

One-step coating of fluoro-containing silica nanoparticles for universal generation of surface superhydrophobicity†

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Stable superhydrophobic surfaces with water contact angles over 170 degrees and sliding angles below 7 degrees were produced by simply coating a particulate silica sol solution of co-hydrolysed TEOS/fluorinated alkyl silane with NH₃·H₂O on various substrates, including textile fabrics (e.g. polyester, wool and cotton), electrospun nanofibre mats, filter papers, glass slides, and silicon wafers.

“Superhydrophobicity” is typically used to describe surfaces with a water contact angle greater than 150 degrees.^{1,2} Nature has imbued the surfaces of some plants and insects, such as lotus leaves and butterfly wings, with superhydrophobicity to show water-repellent and self-cleaning functions. It is of great practical importance to create superhydrophobic surfaces for various synthetic materials so that they can become water/ice/snow repelling, anti-sticking, anti-contaminating, and/or self-cleaning.

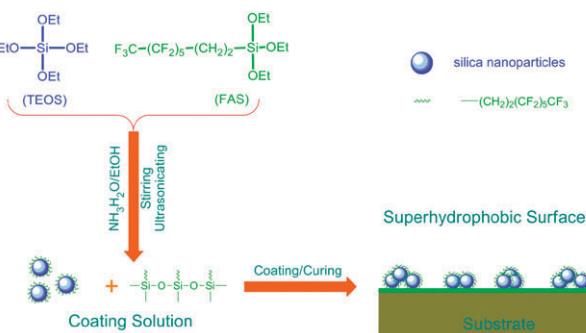
Extensive research has recently been conducted to realise superhydrophobicity on various substrate surfaces. It was demonstrated that superhydrophobicity depends on not only the surface chemistry but also the surface topology. Two distinct theoretical models (Wenzel and Cassie–Baxter)¹ have been used to guide the generation of superhydrophobic surface by either roughening the surface (e.g. etching) or lowering the surface free energy, or both. Examples include using a micro-processing technique^{3–5} to produce rough surface and subsequent chemical treatment with silane⁴ or fluoro-containing polymers⁵ to reduce the surface free energy. Alternatively, a superhydrophobic surface can be generated *via* nano-structured surfaces fabricated by chemical/electrochemical deposition,⁶ self-assembly,^{7,8} or sol–gel process,⁹ followed by further chemical surface modification. However, most of the above techniques involved a tedious and multiple-step procedure, which are impractical for fabrication of superhydrophobic surfaces on a large-scale.

One-step solution treatments using appropriate micellar polymer solutions,¹⁰ phase-separated polymers,¹¹ and nano-

filler-added polymers or sol–gel solutions¹² have been reported. These one-step solution methods are very promising for the large-scale production of superhydrophobic surfaces because of the simplicity in both the process and equipment involved. In this context, we report here a new superhydrophobic coating solution prepared by co-hydrolysis of tetraethylorthosilicate (TEOS) and a fluorinated alkyl silane under the alkaline condition for one-step generation of superhydrophobic surfaces on various substrates, including, but not limited to, textile fabrics (e.g. polyester, wool and cotton), electrospun nanofibre mats, filter papers, glass slides and silicon wafers. The resultant coating of reasonable adhesion to the substrates showed a water contact angle larger than 170° and sliding angle less than 7°. The effect of treatment conditions on the resulting surface hydrophobicity was also discussed in this paper.

The sol solution containing silica nanoparticles was prepared by co-hydrolysis and condensation of two silane precursors, tetraethyl orthosilicate (TEOS) and tridecafluoroctyl triethoxysilane (FAS), in NH₃·H₂O–ethanol solution (see the ESI† for the detailed procedure). This sol solution can be easily coated onto various substrates to form a transparent film simply by dipping, spraying, or spin coating (Scheme 1).

As can be seen in Fig. 1a, the polyester fibres after sol solution treatment show a particulate surface. These particles have average size of *ca.* 50–150 nm, and aggregated randomly over the coated area (see the inset of Fig. 1a and Fig. S1 in ESI†). Fig. 1c clearly shows a nearly sphere-like water droplet that can stay on the treated fabric surface for a long period of time. The contact angle (CA) measurements indicated that the sol-coated polyester surface had a water contact angle of 174 ± 2.7° and a sliding angle of 2.2 ± 0.1°. In contrast, the



Scheme 1 Reaction route of silica sol preparation and coating procedure.

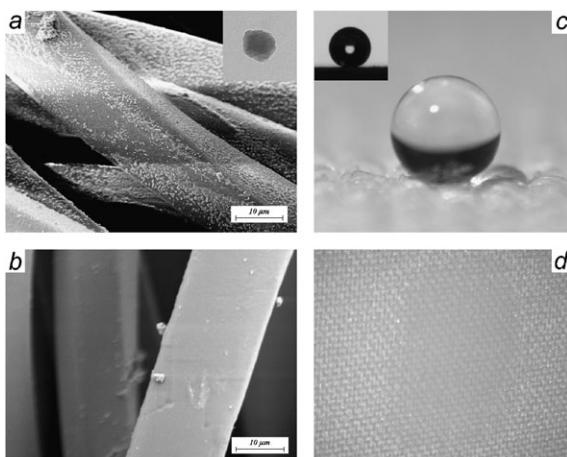


Fig. 1 SEM and photographic images of the polyester fabrics, (a) and (c) after superhydrophobic treatment, (b) and (d) the un-treated pristine fabric.

pristine fabric surface cannot support the formation of any spherical water droplet (Fig. 1d).

To understand the particle formation in the sol preparation, the two silane precursors were hydrolysed separately under the same conditions. It was observed that TEOS in $\text{NH}_3\text{-H}_2\text{O}$ -ethanol solution quickly hydrolysed into silica particles that turned the solution milky, while the FAS formed a thick and clear resin that phase-separated out from the solution, indicating a very slow hydrolysis rate. However, co-hydrolysis of the two silane precursors caused the quick formation of silica particle cores covered with the slowly-hydrolysed FAS resin. There was no separated resin found in the solution even after 12 h reaction time.

The TEM image given in the inset of Fig. 1a (also see Fig. S1 in ESI†) shows a core-shell-like structure for the particles. As expected, the SEM-EDX mapping (Fig. 2) revealed the presence of the surface element O, F, and Si in addition to the bulk C.

Apart from the microscopic investigation described above, the chemical nature of the polyester fabric before and after the coating treatment has also been studied by FTIR and XPS. For the TEOS/FAS coated surface, new FTIR peaks appeared at 1087 and 810 cm^{-1} , corresponding to the Si–O–Si asymmetric and symmetric vibrations, respectively (see the ESI†).¹³ Peaks at 1240 and 1190 cm^{-1} , characteristic of C–F stretching vibrations,¹⁴ were also observed. Fig. 3 shows the high resolution XPS C1s and Si2p spectra of the silica coated polyester fabric. The binding energies of 294 , 292 , 289 , and 285 eV are typical for $-\text{CF}_3$, $-\text{CF}_2$, $-\text{CSi}$ and $-\text{CH}$ moieties, respectively.¹⁵ The XPS peak at 104.6 eV is attributable to Si2p, suggesting that the fabric surface was indeed covered with silica.

The atomic ratio of element F, C and Si on the coating surface can also be calculated from the XPS survey spectrum (see the ESI†) to be $N_{\text{F}}/N_{\text{C}}/N_{\text{Si}} = 37.4/26.9/11.7$ (atomic ratio). This ratio, in conjugation with the corresponding molecular stoichiometric data for FAS molecule ($37.4/23.0/2.8$) allows us to roughly estimate that about 25% of the silicon atoms came from FAS, and the other 75% from TEOS, which is much higher than the FAS/TEOS ratio used for the

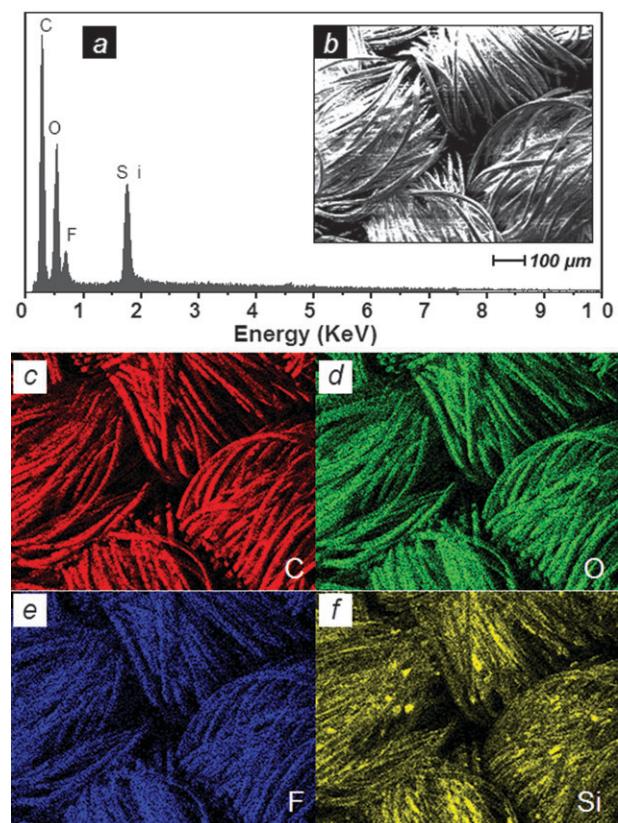


Fig. 2 EDX spectrum (a), SEM image (b) of the coated polyester fibres, and corresponding element mapping (c–f).

sol preparation ($1 : 10$ mol/mol). The presence of the unusually high amount of FAS moieties on the silica coated surface indicated a high concentration of tridecafluoroctyl moieties on the silica surface thus significantly reducing the surface free energy.

To maximise the surface superhydrophobicity, we have further studied the effect of the ratio of FAS to TEOS in the sol preparation on the surface hydrophobicity. Within the range of FAS/TEOS ratios from $1 : 100$ to $1 : 10$ (mol/mol), an increase in the FAS portion led to an increased CA value, suggesting that the surface hydrophobicity increased with increasing amount of FAS used for the sol preparation

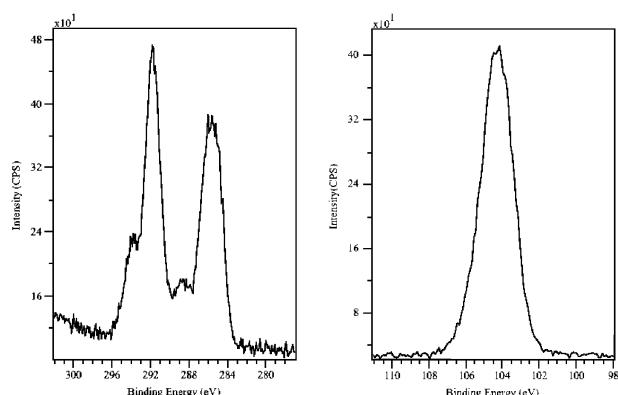


Fig. 3 XPS spectra of C1s and Si2p of the silica coated polyester fabric (FAS/TEOS ratio = $1 : 10$ mol/mol).

Table 1 Water contact angle data on different substrates^a

| Substrates | Loading (mg cm ⁻²) | Contact angle (degree) | | | Sliding angle ^b (degree) |
|------------------|--------------------------------|------------------------|---------------|-----------|-------------------------------------|
| | | Before coating | After coating | | |
| Polyester fabric | 5.02 | 117.1 | 174.2 ± 2.7 | 2.2 ± 0.1 | |
| Cotton fabric | 2.62 | 37.9 | 173.7 ± 3.2 | 4.9 ± 0.4 | |
| Wool fabric | 4.08 | 108.0 | 170.2 ± 2.5 | 5.6 ± 0.4 | |
| Nanofibre mat | 1.30 | 132.6 | 176.9 ± 2.1 | 1.7 ± 0.1 | |
| Filter paper | 1.90 | 0.0 | 172.4 ± 2.3 | 6.3 ± 0.3 | |
| Glass slide | 0.15 | 33.5 | 174.6 ± 1.6 | 2.3 ± 0.3 | |
| Silicon wafer | 0.20 | 63.0 | 174.2 ± 1.4 | 2.4 ± 0.2 | |

^a FAS/TEOS ratio = 1 : 10 (mol/mol). ^b After coating.

(see ESI†). Nevertheless, further increase in the FAS/TEOS ratio from 1 : 10 to 1 : 6.6 (mol/mol) slightly reduced the CA value, presumably due to a reduced surface roughness for the coating layer formed by the silica particles heavily absorbed in the hydrolysed FAS resin. In addition to the FAS/TEOS ratio, multilayer coating was found to have little effect on the CA value, indicating that one-step coating was sufficient to render the substrate surface superhydrophobic.

Similar results were obtained for other substrates, such as cotton and wool fabrics, glass slides, silicon wafers, filter papers, and PAN nanofibre mats. The CA values for the non-treated and treated substrates are listed in Table 1. All the coated surfaces showed very high surface contact angle (>170°) and low sliding angle (<7°). It was interesting to note that surface properties of the pristine substrates had a very little influence on the superhydrophobicity of the resultant coated surface.

The driving force for the formation of the superhydrophobic surface comes from the fluorinated silica nanoparticles aggregated onto the substrate to form a rough surface with a low free energy. Possible effect(s) of the substrate nature on the surface superhydrophobicity can be minimised by uniform coating,¹ while its adhesion to the substrate could be enhanced by the formation of interfacial chemical bonds.¹⁶ For the glass slide, cotton fibre, cellulose filter paper, and silicon wafer with a SiO₂ layer, their surface hydroxyl groups facilitated co-condensation with the partially hydrolysed TEOS/FAS (*via* Si-OH groups) to form interfacial Si-O-Si or Si-O-C bonds. On the other hand, polyester, wool, and PAN could partially hydrolyse under alkaline condition to generate surface carboxylic groups for subsequent co-condensation with the Si-OH groups, leading to the formation of interfacial ester bonds.¹⁷

In summary, we have demonstrated that a coating solution prepared by co-hydrolysis/co-condensation of TEOS and a fluorinated alkyl silane under alkaline condition can effectively generate superhydrophobic surfaces on a wide range of substrates, including textile fabrics (*e.g.* polyester, wool and cotton), electrospun nanofibre mats, filter papers, glass slides and silicon wafers, *via* a one-step coating process. The nature of the substrate had very little influence on the resulting contact angle value. This work will provide a simple and universal method to create superhydrophobic surface on various substrates. Besides the superhydrophobicity, other functionalities can also be produced *via* surface treatment with nanoparticle materials, antibacterial fabric¹⁸ by Ag nanoparticles for instance.

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