
Reversible wettability of hybrid organic/inorganic surfaces of systems upon light irradiation/storage cycles

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Abstract: In this work we present hybrid organic/inorganic structures that can exhibit reversible surface wettability, altered in a controllable manner. In particular, we use the method of photo-patterning to produce polymeric SU-8 pillars of specific geometries, onto which we subsequently deposit colloidal TiO₂ nanorods. In this way, we combine the microroughness of the polymeric pillars with the nanoroughness of the nanorod-coating to create highly hydrophobic surfaces. The hydrophobicity of these systems can be changed reversibly into hydrophilicity upon irradiation of the hybrid structures with pulsed UV laser light. This behaviour is due to the well-known property of TiO₂, that becomes superhydrophilic upon UV light irradiation. This

property is reversible and we monitor the recovery of our hybrid polymeric/inorganic-nanorods structures to their initial hydrophobic character upon dark storage and heating. The wetting behaviour has been modelled and analysed according to the surface geometry. The direct implementation of such structures into microfluidics devices is demonstrated.

Keywords: reversible wettability; hydrophobicity; hydrophilicity; TiO₂ nanorods; SU-8 polymer; photopatterning; UV laser light.

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1 Introduction

The control of the wetting properties of solid surfaces and coatings has attracted much attention in the last years, due its involvement in numerous applications in diverse technological fields, such as, packaging, microelectronics, sensing, microfluidics and self-cleaning surfaces (Gao and McCarthy, 2006; Kim et al., 2008; Athanassiou et al., 2006a, 2006b; Mele et al., 2006; Patankar, 2004a; Cortese et al., 2008; Martines et al., 2005). The wettability can be controlled by designing surfaces with specific geometries or chemistry. Many theoretical and experimental studies have been published on the wetting of rough surfaces with different geometries. Most of these concern the fabrication of superhydrophobic patterns using different approaches, such as the silanisation of prepatterned surfaces, plasma etching and plasma deposition methods, lithographic techniques with the formation of different geometrical structures and layer by layer assembly of surface functionalised particles (Jarn et al., 2008; Zhang et al., 2007a; Barbieri et al., 2007; Lim et al., 2006; Tadanaga et al., 2000; Garrod et al., 2007; Teshima et al., 2005; Huang et al., 2008; Shirtcliffe et al., 2004a; Nakanishi et al., 2008; Yeh et al., 2008; Chen et al., 1999; Bhushan and Jung, 2007; Patankar, 2004b; Lau et al., 2003; Malkov et al., 2008; Roach et al., 2008; Hirvi and Pakkanen, 2007; Bico et al., 2002; Extrand et al., 2007).

Furthermore, in the latest technological developments, surfaces have been utilised that change reversibly their wetting properties by applying external stimuli that affect either the chemistry or the geometry of the surfaces, or both. Several works have been focused onto the investigation of flat and micro/nanostructured surfaces that can undergo a surface transition from a hydrophobic state to a hydrophilic one, upon external stimuli, using both organic molecules and inorganic semiconductor materials (Athanassiou et al., 2006a, 2006b; Mele et al., 2006; Jarn et al., 2008; Zhang et al., 2007; Lim et al., 2006). Titanium dioxide (TiO₂) represents the most studied material due to its ability to offer photocatalytic activity, exploited for the mineralisation of hazardous materials, and its full biocompatibility, coupled with the intriguing property of switchable wettability upon UV light irradiation (Sakai et al., 2001, 2003; Nakajima et al., 2000; Miyauchi et al.,

2000; Wang et al., 1997, 1998). There are few reports that deal with the realisation of appropriately designed structures based on TiO_2 that can exhibit a reversible superhydrophobic to superhydrophilic transition. In these works, the superhydrophobic character is given by the coverage of the flat titanium dioxide surface by means of a hydrophobising agent that is decomposed after UV irradiation, allowing the transition to a superhydrophilic state (Stevens et al., 2003; Zhang et al., 2007b; Notsu et al., 2005). However, these approaches suffered for inhomogeneous coverage of the surface and tedious fabrication steps which make them not convenient for practical applications.

Herein, we report a simple two-step method for the realisation of patterned surfaces with initially highly hydrophobic character and switchable wettability. In particular, we combine the microroughness of a patterned polymeric substrate with the nanoroughness of layers of inorganic TiO_2 nanorods (NRs) that cover the patterned surface. Specifically we use SU-8 pillars covered by surfactant-capped TiO_2 NRs. The NRs were homogeneously accommodated onto the SU-8 pillars as revealed by SEM investigations, making them superhydrophobic. As previously reported (Caputo et al., 2008a, 2008b), coatings of TiO_2 NRs are able to ensure a high degree of hydrophilicity upon UV irradiation without any noticeable photodegradation of the organic surfactants surrounding the nanoparticles. The surface wettability transitions from the highly hydrophobic state to a very hydrophilic one, under selective UV irradiation, have been studied by means of water contact angle (WCA) measurements. Short periods of dark storage allowed the native hydrophobicity to be restored. The SU-8 material, used in this study, is extensively employed into microfluidic structures (Charlot et al., 2008; Liu, 2007), thus, our results open new ways in the fabrication and operation of microfluidic devices.

2 Experimental part

2.1 Preparation of SU-8 masters

Patterns were prepared using SU-8 2010, purchased from MicroChem, employing photolithography on silicon wafer substrates. First the substrates were cleaned by ultrasonication for 10 min in acetone and 10 min in isopropanol and subsequently dried with a N_2 airflow. The SU-8 patterning procedure we followed is reported in the manual from MicroChem Corporation (MicroChem Corp., 2008). Each sample was spin coated using such conditions to obtain the desired thickness of 25.0 μm . The patterning was carried out by using the Karl Suss MJ B3 mask-aligner with UV illumination and a photomask containing the pattern. Post exposure bake (PEB) was performed on a hot plate for ultimate crosslinking of the resist, which in the end was allowed to cool down in order to improve adhesion of SU-8 to the substrate. The wafers were then developed by immersing them in SU-8 developer and isopropanol. The prepared squared micropillars have width $42 \times 42 \mu\text{m}$, height 25 μm and spacing 35 μm .

2.2 Synthesis of TiO_2 NRs

The synthesis was carried out under air-free conditions using the standard Schlenk line setup. Anatase TiO_2 NRs with an average diameter of $\sim 3\text{--}4 \text{ nm}$ and a mean length of $\sim 25\text{--}30 \text{ nm}$ were obtained by low temperature Trimethylamino-N-oxide

(TMAO)-catalysed hydrolysis of titanium tetraisopropoxide (TTIP). In a typical synthesis, 15 mmol of TTIP were dissolved in 70 g of degassed Oleic Acid (OLAC) and the resulting solution was then mixed with 5 mL of an aqueous 2M TMAO solution at 100°C for 72 h (Cozzoli et al., 2003). The TiO₂ NRs were separated from their growing mixture upon 2-propanol addition and were subsequently subjected to repeated cycles of re-dissolution in toluene and precipitation with acetone to wash out surfactant residuals. Finally, optically clear TiO₂ stock solutions in toluene were prepared for the preparation of the thin film coatings.

2.3 Preparation of TiO₂ film coatings

The TiO₂ NR-coatings were fabricated under ambient laboratory conditions as follows. The SU-8 substrates were dipped and withdrawn in a 0.4 M toluene solution of TiO₂ NRs fifty times with a rate of 1 cm/min. Then the as prepared films were gently dried with a nitrogen flow and stored at ambient conditions.

2.4 Irradiation experiments

The TiO₂ coatings were irradiated with the third harmonic wavelength (355 nm) of a pulsed Nd-YAG laser, with pulse duration of 3 ns, repetition rate of 10 Hz and energy density of 5 mJ·cm⁻². The total duration of the irradiation experiments, that was required to detect the largest wettability changes, was found to be 120 min. This period corresponds to 72,000 laser pulses, and hence, to an actual interaction time of UV photons with the TiO₂ samples of only 0.216 ms. Additional irradiation did not influence the wettability of the prepared films any further.

2.5 Scanning electron microscopy (SEM)

Low-resolution SEM characterisation of TiO₂ coatings was performed with a RAITH 150 EBL instrument. Typically, the images were acquired at low accelerating voltages (less than 5 KV) using short exposure times.

2.6 Contact angle measurements

Contact angle characterisation was performed on the SU-8 samples with and without TiO₂ NRs coatings by the sessile drop method using a CAM200-KSV instrument. Bidistilled water (Millipore Q) was used. The WCA value was the average of ten measurements and the estimated error was ±2.

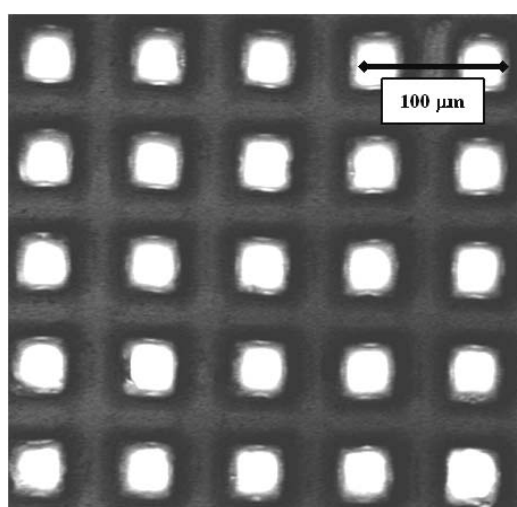
3 Results and discussion

SU-8 was the material of choice for the realisation of the patterns since after processing it becomes strong, stiff and chemical resistant towards the common organic solvents. Moreover, it is commonly used in microfluidic structures (Charlot et al., 2008; Liu, 2007) and in the production of arrays of pillars for the fabrication of super-hydrophobic surfaces (Shircliff et al., 2004b). The dimensions of each pillar were 42 × 42 μm and

25 μm thickness. The distance between successive pillars was 35 μm , as shown in Figure 1.

The micropatterning of the SU-8 substrates with pillar geometries made these substrates more hydrophobic. The wettability of the surfaces was evaluated measuring the water contact angle (WCA) of a water drop on the surface of interest. The WCA on the SU-8 surface was measured to be $80.0 \pm 2.0^\circ$, whereas the patterning of the surface with the pillars increased the WCA to $101.5 \pm 2.0^\circ$. The change in the WCA between the flat and the patterned SU-8 can only be attributed to the change in the geometry of the two surfaces, since the chemistry remains unaffected by the patterning procedure.

Figure 1 Top view, low magnification SEM images of the pillar structures



There are two basic models that describe the wetting behaviour of rough or patterned surfaces, the so-called Cassie-Baxter and Wenzel models. To better assess and explain the wettability changes of our system, we compared the experimental WCA values with the theoretical ones applying first the Cassie-Baxter’s model [equation (1)] (Cassie and Baxter, 1944). The model predicts that a drop placed on a rough surface, resides on a composite surface made of solid and air trapped among the features of the surface. The relation between the contact angle θ_{CB} on the rough surface and the one on the flat surface, θ_{FLAT} , of the same chemistry is described by the relationship:

$$\cos \theta_{CB} = f_s(\cos \theta_{FLAT} + 1) - 1 \tag{1}$$

where f_s is the fraction of the surface area where the solid is in contact with the liquid and is always smaller than 1.

The value of f_s is calculated according to Zhu et al. (2006) and Narhe and Beysens (2007):

$$f_s = \frac{1}{\left(\frac{b}{a} + 1\right)^2} \tag{2}$$

where α is the width and b the spacing of the pillars. For the particular geometry of the pillars used in this work, it was found $fs = 0.3$. The WCA according to the Cassie-Baxter model was found $\theta_{CB} = 130.4^\circ$.

The WCA of the patterned surface was also evaluated using the Wenzel (1936) model approach. This model assumes complete wetting of the rough surface by the liquid and contact angle is given by the following equation:

$$\cos \theta_W = r \cos \theta_{FLAT} \quad (3)$$

where θ_W is the value of the contact angle on the rough surface obtained by multiplying the contact angle on a flat substrate θ_{FLAT} by a factor of roughness r (Athanassiou et al., 2006b; Zhu et al., 2006; Narhe and Beysens, 2007).

The latter is defined as the ratio of the actual area of the rough surface over the geometrically projected one and it is equal or greater than 1. According to Zhu et al. (2006) and Narhe and Beysens (2007), the roughness is calculated using the equation:

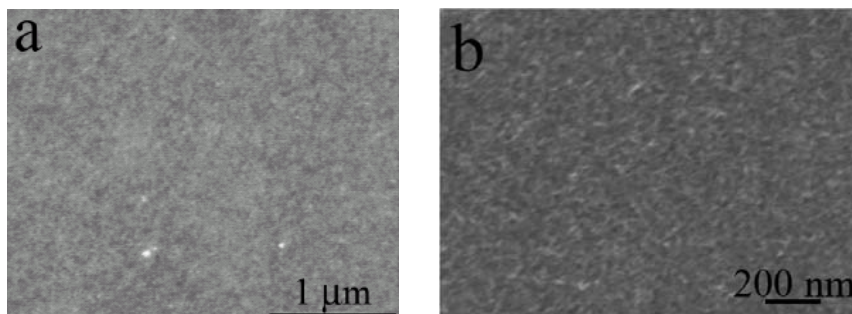
$$r = 1 + \frac{4fs}{(a/H)} \quad (4)$$

where α is the width, H the height of the pillars and fs is the factor in Cassie-Baxter's model. For our samples this value is $r = 1.71$ and the WCA was found $\theta_w = 72.7^\circ$.

There is a considerable disagreement between the theoretical values calculated from both models and the experimental data. The differences are $+29.2 \pm 2.0^\circ$ for the Cassie-Baxter model and $-28.5 \pm 2.0^\circ$ for the Wenzel model. The experimental value lies between the theoretical values given by the two models, indicating that plausibly the real representation of the wetting of the pillar structures stands somewhat between the two models. The Wenzel model predicts a WCA value on the pillars lower than the one on the flat surface, because it assumes complete wetting of the pillar structure, which is apparently a wrong hypothesis. The picture described by the Cassie-Baxter is closer to the description of our system because it evaluates a WCA higher than this on the flat surface, but the predicted WCA value is overestimated. The reason for this is that the water drop does not behave ideally residing exclusively on the top part of the pillars, but instead it starts seeping into the space between the pillars wetting a percentage of their vertical walls, always trapping some air pockets underneath. This permeation of the water drop among the pillar structures occurs possibly due to the gravitational force that becomes larger than the interfacial forces between air and water, forcing the drop to enter into the structures.

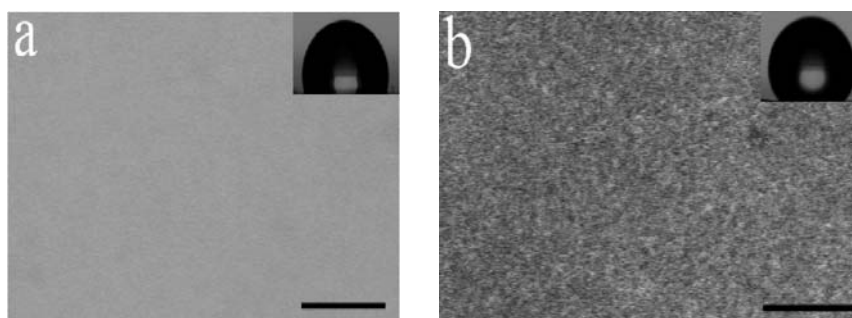
Optically clear solutions of TiO_2 NRs of average diameter $\sim 3\text{--}4$ nm and mean length $\sim 25\text{--}30$ nm in toluene were used for the coverage of the flat and patterned SU-8 samples (Caputo et al. 2008a, 2008b; Cozzoli et al., 2003). Inspection with SEM at low and high magnification, after the realisation of the TiO_2 NR coatings, revealed the formation of a uniform and compact film of NRs without any apparent formation of cracks, as evidenced from Figure 2. The close packing of the NRs can be understood in terms of minimisation of the interfacial energy of the nanocrystals, which are accommodated on the pillars and expose their longitudinal facets to each other strengthening the hydrophobic interactions between the organic capping molecules around the NRs (Caputo et al., 2008a, 2008b).

Figure 2 Low and high resolution SEM images of the TiO₂ NR-coatings on the surface of the pillars taken at different magnifications



After the dipping procedure of the flat and the patterned SU-8 samples into the NRs toluene solution, the NR coating increased noticeably the hydrophobicity of the non-covered systems and the WCA was raised to the values $97.0 \pm 2.0^\circ$ for the flat samples and $139.0 \pm 2.0^\circ$ for the samples patterned with the pillar structures. The increase in the WCA in the first case was $17.0 \pm 2.0^\circ$, whereas in the second case was $37.8 \pm 2.0^\circ$. In Figure 3 is demonstrated the geometry of the top surface of a single pillar before and after the coverage with TiO₂ NRs. The insets show the images of the water drops as they lie on the respective surfaces.

Figure 3 Low resolution SEM images of an uncoated (a) and TiO₂-coated pillar (b)



Note: In the insets drop images are shown with WCA values $101.5 \pm 2.0^\circ$ in panel a and $139.0 \pm 2.0^\circ$ in panel b. The scale bar in both panels is 1 μm.

We used the equation (1) that describes the Cassie-Baxter approach to calculate the theoretical WCA value on the pillar surfaces covered with NRs. As WCA on the flat surface we used the one measured on the TiO₂-covered flat SU-8 surface, $\theta_{FLAT} = 97.0^\circ$. The predicted theoretical WCA is $\theta_{CB} = 137.4^\circ$, a value very close and even slightly lower than the experimental WCA ($139.0 \pm 2.0^\circ$). From the finding we can safely assume that the water droplets reside explicitly on the top surface of the pillars after their coverage with the TiO₂ NRs. The achieved dual, micro and nano-scale roughness, the former being attributed to the pillars' geometry and the latter to the nanoroughness of the NR-coatings, appears to facilitate the trapping of air pockets underneath the water droplet. As a result the liquid is prevented from seeping into the void spaces between the

pillars. This effect is similar to that observed on the lotus leaves, on which the combination of micro-/nano-scale morphological features is ultimately responsible for their superhydrophobic properties (Patankar, 2004a).

As mentioned in the introduction, TiO₂ exhibits the intriguing property of increasing its hydrophilicity reversibly upon UV irradiation. For the explanation of this behaviour it has been proposed that upon UV irradiation the photogenerated holes create oxygen vacancies at the semiconductor surface. Subsequently, these defects promote dissociative adsorption of atmospheric water, which results in an increased degree of surface hydroxylation. The coordinated hydroxyl groups promote the adhesion of further water molecule multilayers, making the surfaces highly hydrophilic. In this work we exploit this mechanism to create surfaces that change between highly hydrophobic to highly hydrophilic in a reversible manner. UV irradiation was performed using a pulsed laser that, as previously demonstrated, does not affect the organic capping of the NRs (Caputo et al., 2008a, 2008b). The third harmonic (355 nm) of a Nd-YAG laser source was employed at energy density of 5 mJ·cm⁻², for 120 min (72,000 pulses) which ensured the highest wettability changes. After two hours of UV irradiation the WCA on the flat surface covered with the NRs becomes 30.0 ± 2.0°, whereas the one on the pillars covered by the NRs coating becomes 32.0 ± 2.0°, exhibiting a decrease of 107.0°. The light-driven WCA excursions measured on the micropillared structures are quite larger than those found for the corresponding flat substrate (Δ WCA = 67.0°). This is another demonstration of the advantageous effect of the micron-scale texturing in combination with the nanoroughness, on the degree of hydrophilicity ultimately achievable. The NR-arrangements on the surfaces are expected to lead to nanocapillary water infiltration (Caputo et al., 2008a, 2008b), due to the alternating distribution of hydrophilic domains (related to the newly introduced Ti-OH groups) and of quite hydrophobic domains (associated with surfactant-protected TiO₂ areas) with nanometre extension throughout the porous film, allowing water droplets to spread out over the coatings. Most likely the droplet spreading over the substrate is facilitated by its front experiencing the highly hydrophilic TiO₂ nanocapillaries located both on the top surfaces and on the sidewalls of the SU-8 pillars. As shown in the sketch of Figure 4(a) after the UV irradiation the surface becomes completely wettable, as the water drop seeps into the pillars, nominating such systems promising candidates for microfluidics devices.

Subsequently to the above-described procedure, and upon dark storage of the samples, their initial hydrophobic state is fully recovered, as demonstrated in Figure 4(b), where the complete mechanism is described graphically. The native superhydrophobic character was regained after a few weeks of dark storage at ambient conditions, since the atmospheric oxygen slowly replaces the hydroxyl groups on the surface of the NRs. This finding is in agreement with the previous works concerning the photoswitchable reversible wettability using TiO₂ NR-coatings (Sakai et al., 2001, 2003; Nakajima et al., 2000; Miyauchi et al., 2000; Wang et al., 1997, 1998). Interestingly, the average recovery time is generally faster for the micropatterned samples (~3 weeks) than for the flat surface counterpart (more than a month), which presumably indicates an easier access of atmospheric oxygen to all the substrate regions functionalised with the TiO₂ NRs. Recovery experiments performed by heating of the samples on a hot plate at temperatures close to 100°C were unable to improve the recovery times of the systems. Moreover, in the latter case the wettability recovery was also incomplete. The mechanism responsible for this behaviour will be presented in a forthcoming paper.

Figure 4a Schematic drawing showing the different drop states (a) before the dipping procedure (b) after the dipping in the TiO₂ NR-solution (c) after the UV irradiation (see online version for colours)

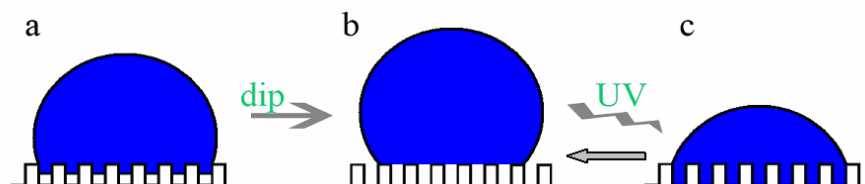
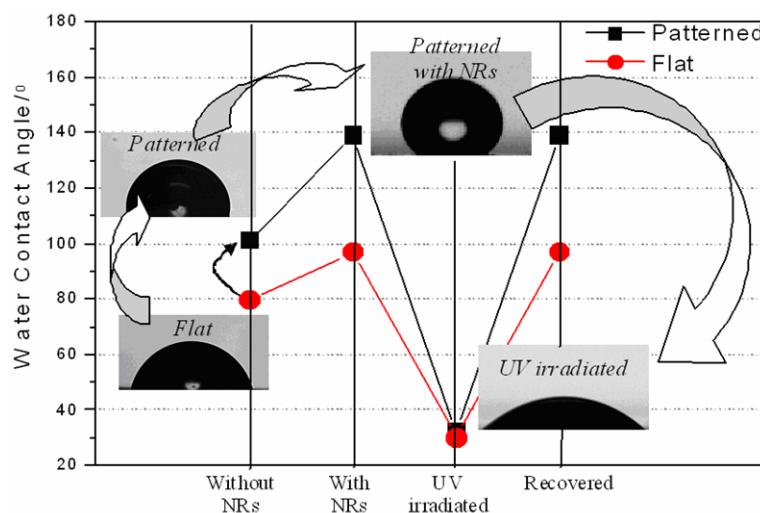


Figure 4b WCA values and drop images for the flat and the patterned samples before and after the dipping procedure, followed by the UV irradiation (see online version for colours)



4 Conclusions

In brief, we manage to realise, in a simple two-step process, SU-8 patterns with microscopic dimensions covered by TiO₂ NRs with nanoscale roughness for the fabrication of highly hydrophobic films. The study was extended to the reversible hydrophobic-hydrophilic transformation induced by UV-laser irradiation and dark storage, with future applications in microfluidics.

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