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ARTICLE

Superhydrophobic Surfaces Based on Polypyrrole with Corrosion Resistance and the Separation of Oil/Water Mixtures Properties

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Frequent oil spillages and the industrial discharge of organic solvents have caused severe environmental and ecological damage. Besides, as another common phenomenon in industry, corrosion of various active metals is of great importance in deciding the service life of such materials. Therefore, for the sake of solving such problems, it is imperative, but also challenging, to find suitable materials with good performance. On the other way, the complicated fabrication procedures generally hindered practical applications of superhydrophobic and superoleophilic materials. Here, we present a simple method for preparing three-dimensional material based on commercially available sponge and other substrates functionalized with depositing of nanoscale polypyrrole (PPy) particles, which is followed by modification of low-surface-energy material such as fluoroalkylsilane (FAS). Such superhydrophobic samples can efficiently separate oils and organic solvents from water and are endowed with good anti corrosion property of several metals to a great extent as well.

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1. Introduction

Owing to one of the most urgent global environmental problems, namely, the oil pollution, enormous efforts have been made to develop effective materials or technologies for separating oils and industrial organic pollutants from water. As traditional methods, oil booms, barriers, and skimmers are usually applied to clean up oil spills or organic pollutants. Nevertheless, the intrinsic hydrophilic property and low absorption selectivity of such materials obviously hold back the efficiency and development of the separation of oil/water mixtures. Moreover, such processes often involve high operation cost which turns out to be another drawback. To dope out a solution to these issues, development of novel strategies with high separation capacity, high selectivity, steady performance and low cost for the removal of oil spillage or industrial pollutants should be brought to the forefront. At

present, multitudinous superhydrophobic absorbents such as sponges¹⁻⁶, activated carbon⁷⁻¹⁰, superhydrophobic graphene^{11,12}, macroporous gels¹³, microporous polymers^{14,15}, cross-linked polymer gels¹⁶⁻¹⁹ and meshes²⁰⁻²³ were developed, which have been reported to possess high absorption selectivity, large absorption capacity, high separation efficiency and facile recyclability. However, the mass commercial application of such superhydrophobic absorbents is hampered on account of the prerequisites of complex fabrication technology or high manufacturing cost. As a consequence of this, probing a simple and low energy-consuming method for fabricating superhydrophobic absorbents for the separation of oils/water mixture can be intensified to combat this environmental problem.

As another ubiquitous problem, corrosion of various active metals is of great importance in deciding the lifetime of such materials. Such as copper material, severe corrosion of copper and its alloys has been reported in various environments, especially in the presence of chloride ions²⁴⁻²⁶. Polypyrrole (PPy) has been deemed to be one of the most promising functional materials on account of aqueous solubility of pyrrole, good redox properties, low oxidation potential, environmental stability and controllable electrical conductivity in comparison with other conducting polymers, thus arousing

mounting interest in the field of scientific research in recent years.²⁷⁻³¹ Taking the advantages of the properties of conductive polymer PPy, plenty of researches are conducted to construct superwetting surfaces. However, there is one difficulty in forming conducting polypyrrole (PPy) on surface of metals, which is the active dissolution of the metal in corrosive media, thus restraining the polymerisation of the pyrrole. To overcome this difficulty, using an electrolyte that includes a suitable anion that deposits the complex compound with the dissolved copper and induces copper passivity is fairly common. Therefore, we introduced aqueous phytate solution to the system for the phytate anion reported to easily form a chelating compound with copper and to possess the inhibitor property of copper.^{32,33} Moreover, in many cases, superhydrophobicity can lead to better anti-corrosion performance.

Generally, PPy films can be synthesised electrochemically, but the pros and cons obviously land on resultant thinner film and higher operation cost, respectively. In this work, the preparation of superhydrophobic surfaces on various substrates including mesh, sponge, filter paper and fabric with simple coating of PPy by in situ polymerization was reported, followed by modification with low-surface-energy material, and furthermore this method can apply to large-scale production simply and facilely. This sort of PPy coated films comprising nano-scale rough coatings and micro-structured porous substrates can separate oil/water mixtures under the force of gravity readily while retaining high separation efficiency and good recyclability. Moreover, such superhydrophobic PPy films on the surfaces of metals can bring about superb corrosion resistance in various extreme environments, which expands their scope of application and prolongs the service life of the metal materials.

2. Experimental section

2.1 materials

The fabrics (containing 65% polyester and 35% cotton) and sponges are uniform, which was purchased from a local store. Copper and Stainless steel meshes with different pore sizes and filter paper were commercially available. The other chemicals were analytical-grade reagents and were used as received without further purification.

2.2 Pre-treatment of substrates

Copper, Stainless steel grids with different mesh number, filter paper, fabric, sponge as substrates were ultrasonically washed with, distilled water, acetone, and anhydrous ethanol in an ultrasonic cleaner before using to remove possible impurities.

2.3 preparation of PPy films on various substrates

Polypyrrole nanoparticles were grown on diverse substrates via in situ polymerization. Taking meshes as an example, in the first step, the following precursor solutions were mixed: Solution A, aqueous solution of oxidative initiator (1.25 mmol 30% H₂O₂ in 1 ml H₂O); Solution B, 5 mmol aqueous solution of pyrrole monomer and 1 mmol phytic acid (50% w/w in water) in 2 ml H₂O. Then, the cleaned meshes were immersed into the mentioned solution at room temperature under constant magnetic stirring. During which the in situ polymerization of PPy took place on the surface of such meshes. Moreover, for the reason of relatively fast polymerization, it was observed that the solution colour changed from light brown to black within merely 3 min. After the stirring process, the PPy coated meshes were fetched out and washed with large excess distilled water at least three times to remove the residual PPy particles or other reactive agents. In the second step, the modification process is implemented by the deposition of trichloro(octadecyl)silane (OTS) after the meshes being dried to produce a superhydrophobic surface. In situ growth of the conductive polymer PPy on other kinds of substrates was realized via employing exactly identical procedures. Additionally, both the concentrations and volumes of the precursors can be altered along with the changes in the size of substrates. This in situ polymerization method is versatile as we have fabricated superhydrophobic coatings on various substrates including filter paper, cotton fabric, metal mesh and sponge. Furthermore, it does not need rigorous conditions, advanced equipments or cumbersome processes, thus making it suitable to manufacture on a large scale.

2.3 Characterizations

The optical images of the PPy coated films and the movies of the separation of the oils and water were obtained using a digital camera (Sony, DSC-HX200). The morphology of uncoated and PPy coated films was observed by a field emission scanning electron microscope (FESEM, JEOLJSM-6701F). The water contact angle was measured with a 5- μ L droplet of distilled water at ambient temperature with JC20001 contact angle system (Zhongchen digital equipment Co. Ltd. shanghai, China) by measuring five different positions on the same sample. The chemical compositions of uncoated and PPy coated surfaces were investigated by X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB 250Xi). Polarization measurements were carried out in a 3.5 wt% NaCl aqueous solution, 0.5M H₂SO₄ solution and 1M NaOH solution at room temperature with a three electrode electrochemical cell setup (CHI660D electrochemical workstation by Shanghai CH Instruments, China). In which the sample acted as working electrode and a platinum foil was employed as the counter electrode. In addition, a saturated calomel electrode (SCE) served as the reference electrode. The exposed area of the working electrode was set to be 1 cm² for all used samples.

3. Results and discussion

3.1 Superhydrophobic PPy-coated sponge

Polypyrrole, as a heterocyclic kind of conjugate polymer materials, has been applied to realize oil/water separation³⁴⁻³⁶. By using commercial sponge as a sort of substrate, fabrication of superhydrophobic PPy-coated sponge was achieved. The choice of sponge is because of its inherent three-dimensional (3D) structure along with the excellent air permeability, softness, flexibility and large internal surface area as well. Owing to the existence of different oxygen groups on the sponge surfaces, the original sponge exhibits fairly hydrophilicity and can easily be attached by PPy from water, thus forming nanosized structure on its microscale rough surface³⁷. Scanning electron microscopy (SEM) was performed to evaluate the morphology of PPy coated sponge. The SEM images of the sponge before and after the hydrophobic modification clearly manifest virtually identical microstructures, which signify that the in situ polymerization do not undermine the original sponge structure. From Fig. 1b, it is clear that the pre-treated sponge shows a macroporous structure with quite smooth and neat surface morphology. After being coated by PPy particles, the prepared PPy film on the sponge surface exhibits lotus-like structure morphology with good roughness, and the pores inside the sponge are hardly blocked. These features will discriminate in favour of the rapid absorption of oil, as the patulous porous network permits quick transportation of gas and liquid inside the sponge. Higher magnification SEM image (Fig. 1a) shows the conductive polymer films is consisted of nanometer-sized PPy particles with average size of around 100 nm and their aggregates simultaneously.

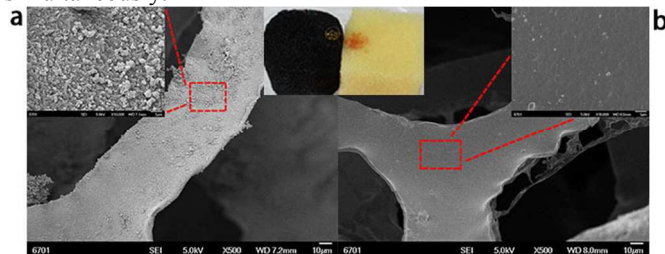


Fig. 1 a) SEM images of the superhydrophobic PPy coated sponge. b) SEM images of the pristine PU sponge. Inset: photograph of the comparison chart of pristine and modified sponge with residue of the dyed water on the surface.

The surface wettability was estimated by the measurement of various contact angles. With the hydrophilic and underwater oleophobic properties of PPy, the unmodified PPy sponge shows a superhydrophilic property with a water contact angle (WCA) of 0°. It is quite apparent that the PPy sponge can barely be put into use for the application of capturing organics and oils from water. In order to render the surfaces of PPy sponge superhydrophobic, the modification of low surface energy material cooperating with nano- or micro-sized roughness on the substrate is of the utmost importance. Recently, such good absorbent sponges with superhydrophobicity and superoleophilicity were achieved by

further surface modification.^{5,38} As a consequence, we modify the coating of PPy nanoparticles with trichloro(octadecyl)silane all over the sponge skeletons, which is anticipated to convert the wettability of the sponge from superhydrophilicity to superhydrophobicity, as is made evident by its WCA of 156°. Furthermore, the manufactured sponge remains its high capacity of absorbing a wide range of oils and organic solvents, thus making the separation of oil/water mixture realized. In addition, the as-prepared sponge exhibits good flexibility and recovers its original shape after anthropogenic compression without apparently damaging the major sponge structure or the porosity. To demonstrate the extreme wettability, we measured the WCA to investigate the surface wettability of modified PPy sponge. As shown in Fig. 1 inset, when two water droplets (dyed with alizarin red) were dripped on the surface of modified PPy sponge and original sponge respectively, the water droplet remained its spherical shape and transparent on the surface of modified sponge, while being immediately absorbed after reaching the surface of the primary one. Apart from its superhydrophobicity, the modified one exhibits excellent oleophilicity after coating of low surface energy material as well.

In contrast to some other substrates, such superhydrophobic PPy-coated sponge is quite stable in withstanding several harsh conditions, including heating at 200 °C for 1 h, freezing at -20 °C for 1 h (Figure. 2).

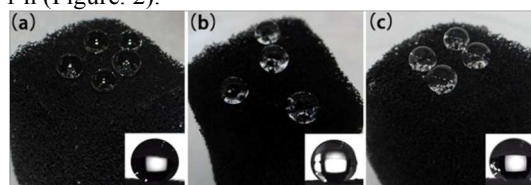


Fig. 2 Photographs of several water droplets on the surface of the original superhydrophobic PPy coated sponges (a), after low temperature (-20 °C) exposure for 1 h (b) and after high temperature (200 °C) exposure for 1 h (c). Inset: the corresponding water contact angles.

Spectrum XPS can provide composition analysis of the top 5 nm of material surface and therefore has been widely used as a kind of material characterization technique. The successful grafting of the hydrophobic molecules on the surface was confirmed by X-ray photoelectron spectroscopy (XPS). From Fig. 3, the peaks appeared at 285.0, 399.88 and 532.3 eV are observed for raw sponge and PPy-coated sponge likewise, being attributed to the C_{1s}, N_{1s} and O_{1s}, respectively^{39,40}. Furthermore, compared to original sponge, the content of C and N elements are increased, the peaks mentioned above verified that the PPy film was triumphantly coated on the pre-treated polyurethane sponge (Fig. 3a, b are the element XPS of C_{1s} and N_{1s} before and after polymerization). In addition to the peaks referred to, some other characteristic peaks were also observed at 199.25 and 102.32 eV in XPS spectra of PPy after modification (Fig. 4c), which indicate the Cl_{2p} and Si_{2p} (Fig. 4a,

are the element XPS of Cl_{2p} and Si_{2p}), and such results were in good agreement with the previous literatures⁴¹.

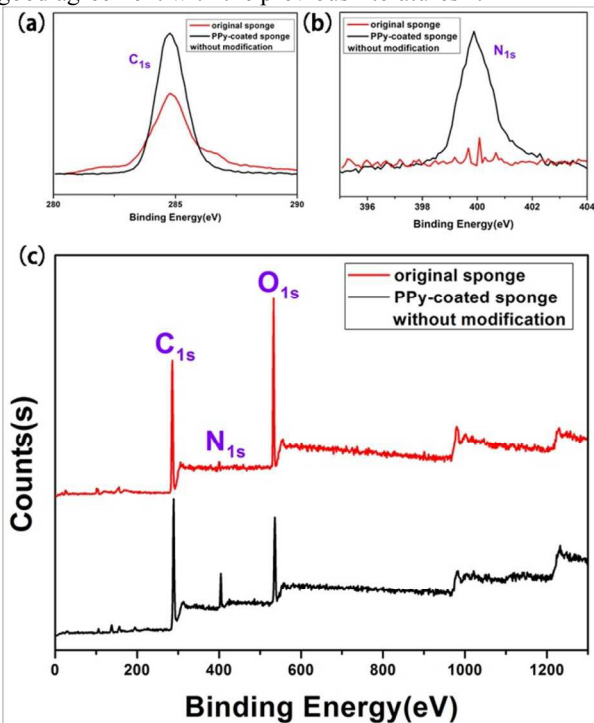


Fig. 3 (a), (b) are the High-resolution XPS of C_{1s} and N_{1s} before and after reaction; (c) is XPS spectra of the raw sponge and PPY coated polyurethane sponge without modification

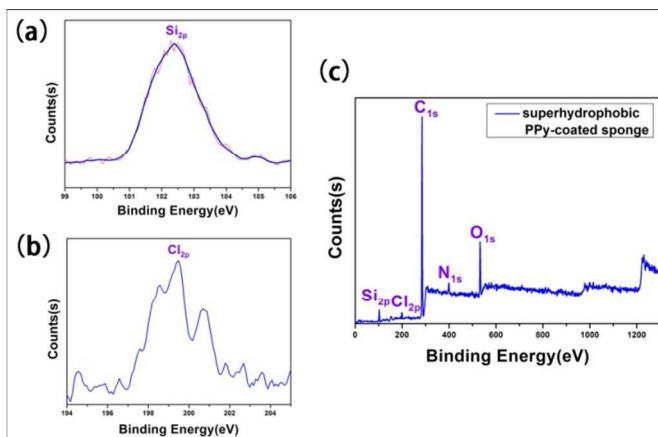


Fig. 4 (a), (b) are the high-resolution XPS of Cl_{2p} and Si_{2p} . (c) is the XPS spectra of the synthesized PPY on the polyurethane sponge after modified treatment

Oil/water separation

It is well known that the surface free energy of water is generally greater than that of oil. Therefore, solid surfaces which possess the surface free energy between that of water and oil may exhibit both of hydrophobicity and oleophilicity concurrently. Via integrating proper surface morphology with materials which possess low surface free energy, thus porous superhydrophobic and superoleophilic materials can be fabricated. By utilizing the properties of superhydrophobicity and superoleophilicity cooperate closely with its instinctive

good porosity, the modified PPY-coated sponge can be deemed to be a superb candidate for capturing various organic solvents and oils from water. Moreover, for the application of the clean-up of oil, there exist some problems that hinder the practical utility and development of it, which incorporate the recyclability of the absorbent and the recoverability of the absorbed liquid.

To demonstrate the feasibility of such superhydrophobic sponge in the practical applications, Dichloroethane and n-hexane (all dyed with Sudan IV) were selected as two representative absorbates on behalf of organic solvents with different densities in the performance of separating oil from water. The experiment details are as follows, when the sponge was dropped on the n-hexane/water surface, it sets out to absorb the red n-hexane fleetly. Thereupon, the black sponge becomes succulent full with red oil (stained n-hexane) after only one minute (Figure. 5). Such rapid absorption process is due to the combined effect of its high porosity, oleophilic nature, and capillary action. Owing to the investitive superhydrophobicity, it was able to be easily fetched out without assimilating any moisture. Then by simple mechanical squeezing or suitable heat treatment, the absorbed matters can be recycled or removed with just a small amount of residual oil retained on the surface of a used sponge. That is undoubtedly to the benefit of the quick and recyclable absorption of variety of organic solvents and oils. While in the case of dichloroethane/water mixture, the dichloroethane can also be removed and recycled efficaciously using such superhydrophobic sponge (Figure. 6). Unlike the case of n-hexane/water mixture, the superhydrophobic sponge is required to be manually pressed to contact the interface between dyed oil and water on account of the dichloroethane's higher density than water.

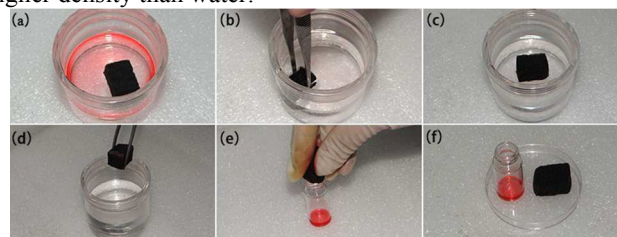


Fig. 5 The absorption and recycling process of n-hexane.

3.2 superhydrophobic films on filter paper, fabric, copper and

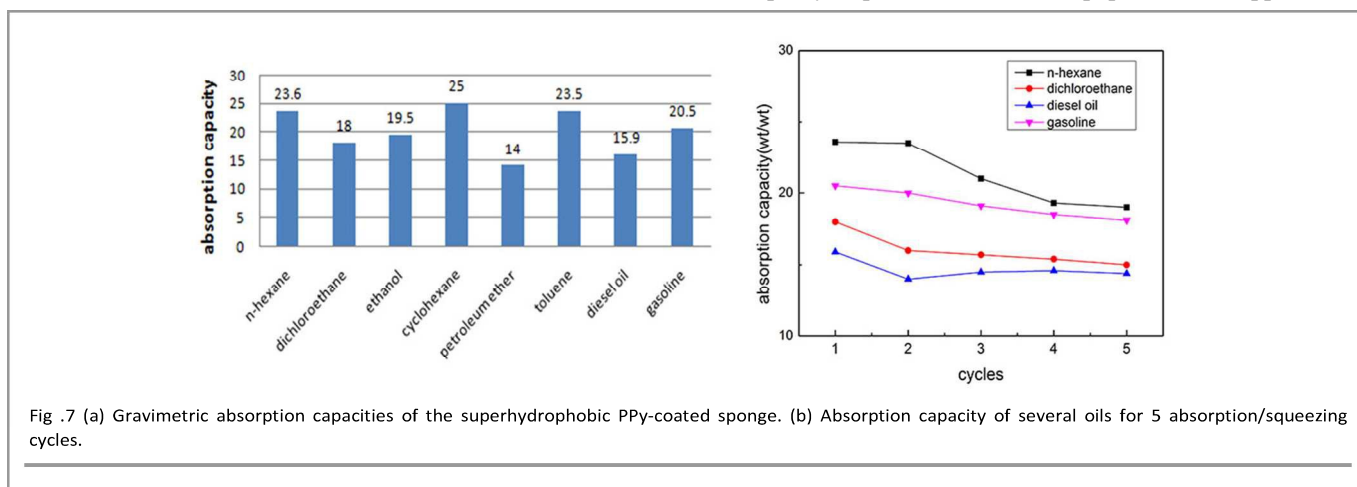


Fig .7 (a) Gravimetric absorption capacities of the superhydrophobic PPY-coated sponge. (b) Absorption capacity of several oils for 5 absorption/squeezing cycles.

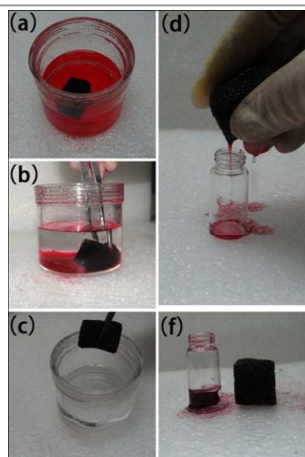


Fig .6 The absorption and recycling process of the underwater dichloroethane.

In addition to the feasibility of such superhydrophobic sponge, we also tested the measurement of the weight of oils and other organic liquids that can be captured by the as-prepared sponges with an in situ growth of PPY film on the main framework via employing the absorption capacity as a criterion. The recyclability of the sponges is measured as well through the same process referred above. The two properties are discussed for the purpose of evaluating the practical utility for various oil/water separation systems. Figure .7a reveals that the absorption capacities of the PPY-coated sponge for oils and organic solvents were 15–25 times its own weight, partly depending on the density and viscosity of the oils and solvents. And it also exhibits that the recyclability of sponges is good since there is no dramatic change in the absorption capacity for various oils, and after several times of cycles the superhydrophobicity of PPY-coated sponge surface can be remained (see Fig .7b).

stainless steel mesh

In virtue of environmental conservation, the solution to oil spill cleanup and oil recovery from industrial effluents, or efficient materials for oil/water separation are in urgent need. Though there have not been a great many oil absorbents fabricated on the base of cellulose, such as the substrates of filter paper or fabric, we successfully coated such substrates with PPY nanoparticles by applying the method referred above (Figure. 8a, b). In the meantime, apart from the substrate of sponge, copper meshes and stainless steel meshes can be covered by PPY via the same way for developing an oil/water filter (Figure .8c, d), which selectively separate oils from water as well. It is obvious that the morphology has no evident difference from the surface of sponge.

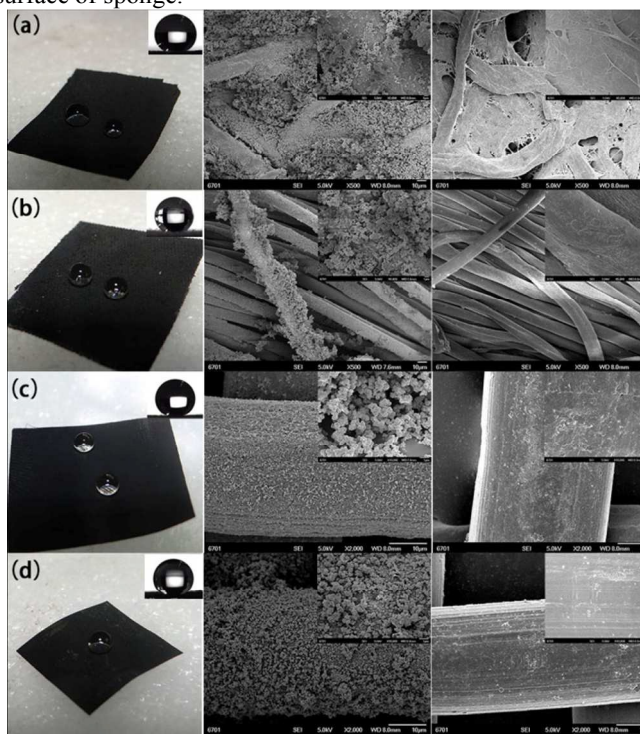


Fig .8 optical photographs and SEM images of as-prepared superhydrophobic surfaces on filter paper (a), fabric (b), copper mesh (c) and stainless steel mesh(d) and the corresponding original samples, respectively. Insets of each optical photographs are the corresponding WCA on them; Insets of each SEM images(scale bar of 10 μ m) are the corresponding higher-magnification SEM images.

Oil/water separation

By utilizing the superhydrophobic property, oil–water separation is carried out through the following processes on modified filter paper, fabric, copper mesh and stainless steel mesh. The experiment details are illustrated in Fig. 9. Firstly, the superhydrophobic PPy-coated films were fixed between two glass tubes, then for a better fixation, Teflon tape was applied to encase the contact area closely. Next, the mixture of water (dyed with Methyl blue) and dichloroethane (dyed with Sudan IV) was poured out of a glass beaker into the upper tube slowly. From the real-time observation, dichloroethane (red) transfluxed through the aforesaid films apace and dropped into the collection beaker underneath, while the water (blue) stay still on top of the films inside the tube above (Movie S1, ESI†). It should be pointed out that the mixture of chloroform/water can be separated successfully as well, so does other mixtures prepared with the oils whose density higher than water. The separation efficiency of the as-prepared substrates for an oil–water mixture was also investigated. The separation efficiency (η) was calculated by $\eta = m/m_0 \times 100\%$, where m_0 is the mass of the water before separation process, m is the mass of the water after separation process. As shown in Fig. 10, the separation efficiencies of the as-prepared substrates are all above 97%. Furthermore, the influence of cycled times of dichloroethane/water separation on the superhydrophobicity of such films (choose 400 mesh copper screen as an example) was inquired into to make an assessment of the repeated utilization factor. As shown in Fig. 11, the copper mesh film still maintained its superhydrophobicity with WCA of about 151° after circulating the separation experiment for 50 times. Note that the as-prepared films show excellent recyclability for oil/water separation without obvious damages of the efficiency and superhydrophobicity, and the complete separation proceeded under the one and only condition of the force of gravity, thus such route can be regarded as economically practical.

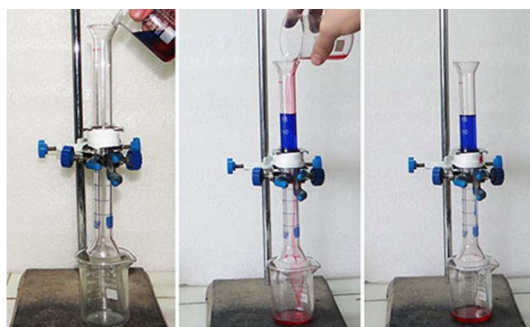


Fig .9 a typical oil–water separation process of PPy-coated meshes. The PPy-coated meshes were fixed between two glass tubes and the oil–water mixtures (water dyed with Methyl blue and dichloroethane dyed with Sudan IV) were

poured into the upper tube. (see the video file provided in the Supporting Information)

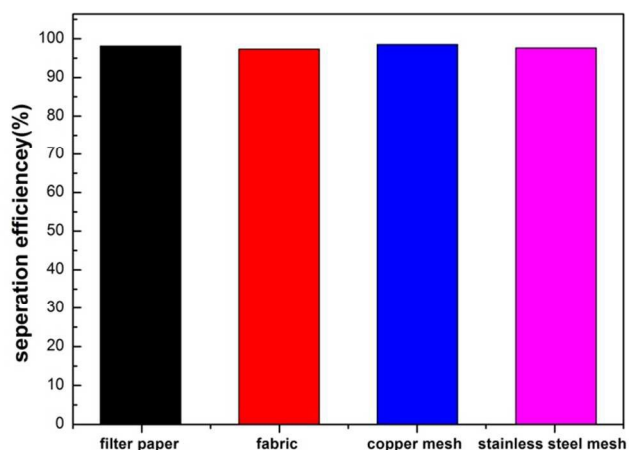


Fig .10 The separation efficiency of the as-prepared filter paper, fabric, copper mesh, stainless steel mesh for a selection of oil–water mixtures.

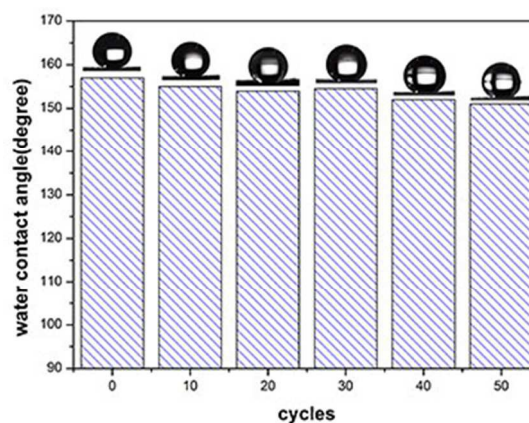


Fig .11 water contact angles of surface of the superhydrophobic PPy-coated copper mesh (400 meshes) during the cycle experiment (50 times).

Evaluation of corrosion resistance

In order to study the stability of as-prepared superhydrophobic surfaces, we applied several corrosive liquids, such as acidic, basic, and salt aqueous solutions to test it. Fig. 12 shows the typical digital images of corrosive liquids on the surface of superhydrophobic PPy-coated substrates. All these corrosive liquids stood uniformly on the surface and maintained a spherical shape. Moreover, all the WCA tested with above solution drops were all larger than 150° .

In addition, we further compared the anti corrosion properties of superhydrophobic PPy coated metal meshes to those of bare metal samples by carrying out polarization measurements. The corrosion characteristics of such samples in 3.5 wt. % NaCl aqueous solution, 0.5 M H_2SO_4 solution and 1 M NaOH solution were given in Table 1. According to Table 1, the i_{corr} values of uncoated surfaces appear to be relatively high. This is because that bare substrate surfaces are in an unstable state and copper or iron becomes ion quickly, thus being suffered from corrosion. Fig .13a illustrates the different E–log i responses of

bare copper mesh, stainless steel mesh, superhydrophobic copper mesh and steel mesh in 3.5 wt. % NaCl solution. The corrosion potential and the corrosion current of the superhydrophobic PPy coated copper meshes was 0.9716 V and 4.172×10^{-6} A, respectively, whereas those of the bare copper meshes were -0.1643 V and 7.817×10^{-5} A, respectively. The shift of the corrosion potential (about 1.13 V) in the positive direction indicates that the superhydrophobic PPy coating act as the effective anodic protective coating rather than the sacrificial corrosion protection. The decrease of the corrosion current by one order of magnitude shows the significant improvement of corrosion resistance of copper mesh by the deposition of superhydrophobic coating on the substrates. When bare copper is immersed in corrosion mediums, the passive oxide is broken down and a severe corrosion begins. However, via coating bare substrates with nanoscale PPy and modifying such coating with low-surface-energy material, the superhydrophobic coating was formed. On the one hand, air can be easily trapped in the pits and cavities between the PPy particles, and the trapped air could serve as a first barrier layer, then the conductive polymer coating can act as the second effective barrier to the inward diffusion of Cl^- , thus inhibiting the corrosion of the substrates. Similarly, as clearly shown in table 1, the i_{corr} of superhydrophobic samples undergo a diminution compared to

corresponding bare substrates while the E_{corr} increase, thus indicating a better anti-corrosion behaviour of superhydrophobic samples than bare substrates. It is believed that the double barrier layers which consist of trapped air layer and PPy layer on the substrates could availably guard against the outside corrosive ions, accordingly improving the resistance of corrosion of such substrates to a great extent.

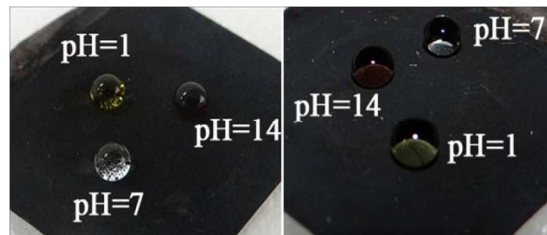


Fig .12 digital images of corrosive liquids on the surface of superhydrophobic PPy-coated substrates (left: copper mesh, right: stainless steel mesh)

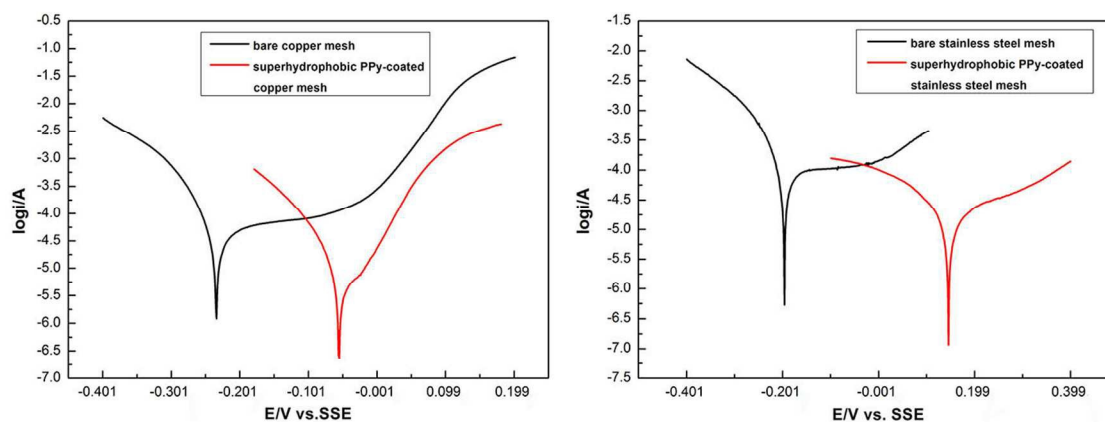


Fig .14 Potentiodynamic polarization curves of pristine copper mesh, pristine stainless steel mesh, superhydrophobic PPy film coated copper mesh and superhydrophobic PPy film coated stainless steel mesh in 0.5M H₂SO₄ solution

Samples	3.5 wt% NaCl solution		0.5M H ₂ SO ₄ solution		1M NaOH solution	
	i_{corr} (A)	E_{corr} (V)	i_{corr} (A)	E_{corr} (V)	i_{corr} (A)	E_{corr} (V)
Bare copper mesh	7.817×10^{-5}	0.1643	1.017×10^{-4}	-0.2352	8.913×10^{-4}	-0.5862
Superhydrophobic copper mesh	4.172×10^{-6}	0.9716	7.160×10^{-6}	-0.0575	5.796×10^{-4}	-0.3357
Bare stainless steel mesh	6.821×10^{-5}	-0.3037	2.400×10^{-4}	-0.1974	5.702×10^{-5}	-0.3092
Superhydrophobic stainless steel mesh	2.224×10^{-5}	0.1224	3.726×10^{-5}	0.1444	1.067×10^{-5}	-0.2106

Table 1 The corrosion characteristics on the surfaces of bare copper mesh, superhydrophobic PPy-coated copper mesh, bare stainless steel mesh, superhydrophobic PPy-coated stainless steel mesh.

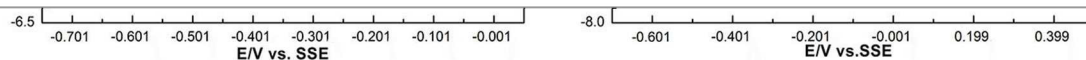


Fig .15 Potentiodynamic polarization curves of pristine copper mesh, pristine stainless steel mesh, superhydrophobic PPy film coated copper mesh and superhydrophobic PPy film coated stainless steel mesh in 1M NaOH solution

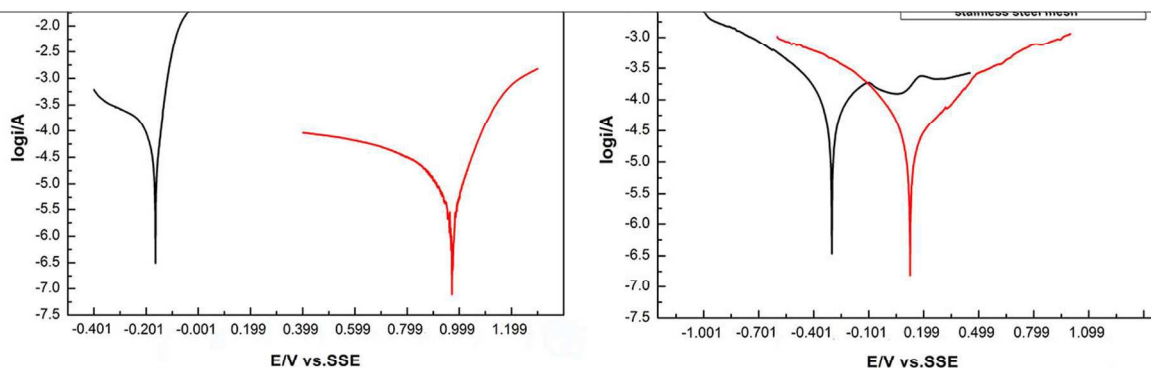


Fig .13 Potentiodynamic polarization curves of pristine copper mesh, pristine stainless steel mesh, superhydrophobic PPy film coated copper mesh and superhydrophobic PPy film coated stainless steel mesh in neutral 3.5wt% NaCl solution.

4. Conclusion

In summary, we demonstrate here a novel and simple two-step design to utilize conductive polymer PPy to produce a three-dimensional superhydrophobic absorbent with multiple functionalities on the basis of sponge. Such method, including an in situ polymerization process for coating a conductive polymer film and a following modification treatment for obtaining superhydrophobicity, is also able to land the stable superhydrophobicity onto many other surfaces via a highly scalable dip coating process. The obtained superhydrophobic property, good absorption or separation performance and robust stability against heating and freezing make such films used for the separation of oils and organic solvents from water, which would have great technological prospect in the field of water pollution rectification, clean-up of huge oil spills and waste oil recovery. Furthermore, the as-prepared superhydrophobic surface on metals exhibited outstanding anti-corrosion properties in various corrosive mediums including neutral NaCl solution, acidic H₂SO₄ solution and basic NaOH solution, thereby endowing this superhydrophobic surface good applicability to be utilized to realize more industrial applications.

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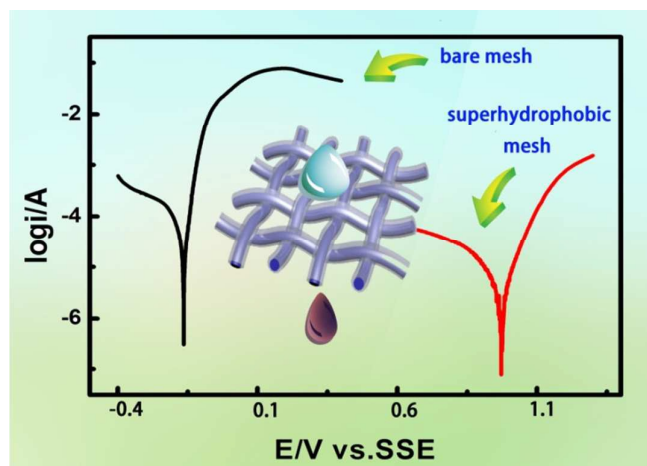
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Graphic Abstract



In this article, we demonstrate a novel and simple two-step design to utilize conductive polymer PPy to produce a superhydrophobic film on various substrates with superb corrosion resistance. Moreover, such as-prepared samples can be good candidate to separate oil/water mixtures.