laser-etching method.[32] When the quadrate laser pulse struck the silicon surface, a pit will form, and, at the same time, the dispersed SiO_2 nanoparticles splashed onto the top, sidewall of the pillars, and the bottom between the pillars. The morphologies of the poly (SP) film grafted from the silicon substrates characterized by SEM are shown in Figure 2. The images show the hierarchical micro- and nanostructures of the surface. The top area of each pillar is about 20 μm × 20 μm. The pillars are about 7 μm high.

XPS analysis was performed to confirm the graft of initiator and polyspiropyran [poly (SP)] from the Si surface (see Supporting Information Fig. S1). It can be found that the intensity of N and C changed obviously for different surfaces. For the etched

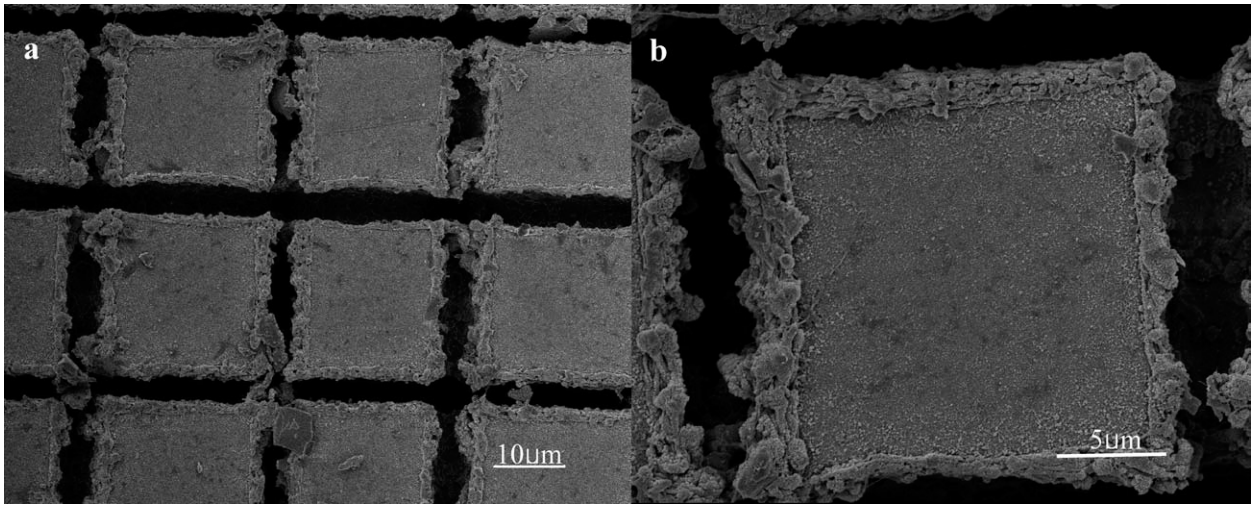


Figure 2 (a) SEM image of the as-prepared surfaces. (b) Magnified part of (a).

wafer, only C1*s* (284.8eV), Si2*p* (~ 99.3 eV for elemental silicon, and ~ 103.0 eV for oxidized silicon), Si2*s* (~ 155.0 eV), and O1*s* (~ 532 eV) were detected. For wafers with initiator, the new peaks of N1*s* (~ 399.9 eV) and Br3d (~ 69 eV) were detected, whereas there was no these peaks for freshly etched Si wafer without any modification. For wafers with poly (SP), the ratio between intensities of C1*s* and Si2*p* increased compared to wafers with initiator, which means successful polymerization of SP from the surfaces. Decomposition of the experimental C1*s* profile was performed for different types of carbon atoms in SP molecules. There were three fitting components centered at 284.8, 286.0, and 288.3 eV (Fig. 3). The main peak at ~ 284.8 eV corresponds to aliphatic and aromatic hydrocarbon backbone and also contaminant containing C. The C1*s* peak at ~ 286.0 eV belongs to the C atom bond to N and O, and the peak at ~ 288.3 can be assigned to the spiro C in the closed form of SP.

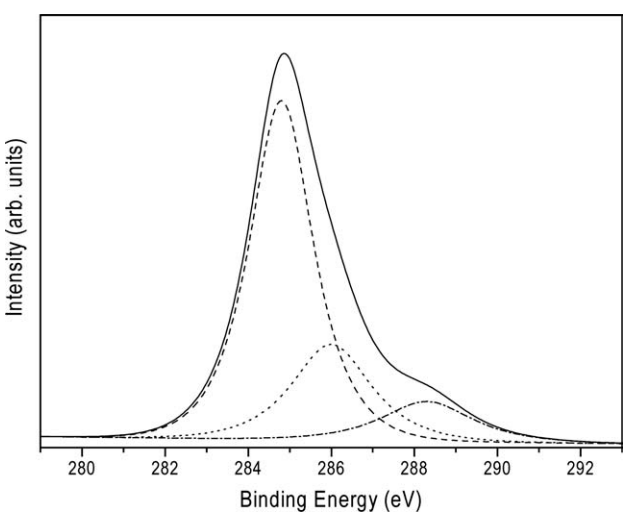


Figure 3 Decomposition of the C1*s* profile of XPS analysis for poly SP film. The main peak at ~ 284.8 eV corresponds to aliphatic and aromatic hydrocarbon backbone and also contaminant containing C. The C1*s* peak at ~ 286.0 eV belongs to the C atom bond to N and O, and the peak at ~ 288.3 can be assigned to the spiro C in the closed form of SP.

A quartz slice was coated synchronously with the silicon substrate to show the conversion between the two states of the SP directly (Fig. 4). It was found that as soon as the UV light irradiated on the surface, the quartz's surface took on a purple color. That means that the SPs undergo a transition from a closed form to an open-ring form (merocyanine) through a heterocyclic ring cleavage caused by the UV irradiation. With the irradiation time continuing, the color increased obviously. It should be noted that the film is optically transparent. After being irradiated by visible light or kept in the darkness for several minutes, the reverse process occurred, and the slice turned back to yellowish.

The water CAs were measured to characterize the wettability of the prepared surfaces on rough silicon substrates. The shape of the water droplets is shown in Figure 5. It can be seen that the water CA of the fabricated surface is ~ 138.8° under visible irradiation, while the CA of the prepared smooth silicon surface with poly (SP) was ~ 87° (see Supporting Information Fig. S2). It means that the hierarchical micro/nanostructures of the substrate enhance the hydrophobic character. When the prepared rough surface was exposed to 365 nm UV light for 5 min, the water CA decreased to ~ 42.7°. Although when the surfaces were irradiated by visible light for 20 min or stored in the dark for hours, the CA came back to the original. This interesting phenomenon is due to the responsive group of SP. Under visible light, the SPs are in a colorless, "closed," and nonpolar form and exhibit water repellency. The

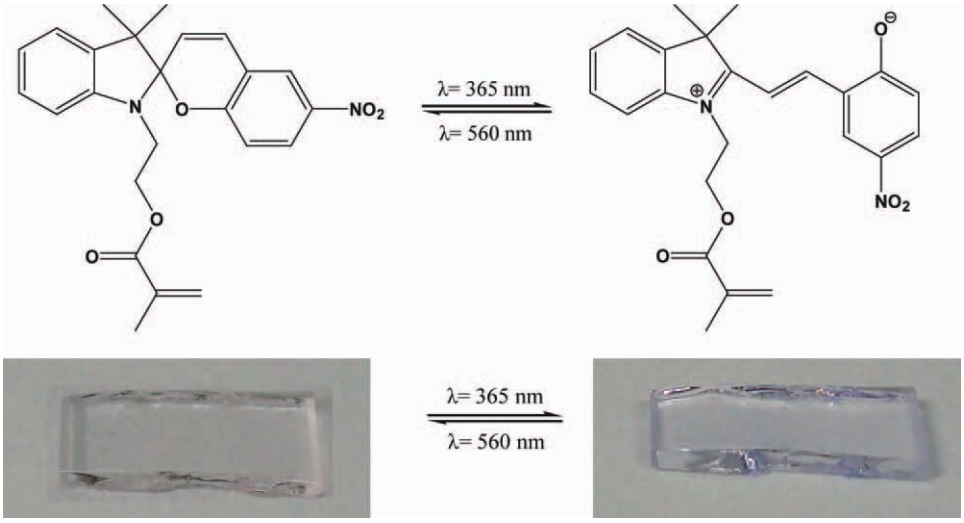


Figure 4 Spiropyran coated quartz slices before (yellowish) and after (purple) UV irradiation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

introduction of the rugged nanoprotrusions on the surface results in more hydrophobic state. This phenomenon can be attributed to the air trapped under the drop at the recessed regions of the surface. When exposed to 365 nm UV light, the SPs molecules undergo a C—O bond cleavage transformation into a colored, open, and high-polar form. This interchange happened on both the top and the side of the pillars, which induce the increase of polarity and hydrophilicity of the surface. There is a time difference between the reverse procedures under visible light for 20 min and stored in the dark for hours. The reverse procedure under visible light may be caused by both photochromic and thermochromic at the same time, while when the surface was kept in dark, thermochromic plays an important role in the change of the CAs. Wang et al.[16] reported the preparation of nanostructured tungsten oxide films with wettability and photochromic dual-responsive properties for the first time. However, the response time is still a bit longer, and the color change is not obvious that can be only observed by UV spectra. The present study of fast photo-switched wettability and color of surfaces may broaden the application of smart surfaces with special wetting property.

CONCLUSIONS

In summary, methacrylate polymer brushes containing SP were grafted from silicon and quartz substrates using ATRP. The smart property of the surfaces is realized by alternating UV-irradiation and visible light irradiation or dark storage. The water CA of the surface of rough silicon substrates changed from 138.8° ± 1.3° to 42.7° ± 1.7° after 5 min under 365 nm UV irradiation and changed back after 20 min of visible light irradiation, which is, to the best of our knowledge, the best results reported for surfaces containing SPs with property of photo-induced reversible wettability and color change. This study may provide the prospect of meeting the

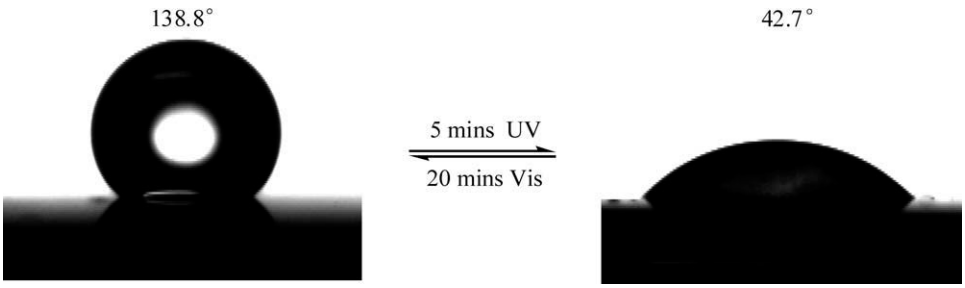


Figure 5 Water droplet profiles on the as-prepared SP-contained silicon substrates before and after UV-irradiation. Water CA of the surface is ~ 138.8° under visible irradiation and decreased to ~ 42.7° when exposed to 365 nm UV light for 5 min. The CA came back to the original when the surfaces were irradiated by visible light for 20 min.

demands of intelligent photoswitches and expanding the applications of SP and its derivates.

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