

Photo-switched wettability on an electrostatic self-assembly azobenzene monolayer†

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A simple electrostatic self-assembly technique was used to fabricate a photo-switched azobenzene monolayer, on which superhydrophobicity and a large reversible CA change could be realized.

It is known that the photo-switched *trans* and *cis* isomers of azobenzene correspond to different dipole moments and surface wettability. Ichimura *et al.* reported light-driven motion of liquids on a flat substrate surface modified with photochromic azobenzene units prepared by the chemisorption self-assembly technique.¹ By the same technique, Brittain and co-workers prepared another kind of azobenzene monolayer, on which the observed change of contact angle (CA) is less than 10° after ultraviolet (UV) irradiation.² Feng *et al.* fabricated an azobenzene polymer film through Langmuir–Blodgett (LB) technique, on which the change of CA is about 10°.³ Although the wettability of azobenzene has attracted great attention, the change of water CA of azobenzene so far reported is limited, almost no more than 10°. Meanwhile, comparing with the chemisorption and LB technique, electrostatic layer-by-layer self-assembly has been considered as a simple, versatile, and effective technique for fabrication of ultra thin organic films by alternately dipping substrates into dilute solutions of cationic and anionic polyelectrolytes.⁴ Rubner *et al.* have fabricated superhydrophobic (CA larger than 150°) polyelectrolyte multilayers through electrostatic self-assembly by coating the highly textured multilayer surface with a semifluorinated silane.⁵ In this communication, a superhydrophobic electrostatic self-assembly azobenzene monolayer is described in which the introduction of roughness structures on the substrate surface results in a large reversible change of wettability (the change of water CA about 66°) after UV and visible (Vis) irradiation.

Azobenzene polyelectrolytes are suitable materials for fabrication of ultra thin organic films through electrostatic self-assembly technology.^{4b,c} Poly{2-[4-phenylazophenoxy] ethyl acrylate-co-acrylic acid} (PPAPE, the ratio of azobenzene unit to acrylic acid unit is 1:1) and poly (diallyldimethylammonium chloride) (PDAC)

were used as polyanion and polycation in this work, respectively. An effective electrostatic self-assembly manner was demonstrated by UV-Vis absorption spectra. The reversible surface wettability on the electrostatic azobenzene monolayer was studied through measuring the water CA. On a flat silicon substrate, the CA change of the monolayer was only about 2°, reversible between $78.3 \pm 1.5^\circ$ and $76.4 \pm 1.3^\circ$ after UV (365 nm) and Vis (494 nm) irradiation, as shown in Fig. 1a and 1b. The photo-switched wettability is a reflection of the change in the dipole moment of the azobenzene unit upon *trans* to *cis* isomerization. The change of the UV-Vis absorption spectra of azobenzene monolayer upon UV and Vis irradiation is shown in Fig. 1c. The azobenzene polyelectrolyte PPAPE exhibited its absorption maxima at about 343 nm and a weak band at about 440 nm, which were related to

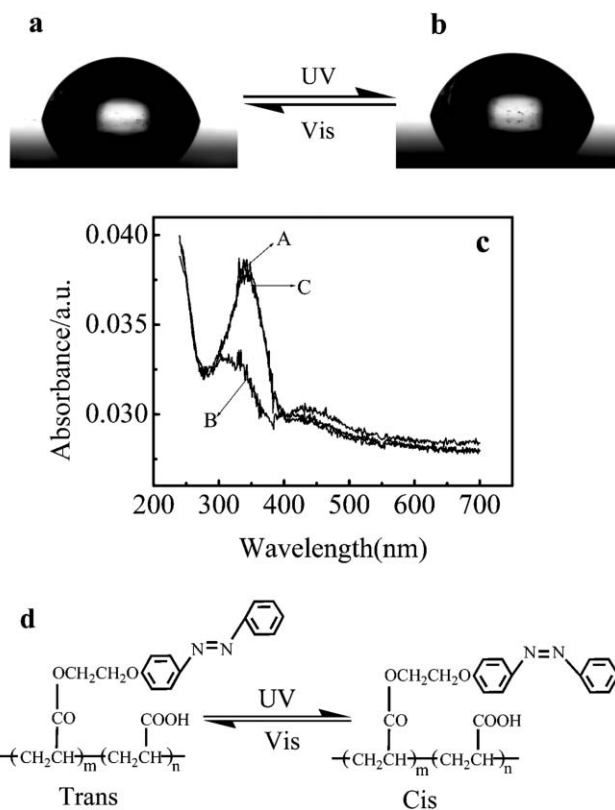


Fig. 1 (a) and (b) The shapes of water drops on a photo-responsive monolayer with flat silicon substrate upon UV and Vis irradiation. (c) UV-Vis absorption spectra of azobenzene monolayer as prepared (curve A), after UV light irradiation (curve B) and then after Vis light irradiation (curve C). (d) The *trans* and *cis* structures of azobenzene upon UV and Vis irradiation.

† Electronic supplementary information (ESI) available: experimental details, chemical structure of polyelectrolytes used, UV-Vis absorption spectra of self-assembly multilayers. See <http://www.rsc.org/suppdata/cc/b5/b504479k/>

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π - π^* and n - π^* transition bands of the *trans* azobenzene, respectively (curve A). Upon UV light irradiation, the intensity of π - π^* transition band at 343 nm decreased and that of n - π^* transition band at 440 nm increased (curve B), indicating the *trans* isomerized to the *cis*. After Vis irradiation, the *cis* recovered to the *trans* (curve C). The structure change between *trans* and *cis* of the azobenzene upon UV and Vis irradiation is shown in Fig. 1d. The *trans* has a small dipole moment and a low surface free energy exhibiting a higher water CA, while the *cis*-form possesses a higher dipole moment and surface free energy exhibiting a lower water CA. Photo-irradiation on the monolayer with UV light will transform the *trans*-rich surface to a polar *cis*-rich surface, which can be reversed by Vis light irradiation. Modifying the chemical structure of the azobenzene, e.g. its substitution and its spacer groups to the main chain, could influence the CA change, since a large change in dipole moment and the high surface density of the azobenzene unit can increase the CA change produced by photoirradiation.⁶ Since the *trans* to *cis* isomer can be cycled by UV and Vis irradiation, the CA change can be adjusted reversibly by light irradiation.

Surface wettability is not only governed by chemical structure but also by surface geometrical structure.⁷ To investigate wettability of the monolayer on rough substrate, we prepared a rough surface introducing geometrical structures with patterned square pillars on a flat silicon wafer, 20 μm high, 10 μm long and with spacing of 5, 10, 15, 20, 30, 40, 50, 60 μm between the silicon pillars (Fig. 2a) by photolithography and the inductive coupling plasma deep etching technique,⁸ and fabricated electrostatic self-assembly azobenzene monolayer on the rough substrate. For the rough films, it was noticed that the wettability and wettability change of the azobenzene monolayer under UV and Vis irradiation greatly depended on the geometrical structure of silicon surface. Fig. 2b shows the relationships between the water CA on the monolayer in *trans* and *cis* states and the pillar spacing, D . Under the *trans* state, the water CAs increased from $78.3 \pm 1.5^\circ$ for a flat substrate (as denoted by pillar spacing of ∞) to $80.1 \pm 1.7^\circ$ ($D = 60 \mu\text{m}$), $92.6 \pm 1.6^\circ$ (50 μm), and to $152.6 \pm 1.9^\circ$ (40 μm), and then the surface kept at a superhydrophobic state when the pillar spacings decreased to 30, 20, 15, 10, and 5 μm , respectively. After UV irradiation, the CAs under *cis* states all decreased for their dipole moments increased and the changes were different with the pillar spacings, which were about 2° (flat substrate), 6° (60 μm), 7° (50 μm), 66° (40 μm), 51° (30 μm), 40°

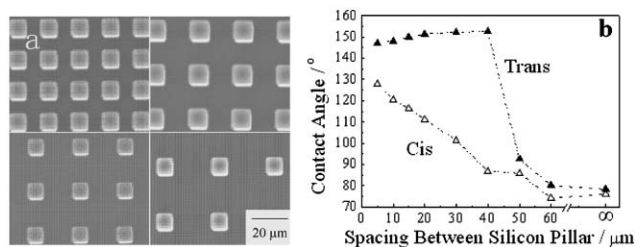


Fig. 2 (a) Scanning electron microscopy images of silicon substrates with well-defined quadrate micropillar array with pillar spacings of 5, 10, 15, 20 μm . (b) The variation of water CA of a photo-responsive monolayer on a patterned substrate with pillar spacing: \blacktriangle represent CA on the monolayer as prepared (*trans* isomer); \triangle represent CA after UV irradiation (*cis* isomer).

(20 μm), 34° (15 μm), 28° (10 μm), and 19° (5 μm). These results indicate that superhydrophobic surface and a great photo-switching between superhydrophobicity and hydrophobicity can be realized when the pillar spacing is properly selected. Surfaces exhibiting a water contact angle $\theta > 65^\circ$ are defined as hydrophobic surfaces by detecting attractive force using surface force apparatus and ancillary techniques.⁹ The *trans* and *cis* monolayers on a flat substrate were both hydrophobic and the hydrophobicity of the *trans* was a little higher than that of the *cis* for their different dipole moments. The micropillars on the patterned silicon increase surface roughness, and air can be present in the microgrooves leading to an increase of the air/water interface and thus to a more hydrophobic surface. The micropillars when spacing decreased to 40 μm or shorter distances made the *trans* monolayer superhydrophobic (CAs were all about 150°), while the *cis* monolayer increased its hydrophobicity gradually with decrease of pillar spacing instead of becoming superhydrophobic because of its higher dipole moment and weaker hydrophobicity.

Compared with the change of CA on the flat films (only about 2°), a large change of CA, about 66° on 40 μm pillar spacing silicon substrate, was induced on the rough substrate by UV irradiation. The roughness can enhance the wettability switching of responsive materials under external stimuli, as has been also observed from thermal-responsive polymer PNIPAAm,¹⁰ photo-responsive ZnO,¹¹ spiropyran,¹² and two-level structured self-adaptive surfaces,¹³ while the photo-switched wettability on an electrostatic self-assembly monolayer has not been reported as far as we know. Fig. 3a and 3b show the shapes of water drop on the monolayer on 40 μm pillar spacing silicon substrate upon photo-irradiation. The CA on the prime monolayer was $152.6 \pm 1.9^\circ$,

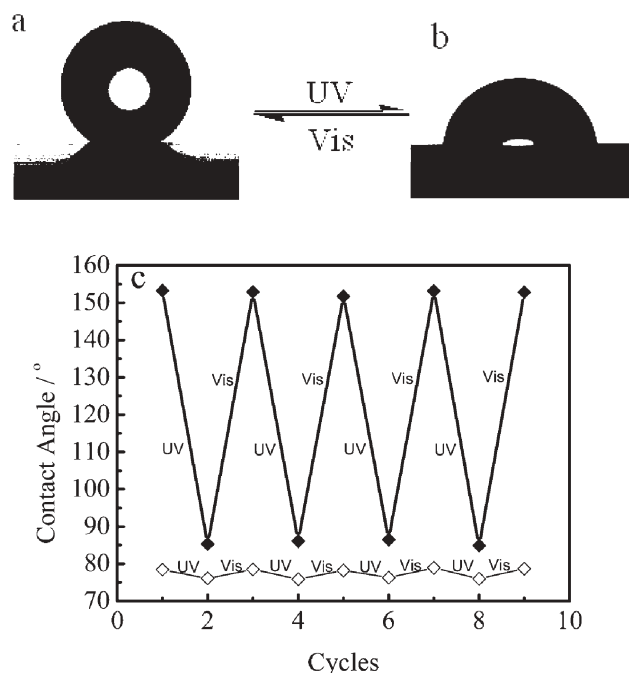


Fig. 3 (a) and (b) The shapes of water drops on photo-responsive monolayer with patterned substrate of 40 μm pillar spacing upon UV and Vis irradiation. (c) Reversible wettability transition of photo-responsive monolayer by UV and Vis irradiation: \diamond represent CA on a flat silicon wafer; \blacklozenge represent CA on a patterned substrate of 40 μm pillar spacing.

after UV irradiation the CA changed to $86.8 \pm 1.5^\circ$, and it came back to the superhydrophobic state after Vis light irradiation. The reversible switching had been repeated several times, and good reversibility of the surface wettability was observed, shown in Fig. 3c.

In conclusion, a simple electrostatic self-assembly technique was used to fabricate a photo-switched azobenzene monolayer on flat and rough substrates. Superhydrophobicity on the monolayer was obtained by introducing geometrical structure (square pillars) on substrate surface and a large reversible CA change of about 66° , 33 times larger than that on the flat film, was realized through UV and Vis irradiation. The superhydrophobicity and large reversible CA change reported here may open up new promising applications of azobenzene, especially in manipulating micro-channels, micro-total analysis systems, microfluidic devices and so on.¹⁴

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