Research Article

Noncovalent Spiropyran Coatings for Photoinduced Wettability Switching

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The noncovalent binding of spiropyran to candle-soot-covered surfaces is investigated for wettability switching using a coating procedure realized with a drop casting process of using 0.001 mol/L spiropyran in a 5 : 1 toluene-acetone mixture. Scanning electron microscopy images reveal a resulting surface with spiropyran flakes in the candle soot. A reversible switching with UV light and blue or green light is achieved, starting from an initial contact angle of $130° \pm 9.68°$. The highest contact angle difference is $41°$ and reversibility has been shown for several switching cycles. Hence, our methods provide an easy-to-use strategy to generate surfaces with switchable wettability.

1. Introduction

The behavior of photochromic molecules on surfaces has been of interest in research since many years given their ability to spatially influence physical properties, such as surface binding or wettability. A technology that allows a simple control of these properties would open new opportunities in bioapplications and sensing applications [1, 2]. Typically, photochromic molecules possess two isomeric states. They switch between these states upon irradiation with light of a specific wavelength. Due to the different dipole moments of each isomer, different contact angles of water droplets are realized on surfaces [1, 3–5]. For surface stability reasons, covalent binding of photochromic molecules to surfaces is typically preferred [6].

Photoinduced wettability changes have been demonstrated for the most commonly studied chromophores azobenzene [7–10] and spiropyran [5, 6]. Covalently bound azobenzenes on silicon surfaces with a nanoscale roughness [9] and on silicon dioxide nanoparticles in a polyelectrolyte matrix [8] allowed for contact angle differences ranging up to

$150°$. On the other hand, azobenzene is quite toxic and shows only a moderate dipole change [7].

Spiropyran undergoes a structural change upon irradiation with ultraviolet (UV) light to the zwitterionic merocyanine, as shown in Figure 1. Its significant increase in dipole moment allows realizing different wettability states on surfaces. Backswitching to spiropyran is achieved by visible light or thermal relaxation, which also means that merocyanine is often not a stable molecule at room temperature. This switching has only been demonstrated for spiropyran mixed into solvents [11], host polymers [12–15], or single molecule layers [16, 17], where steric hindrances are reduced. In its solid crystalline form switching has not been reported.

Switchable surfaces with spiropyran did not show similarly high contact angle differences as with azobenzene so far. Spiropyran was used in structured matrix materials to enhance the switching effect. By this method, a contact angle difference of $10°$ to $18°$ could be shown [18, 19]. Covalently bound spiropyrans on surfaces produced a wettability change of $11°$ to $14°$ [17] on flat surfaces and about $22°$ [20] on structured surfaces such as silicon nanowires. Only with
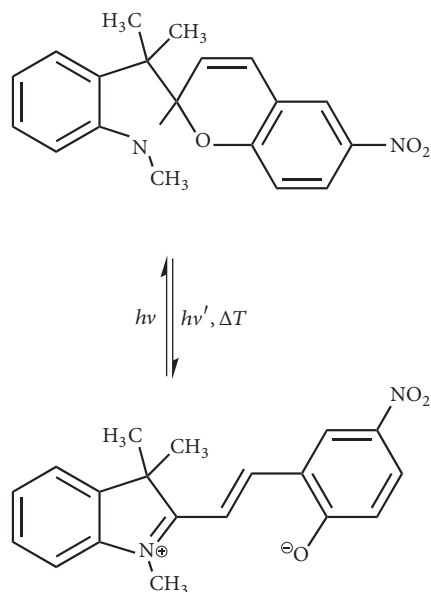
FIGURE 1: Isomerization of spiropyran (top) to merocyanine (bottom).

the use of additional cobalt(II) ions for enhancing the merocyanine form, larger contact angle differences of 32° to 35° were achieved [16, 21]. Noncovalently bound layers are easier to prepare and require less effort on the chemical side. Noncovalently bound spiropyran has been used in combination with graphene [22] and nanotubes [23] to prevent an influence of the electrical properties of the substrate material. Such an influence is more likely for a covalent binding.

Spiropyran has the advantage of being much less toxic than azobenzene and is therefore safer for practical applications. We utilized this in former experiments and observed a contact angle change when spiropyran is switched to merocyanine by UV light. No backswitching of the contact angle could be seen in that study [24].

Here we employ the same coating procedure to bind a thin layer of spiropyran to a candle-soot surface. Candle-soot surfaces can be quickly prepared, are known to exhibit superhydrophobic properties, and are thus promising for contact angle switching [25]. The carbon particles create a complex nanostructure allowing a water droplet to form embedded air cushions and the structure of the candle soot enlarges the contact angle difference of the spiropyran forms [26, 27]. From scanning electron microscopy (SEM) images, the spiropyran deposited on candle-soot surfaces is deposited in the form of flakes. We demonstrate reversible contact angle switching between both molecular states for such spiropyran-coated candle-soot surfaces, which are easy to fabricate and can be switched several times. We see even higher contact angle changes than described in former publications with covalently bound spiropyran [16, 17, 20, 21].

2. Materials and Methods

2.1. Materials.
Ethanol, toluene, and acetone were purchased from Carl Roth. The starting materials for the spiropyran were bought from Sigma Aldrich.

2.2. Synthesis of 1′,3′-Dihydro-1′,3′,3′-trimethyl-6-nitrospiro-[2H-1-benzopyran-2,2′-[2H]indol] (Spiropyran).
The spiropyran is prepared according to well-known synthesis instructions [28–30]. 3.47 g (20.0 mmol) 2-methylene-1,3,3-trimethylindoline and 3.34 g (20.0 mmol) 2-hydroxy-5-methylbenzaldehyde in 70 mL ethanol are refluxed for 5 h. After cooling down to room temperature the deposit is filtered and washed with cold ethanol. Then the product is dissolved in ethanol, heated, cooled to room temperature, and again filtered and washed. The final product has a light green to brown color: yield: 2.83 g (42%); ^{1}H-NMR (200 MHz, CDCl$_3$, TMS): δ = 8.05–7.98 (m, 2H), 7.20 (td, [3]J = 7.5 Hz, [4]J = 1.4 Hz, 1H), 7.13–7.04 (m, 1H), 6.92 (m$_c$, 1H), 6.88 (td, [3]J = 7.5 Hz, [4]J = 1.0 Hz, 1H), 6.77 (m$_c$, 1H), 6.56 (d, [3]J = 7.5 Hz, 1H), 5.86 (d, [2]J = 10.4 Hz, 1H), 2.74 (s, 3H), 1.30 (s, 3H), 1.19 (s, 3H) ppm.

2.3. Sample Preparation.
Microscope glass slides ($25 \times 26 \times 1$ mm^3) are held over the flame of a candle until a fully opaque layer of soot is deposited. The samples are placed in a glass Petri dish (diameter 100 mm) on a hotplate. 25 mL of toluene with 0.001 mol/L of the freshly synthesized spiropyran is filled carefully into the Petri dish, which is then covered with a lid dish. Next, 5 mL acetone is added to the mixture. The Petri dish is covered with a lid dish and Parafilm is used to produce a small gap between the upper and the lower glass dish for control of the solvent evaporation rate. The hotplate then is heated to 40°C to increase the evaporation of the solvent mixture, which is completely evaporated after 90 min. For spectroscopic measurements with the spiropyran layer, the spiropyran is also deposited on an uncoated and thus transparent polyethylene terephthalate (PET) foil.

2.4. Wettability Measurements.
The contact angle is measured with a Dataphysics OCA 50AF in the sessile drop method. First, a water droplet is positioned on top of the surface and, after 60 s, when the droplet is fully rested, the contact angle measurement is performed. The droplet is then removed and the surface exposed to light before the next measurement is performed.

2.5. Irradiation of the Samples.
The surfaces are illuminated with UV light for 100 s (Nichia NSCU033B LED, 365 nm) to switch from spiropyran to merocyanine and with blue (Luxeon LXML PR01 0500 LED, 448 nm) or green (Cree XP-E LED, 525 nm) light for 300 s for the backswitching. The longer irradiation periods are chosen to compensate for the lower radiant flux. The UV LED by Nichia is used with a lens resulting in a radiant flux of 96 mW/cm^2 on the sample surface, while the blue LED applies only 25 mW/cm^2 to the sample.

2.6. Morphology and Mechanical Characterization.
For the preparation of images with a scanning electron microscope (SEM), a 30 nm layer of silver is evaporated on a few samples. The used SEM is a Supra 55VP by Zeiss. The stability of the surface is tested with a scratch test, putting an adhesive test on
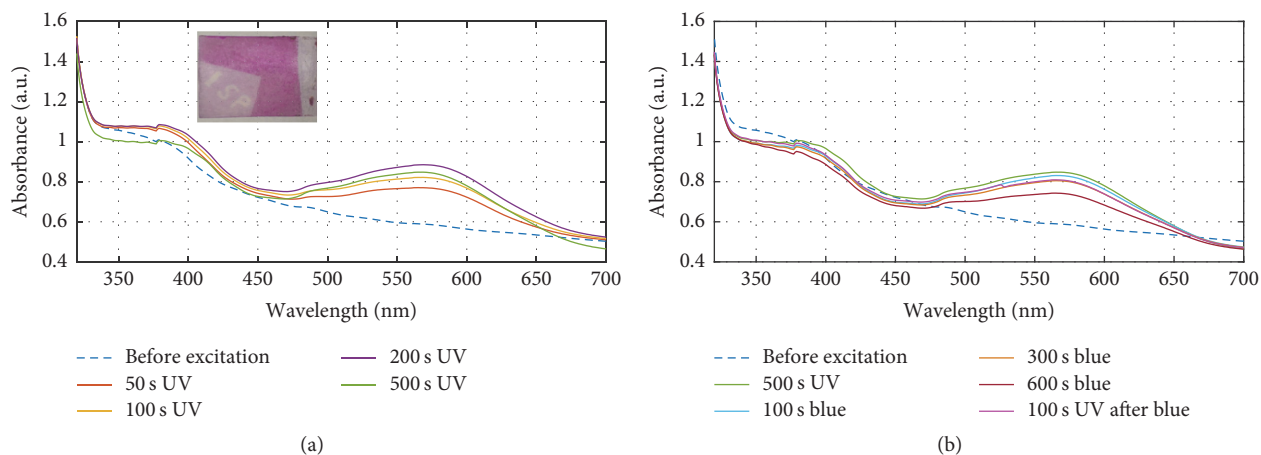
Figure 2: Measured absorption of a spiropyran layer on a PET foil; excitations were performed in the same sequence as shown in the legend; (a) UV exposure; inset: spiropyran-covered PET foil after first UV excitation partly shadowed with a simple mask such that only the lower left corner was covered during the exposure; (b) irradiation with blue light after UV exposure.
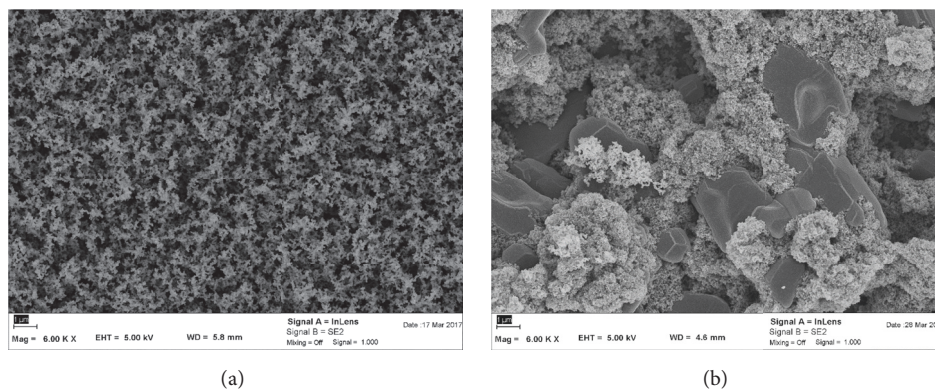

Figure 3: SEM images of candle-soot structure without (a) and with spiropyran coating (b).

the surface and removing it, and with putting a sample under flowing water from a tap.

2.7. Spectroscopic Measurements. The changing absorption of the spiropyran layer was measured with a Perkin Elmer Lambda 650 photospectrometer. For the excitation of the spiropyran layer, the same UV and blue LEDs as for the wettability measurements are used.

3. Results

As the candle soot is a highly absorbing material, it is not possible to see the typical color change of the spiropyran during the switching to merocyanine. For this reason, an uncoated PET substrate is additionally functionalized the same way as the candle-soot surfaces. This allowed performing absorption measurements with a photospectrometer and the results are plotted in Figure 2. The inset in Figure 2(a) shows the homogeneous functionalization on this surface. The sample is first stepwise illuminated with UV light up to 500 s and the measurements show that there is a clear photodegradation after the last UV exposure step (Figure 2(a)). A complete

backswitching to the state before the initial excitation is not possible (Figure 2(b)), not even after weeks of exposure to visible light or heat.

The SEM image in Figure 3(a) shows the obtained candle-soot structure without the spiropyran. On this surface, we measure contact angles with at least 150°, which is in agreement with literature [25].

After the deposition of the spiropyran from the toluene-acetone mixture, there are grayish sediments on top of the surface (Figure 4(a)) and the contact angle on the surface is slightly reduced to around $130° \pm 9.68°$ (Figure 4(b)). Figure 3(b) depicts how the spiropyran is attached on top of the carbon-soot structure coated from the solvent mixture. The molecules form small flakes on the surface, while the form of the flakes varies over the surface and most them are found close to the edges, which correlates with the grayish sediments (Figure 4(a)). Using irradiation with UV light, the droplet contact angle is reduced within seconds to a minimum value. The final state is reached after 2 min of irradiation at latest, which can be seen in Figure 4(b). This stands in contrast to the photoexcitation experiments on the
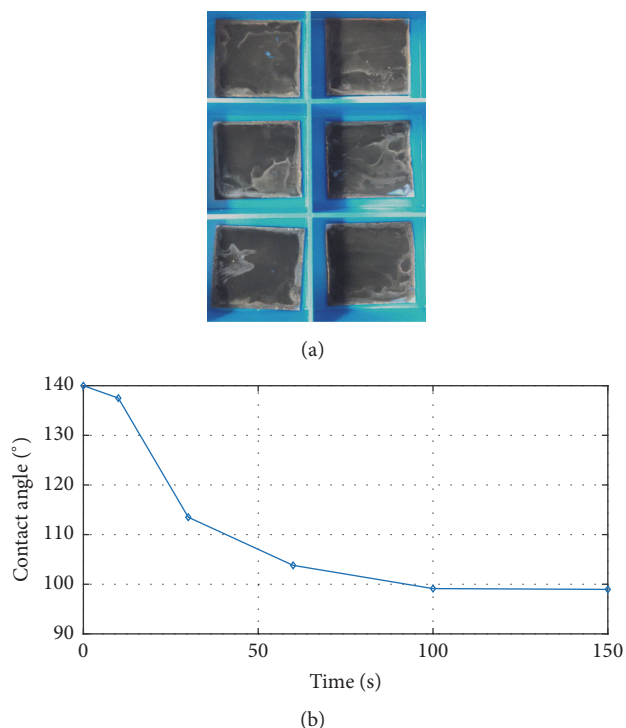
(a)

(b)

FIGURE 4: (a) Candle-soot samples with spiropyran coating; (b) contact angle measurement with stepwise UV excitation.
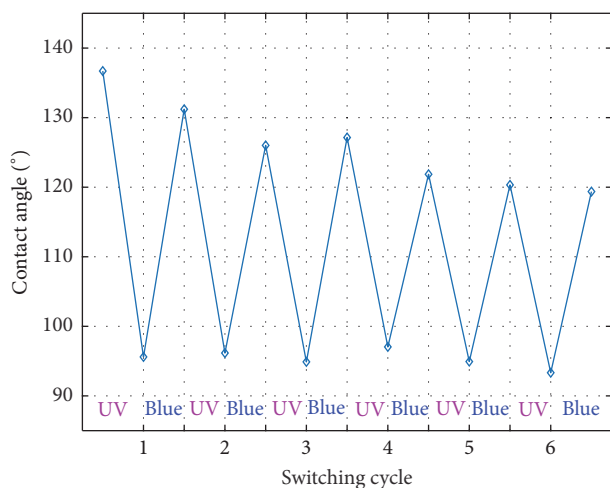

FIGURE 5: Contact angle measurement of water droplets on the spiropyran-coated candle-soot surface for alternating UV and blue light irradiation. Droplets are removed before irradiation. Droplet positions remain unchanged.

PET substrates where the maximal photoconversion is not achieved after just 2 min UV irradiation (Figure 2(a)).

A switching of the contact angle can be almost always observed and works best towards the edges of the sample, but the contact angle difference varies from about 10° to the given maximum of 41° (140° to 99°, Figure 4(b)). Figure 5 plots an example for a contact angle measurement with repeated

switching. Each measurement is performed on the same position of the sample. A slow decrease of the spiropyran contact angle is observed, while the contact angle of the merocyanine state stays in the same range. The backswitching occurs slowly at room temperature with about 2.5° per minute. With the blue light irradiation, this process is accelerated significantly; also with green light the merocyanine returns to spiropyran faster. For red light illumination no effect is observed. This is consistent with the behavior of spiropyran in solutions [11, 21].

The mechanical stability of the produced switchable surfaces is tested with a scratch test and an adhesive tape test. The scratch test shows that candle soot can easily be removed from smooth surfaces but the edges where a lot of the deposited material is found are a bit more robust (Figure 6(a)). In the adhesive tape test, we observe that parts of the functionalization are lifted off (Figure 6(b)). On the other hand, the surface is quite robust against water. A normal stream of water out of the tap cannot destroy the surface (Figure 6(c)) and afterwards the contact angle switching is still possible.

4. Discussion

We demonstrate reversible contact angle switching for non-covalently bound spiropyran molecules. Due to an inhomogeneous coating of surfaces with the candle soot and the spiropyran, the resulting contact angle difference deviates from sample to sample, but there is always a measurable switching observed. The inhomogeneity is mainly an effect of the inexact candle-soot deposition by hand that is hard to control and this results in different thicknesses, where the evaporation of the solvent is different. As the switching works best close to the edges of the sample where also most of the flakes can be seen under a SEM, these flakes seem to be important for the switching. It would be interesting to investigate the influence of the flake form on the contact angle, but this would require more effort in enhancing the homogeneity first. Currently, the areas covered by the same flake forms are too small to conduct these measurements. This will be shown in future studies. On precisely defined surfaces with structures comparable to the candle soot, a much better homogeneity of the contact angle difference is expected. Such defined structures could be achieved by using, for example, a lithographic process or a layer-by-layer technique [8]. The functionalization is already controlled such that a homogeneous surface is obtained. This is demonstrated by the functionalization of a PET substrate (inset Figure 2(a)).

The illumination time to switch from spiropyran to merocyanine and back is just a few minutes which is relatively short but the contact angle measurement on the candle soot and the absorption measurement reveal different excitation periods to achieve a steady state. This might be also due to structural and chemical differences of the substrates. The slow degradation of the surface, shown by a decreased contact angle in the spiropyran state, is most likely caused by photochemical degradation of the photochromic molecule [6]. This problem might be overcome by the usage of another spiropyran which includes an antioxidant group as these
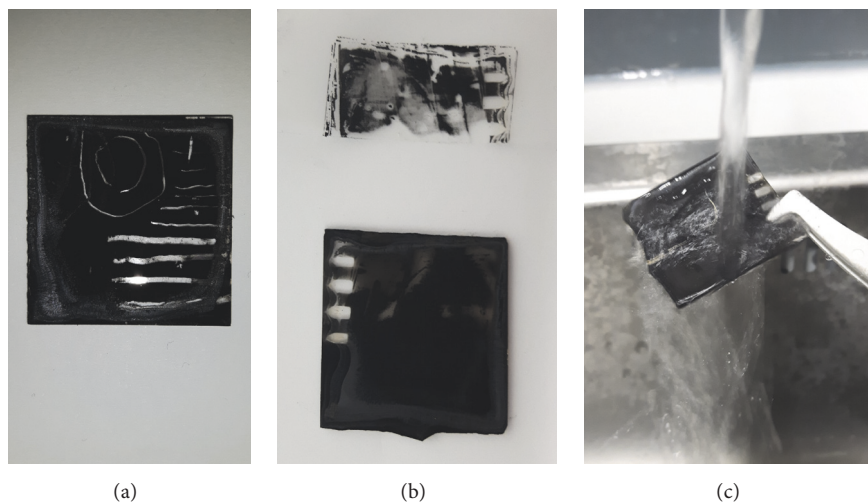
FIGURE 6: Surface stability tests: (a) sample after scratch test; (b) sample (bottom) after attaching and peeling off an adhesive tape (top). The transparent regions are due to holding the samples with tweezers in the candle-soot coating process. (c) Sample under flowing water.

groups are able to prevent degradation of the spiropyran [31]. The additional use of cobald(II) ions might even further reduce the contact angle in the merocyanine state [16, 21] and thereby increase the total contact angle difference.

Although covalently bound azobenzenes show extremely nice switching behavior combined with a suitable structure [8, 9], they have the problem of being more toxic and a covalent binding is generally a more complex surface coating procedure. Our method is simple and less toxic than an azobenzene-based functionalization at a similar or even better switching performance compared to processes where spiropyran was covalently bound to a structured surface [17–21]. As the functionalization is robust towards flowing water, it is well suited for the use in fluidic systems.

5. Summary and Outlook

We functionalized candle-soot-covered glass substrates with spiropyran by a simple drop casting procedure. A 5 : 1 mixture of toluene and acetone as solvent for the spiropyran allows for photoinduced reversible wettability switching with contact angles differences up to around 40°. Although the homogeneity of the coated substrates is low, the switching performance of our very simple preparative approach can compete with results on surfaces with covalently bound spiropyran. Therefore, the described method is an option for systems where a direct chemical bonding to substrate layers is undesired. Due to stability towards flowing water, the usage in fluidic systems, that is, for motion and droplet control, is a future application. Next, the homogeneity of these surfaces has to be increased and the degradation reduced. For an improved surface stability, artificial structures similar to candle-soot structures seem most promising. Furthermore, a study regarding the degree of structuring necessary for switching is interesting. In general, artificial structures promise a much better control of the evaporation of the solvents. The synthesis of a new spiropyran with an antioxidant group will also help to prevent the degradation.

Conflicts of Interest

The authors declare that they have no conflicts interest.

Acknowledgments

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