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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.\textsuperscript{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.\textsuperscript{3,4} 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 superhydrophobic surfaces.\textsuperscript{5} 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.\textsuperscript{6-11} 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.\textsuperscript{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.\textsuperscript{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.\textsuperscript{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\textsubscript{3})\textsubscript{3}. High hydrophobic -CH\textsubscript{3} content make modified DOPA-silica gel superhydrophobic for the lower surface energy.\textsuperscript{25} In order to obtain transparent superhydrophobic 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)}
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particles of around 30 nm in size covered and connected by a thin layer of polydopamine (PDA) though the silica colloid particles are not orderly and easily observable. 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.

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. 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. By providing both, transparency and superhydrophobicity, DSTM gel nanocoating with only a few
Nickel foam as destroyer to deprive its superhydrophobicity by photographs of glass slides with DSTM gel nanocoating of different droplets could not “stand” on the surface and were absorbed (Supporting Information). After mechanical wear treatment, water great brute force, the whole process as shown in Movie S3 (see Supporting Information). There is no significant loss of superhydrophobicity induced by acetone about 3 mins. High-adhesion solvent. Cotton fabric, a common household product, was used to investigate the self-healing ability. Because of 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 immersed in CHCl₃ 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 superhydrophobicity 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 guessimate 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, -C₆H₄, 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.

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 immersed in CHCl₃ 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 superhydrophobicity 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

Notes and references

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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