A transparent and photo-patternable superhydrophobic film†

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A transparent superhydrophobic TiO_2 film, prepared by spin-coating a TiO_2 slurry on a glass substrate and modifying the resultant TiO_2 film with fluoroalkylsilane molecules, was patterned by illumination with ultraviolet light through a photomask, producing a superhydrophobic/superhydrophilic surface micropattern with very small superhydrophilic areas, which we were able to selectively fill with alginate hydrogel.

A surface with patterned wettability has many important technological applications, including cell growth,[1] spotting of biomolecules,[2] fluid microchips,[3] microreactors,[4] and ink-jet printing.[5] In many of these applications, a large wettability contrast on the patterned surface is desired for the accurate manipulation of water-soluble or water-dispersed materials. Recently, several groups have reported the preparation of superhydrophobic/superhydrophilic surface patterns, which exhibit much larger wettability contrast than conventional hydrophobic/hydrophilic patterns[6–12] and are expected to have applications in the site-selective immobilization of biomaterials[9] and other functional materials.[12] However, the preparation of these surface patterns usually requires complicated or time-consuming processes and limited choices of substrate materials.[6–12] Moreover, these surface patterns, except for isolated examples,[8] have seldom been transparent to visible light due to the highly scattering surface morphologies or the non-transparent substrates used; this also restricts the range of practical applications. Here we report a simple method for the preparation of transparent superhydrophobic TiO_2 films, which consists of spin-coating a TiO_2 slurry on a glass substrate and hydrophobically modifying the resultant film with fluoroalkylsilane (FAS) molecules. The superhydrophobic TiO_2 film was able to be conveniently patterned by ultraviolet (UV) light illumination to produce a superhydrophobic/superhydrophilic surface micropattern, which was further converted to an alginate hydrogel pattern on the superhydrophobic surface.

As often mentioned in the literature, a rough surface morphology is necessary to induce superhydrophobicity from a hydrophobic material.[13–15] The rough morphology can trap air pockets, which greatly enhance the hydrophobic properties.[13–15] However, this type of morphology often leads to severe light scattering due to its large roughness which is comparable to or even much larger than the wavelength of the visible light.[13–15] As a result, superhydrophobic materials are seldom transparent to visible light. Therefore, one should reduce the level of surface roughness to a scale much smaller than the wavelength of visible light, without losing the ability to trap air pockets, in order to simultaneously obtain superhydrophobic properties and high transmittance. This is obviously not straightforward, as evidenced by the dearth of reports on transparent superhydrophobic surfaces,[16–20] in contrast to the large volume of publications on superhydrophobic surfaces.[13–15] We, however, found that a TiO_2 film (~500 nm thickness) prepared by spin-coating a TiO_2 slurry on glass substrates (ESI†) exhibited both a rough surface morphology and light transmittance of >78% in the visible light region (400–800 nm), as shown in Fig. 1(a) and (b). After surface modification with FAS molecules by chemical vapor deposition,[21] the film showed a water contact angle of 165° (Fig. 1(c)), and

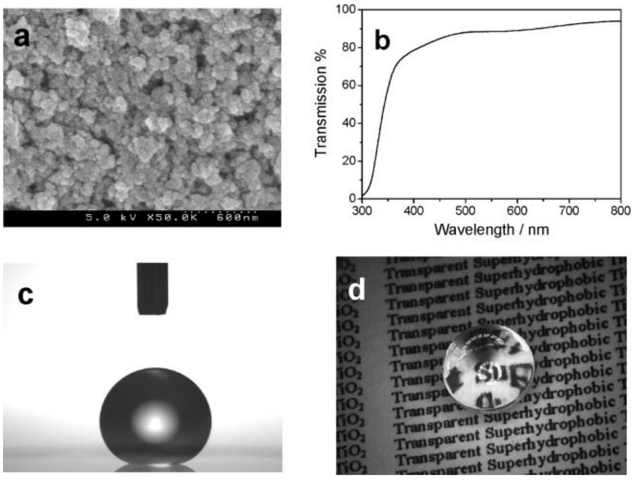

Fig. 1 (a) SEM image of a TiO_2 thin film spin-coated on glass substrate. (b) Transmission spectra of the TiO_2 film shown in (a). (c) Image of a water droplet with a contact angle of 165° on fluoroalkylsilane-modified TiO_2 film. (d) Image of a spherical water droplet placed on a fluoroalkylsilane-modified TiO_2 film showing the transparency and superhydrophobicity of the film.

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† Electronic supplementary information (ESI) available: Experimental details, a TEM image of TiO_2 nanoparticles and a plot of size distribution of aggregated TiO_2 particles analyzed by dynamical light scattering, a cross-sectional SEM image of a TiO_2 film, a surface topographic image of TiO_2 film measured by atomic force microscopy, transmission spectra of TiO_2 films with different thickness, a plot of water contact angle *vs.* UV illumination time for a superhydrophobic TiO_2 film, a plot of transmission spectra of a superhydrophobic TiO_2 film before and after UV irradiation, a micrograph of a surface micropattern that consists of 5 μm-wide superhydrophilic squares, pictures showing the transparency of alginate hydrogel surface pattern, and a plot showing the durability of the superhydrophobic property of the TiO_2 film under room light. See DOI: 10.1039/b713432k

advancing/receding water contact angles of 168/148°. A water droplet placed on the film showed a nearly spherical shape (Fig. 1(d)), and rolled off the film surface with a slight inclination as a result of the small contact angle hysteresis of 20°, calculated from the advancing and receding contact angles.

We measured the particle size of the TiO_2 slurry by transmission electron microscopy and dynamic light scattering techniques, and found that the slurry contains aggregates of TiO_2 nanoparticles (*ca.* 6 nm), with a size range of 40–340 nm (most frequent size, 110 nm) for the aggregates (see ESI†). We thus propose that the fast evaporation of the solvent during the spin-coating process led to the loose packing of TiO_2 aggregates and the porous film structure. The dual-level roughness of the film, based on the nano-size primary particles and the submicrometer-size aggregates, may lead to the efficient trapping of numerous air pockets in the film in contact with water, which contributes greatly to the observed superhydrophobic properties as often discussed in literatures.[13,14] This effect is similar to that involved in the superhydrophobicity of lotus leaves, on which micrometer- and nanometer-level roughness both contribute to the non-wetting properties.[13,14] In addition, the overall surface roughness (rms = 41 nm, measured by AFM), resulted from the packing of submicrometer-sized TiO_2 aggregates with a broad size distribution, is much smaller than the wavelength of visible light; thus, the film only weakly scatters visible light and is transparent to visible light. We consider the knowledge obtained here should be valuable for the design and preparation of transparent superhydrophobic films.

The superhydrophobic TiO_2 film is patternable with the use of UV illumination, as a result of the photocatalytic decomposition of the FAS monolayer (see ESI†).[22,23] Without the FAS monolayer, water spreads completely on the TiO_2 film with a contact angle of $\sim 0°$, which is in marked contrast to the 165° CA of the FAS-modified TiO_2 film; this superhydrophilic state was found to be stable for over 1 month storage due to the rough surface morphology of the film, as discussed in our previous reports.[7,12,24] As a result, we are able to prepare a superhydrophilic pattern on the transparent superhydrophobic TiO_2 film by UV illumination through a photomask, without appreciable change in the film transparency (ESI†). Fig. 2(a) shows such a patterned surface, which consists of 50 μm-width superhydrophilic squares surrounded by superhydrophobic areas. Cooling the patterned film below the dew point led to the selective filling of superhydrophilic squares with condensed water, as shown in the figure. To obtain a clearer image, the surface pattern was developed with metallic nickel by means of electroless plating, which consisted of sensitizing the surface pattern with metallic Pd nuclei and the subsequent catalytic growth of nickel. Since the $PdCl_2$ solution, the precursor of the Pd catalyst nuclei, only adhered to the superhydrophilic squares, a bright nickel pattern was formed on the patterned film, which followed the superhydrophobic/superhydrophilic pattern, with nickel depositing only in the superhydrophilic area, as shown in Fig. 2(b). The scale of superhydrophilic squares, as imaged by water and nickel, is consistent with the photomask, indicating that the resolution of the photocatalytic lithography is sufficient. Further experiments showed that superhydrophilic squares as small as 5 μm in width could be prepared with high resolution (ESI†), and it seems possible to prepare even smaller superhydrophilic features, provided a suitable photomask is used.

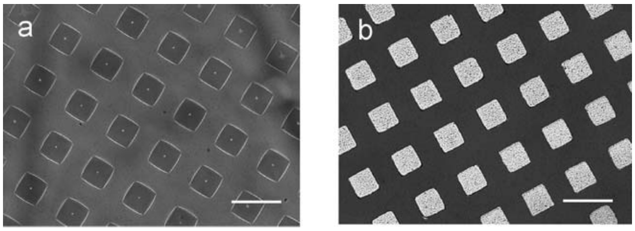

Fig. 2 (a) Optical micrograph of a superhydrophobic/superhydrophilic surface pattern cooled below the dew point. Water is site-selectively condensed in the superhydrophilic area. (b) Optical micrograph of the same surface pattern shown in (a) after having been electrolessly plated with metallic nickel. Scale bars shown correspond to 100 μm.

One may be concerned that the photocatalytic property of TiO_2 material has a negative influence on the durability of the superhydrophobic property of the film. However, we found that the contact angle of water on the superhydrophobic TiO_2 film that was placed in a well-lighted room changed negligibly in a period of ten days, since room-light lamps only emit a very small amount ($\sim 1\ \mu W\ cm^{-2}$) of ultraviolet light (see ESI†). This indicates the quite good stability of the superhydrophobic TiO_2 film under indoor conditions.

One special property of the superhydrophobic/superhydrophilic pattern is its extremely large wettability contrast, which can be employed to selectively fill superhydrophilic areas with water-based functional materials. We selected an alginate hydrogel to examine this idea, which has important biomedical applications for the immobilization of living cells and other biomaterials.[25–28] Generally, alginate hydrogel is prepared by mixing sodium alginate solution with calcium chloride solution. Calcium ions are able to crosslink the polymeric chain of alginate, which leads to immediate gelation. We immersed the patterned TiO_2 film in a 2 wt% sodium alginate solution in water and withdrew it at a speed of 15 cm min^{-1}. By this procedure, the superhydrophilic area of the patterned surface was filled with alginate solution; the superhydrophobic area, however, remained bare, due to the de-wetting of the solution. Next, the film was immersed in a 2% calcium chloride aqueous solution for 20 s and then withdrawn from the solution. Alginate hydrogel was thus site-selectively prepared in the 50 μm-width superhydrophilic squares of the surface pattern (Fig. 3(a)), without appreciable change in the film transparency (ESI†). As shown Fig. 3(a), the hydrogel features are slightly

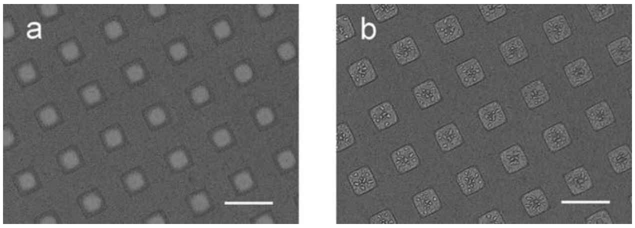

Fig. 3 (a) Optical micrograph of an alginate hydrogel pattern templated by a superhydrophobic/superhydrophilic surface pattern that was the same as that used for the pattern shown in Fig. 2(a), which shows the site-selective deposition of hydrogel in the superhydrophilic areas. (b) Optical micrograph of the same hydrogel pattern cooled below the dew point. Adsorption of condensed water led to the expansion of hydrogel pattern. Scale bars in the pictures are 100 μm.

smaller than the superhydrophilic squares in Fig. 2(a), as a result of the loss of water by evaporation. Cooling the hydrogel pattern below the dew point, however, led to the expansion of hydrogel as shown in Fig. 3(b), due to the re-adsorption of water condensed from the air. No water droplets condensed on the superhydrophobic area surrounding the hydrogel squares, indicating that hydrogel was only deposited in the superhydrophilic squares.

In a control experiment, we patterned a smooth FAS-modified TiO_2 film (water contact angle, 110°) with UV light, and prepared alginate hydrogel on the patterned film by the same method described above. We observed alginate hydrogel covering both hydrophobic and hydrophilic areas, without any selectivity. Therefore, our experiments suggest that the extremely large wettability contrast of the superhydrophobic/superhydrophilic pattern was of great importance for the site-selective deposition of alginate hydrogel.

In summary, we have succeeded in preparing transparent and photo-patternable superhydrophobic TiO_2 films by a simple two-step method, which consists of preparing a porous TiO_2 film by spin-coating and modifying the film with fluoroalkylsilane molecules. The remarkable superhydrophobic properties and the good transparency were believed to result from the special surface morphology of the film, which is characterized by a dual-level roughness dictated by the submicrometer-sized TiO_2 aggregates and nanometer-sized TiO_2 primary particles. The transparent and superhydrophobic TiO_2 film was able to be conveniently patterned with ultraviolet light to produce a superhydrophobic/superhydrophilic surface micropattern, with features as small as 5 μm. It is reasonable to expect that the surface-patterned film may be used to site-selectively immobilize biomolecules such as proteins and nucleotides, cells, hydrophilic polymers, and functional metal or semiconductor nanoparticles. Therefore, the transparent and photopatternable superhydrophobic surface may have promising applications in such areas as cell immobilization and growth, and in chemical or biological sensing. In addition, we consider the possible application of the surface-patterned film in microreactor arrays. For instance, a 50 μm-wide superhydrophilic square is able to contain ∼100 pL aqueous solution, and a 5 μm-wide square can contain a solution at the level of 100 fL. The extremely large wettability contrast ensures that the aqueous solution can be confined within the superhydrophilic area. Therefore, the surface pattern could potentially be used as a pL-level microreactor array that is erasable and recyclable, due to the photocatalytic self-cleaning action of the TiO_2.[22,23]

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