Durable, Self-healing, Superhydrophobic Fabrics from Fluorine-free, Waterborne, Polydopamine/Alkyl Silane Coatings

Hongxia Wang,[a*] Hua Zhou,[a] Shuai Liu,[b] Hao Shao,[a] Sida Fu,[a] Gregory Rutledge,[c] Tong Lin [a*]

[a] Institute for Frontier Materials, Deakin University, Geelong, VIC3216, Australia

[b] School of Mechanical and Electric Engineering, Soochow University, 215000, China

[c] Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139

*Corresponding Authors' E-mail: hong.wan@deakin.edu.au, tong.lin@deakin.edu.au

Electronic Supplementary Information

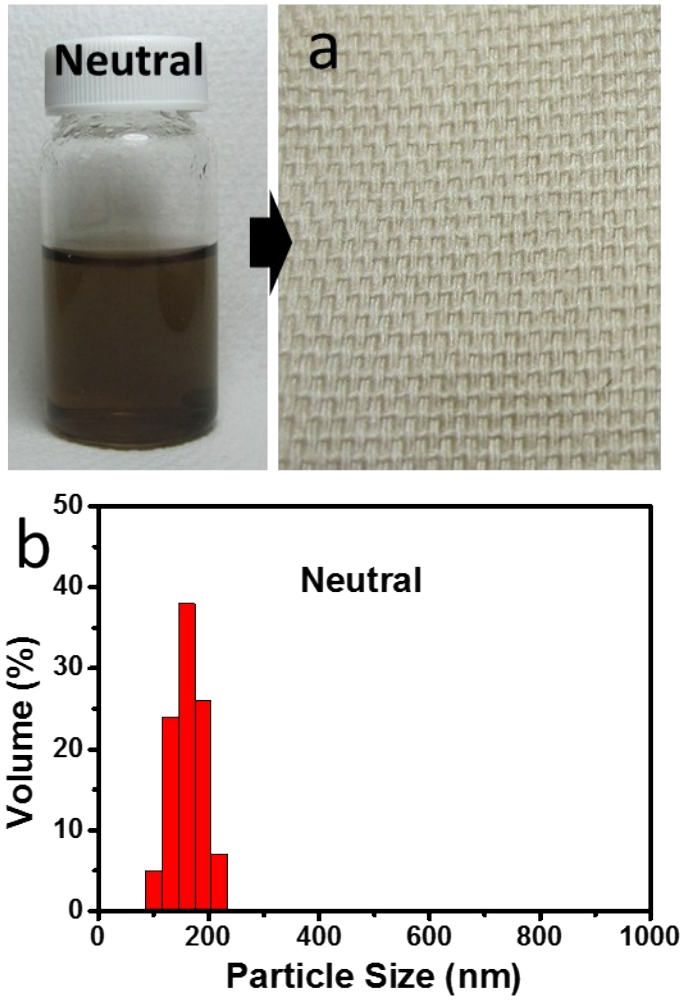


Figure S1. (a) Photo of the dopamine/HDTMS coating solution prepared at neutral condition and the coated cotton fabric, (b) Size distribution of dopamine/HDTMS particles measured by DLS.

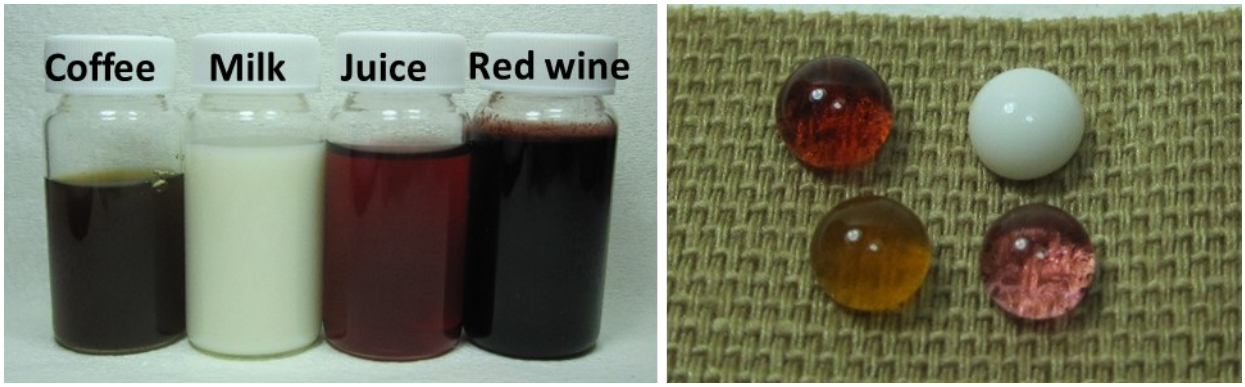


Figure S2. Coffee, milk, cherry juice and red wine on the PDA/HDTMS coated fabric.

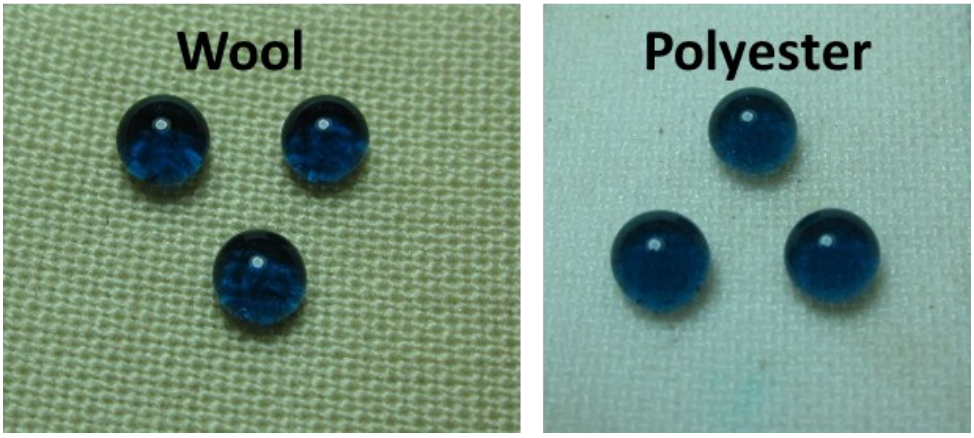


Figure S3. Photos of dopamine/HDTMS-coated wool and polyester fabric.

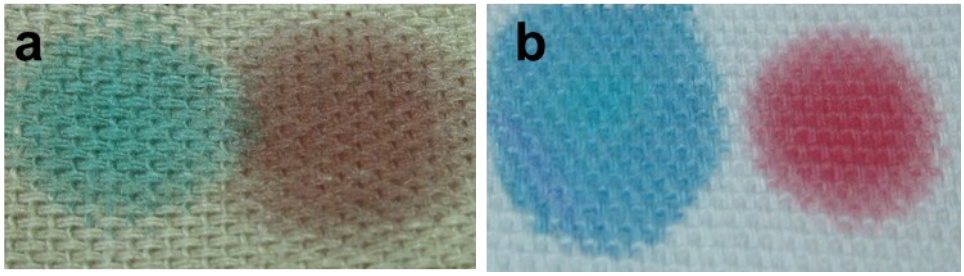


Figure S4. Cotton fabric treated by: (a) PDA without HDTMS, and (b) HDTMS-water without PDA.

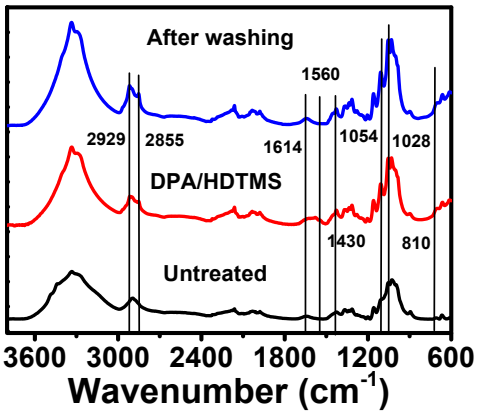


Figure S5. FTIR spectra of cotton fabrics before and after dopamine/HDTMS coating treatment, and after washing treatment.

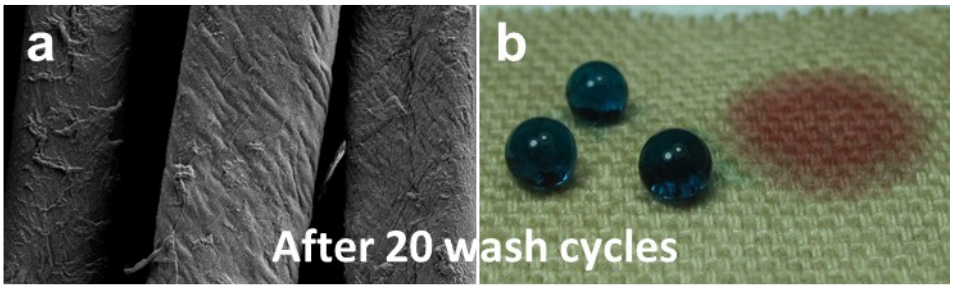


Figure S6. Dopamine/HDTMS coated cotton fabrics after 20 cycles of AATCC standard washing, (a) SEM image, and (b) water and cooking oil on the fabric surface.

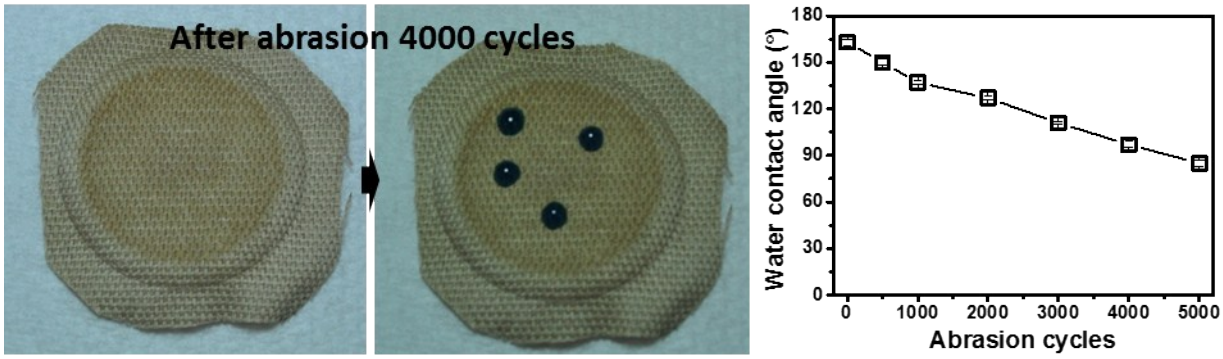


Figure S7. Photo of PDA/HDTMS coated cotton fabric after 4000 cycles of abrasion damages, and effect of abrasion cycles on the water contact angle.

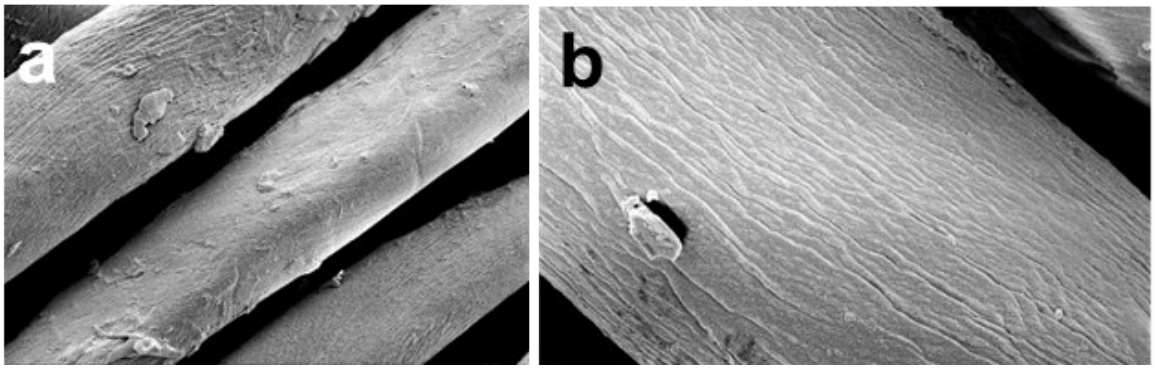


Figure S8. SEM images of fabrics (c) after acid treatment and (d) after acid and heating treatment.

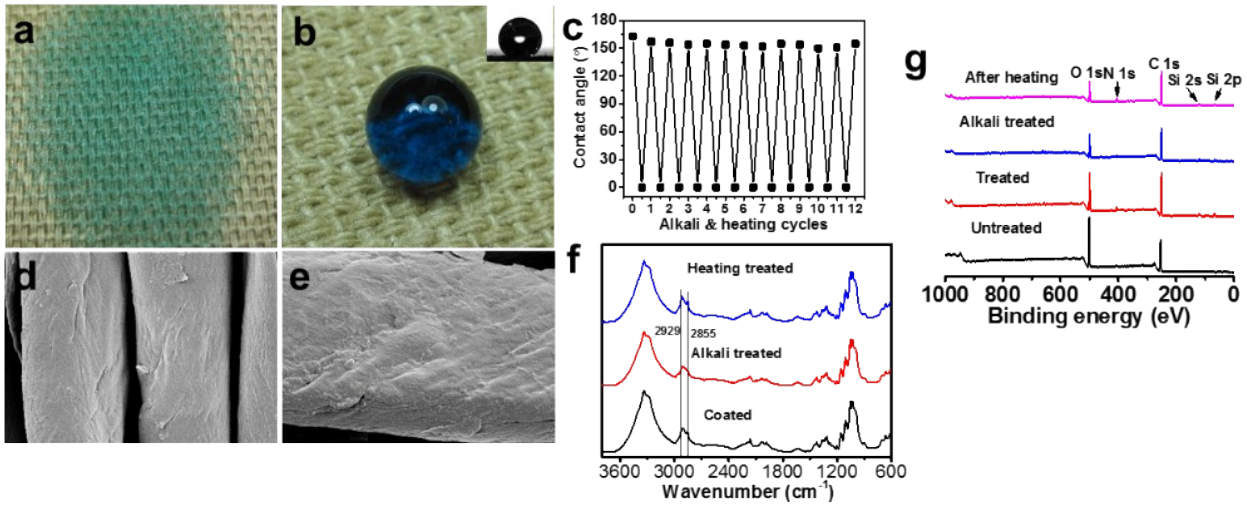


Figure S9. Photos of liquid droplets on fabrics (a) after alkali treatment and (c) after alkali and heat treatment; (c) water contact angles on the coated fabric in the twelve cycles of alkali and heat treatment; SEM images of fabrics (d) after alkali treatment and (e) after alkali and heat treatment; (f) FTIR spectra of the dopamine/HDTMS coated fabric; (g) XPS wide-scan spectra of cotton surface before and after dopamine/HDTMS coating, then alkali treatment and after heat treatment.

Similarly, the coated fabric after immersing in strong alkali solution (pH=14) showed similar self-healing feature (Figure S11b). Such a self-healing property was repeatable and worked for at least 50 cycles (Figure S11c). SEM images of the coated fabric after 50 times alkaline treatment (Figure S11d) and heat treatment (Figure S11e), the alkali etching and self-healing showed little effect on the surface morphology of the coated fiber.

FTIR result is in Figure S11f. The vibration peaks at 2928 and 2855 cm^{-1} appeared, which were assigned to asymmetric and symmetric vibrations of methylene (-CH_2-). When the samples were treated by strong alkali solution, the peaks at 2928 and 2855 cm^{-1} intensity decreased. However, after heat treatment, the peaks at 2928 and 2855 cm^{-1} re-emerged. These results indicate that strong alkali treatment leads to decrease of the -CH_2- bonds on the coating surface, and after the heat treatment the -CH_2- bonds return.

Figure S11g shows the XPS survey spectrum of the cotton fabrics. The presence of a weak N1s peak, Si1s peak and Si2p peak confirmed that PDA and HDTMS were successfully coated on the fiber surface. After alkali treatment, the Si1s peak and Si2p peak are still present but reduced in intensity. After heat treatment, the Si1s peak and Si2p peak recovered again.

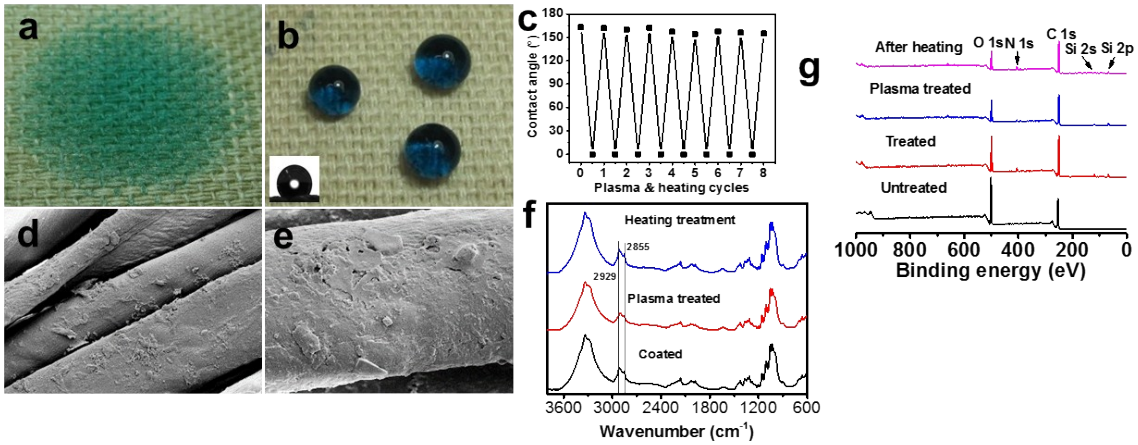


Figure S10. Photos of liquid droplets on fabrics (a) after plasma treatment and (b) after plasma and heating treatment; (c) Contact angle changes in the eight cycles of plasma-and-heat treatments; SEM images of fabrics (d) after plasma treatment and (e) after plasma and heat treatment; (f) FTIR spectra of the dopamine/HDTMS coated fabric; (g) XPS wide-scan spectra of cotton surface before and after dopamine/HDTMS coating, then plasma treatment and after heat treatment.

Figure S10 shows the self-healing result on plasma treatment. The coated fabric was damaged artificially by a plasma treatment using air as O_2 gas source. After 30 seconds of treatment, the surface became hydrophilic with a contact angle of 0° for water in Figure S10a, However, when the plasma-treated fabric was heated at 140° C for 10 minutes, superhydrophobicity was restored (Figure S10b), with contact angles of 151° (Figure S10b inserter). The treated fabric can maintain the superhydrophobicity even after 8 cycles of the plasma-and-heat treatment (Figure S10c).

SEM images of the coated fabric after 15 times plasma treatment (Figure S10d) and heat treatment (Figure S10e) show the hierarchical structure. FTIR result is in Figure S10f. The vibration peaks at 2928 and 2855 cm^{-1} appeared, which were assigned to asymmetric and symmetric vibrations of methylene (-CH_2-). When the samples were treated by plasma, the peaks at 2928 and 2855 cm^{-1} intensity decreased, providing evidence for the generation of -CH_2- bonds via chain scission and chemical bonding induced by the chemical etching of reactive species and bombardment of high energy ions. The fabric became superhydrophilic, with water contact angle = 0°. However, after heat treatment, the peaks at 2928 and 2855 cm^{-1} re-emerged. These results indicate that the introduction of oxygen due to plasma treatment leads to decrease of the -CH_2- bonds on the coating surface, and after the heat treatment the -CH_2- bonds return.

Figure S10g shows the XPS survey spectrum of the cotton fabrics. The presence of a weak N1s peak, Si1s peak and Si2p peak confirmed that PDA and HDTMS were successfully coated on the fiber surface. After plasma treatment, the Si1s peak and Si2p peak are still present but reduced in intensity. After heat treatment, the Si1s peak and Si2p peak recovered again.

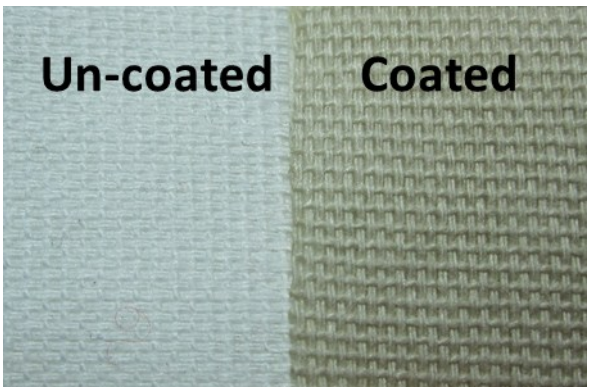


Figure S11. Photo of uncoated and dopamine/HDTMS coated cotton fabrics.

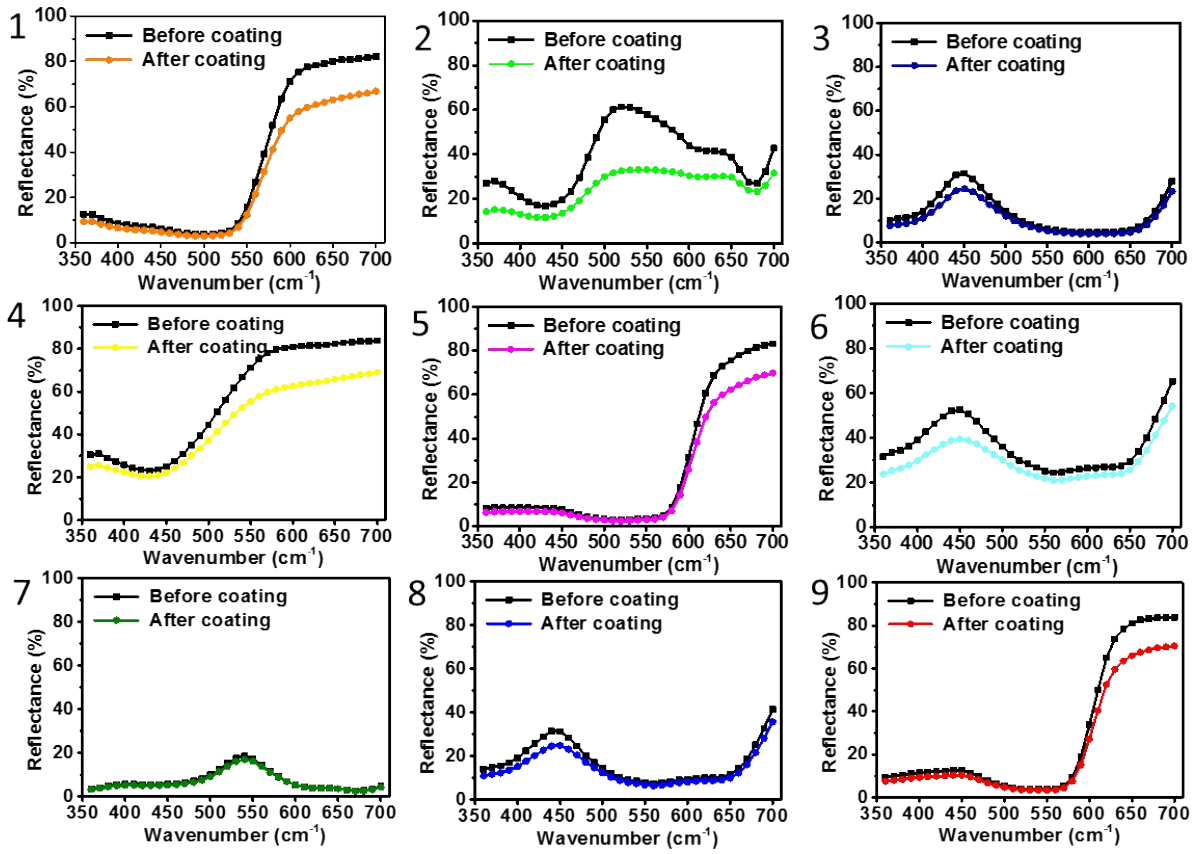


Figure S12. The reflectance of all samples under visible spectral region.

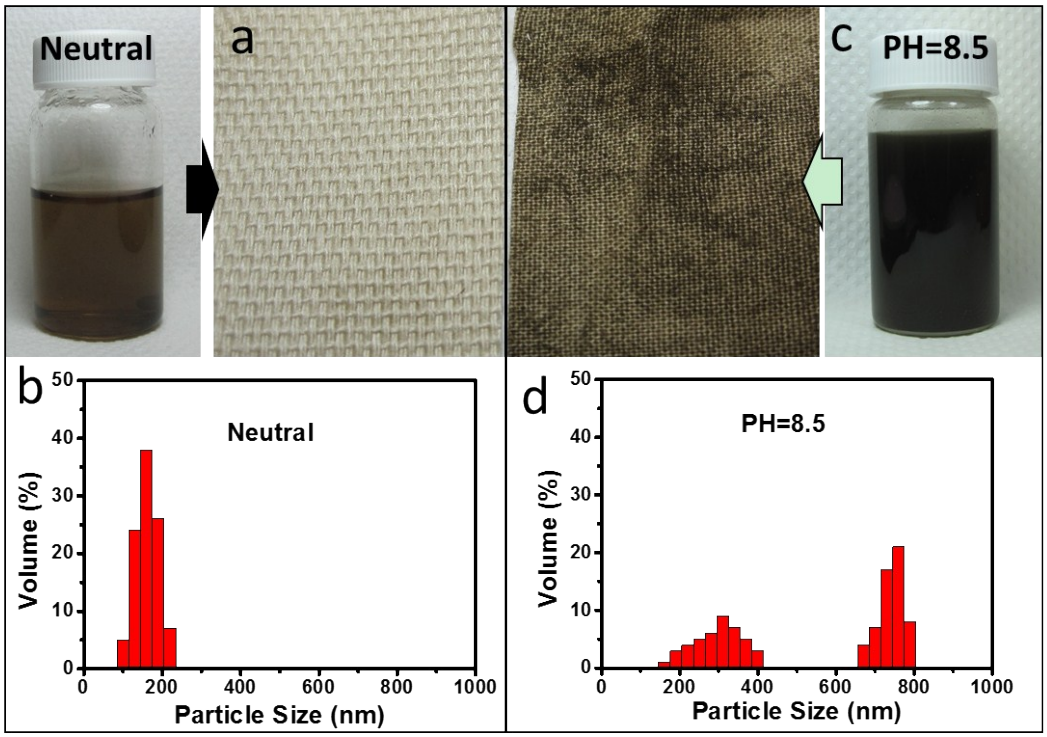


Figure S13. Photo of color difference with dopamine/HDTMS coated cotton fabric with a) neutral aqueous solution (left) and b) pH=8.5 alkali aqueous solution (right); the particle size distribution of dopamine/HDTMS particles size by DLS, c) neutral aqueous solution and d) pH=8.5 alkali aqueous solution.

Two types of reaction have been done and listed in Figure above, Figure S2a shows base dopamine/HDTMS reaction for 12 hour in neutral water, ready for coating. The solution is brown. Figure S2b shows base dopamine/HDTMS reaction in pH=8.5 water for 12 hour ready for coating; the solution is black. After coating treatment, fabrics are shown in Figure S2a & b, neutral solution coated cotton fabric is more uniform and present a tint brown color. For pH=8.5 solution, the coated fabric is black and non-uniform. It is known that HDTMS is insoluble in water and it has a very low hydrolysis rate in neutral condition in water. The presence of dopamine in the solution improved the dispersing ability of HDTMS in water. Figure S2c & d show the average size of PDA/HDTMS particles formed in different conditions, neutral or pH=8.5, respectively. The average particle size increased with increasing the reaction time. In neutral condition, reaction process is slow, and particle size is quite fine and uniform, around 160 nm. In pH=8.5 solution, self-polymerization of the dopamine is very fast, and the solution can change to dark in 10 minutes, the average particle size distribution is bimodal, with one population around 220 nm and the other around 780 nm. As a result, the coating solution is not uniform, and coated fabric is uniform.

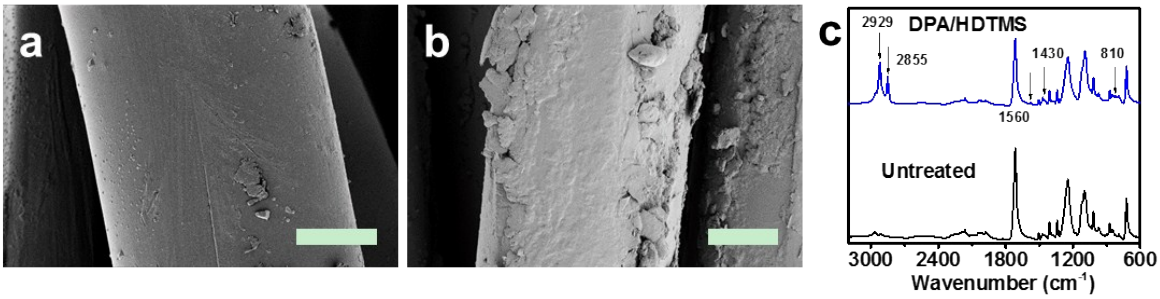


Figure S14. SEM images of polyester fabrics a) untreated, b) treated with PDA/HDTMS (scale bar: 10 μm); c) FTIR spectra of polyester fabrics before and after dopamine/HDTMS coating.

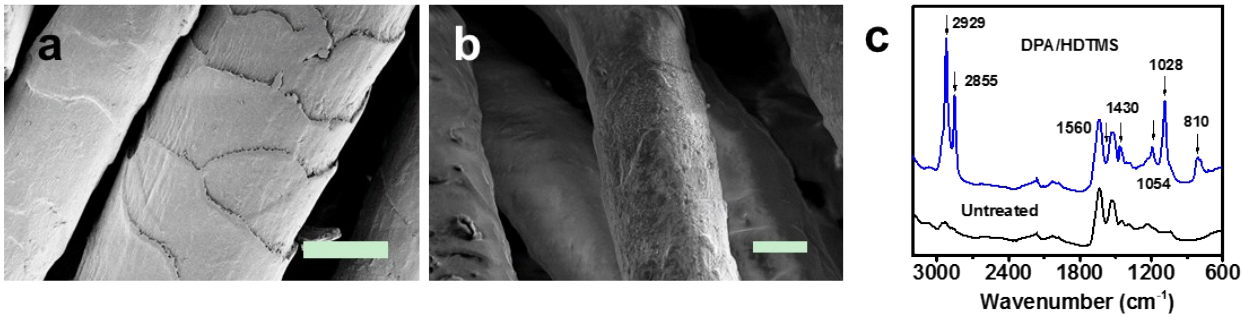


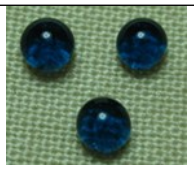
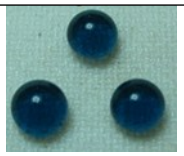
Figure S15. SEM images of wool fabrics a) untreated, b) treated with PDA/HDTMS (scale bar: 10 μm); c) FTIR spectra of wool fabrics before and after dopamine/HDTMS coating.

Table S1. Element contents (%) on the dopamine/HDTMS coated cotton fabric*

Element/groups	Dopamine/HDTMS coated (%)	Acid treated (%)	After heating (%)
O-C-O/C=O	4.6	12.2	4.1
C-O/C-N	20.6	39.7	24.6
C-C/C-H/C-Si	74.8	48.1	71.3

The results was obtained from XPS.

Table S2. CA results of the coated cotton, wool and polyester fabrics before and after washing

Fabric	Without washing			After washing *		
	CA°	SA°	Photo	CA°	SA°	Photo
Cotton	163	8.6		150	15.6	
Wool	165	7.3		154	18.7	
Polyester	160	10.2		148	23.3	

(* AATCC standard washing cycles: 20 cycles)