## Effect of nanostructure on the surface dipole moment of photoreversibly tunable superhydrophobic surfaces<sup>†</sup>

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Fluorinated azobenzene-modified nanoporous substrates were fabricated such that the surface properties were photoreversibly converted between superhydrophobicity and superhydrophilicity as a result of UV irradiation. This result was attributed to the enhanced surface roughness of the nanostructured surface, which supplied sufficient free space within the monolayer for the tethered azobenzenes to facilely isomerize.

Smart materials that change their physicochemical properties and function in response to external-stimuli have received special attention in interdisciplinary studies due to their promise for applications in artificial responsive devices.<sup>1</sup> Environmental stimuli such as heat, light, pH, and electric field have been used to trigger responsive behaviors in particular materials.<sup>2</sup> For example, photosensitive azobenzene molecules undergo reversible trans-cis isomerization, causing large changes in the molecular geometry as a result of UV/visible irradiation.<sup>3</sup> When the azobenzene derivatives are covalently attached to a surface, the wettability of the modified surface can be controlled. We have recently exploited photoswitchable smart surfaces with special wettability and rewritable patterns that could be reversibly controlled between superhydrophobic and superhydrophilic states as a result of UV/visible irradation.<sup>4</sup> These phenomena were attributed to a large photoinduced change in the surface dipole moment of tethered azobenzenes as the molecules converted between trans and cis isomers. The trans isomer of azobenzene has a very small nearly zero, dipole moment, whereas the dipole moment of the cis isomer is around 3.0 Debye.<sup>3</sup> Moreover, the surface roughness induced the wettability difference to a significant enhancement.<sup>5</sup> However, no clear explanation for the relationship between surface dipole moment and wettability of photoresponsive nanotextured substrates, which yield large changes in water attracting/repelling behavior upon UV light irradiation, has yet been presented.

To investigate this behavior in more detail, we focus on the influence of surface dipole moment on the photoswitchable wettability of azobenzene-modified rough surfaces. We fabricated a photoresponsive superhydrophobic surface with a wettability that could be reversibly switched between superhydrophobicity and superhydrophilicity upon UV or visible exposure, respectively. By measuring the difference between the surface dipole moments of the *trans* and *cis* states, we quantitatively elucidated that the extreme wettability change was intimately related to an enhancement in the surface dipole moment due to surface nanostructures.

Photoswitchable azobenzene derivative, 7-[(trifluoromethyl phenylazo)phenoxy]pentanoic acid was synthesized via the diazo-coupling of 4-(trifluoromethyl)aniline with phenol.<sup>6</sup> The procedure for preparation of the phototunable nanostructured substrates is described in Fig. 1a. Building on previous work, porous surfaces were fabricated on negatively charged silicon wafers using a layer-by-layer deposition of ten cycles with the poly(allylamine hydrochloride) (PAH) and silica (SiO<sub>2</sub>) nanoparticles, respectively.<sup>4</sup> Fig. 1b shows a scanning electron microscopy image of an azobenzene-modified (SiO<sub>2</sub>/PAH)<sub>10</sub> polyelectrolyte multilayer, with a nanoporous film, showing the increased surface roughness compared to the smooth substrate. The multi-level structures created hierarchically on the substrate, featured a rough inner structure with many pores, formed by the complicated interconnections between silica nanoparticles. Finally, the introduction of azobenzene molecules to the substrate produced the surface covered with string-like fluorinated azobenzene derivatives on the topmost layer of the nanostructured substrate.

The azobenzene-modified smooth surface underwent limited photoinduced changes in water contact angle (CA) of  $6 \pm 1^{\circ}$ , reduced from  $76 \pm 2^{\circ}$  to  $70 \pm 1^{\circ}$  by irradiation with UV light (Fig. 2). The conformation (cis or trans) of the azobenzene isomers attached to the surface did not significantly affect the hydrophobicity of the functionalized smooth surface. However, the hydrophobic-hydrophilic switching effect was pronounced in the presence of rough underlying nanostructured layers.<sup>5</sup> UV irradiation of the multilayered films promoted a dramatic change in the wetting properties of the substrate, from CAs of  $151 \pm 2^{\circ}$  to below 5°. These observations can only result from a combination of azobenzene trans-cis isomerization on the top surface and the underlying nanostructured layers. In the trans state, azobenzenes containing CF<sub>3</sub> moieties ordinarily align in an array of upright chains, yielding a hydrophobic surface. The air trapped in the porous structures of the rough substrates prevents water droplets from penetrating the surface, thus, water droplets on the surface tend to be spherical. UV illumination induced isomerization of the trans azobenzene molecules to yield the *cis* one. The bent *cis* isomers expose nitrogen atoms at the top layer, which induces a large change in surface dipole moment. The cis-modified surface is more

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**Fig. 1** (a) Fabrication and reversible photoisomerization of a photoreversibly tunable superhydrophobic surface. (b) SEM images of a smooth (left) surface and a rough (right) substrate produced by ten nanoparticle deposition cycles.

hydrophilic than the *trans*-coated surface. Moreover, the porous structures of the rough substrates allow water to penetrate the nanopores by 3D capillary action.

To seek quantitative understanding of the macroscopic nature between these transitions, in particular, the degree of trans-cis photoisomerization and the effect of this switching behavior on surface wettability were studied by measuring a surface potential using secondary electron emission spectra (Fig. 2). The surface potential is closely related to the surface dipole moment oriented normal to the plane of the monolaver of molecules and strongly depends on the areal density of molecules.<sup>7</sup> The onset of secondary electron emission, which corresponded to a surface potential change, was determined by the intersection of the linearly extrapolated background and straight onset in each spectrum. In the trans state, the onset of secondary electron emission occurred at the same kinetic energy, 19.4 eV, for both the flat and nanostructured surfaces. However, when exposed to UV light, the onset for the smooth substrate shifted by 0.1 eV and the onset for the rough surface shifted by 0.4 eV, towards higher kinetic energies, relative to the trans state surface. In rough nanostructured substrates,



**Fig. 2** Water droplet profiles and secondary electron emission spectra on (a) smooth and (b) rough substrates before and after UV exposure.

photoisomerization caused large changes in the surface dipole moment of the azobenzene monolayer, producing a four-fold increase in kinetic energy relative to the smooth film. These results are well consistent with the change of the water CA, shown in Fig. 2.

The enhancement of the photoinduced surface dipole moment changes, induced by the presence of surface nanostructures, was investigated using a series of model monolayer surfaces. Self-assembled monolayers (SAMs) of several ω-terminated alkanethiols (CH<sub>3</sub>, OH, and CF<sub>3</sub>) with a variety of surface dipole moments were prepared on flat or nanostructured substrates.<sup>8</sup> As shown in Fig. 3a, the surface potentials of the OH- and CF<sub>3</sub>-functionalized smooth surfaces were higher than that of the CH<sub>3</sub>-functionalized smooth surface by 0.64 and 1.84 eV, respectively. These differences arose from the surface dipole character of each SAM. Interestingly, we observed the same results for the rough substrate, *i.e.*, the nanostructured surfaces yielded nearly the same kinetic energies as the smooth surfaces (Fig. 3b). These results indicated that the surface potential of the thin film did not depend at all on the nanostructure of the substrates. The results shown in Fig. 3 are surprising, because the nanostructured surface was capable of adsorbing a larger quantity of alkanethiols than the smooth substrate.

This unusual effect was explored by measuring the adsorption behavior of alkanethiols on flat and nanostructured substrates using a quartz crystal analyzer (QCA). Since the surface area of a rough substrate is much larger than that of a smooth substrate, more alkanethiols were expected to react with the nanostructured surface, that is, the number of the adsorbed alkanethiols was expected to be larger on the rough than on the smooth surfaces. Fig. 3c shows the change in resonant frequency as a function of time during the experiments in



**Fig. 3** Secondary electron emission spectra of three films; CH<sub>3</sub>, OH, and CF<sub>3</sub>-functionalized (a) smooth and (b) rough substrates. (c) QCA resonant frequency as a function of time during the adsorption of 1-dodecanethiol onto smooth (black) or rough (nanostructured, red) quartz crystals.



**Fig. 4** X-ray photoelectron spectroscopy spectra of the (a) S 2p and (b) C *Is* levels on the CH<sub>3</sub>-functionalized smooth and rough surfaces.

which 1-dodecanethiol solution was exposed to the flat and nanostructured substrates. The frequency change for the flat substrate,  $\Delta f (= f - f_0)$  was -4 Hz after injecting a 2 mM 1-dodecanethiol ethanolic solution for 15 min. In contrast, the value of  $\Delta f$  for the nanostructured surface was -30 Hz, which constitutes an increase of 7.5 times the frequency change for the flat substrate. This result suggests that the nanostructured surface contained a greater number of 1-dodecanethiols than the flat substrate due to the increased surface area, as expected. The amount of adsorbed 1-dodecanethiol was estimated by measuring the frequency shift of a quartz crystal using Sauerbrey's equation.<sup>9</sup> The quantity of 1-dodecanethiols adsorbed onto the flat gold-coated quartz crystals was calculated to be  $\sim 20 \text{ ng cm}^{-2}$ , whereas the amount adsorbed onto the nanostructured quartz crystals was estimated to be  $\sim 146 \text{ ng cm}^{-2}$ , an increase by a factor of 7.3 relative to the adsorption quantity of the smooth one. These results agreed well with the changes in the resonant frequency for both flat and nanostructured surfaces.

In addition, for comparing the grafting densities of SAMs on the smooth and nanostructured substrates, the S 2p and C Is peaks of the CH<sub>3</sub>-functionalized surfaces were investigated by X-ray photoemission spectroscopy (XPS). The integrated areas of the surfaces' S 2p and C 1s peaks, observed at 160.8 eV and 285.0 eV, respectively, confirmed the quantity of sulfur and carbon atoms per unit area due to the coordination of alkanethiols to the Au layer (Fig. 4). In contrast to the QCA results, the S 2p and C 1s peaks revealed no large differences between the alkanethiol densities present on either substrate, indicating that the alkanethiol adsorbed to the Au surface with a fixed density, irrespective of the surface nanoporosity, even though nanostructured substrates reacted with a larger total quantity of alkanethiols than the flat surface. Therefore, XPS measurements provide evidence that the grafting areal density of alkanethiols adsorbed onto a rough surface is similar to that of a flat surface. From these results, we could infer that the surface potential in the *w*-terminated alkanethiol-modified surfaces did not significantly change with the presence of nanostructure, as was shown in Fig. 3.

By measuring the surface dipole moment of both the *trans*and *cis*-presenting surfaces, however, we found that UV irradiation induced large changes in the molecular dipole moment of the azobenzene-modified nanoporous substrate, although the surface potential did not vary with surface nanostructures. Azobenzene molecules require space for the *trans* to *cis* isomerization. The more ordered and densely packed structure of the monolayer on the smooth surface apparently sterically hindered the isomerization reaction.<sup>1b</sup> On the other hand, nanoporous structures provided sufficient free volume for photoisomerization, which allowed the switching to take place. Therefore, when azobenzene molecules isomerized, the fraction of successful *trans-cis* isomerization events on the nanostructured substrate was expected to be larger than on the flat substrate, such that the actual surface energy of the rough surface tended to increase relative to the smooth substrate. Consequently, on the nanostructured surface azobenzene molecules have a greater ability to reversibly switch between two states than does on the flat surface, leading to a larger variation of the surface dipole moment and water CA upon UV/vis irradiation.

Here, we report a photoreversible surface potential switching effect resulting from the photoinduced *trans-cis* isomerization of azobenzene molecules in a monolayer formed on either a smooth or a nanoporous substrate. The presence of surface nanostructures strongly enhanced the magnitude of the wettability changes resulting from isomerization. This effect was attributed to an increase in available space and a reduction in steric hindrance, for molecules in the monolayer formed on a nanostructured surface. The additional available space allowed for efficient isomerization of tethered azobenzenes, which yielded large changes in the surface dipole moment. This explanation is in good agreement with the extremely tunable wetting properties seen on rough substrates.

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