

Facile fabrication of superhydrophobic polyaniline structures and their anticorrosive properties

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ABSTRACT: We report a simple approach for the preparation of superhydrophobic polyaniline (PANI) and its application for the corrosion protection coatings. First, PANI was synthesized conventionally by oxidative polymerization with APS. Subsequently, PANI with different wettability was obtained by modification with different surfactants. The surface modification of PANI with three different surfactants (sodium dodecylbenzenesulfonate, polyethylene glycol, and cetyltrimethylammonium bromide) provided excellent surface superhydrophobicity (water contact angle $>150^\circ$). The structure and morphology of as-prepared PANI were characterized with Fourier transform infrared, Energy dispersive X-ray spectroscopy, and Scanning electron microscopy. Corrosion protection performance of PANI with different wettability was evaluated in 3.5% NaCl electrolyte using Tafel polarization curves and electrochemical impedance spectroscopy. The results indicated that various superhydrophobic PANI coatings have better anticorrosion performance as compared to the hydrophilic PANI. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 44248.

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INTRODUCTION

Metal corrosion has been considered as one of the most serious threats to both economy and human life.^{1–3} Corrosion control strategies often focus on slowing the kinetics or changing the corrosion mechanism. The use of organic or inorganic coatings is one of the best ways to protect metals against corrosion.^{4–6} Chromate-based organic coatings provide effective corrosion protection, but it has also adverse health and environmental impacts.^{7,8} Considerable interest has been given to the use of conducting polymers for the protection of metals against corrosion. PANI has attracted much attention due to its ease of synthesis, low cost, and environmental stability.^{9–11} PANI has been emerged as one of the most promising conductive polymers for commercial applications,^{10,12} and have been used as protective coatings for corrosion protection. Researchers have found that PANI can protect metals such as stainless steel, iron, mild steel, copper, aluminum, and aluminum alloys from corrosion very effectively.¹³ Lu *et al.*¹⁴ reported that PANI coatings can provide significant corrosion protection to mild steel exposed to the severe corrosion environments of dilute HCl and NaCl. Ansari *et al.*⁷ found that polyaniline/nylon coatings can provide an anodic protection against corrosive environments in which the metals are exposed and the corrosion rate for the polymer coated steel was significantly lower than the bare steel by about 10–15 times. Mechanism for enhanced corrosion protection of

conjugated PANI coatings had been suggested due to the formation of a passive oxide layer induced from the redox catalytic capability of PANI.^{13,15}

Recently, superhydrophobic surfaces with a water contact angle (CA) higher than 150° are arousing much interest because of their high water repellency and practical applications. Superhydrophobic surfaces have been used widely in corrosion protection, self-cleaning, biosensor, metal refining, and low friction coatings.^{16–18} Some researches demonstrated that hydrophobic or superhydrophobic films can protect alloys by forming inhibitive film, which renders surface water repellent to prevent the corrosive attack and significantly enhances corrosion resistance as compared to untreated specimens.⁸ Studies about superhydrophobicity used to protect metal have been focused on managing the surface of metal, yet more and more attention have been paid to coating materials with superhydrophobic structure.^{19,20} It provides a new way to improve the corrosion resistance of metal surface sealed anodic layers. Although, the corrosion protect studies associated with superhydrophobic surface by using PANI coating materials have been reported only a few to date.²¹ Therefore, it is important to combine microstructured and nanostructured PANI with a superhydrophobic function to apply in corrosion protection coatings.

Superhydrophobic surface is governed by both the chemical composition and the geometrical microstructure of the surface.^{17,18}

Various methods have been used to prepare superhydrophobic surfaces, such as imprinting, spray-coating, anodic oxidation, layer-by-layer assembly, radiofrequency-magnetron sputtering, chemical vapor deposition, and casting method.^{17,20} Jiang and coworkers²² found that three-dimensional (3D) microstructures/nanostructures of PANI were self-assembled by template-free method combined with interfacial polymerization in the presence of perfluorosebacic acid (PFSEA) as dopant, the 3D microstructures/nanostructures of PANI show both electrical conductivity and superhydrophobicity. Peng *et al.*²¹ reported that PANI surface with biomimetic superhydrophobic structures was prepared by the nanocasting technique. Weng *et al.*⁸ synthesized advanced anticorrosion coating materials prepared from F-PANI/silica composites with synergistic effect of superhydrophobicity and redox catalytic capability. These PANI-based superhydrophobic surfaces were obtained by lowering surface energy by incorporation of strongly hydrophobic substituent group (fluoro-moieties, PFOA) into PANI chains as well as constructing nanostructured PANI. However, these methods often require complex equipment, toxic fluoride and elaborate syntheses, so a continuing need exists for fast, simple, low-cost and environmentally friendly fabrication approaches of superhydrophobic surfaces. From a practical point of view, the seeking of efficient ways for the creation of superhydrophobic surfaces by facile process should be a priority and be of great importance especially for large-scale practical applications.

Surfactants have special amphiphilic structure, and can be used to control both the material morphology and the surface chemical components. Though, few in-depth works has been reported on PANI modification with surfactants to obtain superhydrophobic surface, and its application on corrosion protection.

In this work, PANI with superhydrophobic surface has been prepared via a facile method using two-step synthetic process by using three different surfactants as modifier. First, PANI was synthesized by conventionally oxidative polymerization of aniline with ammonium persulfate (APS) as oxidant in 0.2M H₂SO₄ aqueous solution. Subsequently, a stimuli-responsive change in wettability for PANI can be simply realized by controlling the modification process of selected surfactants. The method is rapid, cheap and no pollution from fluoride. Sodium dodecylbenzenesulfonate (SDBS), polyethylene glycol (PEG-10000) and cetyltrimethylammonium bromide (CTAB) were chosen to manipulate both wettability and corrosion resistance of PANI. Water contact angles have been measured to study the wettability of the samples. The structure and morphology of the samples have been characterized by FTIR, EDS, and SEM techniques. The detailed anticorrosion performance of the developed PANI coatings was evaluated by a series of electrochemical corrosion measurements in saline condition.

EXPERIMENTAL

Materials

Aniline was double-distilled and stored at -5 °C prior to use. All of the reagents purchased from Tianjin Chemical Industrial Co. Ltd. (Tianjin, China) were analytical grade and used without further purification. Double-distilled water was used for the preparation of solutions.

Preparation of Polyaniline

Aniline (0.2 mL) was distilled in 5 mL 0.2M H₂SO₄, then 0.5071 g APS which was dissolved in 5 mL 0.2M H₂SO₄ was added in one batch, and this solution mixture was immediately subjected to magnetic stirring for 2 min at room temperature. Then the mixture was allowed to proceed without agitation for 8 h at 5 °C. The product was then washed with deionized water and ethanol until the filtrate became colorless, and then dried in vacuum at 45 °C for 24 h.

Preparation of Polyaniline Modified with Surfactants

PANI (0.2 g as prepared) and a predetermined amount of surfactant were added into 50 mL distilled water under magnetic stirring for 8 h at room temperature, respectively, then the products were washed with deionized water and ethanol several times. Finally the products were dried in vacuum at 45 °C for 24 h. Different amounts of SDBS, CTAB, and PEG-10000 in varying range were selected to prepare superhydrophobic PANI and modified PANI with different chemical compositions. Amounts of the PEG-10000 are 0.018 g and 0.012 g for PANI-PEG1 and PANI-PEG2, respectively. Amounts of CTAB are 0.03 mmol and 0.02 mmol for PANI-CTAB1, PANI-CTAB2, respectively. Amounts of SDBS are 0.03 mmol and 0.04 mmol for PANI-SDBS1 and PANI-SDBS2, respectively.

Preparation of Stainless Steel and Coating

Stainless steel (type 316) was used as the working electrode, and the working area was 1 cm² (1 cm × 1 cm). The stainless steel electrode was polished with 600 grit, 1500 grit, and then 2000 grit emery paper, and then rinsed with acetone, ethanol, and distilled water in ultrasonic bath for 10 min, at last dried in the air.

Synthesis procedure of coating is given as following: as-prepared sample were dispersed in *N*-methyl-2-pyrrolidone (5.0 mg/mL) by constantly stirring for 30 min, and then followed by ultrasonically treated for 30 min until a well-proportioned mixture is formed. After that, the mixture was added drop wise onto the surface of the as-prepared stainless steel electrodes and allowed to dry at room temperature, until a thin, flat coating formed.

Characterization of the Samples

The structure was characterized with FTIR (Nicolet, type210, America) which was recorded between 4000 and 500 cm⁻¹. The morphology of the sample was characterized using SEM (JEOL JSM-6701F). Water and oil contact angle measurement were the averages of five measurements obtained at different positions using 3 μL water droplets and performed on a contact angle meter (DSA100, Kruss). Elemental analysis was performed by EDS (JEOL JSM-5600LV).

Corrosion Resistance Testing

Corrosion protection studies were carried out in a three-electrode system with saturated calomel electrode (SCE) used as reference electrode, platinum sheet used as a counter electrode, stainless steel electrode coated with PANI used as a working electrode. Anticorrosion performance was evaluated by the Tafel plot, electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) in a glass cell with 3.5% NaCl aqueous solution as the electrolyte at 25 °C. Tafel measurements were

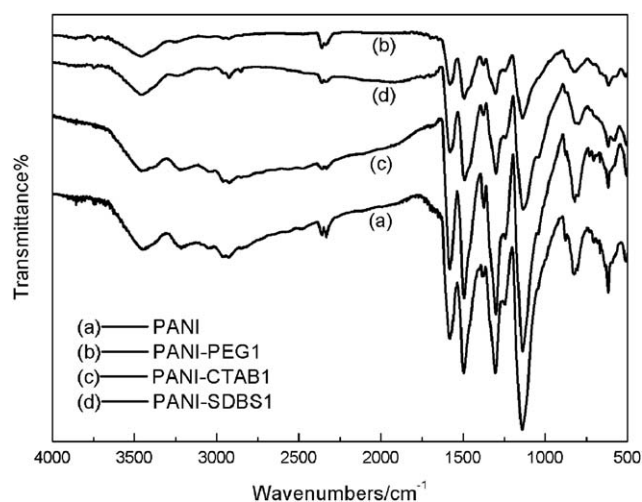


Figure 1. FTIR spectra of PANI (a) and PANI modified with different surfactants (b–d).

performed by scanning the potential from -300 to 300 mV above the open circuit potential (OCP) at a scan rate of 10 mV/s. EIS measurements were recorded in the frequency range from 0.01 Hz to $100,000$ Hz with an excitation signal of 10 mV. The cyclic voltammetry (CV) curves were recorded by scanning the potential from -0.3 to 0.7 V at a scanning rate of 5 mV s^{-1} . All of the above electrochemical measurements were conducted on a CHI660B electrochemical workstation (Chenhua, Shanghai, China). The working electrodes were immersed in a corrosive medium for 30 min before the electrochemical measurement. Each original data was repeated 3 – 5 times to ensure statistical significance and reproducibility.

RESULTS AND DISCUSSION

FTIR

Figure 1 shows the FTIR spectra of PANI, PANI-PEG1, PANI-CTAB1, and PANI-SDBS1. Assignments of the main peaks have been listed in Table I. The FTIR analysis is carried out so as to confirm the characteristic peaks of PANI. The spectra for PANI modified with different surfactants were alike, and similarly resembled that for unmodified PANI. The main characteristic peaks of PANI were assigned as follows: The peaks at 1582 and 1497 cm^{-1} are attributable to the quinoid and benzenoid rings of polyaniline, respectively.²³ The peaks at 1304 cm^{-1} correspond to the C–N stretching vibration in the benzene ring,²⁴

while the absorption peak at 1142 cm^{-1} is from the plane bending vibrations of C–H which belong to quinoid rings.²⁵ Besides, the peaks at 825 cm^{-1} render the existence of 1, 4-bisubstituted benzene ring.^{26,27} Values above are characteristic peaks of PANI. All these peaks can also be found in Figure 1(b–d), and no extra peak for PANI-PEG1, PANI-CTAB1, and PANI-SDBS1 than unmodified PANI. It implies that the samples have similar structure.^{28,29} The main characteristic bands of PANI and PANI-PEG1 contain all individual bands, yet the modification of PEG leads to slightly shift to lower wavenumbers in some bands of PANI.³⁰ Consider the wavenumbers of the main characteristic peaks of CTAB,³¹ they might be covered by some peaks of PANI. When PANI was modified with surfactants, some characteristic bands shifted to lower wavenumbers, this means that there are interactions between PANI and surfactants.

SEM and Contact Angle Measurements

As shown in Figure 2, the morphologies of the samples have been characterized with SEM. It can be seen from Figure 2 that unmodified PANI shows an irregular granular structure with a rough surface, and PANI modified with surfactants exhibits similar structure. Usually, superhydrophobic surfaces are very likely to have phenomenal roughness with microsized or nanosized (or even smaller) protrusions coming out of the surface,¹⁸ yet several morphologies can lead to the same roughness parameter but not the same liquid-repellent properties¹⁷ which results in the difference of wettability between untreated PANI and as-treated PANI.

Double-side tap have been used as substrate with as-prepared samples covered thoroughly upon it to measure water contact angle (CA) in this study. Figure 3 shows the CA of PANI (A) and PANI modified with PEG (B), CTAB(C), and SDBS (D). If the contact angle is below 90° , the surface is intrinsically hydrophilic and if the contact angle is above 90° , the surface is intrinsically hydrophobic, besides, superhydrophobic surfaces are characterized by apparent contact angle above 150° .¹⁷ Unmodified PANI reveals poor surface wettability due to its hydrophilic nature. Obviously, all modified PANI (with water contact angles of 164° , 160° , and 157° for PANI-PEG1, PANI-CTAB1, and PANI-SDBS1, respectively) of which water contact angles $>150^\circ$ that are greater than unmodified PANI (CA = 80°), which means the modification of surfactants have changed PANI from hydrophilic to superhydrophobic successfully. As can be seen from Figure 3, the water droplets (dyed with pigments) remain almost spherical shape when placed on as-modified PANI, on the contrary, oil droplets

Table I. Assignments of the Main Peaks in the FTIR Spectra (cm^{-1}) of PANI Powders in KBr Discs

Assignment	Wavenumber (cm^{-1})			
	PANI	PANI-PEG1	PANI-CTAB1	PANI-SDBS1
Vibrations of NH_2^+	2927	2924	2921	2923
C=C stretching vibrations of quinoid ring	1582	1579	1581	1578
C=C stretching vibrations of benzenoid ring	1497	1493	1494	1491
C–N stretching vibrations	1304	1302	1300	1299
C–H plane bending vibrations	1142	1140	1139	1135
1,4-bisubstituted benzene ring	825	820	820	798

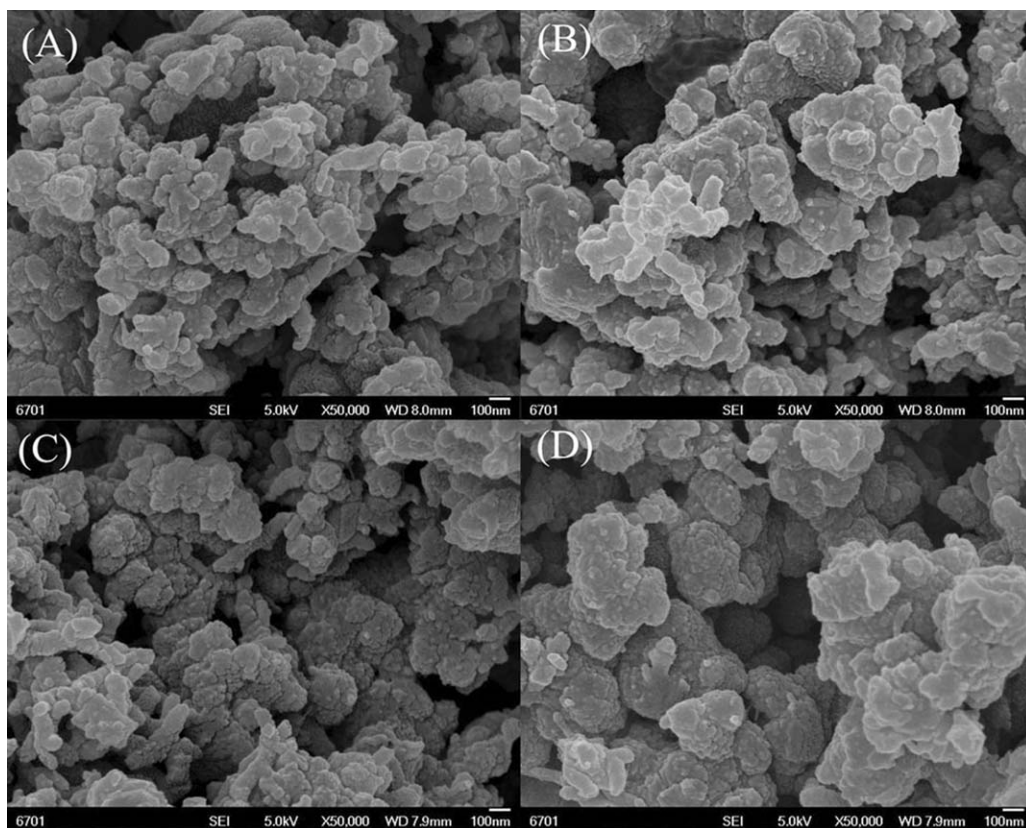


Figure 2. SEM images of PANI (A), PANI-PEG1 (B), PANI-CTAB1 (C), and PANI-SDBS1 (D).

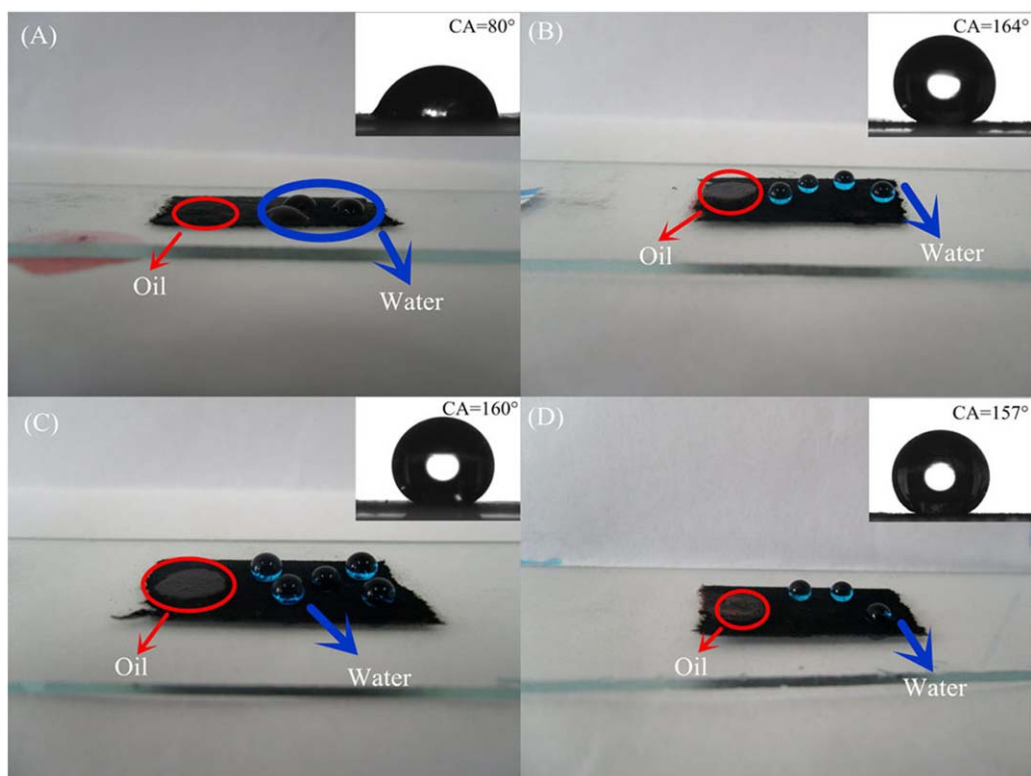


Figure 3. Water contact angles of PANI (A), PANI-PEG1 (B), PANI-CTAB1 (C), and PANI-SDBS1 (D). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

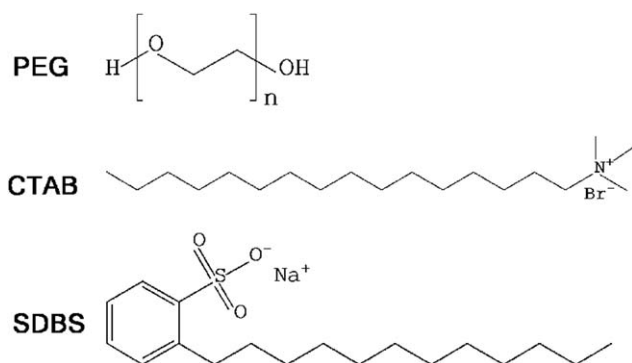


Figure 4. Structural formula of PEG, CTAB, and SDBS.

permeate into the powder instantly leaving an oil contact angle of nearly 0° . The results of water contact angles displayed that the surface of PANI is modified effectively by surfactant and the superhydrophobic surface of PANI has been obtained.

When connected with PANI, hydrophobic alkyl chain of surfactant protruding and lower the surface energy of PANI, the bigger the hydrophobic alkyl chain, the greater the contact angle. The structural formula of PEG is $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$, PEG consists of long hydrophobic alkyl chain and hydrophilic hydroxyl as shown in Figure 4, but hydroxy exists only in the end of the molecule. While the molecular weight increased, the proportion of hydrophilic hydroxyl getting smaller, and hydrophobicity of PEG was increased. In this work, we choose PEG-10000 as one of the modifiers which has much more huge hydrophobic alkyl chain compared with CTAB and SDBS, as a result, PANI-PEG1 revealed best hydrophobicity. CTAB and SDBS have long hydrophobic alkyl chain, so they can also turn PANI from hydrophilic to superhydrophobic, but their molecular chain length are similar, which lead to similar contact angles.

For modification with PEG, the hydroxyl terminal group of PEG connect with $-\text{NH}^+=$ of PANI chains by hydrogen bonding,^{32,33} which caused the PEG hydrophobic alkyl chain protruding, the large hydrophobic group of PEG decreased the free energy of the surface and formed superhydrophobic PANI. Previous researches indicated that the modification of CTAB and SDBS can increase CA over a certain range.^{34–36} For modification with CTAB, the surfactant would adsorb and arranged regularly all around the PANI surfaces because of the quaternary ammonium cation of CTAB. In this study, the protonic acid dopants H_2SO_4 have been used to prepare PANI, anions $-\text{SO}_4^{2-}$ of PANI chain and the quaternary ammonium cation of CTAB link PANI with CTAB by electrostatic interaction, which resulted in the CTAB hydrophobic alkyl chain protruding. For modification with SDBS, the electrostatic interaction between $-\text{SO}_3^-$ of SDBS and $-\text{NH}^+=$ of PANI should play a key role in the formation of the superhydrophobic,³⁷ hydrogen bonding also existed between N and H atoms among PANI chains. The electrostatic interaction and hydrogen bonding immobilized the hydrophilic $-\text{SO}_3^-$ head groups of SDBS around PANI chains and make the hydrophobic chain of SDBS going out.

The results of SEM and contact angle measurements demonstrate that the modification of surfactants did not change the

structure of PANI surface with a two step method, but combined with PANI through electrostatic interaction or hydrogen bonding, which could make the hydrophobic chain of surfactants going out. Then the modification can decrease the surface energy and turn PANI from hydrophilic to superhydrophobic. All modified PANI prepared in the experiment have water contact angles $> 150^\circ$, it implies the method is practicable.

EDS

As shown in Figure 5, EDS has been employed to measure the component of the samples. The results indicate that all four samples are comprised by C, N, O, S elements. The obtained atomic weight percent of C, N, O, S in PANI is 69.76%, 6.94%, 17.22%, and 6.08%, for PANI-PEG they are 77.48%, 4.97%, 12.99%, and 4.57%, meanwhile, they are 73.97%, 7.92%, 13.61%, and 4.50% for PANI-CTAB, and 79.14%, 2.10%, 14.26%, 4.50% for PANI-SDBS1, respectively. The component of the samples changed significantly after the modification of surfactant. Both FTIR and EDS results indicate that the surfactants have been introduced onto the surface of unmodified PANI.

Corrosion Resistance

Potentiodynamic Measurements. Electrochemical tests have been conducted to investigate the effect of surfactants addition on the anticorrosion performance of PANI coating. Corrosion resistance was studied by plotting the polarization curves firstly. Bare stainless steel and those coated with PANI were immersed in a corrosive medium for 30 min before starting. Polarization curves for bare stainless steel and stainless steel coated with PANI in 3.5% NaCl solution are shown in Figure 6. The values of corrosion current density (i_{corr}) and corrosion potential (E_{corr}) are calculated using the Tafel extrapolation from the polarization curves are listed in Table II. The polarization curves for stainless steel electrodes coated with PANI showed remarkable potential shifts to positive values, and the corrosion current density of them decreased slightly compared with that of uncoated electrode. The role of PANI coating is to prevent access by corrosive species to the substrate. Moreover, superhydrophobic PANI modified with surfactant display much better

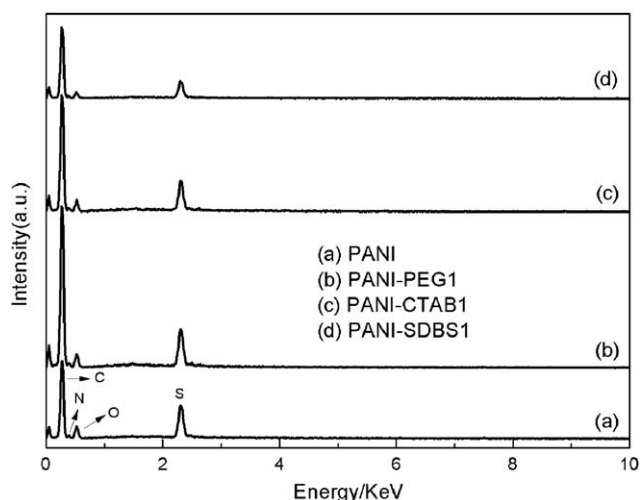


Figure 5. EDS of PANI, PANI-PEG1, PANI-CTAB1, and PANI-SDBS1.

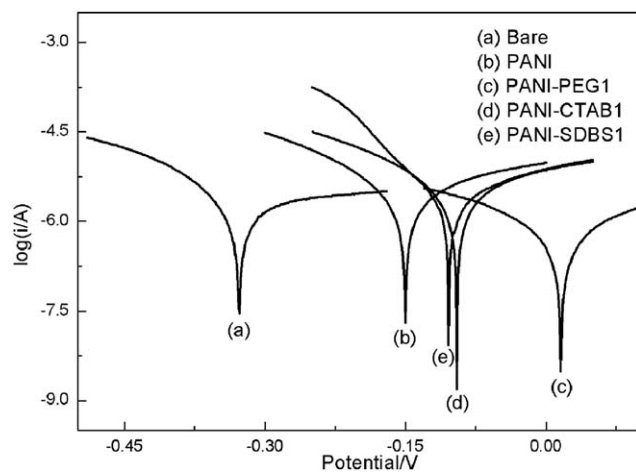


Figure 6. Tafel plots for bare stainless steel, stainless steel coated with PANI, PANI-PEG1, PANI-CTAB1, and PANI-SDBS1.

corrosion protection performance. E_{corr} of PANI-PEG1 and PANI-PEG2 were 0.016 and -0.046 V, respectively. They have been found to be more positive compared with bare stainless steel ($E_{\text{corr}} = -0.320$ V) and untreated PANI ($E_{\text{corr}} = -0.150$ V) with a significant shift of corrosion potential in the anodic region. Higher content of PEG increased the hydrophobicity of PANI, hence higher PEG content showed better anticorrosion performance. The similar phenomenon was also observed while comparing PANI-CTAB1, PANI-CTAB2, as well as PANI-SDBS1, PANI-SDBS2. Among which, PANI-PEG1 have also given the highest corrosion potential, besides, the i_{corr} of PANI-PEG1 was obviously lower than others. The result indicated PANI-PEG coating displays the best corrosion protection performance due to their more positive E_{corr} and lower i_{corr} .

Compared with bare stainless steel and PANI coated stainless steel, the modification of surfactants increased the corrosion potential while superhydrophobicity constructed on surface significantly. Moreover, it was clear that the superhydrophobicity were closely related to their corrosion protection performance. The corrosion potential increased with the increase of the contact angle, and better hydrophobicity corresponded to the better corrosion resistance.

Table II. Corrosion Resistance Testing of bare Stainless Steel, Stainless Steel Coated with PANI and PANI Modified with Different Surfactants

Coating system	Corrosion resistance testing			
	E_{corr} (V)	i_{corr} (A/cm ²)	R_{ct} (k Ω cm ²)	CA (°)
Bare	-0.320	3.271×10^{-6}	0.220	
PANI	-0.150	3.841×10^{-6}	0.894	80
PANI-PEG1	0.016	8.720×10^{-7}	8.751	164
PANI-PEG2	-0.046	3.146×10^{-6}	2.874	161
PANI-CTAB1	-0.095	3.206×10^{-6}	2.252	160
PANI-CTAB2	-0.120	3.383×10^{-6}	0.989	151
PANI-SDBS1	-0.104	3.184×10^{-6}	2.139	157
PANI-SDBS2	-0.134	3.409×10^{-6}	1.636	160

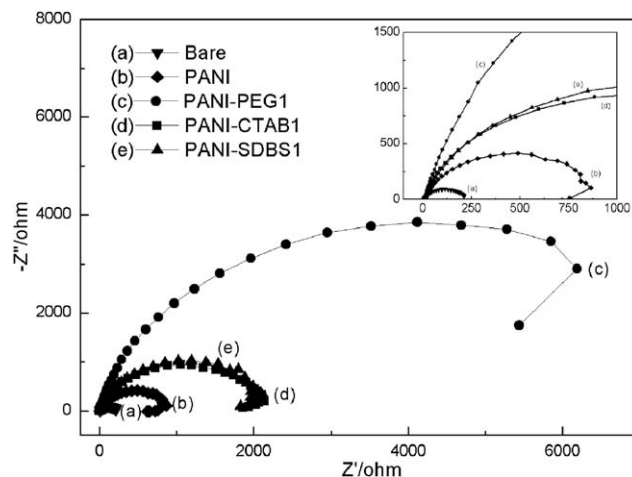


Figure 7. Nyquist plots for bare stainless steel, stainless steel coated with PANI, PANI-PEG1, PANI-CTAB1, and PANI-SDBS1.

The as-prepared superhydrophobic surface has excellent corrosion protection performance, which may be attributed to form dielectric layer like a pure parallel plate capacitor, which repelled the water and further reduce the water/corrosive solution adsorption on the PANI surface, inhibiting the electron transfer between the electrolyte and the metal substrate.

EIS Measurements. In order to further research the anticorrosion performance of the samples, EIS has also been examined. The impedance spectra of bare stainless steel and PANI-coated stainless steel in 3.5% NaCl are shown in Figure 7 in the form of Nyquist plots. The semicircle at low frequency region equals to the response at metal/polymer interface and the one at high frequency region vests in the process at polymer/electrolyte,²⁸ and the high frequency feature can be attributed to the coating.³⁸ It can be seen from Figure 7 and Table II that one semicircle was present, the charge transfer resistance (R_{ct}) of bare stainless steel, stainless steel coated by PANI, PANI-PEG1, PANI-CTAB1, and PANI-SDBS1 are 0.220, 0.894, 8.751, 2.252, and 2.139 k Ω cm², respectively, and other specimens show same trend. That's because the superhydrophobic surface blocks the corrosive medium and the electrode surface and an air protection shield function is achieved, which reduces the electron transfer ability between the electrode and the medium, and slows down the process of corrosion reaction.

Figure 8 shows Bode plots, modulus of impedance phase angle versus frequency (a) and $|Z|$ versus frequency (b). The phase angle value of modified PANI coating is greater than PANI, a bigger phase angle indicates a larger value of Z' , which corresponds to a large diameter in the Nyquist plot.⁴ As observed in Figure 7(b), the as-received superhydrophobic electrode had higher $|Z|$ values, in good agreement with the results presented by Nyquist plots.

Cyclic Voltammetric Test. Figure 9 illustrates the CV curves of PANI before and after modification. It needs to be noted that there are no obvious anodic peaks or cathodic peaks, which is consistent with the previous reports for PANI in neutral medium.³⁹ The CV curves of modified PANI were similar to that of unmodified PANI, yet some considerable disparities were

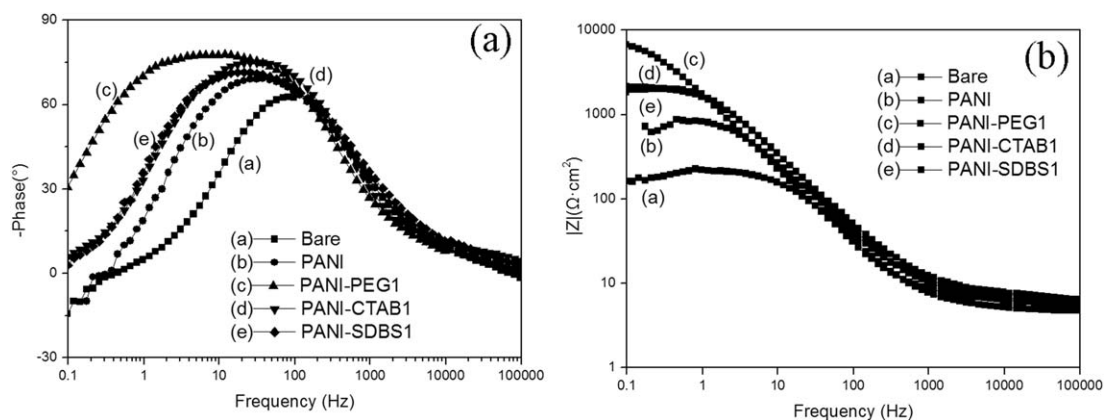


Figure 8. Bode plots for bare stainless steel, stainless steel coated with PANI, PANI-PEG1, PANI-CTAB1, and PANI-SDBS1.

observed. CV curves illustrated that current density of modified PANI is lower than that of unmodified PANI, which means electron transfer capability (ETC) of PANI decreased after modification. This decrease could be attributed to the enhancement of hydrophobicity, the hydrophobic surface repelled the corrosive media and weakened the transmission of electrons between corrosive media and stainless steel, the worse the ETC, the better the corrosion protection performance. Among which, PANI-PEG1 showed lowest current density, and also revealed best corrosion resistance, which further confirms the result revealed by potentiodynamic measurements.

The result indicates that the enhancement of hydrophobicity caused the increase in the value of charge transfer resistance and PANI-PEG has shown the best anticorrosion performance compared with other coatings, which further confirms the result revealed by potentiodynamic measurements.

Equivalent circuit used to fit EIS data for uncoated stainless steel and stainless steel coated with PANI and PANI modified with different surfactants is shown in Figure 10. R_s and R_{ct} are described as solution resistance and charge-transfer resistance, respectively. CPE is known as the double layer capacitance and L is called inductive reactance.

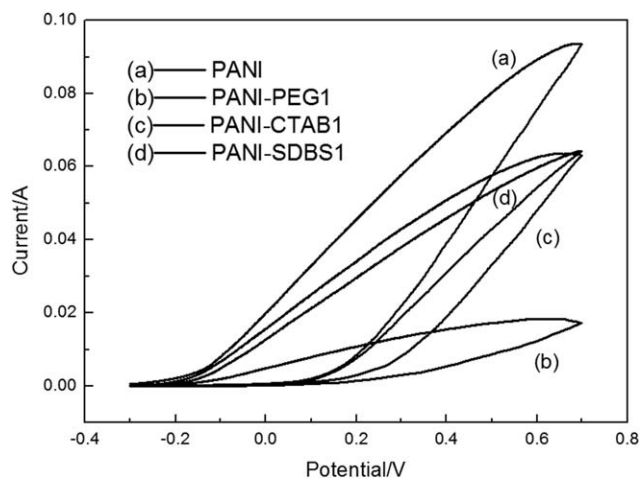


Figure 9. CV curves of PANI, PANI-PEG1, PANI-CTAB1, and PANI-SDBS1.

Considering the results of the measurements above, the increase of anticorrosion performance is attributed to the formation of superhydrophobic surface. The behavior of their anticorrosion performance could be illustrated as following: the first part of the protection is that the hydrophobic surface repelled the moisture and further reduced the water/corrosive media adsorption on the PANI surface, which effectively prevent the underlying metals from corrosion attack.^{20–22} The second is the PANI, which can form a passivation oxide layer on the metal surface to prevent the metal surface from further corrosion.^{8,14} Thus, stainless steel coated with superhydrophobic PANI shows better corrosion protection performance compared with unmodified PANI coating.

CONCLUSIONS

Superhydrophobic PANI structures modified with surfactants has been prepared via a two-step method. The method is facile, cheap, and without fluoride pollution. The morphology, corrosion resistance, and contact angle measurements have been studied. Irregular granular structure with a rough surface has been found from all four samples. Modification with PEG-10000, CTAB, and SDBS can increase the water contact angles from 80° to higher than 150° compared with unmodified PANI, the modification of surfactants does not change the surface structure of the samples, but can be taken as modification lower

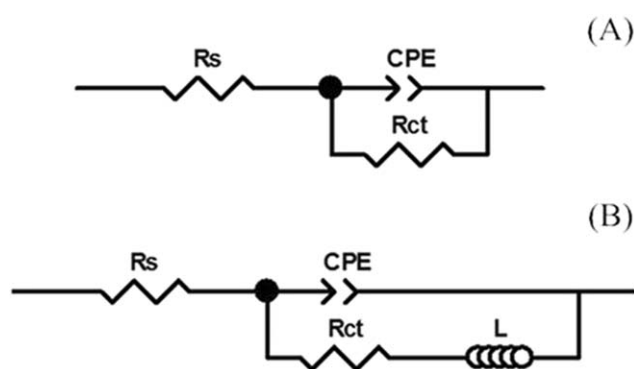


Figure 10. Equivalent circuit used to fit EIS data for uncoated stainless steel (A) and stainless steel coated with PANI and PANI modified with different surfactants (B).

the surface energy of PANI. Moreover, corrosion protection testing demonstrated the significant anticorrosion effect of superhydrophobic PANI with more positive corrosion potential. The study may provide a new way for fabrication of superhydrophobic conducting polymers. And this low-cost and ecofriendly nano-PANI anticorrosive coating can be a promising material to protect metal from corrosion.

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