## Concrete inspired superhydrophobic nanocomposite coating with high robustness

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Fig. S1 (a) The effect of NPs on the wettability of coatings with different resin content. Comparing with sample with organic/inorganic hybrid resin (blue line), the sample without cement clearly have a poor performance in wettability, indicating that cement is also conducive to achieving superhydrophobicity. (b) Sandpaper abrasion test results for the corresponding superhydrophobic samples in S1a.



Fig. S2 Abrasion test results of sample R-40/N-50/P-16, R-40/N-50/P-8 and R-40/N-50/P-8. Clearly, these samples have a better performance when abraded by 180 grit sandpaper with a load of 11.3 kPa.



Fig. S3 Abrasion test results of sample R-35/N-50/P-16, R-35/N-40/P-16 and R-35/N-40/P-8.



Fig. S4 Abrasion test results of sample R-30/N-50/P-16, R-30/N-40/P-16 and R-30/N-40/P-8. Comparing with results ahead, clearly samples with less resin content have a better performance in abrasion test for all test conditions.



Fig. S5 (a) Sample of fabricated with NPs only. (b) Cross-hatch tape peel test performed following ASTM standard D3359-17 for the sample, and ranks 5B. (c) The post-tested sample after abraded by 180 grit sandpaper only for 0.2 m, indicating a poor abrasion resistance. The abrasion test results for sample R-35/N-40/P-8 without the addition of concrete, in both situations, 22.5 kPa load with 180 grit sandpaper for (d) and 22.5 kPa with 600 grit sandpaper for (e), the sample failed after abrasion of 3.2 m.



Fig. S5 Sand impact results of sample R-35/NPs-50/P-16 (a), R-35/NPs-50/P-8 (b), R-35/NPs-40/P-16 (c) and R-35/NPs-50/P-16 (d). Clearly, the results are similar to the results of smaples with resin content of 30 wt.% (shown in Fig. 6a) that samples with higher NPs and PTFE content can guarantee a better performance in sand impact.

Surface	Form	Linear abrasion			San	Ref		
		Pressure/ weight	Sandpaper grit	Cycles /distance	Particle diameter (µm)	Height (cm)	Mass (g)	-
PDMS, SiO <sub>2</sub>	flexible bulk	20 kPa	P240	50 m		       		1
PDMS, SiO <sub>2</sub>	flexible bulk		360	50 m		       		2
PA610, modified SiO <sub>2</sub>	hard bulk	~1.1 kPa	1000	20 m				3
PTFE, CNT	hard bulk	5.6 kPa	1500	6 m		       		4
Octadecyl, SiO <sub>2</sub>	hard bulk	10.5 kPa	P 100	unidirectio nal abrasion				5
Mater-Bi®, HDMS + SiO <sub>2</sub>	coating	2.1 kPa	Plastic disk (M70)	144 cm				6
ABS, HMFS	coating	20.5 kPa	1	86.36 m		I I		7
FPU/F- POSS	coating		   	1000 m		       		8
CNT, PDA, Al <sub>2</sub> O <sub>3</sub> , PTFE	coating	150 kPa	1000	1000 cycles				9
SiO <sub>2</sub> , PTMS	coating	2 kPa	1200	27				10
SiO <sub>2</sub> @TPR- SSM	film	100 g	1000	14				11
SiO <sub>2</sub> , Ep, HMDS	coating	100 g	800	20 cycles		     		12
PDMS, PMMA	film		1     	1     	300	50	50	13
AP, ZnO and PTFE	coating	200 g	1000	5 m	300-600	50	50	14
Graphene, PDMS	coating		1     	1     	50-250	30	50	15
PVA, SiO <sub>2</sub>	film		1	1	100-350	100	80	16
Ep, PS, SiO <sub>2</sub>	coating		     	     	300- 1000		50	17
PS, SiO <sub>2</sub>	coating	7.84 kPa	150	45				18

 Table S1 Comparison of the robustness exhibited by our prepared samples with

 previously reported superhydrophobic sample

PU,	coating	9.8 kPa	2000	150		l		19
modified				1			 	
SiO <sub>2</sub>				 			 	
PU, SiO <sub>2</sub>	coating	300 g	600	35/11.5 m				20
Silicon	coating	2.61 kPa	800	0.8 m		50	100	21
resin, SiO <sub>2</sub>				 			 	
Tape, TiO <sub>2</sub>	coating	2.45 kPa	240	8 m				22
PU,	coating	2.3 kPa	2000	40/1.6 m			 	23
PAL@M-				1			1	
POS				 			 	
TiO <sub>2</sub> , PDMS	coating			1	300	50	50	24
PDMS,	film	12.5 kPa	1000	200				25
carbonyl iron				1			 	
particle, $SiO_2$				 			 	
Ceramic	coating	100g	240	40			 	26
skeleton,				 			 	
PTFE				 			 	
Poly(ethylene	coating		360	27			 	27
-co-acrylic				1			 	
acid), SiO <sub>2</sub>				 			 	
CNT, PTFE	bulk	5.6 kPa	1500	0.3 m			 	28
polyester,	coating	9.6 kPa	220	60			 	29
PTFE				   			 	
PDMS, SiO <sub>2</sub> ,	film	7.6 kPa		500 cycles			 	30
carbonyl iron				 			 	
particle				 			 	
PDMS, Ag	film	50 g		4 m			 	31
PDMS	coating			   	500	20	 	32
This work	coating	22.5 kPa	180/600	10 m/12.8	355-710	30	1400	
				h m		 		

## Reference

[1] Davis, A., Surdo, S., Caputo, G., Bayer, I. S., and Athanassiou, A. Environmentally benign production of stretchable and robust superhydrophobic silicone monoliths [J]. ACS Appl. Mater. Interfaces, 2018, 10, 2907-2917.

[2] Li, Y., Ren, M., Lv, P., Liu, Y., Shao, H., Wang, C., Tang, C., Zhou, Y., and Shuai, M. A robust and flexible bulk superhydrophobic material from silicone rubber/silica gel prepared by thiol–ene photopolymerization [J]. J. Mater. Chem. A 2019, 7, 7242-7255.

[3] Ge, B. A magnetically superhydrophobic bulk material for oil removal [J]. Colloids. Surf. A Physico. chem. Eng. Asp. 2013, 429, 129-133.

[4] Zhu, X. A novel superhydrophobic bulk material [J]. J. Mater. Chem. 2012, 22, 20146-20148.

[5] Ramakrishna, S., Kumar, S., Mathew, D., and Nair, R. A robust, melting class bulk superhydrophobic material with heat-healing and self-cleaning properties [J]. Sci. Rep. 2015, 5, 18510-18517.

[6] Milionis, A., Ruffilli, R., and Bayer, I. S. Superhydrophobic nanocomposites from biodegradable thermoplastic starch composites (Mater-Bi®), hydrophobic nano-silica and lycopodium spores [J]. RSC Adv. 2014, 4, 34395-34404.

[7] Milionis, A., Languasco, J., Loth, E., and Bayer, I. S. Analysis of wear abrasion resistance of superhydrophobic acrylonitrile butadiene styrene rubber (ABS) nanocomposites [J]. Chem. Eng. J. 2015, 281, 730-738.

[8] Golovin, K., Boban, M., Mabry, J. M., and Tuteja, A. Designing self-healing superhydrophobic surfaces with exceptional mechanical durability [J]. ACS Appl. Mater Interfaces 2017, 9, 11212-11223.

[9] Liu, Z., Wang, H., Zhang, X., Lv, C., Wang, C., and Zhu, Y. Robust and Chemically Stable Superhydrophobic Composite Ceramic Coating Repellent Even to Hot Water [J]. Adv. Mat. Interfaces 2017, 4, 1601202.

[10] Liang, Z., Geng, M., Dong, B., Zhao, L., and Wang, S. Transparent and robust SiO2/PDMS composite coatings with self-cleaning [J]. Surf. Eng. 2019, 36, 643-650.

[11] Zeng, X., Yang, K., Yang, K., Xu, S., Xu, M., Pi, P., and Wen, X. Robust superhydrophobic mesh with excellent chemical resistance for separation of complicated boiling water/oil mixtures

[J]. Mater. Res. Express 2019, 6, 085025-085036.

[12] J Jiao, Z., Chu, W., Liu, L., Mu, Z., Li, B., Wang, Z., Liao, Z., Wang, Y., Xue, H., Niu, S., et al. Underwater writable and heat-insulated paper with robust fluorine-free superhydrophobic coatings [J]. Nanoscale 2020, 12, 8536-8545.

[13] Liu, H., Huang, J., Chen, Z., Chen, G., Zhang, K.-Q., Al-Deyab, S.S., and Lai, Y. Robust translucent superhydrophobic PDMS/PMMA film by facile one-step spray for self-cleaning and efficient emulsion separation [J]. Chem. Eng. J. 2017, 330, 26-35.

[14] Liu, M., Hou, Y., Li, J., Tie, L., and Guo, Z. (2018). An all-water-based system for robust superhydrophobic surfaces [J]. J. Colloid. Interface Sci. 519, 130-136.

[15] Wang, P., Yao, T., Sun, B., Fan, X., Dong, S., Bai, Y., and Shi, Y. A cost-effective method for preparing mechanically stable anti-corrosive superhydrophobic coating based on electrochemically exfoliated graphene [J]. Colloids. Surf. A Physico. chem. Eng. Asp. 2017, 513, 396-401.

[16] Ren, T., Geng, Z., He, J., Zhang, X., and He, J. A versatile route to polymer-reinforced, broadband antireflective and superhydrophobic thin films without high-temperature treatment [J].J. Colloid. Interface Sci. 2017, 486, 1-7.

[17] Xue, C.H., Zhang, Z.D., Zhang, J., and Jia, S.T. Lasting and self-healing superhydrophobic surfaces by coating of polystyrene/SiO2 nanoparticles and polydimethylsiloxane [J]. J. Mater. Chem. A 2014, 2, 15001-15007.

[18] Wang, P., Yao, T., Sun, B., Fan, X., Dong, S., Bai, Y., and Shi, Y. A cost-effective method for preparing mechanically stable anti-corrosive superhydrophobic coating based on electrochemically exfoliated graphene [J]. Colloids. Surf. A Physico. chem. Eng. Asp. 2017b, 513, 396-401.

[19] Li, Y., Li, B., Zhao, X., Tian, N., and Zhang, J. Totally waterborne, nonfluorinated, mechanically robust, and self-healing superhydrophobic coatings for actual anti-Icing [J]. ACS Appl. Mater. Interfaces 2018, 10, 39391-39399.

[20] Zhi, D., Lu, Y., Sathasivam, S., Parkin, I. P., and Zhang, X. Large-scale fabrication of translucent and repairable superhydrophobic spray coatings with remarkable mechanical, chemical durability and UV resistance [J]. J. Mater. Chem. A 2017, 5, 10622-10631.

[21] Huang, Q.Z., Fang, Y.Y., Liu, P.Y., Zhu, Y.Q., Shi, J.F., and Xu, G. A novel strategy for durable superhydrophobic coating on glass substrate via using silica chains to fix silica particles [J]. Chem. Phys. Lett 2018, 692, 33-37.

[22] Lu, Y., Sathasivam, S., Song, J.L., Crick, R.C., Carmalt, J.C. and Parkin, P.I. Robust self-cleaning surfaces that function when exposed to either air or oil [J]. Science 2015, 347, 1132-1125.
[23] Zhang, J., Gao, Z., Li, L., Li, B., and Sun, H. Waterborne nonfluorinated superhydrophobic coatings with exceptional mechanical durability based on natural nanorods [J]. Adv. Mater. Interfaces 2017, 4, 1700723-1700731.

[24] Masood, M.T., Heredia-Guerrero, J.A., Ceseracciu, L., Palazon, F., Athanassiou, A., and Bayer, I.S. Superhydrophobic high impact polystyrene (HIPS) nanocomposites with wear abrasion resistance [J]. Chem. Eng. J. 2017, 322, 10-21.

[25] Yao, W., Li, L., Li, O.L., Cho, Y.W., Jeong, M.Y., and Cho, Y.R. Robust, self-cleaning, amphiphobic coating with flower-like nanostructure on micro-patterned polymer substrate [J]. Chem. Eng. J. 2018, 352, 173-181.

[26] Wang, S., Wang, Y., Zou, Y., Chen, G., Ouyang, J., Jia, D., and Zhou, Y. Scalable-Manufactured Superhydrophobic Multilayer Nanocomposite Coating with Mechanochemical Robustness and High-Temperature Endurance [J]. ACS Appl. Mater. Interfaces 2020, 12, 35502-35512.

[27] Luo, H., Yang, M., Li, D., Wang, Q., Zou, W., Xu, J., and Zhao, N. Transparent Super-Repellent Surfaces with Low Haze and High Let Impact Resistance [J]. ACS Appl. Mater. Interfaces 2021, 13, 13813-13821.

[28] Zhu, X., Zhang, Z., Ren, G., Yang, J., Wang, K., Xu, X., Men, X., and Zhou, X. A novel superhydrophobic bulk material [J]. J. Mater. Chem. 2012, 22 20146-20148.

[29] Huang, J., Yang, M., Zhang, H., and Zhu, J. Solvent-Free Fabrication of Robust Superhydrophobic Powder Coatings [J]. ACS Appl. Mater. Interfaces 2021, 13, 1323-1332.

[30] Dai Z., Chen G., Ding S., Lin J., Li S., Xu Y. and Zhou B. Facile Formation of Hierarchical Textures for Flexible, Translucent, and Durable Superhydrophobic Film [J]. Adv. Funct. Mater. 2020, 31, 200857-200868.

[31] Wu, L.S., Luo, J.C., Li, Y.Y., Zhang, W.M., Wang, L., Huang, X.W., Xiao, W., Tang, L.C., and Gao, J.F. Emulsion dipping based superhydrophobic, temperature tolerant, and multifunctional coatings for smart strain sensing applications [J]. Compos. Sci. Technol. 2021, 216, 109045-109055.

[32] Zhang, W.Y., Yan, W.S., Zheng, H.N., Zhao, C.P., and Liu, D. Laser-Engineered Superhydrophobic Polydimethylsiloxane for Highly Efficient Water Manipulation [J]. ACS Appl. Mater. Interfaces 2021, 13,48163-48170.