11.1 Introduction

It is practically impossible to prevent corrosion. Thermodynamically, corrosion is an energetically favorable process that converts a high-energy metal into its low-energy oxide form. Corrosion not only poses serious problems economically and industrially, but also endangers human life. While there is no way to stop corrosion activity, the only option is to slow down its growth rate by preventing the aggressive species from reaching the metal surface, or by having a sacrificial material that preferentially reacts in place of the metal.
11.2 Corrosion Protection

The natural defense of the metal against corrosion is its oxide layer (or rust, in the case of iron). The oxide layer is formed when the metal reacts with the aggressive species from the electrolyte solution. However, most of the time, the oxide layer is not dense enough to prevent further diffusion of aggressive species into the metal surface. Some corrosion protection methods focus on improving the property of the oxide layer. It has been shown that alloying can drastically increase the density and reduce the porosity of the oxide layer. However, alloying is very expensive and can significantly affect the mechanical properties of the metal. Another approach is to use a coating to separate the metal and the corrosive environment. Coatings can be divided into two general areas: conversion coatings and organic coatings.

11.2.1 Conversion Coatings

Conversion coatings are formed by chemically or electrochemically transforming the elemental composition of the metal surface. This coating can function as a stand-alone corrosion protection coating and/or as an adhesion layer for the succeeding organic coating. Two of the most used conversion coatings, especially for iron, are phosphate-based and chromate-based. Phosphate-based coatings involve the immersion of the metal surface in a solution of Ti colloids, and subsequently into a solution containing either zinc phosphate or iron phosphate. The colloids act as nucleation sites for the growth of the phosphate crystals. In the case of zinc phosphate, the immediate metal surface is dissolved into the solution, which decreases the local pH. The decrease in pH drives the equilibrium towards the deposition of Zn(H₂PO₄)₂ on the metal surface. In the case of iron phosphate, the iron is first converted into iron oxide and eventually into iron phosphate. Chromate-based coatings, on the other hand, protect the metal by functioning as a physical barrier against aggressive species. They also effectively prevent the transport of ions because they form bipolar membranes with negatively charged outer layers and positively charged inner layers. Chromate-based coatings can also heal themselves when damaged. Electrolytes that fill the defect produce Cr(IV) from the hydrolysis of Cr(III)-O-Cr(IV) from the porous Cr(OH)₃ networks. The Cr(IV) is then reduced to Cr(III) hydroxide and adsorbs on the defect sites. However, the problem with chromate-based coatings is that they are highly toxic and carcinogenic to human.

11.2.2 Organic Coatings

Organic coatings, on the other hand, can be subdivided into conducting and nonconducting. The basic function of the organic coating is to separate the metal surface from the corrosive environment and to act as a barrier that prevents or slows down
the diffusion of aggressive chemicals and corrosion products. Organic coating can be designed to prevent selectively the diffusion of water, oxygen, ions, or its combination. For the case of nonconducting polymer, the coating itself also functions as an insulating layer that prevents the transfer of electrons from the metal surface into the aggressive species, which is necessary for the formation of the metal oxide or rust. Barrier coatings, such as epoxy, are employed extensively and have been proven to prevent corrosion effectively until coating defects are introduced. Failure starts when pits or holes are formed, usually from mechanical shocks or aging, in the coating. The corrosive species attacks the underlying metal through the defects, increases the exposed surface, and thereby accelerates the corrosion process. The reaction happens not only on the exposed metal surface, but also on the metal underneath the coating. The aggressive species can react with the coating or the metal substrate, which eventually causes cathodic or anodic delamination, respectively. To prevent the delamination of the coating, one can coat the metal with a conducting polymer.

### 11.3 Conducting Polymer as an Anticorrosion Coating

Conducting (or electro-active) polymers are a special type of polymer with extensive π-electron delocalization along their backbones that give rise to interesting optical properties and allows them to become good electrical conductors (typically when oxidized or reduced). Conducting polymers have been utilized in a wide range of applications because they possess both the electronic properties of semiconductors and the processability of conventional polymers. Having a conjugated backbone and/or a backbone that has low oxidation potential is necessary, but not sufficient for the polymer to be conductive. Conjugation provides the orbital system that allows the charge carriers to move because of the continuous overlapping of the pi-orbitals along the backbone. Most organic polymers, including some conjugated polymers, do not have intrinsic charge carriers. Charge carriers can be introduced by partial oxidation (p-doping) of the polymer chain with electron acceptors or by partial reduction (n-doping) with electron donors. Such doping processes mostly introduce charged defects (e.g., polaron, bipolaron, and soliton) along the polymer backbone.

There are several ways to introduce charge carriers or to dope the conjugated polymer to become conducting, but the most widely used are electrochemical and chemical oxidation/reduction. Electrochemical doping offers advantages over other doping techniques: doping level can be precisely controlled by controlling the amount of current passed, and doping and dedoping processes can be done simply by changing the applied potential. Partial oxidation of the conjugated polymer converts the polymer into its cationic salt form, while partial reduction yields the anionic salt form. Both forms are conducting; however, cationic salt form is more stable.
11.3.1 Coating Procedure

Successful use of conducting polymer as an anticorrosion coating depends heavily on how well it can coat the metal substrate. These coatings should have a very good barrier property, are free from any defects where aggressive species can diffuse through, and are strongly adhered on the metal surface to be effective. Next are some of the coating procedures used widely in the industry and in research.

11.3.1.1 Casting-Based Methods

The process of casting involves dissolution of the conducting polymer in a suitable solvent, usually volatile organic solvent or water, and then spreading of the solution over the substrate. Examples include, but are not limited to, dip-coating, drop-casting, spray-coating, and spin-coating. The film of polymer can be obtained after the evaporation of the solvent. This step is commonly followed by an annealing step to make sure that the coating is free of solvent and that the polymer homogenously coats the metal substrate. Coating thickness depends on the polymer concentration, spin speed (for spin-coating), or dipping speed (for dip-coating). One major disadvantage of this technique is that it is hard to find a suitable solvent that can dissolve the conducting polymer.

11.3.1.2 Paint/Resin-Blended Coatings

Alternatives to casting-based methods is to disperse the conducting polymer into a paint or into epoxy or acrylic resins. With this approach, finding a suitable solvent can be bypassed since the conducting polymer can be dispersed in its solid form. In addition, it is possible with this approach to achieve the synergistic effect of the mechanical properties of the paint or resins and the electrical properties of the conducting polymers. This is also the method of choice in expanding the application of conducting polymer to the industrial level, especially in coating large structures.

11.3.1.3 Electropolymerization/Electrodeposition

Electropolymerization is another coating procedure wherein the conducting polymer is formed and deposited from a monomer solution onto a conducting substrate. This is usually the method of choice in coating relatively small areas. Care must be taken in choosing the electropolymerization condition, especially the applied potential and current. The applied potential should be high enough to oxidize the monomer and polymerize it, but low enough not to dissolve the metal or induce corrosion. The electrochemical coating is usually done in an electrochemical cell composed of the substrate to be coated as the working electrode and two inert materials as the counter
electrode (usually platinum) and the reference electrode (usually Ag/AgCl or SCE). The polymerization solution contains the monomer, solvent, and the supporting electrolyte. This method can be further divided into potentiodynamic, galvanostatic, and potentiostatic electropolymerization.

11.3.1.3.1 Potentiodynamic Electropolymerization
Potentiodynamic electropolymerization is characterized by a cyclic regular sweep of potential between the limits of the monomer oxidation and the reduction of the polymerized conducting polymer. The growing polymer film continuously changes from its neutral state to its doped (or conducting) state as the potential is swept back and forth. This process is accompanied by the continuous absorption and desorption of the electrolyte and the solvent to stabilize the growing film.

11.3.1.3.2 Galvanostatic Electropolymerization
Galvanostatic electropolymerization involves the application of constant current to polymerize the conducting polymer at a constant rate. At the beginning of the electropolymerization, the potential rises for a short period and then decreases after a while. It has been explained that the sudden increase in potential is brought about by the formation of the redox-active charged oligomers in front of the electrode. The subsequent decrease in the potential is brought about by the catalytic effect of the charged oligomers to oxidize the monomers. The measured potential also depends on the temperature—the measured potential decreases with decrease in temperature. This can be explained by the decrease of the volume of the solvent, which consequently increases the concentration of the monomer as the temperature decreases.

11.3.1.3.3 Potentiostatic Electropolymerization
Potentiostatic electropolymerization involves the application of constant potential. The rate of polymerization can be controlled depending on the applied potential. This method is similar to the galvanostatic electropolymerization and is different to potentiodynamic electropolymerization because no material is discharged from the deposited film during the coating procedure.

Polypyrrole films polymerized using potentiostatic electropolymerization (and also by galvanostatic electropolymerization) are of dendritic type and have low adhesion strength on the substrate. In contrast, when the polypyrrole is polymerized potentiodynamically, the resulting film is shiny black, adheres strongly on the substrate, and has a smooth and homogenous surface morphology. This has been explained as due to the formation of a large number of equivalent nucleation sites during the growth process. Poly(3-methylthiophene) films, on the other hand, showed better electrical properties (conductivity, charge mobility, number of free carriers, and band gap) when polymerized potentiostatically than when polymerized potentiodynamically.
11.3.2 Mechanism of Protection

There are several proposed reasons why conducting polymer effectively prevents corrosion. Next some of established protection mechanisms are discussed.

11.3.2.1 Barrier Protection

Conducting polymer, when coated properly, can separate the metal substrate and the corrosive environment. The absence of pinholes, cracks, and other coating defects guarantees effective protection. Conducting polymer can also be tuned to prevent diffusion of ions, water, and other aggressive species selectively. This protection mechanism is not unique to conducting polymers; that is, even nonconducting polymer can act as a barrier. The coating blocks the diffusion of the ions and corrosion products, thus preventing the establishment of galvanic coupling between the local anodes and cathodes.

11.3.2.2 Ennobling Mechanism

What differentiates conducting polymer from nonconducting polymer is that the conducting polymer can induce the oxidation of metal surface to form its metal oxide and maintain the metal in its passive or “noble” form. In order for this to happen, the polymer should have lower oxidation potential than the metal it is protecting.\textsuperscript{16} The formed oxide layer, sometimes called the passive layer, prevents further corrosion by functioning as another layer of barrier against diffusion of aggressive species and as an insulating layer that prevents the flow of electrons. Conducting polymer also improves the passivity of the oxide layer and inhibits the cathodic and anodic delamination of the coating.\textsuperscript{17}

11.3.2.3 Polymer is Preferentially Oxidized

This mechanism is similar to the protection mechanism of zinc to iron. Polymer has lower oxidation potential than the metal and therefore the polymer is preferentially oxidized. However, unlike zinc, the oxidized form of the polymer remains insoluble to the corrosive environment and remains intact on the metal surface. The polymer does not dissolve away and therefore protects the metal for a longer time.

11.3.2.4 Self-Healing

The self-healing mechanism was based on the assumption that the conducting polymer releases the doping anions, stored inside the conducting polymer matrix, when a coating defect appears. The doping anions diffuse into the defect site and decrease the
corrosion rate. The passive oxide layer then re-forms between the metal and the conducting polymer brought about by the oxidative capability of the conducting polymer.16

11.3.3 Examples of Conducting Polymers

Interest in conducting polymer research began in the 1970s when films of polyacetylene were found to have semiconductive properties in their reduced form and high electrical conductivity when exposed to iodine vapor.8,18 Exposure to iodine increased conductivity by more than fifteen orders of magnitude and reached a value in the range of $10^4$-$10^6$ S/cm$^2$, which is comparable to that of the metals. For anticorrosion applications, however, polyacetylene is rarely used because it degrades in air. Next some of the conducting polymers that have been used as anticorrosion coatings are examined.

11.3.3.1 Polyaniline

Polyaniline (PANI) is considered one of the conducting polymers most used as an anticorrosion coating. It has the following advantages over other conducting polymers: (1) it can be synthesized easily via chemical or electrochemical means, (2) it can be doped and dedoped easily by treatment with aqueous acid and base, (3) it cannot be degraded easily, and (4) the aniline monomer is relatively cheap.19 First report of its synthesis dates back to 186220 and its primary application was as textile dye. It was only during the 1960s that the electrical property of PANI was realized.21

PANI can be synthesized either chemically or electrochemically. Chemical synthesis of PANI involves the oxidation of aniline in acidic medium with an oxidizing agent such as ammonium persulfate and tetrabutyl ammonium periodate.22,23 First report of electrochemical oxidation of aniline was done by Letheby and was later extended to polymerize alkyl, alkoxy, and dimethoxy-substituted aniline.20 It has been proven that chemical oxidation of aniline yields linear PANI, while electrochemical oxidation of aniline yields a cross-linked polymer network.24,25 PANI can exist in a number of well-defined oxidation states.26 PANI can either be fully reduced (leucoemeraldine), fully oxidized (pernigraniline), or partially oxidized (protoemeraldine, emeraldine, nigraniline). None of these are conducting. PANI becomes moderately conducting when the partially oxidized states, specifically the emeraldine base, are protonated by adding an aqueous acid solution.

Recently, Sakhri et al.27 compared the efficacy of PANI to zinc phosphate as an anticorrosion pigment by mixing each into a chlorinated rubber paint and applying the composite paint onto the carbon steel substrates. They found out that PANI performs better even with a very low loading of 1.5 wt.% compared to zinc phosphate. They also reported that although the coating with PANI pigment absorbs more water, the high electroactivity of PANI increases the alkalinity at the polymer/metal interface, which increases the stability against cathodic disbondment of the coating.
Adhesion of PANI on the metal substrate can easily be improved by combining it with silica sol-gel as demonstrated by Akid et al.\textsuperscript{28} The PANI/silica sol-gel composite coating offers both the anticorrosion resistance of PANI and the mechanical property of the silica sol-gel. Even with low PANI/sol-gel ratio, the composite passed the 500 h in the salt spray testing without any visible sign of corrosion or any undercutting (see Figure 11.1). Scanning vibrating electrode technique (SVET) also confirms the self-healing capability of the PANI/sol-gel composite due to the ability of the

\textbf{Figure 11.1} Images of the scribed aluminum substrate coated with sol-gel only (a), and PANI/sol-gel (b).\textsuperscript{28}
PANI to undergo oxidation-reduction reaction. Finally, they reported that high PANI content (more than 2.5%) could greatly reduce both the corrosion protection and the adhesion of the composite coating.

Titania/PANI/polyvinyl butyral hybrid coating has also been proven to provide superior anticorrosion performance. Radhakrishnan et al. claimed that the effectiveness of this hybrid coating is brought about by (1) the improvement of its barrier properties, (2) the redox capability of PANI, and (3) the formation of p-n junction that prevents the charge transport when the coating is damaged. The developed hybrid coating can release the PANI to heal the defects and prevent catastrophic failure.

### 11.3.3.2 Polypyrrole

Polypyrrole is an example of heterocyclic conductive polymer. The earliest report of its synthesis was in 1968. Electrochemical synthesis of polypyrrole in sulfuric acid yielded a black conducting film, which is stable under ambient conditions and even at temperatures above 200 °C. Electrical and mechanical properties of the electropolymerized polypyrrole film depend heavily on the counter-ion used. Using perchlorate instead of oxalate can increase its conductivity by 10 times. Commercially available polypyrrole films with tosylate counter-ions are highly conductive (15 S/cm) and are very stable under ambient conditions (conductivity only decreased by 15% after 1 year).

To increase the processability of polypyrrole, soluble forms were synthesized by adding flexible side chains along the ring. Addition of various functionalities at the nitrogen can also improve its solubility; however, the conductivity of the resulting film can be reduced drastically because of the strong steric interactions of the substituent at the nitrogen and the hydrogens at the 3- and 4-positions of the adjacent pyrrole rings. The adjacent rings are forced out of the plane, which results in loss of conjugation and ultimately drastic reduction of its conductivity.

Recently, Gonzalez et al. studied the electropolymerization of pyrrole in the presence of nitrate and molybdate anions and evaluated the anticorrosion property of the resulting film. They reported that only the film electropolymerized potentiostatically has the strong adhesion on the stainless steel substrate and can completely prevent the pitting corrosion in chloride solution. There are no observable pits or defects on the coating as seen in Figure 11.2 after 12 h of polarization at 0.60 V versus Ag/AgCl in 0.15 M NaCl. It has also been suggested that the presence of nitrate and molybdate provided the polymer coating with fixed negative charge, which prevents the diffusion of the negative chloride ions through the polymer matrix.

Mrad et al. found out that addition of hydroxyquinoline or molybdate anions drastically changes the morphology and the thickness of the electropolymerized
polypyrrole and moderates the resistance of the coating against pitting corrosion of the aluminum alloy. Hybrid coating comprising polypyrrole and titania nanotubes has been recently studied by Herrasti et al. They reported that addition of titania nanotubes increases the polymerization rate of pyrrole because the nanotubes act as nucleation sites. Also, the hybrid coating improved the corrosion resistance of stainless steel by 400 times as compared to the uncoated steel, and by twice as compared to the stainless steel coated with just polypyrrole.

Figure 11.2  SEM images of the surface of the PPy-coated steel electrode after 12 h of polarization at 0.60 V versus Ag/AgCl.
11.3.3.3 Polythiophene

Polythiophene is similar to polypyrrole, but with sulfur in place of the nitrogen in the aromatic ring. Chemical synthesis of polythiophene can be performed by mixing thiophene monomer and sulfuric acid to yield a dark insoluble material or by using a Grignard-type coupling of 2,5-dibromothiophene.\(^{39-41}\) A highly conducting form of polythiophene is composed of monomers linked at the 2- and 5-positions. Defects like 2,4- and 2,3-linkages reduce the degree of conjugation and, in effect, reduce the conductivity of the resulting film.\(^{42}\) In terms of processability, addition of flexible side chains at the 3- and/or 4-position can improve the solubility of polythiophene. Electropolymerization of thiophene monomer is rarely done because it requires high oxidation potential (2.07 vs. SCE). Instead, thiophene oligomers, such as bithiophenes and terthiophenes with oxidation potentials of 1.05 and 1.31 V versus SCE, respectively, are used.\(^{43}\)

In terms of anticorrosion property, poly(thiophene) was recently used as part of a polymer alloy that was used as a coating on mild steel.\(^{44}\) It has been shown that the resulting polymer alloy coating has very high heat resistance and is stable at 380°C. Also, impedance spectroscopy measurement was used to prove that the coatings were initially capacitance in nature with very high resistance (10\(^7\)-10\(^8\) Ω cm\(^2\)). These resistances decreased only by two- to threefold after immersion in 3 wt.% NaCl. Leon-Silva et al. recently reported that thermal annealing of poly(3-octylthiophene) can drastically improve its anticorrosion property.\(^{45}\) This was due to the densification of the conducting polymer coating, through which the diffusion resistance of aggressive species becomes a lot higher.

11.4 Superhydrophobic Coating as an Anticorrosion Coating

Interest in using superhydrophobic coatings developed from its application as a self-cleaning surface and as an antisticking, anticontamination, and anticorrosion coating.\(^{46}\) A direct measure of the wettability of the surface is the contact angle. Surfaces with a water contact angle of >150° are superhydrophobic, while surfaces with a water contact angle of about 0° are superhydrophilic. In nature, there are many species that exhibit superhydrophobicity, such as leaves of a lotus plant, legs of a water strider, and wings of a cicada.\(^{47}\)

11.4.1 Theoretical background

In-depth understanding of superhydrophobicity requires the examination of the relationship between the surface energy and the surface roughness and the wettability of the surface. The most basic equation is the Young’s equation. Derivation of the
Young’s equation starts with the consideration of the sessile drop on an ideal, rigid, homogeneous, flat and inert surface.\textsuperscript{47} When a liquid is dropped on a solid substrate, there exists a three-phase contact line where the air, liquid, and solid contacts each other. Young’s equation is given by

$$\cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}$$

where $\gamma_{SV}$, $\gamma_{SL}$, and $\gamma_{LV}$ refer to the interfacial surface tensions between the solid and the gas, the solid and the liquid, and the liquid and the gas, respectively. The $\theta$ is called the Young’s contact angle (or just contact angle). The value of the contact angle is the result of the thermodynamic equilibrium of the free energies at the solid-liquid-gas phase. If water is used as the liquid, then the surfaces with $\theta < 90^\circ$ are hydrophilic, while surfaces with $\theta > 90^\circ$ are hydrophobic.

Real surfaces are most of the time neither perfectly flat nor homogeneous (see Figure 11.3). Wenzel proposed an equation that considers both the surface roughness and surface energies.\textsuperscript{48} The Wenzel equation (11.1) is given as

$$\cos \theta^W = r \cos \theta$$

where $\theta^W$ corresponds to the apparent (Wenzel) contact angle, $r$ represents the roughness factor, and $\theta$ refers to the Young’s contact angle. The basic assumption of the Wenzel’s theory is that the liquid follows the roughness of the surface by permeating into the grooves. The roughness factor ($r$) is defined as the ratio of the actual surface area and the projected surface area. Therefore, for perfectly flat surfaces, the value of $r = 1$, while for rough surfaces the value of $r > 1$. As can be seen from the Wenzel’s equation, roughness can enhance the hydrophobicity and hydrophilicity of the surface depending on its surface energy. It has been demonstrated that the apparent contact angle increases as the roughness factor increases, until it exceeds $r = 1.7$, wherein deviations from the Wenzel’s theory become apparent.\textsuperscript{49}

As the surface becomes rougher, it becomes hard for the water to permeate through the grooves mostly because of the packets of air that are trapped. As a result, the liquid droplet rests on a “composite” surface comprising the trapped air and the tip of the surface. Cassie-Baxter proposed that the apparent contact angle is related to the fraction of the surface that is in contact with the liquid as shown in the following equation.

$$\cos \theta^{CB} = f (1 + \cos \theta) - 1$$

where $\theta^{CB}$ corresponds to the apparent (Cassie-Baxter) contact angle, $f$ is the fraction of the solid surface that is in contact with the liquid, and $\theta$ refers to the Young’s contact angle.\textsuperscript{47} Following the Cassie-Baxter equation, we can see that to have a superhydrophobic surface, $f$ should be as small as possible or the surface is comprised of a solid material with very high contact angle.
11.4.2 Fabrication procedures

Most of the procedures in fabricating superhydrophobic surfaces involve either roughening the surface (to make $f$ as small as possible) followed by hydrophobization (to make $\theta$ as high as possible) or roughening the low-surface energy materials. Next some of the methods that have been used in fabricating superhydrophobic coatings for anticorrosion applications are presented.

11.4.2.1 Chemical Deposition

Chemical deposition involves a reaction wherein the product self-assembles and coats the substrate. It can be further divided into chemical vapor deposition, chemical bath deposition, and electrochemical deposition. Recently, Wang et al. deposited zinc
tetradecanoate film via potentiostatic electrolysis of tetradecanoic acid using zinc as the working electrode.\cite{50} Deposition of Zn(CH$_3$(CH$_2$)$_{12}$(COO)$_2$) on the zinc surface caused its contact angle to change from 62° ± 3° for bare zinc to 152.5° ± 3°. The petal structures (see Figure 11.4) with low surface energy found on the zinc surface caused the superhydrophobicity. They observed a five orders of magnitude decrease in capacitance and dramatic increase in the resistance because of the air trapped between these structures.

Zhang et al. deposited $1H,1H,2H,2H$-perfluorooctyltriethoxysilane (PTES) onto the roughened surface of titanium to render it superhydrophobic.\cite{51} The rough surface of the titanium was brought about by the formation of anodic titania films grown by potentiostatic anodization. The contact angle before and after the deposition of the fluorinated silane is about 10° and as high as 160°, respectively. The superhydrophobic film prevented the corrosion of the underlying titanium metal even after 90 days of immersion in 3.5 wt.% NaCl. The excellence corrosion resistance was attributed to the trapped air in between the nanopores that limits the water accessibility and the diffusion of Cl$^-$ ions. Carbon fiber can also be used to fabricate superhydrophobic coating on zinc, as demonstrated by Qiu et al.\cite{52} The surface of the zinc substrate was roughened by immersing it into 0.1 M CuCl$_2$ solution. Metallic copper dendritic structure was formed on the zinc surface and became the catalyst for the deposition of the carbon fiber on it. Polarization scans revealed that the current density for the Zn coated with superhydrophobic carbon fiber is $2.83 \times 10^{-11}$ A/cm$^2$, while the current density for bare Zn is $3.05 \times 10^{-5}$ A/cm$^2$. Similar to previous cases, the trapped air is the one responsible for the six orders of magnitude decrease of current density. Liu et al. showed that coating zinc foil with superhydrophobic coating could decrease the corrosion current to $1.62 \times 10^{-7}$ versus $1.09 \times 10^{-5}$ A/cm$^2$ for the uncoated zinc.\cite{53} The superhydrophobic coating was fabricated by immersing the zinc foil into the hydrolyzed solution of $1H,1H,2H,2H$-perfluorooctyltrichlorosilane for 5 days. The contact

Figure 11.4  Contact angle photographs of zinc coated with superhydrophobic film (left) and surface morphology of the superhydrophobic coating (right).\cite{50}
angle increased from $64^\circ$ to $151^\circ$. SEM image of the zinc surface after immersion in 3% NaCl for 1 day shows the formation of dense film of ZnO structures all over the surface. On the other hand, similar structures are visible only on some areas on the SH-coated zinc immersed in the same solution for 29 days.

### 11.4.2.2 Colloidal Assemblies

Micro- and nanoparticles can provide surface roughness when deposited on the metal surface. Further treatment of these particles to decrease their surface energy can render the surface with superhydrophobicity. Recently, Weng et al. employed the use of organic fluorinated polyacrylate and methyltriethoxysilane (MTES)-based silsesquioxanes particles to fabricate superhydrophobic coating on cold-rolled steel.\(^{54}\) Because of the surface roughness provided by the particles (about 400 nm in diameter) and the low surface energy provided by the fluorinated polyacrylate, the contact angle increased from $74.1^\circ$ for bare steel to $153.2^\circ$ (Figure 11.5). Potentiodynamic

![Figure 11.5](image_url)  
SEM image (a) and AFM image (b) of the superhydrophobic coating on CRS. Contact angle photograph in the inset.\(^{54}\)
measurements revealed that the corrosion rate was decreased from 12.77 mm/year for bare steel to 0.02 mm/year for the coated steel.

Silica colloids can also be used to fabricate superhydrophobic coating on aluminum foil, as demonstrated by Xu et al.\textsuperscript{55} They dip-coated the cleaned aluminum substrate with a sol-gel containing 2.5 wt.% silica colloid particles and 0.2 wt.% polystyrene microspheres. The polystyrene microspheres were used as a removable template to control the surface roughness of the coating. After the removal of the polystyrene microspheres by heating the coating at 550°C, the surface energy of the coating was lowered by chemical vapor deposition of perfluoroalkylsilane. The resulting coating can protect the underlying aluminum foil from acid attack for at least 5 h. Rao et al. coated the copper substrate with a superhydrophobic coating by immersing the substrate into solution containing MTES, methanol, water, and ammonium hydroxide.\textsuperscript{56} The gel network was then densified by sintering at 250°C for 3 h. To test the long term stability of the coating, the coated substrate was immersed in 50% HCl solution. No change in wettability was observed after 100 h of immersion, however, the contact angle decreased from 158° to 146° after 120 h of immersion.

\textbf{11.4.2.3 Other Methods}

Yuan et al. demonstrated that surface energy can be effectively lowered by growing a polymer brush on the roughened surface of copper.\textsuperscript{57} A copper surface was roughened by etching in solution of nitric acid and hydrogen peroxide. The vinyl-terminated silane was then self-assembled on the surface and subsequently, fluorinated polymer brush was grown from it. Polymerization for 6 h resulted in very rough surface with contact angle value of 159° (Figure 11.6). The superhydrophobic coating shows 95.3% corrosion inhibition efficiency after immersion in 3.5 wt.% NaCl for 1 day and 91.3% after immersion for 21 days.

Electrospun nanofibers can also be used to fabricate superhydrophobic anticorrosion coating.\textsuperscript{58} They showed that superhydrophobic coating can be fabricated by using (heptadecafluorodecylacrylate-co-acrylic acid)-b-poly(acrylonitrile) nanofiber. Acetic acid salt spray test was used to test the adhesion of the coating. After the accelerated corrosion test, they saw that the contact angle of the substrate coated with thick nanofiber mat remained unchanged.

\textbf{11.5 Superhydrophobic Conducting Polymers as Anticorrosion Coatings}

Conducting polymer protects the metal from corrosion because aside from being a barrier against aggressive species, it also induces the formation of the passive oxide layer at the metal and coating interface. On the other hand, superhydrophobic
coatings protect the underlying substrate by preventing the diffusion of water that acts as a medium for diffusion of aggressive species towards the metal. It is therefore reasonable to think that by making a superhydrophobic coating from a conducting polymer, one can have a coating with enhanced corrosion protection ability.

Figure 11.6 SEM images of the coating after the growth of the polymer brush: low magnification (a) and high magnification (b). Insets are the contact angle photographs and optical image of water on the Cu substrate.
The fabrication of superhydrophobic coating from conducting polymer has been
the focus of interest of some research. Qu et al. demonstrated that superhydrophobic
PANI nanowires can be prepared by adsorbing low-surface energy molecules on it.59
PANI nanowire film was prepared by electropolymerization of aniline in sulfuric
acid on titanium-coated silicon wafer with anodized aluminum as the hard template.
The resulting PANI was then immersed in solution containing perfluorooctanoic acid
and N,N′-dicyclohexylcarbodiimide in methanol for 2h. The resulting film has con-
tact angle of 160°±1°. Alternative procedure in fabricating superhydrophobic PANI
was developed by Zhu et al.60 They reported a template-free approach to synthesize
3D box-like microstructures of PANI by self-assembly of PANI nanofibers in the
presence of perfluorosebacic acid with contact angle of 151.7°. They proposed that
the self-assembly of PANI nanofibers to box-like structures was brought about by the
cooperation between the perfluorosebacic acid and aniline. Hydrogen bonding and
hydrophobic interactions hold the nanofiber together to form the box.

Xu et al. demonstrated that the wettability of rough PPy film can be effec-
tively controlled by applying potential in the presence of fluorinated dopant. 61
Superhydrophobic PPy was fabricated by galvanostatic electropolymerization of
pyrrole with perfluorooctanesulfonate as the dopant. The resulting film has contact
angle of 152°±2°. Applying −0.6 V versus SCE converts the superhydrophobic into
its superhydrophilic neutral form. Applying 1.0 V in the presence of perfluorooctane-
sulfonate converts it back to being superhydrophobic (Figure 11.7).

The number of studies on application of superhydrophobic conducting coating to
corrosion is still limited. Weng et al. used nanocasting technique to mold an electroac-
tive epoxy to have morphology derived from Xanthosoma sagittifolium leaves.62 The
resulting coating has contact angle of about 155°. Immersion of the coated cold-rolled
steel to neutral 3.5% aqueous NaCl for one day shows 86.77% protection efficiency.
Increasing the acidity of the NaCl solution reduces the protection efficiency by a min-
imal amount, with the lowest at 84.66% for pH=1. Immersion for 7 days in neutral
NaCl solution caused the protection efficiency to drop to 86.31%. They also compared
the anticorrosion performance of the superhydrophobic electroactive coating to the flat
(hydrophobic) electroactive coating. The protection efficiency of the flat (hydrophobic)
electroactive coating is just 69.1% and 52.3% after immersion in neutral NaCl solution
for 1 and 7 days, respectively. Alternative approach in fabricating superhydrophobic
conducting coating involves the combined colloidal assembly and electropolymeriza-
tion.63 Monolayer of polystyrene nanospheres (d=500 nm) was deposited by Langmuir-
Blodgett-like technique onto the stainless steel. The polystyrene nanoparticles provide
the microscale roughness and also act as another layer of barrier against diffusion of
aggressive chemicals. Terthiophene-derivative monomer was then electopolymerized
on top of it. This provides the low surface energy coating, additional nanometer scale
roughness, and anodic protection of the underlying stainless steel substrate. The result-
ing film has contact angle of 152°±1°. Corrosion protection of the resulting film was
tested by immersing the coated steel in 3.5 M NaCl solution of varying pH and temperature. Potentiodynamic measurements reveal that the superhydrophobic coatings have protection efficiency of 96.6%, 96.9%, 96.2%, and 95.8% for pH 1, 7, 14, and $T=60^\circ$C, respectively, after immersion for 1 day. Immersion for 7 days reduced the protection efficiency minimally. The superior corrosion protection is brought about by the redox catalytic ability of the conducting polymer and the water-repellant property of the superhydrophobic coating acting synergistically.

### 11.6 Conclusion

In summary, enhanced corrosion protection can be derived by combining the outstanding redox capability of conducting polymer and water-repellant property of superhydrophobic coatings. The superior performance can be attributed to the high water repellency of the polymer coating combined with its capability to protect the
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The ability of the coating to prevent the adhesion of water is important to its anticorrosion property as water serves as the medium for diffusion of aggressive chemicals and corrosion products, from being absorbed by the coating.

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