# Electrospun Nanofibers for Coating and Corrosion

**Subhash B. Kondawar, Hemlata J. Sharma, Sushama M. Giripunje, and Pravin S. More**

**Abstract** Metallic and alloy materials are needed special surface treatments and coatings to be acted as environmentally anticorrosion. Corrosion is a typical critical issue in the performance of metallic components used in industrial applications. Surface engineering techniques have been well developed with the advent of nanotechnology for the improvement of corrosion resistance. Traditional techniques of coating used chromates which are environmentally creating human health problems. To resolve this issue, surface modification by using nanostructure coating is the hot topic of research in the field of anticorrosion properties of nanomaterials. Among the various nanoscale deposition on the metallic or alloy materials such as sputter deposition, physical vapor deposition, chemical vapor deposition, laser-assisted ablation, electrodeposition, atomic layer deposition, spin-coating, chemical bath deposition, etc., the deposition by polymeric fibrous materials at the nanoscale has found to be well anticorrosive. The polymeric nanofibers coating on metal by electrospinning is an effective technique used for the reduction of corrosion rate. This chapter is mainly focused on the fabrication technique of electrospun nanofibers which can be efficiently used as corrosion inhibitors as well as self-healing agents to reduce the corrosion rate and compared with other coating techniques.

**Keywords** Polymers · Nanofibers · Electrospinning · Coating · Corrosion

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S. K. Tiwari et al. (eds.), *Electrospun Nanofibers*, Springer Series on Polymer and Composite Materials, https://doi.org/10.1007/978-3-030-79979-3_5

## 1 Introduction

The corrosion can be well defined as the electrochemical oxidation of metal in reaction with oxygen that converts the refined metal to a more chemically stable form. Corrosion is not limited to metal. It can be found in polymer, ceramic, and steel. Due to chemical or physical interactions of the material with the environment, there is a gradual destruction of metal. Corrosion of metals is one of the most serious problems and several techniques have been used to protect metals from corrosion. To control and prevent the corrosion of metals, it needs to be properly coated. The durability of the metal used as current collector electrodes in most of the applications including solar power generation panels and electrodes for capacitors and supercapacitors is greatly affected by environmental corrosion. Therefore, there is a demand to protect the metals by using suitable self-healing anticorrosion coatings. Metallic structures in the modern industry rely on organic coatings for corrosion protection. To prevent corrosion on the surface of metals exposed to a corrosive environment, polymer coatings are widely applied as such coatings are cost-effective and environmentally friendly. These coatings have the ability to self-heal after suffering mechanical damage. The ability to self-heal can be obtained by adding corrosion inhibition substances to the coating system. Nanocomposites containing active protective components that have self-healing properties became the top priority in organic coating systems for corrosion protection. Due to the synergistic effect of components forming polymeric nanocomposites, more attention has been devoted to organic–inorganic coatings. The organic component provides excellent conductivity, high mechanical flexibility, and improved adhesion on the metallic surface, whereas the inorganic nano-filler provides a high aspect ratio and improves the electrical and electrochemical performances by creating the active sites for reaction. The corrosion resistance of metallic materials can be well improved by the surface engineering techniques by using chromates. But these techniques are not suitable as the use of chromates is found to be dangerous for human health [1]. With the advent of nanotechnology, the materials behave differently at nanoscale as nanomaterials posses very large surface area to volume ratio and very large number of surface atoms in comparison with the interior or bulk atoms. And therefore, coating of such nanomaterials over the metallic surface will definitely improve the corrosion resistance.

The main purpose of coatings for corrosion inhibition is to create a functional barrier in environments to protect against corrosion of the materials. Generally, coatings can be categorized as metallic, inorganic, organic, and hybrid coatings depending on the materials which are to be used for coating. Since the materials behave differently at the nanoscale, the coating by nanostructure can improve coating properties, and therefore, nanomaterials are studied for nanocoating with improved strength, hardness, and corrosion behavior.

The nanofibers are found to be very good resistive to prevent corrosion due to their remarkable properties such as large surface area, high porosity with good elasticity, and mechanical strength. They are lightweight with small diameters and controllable pore structures making them ideal for a wide range of applications [1]. In recent years, a number of processing techniques have been used to prepare polymeric nanofibers such as drawing, template synthesis, phase separation, self-assembly, and electrospinning [2]. Among them, electrospinning is an advancement in the field of nanotechnology and is a popular technique that allows the deposition of synthesized polymeric nanofibers onto metallic surfaces. The deposited electrospun nanofibers can act as an effective barrier coating to reduce the rate of corrosion of metals. Zhao et al. reported the improvement of corrosion resistance when the healing agent is mixed in core–shell nanofibers [3]. Harb et al. suggested that nanocomposites have high-efficiency protective coatings. Inorganic oxides modified polymeric materials coatings have proved to be very good corrosion protection [4]. Aldabbagh et al. mentioned that polyamide coatings can be a good corrosion resistance for aluminum [5]. Electrospun polyvinyl alcohol (PVA) and polyvinyl chloride (PVC) fibers coating works as corrosion passivation application under chloride solution [6].

The selected coating material should be environmentally friendly to which it will be exposed to and should be pollution-free. By electrospinning technique, polyvinyl alcohol (PVA) fibrous material was successfully deposited on aluminum alloy and the corrosion behavior was studied in 3 wt % NaCl solution by means of electrochemical impedance spectroscopy (EIS). It is not only a cost-effective approach to provide a protective layer onto metallic surfaces but also provides new coating methods in which polymeric mats that are corrosion inhibitors developed self-healing functionalities [7]. Recently, it has been reported that ZnO-polymeric composite materials bilayer coating with a p-n heterojunction produce various effects of corrosion inhibition through various mechanisms on carbon steel substrate [8]. Superhydrophobic carbon nanofibers coatings have been reported as potential candidates for protecting metal and alloy surfaces in various engineering and environmental applications [9]. PANI microfibers blended with PMMA doped with DBSA and CSA can also be used as anticorrosion coatings of carbon steel. The coating is said to be reliable if it has low moisture penetration and chemically resistive [10, 11].

Corrosion mostly occurs in aqueous environments. In that condition, a metal can experience a number of degradations in the environment. The best coating or deposition technique which shields metallic surfaces against corrosion is electrospinning.

This chapter is mainly focused on various types of coating techniques in general and particularly the electrospun nanofibers coating along with the fabrication technique of electrospun nanofibers used as self-healing agents to prevent corrosion and for encapsulation of corrosion inhibitors.

## 2 Techniques of Nanostructure Coating

To prevent the corrosion of metals, the covering to the metallic surface by a certain substance is termed to be coating. There are various techniques for coating on the surface of metals. In most of the available techniques, chromates are used which create human health and environmental problems. To resolve this issue, various techniques of coating have been developed in accordance with the understanding of methods of nanostructure materials and the emergence of instrumentation to characterize the materials at the nanoscale. The development of preparation of nanostructure materials has proved to be very successful for deposition over the surface of the substrate which was later found to be useful for coating the metallic substrates against corrosion. Nanostructure deposition over the surface of metal has proved to be an anticorrosive coating which supports the metal against corrosion. The nanostructure coating over the metallic substrates can be done by various processes such as atomic layer deposition, laser thermal spray-coating, laser ablation coating, sol–gel coating, sputter deposition, chemical vapor deposition (CVD), physical vapor deposition (PVD), and electrospun nanofibers coating.

## *2.1 Atomic Layer Deposition*

The atomic layer deposition (ALD) technique is a homogeneous and conformal technique that has been recently accepted compared to other deposition techniques with precise control over thickness and composition. It considers self-limiting surface reactions and adsorbing molecular monolayer in sequence, i.e., the growth rate of a thin film can be precisely limited to only one molecular layer at one time. Also, surfaces can be uniformly coated by adjusting the number of ALD cycles and only one monolayer of the precursor is adsorbed on the surface during each pulse, regardless of whether there is an excess of precursor on the substrate [12]. We can introduce ALD coatings on metallic surfaces for the purpose of enhancing the chemical resistance against corrosion and oxidation and to improve the chemical stabilities of other nanostructure metals [13]. The pinhole-free films produced by ALD technique have better protection to the metallic surfaces because they can entirely prevent the direct contact of the metal and the corrosive media [14]. Shan et al. reported the coating of $TiO_2$ by using the ALD technique on stainless steel to show its lower corrosion rate [15]. Gao et al. investigated the anticorrosion effect of coating of various metal oxides such as $Al_2O_3$, $ZrO_2$, $HfO_2$, and $TiO_2$ deposited by the ALD technique on the surface of silver nanoparticles and found that all of these metal oxide coatings exhibited a significant reduction of corrosion current density by a magnitude of tens of orders in a neutral NaCl solution [16]. Jeong et al. reported atomic layer deposition of $TiO_2$-$Al_2O_3$ core–shell nanoparticles uniformly on silicon wafer used as a substrate (Fig. 1) [17]. This ALD technique can be extended for the study of anticorrosion properties of the metals coated with core–shell nanoparticles.

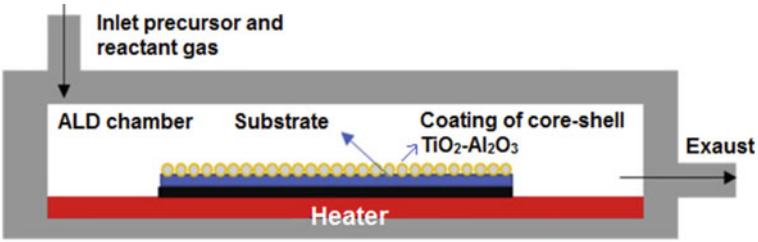


**Fig. 1** Atomic Layer Deposition process (Reproduced with permission from Ref. [17])

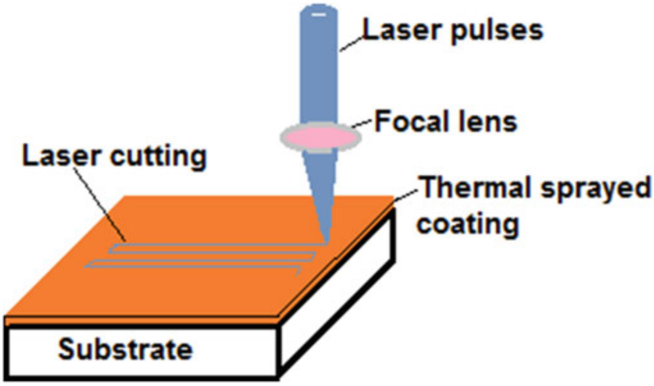


**Fig. 2** Schematic diagram of laser-assisted thermal spray-coating

## *2.2 Laser Thermal Spray-Coating*

The laser-assisted thermal spraying process is a technique of deposition of nanostructure material on the metal substrate by using laser and spray mechanism. Amorphous nanostructure can be coated by using laser thermal spray-coating [18]. Figure 2 shows the schematic diagram of laser-assisted thermal spray-coating. Zhao et al. used laser thermal spray-coating for deposition of AlFeSi coating on steel and studied the effect of laser power on corrosion performance of coating [19].

## *2.3 Sol–Gel Coating*

Sol represents the solute colloidal particles dispersed in liquid and gel represents the network of sol filled with liquid. Nanomaterials of 0D (quantum dots), 1D (quantum wires), and 2D (quantum well) can be easily prepared. Preparation of 2D thin film by sol–gel is used for coating the surface of the metallic substrate. In the case of sol–gel coating, the nanoparticles are prepared by sol–gel technique followed by either

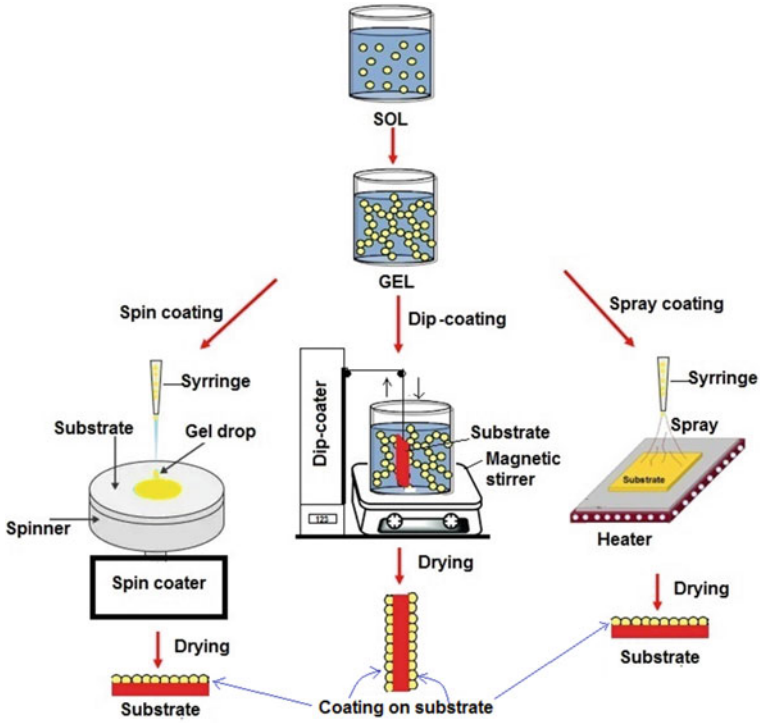


**Fig. 3** Schematic diagram of sol–gel spin-coating, dip-coating, and spray-coating of nanostructure thin film on substrate

spin-coating or dip-coating or spray-coating to deposit the nanostructure material on the substrate as shown in Fig. 3. In the case of sol–gel dip-coating process, the substrate on which the coating is required is dipped in solution and taken out periodically for multilayer coating. In the case of sol–gel spin-coating process, the syringe is used to drop the sol on the surface of the substrate which is kept under spinning and heating for uniform coating on the substrate. In the case of sol–gel spray-coating, the sol is sprayed on the substrate and the subsequent heating by the heater gives the uniform coating of nanostructure thin film on the substrate. Zhang et al. reported the preparation of $TiO_2$-PTFE nanocomposites coating on stainless steel substrate by using a sol–gel dip-coating technique and studied anticorrosion properties [20]. Conceicao et al. showed the corrosion behavior of magnesium alloy (AZ31) sheets coated with PEI by sol–gel spin-coating process and the corrosion protection of the coatings was evaluated by impedance analyses. According to them, all tests were done under $N_2$ atmosphere in NaCl solution, using 15 wt.% solution in N'N'- dimethylacetamide (DMAc), and 2 μm thickness of film has been achieved. It has also been noted that value of impedance also decreases as the time increased during exposure of NaCl solution [21].

Sol–gel process is used for increasing the corrosion resistance of the metal, and it has good surface protection, good chemical stability, and good oxidation control for metal substrates [22]. But the drawback with metal oxide-based coatings is that they are brittle and thicker and often works at high temperature; so to overcome with these limitations, the sol–gel coatings by hybrids are of an interesting area which works at room temperature and have good thermal as well as environmental stability due to synergistic effect of organic and inorganic materials. Copper and bronze are oftenly used metals in kitchen utensils but in the wet environment, they form hydroxides and harmful complexes and accelerate corrosion process [23]. The corrosion inhibition efficiency was found to increase with increasing 3-mercaptopropyltrimethoxysilane (MPTS) concentration which was used as a precursor in the formation of sol–gel coating over aluminum and copper surfaces. In a similar way, nanofibers synthesized by electrospinning technique and calcination procedure dissolved in a solvent can be coated on metal surfaces to protect it from corrosion in the neutral environment at room temperature by sol–gel technique [24]. The particles of hydroxylated nanodiamond (HNDs) contained in the sol–gel coating diminished the corrosion effect on magnesium surface [25]. Because sol–gel itself contains a large number of defects and cracks in the coating but as we inculcate nanoparticle, then it overcomes defects in the material and enhanced corrosion resistance of the synthesized coated film. It has been reported that with the heat treatment, the stabilized polyacrylonitrile (PAN) nanofibers synthesized by sol–gel via electrospinning were uniform and continuous to improve the oxidation resistance of the carbon nanofibers [26].

## *2.4 Laser Ablation Coating*

In the laser ablation process, the material is removed from the surface by irradiation of the laser beam. In this method, the ablation or vaporization of the bulk material by the laser beam of high power in the UV range of wavelength is used to produce the nanoparticles film deposited on the substrate. The temperature of the irradiated spot increases when the laser beam is irradiated on the target which then evaporates the atoms from the target. The interaction of evaporated atoms with the atoms of inert gas creates a plasma plume near to the target. Sufficient pressure of gas carries the vaporized atoms toward the cool substrate for condensation on the surface of the substrate to produce film of nanoparticles. Particle size distribution is determined by gas pressure and laser pulse. Usually, the gas pressure in the range of 0.1 to 1.0 torr is used for narrow particle size distribution. Shortening the laser pulse 20–30 ms gives a smaller particle size. Generally, $CO_2$ laser, Nd-YAG laser, ArF excimer laser, or XeCl excimer laser of shorter wavelength of the UV spectrum of the order of 200 nm are used in the laser ablation process for the preparation of nanoparticles. Figure 4 shows the schematic of laser-assisted ablation coating of nanostructure thin film on the substrate. Claries et al. demonstrated the laser ablation technique for coatings of amorphous calcium phosphate and crystalline hydroxyapatite with different morphologies [27].

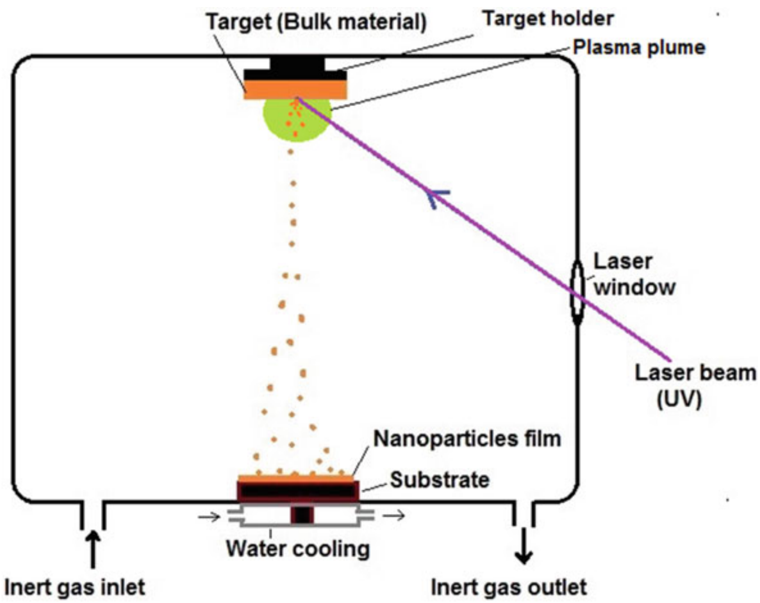


**Fig. 4** Schematic of laser-assisted ablation coating of nanostructure thin film on substrate

## *2.5 Sputter Deposition*

Interaction of an ion with the target causes the formation of plasma which is the mixture of photons, electrons, atoms, ions, and molecules in the space between the target and substrate (two electrodes) with the application of DC or AC. The density of plasma depends on the pressure of the inert gas. More the plasma density, sputtering of atoms will be more and hence more deposition of nanoparticles on the substrate takes place. Electrons are emitted from target due to high potential of DC source applied between target and substrate. These electrons ionize the inert gas which causes the formation of plasma between target and substrate. The ionized gas then strikes on the target to sputter the atoms to be deposited on the substrate. DC sputtering is not suitable for sputtering of insulating or even semiconducting target. In this case, electron oscillates with the radio frequency (13.56 MHz) of RF generator between the target and substrate causing more ionization of inert gas, even the target is an insulator thereby increasing the efficiency of the sputtering of target atoms as compared to that of DC sputtering. Electron is subjected to E and B simultaneously. Electron moves in a helical or spiral path and is able to ionize more atoms of the gas, thereby increasing the efficiency of the sputtering of target atoms for enhancing deposition of nanoparticles on the substrate. Baldwin et al. highlighted the versatility of the magnetron sputtering process to produce novel multilayer pyrotechnic coatings and corrosion-resistant supersaturated Al/Mg alloy coatings [28]. Figure 5 shows the schematic of magnetron sputter deposition. Further, the plasma density can be

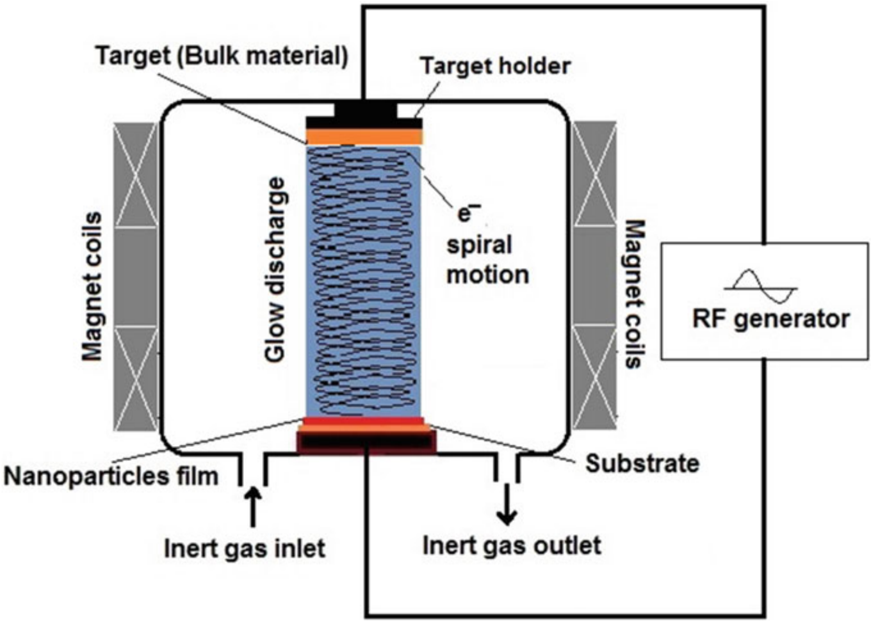


**Fig. 5** Schematic of magnetron sputter deposition

increased by using microwaves of frequency 2.45 GHz in a direction such that the plasma density can be enhanced due to more radius of spiral motion of electron at resonance when microwave frequency coincides with the natural frequency of rotation of electrons in magnetic fields. Therefore, this technique is known to be a microwave ECR (Electron Cyclotron Resonance) excited plasma deposition.

## 2.6 *Physical Vapor Deposition (PVD)*

Physical vapor deposition is a vaporization coating technique that involves the transfer of material at the atomic level. The process can be described by the following steps; (i) the material to be deposited is converted into vapor by physical means (high-temperature tube furnace), (ii) the vapor is carried by the inert gas to a region of low pressure toward substrate, and (iii) the vapor condenses on the cool substrate to form a thin film. PVD processes are used to form multilayer coatings, composition deposits, very thick deposits, and freestanding structures. Physical vapor deposition is used to produce thin, corrosion-resistant coatings. The metallic behavior can be modified by the deposition of PVD layers to improve surface hardness, wear resistance, and corrosion resistance of PVD-coated materials when deposited on magnesium and their alloys; their application has extended to the biomedical field. A typical PVD process is shown in Fig. 6.

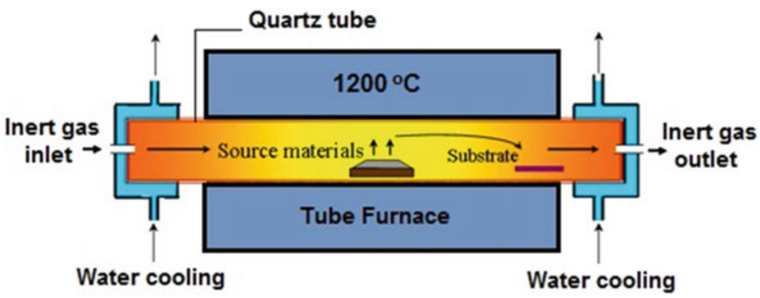


**Fig. 6** Schematic of PVD process for coating nanoparticles on the substrate

## *2.7 Chemical Vapor Deposition (CVD)*

To improve the quality of coating, the aerosol-assisted CVD method can be used to create ordered nanostructured material and deposit a thin layer of hydrophobic compound on the surface [29]. CVD is used to deposit various types of materials that may be nanocomposites onto metallic surfaces. The production of uniform thickness of films with fine coating and complicated shapes can be enabled to protect against oxidation and corrosion due to its excellent throwing power and low porosity. Its uniqueness lies in its ability to control and check the quality of the coating at various stages of processing. The schematic diagram of chemical vapor deposition is shown in Fig. 7. Chemical vapor deposition involves the deposition of solid material at the nanoscale from the gaseous phase. In this method, precursor gases are diluted with a carrier gas (inert gas) and delivered to the reaction chamber (quartz tube) at ambient temperature and they react with processing gas or decompose to form a solid phase to be deposited on the heated substrate place on a quartz boat at the middle of the tube furnace. In CVD, the volatile metal compound from the gas mixture is introduced into the reaction chamber deposits in the form of thin film on the surface of substrate placed at the center in the chamber.

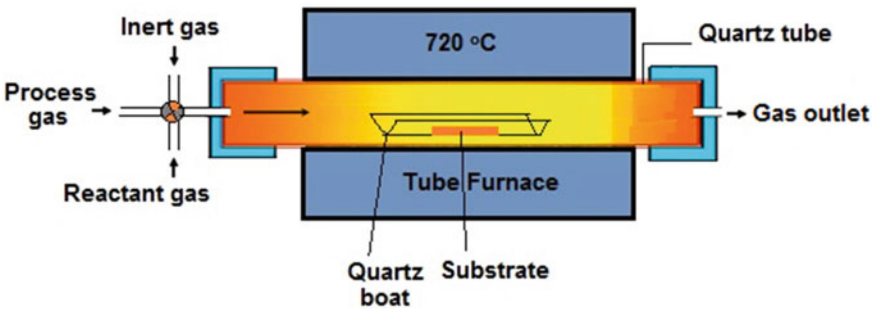


**Fig. 7** Schematic diagram of chemical vapor deposition

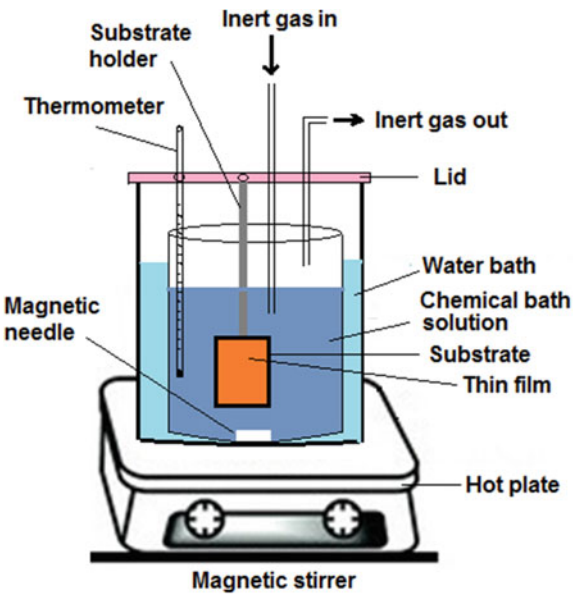


**Fig. 8** Chemical bath deposition (CBD) technique

## 2.8 *Chemical Bath Deposition*

The chemical bath deposition (CBD) technique as shown in Fig. 8 involves the controlled precipitation from theTsolution of a compound on a suitable substrate inserted in a chemical bath solution. The reaction and the deposition occur simultaneously inside the chemical bath. Hence, it is named as CBD. It offers many advantages of preparing semiconducting nanoparticle thin films over CVD and PVD due to control of film thickness and deposition rate by varying pH, temperature, and reagent concentration of the solution.

## 2.9 *Ionized Cluster Beam Deposition*

Nanoparticles thin film can also be deposited on the surface of the substrate using ionized cluster beam deposition. Figure 9 shows the schematic of the deposition of nanoparticles thin film by ionized cluster beam deposition technique. It consists of an evacuated chamber which has the source of evaporation, a crucible with a fine nozzle through which material evaporates, the beam of clusters through which the nozzle gets ionized by electrons, and the accelerated ionized beam of cluster deposited on the substrate to form nanoparticles film.

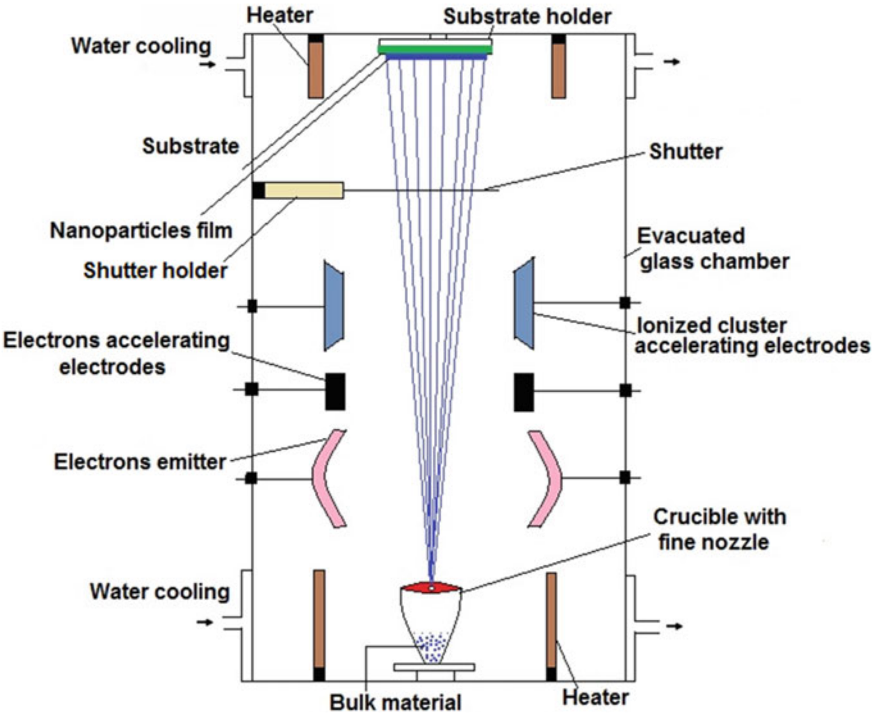


**Fig. 9** Schematic of ionized cluster beam deposition technique

## 3 Electrospun Nanofibers Coating

There are various techniques available for the fabrication of nanofibers, but electrospinning is the simplest and cost-effective technique with facile control of the diameter of fiber [30]. Electrospun nanofibers coating is a versatile technique of nanostructure coating on the metallic substrate. Ultrafine electrospun polymeric or composite nanofibers can be coated on the metal surface by electrospinning technique, which is an efficient technique to synthesize uniform, conductive nanofibers with an average diameter between tens to hundreds of nanometer range by using electrostatic forces [31]. Figure 10 shows the electrospinning setup for aligned and randomized nanofibers coating on metal. The basic principle of this electrospinning technique is “electrostatic interactions”. The peristaltic pump, where a high voltage power supply is connected, pushes the solution from the needle. Single droplet ejected at the tip of needle will be collected in a counter electrode called collector. Electrospinning instrument consists of three major parts; first and foremost influencing part is high voltage power supply, the second one is the syringe and needle assembly (collectively called as spinneret in needleless type), and the last one is the collector. Many types of electrospinning instruments are available in the market nowadays. They differ only in the type of spinneret and collector. Some instruments employ

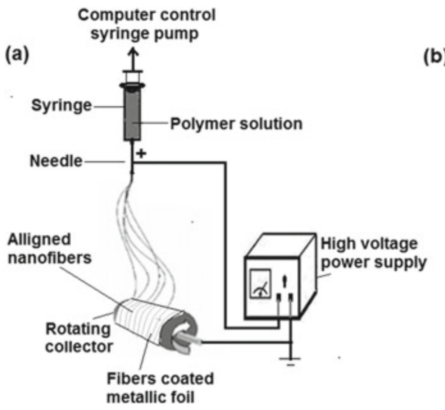


**Fig. 10** Electrospinning setup for **a** aligned nanofibers and **b** randomized nanofibers coating on metallic foil

an electrode material as spinneret while few others contain needleless spinneret. Many parameters influence the electrospinning of fibers. The selection of a suitable polymer for electrospinning depends on the enduse of nanofibers. The molecular weight (M. wt.) of the chosen polymer is an important factor that alters the characteristics of nanofibers. The same polymer of different molecular weights produces fibers of different diameters. The diameter of the nanofibers prepared by electrospinning technique is dependent on the physical (distance, voltage, flow rate, and collector), chemical (concentration, conductivity, molecular weight, viscosity, solvent volatility, and molecular structure), and environmental (humidity and temperature) parameters. It consists of three main parts namely high voltage power supply, syringe pump, and metallic collector. The polymeric solution in the syringe generates an electrically charged jet when flowing through the capillary needle under a high electric field.

Bhute et al. reported the synthesis of polyvinylidene fluoride/cellulose acetate (PVdF/CA) and PVdF/CA-AgTi$O_2$ polymer nanofibers coating on aluminum substrate by electrospinning [32]. SEM images and histograms of electrospun PVdF/CA and PVdF/CA-AgTi$O_2$ polymer nanofibers membranes are shown in Fig. 11. It is concluded from the SEM images histograms that the diameter of the nanofibers coated on the metallic substrate can be easily controlled by changing the electrospinning parameter. The smaller fiber diameter due to the increase in viscosity of the electrospinning solution possess a large surface area beneficial for increasing adsorptive properties toward increasing the corrosion resistance of the metals on which it has been coated.

It has been found that polyamide (PA) coated on the aluminum surface by electrospinning technique is found to be good corrosion resistance [5]. Coating of nanofibers is used for improving the corrosion resistance of the coated metallic surfaces and used in various industries such as coating of pipes and tanks [33]. Metal oxide polymer nanocomposite, PCL/ZnO-NiO-CuO (polycarprolactone/ zinc

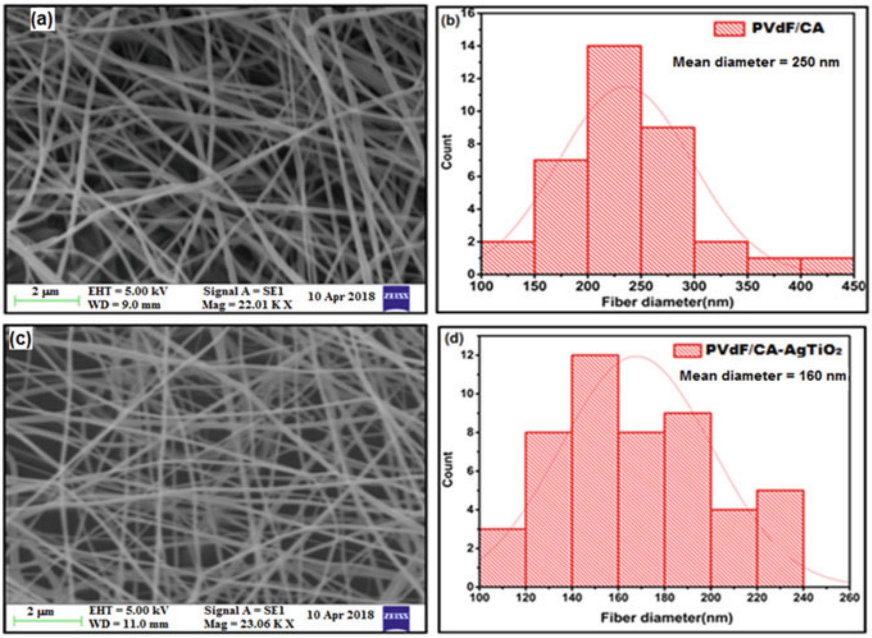


**Fig. 11** SEM images of **a** PVdF/CA, **c** PVdF/CA-Ag$TiO_2$ and histograms of **b** PVdF/CA, **d** PVdF/CA-Ag-$TiO_2$ nanofibers membranes (Reproduced with permission from Ref [32], Bhute MV, Kondawar SB, *Solid State Ionics* 333, 38–44 (2019) Copyright (2019) Elsevier)

oxide–nickel oxide–copper oxide) have been successfully synthesized through electrospinning technique and deposited on mild steel and found excellent corrosion resistance in HCl solution. Nanofibers of other polymers such as PCL, PAN-$Al_2O_3$, and polyaniline/poly(methylmethacrylate) PANI/PMMA could also be deposited by electrospinning technique to increase the corrosion resistance of metal surface [12]. Nanofibers coatings have good electrical and thermal conductivity, good environmental or thermal stability, good surface appearance, good chemical resistance, and better corrosion resistance. Self-healing coatings have been recently proposed. The principle of anticorrosion coatings on the metallic surface is to protect the coated sample from corrosive agents present in the corrosive environment. Coating allowed the flow of corrosive agents to the metal surface, but coating materials must have high electric resistance and high adhesion to the substrate. The nanocomposites coating, epoxy/polyaniline-ZnO nanorods, polyaniline-$TiO_2$ composite, organic–inorganic hybrid coatings, and sandwiched polydopamine for $TiO_2$ create a synergistic effect and have enhanced the corrosion resistance.

## 4 Corrosion

Natural conversion of a refined metal to a more stable in the form of oxide, hydroxide, or sulfide state which causes the metal deterioration is often called as corrosion. Corrosion is an irreversible interfacial reaction of a material with its environment, resulting in the loss of material [34]. Corrosion is the surface wastage that occurs when metals are exposed to reactive environments due to interaction between a metal and environments which results in its gradual destruction. The decay of materials by chemical or biological agents is also done by corrosion. Corrosion is a threat to the environment. For instance, water can become contaminated by corrosion products and unsuitable for consumption. Corrosion prevention is integral to stop contamination of air, water, and soil. The most common type of iron corrosion occurs when it is exposed to oxygen and in the presence of water, which creates a red iron oxide commonly called rust. Rust can also affect iron alloys such as steel. The term corrosion can be applied to all materials, including non-metals. But in practice, the word corrosion is mainly used in conjunction with metallic materials. Mechanical properties of metals reduce due to corrosion and therefore, it is necessary to study the anticorrosion coating and corrosion protection [35]. Based on corrosion mechanism, corrosion of metals can be divided into four categories; chemical, physical, electrochemical, and biological corrosion as shown in Fig. 12.

Due to oxidation–reduction reactions, chemical corrosion takes place when metal meets corrosive media directly. The entire reaction surface is covered by the corrosion product and protective film is formed in the process of chemical corrosion. Physical corrosion changes the shape, size, or phase of a substance due to the metal melting process. The electrochemical reaction between metal and electrolyte solution (mostly aqueous solution) is responsible for electrochemical corrosion. Biological

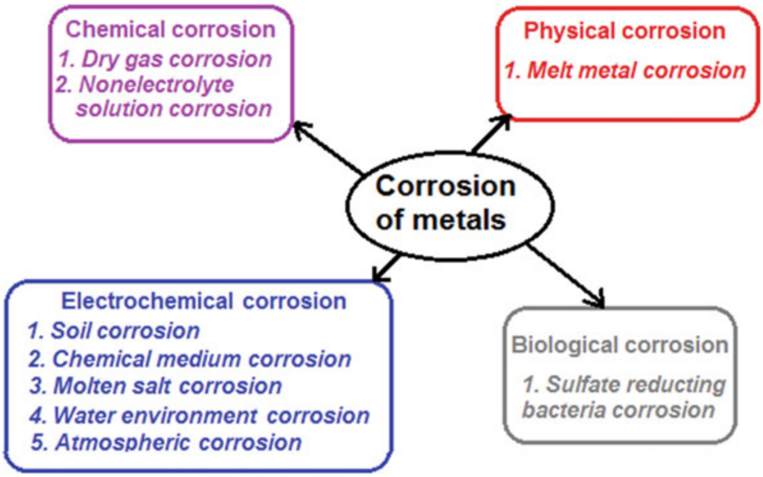


**Fig. 12** Categories of metal corrosion based on corrosion mechanism

corrosion is the corrosion affected by the presence or activity of microorganisms such as bacteria on the surface of the metal.

## 4.1 Corrosion Resistance

Corrosion resistance is the ability to prevent environmental deterioration by chemical or electrochemical reactions. Desirable characteristics of corrosion-resistant alloys, therefore, include high resistance to overall reactions within the specific environment. As far as corrosion resistance of stainless steel is concerned, it is highly resistive for corrosion in many environments. On the other hand, carbon and low alloy tool steels will corrode in the same environment. The very thin oxide layer of the order of nanometer on stainless steel plays the role of its corrosion resistance. In the corrosive environment, the oxide layer act as a passive layer which forms because of the chromium added to stainless steel. For better corrosion resistance, there should be more than 10.5% chromium added to have a more stable passive layer in stainless steel. To further enhance the corrosion resistance of the stainless steel, the elements such as nickel, molybdenum, manganese, etc. can be added. Similarly, if the passive layer of the stainless steel is exposed to oxygen, corrosion resistance can be maintained. By boldly exposing the steel surface, the corrosion resistance will be greatest. During well exposing the surface of stainless steel, the passive layer on the surface at some localized spots may be broken under certain circumstances. The corrosion under this condition at localized spots is said to be pitting corrosion. Under some aqueous environments containing chloride, pitting corrosion is common for this situation. There are various examples of pitting-type corrosion which includes coastal atmospheres and road salt combined with rainwater or tap water which contains chloride mostly. Stainless steels are very popular for various applications but the elements it contains mostly chromium and nickel in high concentration may be very harmful to human beings as concerned health due to their carcinogenic and toxic effects [36].

## 4.2 Corrosion Measurement

By using electrochemical impedance spectroscopy (EIS), the important electrochemical parameters such as coating capacitance (*Q*c), coating resistance (*R*c), double-layer capacitance, and charge transfer resistance are considered for the evaluation of corrosion resistance of organic coatings. For the evaluation of these parameters for the coating, an electrochemical cell consisting of three electrodes namely platinum wire as a counter electrode, Ag/AgCl as a reference electrode, and a working electrode made of coating is used in an instrument called as potentiostat. [7]. The impedance of the coated materials can be determined using this technique in which the response of the coated material can be detected in terms of a small amplitude *ac* perturbation as a function of frequency. A physical method is required to interpret the impedance–frequency response for metal–coating–electrolyte interface by an electrical equivalent circuit which provides a clear description of the different contributions to the impedance. Reproducibility of the measurement of the impedance of coating in this technique is an issue to obtain the results with high accuracy for which statistical methods to interpret the data can be used.

The type of methods for expressing the degree of metal corrosion depends on corrosion types. Generally, for general corrosion, it can be expressed by the average corrosion rate. The corrosion rate can be calculated by expressing the average corrosion rate in general for any type of corrosion using Eq. (1) [5].

$$\text{Corrosion rate} = \frac{I_{corr}\,K\,E_w}{D\,a} \quad (1)$$

where $I_{corr}$ is the current of corrosion, K is a constant according to units of corrosion rate, $E_w$ is the equivalent weight, D = density, and a is the area of the sample.

There are several ways to prevent and control corrosion which are summarized in Fig. 13.

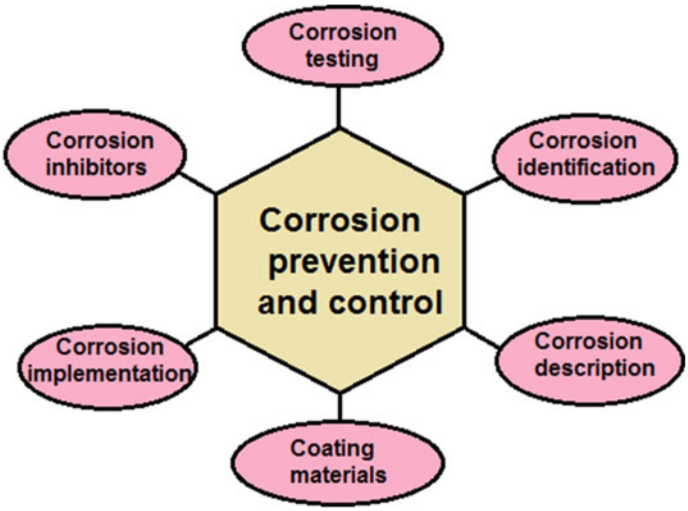


**Fig. 13** Schematic of the ways for corrosion prevention and control

### *4.3 Corrosion Inhibitor*

The best way of corrosion protective coatings is the self-healing of the damage caused by corrosion. As a coating suffers mechanical damage, which is automatically repaired by a chemical component that acts as a corrosion inhibitor in the coating. Corrosion inhibitor is a chemical mixed with an environment that contains liquid or gas which decreases the corrosion rate of the metal when it is exposed to that environment. To prevent or control corrosion, the effective way is the corrosion inhibitor as it allows one to use less expensive metals for a corrosive environment. Though there are several corrosion inhibitors, but the process of selecting a particular corrosion inhibitor is quite difficult when it is the first time selected for the material to prevent its corrosion as the effectiveness of a corrosion inhibitor depends on the fluid composition. Formation of coating is a common mechanism for inhibiting corrosion which prevents the access of the corrosive substance to the metal [37–39].

The corrosion rate can be slowed down in the presence of an inhibitor. The inhibition efficiency can be determined by finding the difference between the rate of corrosion in the absence and presence of the inhibitor to reduce the rate of corrosion expressed by Eq. (2);

$$R_i = \frac{\vartheta_0 - \vartheta}{\vartheta_0} \tag{2}$$

where $\vartheta_0$ and $\vartheta$ are the corrosion rate measured in the absence of inhibiter and in the presence of inhibitor, respectively. The inhibition efficiency mostly depend on an important parameter inhibitor concentration. In many ways, the inhibitors can be applied to prevent corrosion. The most common corrosion inhibitors are acid pickling baths which are used to chemically deposit the iron oxide scale on steel which adsorb onto the metal surface thereby blocking the electrochemical attack of the steel. The effect of the inhibitor on the corrosion process can be understood and classified by comparing polarization curves in environments with and without the inhibitor added. Figure 14 shows the schematic examples of the types of inhibition and their effects on the polarization curves. Inhibitors can be classified as an anodic, cathodic, or mixed inhibitor as shown in this figure. An anodic inhibitor reduces the rate of the anodic reaction with less effect on the cathodic reaction. A cathodic inhibitor reduces the rate of the cathodic reaction with less effect on the anodic reaction. A mixed inhibitor reduces both the rates of cathodic and anodic reactions equally. The corrosion potential (Ecorr) is different in a solution containing an inhibitor compared to that solution which does not have an inhibitor. Ecorr will be more for an anodic inhibitor, less for a cathodic inhibitor, but there is no change for a mixed inhibitor. The change in Ecorr is used as an diagnostic for the type of inhibitor as long as the corrosion rate is reduced from the metal.

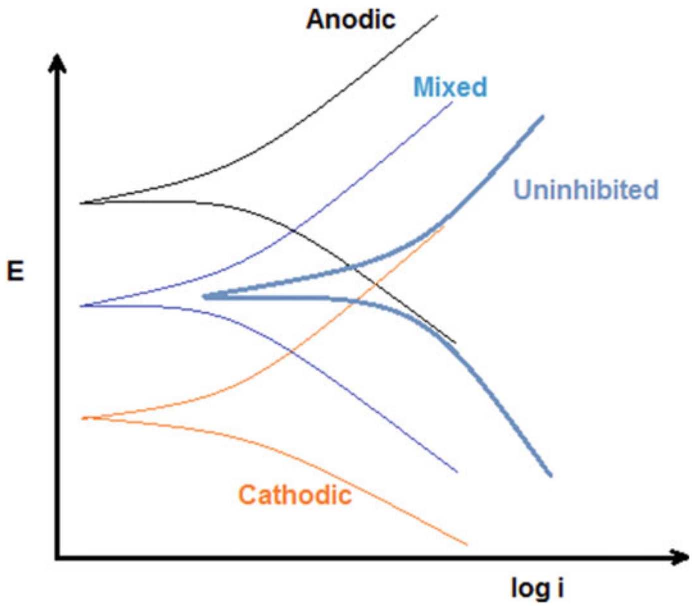


**Fig. 14** Effect of anodic, cathodic, and mixed type of inhibition on the polarization curves

## 5 Electrospun Nanofibers Coating for Corrosion Protection

A new and innovative way of fighting against corrosion is electrospun nanofibers-based coatings. Electrospinning is a versatile and flexible low-cost process for producing nanostructure ultra-thin fibers from a wide range of materials (polymers, composites, and ceramic) onto any type of surface with arbitrary geometries. Recently, with the advent of nanotechnology, the fabrication of nanofibers has been progressed with excellent control of their morphology for the applications toward the control of the rate of corrosion. The corrosion rate of metal (steel, aluminum, and magnesium alloys) can be reduced by the effective barrier coating produced by these electrospun nanofibers which have a large surface area, good mechanical strength, and high elasticity can improve the mechanical properties of the coating. As compared to polymeric coating, the electrospun composite coating layers on magnesium alloy via electrospinning have proved to enhance the corrosion resistance. Electrochemical evaluation and salt-spray test are the tests that can be conducted to evaluate the corrosion resistance of different samples [3, 40]. Pure PANI and PANI/PMMA nanofibers synthesized by the electrospinning technique displayed superior anticorrosion properties. Polyaniline (PANI) is one of the most interesting conducting polymers due to the ease of chemistry, redox behavior, and excellent anticorrosion properties. The mechanism behind this is the enhanced anticorrosion behavior of PANI as it has the ability to form a protective layer due to its redox catalytic properties and to reduce the amount of $H^+$ at the metal/PANI interface and due to their doping–dedoping structural morphology [11].

The degradation of Mg alloy covered with poly(lactic acid) was studied to find the influence of electrospinning and dip-coating approaches for enhancement of the corrosion resistance. The electrospinning technique to fabricate nanofibrous materials further found to be beneficial in improvement for prolonged immersion periods [41]. Es-saheb et al. investigated the fabrication of nanofiber coating of polyvinyl alcohol (PVA) and polyvinyl chloride (PVC) on the pure aluminum surface using the electrospinning deposition technique. They have prepared NaCl solution and studied the effect of coating of PVA and PVC nanofibers on the corrosion resistance of aluminum in this solution. The surface analysis of the fabricated nanofibers was studied by using scanning electron microscopy. The corrosion test was studied using cyclic potentiodynamic polarization by electrochemical impedance spectroscopy measurements. Actually, chloride solution corrodes the aluminum when it is placed in NaCl solution, but the results obtained from corrosion tests confirmed that the presence of PVA and PVC nanofibers coatings on top of aluminum surface acted as corrosion resistance and hence it was greatly precluded this corrosion. It was also confirmed from this test that the polarization resistance of aluminum in NaCl solution was found to be increased due to PVA and PVC coating which decreases the rate of corrosion drastically. This study concluded that PVA and PVC nanofibers coatings can protect the aluminum surface against corrosion [42]. Muthirulan et al. reported the preparation of poly-o-phenylenediamine (PoPD) nanofibers by the electrospinning technique and studied corrosion protection properties of synthesized nanofibers-coated stainless steel in NaCl solution. The comparison of uncoated stainless steel and coated stainless steel was studied for the detection of corrosion resistance and found the strong adherent and inhibition effect of PoPD nanofiber film-coated stainless steel substrate which exhibited good corrosion resistance. Thus, for chloride-containing solution, PoPD nanofiber coatings by electrospinning were found to be a potential coating material for stainless steel against corrosion [43]. Figure 15 shows the potentiodynamic polarization curves for uncoated and PoPD nanofiber-coated 316L SS steel in 3.5% NaCl solution. The corrosion potential (Ecorr) and current density (Icorr) were found to be higher for PoPD nanofiber-coated 316L SS compared to uncoated 316L SS. From the potentiodynamic polarization curves, it was observed that the value of Ecorr shifted toward a more positive value when the steel surface was coated by the PoPD nanofiber film. This confirmed that the best protection against corrosion was provided by the coating of PoPD nanofiber on the surface of stainless steel. The protective layer on the stainless steel by PoPD nanofiber coating may be to the presence of p electrons in the aromatic ring and the lone pair of electrons in the nitrogen atom responsible for the surface modification of stainless steel against corrosion.

Grignard et al. reported the fabrication of poly-(heptadecafluorodecylacrylate-co-acrylic acid)-bpoly(acrylonitrile) nanofibers coated on the aluminum surface by using electrospinning technique for the study of superhydrophobicity and corrosion resistance [44]. Firouzi et al. reported the fabrication of polyvinyl alcohol (PVA) nanofibers coating on aluminum alloy by using electrospinning technique and studied

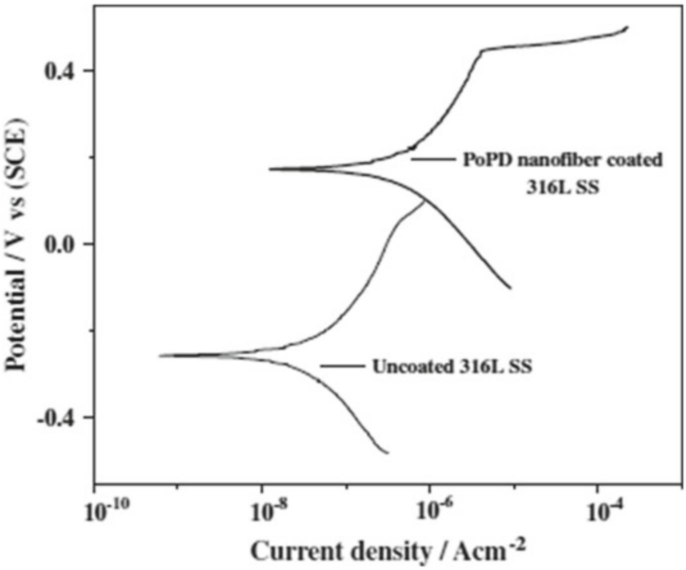


**Fig. 15** Potentiodynamic polarization curves for uncoated and PoPD nanofiber-coated 316L SS steel in 3.5% NaCl solution (Reproduced with permission from Ref [43], Muthirulan P, Kannan N, Meenakshisundaram M, *J. Adv. Res.* 4, 385–392 (2013), Copyright (2013) Elsevier)

the anticorrosion performance of NaCl solution by using electrochemical impedance spectroscopy (EIS) [7]. Electrochemical tests revealed that the corrosion resistance of electrospun PVA nanofibers-coated aluminum in NaCl solution was found to be 26 kΩ after 20 h as compared to the corrosion resistance of uncoated aluminum in the same solution (3.8 kΩ).

Aldabbagh et al. prepared polyamide (PA-6) nanofiber coatings on aluminum surface using the electrospinning technique under two different voltages (24 kV and 34 kV). They studied the coating morphology roughness, 3D structural properties, and hydrophobic behavior. The electrochemical corrosion of aluminum without and with PA-6 nanofibers coating in NaCl solution was investigated. It was found that the PA coating decreased the corrosion current and corrosion rate as well as increased the corrosion resistance for aluminum in the NaCl solution. PA-6 electrospun nanofibers are very efficient for protecting the metal surface from corrosion, also the high voltage prepared electrospun nanofibers to lead to an increase in the corrosion resistance of the metal surface [5]. Castro et al. reported the fabrication of electrospun PHBV nanofibers-coated magnesium alloy by using electrospinning technique and studied for biodegradable implant applications. Their study concluded that the electrospun-coated PHBV nanofibers-coated magnesium alloy showed better corrosion resistance than uncoated magnesium alloy and also verified that the porous structure of PHBV nanofibers was obtained by electrospinning technique provided extracellular matrix which promoted cell growth for tissue healing [45]. Nafi et al. prepared electrospun PLLA nanofibers coating on pure magnesium and magnesium alloy (AZ91) using electrospinning technique and studied the corrosion behavior in Hanks' solution. The results confirmed the reduction in the corrosion rate of the materials coated with PLLA nanofibers [46]. The preparation of PCL nanofibers coated on $HNO_3$ treated magnesium alloy (AZ31) by electrospinning is reported by Hanas et al. Previously treated with $HNO_3$ magnesium alloy (AZ31) has provided a good adhesion between the coating of electrospun PCL nanofibers and the metallic substrate. The results obtained from corrosion tests confirmed that the bioactivity of electrospun PCL nanofibers coating is enhanced due to $HNO_3$ pre-treatment which was further found to be very effective in controlling the degradation rate [47]. In another study, they have demonstrated that the coating of electrospun PCL nanofibers on AZ31 magnesium alloy was protected from chloride ion attack and avoided the formation of pitting corrosion when the materials were exposed to supersaturated simulated body fluid [48].

Polymers possess very high molecular weight and therefore they are used to prepare nanofibers using electrospinning. Electrospun nanofibers of polymers including conducting polymers, hydrophobic polymers, and superhydrophobic polymers are found to be good corrosion resistant when coated on metallic surfaces. Zhao et al. reported the fabrication of blended electrospun polyaniline (PANI) microfibers with poly(methyl methacrylate) (PMMA)-coated carbon steel and studied for corrosion behavior in 0.1 M $H_2SO_4$ solution. They have well compared the corrosion protection efficiency of blended electrospun polyaniline (PANI) microfibers with poly(methyl methacrylate) (PMMA)-coated carbon steel with that of traditional drop-casting PANI/PMMA coating on carbon steel and confirmed that nearly 500 times higher corrosion protection efficiency for blended electrospun nanofibers coating. The efficiency of the corrosion protection for blended electrospun nanofibers coating was found to be 99.96 even after 20 days of immersion in the acidic solution. The increased anticorrosion behavior of blended electrospun nanofibers coating is due to cathodic protection by releasing $H_2$ gas occupying holes of the PANI/PMMA coating because of blocking $H^+$ diffusion on the surface of carbon steel. Trapping of $H_2$ in the holes of PANI/PMMA coating limits the diffusion of the anodic reaction produced by $Fe^{2+}$ ions which also retard the anodic reaction [11]. Tafel polarization curves for carbon steel, PANI/PMMA-coated carbon steel, and blended electrospun PANI/ PMMA microfibers with 25 wt% PANI-coated carbon steel in 0.1 M $H_2SO_4$ aqueous solution are shown in Fig. 16. Due to extraordinary compact microstructure of blended electrospun PANI/ PMMA microfibers coatings with 25 wt% PANI, the superior corrosion protection property was observed. This is also responsible for effective anticorrosion protection.

The intrinsically ultrahigh hydrophobic or superhydrophobic polymers used to fabricate nanofibers by electrospinning provide long-term anticorrosive protection to the metallic surfaces. Polyvinylidenefluoride (PVDF) has high hydrophobicity with excellent antioxidation and anticorrosion properties and therefore, it is favorable to have electrospun for coating over the metallic surfaces [49]. Cui et al. could fabricate electrospun blended polyvinylidenefluoride (PVDF)/stearic acid (SA) nanofibers coated on aluminum (Al) and studied its long-term anticorrosion property. Even after 30 days, they found that PVDF/SA nanofibers-coated aluminum exhibited lower

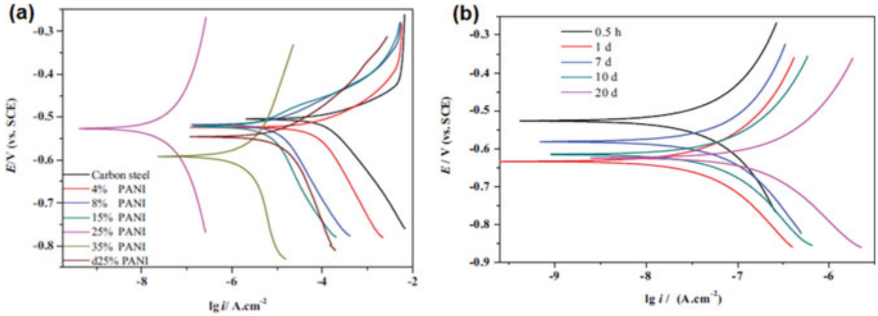


**Fig. 16** Tafel polarization curves **a** for carbon steel, coated carbon steel with PANI/PMMA coatings in 0.1 M $H_2SO_4$ aqueous solution and **b** for coated carbon steel with electrospun PANI/ PMMA coating at 25 wt% PANI after different days of immersion (Reproduced with permission from Ref [11], Zhao Y, Zhang Z, Yu L, Tang Q, *Synth. Met.* 212, 84–90 (2016) Copyright (2016) Elsevier)

corrosion current density in comparison with PVDF nanofibers-coated aluminum in NaCl solution. From the Tafel polarization curves as shown in Fig. 17 for bare Al sheet after immersion in NaCl aqueous solution for 2 h, pure PVDF nanofibers-coated Al sheet after immersion in NaCl aqueous solution for 6 h, and PVDF/SA nanofibers-coated Al sheet after immersion in NaCl aqueous solution for 6 h as well as 30 days, it is concluded that a superior anticorrosion performance for long-term anticorrosion of aluminum sheet was obtained from PVDF/SA nanofibers coating [50].

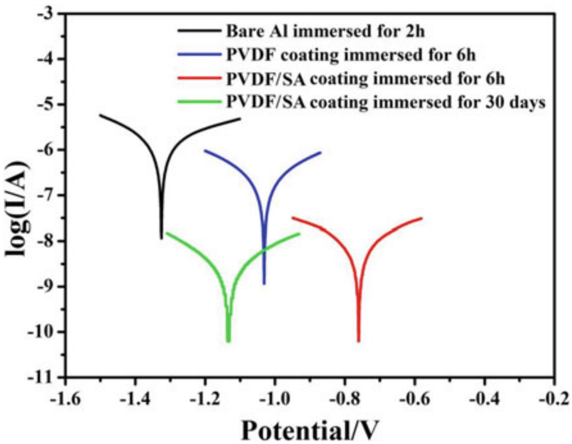


**Fig. 17** Tafel polarization curves of a bare Al sheet after immersion in NaCl aqueous solution for 2 h, pure PVDF nanofibers-coated Al sheet after immersion in NaCl aqueous solutions for 6 h, and PVDF/SA nanofibers-coated Al sheet after immersion in NaCl aqueous solutions for 6 h and 30 days (Reproduced with permission from Ref [50], Cui M, Xu C, Shen Y, Tian H, Feng H, Li J, *Thin Solid Film.* 657, 88–94 (2018) Copyright (2018) Elsevier)

Polyvinyl chloride (PVC) or polystyrene (PS) nanofiber coatings fabricated by electrospinning with superhydrophobic behavior on brass surfaces confirmed good anticorrosion property. The coating of electrospun polymer nanofibers made of PVC is found to be a corrosion inhibitor when they are deposited on metallic substrates such as aluminum, steel, and brass surfaces [51, 52]. Yabuki et al. reported pH-controlled self-healing polymer coatings with cellulose nanofibers as corrosion inhibitor to protect corrosion of carbon steel by varying the pH values of the polymer coatings to control the adsorption and desorption of the corrosion inhibitor from the cellulose nanofibers. By scratching the coatings, the polarization resistance was measured in a sodium chloride solution for evaluation of the self-healing ability of polymer coatings with cellulose nanofibers. The resistance of the scratched coatings was largely dependent on the pH of the polymer. A drastic increase in polarization resistance was observed when the scratched polymer coating was prepared at pH 11.4 after 24 h corrosion test. The polarization curves of the scratched polymer coating were measured in sodium chloride solution using the same system as that used for the measurement of electrochemical impedance [53]. Doan et al. reported the fabrication of electrospun core–shell nanofibers as a self-healing coating material for the protection of steel against corrosion. They have prepared two types of core–shell nanofibers. In A type core–shell nanofibers, the corrosion healing agent core contains a stoichiometric mixture of poly(dimethylsiloxane) and crosslinker poly(diethoxysiloxane) (PDES) with PVA as shell, while in B type core–shell nanofibers, the corrosion healing agent core contains the crosslinking catalyst dibutyltindilaurate (DBTL) with the same PVA as shell. The schematic of fabrication of core–shell electrospun nanofibers of PVA as shell and healing agent as core along with SEM images is shown in Fig. 18.

The technique of coating of core–shell nanofibers on steel is shown in Fig. 19. The technique of coating consisting of core–shell nanofibers was prepared on clean sandblasted steel by electrospinning and then silicone binder was deposited to affix fibers on steel followed by scribing the coating with a corrocutter and allowing the coating to heal for 24 h. The linear polarization experiment was performed to find the effectiveness of the healed coating toward preventing corrosion by observing the corrosion current increased with applied potential. The corrosion inhibition efficiency of the healed coating was found to be 88% indicating the effective healing behavior against corrosion [54].

## 6 Conclusion

With the advent of nanotechnology, the nanostructure coating on metallic and alloy materials significantly improved the corrosion resistance. The control of the coating structure at the nanoscale level allows improving the intrinsic properties of the surface compared to bulk materials. A nanostructure deposition technique with increasing popularity in the field of nanotechnology is electrospinning. Electrospinning is a popular and cost-effective technique used for the deposition of synthesized polymeric

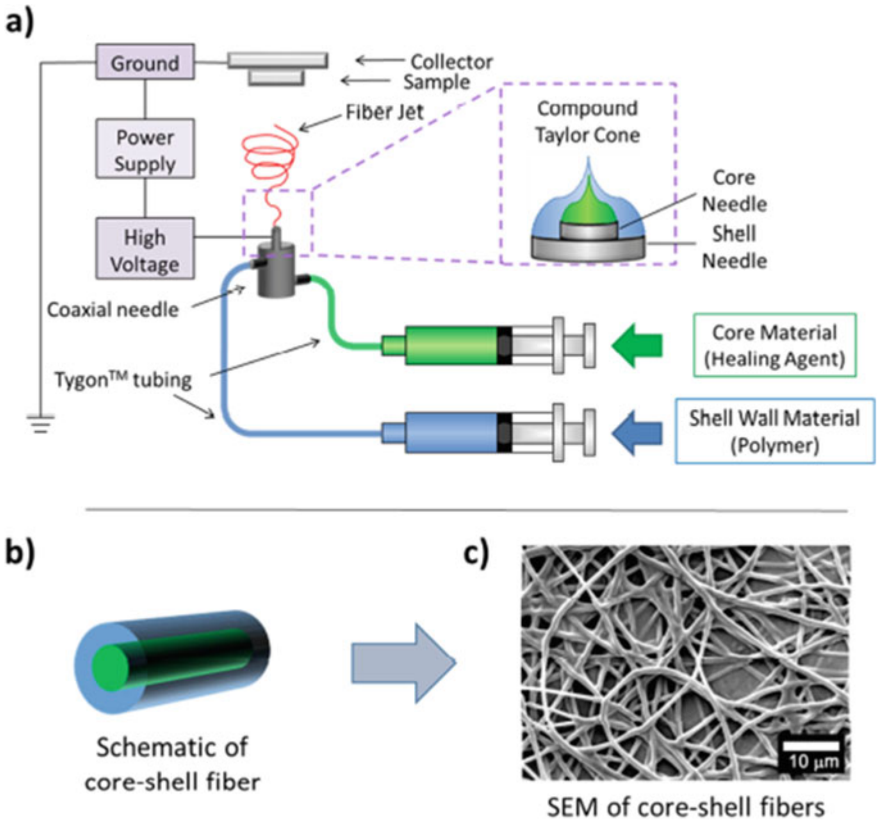


**Fig. 18** Schematic of fabrication of core–shell electrospun nanofibers: **a** schematic of coaxial electrospinning setup, **b** schematic of core–shell fibers of PVA (shell) and healing agent (core), and **c** SEM image of randomly deposited core–shell fibers (Reproduced with permission from Ref [54], Doan TQ, Leslie LS, Kim SY, Bhargava R, White SR, Sottos NR, *Polymer* 107, 263–272 (2016), Copyright (2016) Elsevier)

nanofibers onto metallic surfaces. The deposited electrospun nanofibers reduce the corrosion rate of the metal by acting as an effective barrier coating. Corrosion protection of metallic surfaces can be well controlled by depositing electrospun nanofibers. The deposited electrospun nanofibers reduce the corrosion rate of the metal by acting as an effective barrier coating. Some of the coating or deposition techniques which shield metallic surfaces against corrosion are electrospinning, atomic layer deposition, sol–gel coating, sputters coating, laser-assisted ablation coating, chemical vapor deposition (CVD), and physical vapor deposition (PVD). Electrospun polymeric nanofibers coating have demonstrated the potential deposition technique useful for superior anticorrosion performances for long term metal substrate preservation.

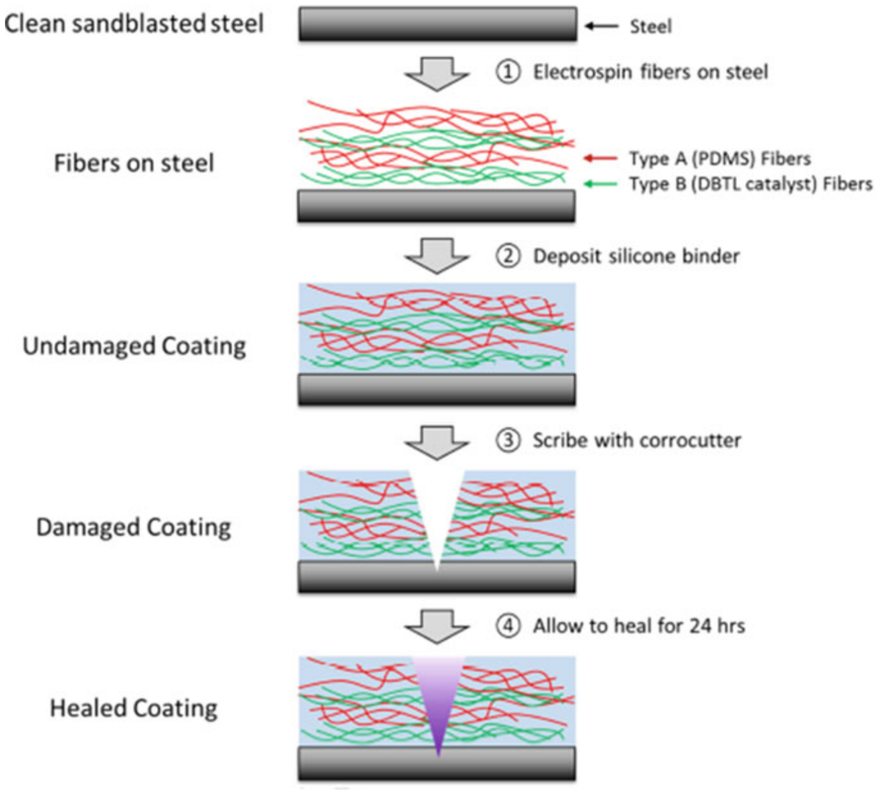


**Fig. 19** Schematic of coating fabrication process (Reproduced with permission from Ref [54], Doan TQ, Leslie LS, Kim SY, Bhargava R, White SR, Sottos NR, *Polymer* 107, 263–272 (2016), Copyright (2016) Elsevier)

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