Supporting Information

A Nature-Inspired Strategy Toward Superhydrophobic Fabrics for Versatile Oil/Water Separation

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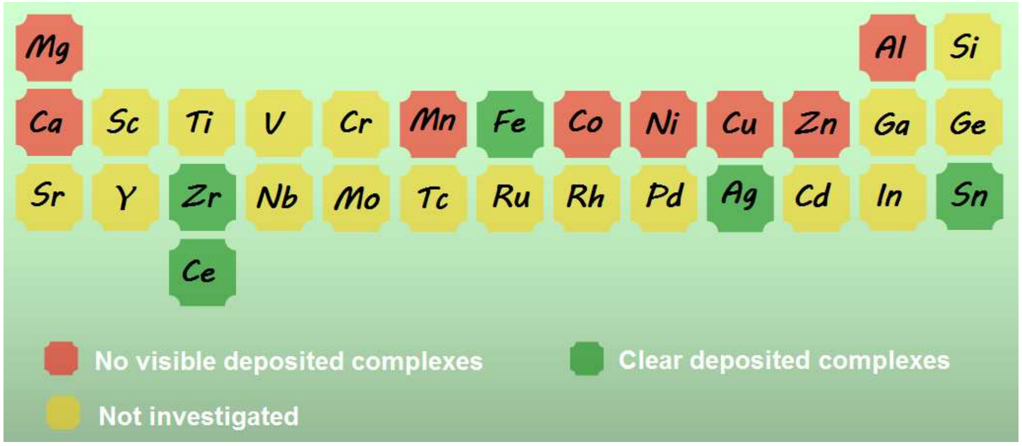

Figure S1. Graph showing a portion of the periodic table of elements.

Thirteen kinds of metal ions (including Mg^{2+}, Al^{3+}, Ca^{2+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Zr^{4+}, Ag^{+}, Sn^{4+}, Ce^{3+}) were chosen to combine with PA. The concentration of PA was 0.013 mol/L. The concentrations of metal ions were increased from 0.0065 mol/L to 0.3 mol/L gradually to investigate whether the visible precipitate formed. The volume ratio of PA solution and metal ions solution is 1:1. As shown in Fig. S1, five kinds of metal ions including Ag^{I}, Fe^{III}, Ce^{III}, Zr^{IV}, and Sn^{IV} can combine with PA to form visible precipitate. However, in the widely range of concentrations, the other eight kinds of metal ions could not form visible precipitate when added them into PA solution.

The reagents for supplying metal ions are as follows: $MgSO_4$, $AlCl_3 \cdot 6H_2O$, $CaCl_2$, $MnCl_2 \cdot 4H_2O$, $FeCl_3 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $CuSO_4 \cdot 5H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, $ZrCl_4$, $AgNO_3$, $SnCl_4 \cdot 5H_2O$, $Ce(NO_3)_3 \cdot 6H_2O$. All the reagents are of analytical grade and used without further purification.

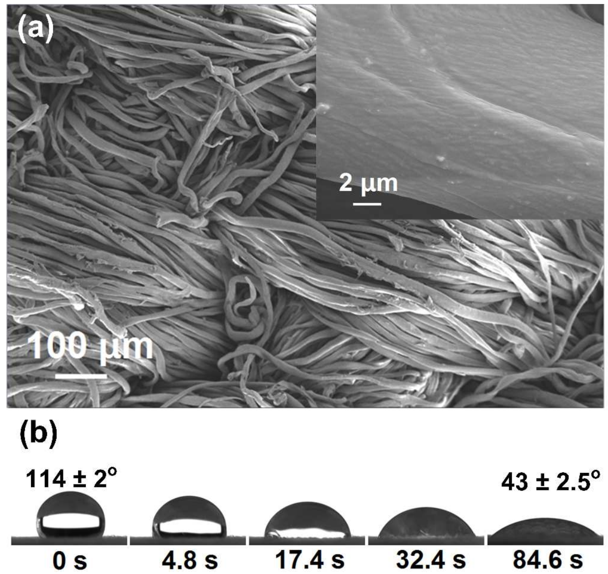

Figure S2. (a) SEM image of the cotton fabric directly modified with PDMS. The inset clearly displays the smooth morphology of the fabric surface. (b) Sequent captures of a water droplet placed on the PDMS modified cotton fabric.

Table S1. Summary of experimental detail for superhydrophobic cotton fabric preparation

Metal ion	$C_{M^{n+}}$ (mol/L)	C_{PA} (mol/L)	Assembly cycles	Contact Angle (°)	SEM image
Ag^+	0.01	0.013	1	142.2 ± 2.8	Figure S5a
Ag^+	0.05	0.013	1	144.1 ± 2.4	Figure S5b
Ag^+	0.15	0.013	1	146.3 ± 2.0	Figure S5c
Ag^+	0.3	0.013	1	148.8 ± 2.4	Figure 4a,b
Fe^{3+}	0.01	0.013	1	142.1 ± 2.5	Figure 3a
Fe^{3+}	0.01	0.013	2	144.2 ± 2.3	Figure 3b
Fe^{3+}	0.01	0.013	3	147.2 ± 1.5	Figure 3c
Fe^{3+}	0.01	0.013	4	150.4 ± 1.7	Figure 3d
Fe^{3+}	0.01	0.013	5	151.5 ± 1.3	Figure 1b
Fe^{3+}	0.01	0.013	8	152.9 ± 1.8	Figure 3e
Fe^{3+}	0.01	0.0065	5	152.3 ± 1.3	Figure S4a,b
Fe^{3+}	0.01	0.02	5	148.1 ± 1.6	Figure S4c,d
Ce^{3+}	0.01	0.013	1	149.0 ± 1.6	Figure S7a,b
Ce^{3+}	0.01	0.013	3	151.3 ± 1.5	Figure S7c,d
Ce^{3+}	0.01	0.013	5	152.4 ± 1.3	Figure 4c,d
Zr^{4+}	0.01	0.013	1	148.1 ± 1.7	Figure S9a,b
Zr^{4+}	0.01	0.013	3	149.5 ± 1.9	Figure S9c,d
Zr^{4+}	0.01	0.013	5	150.2 ± 2.1	Figure 4e,f
Sn^{4+}	0.01	0.013	5	147.4 ± 1.4	Figure S11a,b
Sn^{4+}	0.03	0.013	5	148.0 ± 1.8	Figure S11c,d
Sn^{4+}	0.05	0.013	5	151.6 ± 2.6	Figure 4g,h

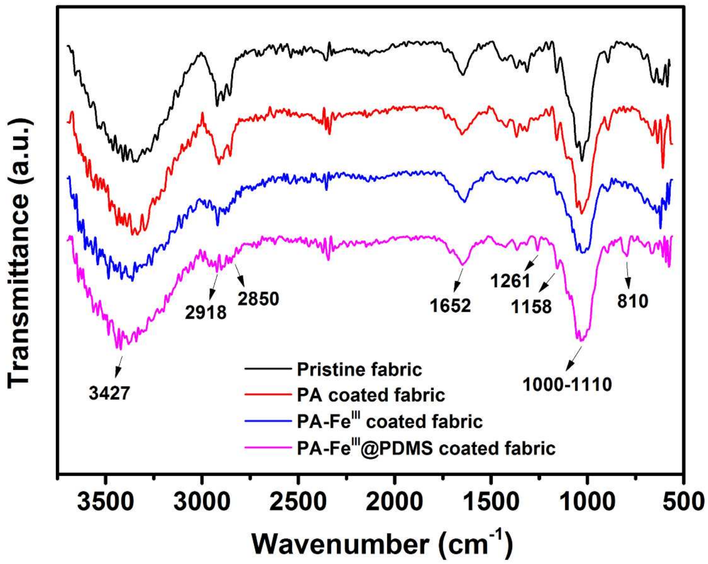

Figure S3. ATR-FTIR spectra of the cotton fabrics.

The chemical components on the surface of cotton fabrics were verified by the ATR-FTIR spectra. The broad band at approximate 3427 cm^{-1} is the peak of –OH. The vibration peaks at 2918 cm^{-1} and 2850 cm^{-1} were attributed to –C–H stretching vibrations of $–CH_2$ and $–CH_3$ groups, which come from cellulose or the added PDMS. The peaks at about 1652 cm^{-1} and 1158 cm^{-1} presented in all the spectra could be attributed to the –C(=O)O and C(=O)O–C stretching vibrations, respectively. The absorption band at 1000-1110 cm^{-1} should be related to the C–O band from cellulose.[1] Additionally, stretching frequencies of the P=O groups which come from $–HPO_4^{2-}$ in the fabrics containing with PA appear to be overlapped by the –C=O band near 1652 cm^{-1}. Meanwhile, the characteristic peak of the $–PO_4^{3-}$ at about 1100 cm^{-1} presented to be overlapped by the C–O band.[2] After modification by PDMS, the absorption bands at 1261 cm^{-1} and 810 cm^{-1} appeared, which associated with the bending vibration of $Si–CH_3$ and the symmetric stretching vibration of Si–O–Si in PDMS, respectively.[3]

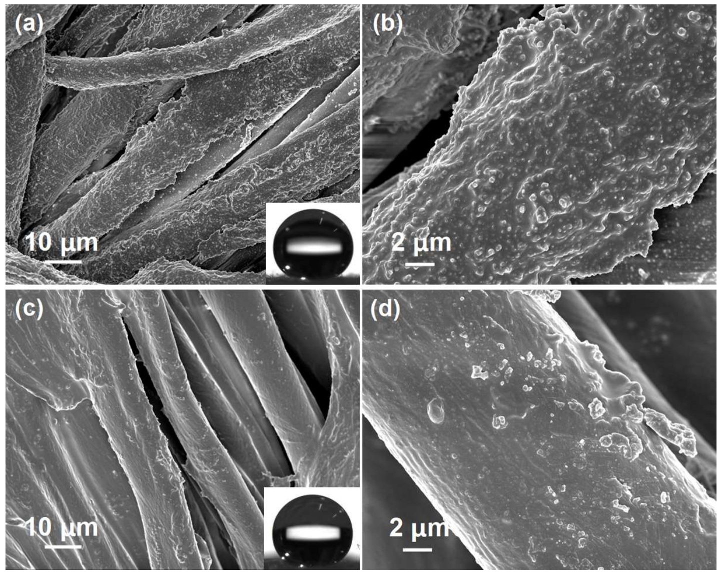

Figure S4. SEM images of the PA-Fe^{III}@PDMS coated cotton fabrics prepared with different concentrations of PA: (a, b) 0.0065 mol/L, (c, d) 0.02 mol/L. The insets of (a) and (c) are the photographs of static water contact state on the corresponding fabrics.

As shown in Fig. S4a,b, complete coating on the fabric fibers could be found when using lower concentration of PA (0.0065 mol/L). Increase the concentration of PA to 0.02 mol/L, which is twice as much as that of Fe^{III}, a small quantity of aggregations packed on the fabric surface (Figure S4c,d). Results indicated that decreasing concentration of PA (increasing the concentration of metal ion relatively) is helpful to form precipitate, the same conclusion can be obtained from the experiments of PA-Ag^{I} shown in Figure S5.

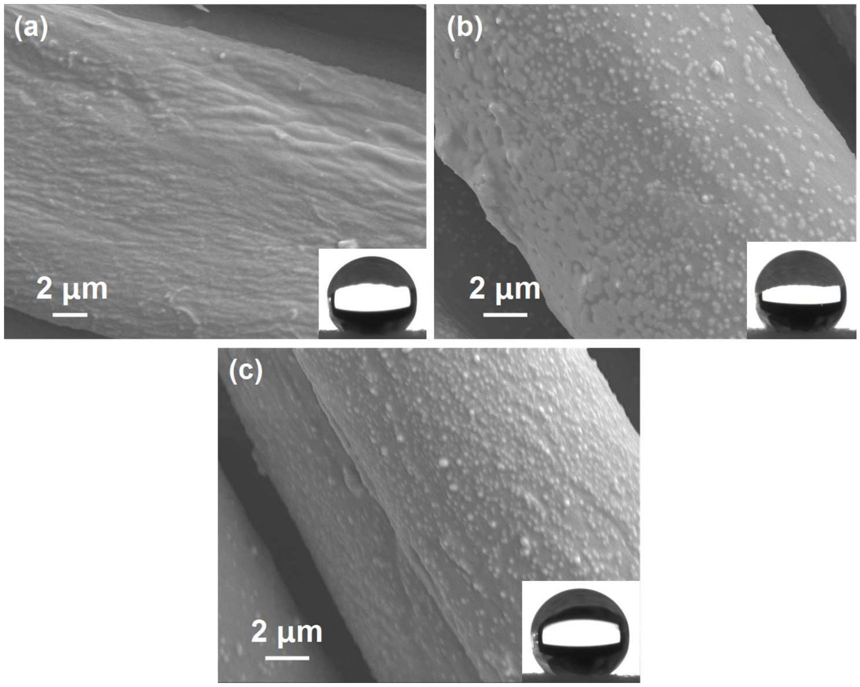

Figure S5. SEM images of PA-Ag^{I}@PDMS cotton fabrics prepared with different concentrations of Ag^{+}: (a) 0.01 mol/L, (b) 0.05 mol/L, (c) 0.15 mol/L.

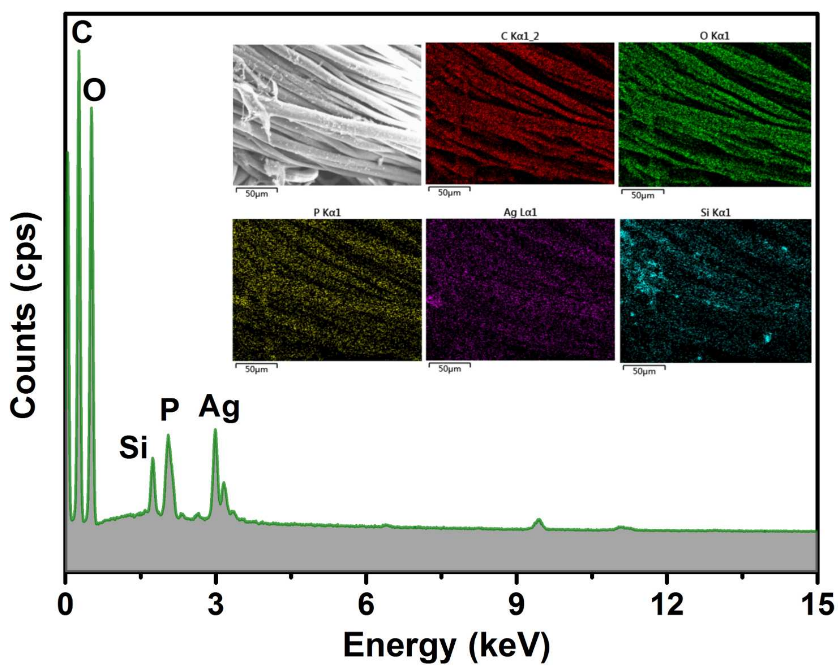

Figure S6. EDS spectrum of the PA-Ag^{I}@PDMS cotton fabric. Insets are the EDS maps of C, O, P, Ag and Si elements on the PA-Ag^{I}@PDMS fabric.

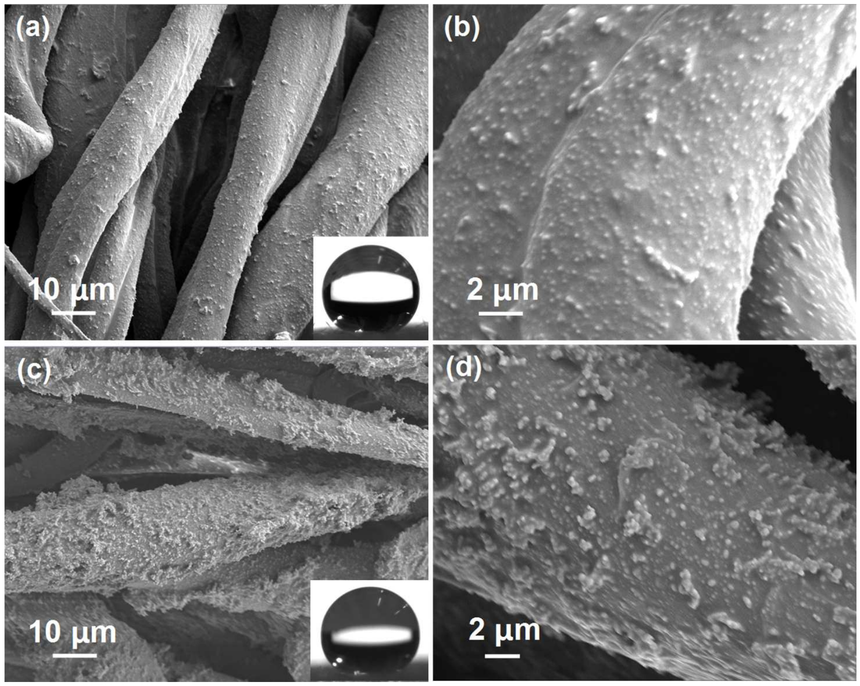

Figure S7. SEM images of PA-Ce^{III}@PDMS cotton fabrics prepared with different assembly cycles: (a, b) one, (c, d) three. The concentration of Ce^{3+} was 0.01 mol/L.

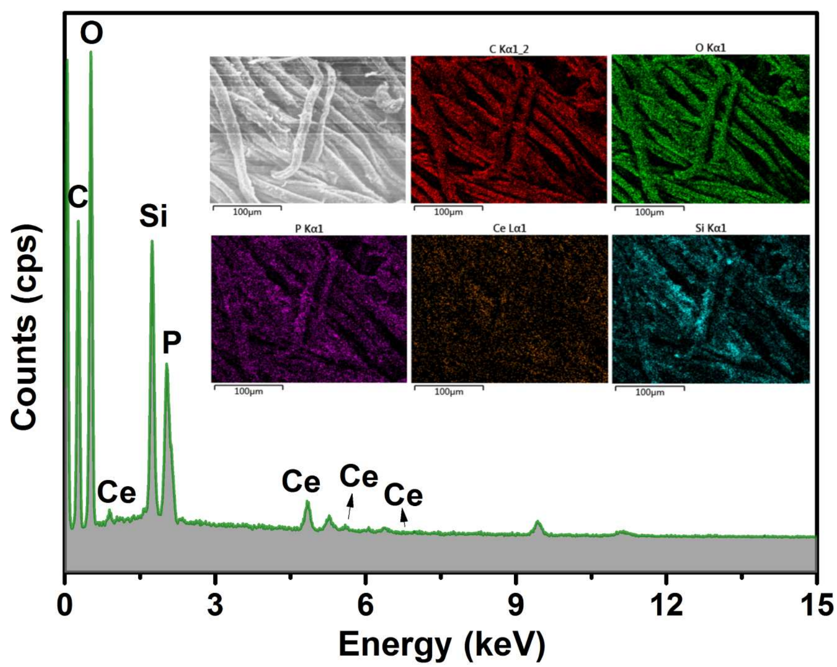

Figure S8. EDS spectrum of the PA-Ce^{III}@PDMS cotton fabric. Insets are the EDS maps of C, O, P, Ce and Si elements on the PA-Ce^{III}@PDMS fabric.

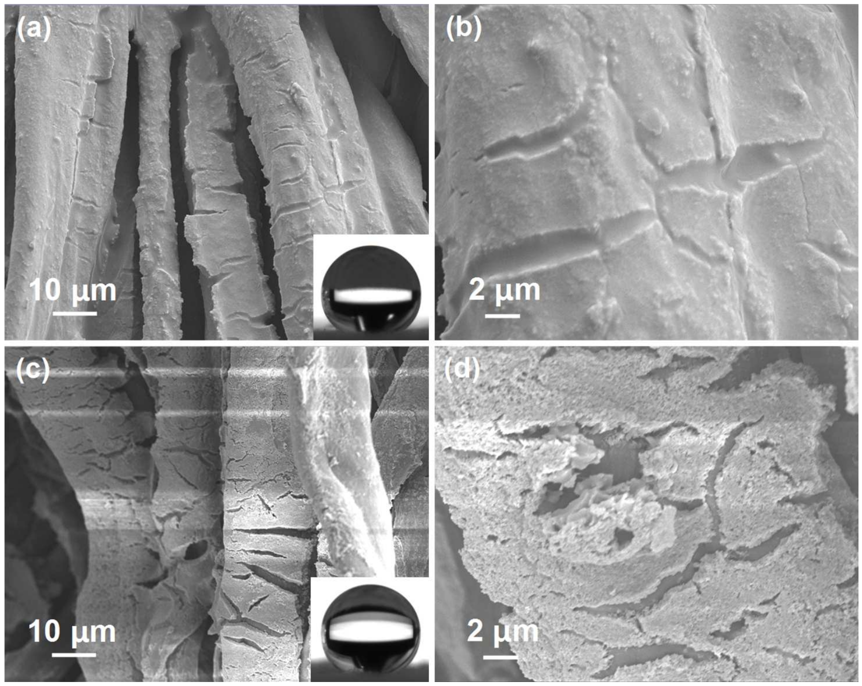

Figure S9. SEM images of PA-Zr^{IV}@PDMS cotton fabrics prepared with different assembly cycles: (a, b) one, (c, d) three. The concentration of Zr^{4+} was 0.01 mol/L.

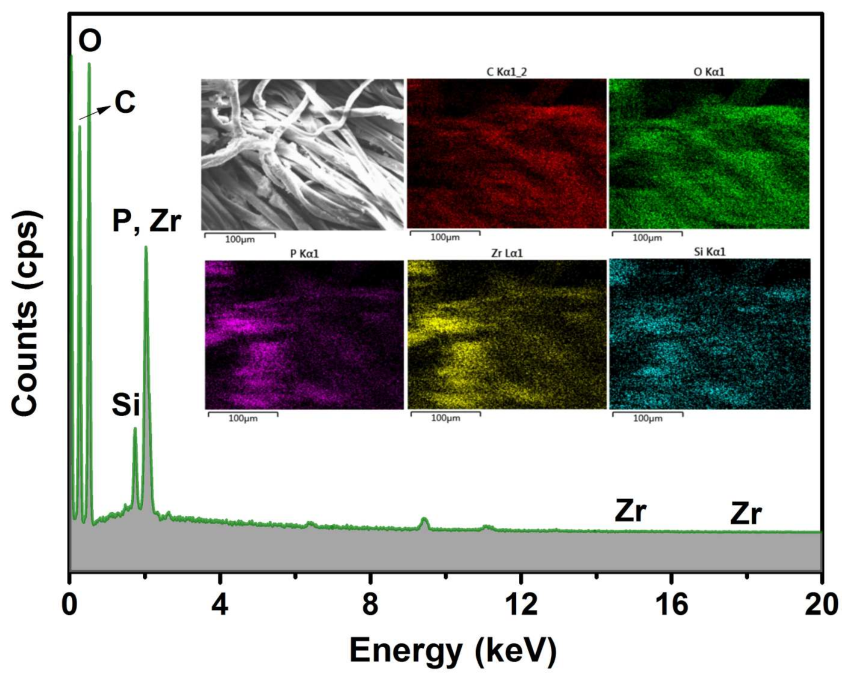

Figure S10. EDS spectrum of the PA-Zr^{IV}@PDMS cotton fabric. Insets are the EDS maps of C, O, P, Zr and Si elements on the PA-Zr^{IV}@PDMS fabric.

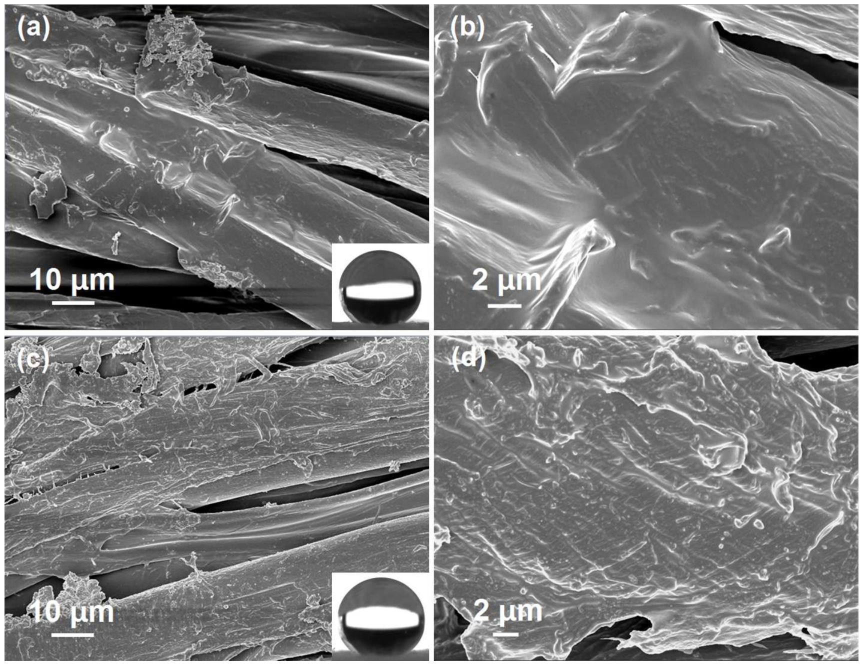

Figure S11. SEM images of PA-Sn^{IV}@PDMS cotton fabrics prepared with different concentrations of Sn^{4+}: (a, b) 0.01 mol/L, (c, d) 0.03 mol/L.

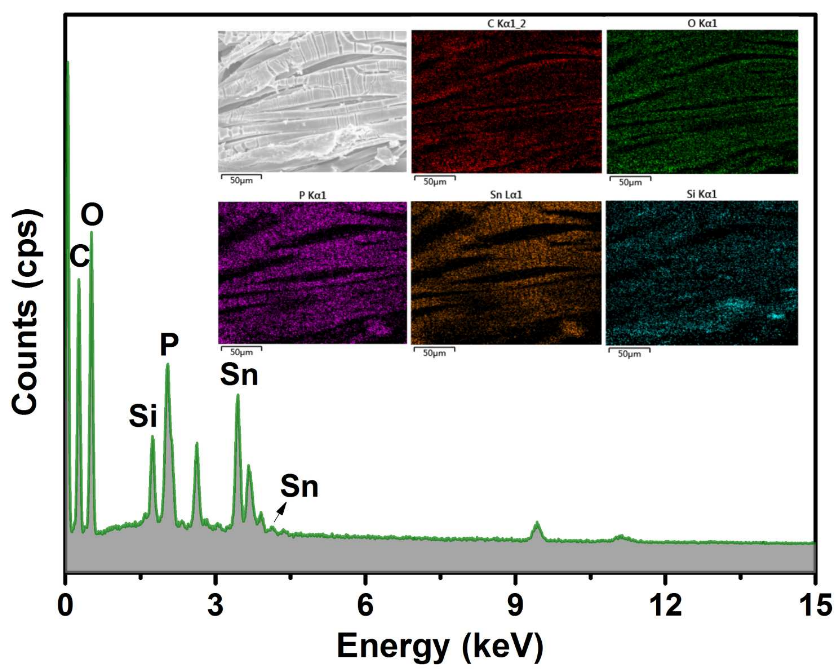

Figure S12. EDS spectrum of the PA-Sn^{IV}@PDMS cotton fabric. Insets are the EDS maps of C, O, P, Sn and Si elements on the PA-Sn^{IV}@PDMS fabric.

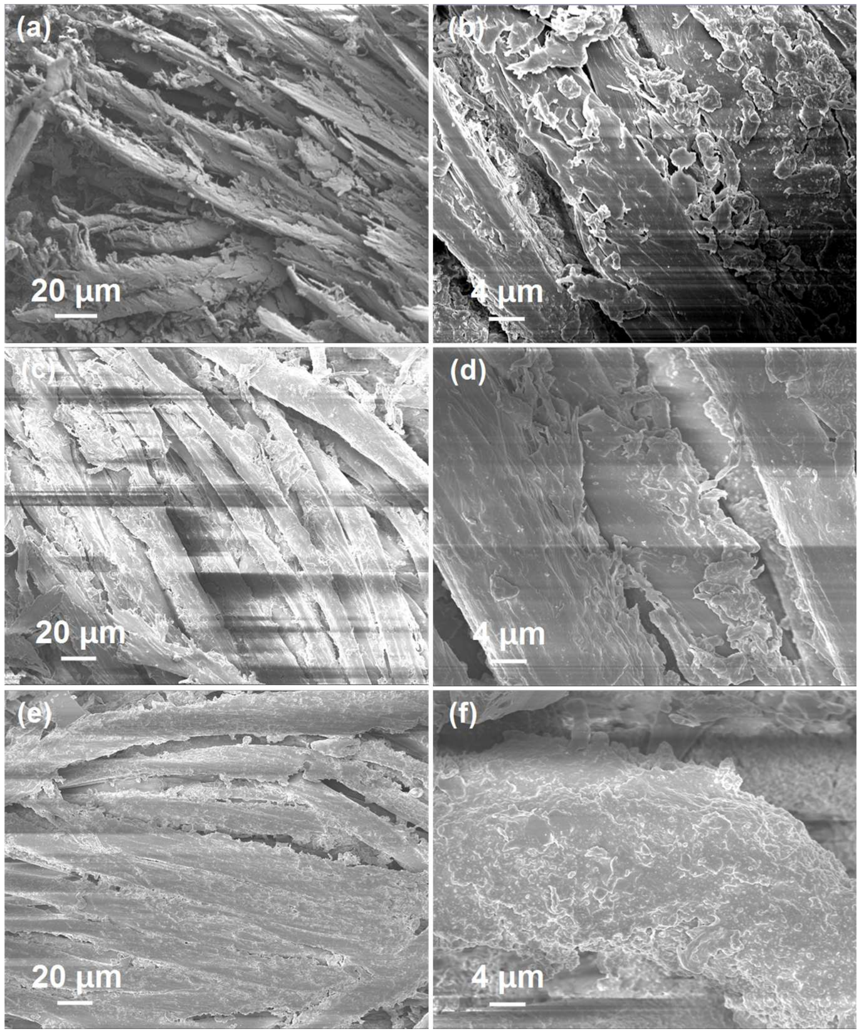

Figure S13. SEM images of PA-Fe^{III}@PDMS coated cotton fabrics after abrasion for 30 cycles using different meshes of sandpaper: (a),(b) 600 mesh; (c),(d) 1000 mesh; (e),(f) 2000 mesh.

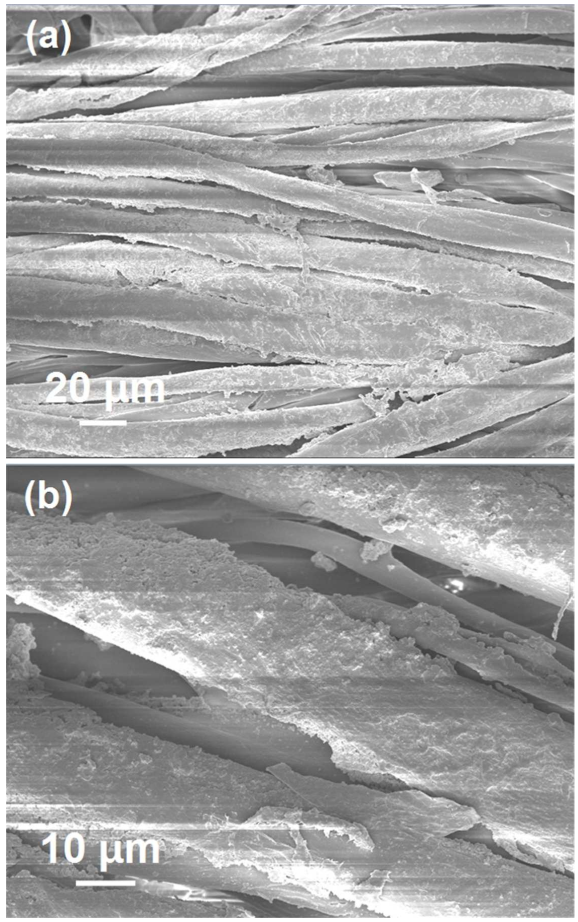

Figure S14. SEM images of PA-Fe^{III}@PDMS coated cotton fabric after repeated torn by the adhesive tape for 300 cycles.

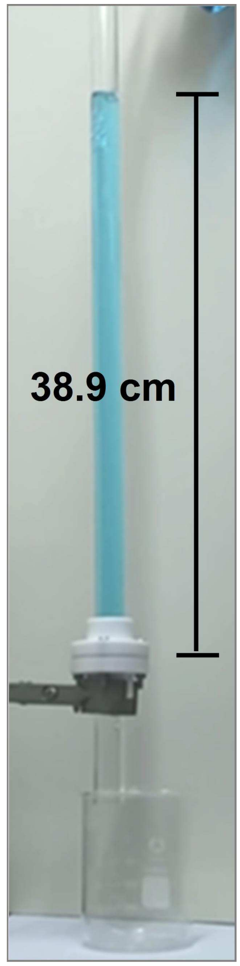

Figure S15. Photograph of the measurement of water intrusion pressure on the as-prepared PA-Fe^{III}@PDMS cotton fabric. Water was colored with methylene blue.

References

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(2) Chen, Y. Q.; Zhao, S.; Liu, B.; Chen, M. Y.; Mao, J. L.; He, H. R.; Zhao, Y. C.; Huang, N.; Wan, G. J. Corrosion-Controlling and Osteo-Compatible Mg Ion-Integrated Phytic Acid (Mg-PA) Coating on Magnesium Substrate for Biodegradable Implants Application. *ACS Appl. Mater. Interfaces* **2014**, *6*, 19531-19543.

(3) Lee, J. H.; Kim, D. H.; Han, S. W.; Kim, B. R.; Park, E. J.; Jeong, M-G. Ju Hwan Kim, J. H.; Kim, Y. D. Fabrication of Superhydrophobic Fibre and Its Application to Selective Oil Spill Removal. *Chem. Eng. J.* **2016**, *289*, 1-6.