DEVELOPMENT OF POLYMER NANOCOMPOSITE-BASED COATING FOR CORROSION PROTECTION

CHEN TZE XIANG

UNIVERSITI SAINS MALAYSIA

2022

SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING

UNIVERSITI SAINS MALAYSIA

DEVELOPMENT OF POLYMER NANOCOMPOSITE-BASED COATING FOR CORROSION PROTECTION

By

CHEN TZE XIANG

Supervisor: Prof. Madya. Ts. Ir. Dr Anasyida Abu Seman @ Hj Ahmad

Dissertation submitted in partial fulfilment of the requirements for the degree of

Bachelor of Engineering with Honours

(Materials Engineering)

Universiti Sains Malaysia

September 2022

DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled 'Development of Polymer Nanocomposite-Based Coating for Corrosion Protection'. I also declare that it has not been previously submitted for the award of any degree and diploma or other similar title of this for any other examining body or University.

Name of Student: Chen Tze Xiang Signature:

Date: 25 July 2022

Witness by

Supervisor: Prof. Madya. Ts. Ir. Dr Anasyida Abu Seman @ Hj Ahmad Signature:

Prof. Madya Ir. Ts. Dr. Anasyida Abu Seman @ Hj Ahmad
Pensyarah
Pusat Pengajian Kejuruteraan Bahan & Sumber Mineral
Kampus Kejuruteraan , Universiti Sains Malaysia,
14300 Nibong Tebal, Pulau Pinang.
Tel : 04-5995216 Fax : 04-5996907
Email : anasyida@usm.my

Date: 25 July 2022

ACKNOWLEDGEMENT

I would firstly like to express my sincere appreciation to my research supervisor, Prof. Madya Ir. Ts. Dr. Anasyida Bt. Abu Seman for the academic guidance and constant encouragement throughout the project. I also want to thank her for sharing her knowledge and experiences through presentations and advice. Furthermore, I want to express my deep gratitude to Ms. Siti Aminah Zakaria. She has led me in the handling of experimental and material for this work. Besides, I am appreciated for her willingness to freely share the knowledges and suggestions. Other than that, special thanks to all the technicians and supporting staffs especially Encik Mohd Azam Rejab, Encik Muhammad Azrul Zainol Abidin, Encik Muhammad Khairi Khalid, Encik Abdul Rashid Selamat, Encik Meor Mohamad Noh and Encik Mohd Farid Abd Rahim from School of Materials and Mineral Resources Engineering for their kind assistance and cooperation provided in completing my final year project. Finally, I would like to express my deepest respect to my family and friends for their endless support, understanding, and encouragement to complete this thesis.

TABLE OF CONTENTS

DECLARATION .... **i**

ACKNOWLEDGEMENT .... **ii**

TABLE OF CONTENTS .... **iii**

LIST OF TABLES .... **vi**

LIST OF FIGURES .... **vii**

LIST OF SYMBOLS .... **x**

LIST OF ABBREVIATIONS .... **xi**

ABSTRAK .... **xii**

ABSTRACT .... **xiii**

CHAPTER 1 INTRODUCTION **1**

1.1 Background 1

1.2 Problem Statement 7

1.3 Objectives 8

1.4 Thesis Outline 8

CHAPTER 2 LITERATURE REVIEW **9**

2.1 Introduction 9

2.2 Mild Steel 10

2.3 Superhydrophobic Surface 11

2.4 Wettability 14

2.5 Fabrication Method for Superhydrophobic Coating 18

2.6 Types of Nanoparticles Used in Polymer Coating 19

2.6.1 Silica Nanoparticles 20

2.6.2 Tungsten Oxide Nanoparticles 24

2.6.3 Octadecylamine 27

2.6.4 Zinc Oxide 28

2.6.5 Titanium Dioxide 30

2.7 Corrosion Resistance of Polymer Coating 32

2.7.1 Electrochemical Impedance Spectroscopy (EIS) 33

2.7.2 Tafel Analysis 36

2.7.3 Linear Sweep Voltammetry (LSV) 38

CHAPTER 3 METHODOLOGY 40

3.1 Introduction 40

3.2 Raw Materials 40

3.2.1 Mild Steel Substrate 40

3.2.2 Octadecylamine (ODA) 41

3.2.3 Silica Nanoparticles (SiO_2) 41

3.2.4 Tungsten Oxide Nanoparticles (WO_3) 42

3.2.5 Dimethyldichlorosilane (DMCS) 42

3.2.6 (3-glycidyloxypropyl)trimethoxysilane (3-GPTMS) 43

3.3 Coating Process 44

3.3.1 Substrate Preparation 46

3.3.2 Treatment Process for Silica Nanoparticles 46

3.3.3 Treatment Process for Tungsten Oxide Nanoparticles 48

3.3.4 Suspension Preparation 49

3.3.4(a) Suspension with Octadecylamine (ODA) 50

3.3.4(b) Suspension with Octadecylamine and Silica Nanoparticles 50

3.3.4(c) Suspension with Octadecylamine, Silica and Tungsten oxide Nanoparticles 50

3.3.5 Coating and Curing Process 50

3.4 Characterization 51

3.4.1 Fourier-Transform Infrared Spectroscopy (FTIR) 51

3.4.2 Contact Angle Measurement (CA) 52

3.4.3 Atomic Force Microscopy (AFM) 54
3.4.4 Scanning Electron Microscopy (SEM).. 55
3.4.5 Linear Polarization Corrosion Test 57
CHAPTER 4 RESULTS AND DISCUSSION.. 60
4.1 Introduction 60
4.2 Materials Characterization of Modified Nanopowder 60
4.2.1 Silica Nanoparticles.. 61
4.2.2 Tungsten Oxide Nanoparticles... 61
4.3 Investigation on Surface Energy of Coating with Epoxy and ODA............. 62
4.3.1 Contact Angle Measurement (CA).. 62
4.3.2 Atomic Force Spectroscopy (AFM) 64
4.4 Addition of Nanoparticles for Hydrophobic Surface................................... 66
4.4.1 Contact Angle Measurement (CA).. 66
4.4.2 Scanning Electron Microscopy (SEM).. 68
4.4.3 Linear Polarization Analysis... 70
CHAPTER 5 CONCLUSION AND FUTURE RECOMMENDATIONS...... 72
5.1 Conclusion... 72
5.2 Recommendations for Future Research 73
REFERENCES... 74

LIST OF TABLES

Page

Table 3.1 Weight of epoxy and nanoparticles used for coating 49

Table 4.1 Water contact angle and surface energy of coated sample with ODA63

Table 4.2 Surface roughness average calculated from AFM analysis...............64

Table 4.3 Water contact angle and surface energy of coated sample with ODA, treated SiO_2 and WO_3 nanoparticles 67

Table 4.4 Corrosion potential (E_{corr}), current density (i_{corr}) and corrosion rate of sample AO20S6, AO20S6W1, AO20S6W2, and AO20S6W3.........71

LIST OF FIGURES

Page

Figure 1.1 Coloured scanning electron microscopy (SEM) image of lotus leaf surface (*Lotus leaf surface, SEM - Stock Image - C006/6469 - Science Photo Library*, 2022) 3

Figure 1.2 Timeline of key developments of models on wettability (Parvate, Dixit & Chattopadhyay, 2020) 4

Figure 1.3 Numbers of papers published (A) and numbers of times cited (B) from 2009 to 2018 under the topics of self-cleaning (Dalawai *et al.*, 2020) 4

Figure 2.1 Microstructures of plain low carbon steel (Phoumiphon, Othman & Ismail, 2016). 10

Figure 2.2 (a) Schematic diagram of contact angle. (b) Schematic diagram of Young model. (c) Schematic diagram of Wenzel model. (d) Schematic diagram of Cassie-Baxter model. (e) The driving force of chemical gradients. (f) The driving force generated by the structural gradient. (Yang *et al.*, 2022) 12

Figure 2.3 The states of droplets on texture surface (Zhang & Lv, 2015) 13

Figure 2.4 Contact angle on different types of surfaces 14

Figure 2.5 Schematic represent hydrophilic, hydrophobic and superhydrophobic surfaces (Das *et al.*, 2018). 15

Figure 2.6 Wettability on (a) hydrophilic surface and (b) hydrophobic surface (Kwok, 2020) 16

Figure 2.7 Fabrication methods to prepare superhydrophobic coating (Meena *et al.*, 2020) 18

Figure 2.8 Schematic illustration of KH560 functionalization of silica nanoparticles (Zhi *et al.*, 2019) 21

Figure 2.9 Silica-coating strategies (Liu & Han, 2010) 23

Figure 2.10 SEM image of tungsten oxide nanoparticles 25

Figure 2.11 EDAX spectrum of pure WO_3. 25

Figure 2.12 Variation of contact angle on zinc-plated steel with a superhydrophobic coating in the course of tests in 0.5 M NaCl (Polyakov *et al.*, 2021) 28

Figure 2.13 Overall EIS experimental setup using three electrode mode (Acord, 2021)..34

Figure 2.14 Equivalent circuit for Simplified Randles Cell (Acord, 2021). 34

Figure 2.15 Randles circuit's Nyquist plot (Acord, 2021) 35

Figure 2.16 Tafel equation 36

Figure 2.17 Typical cathodic and anodic polarization plots used to extract corrosion rate (Namboodiri, 2020)..36

Figure 2.18 Linear Sweep Voltammetry (LSV) Waveform Field Diagram (Paschkewitz, 2020) 39

Figure 3.1 Mild steel substrate (a) before grinding and (b) after grinding..........40

Figure 3.2 Octadecylamine (ODA) powder 41

Figure 3.3 Silica nanoparticles 41

Figure 3.4 Tungsten oxide nanoparticles 42

Figure 3.5 (3-glycidyloxypropyl)trimethoxysilane (3-GPTMS) 43

Figure 3.6 Flowchart of the research 45

Figure 3.7 Grinding machine..46

Figure 3.8 Vacuum oven 47

Figure 3.9 Vacuum filtration of silica nanoparticles suspension.......................47

Figure 3.10 Stirring of tungsten oxide suspension with magnetic stirrer 48

Figure 3.11 Fourier Transform Infrared Spectroscopy (FTIR) Machine.............51

Figure 3.12 Variables that determine image quality...52

Figure 3.13 Goniometer 53

Figure 3.14 Atomic Force Microscopy (AFM) Principle 54

Figure 3.15 Radiation from the Incident beam for Scanning Electron Microscope (SEM) 55

Figure 3.16 Scanning Electron Microscope (SEM) 56

Figure 3.17 Setup of sample for SEM analysis 56

Figure 3.18 Setup for linear polarization corrosion test 59

Figure 3.19 Electrode setting for linear polarization test 59

Figure 4.1 Morphology of silica nanoparticles a) before treatment and b) after treatment 61

Figure 4.2 Morphology of tungsten oxide nanoparticles a) before treatment and b) after treatment 61

Figure 4.3 3D image of surface roughness of coated sample of (a) AE, (b) AO5 and (c) AO10 65

Figure 4.4 SEM image of coated surface of (a) AO20S6, (b) AO20S6W1, (c) AO20S6W2, and (d) AO20S6W3 69

Figure 4.5 Linear polarization curve (Tafel plot) of coated samples AO20S6, AO20S6W1, AO20S6W2, and AO20S6W3 71

LIST OF SYMBOLS

°	Degree
°C	Degree Celcius
cm	Centimeter
mm	Millimeter
mm/year	Millimeter per year
nm	Nanometer
wt.%	Weight percentage
i_{corr}	Corrosion Current Density
E_{corr}	Corrosion Potential
A/cm^2	Current per centimeter square
J/m^2	Joule per meter square
g	Gram

LIST OF ABBREVIATIONS

3-GPTMS	(3-glycidoxypropyl)trimethoxysilane
BCC	Body-centered cubic
AC	Alternating current
AFM	Atomic Force Microscopy
CE	Counter electrode
DC	Direct current
DMCS	Dimethyldichlorosilane
EDX	Energy Dispersive X-ray Spectroscopy
EIS	Electrochemical Impedance Spectroscopy
EP	Epoxy resin
EPD	Electrophoretic Deposition
FTIR	Fourier Transform Infrared Spectroscopy
HDPE	High Density Polyethylene
LSV	Linear Sweep Voltammetry
NPs	Nanoparticles
ODA	Octadecylamine
PMHS	Poly(methylhydrogen)siloxane
RE	Reference electrode
SA	Sliding angle
SCE	Saturated calomel electrode
SEM	Scanning Electron Microscopy
SHE	Standard hydrogen electrode
SNF	Silicon Nanofilaments
USM	Universiti Sains Malaysia
WCA	Water contact angle
WE	Working electrode
XPS	X-ray Photoelectron Spectroscopy

DEVELOPMENT OF POLYMER NANOCOMPOSITE-BASED COATING FOR CORROSION PROTECTION

ABSTRAK

Keluli digunakan dalam pelbagai tetapi ia adalah logam aktif dengan aktiviti kimia dan elektrokimia yang mudah terhakis. Matlamat penyelidikan ini adalah untuk menilai morfologi permukaan dan taburan zarah nano dalam salutan superhidrofobik, untuk mengukur sifat superhidrofobik salutan berasaskan nanokomposit polimer dan menyiasat ketahanan salutan superhidrofobik dalam persekitaran yang menghakis. Oleh sebab kualiti mekanikalnya yang unggul, epoksi (EP) dipilih sebagai salutan asas untuk projek ini. Salutan boleh diperolehi dengan mengubah kekasaran permukaan nanozarah di mana medium berfungsi telah diperkenalkan kepada nanozarah. Octadecylamine (ODA) diperkenalkan untuk meningkatkan hidrofobisiti salutan. Untuk meningkatkan kekasaran permukaan, nanopartikel nanosilica dan tungsten oksida telah digunakan sebagai prekursor yang disepadukan ke dalam epoksi selepas pengubahsuaian permukaan. Campuran antara epoksi, ODA dan nanopartikel komposisi berbeza disalut pada substrat keluli lembut dengan kaedah memberus. Sampel bersalut dicirikan untuk sudut sentuhan air, kekasaran permukaan, morfologi dan kadar kakisan menggunakan goniometer, AFM, SEM dan potensiostat. Salutan epoksi dengan 20g ODA mempunyai sudut sentuhan air tertinggi 122.57° dan tenaga permukaan terendah 10.28 J/m^2. Salutan epoksi dengan nanopartikel ODA, SiO_2 dan WO_3 mempunyai sudut sentuhan 97.85° dan tenaga permukaan 24.36 J/m^2. Kedua-dua sampel adalah salutan hidrofobik walaupun ia tidak memenuhi kriteria superhidrofobik. Kadar kakisan sampel bersalut ODA dan 6g SiO_2 adalah paling rendah (0.41042 mm/tahun). Kadar kakisan meningkat apabila ketumpatan arus meningkat.

DEVELOPMENT OF POLYMER NANOCOMPOSITE-BASED COATING FOR CORROSION PROTECTION

ABSTRACT

Steel is utilised in a wide range of applications, but it is an active metal with significant chemical and electrochemical activity which it is easily be corroded. The aim of this research is to evaluate the surface morphology and distribution of nanoparticles in the superhydrophobic coating, to measure the property of polymer nanocomposite-based coating and investigate the durability of the superhydrophobic coating in corrosive environment. Because of its superior mechanical qualities, epoxy (EP) was chosen as the foundation coating for this project. The coating can be obtained by altering the surface roughness of nanoparticles where a functionalized medium has been introduced to the nanoparticles. Octadecylamine (ODA) is introduced to improve the hydrophobicity of the coating. To improve the surface roughness, nanosilica and tungsten oxide nanoparticles were utilised as a precursor that was integrated into epoxy after surface modification. The mixture between epoxy, ODA and nanoparticles of different compositions were coated onto mild steel substrate by brushing method. The coated sample were characterized for water contact angle, surface roughness, morphology and corrosion rate using goniometer, AFM, SEM and potentiostat. The epoxy coating with 20g ODA have the highest water contact angle of 122.57° and the lowest surface energy of 10.28 J/m^2. The epoxy coating with ODA, SiO_2 and WO_3 nanoparticles have contact angle of 97.85° and surface energy of 24.36 J/m^2. Both samples are hydrophobic coating although it does not meet the superhydrophobic criteria. The corrosion rate of coated sample of ODA and 6g SiO_2 is the lowest (0.41042 mm/year). The corrosion rate increase as the current density increases.

CHAPTER 1
INTRODUCTION

1.1 Background

Steel is an alloy of iron and carbon containing less than 2% carbon and 1% manganese and small amounts of silicon, phosphorus, sulphur, and oxygen. It is the most important construction and engineering material in the world. It is used in almost every aspect of our lives, including transportation, the building sector, and the oil and gas sector. Due to its affordability and superior mechanical qualities as compared to high alloy alloys, steel is a widely used material. According to data from the World Steel Association, worldwide crude steel output fell by 0.9% from 2019 to 1864 million tonnes in 2020. (World Steel Association, 2021). Because of their exceptional ductility, mild steels, for instance, are a great option for producing steel pipes for a variety of purposes. This enables the pipes to be quickly welded while remaining flexible enough to resist collapsing under pressure. These pipes may be insulated to improve the long-term durability of the piping and to sustain performance in colder climates and challenging conditions. However, in regular or extreme situations, mild steel may rust quickly. The mechanical properties of metal materials are significantly reduced, electronic and optical properties are destroyed, and the service life of mechanical equipment is shortened as a result of chemical or electrochemical reactions on the metal surface that turn the metal into an oxidation or ionic state. These reactions cause stress corrosion cracking and corrosion fatigue in the metal material (Jiang *et al.*, 2015). Corrosion-related failures of metallic components may lead to monetary losses, environmental damage, injury, or even death.

Surface coating is one of the most practical methods of preventing steel corrosion. It prevents the formation of corrosion by obstructing the transit of corrosive liquid to the substrate. For example, chromate, a typical pre-process coating, can provide the maximum anti-corrosion ability because hexavalent chromium can react with other elements to generate some insoluble chromium compounds that can hide defects and prevent defects corrosive solution penetration. Yet, hexavalent chromium's severe toxicity and carcinogenicity are the significant problems limiting its use. The usage of chromate is gradually being eliminated due to its high toxicity, significant environmental threats, and pollution control legislation. As a result, it is vital to select a non-toxic and environmentally friendly coating.

In past few years, to replace the chromate-containing coatings used in metal anti-corrosion coatings, many scientists have been concentrating on the fabrication of passivation films such as metallic compound films, organic films, nanoparticle films, and other composite passivation films (Zhan-Fang *et al.*, 2017). Nevertheless, several of these coatings remain vulnerable to corrosive media such as water, oxygen, and corrosion ions such as chloride ion. In spite of the presence of passivation coatings, electrolyte solution penetrates the surface coating and reaches the metal/coating contact, resulting in corrosion of the metallic substrate. Wettability, which relates to a surface's affinity for water, is one of the most important characteristics of the material's surface. It is well known that the surface energy, surface roughness, and surface micro-nano structure of a surface play a significant impact in determining its wettability. Superhydrophobic surfaces, also referred to as surfaces with contact angles greater than 150° according to Young's equation, have attracted the attention of scientific researchers and have become an integral part of fundamental research and practical applications due to their remarkable water repellence, self-cleaning capability, corrosion resistance, and mechanical robustness.

When water droplets are prevented from wetting a surface due to the micro- and nanostructure known as hierarchical surfaces, this is referred to as superhydrophobicity. A superhydrophobic surface has a water contact angle (WCA) greater than 150°, a sliding angle (SA) less than 10°, and a low surface energy. The superhydrophobic phenomenon was first observed in nature. From Figure 1.1, SEM analysis of the surface of lotus leaf revealed that the surfaces are not smooth but rather covered by wax nanocrystals. The roughness of the surface contributes to the formation of the water repellent layer by these crystals. Figure 1.2 shows the developments of models on wettability from 1805 to 2010 while Figure 1.3 illustrates the increasing number of research papers related to superhydrophobic coating from 2009 to 2018.

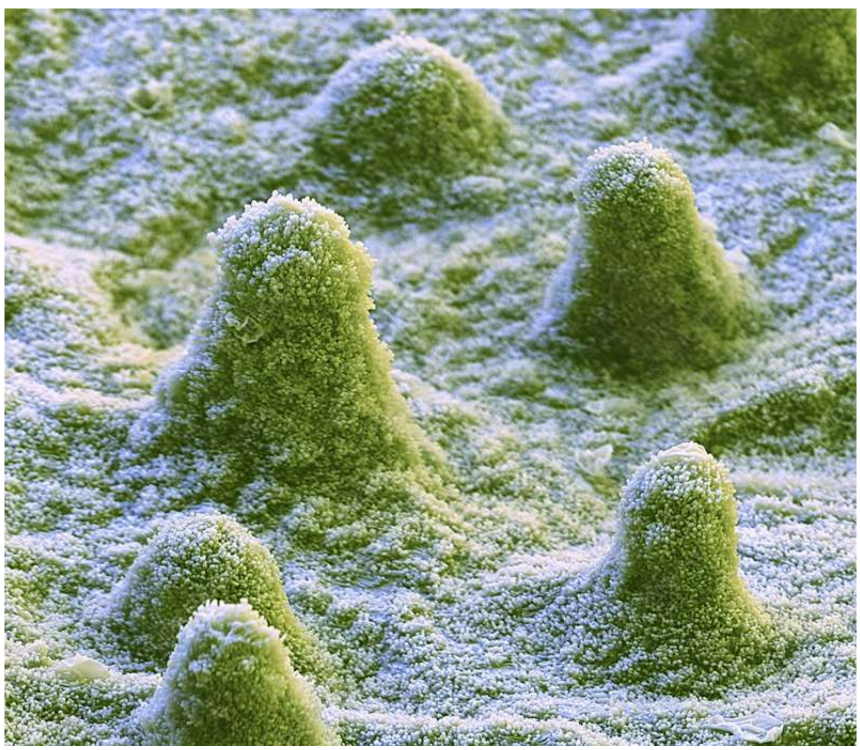

Figure 1.1 Coloured scanning electron microscopy (SEM) image of lotus leaf surface (*Lotus leaf surface, SEM - Stock Image - C006/6469 - Science Photo Library*, 2022)

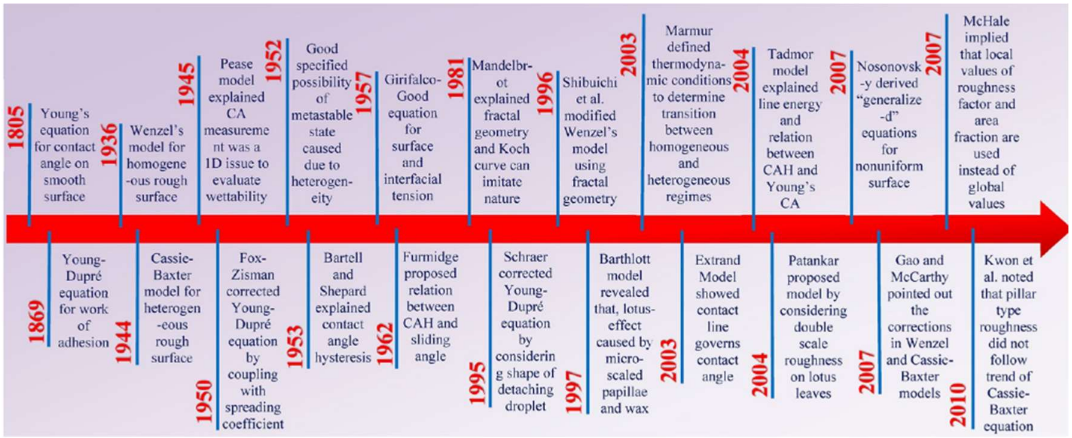

Figure 1.2 Timeline of key developments of models on wettability (Parvate, Dixit & Chattopadhyay, 2020)

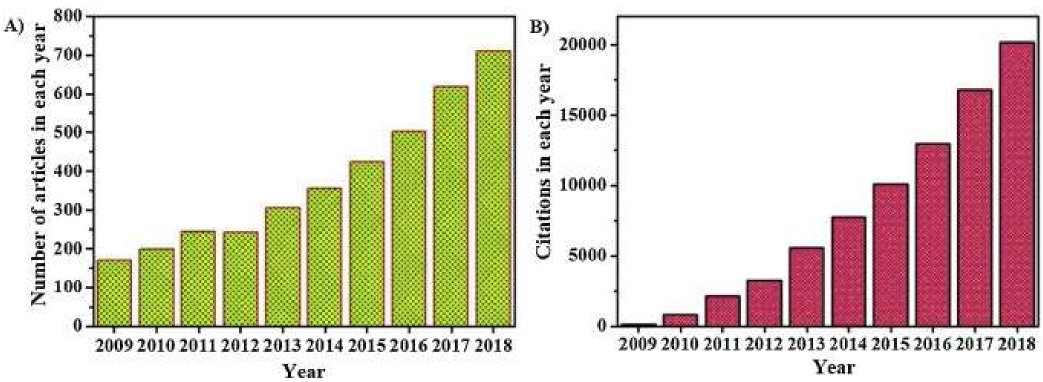

Figure 1.3 Numbers of papers published (A) and numbers of times cited (B) from 2009 to 2018 under the topics of self-cleaning (Dalawai *et al.*, 2020)

Chemical etching, spray coating, dip coating, layer-by-layer assembly, sol–gel technique, chemical vapour deposition, and electrodeposition are all used to make superhydrophobic coatings (Kumar *et al.*, 2020). The spray approach offers the advantages of cost effectiveness, simplicity, and industrial application suitability.

It has been shown that surface roughness and low surface energy are two critical components for the development of superhydrophobicity (Li *et al.*, 2020). Surface free energy is the key factor of whether a surface is hydrophobic. The lower the surface's free energy, the greater its hydrophobicity. Moreover, the strength of the hydrophobic is governed by the microroughness of the surface; the rougher the surface, the more exposed surface area, and the stronger the hydrophobic. To make a very hydrophobic surface, the surface energy and surface roughness must be altered. In general, there are two methods for creating superhydrophobic surfaces: producing a rough surface with a micro–nano structure on a low surface energy material and changing the rough surface with materials containing a low surface energy material (Ragesh *et al.*, 2014). To prepare rough structures, various techniques such as etching, electro-deposition, template imprinting, nanoparticle deposition, and so on are commonly used. Academic and industrial applications are very interested in the creation of superhydrophobic surfaces based on nanocomposite films. This is accomplished by trapping micro/nanoparticles in hydrophobic polymer-based materials, which are accountable for surface roughness. Nanoparticles such as SiO_2, CNT, TiO_2, Al_2O_3, ZnO, ZrO_2, and Fe_2O_3 have been employed as reinforcement in a number of studies to regulate surface roughness and produce superhydrophobic coatings.

Corrosion is a widespread occurrence with significant economic ramifications. All industries, including oil and gas, chemical, food, fertiliser, maritime, and construction, employ metals in their goods, machinery, and equipment. If not properly planned and maintained, storage and working conditions may expose metals to corrosion. An effective and affordable way to stop metal corrosion is by using protective coatings. Coatings need to have high mechanical, thermal, and anticorrosive qualities in order to endure corrosive conditions. Polymer nanocomposite-based coatings have generated a lot of research attention due to their effective anti-corrosion performance on metal surfaces. Unique mechanical, physical, and chemical characteristics of nanoscale materials may improve the degree of corrosion resistance in bulk materials. Additionally, the adoption of sophisticated nano-structured coatings offers numerous additional benefits, such as improvements in the mechanical, optical, hydrophobic, tribological, and electrochemical characteristics of the materials used to shield industrial components (Pourhashem, Vaezi & Rashidi, 2017).

1.2 Problem Statement

Superhydrophobic coatings should be long-lasting and resistant to mechanical damage and corrosive environments. The mechanical characteristics and water repellent behaviour of the coatings are significant. The present superhydrophobic coatings are not able to sustain their superhydrophobic properties for a long period of time, especially after being exposed to the external environment, where the coatings are sensitive to pollutants and severe conditions. Few studies have shown that by nanoparticles into polymer matrix, the surface roughness is increased, and surface energy of polymer nanocomposite coating can be lowered and achieved superhydrophobic surface. The epoxy nanocomposite coating improved the protection performance against corrosion and the corrosion resistance increases when the weight ratio of WO_3 nanoparticles increases. Jiang & Guo (2016) states that before modification, the water droplets penetrated the WO_3 particles quickly because of their intrinsic hydrophilicity. Both silica and tungsten oxide nanoparticles can contribute to increase in hydrophobicity of the surface and improve mechanical properties. Liu et al. (2019) have produced SiO_2/grafted epoxy resin-octadecylamine (SiO_2/EP-ODA) coatings with superhydrophobicity. The combination of ODA, silica and tungsten oxide nanoparticles in polymer matrix is expected to give a better coating performance and lower corrosion rate.

1.3 Objectives

The objectives of this study are:

i. To evaluate the surface morphology and distribution of nanoparticles in the superhydrophobic coating.

ii. To measure the hydrophobic property of polymer nanocomposite-based coating.

iii. To investigate the durability of the hydrophobic coating in corrosive environment.

1.4 Thesis Outline

This research work was classified into five chapters. In this chapter, an introduction associated with superhydrophobicity, and corrosion is presented. In Chapter 2, a comprehensive literature review from recent studies is presented along with explanation about wettability model and how it affects the superhydrophobicity. Different results using different nanofillers are presented in this chapter. Corrosion resistance of polymer nanocomposite-based coating is also be presented in this chapter. Next, Chapter 3 explains the experimental activity that have been carried out throughout this project. Raw materials characterization, coating processes and characterization techniques were elaborated. Following that, the data are analysed and discussed in Chapter 4. The results from this project and outcomes from previous studies are also being used to support the explanations. Moving on, Chapter 5 is conclusion, meaning that this chapter will summarize the whole project activities and outcomes. This thesis is then ended with future works recommendation for further improvement.

CHAPTER 2
LITERATURE REVIEW

2.1 Introduction

Steels, particularly mild steel, are important building materials that are used in nearly every bridge, building, and transportation vehicle. As a result, metal corrosion protection has become a critical issue, not only for the safety of structures and vehicles, but also for economic reasons. The use of chromium (VI) ions in chromating has been shown to be harmful to both humans and the environment, and its use has been severely limited since around the year 2000. These regulations necessitate the development of non-toxic, efficient, and environmentally friendly corrosion protection systems. Polymeric coatings are one strategy that is gaining popularity due to their flexibility, ability to be water-based or solvent-free, and low cost. Recently, there has been a significant increase in research activity on the characteristics, uses, and properties of superhydrophobic polymer coatings. Hydrophobic surfaces can protect metal and alloy surface coatings that are resistant to natural degradation because they limit water exposure and surface interaction. Therefore, this characteristic can make the hydrophobic surface to be anticorrosive, and eventually increase the lifespan of metal.

2.2 Mild Steel

Mild steel has a carbon content of less than 0.25 weight percent. It is an interstitial-free steel with a ferrite microstructure and a body-centered cubic (BCC) crystal structure because carbon atoms fill only a small fraction of the interstices between the iron lattices. As a result, iron accounts for more than 99 wt.% of the microstructure in mild steel, while the remaining elements account for less than 1wt.% of the total composition (Schaeffler, 2016). It is produced from steel which is been extracted from pig iron and less expensive to produce and it is readily available. It has outstanding ductility and toughness, high machinability and weldability which make its applications possible in the engineering fields. Although mild steel is widely used, the main disadvantage of ferrous alloys is they are susceptible to corrosion especially when mild steel allows only a few carbon atoms to fit inside the iron lattice interstices. Therefore, mild steel is easily oxidized or corroded. The microstructure of mild steel is shown in Figure 2.1.

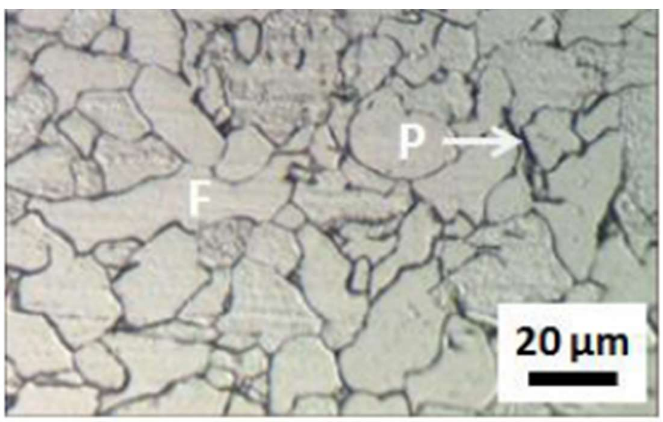

Figure 2.1 Microstructures of plain low carbon steel (Phoumiphon, Othman & Ismail, 2016).

2.3 Superhydrophobic Surface

Superhydrophobic is an intelligent surface with a low surface energy and a high contact angle. The superhydrophobic was founded on the lotus leaves in the nature of the world, which is very special phenomenon. To produce a superhydrophobic surface or coating, the surface must simultaneously contain hierarchical micro- and nano-roughness and low surface energy. The distinctive surface structure of the lotus leaf and the existence of a substance with low surface energy were the primary causes of this occurrence.

Water droplets often retain high contact angles when resting on superhydrophobic surfaces, and the surface's decreased contact angle hysteresis makes it possible for them to roll extremely swiftly. In situ detection, biochemical separation, microfluidics, and flow of the liquid inside or in open area will all benefit greatly from the study of superhydrophobic surfaces on the lotus leaves in the nature that response to external stimuli, which has produced numerous promising breakthroughs in this area. Superhydrophobic surfaces are typically contact angles 150° and rolling angles of 10°, and the contact angles which is shown in Figure 2.2(a). In most cases, the wettability of a surface is determined by the contact angle of a droplet with a solid surface. The main theoretical for the superhydrophobic surface is known as Young model, the Wenzel model, and the Cassie-Baxter model which is shown in Figure 2.2(b, c, d) (Yang et al., 2022).

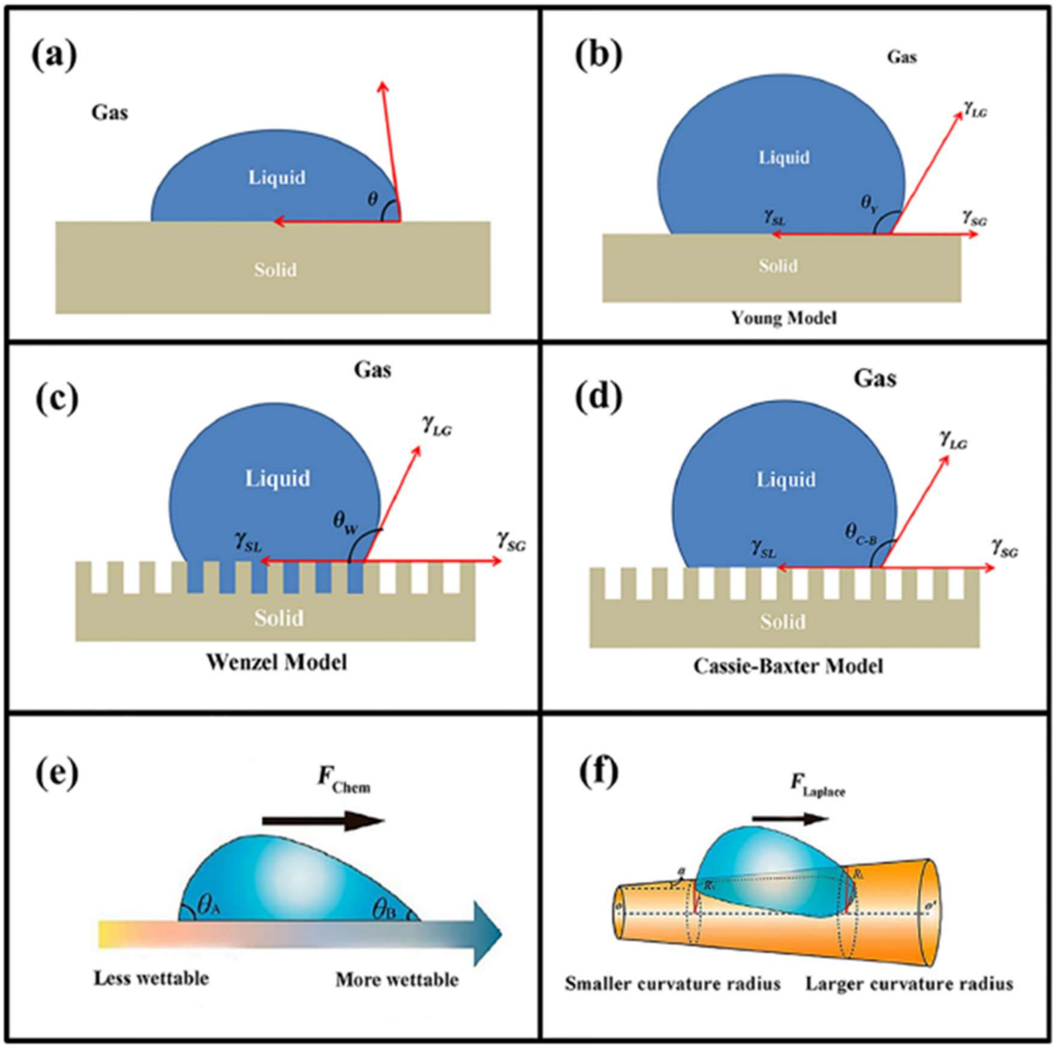

Figure 2.2 (a) Schematic diagram of contact angle. (b) Schematic diagram of Young model. (c) Schematic diagram of Wenzel model. (d) Schematic diagram of Cassie-Baxter model. (e) The driving force of chemical gradients. (f) The driving force generated by the structural gradient. (Yang *et al.*, 2022)

Normally, the contact angle is assessed when there is a water droplet rests on top of a solid surface. The Wenzel state and the Cassie-Baxter state are two different kinds of states for water droplet rest on top of a solid surface, as seen in Figure 2.3. In the Wenzel state, water penetrates the textured or structured surface, immobilizing water droplets and preventing them from easily rolling off the surface. The water droplets floating on the surface of the texturing under Cassie-state Baxter's are likely to slide off effortlessly. After that, for the equivalent contact angles of Cassie-Baxter state would be greater than those for the Wenzel state because of the surface structure either is smooth or having some tiny, small holes or scratches (Zhang & Lv, 2015). The two main factors that determine a surface's super hydrophobicity are hierarchical structures or nanostructures and coatings with low surface energy, as the modification applied to the structure with a hydrophobic substance can significantly reduce the surface energy and also increase the property of repellent.

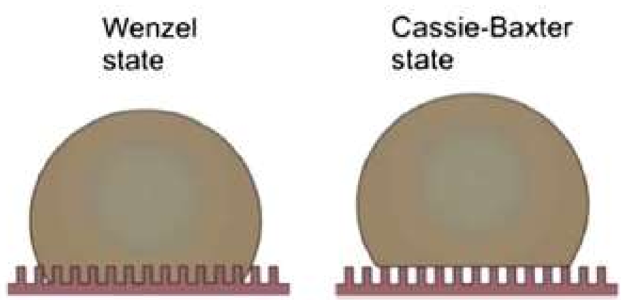

Figure 2.3 The states of droplets on texture surface (Zhang & Lv, 2015)

2.4 Wettability

Wettability is a liquid's capacity to spread over a surface. It may be measured by the liquid's contact angle with the surface. There is a clear correlation between contact angle and surface energy, such that contact angle decreases as surface energy increases.

Wettability is a key feature of solid-state surfaces with significant industrial applications. In general, the wettability of a surface is determined by the contact angle between solid and liquid surfaces. The wettability of shale oil is a crucial aspect in its exploration and production. Shale wettability has not yet attained a unifying concept. Research on the wettability of shale often makes use of contact angle. However, the shale's pre-treatment has a significant impact on the contact angle (Richard, 2016).

If a liquid is applied to a surface, it tends to spread and cover it. When seen on a microscopic scale, the border of the liquid displays a distinctive form. A knife-shaped edge implies moist conditions, but a beaded edge indicates dry conditions. This is shown in Figure 2.4, which depicts a drop of water touching a solid surface while surrounded by oil.

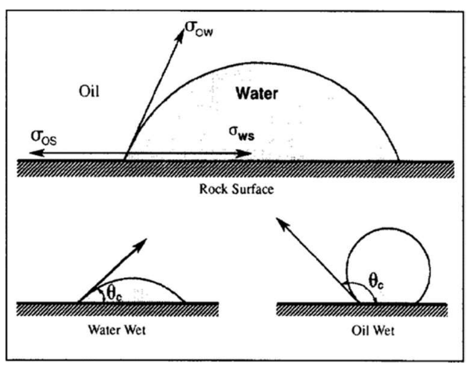

Figure 2.4 Contact angle on different types of surfaces

According to the study, oil-wet has a favourable relationship with thermal maturity and the presence of organic content. Besides, the clay or the carbonate minerals react negatively with moist water while the silica minerals are the positively related with water-wet. The shale's mineralogical makeup, the characteristics of aqueous media, the oil's makeup, temperature, or pressure all will be affected to the wettability. Following iron minerals in terms of hydrocarbon affinity are clay minerals, carbonate minerals, and silica minerals. In conditions of low salinity, minerals are more hydrophilic. The build-up of non-hydrocarbons makes the surface hydrophilic. In addition, the hydrophilic properties of the "oil-water rock" will decrease as the temperature rises (Göhl *et al.*, 2018).

Based on the water contact angle, four different wetting regimes may be distinguished in the wetting behaviour (WCA). As illustrated in Figure 2.5, the WCA may be characterised as superhydrophilic, hydrophilic, hydrophobic, and superhydrophobic with a starting range of 0° 10°, 10° 90°, 90° 150°, and 150° 180°. Superhydrophobic coatings are impervious to water droplets (Das *et al.*, 2018).

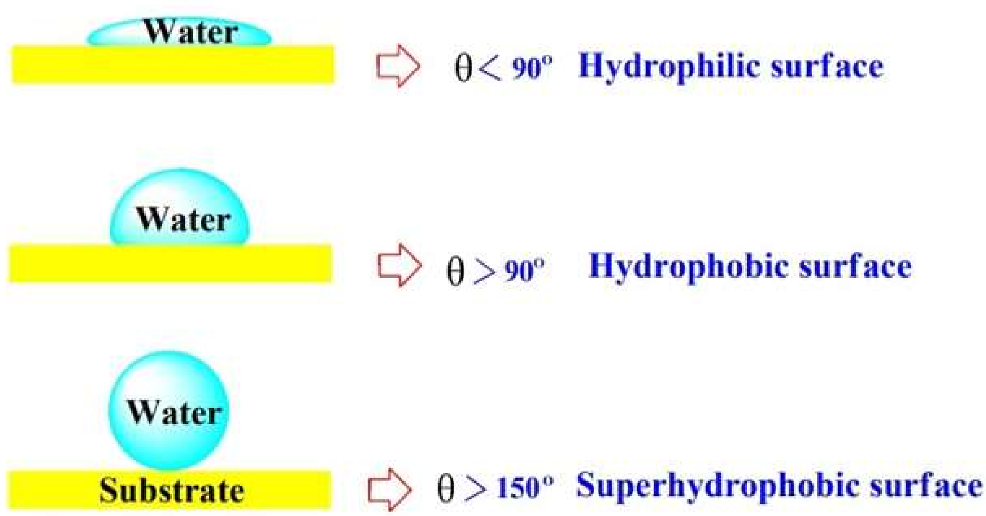

Figure 2.5 Schematic represent hydrophilic, hydrophobic and superhydrophobic surfaces (Das *et al.*, 2018).

Young's equation is a formula created by the English physicist Thomas Young that describes the link between the contact angle, the surface tension, the interfacial tension between a liquid and a solid surface, and the surface free energy of the solid. The equation aids in describing the structure and behaviour of a liquid when the liquid-vapor interface meets a solid surface in simpler words. Based on the figure, the surface of the solid is wetted by the three-surface come into contact. The three surface is labelled as liquid to solid (ls), liquid to liquid (ll), and solid to liquid (sl), which also called as (lv). The contact angle between the interfaces of sl and lv must have a certain value in order to meet the equilibrium state of the three interfacial tensions. Young said that two requirements must be satisfied for balance to exist. The force per unit length (γ) and the contact angle (θ) at a point where the tangent line at the liquid-air (lv) interface intersects the solid surface, as shown in Figure 2.6, are both given by Young's equation 2.1.

$$\gamma_{lv} \cos\theta = \gamma_{sv} - \gamma_{sl} \qquad \text{(Equation 2.1)}$$

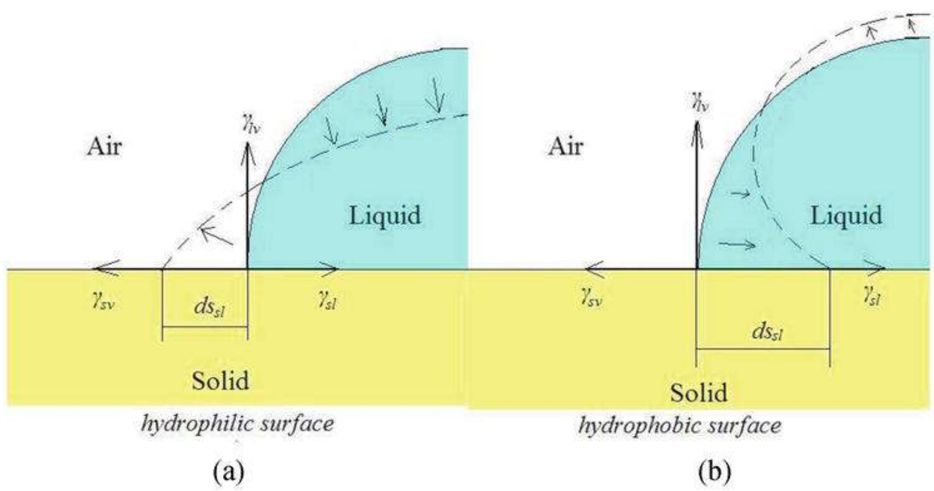

Figure 2.6 Wettability on (a) hydrophilic surface and (b) hydrophobic surface (Kwok, 2020)

The second aspect of the interface energy relates to dynamic equilibrium, which can be calculated using Equation 2.2. This equation calculates dynamic equilibrium. This equates the dynamic equilibrium area (in terms of interface area) of the two interfaces (sl and lv).

$$(\gamma_{sv} - \gamma_{sl})\, ds_{sl} = \gamma_{lv}\, ds_{lv} \qquad \text{(Equation 2.2)}$$

Therefore, contact angle can be determined by combining equation 2.1 and equation 2.2, as shown below,

$$cos\theta = \frac{ds_{lv}}{ds_{sl}} \quad \text{(Equation 2.3)}$$

Where, $\frac{ds_{lv}}{ds_{sl}}$ is the area changing rate of the lv interface with the sl interface increasing.

2.5 Fabrication Method for Superhydrophobic Coating

Based on the research (Kumar *et al.*, 2020), surface roughness and low surface energy materials are two key determinants of superhydrophobicity, and they are often produced through chemical etching, spray coating, dip coating, layer-by-layer assembly, the sol-gel technique, chemical vapour deposition, and electrodeposition which is shown in Figure 2.7. The dip-coating procedure is simple, but if the withdrawal speed is too high, it produces a thick, non-homogeneous layer. A non-homogeneous covering is also produced via spray coating. By forming a multi-layer coating, the layer-by-layer assembly approach may improve the mechanical characteristics, but it necessitates a difficult pre-processing step. On the other hand, spin coating offers clear coatings and a thin, homogeneous coating on solid objects. It is a relatively straightforward method that works well for large-scale manufacture and is quite economical.

fabrication method	advantages	disadvantages
sol–gel method	provides high quality films, synthesis at normal temperature, less deterioration	limiting thickness, less durable to mechanical stress, costly
immersion coating	industrially feasible, low cost	non-uniform
spin coating	quick drying, controllable thickness	provides a smooth surface, only for laboratory scale, needs a large amount of solvent
dip coating	industrially feasible, reusable, low cost	requires more time, only for soluble polymers, not suitable for the environment
spray coating	high quality coating, repairable	requires more capital, non-uniform thickness
layer-by-layer assembly	controllable thickness	high cost

Figure 2.7 Fabrication methods to prepare superhydrophobic coating (Meena *et al.*, 2020)

2.6 Types of Nanoparticles Used in Polymer Coating

Polymer coating that covered on the surface of consumer goods served as a protective and decorative layer. High-performance and super durable coatings are needed for outdoor applications because photo degradation frequently reduces a polymer coating's durability. A recent innovation in the production of coating systems with better performance is the incorporation of nanoparticles in coating.

For a variety of applications, the quick advancement of nanotechnology and nanomaterials has necessitated the modification of nanoparticle surfaces. Therefore, nanoparticles employed in polymer coating are very tiny, have a high surface energy, and have a large surface area, they provide significant hurdles. The regulated release of drugs, genes, and other bioactive molecules is found to be especially fascinating when nanoparticles are coated or enclosed. Protection against rapid degradation, targeted administration, control over the rate of release, and a prolonged half-life for bioactive substances are all benefits of controlled release systems (Wang, Dave & Pfeffer, 2004).

Superhydrophobic coating was produced using a variety of techniques, including layer-by-layer assembly, the sol-gel method, chemical vapour deposition, brushing, spray coating, dip coating, and electrodeposition. The brushing technique, among others, has the advantages of being straightforward, economical, and appropriate for industrial applications.

2.6.1 Silica Nanoparticles

Silica nanoparticles (SiNPs), it is also known as silicon dioxide, are spherical amorphous solids. Silica-coated metal nanoparticles have become increasingly important during the last ten years for a variety of potential catalytic and biological uses. The properties of their surfaces may be readily changed to suit a variety of purposes, and they can be produced in a variety of sizes and shapes. Nanoparticles of nonporous silica are both abrasive and absorbent. Silica nanoparticles with a size range of 10-500 nm and a variety of morphologies and physicochemical characteristics may be made in a number of ways. The most popular methods for creating SiNPs are Stober's approach and the micro emulsion method. The Stober's technique for the creation of monodisperse silica particles with a sub-micrometer size was originally reported in 1968. This method produces non-porous silica particles smaller than 200 nm by hydrolyzing tetraethyl orthosilicate (TEOS), a precursor to silica, in the presence of ethanol and ammonium hydroxide (NH_2OH). User-specific requirements have been taken into account while changing this synthesis approach.

Silicon dioxide nanoparticles, also known as silica nanoparticles, are desirable for biological applications due to their good biocompatibility, heat resilience, low toxicity, straightforward synthetic method, and huge synthetic supply. Furthermore, natural silica and silicates, which are predominantly crystalline, are the most abundant elements of the Earth's crust.

Zhi et al. (2019) shows that the fabricated silica nanoparticles having surface reactive groups capable of reacting further with epoxy resin. Consequently, the hydrophobic silica nanoparticles were firmly fixed and retained in the cured resin matrix, generating nanometer-scale roughness of a nanostructures. After mechanical abrasions, the produced silica-decorated epoxy resin coating exhibits excellent durability, water resistance, and substrate adherence.

As shown schematically in Figure 2.8, the surface functionalized silica nanoparticles were produced utilising an in situ surface modification method. In a nutshell, the 2,3-epoxypropoxypropyltrimethoxysilane (KH560) modifier was dissolved in absolute alcohol, while sodium metasilicate and hydrochloric acid were each individually dissolved in deionized water. After that, the sodium metasilicate solution received drop-by-drop additions of the KH560 and hydrochloric acid solution. This solution was heated and stirred at the required temperature for four hours before foam started to form on the surface. The suspension split into two layers right away, with a layer of white floc floating on top. Filtering was used to recover and fully clean the floc. In order to generate an emulsion, the filtered substances will then divide once again into a quantity of mixed solution. The emulsion was then spray-dried at 140 °C to produce white SiO_2 nanoparticles. 0.3 mol L^{-1} sodium metasilicate, 0.72 mol L^{-1} hydrochloric acid, and 0.05 mol L^{-1} modifier were employed as the standard formula. There is a wealth of information on surface-functionalized SiO_2 nanoparticles in S1 of the ESI.

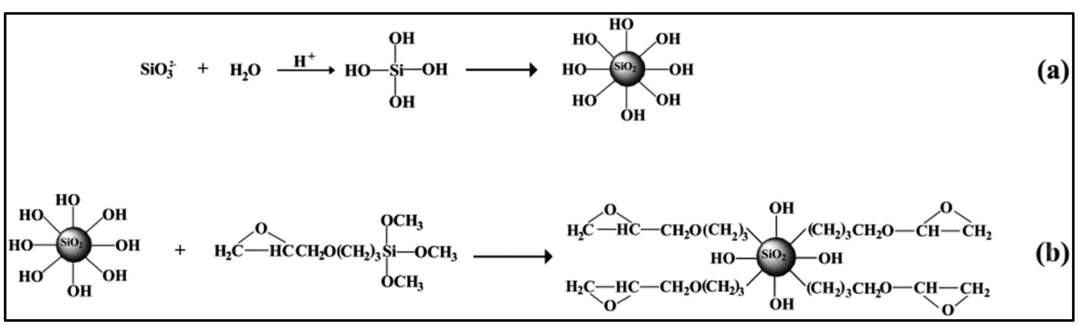

Figure 2.8 Schematic illustration of KH560 functionalization of silica nanoparticles (Zhi *et al.*, 2019)

In the late 1960s, Stober and coworkers discovered the sol-gel chemistry of silicon alkoxides, which enabled the synthesis of monodisperse spherical silica nanoparticles in simple aqueous solutions containing several alcohols, including methanol, ethanol, and isopropanol. The innovative silica-coating of the researcher follows the well-known Stober strategy and starts with the bi-functional (3-aminopropyl)trimethoxysilane's flimsy surface attachment in aqueous solution. In order for the gold nanoparticles to be transferred into alcohols to create a stable water/alcohol solution, the -NH_2 groups are joined to the gold surface and when it combined with sodium silicate, the extended -Si3 groups are hydrolyzed and condensed to form a very thin layer of surface-protective silica. Tetraethyl orthosilicate, a typical precursor of silicon alkoxides, may be further hydrolyzed or condensed to produce thicker silica shells that can support the surface of gold nanoparticles (Liu & Han, 2010).

A variety of surface-attachment techniques have been established in aqueous solutions before silica coating, using bi-functional molecules, strong surface coordination, or electrostatic interaction with metal nanoparticles. These methods produce colloidally stable, surface-protected nanoparticles in alcoholic solutions. Tetraethyl orthosilicate must include reactive hydroxyl groups at this surface-protected nanoparticles contact in order to be hydrolyzed or condensed. Utilizing the surface chemistries and interface properties of metal nanoparticles to generate solid interfaces for generating effective surface-coatings has become the most important task (Figure 2.9). Small compounds, synthetic polymers, and biopolymers are used in combination with several straightforward procedures to provide metal nanoparticles beneficial surface groups for upcoming silica deposition (Liu & Han, 2010).

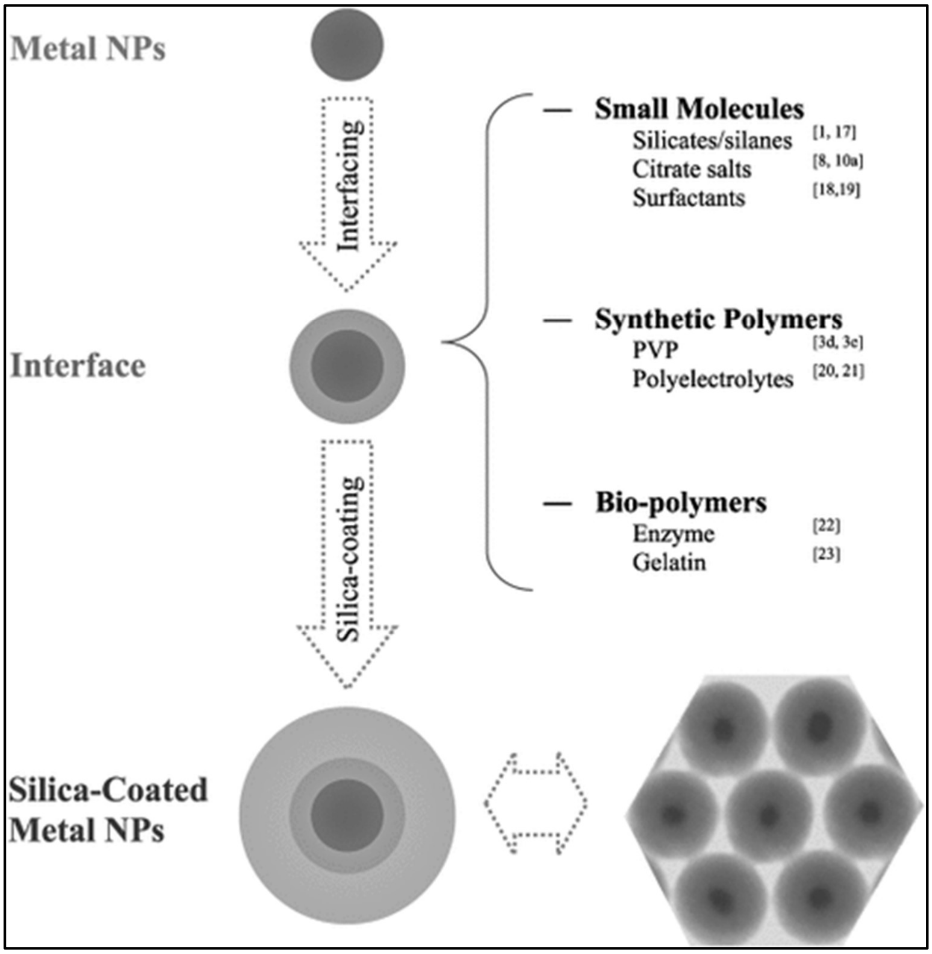

Figure 2.9 Silica-coating strategies (Liu & Han, 2010)

2.6.2 Tungsten Oxide Nanoparticles

Tungsten and tungsten oxides have been investigated since the early 20th century. Due to its appropriateness for a vast array of applications, there has been an increase in study on tungsten alloys and oxides with diverse stoichiometries during the last 50 years. This transition metal oxide is plentiful in nature, inexpensive, and non-toxic to living creatures. It is also ecologically beneficial. These characteristics, together with its strong chemical stability in a pH range relevant to many applications and its semiconducting properties, have resulted in a considerable number of publications during the last 15 years (Mardare & Hassel, 2019). Therefore, tungsten-based superhydrophobic is a relative newcomer to the world of superhydrophobic. Until now, there have not been many papers that report on superhydrophobic coatings based on tungsten nanoparticles.

Based on the researcher (Tesler *et al.*, 2015), nanomaterial containing tungsten oxide (WO_3) is an effective corrosion inhibitor due to its numerous advantageous properties, including high inhibition efficacy, cheap cost, low toxicity, and simple manufacture. The deposition of metal or metal oxide nanoparticle composites has permitted advancements in the area of protective coatings. The reseacher increased the corrosion resistance of zinc by co-depositing TiO_2 nanoparticles, whereas improved the corrosion behaviour of nickel coatings by including CeO_2 nanoparticles. Thus, the authors are unaware of any other publications in the scientific literature in which Electrophoretic Deposition (EPD) has been employed to deposit WO_3 nanoparticles as protective coating films. The researcher used Scanning Electron Microscopy (SEM) to determine the particle size of the tungsten oxide and it is clearly observed that sample show rod by referring to Figure 2.10.