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DEVELOPMENT OF SUPERHYDROPHOBIC AND SELF-CLEANING SURFACES USING SILANE-BASED MATERIAL AND Cu-doped TiO_2 NANOPARTICLES FOR CERAMIC WALL TILES

By

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitles "**Development of Superhydrophobic and Self-Cleaning Surfaces using Silane-based material and Cu-doped TiO_2 nanoparticles for Ceramic Wall Tiles**". I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this for any other examining body or university.

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LIST OF SYMBOLS

°	Degree
°C	Degree Celsius
N/m^2	Newton per meter
J/m^2	Joule per meter
γ_{lv}	Liquid-Vapour Surface Energy
θ_E	Equilibrium Contact Angle
γ_{sv}	Solid-Vapour Surface Energy
γ_{sl}	Solid-Liquid Surface Energy
θ_w	Contact Angle of Rough Surface by Wenzel
θ_{CB}	Contact Angle of Rough Surface by Cassie-Baxter
f	Fraction
θ	Water Contact Angle
µm	Micro meter
rpm	Revolutions per Minute
min	Minute
eV	Electrovolt
°C/min	Degree Celsius per Minute
s	Second
h	Hour
M	Molarity
mL	Millilitre
mmol	Millimol
pH	Potential of Hydrogen
mm/s	Millimetre per second
kV	Kilovolt
nm	Nanometre
ppm	Parts per Million
g	Gram
Å	Armstrong

LIST OF ABBREVIATIONS

NPEs	Nonylphenol Ethoxylates
VOCs	Volatile Organic Compounds
WCA	Water Contact Angle
Cu-doped TiO_2	Copper doped Titania
TiO_2	Titania
UV	Ultraviolet
XRD	X-Ray Powder Diffraction
FESEM	Field Emission Scanning Electron Microscopy
EDX	Energy Dispersive X-Ray
TEM	Transmission Electron Microscopy
UV-vis	Ultraviolet Visible Spectroscopy
UV-DRS	Ultraviolet Diffuse Reflectance Spectroscopy
MO	Methyl Orange
COF	Coefficient of Friction
CuO	Copper Oxide
Cu^{2+}	Copper ion
Ni^{2+}	Nickel ion
Co^{2+}	Cobalt
NaOH	Sodium Hydroxide
ROS	Reactive Oxygen Species
$O^{2\bullet-}$	Anions
H_2O_2	Hydrogen Peroxide
HO●	Hydroxyl Radical
CO_2	Carbon Dioxide
VB	Valence Band
CB	Conduction Band
h^+	Holes
e^-	Electrons
H_2O	Water
O_2	oxygen
Cu	Copper

HAIs	Healthcare Associated Infections
HCl	Hydrochloric Acid
MTCS	Methyltrichlorosilane
LiOH	Lithium Hydroxide
atm	Atmospheric pressure
ICDD	International Centre for Diffraction Data

PENGHASILAN PERMUKAAN SUPERHIROFOBIK DAN PEMBERSIHAN DIRI MENGGUNAKAN ZARAH Cu-doped TiO_2 BAGI JUBIN DINDING SERAMIK

ABSTRAK

Permukaan yang mempunyai ciri superhidrofobik membuatkan permukaan itu senang di bersihkan dengan bertindak sebagai penangkis air apabila titisan air menyentuh permukaan tersebut. Titisan air akan membentuk seperti mutiara apabila ia menyentuh permukaan pepejal, kemudian titisan air tersebut akan berguling dan membawa sekali kotoran keluar. Fokus utama dalam kerja ini adalah untuk menghasilkan permukaan superhidrofobik baru di atas jubin dinding seramik supaya mudah untuk di bersihkan. Penghasilan salutan yang baru perlu memenuhi keperluan permukaan superhidrofobik iaitu permukaan kasar dan tenaga permukaan yang rendah. Kuprum-dop titanium dioksida (Cu-dop TiO_2) tiub nano telah menjalani sintesis menggunakan kaedah hidroterma untuk di gunakan bersama bahan salutan. Penambahan Cu-dop TiO_2 tiub nano adalah untuk mewujudkan permukaan kasar dan bertindak sebadai ejen pembersih diri dan antibakteria di atas permukaan substrat. Dua pelarut berlainan bahan (silika koloid dan bahan silana) yang digunakan sebagai pengikat untuk memegang Cu-dop TiO_2 tiub nano di atas jubin dinding seramik (licau dan tidak licau) substrat. Cu-dop TiO_2 tiub nano telah diletakkan di atas jubin dengan menggunakan teknik salutan celup dan dengan meningkatkan bilangan kitaran salutan celup, kekasaran pada permukaan akan terbentuk. Lapisan silica koloid yang di perbuat dari Ludox AS-40 dan Cu-dop TiO_2 tiub nano didedahkan sebagai permukaan hidrofilik akibat daripada kekasaran permukaan yang rendah dan tenaga permukaan yang tinggi (57.88 ± 0.03 J/m^2) serta sudut sentuh air yang rendah iaitu $42.73° \pm 0.06$. Sementara itu, lapisan bahan silana yang diperbuat daripada methyltrichlorosilane (MTCS), toluena dan Cu-dop TiO_2 tiub nano didedahkan sebagai permukaan superhidrofobik kerana kekasaran permukaan yang tinggi dan tenaga permukaan yang rendah (0.00 J/m^2) serta sudut sentuh air yang tinggi hingga 153.96°. Oleh itu, salutan berasaskan silana dipilih sebagai pelarut terbaik untuk mendepositkan TiO_2 tiub nano pada jubin dinding untuk mengahasilkan kesan superhidrofobic, yang boleh menyebabkan aplikasi pembersihan diri.

DEVELOPMENT OF SUPERHYDROPHOBIC AND SELF-CLEANING SURFACES USING Cu-doped TiO_2 PARTICLES FOR CERAMIC WALL TILES

ABSTRACT

Superhydrophobic property make surfaces easy to clean that act as a water repellent when water droplet is in contact to the surface. The water droplet will formed bead-like shape when hitting the surface then roll-off and collect the dust while on the way. The main focus of this work is to develop a new superhydrophobic surfaces on ceramic wall tiles for easy cleaning. The newly developed coating need to satisfy hydrophobic surface requirements which are rough surface and low surface energy. Copper doped Titania (Cu-doped TiO_2) nanotubes was synthesized using hydrothermal method to be used as incorporation with coating materials. The addition of Cu-doped TiO_2 nanotubes is to create surface roughness and serve as self-cleaning and antibacterial agent on the substrate. Two different solvents (colloidal silica and silane-based materials) were used as a binder that will hold the Cu-doped TiO_2 nanotubes on the ceramic wall tiles (glazed and unglazed) substrate. The Cu-doped TiO_2 nanotubes were deposited on the tiles by dip coating method and by increased the number of dipping cycle, surface roughness will be formed. Colloidal silica coating that was made from Ludox AS-40 and Cu-doped TiO_2 nanotubes was revealed to be a hydrophilic surface due to low surface roughness and high surface energy (57.88 ± 0.03 J/m^2) with low water contact angle (WCA) of 42.73° ± 0.06. While, silane-base coating that was made from methyltrichlorosilane (MTCS), toluene and Cu-doped TiO_2 revealed to be a superhydrophobic surface because of high surface roughness and low surface energy (0.00 J/m^2) with high WCA up to 153.96°. Therefore, silane-based coating is chosen as the best solvent to deposit TiO_2 on the wall tiles in order to create the superhydrophobic effect, which can lead to self-cleaning applications.

CHAPTER 1

INTRODUCTION

1.1 Research Background

Tiles had been used for many years ago from the earlier 13^{th} century (The Victorian Emporium, 2011). Tiles are often used to give the aesthetic value to decoration of wall, floor and roof coverings. Tiles can be divided into wall, floor and multipurpose tiles which can be made from materials such as ceramic, porcelain, quarry, mosaic, marble and many more (Imam, 2017). Ceramic tile is made up of plastic and non-plastic raw materials. Plastic materials such as ball clay and china clay acts as binder and form plasticity when mixed with water. Non-plastic materials such as quartz and feldspar serve as filler and flux, respectively. Filler is important in reducing high plasticity or shrinkage of the body during drying and firing, while flux provides glassy phase (Ceramic Research Company, 2012). Ceramic tiles are typically glazed for internal uses (such as tiles used in the kitchen, toilets, and house decoration) and unglazed for outdoor application (such as roofing, wall, and floor). Glazing is very important to floor and wall tiles to enhance the aesthetic value, less staining and to protect the porous body with its impermeable outer surface (Build Direct, 2017).

However, tiles need regular cleaning in order to reduce dirt, dust and stains to keep its feature like new. Unglazed tiles with permeable surfaces make it even harder to clean because water can be absorbed by the tile body. Thus, the unglazed tiles will worn out faster than using glazed tiles. Although glazed tiles has shiny and smooth surfaces, dirt and stains can still stick to the surface. Thus, cleaning is required. In practical, most people use detergents or cleaning products which contains chemical substances.

These chemicals make cleaning tiles much easier rather than the use of only water alone.

However, the detergents typically used as cleansing substances can cause water pollution when it discharge into the receiving running water, seas, and also lakes. Detergents may contain surfactants, bleaches, dyes phosphate and many more that can cause the water pollution to happen (Nelson, 2018). Polluted water can be dangerous to the ecosystem and also human health. Phosphate in the detergents can cause rapid growth of algae producing massive growths or ‘bloom’ on the water surfaces and cause eutrophication. Eutrophication happen when the water surface was blocked by the algae that prevent oxygen into the water causing the death of other organisms inside the water (Bagai, 2018). Polluted algae can be harmful to fish, animals and also mankind because it is toxic (Sen *et al.*, 2013). Nonylphenol ethoxylates (NPEs) which is a group of surfactant petrochemical that slowly biodegrade into more toxic compounds and interfering with the fish and shellfish hormones. Bleach which is sodium hypochlorite will react with other cleaning chemical and generate chlorinated volatile organic compounds (VOCs) which are very toxic and considered as human carcinogens (able to cause cancer in living tissue) (Nelson, 2018).

One approach to avoid water pollutant is by creating tiles that can clean the surface by its self without the use of detergent. Superhydrophobic surfaces can be developed on the tiles to make water droplets bounce on the surface and carry dirt while rolling-off and provide self-cleaning effect. Superhydrophobic properties are considered as smart coating having great interest since it is easy to clean and thus require low maintenance (Zhang *et al.*, 2016). Superhydrophobic surfaces normally involve the combination of high surface wetting angle and low surface energy which is water contact angle (WCA) more than 150° and tilt angle less than 10° (Martin and Bhushan, 2017). In recent years, superhydrophobic surfaces have drawn much attention around the world both in scientific research and commercial applications. There are many methods or techniques for the fabrication of superhydrophobic surfaces such as simple dip-coating, spin coating, spray coating and many more (Mahadik *et al.*, 2013; Gurav *et al.*, 2015; Söz, Yilgör and Yilgör, 2016; Martin and Bhushan, 2017; Zhao, Hu and Zhang, 2018). Superhydrophobic coating has been used in many industrial and household applications such as self-cleaning windows, windshields, exterior paints for buildings and navigation of ships, utensils, roof tiles, textiles, solar panels and applications requiring a reduction of drag in fluid flow (Zhang *et al.*, 2016).

During the current approach, coating surfaces was developed on the glazed and unglazed ceramic wall tiles by dipping the tiles in the coating solution. The coating solution was made up of silane-based solution combined with Cu-doped TiO_2 nanotubes to create superhydrophobic and self-cleaning effect. By having superhydrophobic surface, it is useful for water repellent and self-cleaning surfaces when water droplet that in contact with the surface will roll-off and picking up dirt along the way (Zhang *et al.*, 2016). TiO_2 nanotubes act as photocatalyst to give self-cleaning effect on the coating surfaces by photodegradation process. When the surface was exposed to the (ultraviolet) UV light, the volatile organic compounds will be decomposed (Xu *et al.*, 2017). Doping metal ions (such as Cu and Zn) into TiO_2 lead to a decrease in band gap energy of the TiO_2 nanoparticles and increase the absorption edge wavelength. The doping ions and the small crystallite size inhibited any phase transformation and promote growth of the TiO_2 anatase phase (Khairy and Zakaria, 2014). Doping metal ions would also possess antibacterial property and reduces bacterial growth (Hikku, Jeyasubramanian and Vignesh Kumar, 2017a).

1.2 Problem Statement

Since tiles were first developed, it had been increasingly being utilized as a wall cover because of its durability, stain proof, long lasting and environmental friendly (Tile Direct, 2015). Other than that, tiles are relatively cheap for a long term and has variety of designs and colours to be chosen to decorate houses, restaurants, offices and many other places. To keep the beautiful feature of the tiles in like-new shape, regular cleaning is required. Due to the exposure to the outdoor surrounding like dirt, dusts, and moisture that lead to moss formation, people tend to use detergent or other cleaning products that contain chemical to clean their tiles.

Detergents are the most common cleaning agent that are commonly use to clean tiles. However, the use of these detergents gives bad impact to the environment which cause pollution due to the accumulation in organisms, resilience to biodegradation and higher solid content compared to other cleaning compound (Giagnorio *et al.*, 2017). Phosphate salts in the detergents can cause water pollution which it tends to inhibit the biodegradation of organic substances. It also can cause eutrophication which prevent the water from available oxygen, causing the death of aqua organisms. Detergents also gives bad impact to human health. Drinking water that contaminated by detergents that contain chemicals can be hazardous to human health (Bagai, 2018). The tiles surfaces need to be improved or modify to be cleaned easily. Thus, by introducing superhydrophobic coating surfaces on the tiles, it can be a lot easier to clean by only water and reduce the use of detergent.

Many researchers has studied on superhydrophobic surfaces using various materials and method such as SiO_2, ZnO and TiO_2 by dip coating, spin coating, sol-gel method and many more (Han *et al.*, 2012; Mahadik *et al.*, 2013; Gurav *et al.*, 2014, 2015; Söz, Yilgör and Yilgör, 2016). Özcan, Açıkbaş and Çalış Açıkbaş, (2018) had produced a superhydrophobic surface of wall tiles by inducing metallic zinc powder in the glaze composition before firing. However, methods to produce superhydrophobic surface on wall tiles after firing has not been widely explored yet. Many research has developed superhydrophobic on substrates such as glass, fabric and metal. Therefore, this study aim to develop a superhydrophobic surfaces on wall tiles with self-cleaning and antibacterial properties by combining Cu-doped TiO_2 nanotubes in colloidal silica and silane-based coating. Cu-doped TiO_2 were used to create surface roughness and it also gives better photocatalytic activity due to its lower band gap energy compared to commercial TiO_2. Doping copper to the TiO_2 is to increase the antibacterial properties. A simple dip coating technique was used in this study. The coating were applied on glazed and unglazed wall tiles. The wall tiles surface of silica coating with Cu-doped TiO_2 were compared to colloidal silica with Cu-doped TiO_2 coated tiles.

1.3 Research Objectives

The aim of this research is to develop a superhydrophobic coating on different types of wall tiles (glazed and unglazed). With this main goal, the following objectives were set:

i. To synthesize Cu-doped TiO_2 nanotubes by hydrothermal method.
ii. To develop a new superhydrophobic coating on different ceramic wall tiles body using Cu-doped TiO_2/silane and Cu-doped TiO_2/colloidal silica coating materials via simple dip-coating method.
iii. To investigate the functionality of the newly develop coated tiles for self-cleaning and antibacterial properties.

1.4 Scope of Research Work

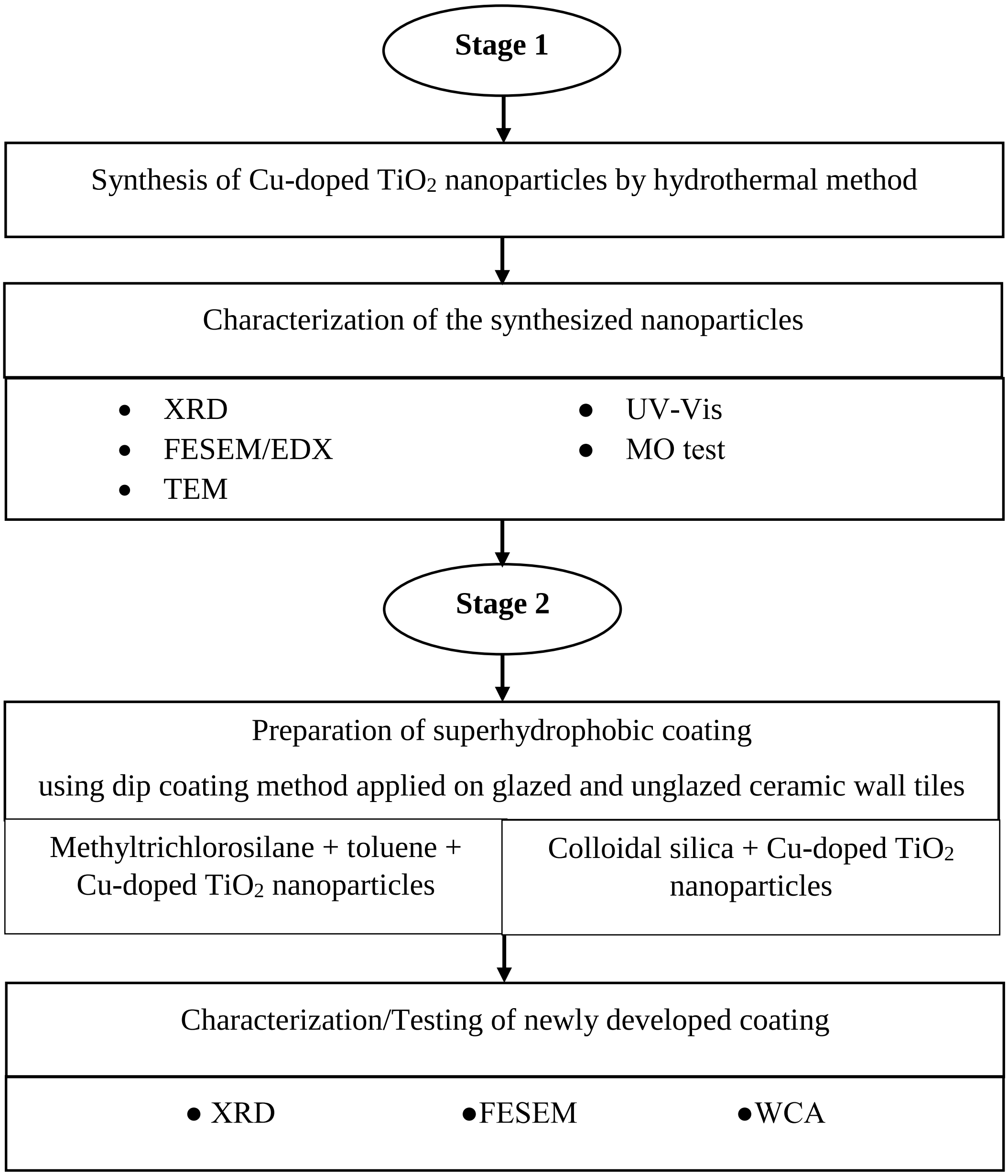


Figure 1.1 Flowchart of research work.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter is on the review of relevant literature on introduction to tiles, types of tiles and manufacturing of ceramic tiles. The fundamental of hydrophobicity and hydrophilicity was explained on how the wetting of water droplet happen. Natural and fabrication of superhydrophobic surfaces and its wetting capability were included in this chapter. The introduction of TiO_2 and its properties which are self-cleaning by TiO_2 photocatalyst, antibacterial activity and the band gap energy of the particles. Some of methods to produce TiO_2 nanoparticles such as hydrothermal, sol gel and chemical vapor deposition techniques.

2.2 Introduction to tiles

Tile is a manufactured thin slab piece that can be made up of many different materials such as ceramic, porcelain, quarry (natural stone), and marble (The Victorian Emporium, 2011). Tiles had widely been used as covering and decoration for wall, floor, roof, bathroom, kitchen and countertops (Imam, 2017). Tiles are cost effective because of hard-wearing, easy to clean, low maintenance, long lasting and cheaper for a long term investment (Tile Direct, 2015). Ceramic tiles (Figure 4.1(a)) are manufactured by mixing clay, sand and feldspar, pressed into shape and fired at high temperature in a kiln. Porcelain tiles (Figure 4.1(b)) are manufactured by mixing clay, sand and other minerals fired at high temperature (Imam, 2017). The difference between porcelain and ceramic tiles are porcelain is a type of ceramic made by the fusion of clays whereas ceramic is a semi-crystalline, amorphous and inorganic materials. The porcelain tiles were also has higher durability compared to ceramic tiles and porcelain tiles are more expensive (Sebring, 2016). Quarry tiles (Figure 4.1(c)) are manufactured by using natural stones and often referred to as an unglazed ceramic tiles due to same durability features. Natural stones tiles required only a little amount of waxing for fitting to prevent them from damage. Whereas marble tiles (Figure 4.1(d)) manufactured of two or more colours of metamorphic rocks and used to create luxurious look. Marble tiles were used to make a space look spacious because it has the ability to reflect light (Imam, 2017).

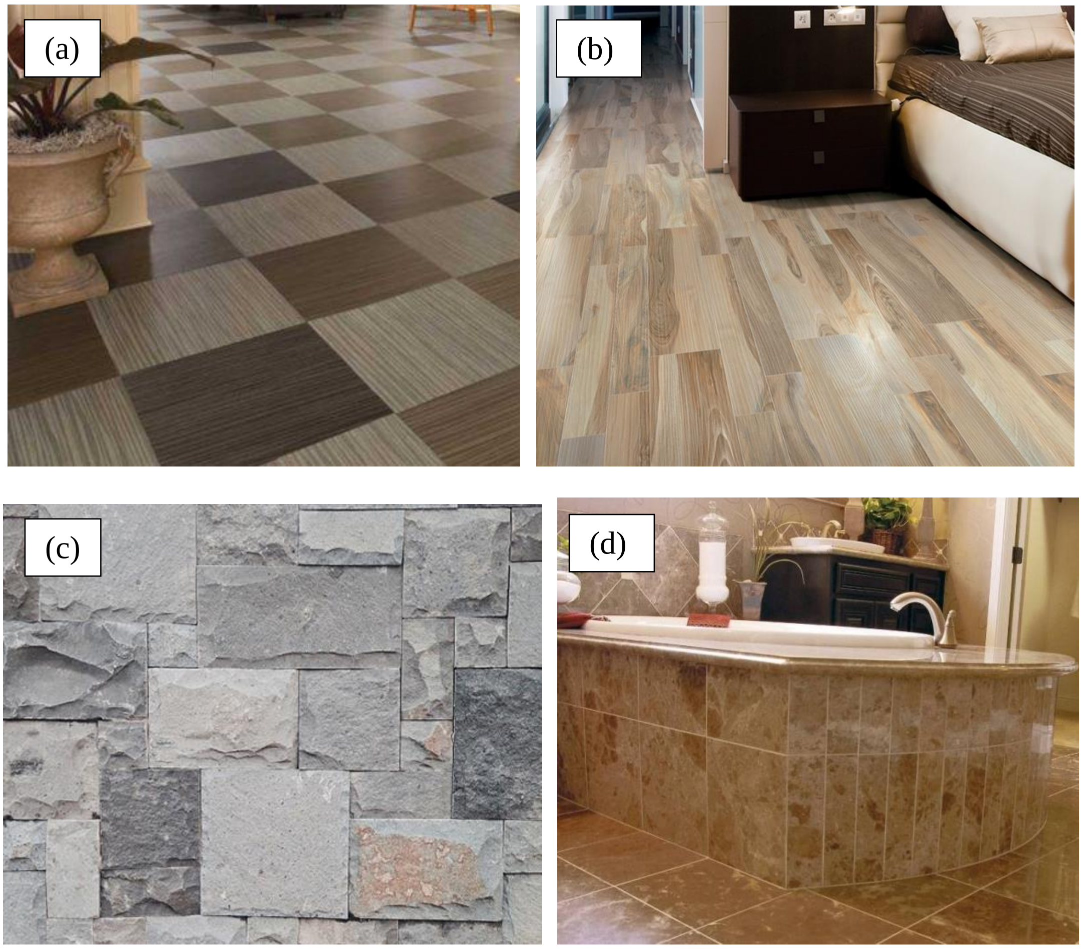


Figure 2.1 Example of (a) ceramic, (b) porcelain, (c) quarry (natural stone), and (d) marble tiles (Imam, 2017).

2.2.1 Manufacturing process of ceramic tiles

Ceramic tiles are the most popular tiles used in the living area, schools, hospitals and other places (El Nouhy, 2013). Ceramic tiles are made up of clays, feldspar and silica. Clay is the most important component of a ceramic tile body. Ball clay, china clay and bentonite are the plastic raw materials which have the plasticity properties and act as a binder when mixed with water. Ball clay has fine particles that led to high plasticity and green strength which is good for shaping. Ball clay also has thin and platey shape that led to high shrinkage and if the shrinkage is non-uniform will lead to shape deformation. Whereas china clay has coarse particles which can balance the shrinkage and minimize deformation. Flux (such as feldspar, nephtaline, and synite) and filler (such as silica and alumina) are the non-plastic raw materials which can control the firing temperature and reduce shrinkage. Then, the raw materials undergo step processing of batching, grinding, spray drying, pressing, drying, firing, then sorting and packaging as in Figure 2.1 (Ceramic Research Company, 2012).

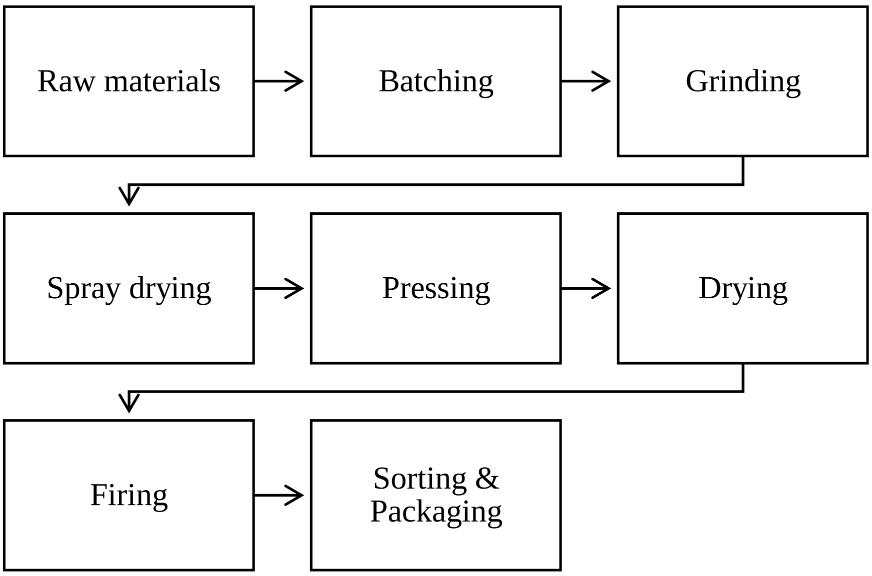


Figure 2.2 Flow of ceramic tiles manufacturing process.

The raw materials going through proportioning or batching process and undergo wet grinding where it being mixed and milled to reduce the size particle. The plastic and non-plastic raw materials were mixed to produce physically and chemically homogeneous materials. Slip was formed by adding water and deflocculant to ease dispersion. Spray drier was used for atomization to form granulated particles. Fine granulated particles can be achieved by using nozzles and sprayed towards the drying chamber. Then, the spray dried powder were pressed during the pressing stage to produce compacted piece of unfired tile using hydraulic presses with constant pressure. The compacted tiles undergo drying to increase strength and reduce deformation and avoid cracks which can happen as moisture from green body vaporized rapidly. Dried tiles will undergo firing at high temperature in a kiln to get denser and sturdier body (Ceramic Research Company, 2012). For glazed tiles, there are single, double and third firing. For single firing, dried tiles will undergo glazing which contain frits in the glazing slip before glazed firing at high temperature (1000-1100°C) in the kiln (Torrecid Group, 2018). For double firing, dried tiles will undergo bisque firing (temperature lower than glaze firing) before glazing and glaze firing make it more durable than the single firing (D'souza, 2017). For third firing, the dried tiles will undergo bisque firing, glazing, glaze firing and decoration before pattern firing at 850-1050°C (Materiali Speciali, 2013).

The difference between ceramic wall tiles and floor wall tiles is that wall tiles are high porosity, less dense and high water absorption. While, floor tiles need to be dense and more sturdier to withstand from cracks and heavy load (Bayer Ozturk and Eren Gültekin, 2014; Tarhan, Tarhan and Aydin, 2016). Floor tiles must have certain level of Coefficient of Friction (COF) to make it safe to walk which is COF of 0.5 or higher. Friction for wall tiles are not important thus it can be as slick as glass

(Wallender, 2018). Wall tiles were chosen in this study to develop the newly superhydophobic surfaces because wall tiles does not need frictions thus, the tiles surface can be covered with new coating surface. If floor tiles were chosen, the COF will be covered by the new superhydrophobic coating and people with wet feet can slip and fall.

To keep the tiles like new and minimize dirt, dust and stains, the tiles need to be cleaned often. Due to the exposure to surrounding like dirt, dust, stains and moisture that lead to the formation of moss on the tiles. In practical, detergent and other products which usually contain chemicals were used to clean the tiles. These detergents makes cleaning tiles much easier compared to the use of water alone. However, detergents contain chemicals that are harmful to the ecosystem and human health.

2.3 Impacts of detergent to ecosystem

Detergents are the most common cleaning agent that are usually used to clean tiles and remove dirt. However, the use of these detergents gives bad impact to the environment which cause water pollution due to the accumulation in organisms, resilience to biodegradation and higher solid content compared to other cleaning compound (Giagnorio *et al.*, 2017). Detergents may contain surfactants, bleaches, dyes phosphate and many more that can cause the water pollution (Nelson, 2018). Phosphate salts in the detergents can cause water pollution which contributes to the growth of algae in water. The rapid growth of algae producing massive growths or ‘bloom’ on the water surfaces and cause eutrophication. Eutrophication happen when the water surface was blocked by the algae that prevent oxygen into the water causing the death of other organisms inside the water (Bagai, 2018). Polluted algae can be harmful to fish, animals and also mankind because it is toxic (Sen *et al.*, 2013). Detergents also gives bad impact to human health. Drinking water that contaminated by detergents that contain chemicals can be toxic and hazardous to human health (Bagai, 2018). Polluted water can be dangerous to the ecosystem and also human health. Nonylphenol ethoxylates (NPEs) which is a group of surfactant petrochemical that slowly biodegrade into more toxic compounds and interfering with the fish and shellfish hormones. Sodium hypochlorite in the bleach will react with other cleaning chemical and generate chlorinated volatile organic compound (VOCs) which are very toxic and can cause cancer (Nelson, 2018). Thus, by introducing superhydrophobic coating surfaces on the tiles, it can be a lot easier to clean by only water then the used of detergent can be reduced.

2.4 Fundamental hydrophobicity and hydrophilicity

Hydrophobic and hydrophilic surfaces can be determined by the surface tension or surface energy which is a tensile or contractile force in the units of Newton per meter [N/m^2] or Joule per meter [J/m^2] which is energy per unit area. Surface tension can be caused by attractive or cohesive force between the water molecules (Ranowsky, 2016). For example, molecules that are inside a pool of liquid experiencing cohesive forces. Molecules that are surrounded by other molecules has lower energy state of water molecules. While molecules that are near the surface has higher energy state because the molecules were surrounded by half number of the other molecules. Water drops are sphere because water molecule will adjust their shape to expose the smallest possible surface area. When water droplet contact a surface it produce a spherical cap as in Figure 2.3. Surface energy between solid-liquid-vapour can be determined when liquid droplet is in contact with a solid surface. Mechanical equilibrium of the contact angle of a liquid droplet on ideal solid surface was described by Thomas Young in Equation 2.1 (Bracco and Holst, 2013).

$$\gamma_{lv} \cos \theta_E = \gamma_{sv} - \gamma_{sl} \qquad \text{Equation 2.1}$$

where the γ_{LV}, γ_{SV} and γ_{SL} represents liquid-vapor, solid-vapor and solid-liquid surface energy, respectively. While, θ_E is the equilibrium contact angle.

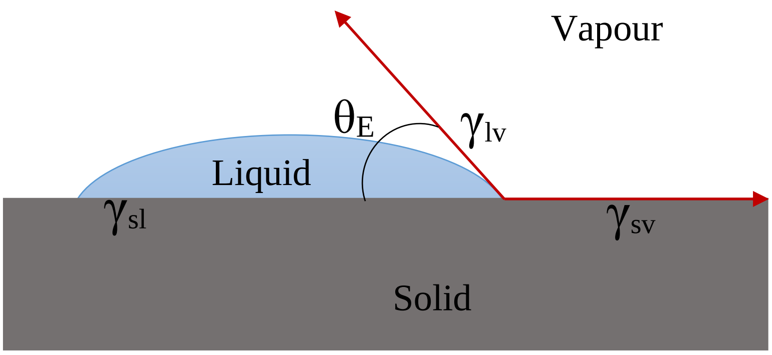


Figure 2.3 Young's contact angle of liquid droplet on an ideal solid surface.

A test that can prove a surface is superhydrophobic is by testing the wettability. Wettability is the wetting ability of a liquid to maintain in contact with a solid surface (Fuchs, 2015). Wenzel and Cassie-Baxter models has provide a framework on the effect of surface roughness on wetting and the contact angles (Ma and Hill, 2006). Wenzel model explained that there is no air bubble or air pocket underneath the liquid droplet. The liquid droplet will completely in contact to the surface (Figure 2.4 (a)). Average surface roughness is very important to determine superhydrophobicity. Young's equilibrium contact angle equation by Wenzel model can predict the contact angle of rough surface (θ_w) using Equation 2.1. Young's contact angle (θ_E) has been modified by incorporating a roughness factor (r).

$$\cos \theta_w = r \cos \theta_E \qquad \text{Equation 2.2}$$

Cassi-Baxter model explained that underneath a fluid droplet has air entrapped (air pocket) in the rough texture that forms a composite air and solid interface(Figure

2.4 (b)) (Gurav *et al.*, 2015). In this state, liquid droplet will bounce and roll-off. This is useful for water repellent and self-cleaning surfaces. The surface can be self-cleaning because any liquid that in contact to the surface will roll-off and picking up any dirt along the way. Contact angle on the rough surface (θ_{CB}) given by the Cassie-Baxter equation for wetting on composite made of solid and air (Zhang *et al.*, 2016). Equation 2.2 shows (f) as the fraction of the surface on top of the protrusions, (1-f) is the fraction of air pockets and ($\theta_{g)}$ is the contact angle on the air (Söz, Yilgör and Yilgör, 2016). Figure 2.6 shows the illustration of the wetting droplet on a superhydrophobic surfaces by Wenzel and Cassie-Baxter.

$$\text{Cos}\theta_{CB} = (f \cos\theta\ ) + (f\text{-}1) \qquad \text{Equation 2.3}$$

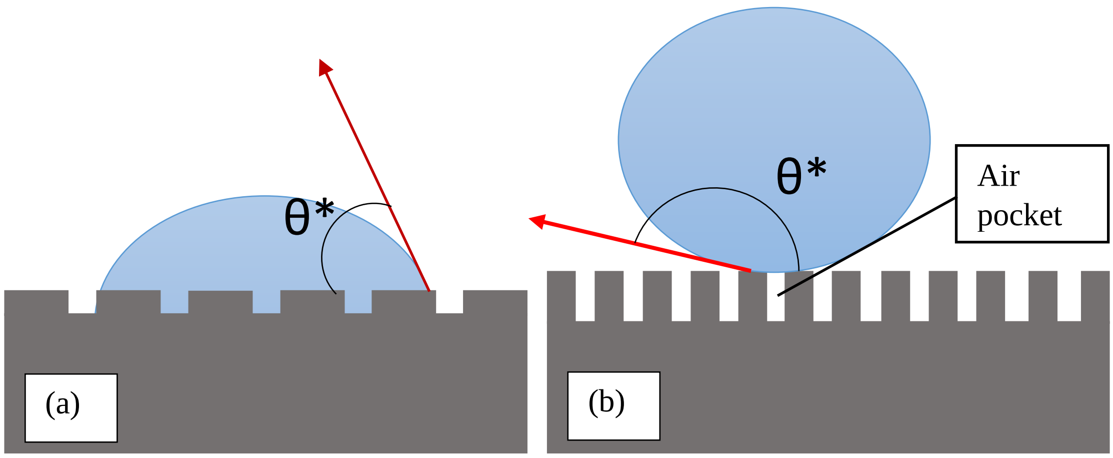


Figure 2.4 Illustration diagram of liquid droplet on a superhydrophobic surfaces by (a) Wenzel and (b) Cassie-Baxter.

In recent years, solid surfaces with both superhydrophobicity and self-cleaning functionality have become necessary because of their various valuable and promising practical applications. The valuable and promising practical applications are dust-free and self-cleaning surfaces for solar cells, in automobile windshields, micro/nano-fluidic devices, building walls and roof glass and self-cleaning windows (Gurav *et al.*, 2014).

Superhydrophobic or ultrahydrophobic is highly hydrophobic which has non-wettable surfaces with high water contact angles (WCAs) exceed 150° and facile sliding drops (Ma and Hill, 2006; Söz, Yilgör and Yilgör, 2016; Zhang *et al.*, 2016). Droplets that hit this kind of surface can fully rebound in the shape of column or bead like structure and carry away dust particles leaving a clean surface (Hikku, Jeyasubramanian and Vignesh Kumar, 2017a). Surfaces which can repel contaminants such as solid particles, organic liquids, and biological contaminants by the action of rolling-off water drops is one of the superhydrophobic fascinating properties (Zhang *et al.*, 2016). Superhydrophobic property is the requirement for a self-cleaning surface because it has a very low roll-off angle less than 10° and a very high static water contact angle greater than 150° (Zhang *et al.*, 2016). The two main properties of superhydrophobic surfaces are surface roughness and low surface energy (Gurav *et al.*, 2014, 2015; Wang *et al.*, 2014; Zhang *et al.*, 2016). Based on Law (2014), hydrophobic means when the static water contact angle, θ is more than 90° and hydrophilic is when the θ is less than 90°. The differences of superhydrophobic, hydrophobic, hydrophilic and superhydrophilic can be seen from the Figure 2.5.

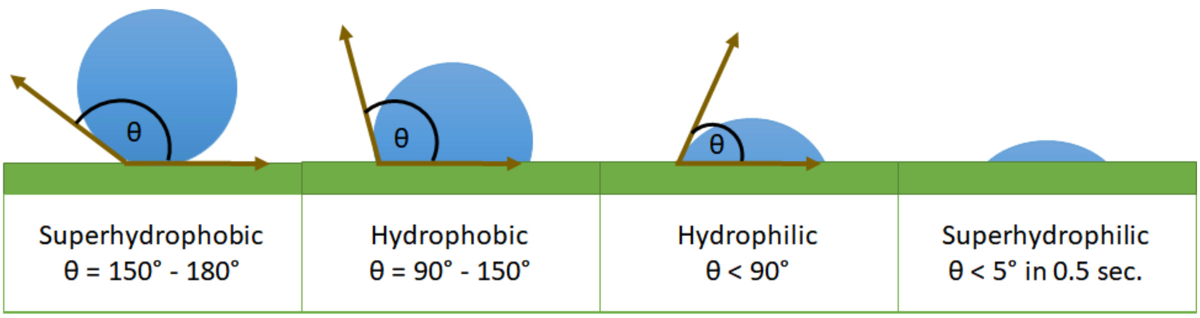


Figure 2.5 Schematic diagram of macroscopic contact angle of water droplet on super-hydrophobic, hydrophobic, hydrophilic and superhydrophilic surfaces.

2.4.1 Natural superhydrophobic surfaces

Many surfaces in nature are highly hydrophobic and self-cleaning including plants and animals (Ma and Hill, 2006). Examples of a hydrophobic self-cleaning surface including the wings of butterflies, fish scales, mosquito eyes, rice leaves, and the best known example is the leaves of lotus plant which is known as “Lotus effect”. Lotus leaves are the best known natural superhydrophobic and self-cleaning phenomenon. They revealed their efficient self-cleaning ability which the water droplets will form nearly spherical drops and immediately roll off carrying away any dust particles when the water droplet contact the leaf surface (Gurav *et al.*, 2014; Wang *et al.*, 2014; Zhang *et al.*, 2016).

The presence of multi-scale roughness, low energy waxes and the nanoscale hair-like structure as in Figure 2.6 are responsible to the superhydrophobic and self-cleaning properties of the lotus leaf surfaces (Zhang, et al., 2016). The protruding nubs on the lotus leaves showed that it was 20-40 µm apart each covered with a smaller scale roughed surface of epicuticular wax crystalloids (Ma and Hill, 2006). The combination of the micro/nano-scale patterned structures and low surface energy which keep the lotus leaf clean and dry even in dirty water (Gurav *et al.*, 2014).

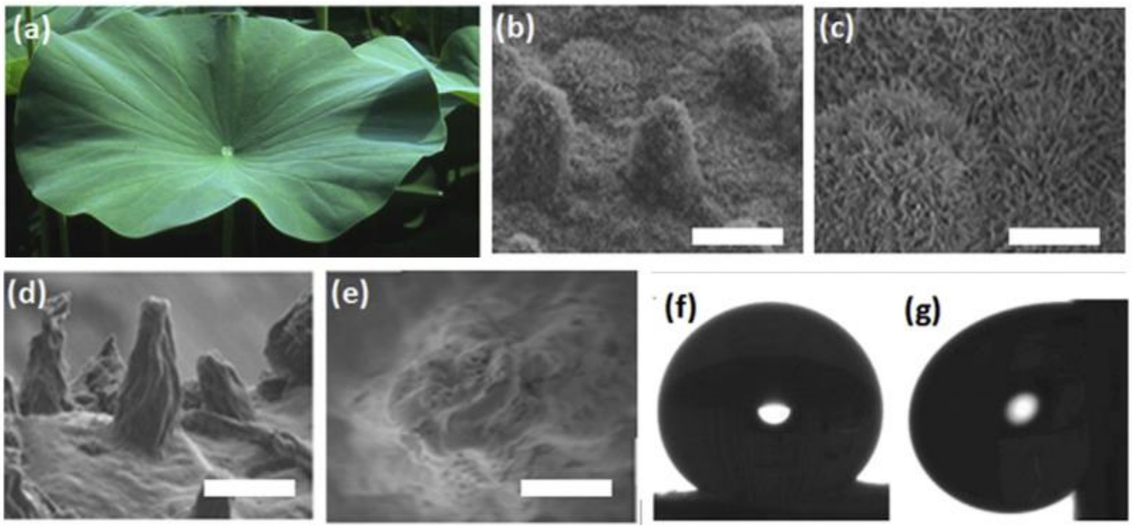


Figure 2.6 Image and SEM images of lotus leaf surface. (a) A fresh lotus leaf in nature, (b) the micro-structure of lotus leaf, (c) the nanostructure of lotus leaf (d) the micro-structure of annealed lotus leaf (e) the nanostructure of annealed lotus leaf (f) a droplet placed on an untreated lotus leaf, and (g) a droplet placed on an annealed lotus leaf, then, tilted to an angle of 90° (Zhang *et al.*, 2016).

2.4.2 Fabrication superhydrophobic surfaces

Nowadays, superhydrophobic coating have been gaining attraction with their amazing properties which can repel water with its water contact angle more than 150° and have low surface energy (Ma and Hill, 2006). Studies on the natural plant leaves shows that the surface morphologies is an important properties for constructing superhydrophobic surfaces with hierarchal unitary structure. Thus, many researchers are attempted to duplicate the superhydrophobic and self-cleaning system inspired by the nature (Mahadik *et al.*, 2013; Gurav *et al.*, 2014; Niu and Kang, 2018; Zhao, Hu and Zhang, 2018). New superhydrophobic surface has been developed on a lot of material surfaces such as glass, quartz, metal, utensils and many more using various coating method such as dip-coating, spray-coating, spin-coating. Many researchers used materials such as SiO_2, ZnO and TiO_2 particles to create surface roughness. However, SiO_2 and ZnO does not give photocatalytic properties that can degrade organic pollutants while TiO_2, although it has photocatalytic properties, it does not give optimum function due to larger band gap energy. In this study, Cu-doped TiO_2 were used to create surface roughness and to provide better photocatalytic activity due to the doping with copper that lower the band gap energy. Also, silane-based material such as methyltrichlorosilane (MTCS), polydimethylsiloxane (PDMS) and methyltrimethoxysilane (MTMS) had been widely used as binder to adhere particles on the surface and provide low wettability (Ma and Hill, 2006; Mahadik *et al.*, 2013; Gurav *et al.*, 2014).

2.4.2.1 Dip-coating method

Gurav, et al (2015) and Mahadik *et al.* (2013) have developed superhydrophobic surfaces from silica coating using simple dip-coating method (Figure 2.7) and applied it on a glass and quartz substrates. From their studies, increasing the dipping steps allows a larger number of silica particles to assemble gradually on the substrate surface and using double step sol-gel route able to produce a rough surface morphology. The water contact angle reached 153° ± 2° and roll-off angle of 8° ± 1° for the silica coating prepared after three dips while for sol-gel coating water contact angle reached 168° ± 2° and roll-off angle of 3° ± 1°, indicating the formation of a superhydrophobic surface (Mahadik *et al.*, 2013; Gurav *et al.*, 2015).

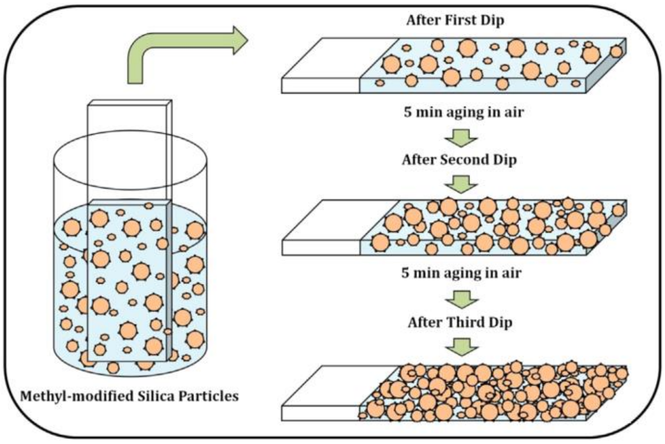


Figure 2.7 Schematic diagram showing simple dip-coating process for deposition of methyl-modified silica particles on glass substrate (Gurav, et al., 2015).

2.4.2.2 Spray coating method

Zhao, Hu and Zhang, (2018) have developed superhydrophobic coating using spray coating method prepared from wax suspensions and annealed at 40°. Spray coating was performed with nozzles and pressure to produce continuous flow of droplets. Spray processes can improve the coating quality by having higher density due to greater particle impact velocities. Thus, create robust, harder and high hardness coating. From their study, the water contact angle achieved is 158.2° and 7.3° sliding angle.

2.4.2.3 Spin Coating

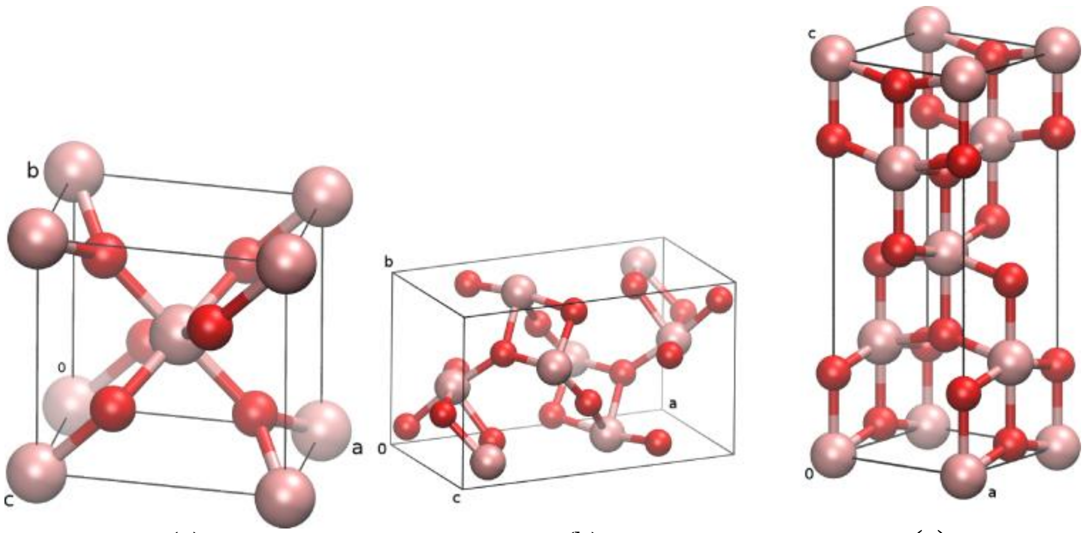
Söz, Yilgör and Yilgör, (2016) have developed a superhydrophobic coating from polymer based materials (polystyrene/hydrophobic silica dispersed in toluene and epoxy resin/hydrophobic silica dispersed in methylene chloride) using spin coating that applied on glass substrate. Spin coating technique require a spin coater machine (Figure 2.8) to develop the coating. Substrates were taped on the machine and performed while spinning. Spin coating can produce uniform coating and the thickness can be controlled.

From their studies, a few drops of silica dispersion was placed on the substrate and performed at 1000 rpm for 1 min. The samples were then dried and cured at room temperature and 150°C, respectively. They obtained robust and durable coated surface with static water contact angle above 150° and contact angle hysteresis value lower than 10° (Söz, Yilgör and Yilgör, 2016).

Figure 2.8 Spin coater machine

2.5 Introduction to TiO_2

TiO_2 has attracted considerable attention due to its interesting properties, such as chemical inertness, non-toxicity, high refractive index, low cost, and unique electrical and optical properties (Zanganeh *et al.*, 2011). There are three main phases of crystallized TiO_2 including Anatase, Rutile, and Brookite (Figure 2.9) (Moellmann *et al.*, 2012; Malekshahi Byranvand *et al.*, 2013). Anatase has crystalline structure with tetragonal system (with dipyramidal habit). Rutile has tetragonal crystal structure with prismatic habit. While, brookite has orthorhombic crystal structure. These main phases can be understood with (TiO_6^{2-}) octahedral terms differing by the distortion and connectivity of the octahedral chains (Moellmann *et al.*, 2012). Anatase showing a greater photocatalytic activity than the other types of TiO_2 polymorph because it has wider band gap energy ~3.2 eV (De Niederhãusern, Bondi and Bondioli, 2013; Miljevi *et al.*, 2017).



(a) (b) (c)

Figure 2.9 Unit cells of TiO_2 phases (a) rutile, (b) brookite and (c) anatase (Moellmann *et al.*, 2012).

2.5.1 Methods to produce TiO_2 nanoparticles

Morphologies of TiO_2 nanostructures can be affected from the method used to produce them. Several methods can be used to produce TiO_2 powder such as hydrothermal method, sol-gel, solvothermal, and many more (Askari, et al., 2017).

2.5.2.1 Hydrothermal method

In this study, hydrothermal method had been used to synthesize the nanostructures powder of Cu-doped TiO_2. Copper oxide (CuO) nanomaterials are effective in inhibiting bacterial activity (Ananth *et al.*, 2015; Hikku, Jeyasubramanian and Vignesh Kumar, 2017a; Lin *et al.*, 2017) and titanium dioxide (TiO_2) nanomaterials are effective in self-cleaning and photodegradation properties . From the previous studies done by Razali *et al.*, 2014, it was found that introducing metal ion to the TiO_2 able to increase the photocatalytic activity with Cu^{2+} showed the highest degradation of 98.82% compared to Ni^{2+} and Co^{2+} with 96.14% and 95.12% respectively (Razali *et al.*, 2014a).

Hydrothermal technique is one of the most important method in synthesizing nanostructured materials due to of their advantages in processing which has appropriate crystallization temperature, controllability o reaction conditions, environment friendly, low consumption and low cost (Zanganeh *et al.*, 2011). Hydrothermal can be defined as any heterogeneous reaction in the presence of aqueous solvents to recrystallize or recover materials that are relatively insoluble under ordinary conditions and it must be carried out in controlled temperature and pressure and closed system (Razali *et al.*, 2014b). Hydrothermal reaction usually performed in a closed steel pressure vessels called autoclaves with or without Teflon vessels. By using the hydrothermal technique it is possible to grow nanostructured metal oxides as the activating agent sodium hydroxide (NaOH) solvent enhanced the decomposition of starting material, thereby creating distinctive difference in their characteristics at nano-scale level (Zanganeh *et al.*, 2011; Murali and Perumal, 2018).

2.5.2.2 Sol-gel method

Sol-gel method can be used to make various ceramic materials. The colloidal suspension can be called sol, are usually inorganic metal salts or metal organic compound formed from hydrolysis and polymerization reactions of the precursors. Ultrafine and uniform TiO_2 powders are formed through precipitation, emulsion technique or spray pyrolysis. Nanostructed TiO_2 and highly crystalline anatase TiO_2 in different sizes and shapes can be obtained. This technique is relatively cheap and low temperature technique allow fine control on chemical composition (Vijayalakshmi and Rajendran, 2012)

2.5.2.3 Solvothermal method

Solvothermal is almost the same with hydrothermal except that they used nonaquoeous solvent while hydrothermal used water as solvent and solvothermal has higher elevated temperature since the organic solvents with high boiling point can be chosen. Solvothermal has better control of the size, shape distribution and crystallinity of TiO_2. This method can be used to produce nanoparticles, thin film, bulk powders and single crystal TiO_2 (Vijayalakshmi and Rajendran, 2012)

2.5.2 TiO_2 particles properties

TiO_2 has the ability to oxidize and decompose organic and inorganic materials or pollutants. Reactive oxygen species (ROS) like $O_2^{\bullet -}$, H_2O_2 and HO● (which are harmful) are produced on the TiO_2 surface when illuminated by photons with energy greater than its band gap. The irradiated TiO_2 photocatalyst can decompose and mineralize organic compounds by oxidation reaction and produce harmless gas of carbon dioxide (CO_2). As in Figure 2.10, electron from the valence band (VB) will be excited to the conduction band (CB) thus creating electron and hole pairs. Holes (h+) and hydroxyl radicals (OH●) will be generated in the valence band due to oxidation of water (H_2O) and electrons (e^-) and anions ($O_2^{\bullet -}$) will be generated in the conduction band due to reduction of oxygen (O_2) (Haider, AL– Anbari, *et al.*, 2017). Studies have proved that TiO_2 nanostructures have better performance compared to other forms of TiO_2 for the photocatalytic degradation (Zanganeh *et al.*, 2011; Razali *et al.*, 2014b; Haider, Al-Anbari, *et al.*, 2017).

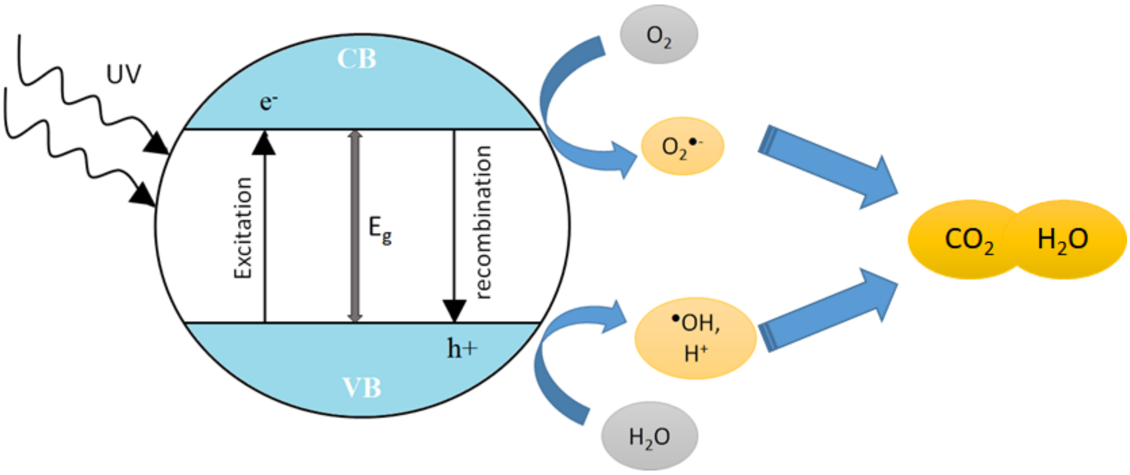


Figure 2.10 Mechanism of electron-hole pair formation in TiO_2 particle.

Narrow band gap is very crucial for TiO_2 applications to conduct efficient photocatalytic activity. However, anatase, rutile and brookite has wider band gap larger than ~3.0 eV. Attempt to reduce the band gap is by increase its absorption of visible light. One of the approach is by doping the TiO_2 material with metal or non-metal impurities which can reduce the carrier recombination centers. Hexagonal phase of TiO_2 possess much smaller band gap energy of 1.7 eV. This hexagonal phase TiO_2 has crystal structure of metastable TiO_2 layers that is similar to the graphite (Lu *et al.*, 2011). Thus, the purpose of doping Cu metal ion is to narrow the anatase TiO_2 band gap energy then transform it to hexagonal phase TiO_2.

Utilizing metal oxide nanostructures also possess photocatalytic and antibacterial property (Hikku, Jeyasubramanian and Vignesh Kumar, 2017b). TiO_2 coating has excellent self-cleaning property from the redox reaction of photocatalyst surface. Thus, inorganic dirt and stains on the surface can be easily removed as it soaked with water (Haider, Al-Anbari, *et al.*, 2017). Developing coating with antibacterial property by adding inorganic material such as Copper Oxide (CuO) (Ananth *et al.*, 2015), Zinc Oxide (ZnO) (Lin *et al.*, 2017), Iron Oxide (Fe_2O_3) and