Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Versatile fabrication of superhydrophobic and ultralight cellulose based aerogel for oil spillage cleanup

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Supplementary table and movie captions:

Table S1. The changes of water contact angle (WCA) at different plasma treatment time (the first plasma treatment).

Table S2. The changes of water contact angle (WCA) after the second plasma treatment.

Table S3. The changes of water contact angle (WCA) after the third plasma treatment.

Table S4. The changes of water contact angle (WCA) at different silane reagents concentration and solvents.

Table S5. Comparison of various superabsorbents.

Movie S1. The dynamic measurements of water adhesion on the sample surface.

Movie S2. The dynamic measurements of oil permeation on the sample surface.

Movie S3. The selective oil absorption process of superhydrophobic cellulose aerogel in the soybean oil-water mixture (the oil was colored with orange).

Movie S4. The selective oil absorption process of superhydrophobic cellulose aerogel in the chloroform-water mixture (the chloroform layer was colored with blue).

Movie S5. The abrasion test of the as-prepared superhydrophobic surface (the aluminium oxide sandpaper of 600 mesh as an abrasion surface).

The OTMS concentration, the activation time of cellulose hydroxyl and the plasma radiation time were all tested during the experiment process and shown in Tables S1-S4.

In order to make the cellulose hydroxyl activated, the as-prepared cellulose aerogel was firstly placed into the plasma treatment system (KSUN, 50kw) for treating a certain time under the argon atmosphere. The changes of water contact angle (WCA) at different plasma treatment time were tested and listed in Table S1. All the CA values were obtained by measuring five different positions for each sample.

Table S1 The changes of water contact angle (WCA) at different plasma treatment time (the first plasma treatment).

Function	Samples	Plasma treatment time /min	CA(°)
activation of cellulose hydroxyl	1	5	123.6 ± 7.5
	2	15	132 ± 0.95
	3	25	138.9 ± 0.36
	4	30	148.8 ± 0.11
	5	40	141.1 ± 0.12
	6	60	140.9 ± 0.06

Note: Silane modifier concentration: 0.5% (v/v) OTMS dissolved in n-hexane.

It can be seen from Table S1, the CA values increased gradually with the increase of activation time from 5min to 30min. However, when the activation time was more than 30 minutes, the CA values have a slight decline. The possible reasons can be explained as follows: with the extension of the plasma processing time, the hydroxyl groups on the fiber surface were activated and exposed gradually. The hydrolyzed –Si–OH of silane was very reactive toward the activated hydroxyl groups (C–OH). After modified by the silane reagent (OTMS), the hydrophobic property of the sample was greatly improved. However, when the radiation time exceeds a certain value, the increase of the activated hydroxyl number does not improve the hydrophobicity of sample, contrary, too much plasma radiation may also destroy the fiber surface structure, resulting in a decline of the CA values. Thus, 30min was chosen as the optimal activation time for the cellulose aerogel.

After the cellulose hydroxyl activated, the sample was placed into 0.5% (v/v) OTMS for modification. Thereafter, the sample was etched by plasma for another 5 min (the second plasma treatment) in order to keep the sample surface a certain roughness. The changes of water contact angle (WCA) at the second plasma treatment were listed in Table S2.

Table S2 The changes of water contact angle (WCA) after the second plasma treatment.

Function	Samples	Plasma treatment time /min	CA(°)
keep the surface a certain roughness	1	5	133.8 ± 0.29
	2	5	137.6 ± 0.11
	3	5	142.9 ± 0.36
	4	5	152.4 ± 0.13
	5	5	148.6 ± 0.13
	6	5	142.3 ± 0.36

Note: Silane modifier concentration: 0.5% (v/v) OTMS dissolved in n-hexane.

It can be seen from Table S2, the CA values of samples were all increased when etched by plasma for another 5 min. When the samples were firstly activated for 30 minutes and secondly etched by plasma for another 5 minutes, the superhydrophobic state could be achieved, for example, the CA value of sample 4 increased from 148.8°to 152.4°.

In order to study the strengthen effect of the plasma, the samples were continued to be etched by plasma for another 5 minutes (the third plasma treatment) after modification by silane modifier. The changes of water contact angle (WCA) after the third plasma treatment were also listed in Table S3.

Table S3 The changes of water contact angle (WCA) after the third plasma treatment.

Function	Samples	Plasma treatment time /min	CA(°)
keep the surface a certain roughness	1	5	141.7 ± 0.05
	2	5	144.5 ± 0.06
	3	5	150.9 ± 0.11
	4	5	156.8 ± 0.06
	5	5	149.5 ± 0.12
	6	5	144.3 ± 0.16

Note: Silane modifier concentration: 0.5% (v/v) OTMS dissolved in n-hexane.

It can be seen from Table S3, the hydrophobility of the samples were increased greatly and the CA values of samples were all greater than 140°. Among which, the sample 3, 4 and 5 have reached the superhydrophobic state (WCA>150°), indicating the positive strengthen effect of the plasma treatment. The reason can be explained as follows: after the plasma etching for a short time, the surface of the samples became coarser, forming many micro/nano-structures. Due to the rough nanostructures, the water droplets have no direct contact with the wall surface, resulting in the formation of Cassie impregnating wetting area. Therefore, the water droplets exhibited the superhydrophobic state and the hydrophobility could be strengthened by plasma etching for several times.

The changes of CA values with the OTMS concentration were also tested in this study and listed in Table S4. It can be seen from Table S4, the water contact angle reached its maximum value when the concentration of OTMS was 0.5% and the plasma treatment time was 30min. However, with the concentration of OTMS increased from 0.5% to 2.5%, the CA values have a slight decline from 148.8° to 116.3°. This phenomenon may be associated with the hydrolysis and condensation reactions rate of silane reagents. When increased the concentration of OTMS, the hydrolysis rate increased rapidly. Its own polymerization reaction was mainly occurred on the hydrolyzed –Si–OH of silane, reducing its combined rate with the cellulose hydroxyl group. Therefore, the water contact angle will decrease.

Table S4 The changes of water contact angle (CA) at different silane reagents concentration and solvents.

Samples	OTMS concentration	Solvent	Plasma treatment time /min	CA(°)
1	0.5%	n-hexane	30	148.8 ± 0.11
2	1%	n-hexane	30	119.2 ± 0.11
3	1%	n-hexane	—	98.9 ± 1.17
4	2.5%	n-hexane	30	116.3 ± 0.93

Table S5 Comparison of various superabsorbents.

Oil absorbents	**Density (mg/cm^3)**	**$M_{\text{oil/org}}$ (g/g)**	**$V_{\text{oil/org}}$ (cm^3/cm^3)**	**Oil recovery method**	**Ref.**
PDMS sponge	180	4~11	0.89~1.34	squeezing	12
Swellable porous PDMS	180	18~22	3.9~5.3	solvent extraction or squeezing	13
PU-based graphene foam	---	9~27	0.7~0.96	solvent extraction	15
PU sponges	---	13~26	---	squeezing	44,45
functionalized graphene aerogel	14.4	30~112	---	drying	7
Silylated nanocellulose sponge	17.3	49~102	---	solvent extraction	23
Superabsorbent from microfibrillated cellulose fibers	2.4	88~228	---	squeezing	4
cotton towel	240	5	1.43	squeezing	11
cellulose aerogel from waste paper fibers	40	18~20	---	squeezing	17
cellulose based aerogel	34	19~42	0.72~0.99	solvent extraction or burning	this work
organic nanocomposites	---	2~14	---	---	41,42
3D macroporous Fe/C	---	4~10	---	solvent extraction	43
nanocellulose/TiO_2 aerogel	30	27	0.88	solvent extraction	22
graphene/α-FeOOH aerogel	---	12~27	---	burning	46

Noting: “$M_{\text{oil/org}}$” mass-based adsorption capacity, “$V_{\text{oil/org}}$” volume-based absorption capacity
“----” unmentioned in the reference.