A manuscript submitted to Green Chemistry

Supporting information

Development of a Facile and Bi-functional Superhydrophobic Suspension and its Applications as Superhydrophobic Coating and Aerogel in high-efficiency Oil-water Separation

Xin Wang,^a Feng Liu,^a Yudong Li,^a Wenbo Zhang,^a Shunwen Bai,^b Xuelian Zheng,^a Jinmu Huan,^a Guoliang Cao,^b Tinghan Yang,^a Meng Wang,^a Zishuai Jiang,^a Chengyu Wang,^{a*}and Shih-Hsin Ho^{b*}

^a Key Laboratory of Bio-Based Material Science and Technology of Ministry of

Education, Northeast Forestry University, Harbin, 150040, P. R. China

^b State Key Laboratory of Urban Water Resources and Environment, Harbin Institute of Technology, Harbin, 150040, P. R. China

Supplementary Information contains:

Supplementary Methods

Supplementary Figure 1–7 and Table 1-5

Supplementary Movie explanation

Supplementary References

*Corresponding Author

*Email: <u>wangcy@nefu.edu.cn</u>

*Email: stephen6949@hit.edu.cn

1. Supplementary Methods

1.1 Superhydrophobic suspension fabrication with different solvents

Preparations of SH suspension with solvent ethanol, n-hexane, acetone, and water were divided into two parts: pretreatment reaction and prolonged reaction. In the pretreatment reaction process, 0.02 kg of fumed silica was treated by 0.02 kg of HDTMS with a small volume of solvent (Table S1-S4). Then, 0.0011 kg of formic acid was added into the above mixed solution in the manner of HDTMS to generate a homogenous suspension after magnetic stirring for 10 min. Afterward, a large volume of solvent (Table S1-S4) was added to reduce SH suspension concentration, and organic solvent routes required 4h of mechanical stirring in the prolonged reaction part. However, as demonstrated by Li et al,¹ waterborne SH suspension production only needed a long time static reaction owing to water reaction conditions, which facilitated HDTMS methoxy group hydrolysis. Energy consumption was calculated only in the forms of electricity depletion throughout the whole preparation.

1.2 Life cycle assessment

(1) Hexadecyltrimethoxysaliane synthesis route



Scheme 1. Reagent and conditions: (a) Toluene as solvent, 35 bar of ethylene pressure, 100° C, 60 min; (b) CH₂Cl₂ as solvent, methanol, room temperature, 2h; (c) CH₂Cl₂ as solvent, sodium hypochlrite, 0°C, 30 min; (d) Tetrahydrofuran as the solvent, thionyl chloride, methanol, room temperature, 4h; (d) Currents density 200 mA cm⁻², 40-45°C; (e) Tetrahydrofuran as solvent, 50 bar of H₂ pressure, 100° C, 2.5h; (f) Dimethyl sulfoxide as the solvent, 1,5-Dibromopentane, trichlorosilane; (g) Without solvent, methanol, room temperature.

Since no HDTMS LCIA EIs results are acquirable in the LCA database, HDTMS synthesis route is built based on reported several works in laboratory scale, and EIs of 1kg production are calculated via the stoichiometry.²⁻⁹ The HDTMS production requires ethylene, methanol, thionyl chloride, tetrahydrofuran 1,5-dibromopentane, and trichlorosilane. However, 1,5-dibromopentane

and trichlorosilane do not exist in the eco-invent 3.4 database. Therefore, ramification materials synthesis routes need to be established, which is described below according to papers. Dodecene is prepared directly by ethylene, and 1 kg of dodecene synthesis requires 1.149 kg of ethylene. The dodecene and methanol are raw material fabricated dodecan-1-ol, and 1kg of dodecan-1-ol synthesis requires 0.931kg of dodecene and 0.177 kg of methanol. Lauric acid is prepared by dodecan-1-ol. 1kg of lauric acid needs 0.930 kg of dodecan-1-ol and 0.5025 kg of sodium hypochlorite as an oxidizing agent. Dodecanedioic acid monomethyl ester is prepared by lauric acid, methanol, and thionyl chloride. 1 kg of dodecanedioic acid monomethyl ester production requires 1.4886 kg of lauric acid, 0.205 kg of methanol, and 0.387 kg of thionyl chloride. Methyl undecenate is prepared by electrolysis dodecanedioic acid monomethyl ester. 1 kg of Methyl undecenate needs 1.232 of kg dodecanedioic acid monomethyl ester. 10-Undecen-1-ol is prepared by methyl undecenate through an electrolytic process. 1kg of 10-undecen-1-ol needs 1.164 kg of methyl undecenate. Hexadecyltrichlorosilane is prepared by 10-undecen-1-ol, 1,5-dibromopentane, and trichlorosilane. 1 kg of hexadecyltrichlorosilane requires 0.473 kg of 10-undecen-1-ol, 0.638 kg of 1,5dibromopentane and 0.376 kg of trichlorosilane. 1 kg of hexadecyltrimethoxysilane is prepared by 1.282 kg of hexadecyltrichlorosilane and 0.342 kg of methanol without solvent.

(2) 1,5-Dibromopentane synthesis route



Scheme 2. Reagent and conditions: (a) Acetone as solvent, room temperature, 2h; (b) Tetrahydrofuran as the solvent, room temperature, 0.5h; (c) Toluene as solvent, bromine.

1,5-Dibromopentane and trichlorosilane as ramification materials are not accessible in the eco-invent 3.4 database. Production of trichlorosilane and 1,5-dibromopentane are also studied as part of this synthesis route.¹⁰⁻¹³ To produce 1kg of 1,5-dibromopentane, 0.453 kg of 1,5-pentanediol is required as direct original supplement. Due to lack of LCIA data of 1,5-pentanediol in the existed database, further details about the synthesis of 1,5-pentanediol should be detected and simple chemical reagents that can be accessible to ecoinvent 3,4 database should be searched. Delta-Valerolactone which is the upstream substance to prepare 1,5-pentanediol can be prepared by more ordinary chemical tetrahydrofuran.

(3) Trichlorosilane synthesis route

 $Si + 3HCl \rightarrow SiHCl_3 + H_2$

Scheme 3. Reagent and conditions: hydrogen chloride, silicon, heated to 300°C~400°C.14

The trichlorosilane is obtained by passing hydrogen chloride through an iron tube filled with silicon and heated to 300°C~400°C. 1kg trichlorosilane is prepared by 0.207 kg of silicon and 0.807 kg of hydrogen chloride. 0.015kg of hydrogen which is released to air is the by-product of the reaction.

(4) Fumed silica nanoparticles synthesis route

 $SiCl_4 + 2H_2 + O_2 \rightarrow SiO_2 + 4HCl$

Scheme 4. Reagent and conditions: silicon tetrachloride, hydrogen, oxygen, temperature over 1500 °C

Fumed silica is made from flame pyrolysis of silicon tetrachloride or from quartz sand vaporized. Production of 1kg fumed silica which prapered by this route requires 2.828 kg of silicon tetrachloride, 0.067 kg of hydrogen, and 0.533 kg of oxygen.

2. Supplementary Figure 1–7 and Table 1-5



Figure S1. TEM photograph of NCF.



Figure S2. Two boundaries of four manufacturing routes of SH suspension.



Figure S3. (a) Comparative results of HDTMS synthesis. (b) Comparative results of fumed SiO₂ nanoparticle synthesis.

Process n-hexane	Input		Unit	
Pretreatment	n-hexane mass		kg	0.165
	mixing electricity	energy	kWh	0.02025
	dispersing electricity	energy	kWh	1.875
	formic acid	mass	kg	0.0011
	SiO ₂ nanoparticles	mass	kg	0.02
	HDTMS	mass	kg	0.02
Prolonged reaction	n-hexane	mass	kg	0.79625
	reaction electricity	energy	kWh	2.863
Process n-hexane	Output		Unit	
	SH suspension	mass	kg	1

Table S1. Input and output of SH suspension preparation using n-hexane as solvent.

Process acetone	Input		Unit	
Pretreatment	acetone mass		kg	0.196
	mixing electricity	energy	kWh	0.02025
	dispersing electricity	energy	kWh	1.875
	formic acid	mass	kg	0.0011
	SiO ₂ nanoparticles	mass	kg	0.02
	HDTMS	mass	kg	0.02
Prolonged reaction	acetone	mass	kg	0.765
	reaction electricity	energy	kWh	2.863
Process acetone	Output		Unit	
	SH suspension	mass	kg	1

Table S2. Input and output of SH suspension preparation using acetone as solvent.

Process ethanol	Input		Unit	
Pretreatment	ethanol	ethanol mass		
	mixing electricity	energy	kWh	0.02025
	dispersing electricity	energy	kWh	1.875
	formic acid	mass	kg	0.0011
	SiO ₂ nanoparticles	mass	kg	0.02
	HDTMS	mass	kg	0.02
Prolonged reaction	ethanol	mass	kg	0.79375
	reaction electricity	energy	kWh	2.863
Process ethanol	Output		Unit	
	SH suspension	mass	kg	1

 Table S3. Input and output of SH suspension preparation using ethanol as solvent.

Process water	Input		Unit	
Pretreatment	water mass		kg	0.25
	mixing electricity	energy	kWh	0.02025
	dispersing electricity	energy	kWh	1.875
	formic acid	mass	kg	0.0011
	SiO ₂ nanoparticles	mass	kg	0.02
	HDTMS	mass	kg	0.02
Prolonged reaction	water	mass	kg	0.71125
	reaction electricity	energy	kWh	0.66
Process water	Output		Unit	
	SH suspension	mass	kg	1

Table S4. Input and output of SH suspension preparation using water as solvent



Figure S4. EIs results of SH suspension fabrication using acetone processed by Monte Carlo method.

Categories	Unit	Acetone	Ethanol	n-Hexane	Water
AP	kg SO ₂ -Eq	0.018590009	0.012610084	0.013278589	0.00671524
GWP	kg CO ₂ -Eq	4.310499074	1.95516054	2.257785345	1.310504385
EP	kg NOx-Eq	0.014497129	0.017241838	0.010957057	0.005320238
FAETP	kg 1,4-DCB-Eq	0.030576614	0.0923436	0.034205939	0.015767551
FSETP	kg 1,4-DCB-Eq	0.059060779	0.05891405	0.071765644	0.026763664
HTP	kg 1,4-DCB-Eq	1.120072075	2.748095556	0.700928956	0.304441888
IR	DALYs	1.42223E-08	1.31455E-08	1.65358E-08	4.46996E-09
LU	m ² a	0.012925972	0.011456341	0.007944508	0.004248171
MA	m ³ air	61480.93146	257093.6125	43282.57902	35287.7026
MAETP	kg 1,4-DCB-Eq	0.305066052	0.172401321	0.277662076	0.100299084
MSETP	kg 1,4-DCB-Eq	0.350377914	0.211747891	0.321097868	0.113448895
PCO	kg formed ozone	0.019715212	0.001234693	0.001752663	0.000198861
R	kg antimony-Eq	0.048554708	0.015919472	0.033357084	0.011902708
ODP	kg CFC-11-Eq	3.44785E-07	2.32949E-07	6.39105E-07	1.93469E-07
TAETP	kg 1,4-DCB-Eq	0.000624707	0.005361996	0.000565621	0.000325523

Table S5. EIs results of four SH suspension fabrication processed by Monte Carlo method.



Figure S5. (a) Malodours air EIs of 1 kg SH suspension fabrication and solvent volatilization after utilization. (b) Photochemical oxidation EIs of 1 kg SH suspension fabrication and solvent volatilization after utilization.



Figure S6. (a) FT-IR graph of SiO₂ and HDTMS@SiO₂ (b) High-resolution XPS spectra of C 1s of HDTMS@SiO₂ (c) High-resolution XPS spectra of Si 2p of HDTMS@SiO₂ (3) High-resolution XPS spectra of Si 2p of HDTMS-AS@NCF



Figure S7. (a) Model of 6160 oscillating Abrasion Tester. (b) Experimental procedure of abrasion device. (c) 800 mL abrasion sands used as wear medium.

Oil absorbent	Adsorption	Method	Comments	Solvent	Biodegradability	ref
	capacity (g/g)					
PDMS sponges						
Superhydrophobic PDMS sponge	4.72-20	Templating of NaCl method	Complicated	Dimethicone	No	15
Superhydrophobic PDMS sponge	4-34.0	Templating of saccharose method	Complicated	p-Xylene	No	16
Superhydrophobic PDMS sponge	4.0-11.0	Templating of sugar method	Complicated	Water	No	17
Modified PU Sponges						
PU@Fe3O4@SiO2@FP Sponge	13.26-44.50	Two steps of dip-coating method, CVD and annealed at high temperature	Complicated	Acetone	No	18
Superhydrophobic PU sponge	13	Two steps of dip-coating method and electroless deposition	Complicated	HCl	No	19
PPy-PTES sponge	21-31	Dip-coating method, CVD and heated drying	Complicated	Ethanol	No	20
Superhydrophobic PU Sponge	24.9-86.7	Dip-coating method heated drying	Easy	H ₂ O/ethanol (1:1)	No	21
PU@TiO ₂ sponge	3.0-7.0	Dip-coating method heated drying	Easy	Ethanol	No	22
Magnetic PU sponge	10-35	Two steps of dip-coating method	Complicated	Ethanol	No	23
Superhydrophobic PU sponge	18-26	Dip-coating method and heated drying	Easy	H ₂ O/ethanol (1:1)	No	24
Modified Melamine Sponges						
Superhydrophobic melamine Sponge	103-179	Dip-coating method and photocuring	Easy	CH_2Cl_2	No	25
PDMS functionalized melamine sponge	45-75	Dip-coating method and heated drying	Easy	n-Hexane	No	26
TPU-GO-TDA Foam	25.6-28.5	Dip-coating method	Easy	Water and ethanol	No	27
Polybenzoxazine functionalized melamine sponge	50-90	Dip-coating method and heated drying	Easy	Acetone	No	28
Modified other sponges						
Nanoporous divinylbenzene/SiO ₂ hybrid material	7.8-21.9	One-pot solvothermal method	Easy	Ethyl acetate	No	29
Shish-kebab Membrane	15-32	Modified flow-induced crystallization method	Complicated	Xylene	No	30
PP/PTFE composite foam	8.0-9.0	CO ₂ foaming process	Easy	Without	No	31
PLA foam	12.0-31	Freeze-drying treatment	Easy	Dioxan	Yes	32
Wood Sponge	16-41	Delignified and freeze-drying and CVD	Complicated	8% NaOH solution	Yes	33
Modified aerogels						
MTCS-modified chitin aerogel	29-58	Freeze-drying treatment and CVD	Complicated	11 wt % NaOH/4 wt % urea solution	Yes	34
Composite aerogel	33-36	Freeze-drying treatment and dip-coating method	Complicated	Water and acetone	Yes	35
Graphene/carbon nanotube hybrid aerogel	80-130	CVD and templating method	Complicated	Ethanol	No	36
Carbonaceous nanofiber aerogel	50-140	Template hydrothermal method, freeze-drying and pyrolysis	Complicated	Acetone	No	37
Cellulose aerogel	83-176	Long time solvent exchange and freeze-drying	Complicated	Water and	Yes	38

Table S6. the comparison between SHNCF aerogel and previous reported oil absorbents.

		method		tert-butanol		
SHNCF aerogel	13.03-32.95	One-pot freeze-drying method	Easy	Water	Yes	This
						work



Figure S8. (a) WCA of SHNCF aerogels with different degree of SiO_2 modification. (b) Oil adsorption capacity of SHNCF aerogels with different degree of SiO_2 modification



Figure S9. (a, b, c) N_2 adsorption-desorption isotherms of NCF, HDTMS-AS@NCF, and SHNCF aerogel. (d, e, f) Pore diameter distribution of NCF, HDTMS-AS@NCF, and SHNCF aerogel.



Figure S10. (a) Water contact angles of NCF, HDTMS-AS@NC, and SHNCF aerogel. (b) Oil adsorption capacities of NCF, HDTMS-AS@NCF, and SHNCF aerogel.

Sample	BET surface aera	Pore diameter	Pore volume
	(m^{2}/g)	(nm)	(cm^{3}/g)
NCF aerogel	6.864	6.04299	0.01923
HDTMS-AS@NCF	1.599	5.90642	0.00598
aerogel			
SHNCF aerogel	46.486	8.09398	0.12975

Table S7. BET surface area, pore diameter and pore volume of NCF, HDTMS-AS@NCF, and SHNCF aerogel.

3. Supplementary Movie explanation

Movie 1. Interaction between a 5µl water drop and the NCF-composited SH coating.

Movie 2. Superhydrophobicity of NCF-composited SH coating after scratched with a knife.

Movie 3. Self-cleaning performance test for NCF-composited SH coating.

Movie 4. Experimental process of abrasion device.

Movie 5. Oil suction process with the aid of an electric pump.

4. Supplementary References

- 1. Y. Li, B. Li, X. Zhao, N. Tian and J. Zhang, *ACS Appl Mater Interfaces*, 2018, **10**, 39391-39399.
- 2. N. Balachander and C. N. Sukenik, *Tetrahedron Letters*, 1988, **29**, 5593-5594.
- 3. K. Albahily, S. Licciulli, S. Gambarotta, I. Korobkov, R. Chevalier, K. Schuhen and R. Duchateau, *Organometallics*, 2011, **30**, 3346-3352.
- 4. J. M. Clay and E. Vedejs, *Journal of the American Chemical Society*, 2005, **127**, 5766-5767.
- 5. T. Vijai Kumar Reddy, B. L. A. Prabhavathi Devi, R. B. N. Prasad, M. Poornima and C. Ganesh Kumar, *Bioorganic & Medicinal Chemistry Letters*, 2012, **22**, 4678-4680.
- 6. A. Gheorghe, A. Matsuno and O. Reiser, *Advanced Synthesis & Catalysis*, 2006, **348**, 1016-1020.
- A. Weiper-Idelmann, M. aus dem Kahmen, H. J. Schäfer, M. Gockeln, P. H. Nielsen, A. Püschl, K. V. Mikkelsen and A. Senning, *Acta Chemica Scandinavica*, 1998, **52**, 672-682.
- 8. United States Pat., 6,150,551A, 1999.
- 9. *Germany Pat.*, WO2004/87655 A1, 2004.
- M. Hojo, C. Murakami, A. Fujii and A. Hosomi, *Tetrahedron Letters*, 1999, 40, 911-914.
- 11. S. Lai and D. G. Lee, *Tetrahedron*, 2002, **58**, 9879-9887.
- 12. J. M. Chong, M. A. Heuft and P. Rabbat, *The Journal of Organic Chemistry*, 2000, **65**, 5837-5838.
- 13. L. A. Saudan, C. M. Saudan, C. Debieux and P. Wyss, *Angewandte Chemie*, 2007, **119**, 7617-7620.
- 14. United States Pat., 2380995A, 1945.
- 15. X. Zhao, L. Li, B. Li, J. Zhang and A. Wang, J. Mater. Chem. A, 2014, 2, 18281-18287.
- A. Zhang, M. Chen, C. Du, H. Guo, H. Bai and L. Li, *ACS Appl Mater Interfaces*, 2013, 5, 10201-10206.
- 17. S. J. Choi, T. H. Kwon, H. Im, D. I. Moon, D. J. Baek, M. L. Seol, J. P. Duarte and Y. K. Choi, *ACS Appl Mater Interfaces*, 2011, **3**, 4552-4556.
- L. Wu, L. Li, B. Li, J. Zhang and A. Wang, ACS Appl Mater Interfaces, 2015, 7, 4936-4946.
- 19. Q. Zhu, Q. Pan and F. Liu, *The Journal of Physical Chemistry C*, 2011, **115**, 17464-17470.
- 20. X. Zhou, Z. Zhang, X. Xu, X. Men and X. Zhu, *Industrial & Engineering Chemistry Research*, 2013, **52**, 9411-9416.
- 21. S. Huang, ACS Appl Mater Interfaces, 2014, 6, 17144-17150.
- Y. Wang, Y. Zhu, C. Yang, J. Liu, W. Jiang and B. Liang, ACS Appl Mater Interfaces, 2018, 10, 24149-24156.
- 23. S. Liu, Q. Xu, S. S. Latthe, A. B. Gurav and R. Xing, *RSC Advances*, 2015, **5**, 68293-68298.
- 24. Q. Zhu and Q. Pan, ACS Nano, 2014, 8, 1402-1409.
- 25. J. Peng, J. Deng, Y. Quan, C. Yu, H. Wang, Y. Gong, Y. Liu and W. Deng, ACS Omega,

2018, **3**, 5222-5228.

- 26. X. Chen, J. A. Weibel and S. V. Garimella, *Industrial & Engineering Chemistry Research*, 2016, **55**, 3596-3602.
- 27. Q. Wei, O. Oribayo, X. Feng, G. L. Rempel and Q. Pan, *Industrial & Engineering Chemistry Research*, 2018, **57**, 8918-8926.
- 28. J. Ge, F. Wang, X. Yin, J. Yu and B. Ding, *ACS Appl Mater Interfaces*, 2018, **10**, 40274-40285.
- 29. Y. Li, Z. Zhang, B. Ge, X. Men and Q. Xue, *Separation and Purification Technology*, 2017, **176**, 1-7.
- S. Sun, L. Zhu, X. Liu, L. Wu, K. Dai, C. Liu, C. Shen, X. Guo, G. Zheng and Z. Guo, ACS Sustainable Chemistry & Engineering, 2018, 6, 9866-9875.
- 31. H.-Y. Mi, X. Jing, Y. Liu, L. Li, H. Li, X.-F. Peng and H. Zhou, *ACS Applied Materials & Interfaces*, 2019, **11**, 7479-7487.
- 32. X. Wang, Y. Pan, X. Liu, H. Liu, N. Li, C. Liu, D. W. Schubert and C. Shen, *ACS Appl Mater Interfaces*, 2019, **11**, 14362-14367.
- 33. H. Guan, Z. Cheng and X. Wang, *ACS Nano*, 2018, **12**, 10365-10373.
- 34. B. Duan, H. Gao, M. He and L. Zhang, *ACS Appl Mater Interfaces*, 2014, **6**, 19933-19942.
- 35. G. Zhu, H. Xu, A. Dufresne and N. Lin, *ACS Sustainable Chemistry & Engineering*, 2018, **6**, 7168-7180.
- X. Dong, J. Chen, Y. Ma, J. Wang, M. B. Chan-Park, X. Liu, L. Wang, W. Huang and P. Chen, *Chem Commun (Camb)*, 2012, 48, 10660-10662.
- Z. Y. Wu, C. Li, H. W. Liang, Y. N. Zhang, X. Wang, J. F. Chen and S. H. Yu, *Sci Rep*, 2014, 4, 4079.
- 38. R. Gao, S. Xiao, W. Gan, Q. Liu, H. Amer, T. Rosenau, J. Li and Y. Lu, ACS Sustainable Chemistry & Engineering, 2018, 6, 9047-9055.