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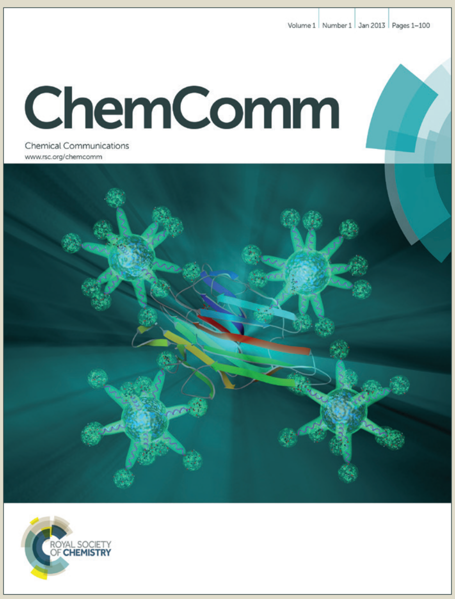




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ARTICLE TYPE

# Multifunctional Transparent Superhydrophobic Gel Nanocoating with Self-healing Property

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**Inspired by mussel we designed a novel green superhydrophobic gel nanocoating with good transparency and stability through facile copolymerization reaction at room temperature and a subsequent trimethyl silyl modified process, which is applicable to various substrates via simple spray process without toxic substances required. Importantly, this well-designed nanocoating has rapid self-healing superhydrophobicity induced by usual organic solvent to face complicated work condition which satisfies the need of daily life and can be applied in industry as well.**

Nature, the forerunner and headspring of all the progress of science and technology, is always directing human to create various multifunctional materials. Superhydrophobic surface with a water contact angle (WCA) larger than 150° and a sliding angle (SA) lower than 10° is one of the most characteristic examples.[1-2] Over the course of thousands of years of evolution, there are abundant biological surfaces with superhydrophobicity in nature, such as lotus leaves, water strider and so on. Both of them show many excellent properties including self-cleaning, corrosion resistance, anti-drag, anti-bacteria and so forth.[3-8] Therefore, artificial functional superhydrophobic surface has been a hot area of research for several years. There is no doubt that the extreme goal for research is to serve to our daily life. That way, transparency becomes a fundamental characteristic for superhdrophobic surfaces.[9] Otherwise, the practical application on everyday objects like fibers, glass or solar cells will fail to achieve. Based on this understanding, researches are always on the way and never stop. Electrospinning, electrodeposition and CVD (Chemical Vapor Deposition) are common technologies to create superhydrophobic surfaces. But when taking the universality and convenience into considering, spray coating technology must be the best choose.[10-11] However, the inescapable problem of this method is usually weak adhesion between the coating and substrate. Usual mechanical wear will always cause fatal damage to superhydrophobic surfaces. To solve this issue, inspired by mussel from nature, polydopamine is a wonderful answer for its robust and strong adhesion to virtually all types of surfaces which can be a strong bridge between coating and substrates.[12-16] Furthermore, if we turn our sights on the industrial applications of superhydrophobic surfaces, preferable performances are essential, for example, the self-healing ability to extreme environment.[17-20] Combining all of these superior properties into one multifunctional material is extraordinarily difficult which has been the dream and pursuit of researchers for many years as well.[21-24]

To this end, inspired by mussel we present a novel transparent fluoride-free superhydrophobic gel nanocoating with excellent adhesive force and thermostability without high temperature and toxic substances required. This multifunctional nanocoating not only is applicable to various substrates via a simple and easy spray method but also shows the quick self-healing superhydrophobicity induced by usual organic solvent after it is damaged by mechanical wear or strong acid. This means that this well-design superhydrophobic gel nanocoating satisfies the need of daily life and can be applied in industry as well.

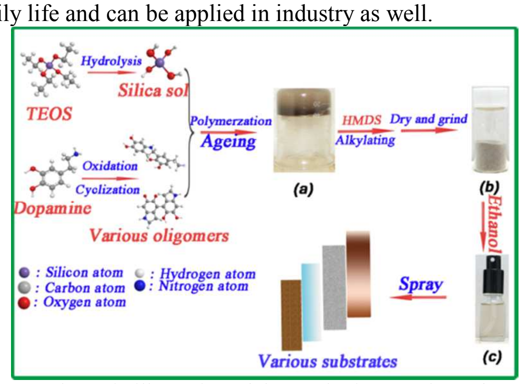


**Figure 1.** Schematic illustration of the synthesis procedure of DSTM gel nanocoating. Optical photographs of (a) DOPA-silica gel. (b) DSTM gel powder. (c) DSTM gel nanocoating.

This multifunctional superhydrophobic gel nanocoating is obtained by copolymerization reaction at room temperature and a subsequent trimethyl silyl modified process. At first, silica sol was prepared via a typical tetraethoxysilane (TEOS) hydrolysis reaction at alkaline environment. Putting dopamine (DOPA) into silica sol system, then one kind of brown opaque DOPA-silica gel was formed because of the existence of -OH group both of them after ageing. Similarly, the DOPA-silica gel can react with 1,1,1,3,3,3-hexamethyl disilazane (HMDS) to convert the rest -OH group of the surface of gel by $-OSi(CH_3)_3$. High hydrophobic $-CH_3$ content make modified DOPA-silica gel superhydrophobic for the lower surface energy.[24] In order to obtain transparent superhdrophobic gel nanocoating, the DOPA-silica gel was dried at 60 °C and grinded to get DOPA-silica trimethylsilyl modified (DSTM) gel powder (Fourier transformer infrared spectra (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS) spectra are shown in Figure S1-S2, Supporting Information). In the end, taking environmentally friendly nontoxic ethanol as a solvent, varying mass ratios transparent superhydrophobic DSTM gel nanocoating was prepared which can be sprayed on various engineering material substrates without any pre-treatment regardless of the composition and morphology (the synthesis process is illustrated in Figure 1 and the preparation details are introduced in Experimental Section in Supporting Information). To demonstrate the extraordinary superhydrophobic properties, tiny amounts of water were deposited on virtually any coated substrates (WCA of various primitive substrates and WCA/SA of various coated substrates are shown in Figure S3, Supporting Information). According to Optical photographs, it is clear that all the water droplets “stand” on the coated area in near-perfect sphere (Figure 3a-h).

Here, the unique self-roughness DSTM gel nanocoating only needs air desiccation at room temperature and can make the coated surface with nanoscale roughness for the silica colloid particles of around 30 nm in size covered and connected by a thin layer of polydopamine (PDA) though the silica colloid particles has not yet taken regular sphere because we take TEOS and PODA copolymerization method to prepare the gel. Transmission Electron Microscopy (TEM) can be used to detect the microstructure of DSTM gel and results shown in Figure 2a-b. The net-like thin layer of PDA acts as cross linking agent to arrest half-formed silica colloid particles. The Field Emission Scanning Electron Microscopy (FESEM) images can also give proof of it. The copper wire mesh covered DSTM gel nanocoating, for example, does not show obvious roughness structure at low magnification but we can still observe silica particles about 30 nm at high magnification (Figure 2c-d). Of course, for the amorphous half-formed shape and hided by thin layer of PDA, silica colloid particles are not orderly and easily observable.

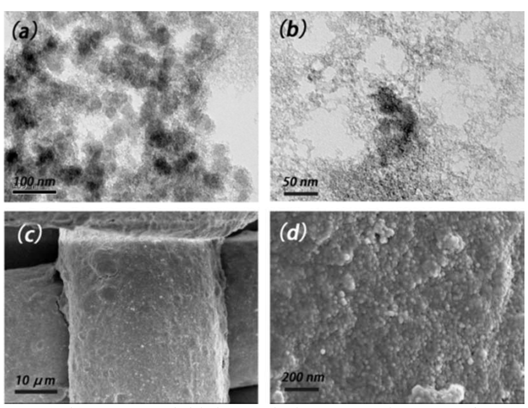


**Figure 2.** (a-b) Low and high resolution TEM images of DSTM gel particle. (c-d) Low and high resolution FESEM images of copper wire mesh with DSTM gel nanocoating.

TEM, FESEM studies are also unimpeachable theory evidences for the realizability of transparency to DSTM gel nanocoating. In fact, the transparency and superhydrophobicity are two competitive factors for same surface due to the light scattering which increases with the growth of surface roughness.[25] Mie scattering theories and Rayleigh scattering can depict the light scattering behavior and indicate that roughness at the scale of sub-100-nm is more conductive to achieve higher transparency.[26-28] By providing both, transparency and superhydrophobicity, DSTM gel nanocoating with only a few tens of nanometers roughness does not cause any damage of various common substrates that can be recognizable Figure 3a-h. The Figure 3i is the optical images of glass slides with DSTM gel nanocoating of different DSTM gel powder concentrations (1 g/L, 2.5 g/L and 4 g/L). Remarkably enough, by the naked eye, all the water droplets have high CAs on the coated glass slides no matter what concentration is and all the letters show good readability under the coated glass slides. The transmittance spectrum of the coated glass slides in the visible region (300-800 nm) is one rational characterization of transparency (Figure 3j). When the DSTM powder concentrations were 1 g/L, 2.5 g/L, the transmittance spectrum of the coated glass slides were very close to but a little lower than the uncoated one. While when the DSTM gel powder concentration was increased to 4 g/L, the transmittance of the coated glass decreased to 70%. This result is enough to meet the need of actual applications.

Weak adhesion between the spray transparent coating and substrate is one of its top concerns. This is why seldom researchers dared to test this property. Here, we use the fabric with DSTM gel nanocoating as the impacting object under running water. When the water flow is puny, a thin stream slides down without residual. Increasing the water flow make water spread out on the fabric surface then slipped off (Movie S1, Supporting Information). This impact process can last several hours without losing their superhydrophobicity. Sandpaper abrasion test under 100 g load to modified fabric were adopted as well. The damage of superhydrophobicity of modified fabric was not significant after 30 times cycles. The experiment detail was showed in Figure S4 and Movie S2. The existence of the net-like thin layer of PDA is the major reason for the high adhesion force.[29-30] As is well known, one of the most important properties of PDA is its strong adhesion to virtually all types of surfaces, no matter what the substrate’s chemistry is. Under ambient conditions DPA is prone to diffusion on substrates through noncovalent binding interaction such as $\pi - \pi$ stacking, Van der Waals interactions and quinhydrone charge-transfer complexes to create an effective adlayer.[31-33] In particularly, we creatively designed novel net-like PDA gel which could clad the coated surface to further enhance the adhesion force between the DSTM gel nanocoating and substrate. The possible combination form of DSTM gel nanocoating and substrate has been illustrated in Figure 3k.

The thermal stability of the DSTM powder has been tested by thermogravimetry (TG) and differential thermal analysis (DTA) studies (Figure S5, Supporting Information). It is clear that TG curve appears to decline at 456 °C and DTA shows exothermic peak at 458 °C. That is to say the decompose process will not happen until this temperature. So, we have every reason to believe that the DSTM gel nanocoating can maintain the excellent performance under this temperature. We also measured the WCA of copper wire mesh with DSTM gel nanocoating after thermal treated in the range 0 ~ 150 °C with 6 h, and the result was shown in Figure S6 (see Supporting Information). Heat-treated coated copper wire meshes still hold a high WCA and low SA. When the temperature reached 90 °C, the SA value will be increased markedly and the surface of copper wire mesh started to go black slightly because it has been oxidized. The increment of oxygen-containing groups was the reason why the SA will be increased. However, subtle change of this surface composition does not cause significant damage to WCA value due to the



 

DSTM gel nanocoating keeps consistent performance as excellent as before. Thus, there are no temperature limitations for our multifunctional DSTM nanocoating in the general case.

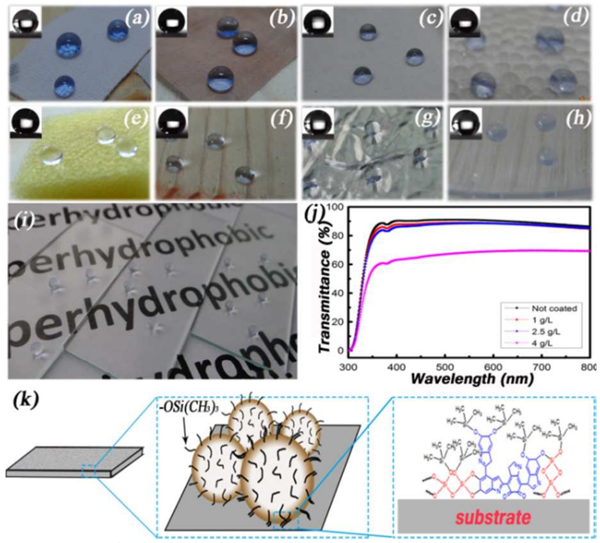


**Figure 3.** Optical photographs of various substrates with DSTM gel nanocoating (The insets show the water CA of various substrates). (a) Cotton fabric; (b) Copper wire mesh; (c) Filter paper; (d) Foam; (e) Sponge; (f) Wood; (g) Al foil; (h) PP (Propene polymer). (i) Optical photographs of glass slides with DSTM gel nanocoating of different DSTM gel powder concentrations (left to right, 1 g/L, 2.5 g/L and 4 g/L). (j) The transmittance spectrum of uncoated glass slide and glass slides with DSTM gel nanocoating of different DSTM powder concentrations. (k) Schematic illustration of the possible combination form of DSTM gel nanocoating and substrate.

What surprised us is that the DSTM nanocoating displays good self-healing superhydrophobicity induced by usual organic solvent. Cotton fabric, a common household product, was used to investigate the self-healing ability. Because the high adhesion force as mentioned, a mild mechanical wear will do little harm to superhydrophobicity of coated cotton fabric. We have to choose Nickel foam as destroyer to deprive its superhydrophobicity by great brute force, the whole process as shown in Movie S3 (see Supporting Information). After mechanical wear treatment, water droplets could not “stand” on the surface and were absorbed slightly. This hydrophilic cotton fabric regained its superhydrophobicity induced by acetone about 3 mins. High-strength mechanical wear treatment even made macroscopic deformation to cotton, but the superhydrophobicity survived for self-healing process (see Figure 4a). In the further experiments, the DSTM gel nanocoating modified copper wire mesh was damaged by 1M HCl. After the treatment, the superhydrophobic copper wire mesh turns to be hydrophobic one with WCA about 127°. However, this obtained hydrophobic copper was immerged in $CHCl_3$ for 1 min. Then the superhydrophobicity will be restored with WCA above 150° and low SA (Movie S4, Supporting Information). There is no significant loss of superhydropbobicity after repeat the self-healing procedure many times and here we just present 8 times results shown in Figure 4b. Besides, other organic solvents, such as cyclohexane, 1, 2-dichloroethan, have the same good effect.

Surface roughness and surface energy are two determining factors of surface superhydrophobicity which are determined by surface morphology and surface chemical composition. In order to reveal the self-healing mechanism, the FESEM images of the coated copper wire mesh after damaged were presented in Figure S7 (see Supporting Information). According to the comparison of high and low magnification images, the microstructure of damaged copper wire mesh has not been any changed and we still can see silica particles about 30 nm. That is to say the destruction of superhydrophobicity is not because of the change of surface roughness. So, we put a reasonable guesstimate that the change of chemical composition of surface ultimately results in the loss of superhydrophobicity. Because of the initiation of organic solvent, wrapped hydrophobic group or hydrophobic bond, such as Si-C, C-C, -$C_6H_5$, will move to organic solvent and migrate to surface of DSTM gel nanocoating. So, this self-healing process will greatly reduce the surface energy of DSTM gel nanocoating and re-give the superhydrophobicity to the surface. This is the possible reason of the regeneration mechanism. Of course, it is just our reasonable speculation and we will further explore the mechanism accurately in upcoming studies.

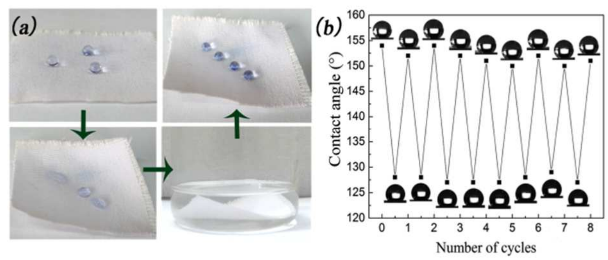


**Figure 4.** (a) Demonstration of self-healing superhydrophobicity of coated cotton fabric induced by acetone. (b) WCAs on the coated copper wire mesh in the eight cycles of 1 M HCl treatment.

In conclusion, inspired by mussel, we created a novel transparent green superhydrophobic DSTM gel nanocoating with excellent adhesive force and stability through a facile process which can be applied to various substrates in large scale by simple spray method. More attractively, this multifunctional nanocoating has rapid self-healing superhydrophobicity induced by usual organic solvent which can increase the service life of any coated surface no matter in daily life or industry. This work has not only broad practical application prospect but also precious research value in super-wettability materials field.

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## Notes and references

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1 L. Feng, S. H. Li, Y. S. Li, H. J. Li, L. J. Zhang, J. Zhai, Y. L. Song, B. Q. Liu, L. Jiang and D. B. Zhu, *Adv. Mater.*, 2002, **14**, 1857.
2 H. Yang, F. Liang, Y. Chen, Q. Wang, X. Qu, Z. Yang, *NPG Asia Materials*, 2015, 7, DOI:10.1038/am.2015.33.
3 L. P. Wen, Y. Tian, L. *Jiang, Angew. Chem. Int. Ed.*, 2015, **54**, 3387-3399.
4 Z. L. Chu, S. Seeger, *Chem. Soc. Rev.*, 2014, **43**, 2784-2798.
5 B. Su , W. Guo , L. Jiang, *Small*, 2015, **11**, 1072-1096.
6 Z. Chu, Y. Feng, S. Seeger, *Angew. Chem. Int. Ed.*, 2014, **53**, 2-13.
7 X. F. Gao, L. Jiang, *Nature.*, 2004, **432**, 36.
8 L. Tie, Z. G. Guo, W. M. Liu, *ACS Appl. Mater. Interfaces*, 2015, **7**, 10641-10649.
9 Y. Rahmawan, L. B. Xu, S. Yang, *J. Mater. Chem. A*, 2013, **1**, 2955-2969.
10 Y. F. Si, Z. G. Guo, *Nanoscale*, 2015, **7**, 5922-5946.
11 H. S. Hwang, N. H. Kim, S. G. Lee, D. Y. Lee, K. Cho, I. Park, *ACS Appl. Mater. Interfaces*, 2011, **3**, 2179-2183.
12 H. Lee, S. M. Dellatore, W. M. Miller, P. B. Messersmith, *Science*, 2007, **318**, 426-430.
13 Z. X. Wang, Y. C. Xu, Y. Y. Liu, L. Shao, *J. Mater. Chem. A*, 2015, **3**, 12171–12178.
14 Q. Zhu, Q. M. Pan, *ACS Nano*, 2014, **8**, 1402-1409.
15 Y. H. Liu, Y. P. Liu, H. Y. Hu, Z. L. Liu, X. W. Pei, B. Yu, P. X. Yan, F. Zhou, *J. Phys. Chem. C*, 2015, **119**, 7109-7114.
16 Y. H. Liu, Z. L. Liu, Y. P. Liu, H. Y. Hu, Y. Li, P. X. Yan, B. Yu, F. Zhou, *Small*, 2015, **11,**426-431.
17 J. Wu, J. Li, B. Deng, H. Jiang, Z. Wang, M. Yu, L. Li, C, Xing, Y, Li, *Sci. Rep.*, 2013, **3**, 2951-2956.
18 S. Chen, X. Li, Y. Li, J. Sun, *ACS Nano*, 2015, DOI:10.1021/acsnano.5b00121.
19 J. A. Flores, A. Pavía-Sanders, Y. Chen, D. J. Pochan, K. L. Wooley, *Chem. Mater.*, 2015, DOI: 10.1021/acs.chemmater.5b01523.
20 F. Luo, T. Sun, T. Nakajima, T. Kurokawa, Y. Zhao , K. Sato , A. B. Ihsan , X. Li , H. Guo, J. P. Gong, *Adv. Mater.*, 2015, **27**, 2722-2727.
21 B. Wang, Y. B. Zhang, L. Shi, J. Li, Z. G. Guo, *J. Mater. Chem.*, 2012, **22**, 20112-20117.
22 L. Ionov, A. Synytska, *Phys. Chem. Chem. Phys.*, 2012, **14**, 10497-10502.
23 H. X. Wang, Y. H. Xue, J. Ding, L. F. Feng, *Angew. Chem.*, 2011, **123**, 11635-11638.
24 D. Goswami, S. K. Medda, G. De, *ACS Appl. Mater. Interfaces* ,2011, **3**, 3440-3447.
25 Y. Lu, S. Sathasivam, J. Song, C. R. Crick, C. J. Carmalt, I. P. Parkin, *Science*, 2015, **347**, 1132-1135.
26 S. Yu, Z. G. Guo, W. M. Liu, *Chem. Commun.*, 2015, **51**, 1775-1794.
27 R. G. Karunakaran, C. H. Lu, Z. Zhang, S. Yang, *Langmuir*, 2011, **27**, 4594-4602.
28 X. Deng, L. Mammen, H. Butt, D. Vollmer, *Science*, 2012, **6**, 67-70.
29 Q. F. Xu, J. N. Wang, K. D. Sanderson, *ACS Nano*, 2010, **4**, 2201-2209.
30 Q. Wei, K. Achazi, H. Liebe, A. Schulz, P. M. Noeske, I. Grunwald, R. Haag, *Angew. Chem. Int. Ed.*, 2014, **53**, 11650-11655.
31 N. F. D. Vecchia, A. Luchini,; A. Napolitano, G. D'Errico, G. Vitiello, N. Szekely, M. d'Ischia,; L. Paduano, *Langmuir*, 2014, **30**, 9811-9818.
32 L. Klosterman, J. K. Riley, C. J. Bettinger, *Langmuir*, 2015, **31**, 3451-3458.
33 J. Liebscher, R. Mrówczyński, H. A. Scheidt, C. Filip, N. D. Hădade, R. Turcu, A. Bende, S. Beck, *Langmuir*, 2013, **29**, 10539-10548.