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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Dissertation submitted in partial fulfilment of the requirements for the degree of Bachelor of Engineering with Honours (Materials Engineering)

Universiti Sains Malaysia
JUNE 2018
DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled “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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Date : 25$^{th}$ June 2018

Witness by

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LIST OF SYMBOLS

° Degree
°C Degree Celsius
N/m² Newton per meter
J/m² Joule per meter
γlv Liquid-Vapour Surface Energy
θE Equilibrium Contact Angle
γsv Solid-Vapour Surface Energy
γsl Solid-Liquid Surface Energy
θw Contact Angle of Rough Surface by Wenzel
θCB 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**

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<thead>
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<td>NPEs</td>
<td>Nonylphenol Ethoxylates</td>
</tr>
<tr>
<td>VOCs</td>
<td>Volatile Organic Compounds</td>
</tr>
<tr>
<td>WCA</td>
<td>Water Contact Angle</td>
</tr>
<tr>
<td>Cu-doped TiO₂</td>
<td>Copper doped Titania</td>
</tr>
<tr>
<td>TiO₂</td>
<td>Titania</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray Powder Diffraction</td>
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<td>FESEM</td>
<td>Field Emission Scanning Electron Microscopy</td>
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<td>EDX</td>
<td>Energy Dispersive X-Ray</td>
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<td>TEM</td>
<td>Transmission Electron Microscopy</td>
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<td>UV-vis</td>
<td>Ultraviolet Visible Spectroscopy</td>
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<tr>
<td>UV-DRS</td>
<td>Ultraviolet Diffuse Reflectance Spectroscopy</td>
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<td>MO</td>
<td>Methyl Orange</td>
</tr>
<tr>
<td>COF</td>
<td>Coefficient of Friction</td>
</tr>
<tr>
<td>CuO</td>
<td>Copper Oxide</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>Copper ion</td>
</tr>
<tr>
<td>Ni²⁺</td>
<td>Nickel ion</td>
</tr>
<tr>
<td>Co²⁺</td>
<td>Cobalt</td>
</tr>
<tr>
<td>NaOH</td>
<td>Sodium Hydroxide</td>
</tr>
<tr>
<td>ROS</td>
<td>Reactive Oxygen Species</td>
</tr>
<tr>
<td>O²⁻</td>
<td>Anions</td>
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<tr>
<td>H₂O₂</td>
<td>Hydrogen Peroxide</td>
</tr>
<tr>
<td>HO●</td>
<td>Hydroxyl Radical</td>
</tr>
<tr>
<td>CO₂</td>
<td>Carbon Dioxide</td>
</tr>
<tr>
<td>VB</td>
<td>Valence Band</td>
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<tr>
<td>CB</td>
<td>Conduction Band</td>
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<td>h⁺</td>
<td>Holes</td>
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<tr>
<td>e⁻</td>
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<td>H₂O</td>
<td>Water</td>
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<td>O₂</td>
<td>oxygen</td>
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<td>Cu</td>
<td>Copper</td>
</tr>
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<td>Abbreviation</td>
<td>Description</td>
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</tr>
<tr>
<td>HAIs</td>
<td>Healthcare Associated Infections</td>
</tr>
<tr>
<td>HCl</td>
<td>Hydrochloric Acid</td>
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<tr>
<td>MTCS</td>
<td>Methyltrichlorosilane</td>
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<tr>
<td>LiOH</td>
<td>Lithium Hydroxide</td>
</tr>
<tr>
<td>atm</td>
<td>Atmospheric pressure</td>
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<tr>
<td>ICDD</td>
<td>International Centre for Diffraction Data</td>
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PERHATIAN PERMUKAAN SUPERHIROFOBIK DAN PEMBERSIHAN
DIRI MENGGUNAKAN ZARAH Cu-doped TiO₂ BAGI JUBIN DINDING
SERAMIKN

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 TiO₂) tiub nano telah menjalani sintesis menggunakan kaedah hidroterm untuk di gunakan bersama bahan salutan. Penambahan Cu-dop TiO₂ tiub nano adalah untuk mewujudkan permukaan kasar dan bertindak sebagai 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 TiO₂ tiub nano di atas jubin dinding seramik (licau dan tidak licau) substrat. Cu-dop TiO₂ 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 TiO₂ tiub nano didedahkan sebagai permukaan hidrofilik akibat daripada kekasaran permukaan yang rendah dan tenaga permukaan yang tinggi (57.88 ± 0.03 J/m²) serta sudut sentuh air yang rendah iaitu 42.73° ± 0.06. Sementara itu, lapisan bahan silana yang diperbuat daripada methyltrichlorosilane (MTCS), toluena dan Cu-dop TiO₂ tiub nano didedahkan sebagai permukaan superhidrofobik kerana kekasaran permukaan yang tinggi dan tenaga permukaan yang rendah (0.00 J/m²) serta sudut sentuh air yang tinggi hingga 153.96°. Oleh itu, salutan berasaskan silana dipilih sebagai pelarut terbaik untuk mendepositkan TiO₂ tiub nano pada jubin dinding untuk menghasilkan 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\textsuperscript{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,
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

![Flowchart of research work.](image-url)

**Stage 1**

Synthesis of Cu-doped TiO$_2$ nanoparticles by hydrothermal method

Characterization of the synthesized nanoparticles

- XRD
- FESEM/EDX
- TEM
- UV-Vis
- MO test

**Stage 2**

Preparation of superhydrophobic coating using dip coating method applied on glazed and unglazed ceramic wall tiles

Methyltrichlorosilane + toluene + Cu-doped TiO$_2$ nanoparticles

Colloidal silica + Cu-doped TiO$_2$ nanoparticles

Characterization/Testing of newly developed coating

- XRD
- FESEM
- WCA

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](image1.png)

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).

![Diagram of ceramic tiles manufacturing process](image)

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 $[\text{N/m}^2]$ or Joule per meter $[\text{J/m}^2]$ 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).
\[ \gamma_{lv} \cos \theta_E = \gamma_{sv} - \gamma_{sl} \]  \hspace{1cm} \text{Equation 2.1}

where the \( \gamma_{lv} \), \( \gamma_{sv} \) and \( \gamma_{sl} \) represents liquid-vapor, solid-vapor and solid-liquid surface energy, respectively. While, \( \theta_E \) is the equilibrium contact angle.

![Diagram of Young's contact angle](image)

**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 have provided 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 with 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 (\( \theta_w \)) using Equation 2.1. Young’s contact angle (\( \theta_E \)) has been modified by incorporating a roughness factor (\( r \)).

\[ \cos \theta_w = r \cos \theta_E \]  \hspace{1cm} \text{Equation 2.2}

Cassie-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
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 ($\theta_{CB}$) 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.

\[
\cos \theta_{CB} = (f \cos \theta_g) + (f-1)
\]  

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 TiO₂

TiO₂ 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 TiO₂ 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 \((\text{TiO}_6^{2-})\) 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 Niederhäusern, Bondi and Bondioli, 2013; Miljevi
et al., 2017).

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 of 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. Nanostructured 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 nonaqueous 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 TiO₂. This method can be used to produce nanoparticles, thin film, bulk powders and single crystal TiO₂ (Vijayalakshmi and Rajendran, 2012)

2.5.2 TiO₂ particles properties

TiO₂ has the ability to oxidize and decompose organic and inorganic materials or pollutants. Reactive oxygen species (ROS) like O₂●⁻, H₂O₂ and HO● (which are harmful) are produced on the TiO₂ surface when illuminated by photons with energy greater than its band gap. The irradiated TiO₂ photocatalyst can decompose and mineralize organic compounds by oxidation reaction and produce harmless gas of carbon dioxide (CO₂). 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 (H₂O) and electrons (e⁻) and anions (O₂●⁻) will be generated in the conduction band due to reduction of oxygen (O₂) (Haider, AL– Anbari, et al., 2017). Studies have proved that TiO₂ nanostructures have better performance compared to other forms of TiO₂ for the photocatalytic degradation (Zanganeh et al., 2011; Razali et al., 2014b; Haider, Al-Anbari, et al., 2017).
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 $\sim$3.0 eV. Attempt to reduce the band gap is by increase its absorption of visible light. One of the approach is by doping the TiO$_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$_2$O$_3$) and
Cerium Oxide (CeO$_2$) (Shu et al., 2017) can reduce the spreading of bacteria, viruses, fungi, and the risk of healthcare associated infections (HAIs) from places that need hygiene conditions especially hospitals, kitchen, bathroom and other locations where bacterial population is high. There are many other materials that employ the use of photocatalytic and anti-bacterial properties but based on Hikku, Jeyasubramanian and Vignesh Kumar (2017), less studies have discussed about both properties. Some of it are mixture of nano TiO$_2$ and ZnO particles in aqueous acrylic interior paints which have multi-functional properties (Hochmannova and Vytrasova, 2010), and magnesium oxide alone possessing both photocatalytic and anti-microbial properties (Hikku, Jeyasubramanian and Vignesh Kumar, 2017b).
CHAPTER 3

MATERIALS AND METHODOLOGY

3.1 Introduction

This chapter provides detailed descriptions on the preparation of superhydrophobic coating and characterization study. Generally, this chapter can be divided into three main sections. The raw materials and preparation for synthesis of Cu-Doped TiO$_2$ nanopowders will be discussed in Section 3.2 while Section 3.3 and Section 3.4 in this chapter focused on the development of superhydrophobic coating and characterization techniques that were performed in this study. Figure 3.1 and Figure 3.2 summarized the experiments involved in this study; Stage 1: involve the synthesis of Cu-Doped TiO$_2$ nanopowders by hydrothermal method followed by the characterization of the calcined Cu-Doped TiO$_2$ nanopowders; Stage 2: is the development of superhydrophobic coating by dip coating method and finally the characterization of newly develop superhydrophobic coating in terms of physical and chemical properties.

Basically, several characterization techniques were used to characterize calcined nanopowders and superhydrophobic coating such as X-Ray Diffraction analysis (XRD), Field Emission Scanning Electron Microscopy Energy (FESEM), Energy Dispersive X-ray (EDX) analyser, Transmission Electron Microscopy (TEM), Ultraviolet-visible Spectroscopy or Ultraviolet-Diffuse Reflectance Spectroscopy (UV-vis/UV-DRS), Methyl Orange (MO) Test and Water Contact Angle (WCA) Test.
Figure 3.1 Flowchart for the synthesis of Cu-doped TiO₂ nanoparticles.
Figure 3.2 Flowchart for the preparation of superhydrophobic coating.

**Preparation of superhydrophobic coating**

- **Stage 2**

**Silica coating + Cu-doped TiO$_2$**
- Tiles were sterile with acetone, 70% ethanol, soap and distilled water
- A solution of 1 g Cu-doped TiO$_2$ with 100 ml toluene was prepared and ultrasonicated for 1 h
- 0.6 ml MTCS were added in the solution and further sonicated for 3 h
- A cleaned tile was dipped into the mixture for 5 s and let dry at room temperature (repeat for 3 and 5 dipping cycle)
- Cured at 70°C for 3 h and annealed at

**Colloidal silica + Cu-doped TiO$_2$**
- Tiles were sterile with acetone, 70% ethanol, soap and distilled water
- A solution of 20 ml LUDOX-AS40 with 1 g Cu-doped TiO$_2$ nanopowder was prepared
- A cleaned tile was dipped into the mixture for 5 s and let dry at room temperature (repeat for 3 and 5 dipping cycle)
- Cured at 60°C for 3 h

**Characterization/Testing**
- Field Emission Scanning Electron Microscopy (FESEM)
- X-ray Diffraction (XRD)
- WCA Test
3.2 Synthesis of Cu-Doped TiO$_2$ nanopowders by hydrothermal method

3.2.1 Raw Materials

General information of raw materials and chemicals used for the synthesis of Cu-doped TiO$_2$ are summarized in Table 3.1.

Table 3.1. List of raw materials and chemicals for synthesis of Cu-doped TiO$_2$.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Chemical Formula</th>
<th>Function</th>
<th>Source</th>
<th>Purity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titanium Dioxide powder</td>
<td>TiO$_2$</td>
<td>Precursor</td>
<td>Merck</td>
<td>99.0</td>
</tr>
<tr>
<td>Sodium Hydroxide</td>
<td>NaOH</td>
<td>Solvent to extract Cu-Doped TiO$_2$</td>
<td>Merck</td>
<td>99.0</td>
</tr>
<tr>
<td>Hydrochloric Acid</td>
<td>HCl</td>
<td>Cleaning agent</td>
<td>Merck</td>
<td>99.0</td>
</tr>
<tr>
<td>Cupric Nitrate Trihydrate</td>
<td>Cu(NO$_3$)$_2$.3H$_2$O</td>
<td>Source of Cu$^{2+}$ dopant</td>
<td>Merck</td>
<td>99.5</td>
</tr>
</tbody>
</table>

3.2.2 Preparation of Cu-Doped TiO$_2$ nanopowders

All chemical and solvents were used as received without further purification. Commercial titanium dioxide (TiO$_2$) powder were used as precursor. Sodium Hydroxide (NaOH) pellet were diluted in distilled water to obtain 10 M NaOH aqueous solutions. Hydrochloric acid (HCl, 37% solution in water) was diluted in distilled water to obtain 0.1 M HCl aqueous solutions. Cupric nitrate trihydrate [Cu(NO$_3$)$_2$.3H$_2$O] precursor was used as source of Cu$^{2+}$ metal ion dopant. In this study, the technique used to produce Cu-doped TiO$_2$ was adopted from the previous study of research group Razali, Ahmad-Fauzi, Mohamed, & Sreekantan, (2014).
Cu-doped TiO₂ nanopowders were prepared by in-situ doping using hydrothermal method. Hydrothermal synthesis is a method that is able to grow single crystals materials by mixing the starting material in aqueous solvent like NaOH and LiOH, and undergo treatment in closed system autoclave (with a thick wall steel vessel) at high temperature and pressure (Royal Society of Chemistry, 2018). Hydrothermal method was used due to their appropriate crystallization temperature, able to synthesize large crystal, controllability of reaction condition, environment friendly and low energy consumption. This method had been used by many researchers to produce nanostructured material such as TiO₂ and ZnO (Zanganeh et al., 2011; Vijayalakshmi and Rajendran, 2012; Kavitha, Gopinathan and Pandi, 2013).

Figure 3.3 Autoclave machine for hydrothermal synthesis.
In this study, Cu-doped TiO$_2$ was prepared by mixing 2 g of the commercial TiO$_2$ powder in 100 mL aqueous solution consists of 10 M NaOH and 0.25 mmol Cu(NO$_3$)$_2$·3H$_2$O. The mixture was stirred for 30 minutes to obtain homogeneous solution. Then, the solution was transferred into Teflon vessel and subjected to hydrothermal treatment at 150°C for 24 hours in an autoclave. When the reaction was completed, the solid precipitate were collected and washed with 0.1 M HCl (200 mL) followed by distilled water until pH 7 of washing solution was obtained. The final products were obtained by the filtration and subsequent drying in the oven for 24 hours at 80°C. The sample was calcined at 300°C for 2 hours to produce Copper-doped titania (Cu-doped TiO$_2$) nanopowders. Figure 3.3 showed the Cu-doped TiO$_2$ nanopowders synthesis flow. Calcination was performed in air pressure (atm) following the heat treatment profile shown in Figure 3.4.
Figure 3.4 Flow of Cu-doped TiO\textsubscript{2} nanopowders synthesis.

Figure 3.5 Heat treatment profile for calcination of Cu-doped TiO\textsubscript{2} nanoparticleless.
3.3 Development of Superhydrophobic Coating

3.3.1 Raw Materials

General information of raw materials used to create coating surface on wall tiles are shown in Table 3.2.

Table 3.2: Raw materials for the coating solution.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Chemical Formula</th>
<th>Function</th>
<th>Source</th>
<th>Purity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wall tiles</td>
<td>-</td>
<td>Substrate</td>
<td>Ceramic Research Company (CRC)</td>
<td>-</td>
</tr>
<tr>
<td>Copper-doped titania</td>
<td>Cu-doped TiO₂</td>
<td>Self-cleaning and antibacterial agent</td>
<td>In-house synthesized powders</td>
<td>-</td>
</tr>
<tr>
<td>Methyltrichlorosilane (MTCS)</td>
<td>CH₃Cl₃Si</td>
<td>Precursor silane based</td>
<td>Fluka</td>
<td>97.0</td>
</tr>
<tr>
<td>Toluene (anhydrous)</td>
<td>C₆H₅CH₃</td>
<td>Solvent</td>
<td>J.T.baker</td>
<td>98.8</td>
</tr>
<tr>
<td>Ludox AS-40 colloidal silica 40 wt % suspension in H₂O</td>
<td>SiO₂</td>
<td>Solvent to create superhydrophobic surface</td>
<td>Aldrich</td>
<td>99.0</td>
</tr>
<tr>
<td>Acetone</td>
<td>C₃H₆O</td>
<td>Cleaning agent</td>
<td>J.T.baker</td>
<td>99.0</td>
</tr>
<tr>
<td>Ethanol 90%</td>
<td>C₂H₅O</td>
<td>Cleaning agent</td>
<td>J.T.baker</td>
<td>99.0</td>
</tr>
</tbody>
</table>
3.3.2 Preparation of superhydrophobic silica coating

Silicon dioxide particles, Methyltrichlorosilane (MTCS), Toluene (anhydrous), Ludox AS-40 colloidal, acetone and ethanol were used as received without any further purification. The glazed and unglazed wall tiles were provided by the Ceramic Research Company (CRC), Malaysia.

Prior to coating, the glazed and unglazed wall tiles were cleaned thoroughly by sequential rinsing with acetone, ethanol, soap and water to remove surface contaminants such as dirt and dust. Then, the tiles were dried at 60°C in oven for 30 minutes. Coating were performed using a simple dip-coating method at room temperature (~27°C).

Cu-doped TiO$_2$ nanotubes were added into binder

Stir

Binder:
1. Ludox AS-40 (Colloidal silica)
2. MTCS + toluene

Cleaned ceramic wall tiles were dip into the coating solution with dipping cycle 0, 1, 3, and 5

Ceramic tiles:
1. Glazed
2. Unglazed

Coated tiles were cured (80°C, 3 h) and annealed (150°C, 5 h)
3.3.2.1 Preparation of colloidal silica coating

1 g of Cu-Doped TiO$_2$ nanopowders were dispersed in a 20 ml Ludox AS-40 and stirred for 30 minutes. A well-cleaned wall tiles was dipped into the coating solution for 5 s and then withdrawn at a constant speed of ~5 mm/s after that, kept in air at room temperature for 5 min. The same coating procedure were repeated with 3 and 5 dipping cycle on glazed and unglazed wall tiles under a fixed condition with the same sample to obtain a uniform and rough-textured coating. The coated tiles were finally cured at 80°C for 3 h to stabilize the coatings.

![Figure 3.6 Flow process of colloidal silica coating.](image)

Characterized using XRD and SEM
3.3.2.2 Preparation of methyl modified Cu-doped TiO$_2$ nanoparticles coating

1 g of Cu-doped TiO$_2$ nanopowder were dispersed in 100 ml of toluene and ultrasonicated for 1 h. Next, 3 ml of MTCS were added slowly to this mixture, which again ultrasonicated for another 3 h to obtain homogenous solution. The coatings were prepared using a simple dip-coating method at room temperature (~27 °C). A well-cleaned wall tile was dipped into the coating solution for 5 s and then withdrawn at a constant speed of ~5 mm/s after that, kept in air at room temperature for 5 min. The same coating procedure were repeated with 3 and 5 dipping cycle on glazed and unglazed wall tiles under a fixed condition. The coated tiles were cured at 80°C in the oven for 1 hour and further annealed at 150°C for 5 hours at 2°C/min. Toluene is a solvent which can be used to dissolve many organic compound but it is toxic. Thus, 150°C temperature for the annealing was used in order to decompose the toluene (with boiling point of 110°C).
1 g of Cu-doped TiO$_2$ nanopowder + 20 ml of toluene

Ultrasonicate for 1 hour

Add 3 ml of MTCS

Ultrasonicate at 3 hours

Dip cleaned tiles (glazed and unglazed) into coating solution

Repeat with 3 and 5 dipping cycle

Cured at 80° for 1 hour

Annealed at 150°C for 5 hours (2°C/min)

Characterize using XRD, SEM, WCA

Figure 3.7 Flow process of silane-based coating.
3.4 Characterization of Techniques

The Cu-Doped TiO\textsubscript{2} nanopowders samples were characterized using XRD, FESEM/EDX, TEM, UV-vis/UV-DRS and MO test to study their crystallographic structure, morphology of the samples, elemental composition, photon energy and photodegradation, respectively. For the superhydrophobic coating, the surface of the coatings was analysed using XRD, FESEM and WCA. The static water contact angles will be measured over three different areas on a sample using a contact angle meter (Ramehart Instrument Co., USA), and the average value of the measurements will be selected as the final value.

3.4.1 X-Ray Diffraction

X-ray powder diffraction (XRD) analysis is a rapid analytical technique primarily used for phase identification, determine strain, preferred orientation, crystallographic structure and grain size of a crystalline material (Material Interface inc, 2013). This analysis was used to characterize the Cu-doped TiO\textsubscript{2} nanopowder and the newly developed coating surface. XRD is based on constructive interference of monochromatic X-rays and crystalline sample. When the ray hit the sample, it will produce constructive interference and a diffracted ray when the conditions fulfil Bragg’s Law (n\lambda=2d \sin \theta) as in Figure 3.5 (Dutrow & Clark, 2018). This law stated that the angle of incidence, \theta reflect back with the same angle of scattering, \theta and the wavelength, \lambda will occur as the path different, d is equal to the whole number, n (Libre Texts, 2017).

In this work, XRD pattern of the calcined nanopowders was observed using X-ray diffractor (Bruker D8 Advanced X-ray Diffractometer, Cu Ka, \lambda = 0.154 nm). The diffractometer was operated at 40 kV and 110 mA at 2\theta range from 10° to 90°.
XRD pattern obtained was analysed by using X’pert HighScore Plus V.2.2.5 Software and compared with the standard reference which is International Centre for Diffraction Data (ICDD) data base. The ICDD used in this work are ICDD 98-000-5225 for anatase TiO$_2$ and ICDD 98-005-5018 for hexagonal TiO$_2$. Crystallite sizes were extracted from X-ray diffraction line profile using Scherrer equation at Equation 3.1.

$$D\,(nm) = \frac{K\lambda}{\beta \cos \theta}$$ Equati 3.1

Where:

D = mean size of the ordered (crystalline) domain

K = dimensionless shape factor

$\beta$ = line broadening at half the maximum intensity

$\theta$ = Bragg angle (°)

Figure 3.8 Diagram of Bragg’s Law.
3.4.2 Field Emission Scanning Electron Microscopy/Energy Dispersive X-ray

Morphological evaluation of the synthesized Cu-doped TiO$_2$ nanopowders and the superhydrophobic coating were examined by field emission scanning electron microscopy (FESEM). In this study, Zeiss Supra 55VP Field Emission Scanning Electron Microscope was used to characterize the samples.

The synthesized Cu-doped TiO$_2$ nanopowders and the superhydrophobic coated tiles were coated with gold during sample preparation before evaluated in FESEM machine to lower sputter rates. For non-conductive materials, it required thin conductive coating to prevent electrical changing of the sample and to achieve optimum performance (Micro to Nano, 2018). The sputtered samples were then inserted into the sample chamber. Tungsten needle as the field emission cathode has thin and sharp tip provides narrower probing beams resulting in minimizing sample charging and getting better resolution also reduce damages (Janssen, 2015). The surface morphologies of nanopowders and superhydrophobic coatings were observed at various magnifications using secondary electron mode.

Besides that, Energy Dispersive X-ray analysis (EDX) was used as secondary results to provide the elemental identification and quantitative compositional information during characterization of the synthesized Cu-doped TiO$_2$ nanopowders. Electron beam in SEM will hit samples and transfer energy to atoms of the sample. Electrons in the atoms will receive the energy and “jump” to an energy shell with higher energy or be knock-off from the atom. Holes will be created as the electrons leave the shell and attract electrons from higher energy levels. Thus, the energy difference of the transition of high energy levels electrons can be released in the form of x-ray (Nanakoudis, 2017).
3.4.3 Transmission Electron Microscopy (TEM)

TEM used to observe features like crystal structure and features in the crystal structure such as dislocations and grain boundary, growth of layers, their composition and defects. TEM uses electrons instead of light because the wavelength of electrons is much smaller than light. The beam will pass through condenser lens, condenser aperture to focus into small, thin and coherent beam also to exclude high angle electrons. Then, the beam strikes the specimen and transmitted depending the thickness and electron transparency of the specimen (Leadley, 2010).

TEM (Zeiss, Libra 120) was used to observe the calcined Cu-doped TiO₂ nanoparticles. The as-prepared TiO₂ powder were mixed in ethanol then send to ultrasonic to break the nanoparticles. Then, one drop of the suspension was placed on carbon-coated grids and inserted it in machine chamber.

3.4.4 UV-Visible Spectroscopy or Diffuse Reflectance Spectroscopy (UV-Vis/UV-DRS)

Ultraviolet-visible spectroscopy also called UV-vis is a spectrophotometer that most often refers to absorption spectroscopy, whereas UV-DRS specifically refers to diffuse reflection spectroscopy. UV-vis measures the absorption of light across the ultraviolet and visible light wavelength through a liquid sample while UV-DRS measure the reflectance of light that reflected on surface of opaque (solid) sample (Shimadzu Scientific Instrument, 2016).

UV-vis Perkin Elemer Lambda 35 (Figure 3.9a) was used to measure the degradation percentage of the liquid from the MO test. UV-DRS Perkin Elmer Lambda 35 (Figure 3.9b) was used to measure the band gap of the Cu-doped TiO₂ nanopowder
determined from the reflectance data. A graph of \[ \ln \left( \frac{R_{\text{max}} - R_{\text{min}}}{R - R_{\text{min}}} \right) \] versus photon energy (band gap energy) was plotted where \( R_{\text{max}} \) represents the maximum reflectance value and \( R_{\text{min}} \) represents the minimum reflectance in desired wavelength. The energy band gap is determined based on the intersection from the extrapolation of the straight line of the curve to the y-axis = 0 (Joshi et al., 2003).

Figure 3.9 (a) UV-vis and (b) UV-DRS Perkin Elmer Lambda 35.
3.4.5 Methyl Orange (MO) Test

Methyl orange (MO) is an acid base dye work as an indicator (Eumann and Schaeberle, 2016) that was used in this study to determine the photodegradation of Cu-doped TiO$_2$ nanopowder. The Cu-doped TiO$_2$ nanopowder worked as photocatalyst for the degradation of methyl orange. A 20 ppm of methyl orange solution was prepared by mixing methyl orange powder in distilled water, then, kept in a dark place for 30 min without any radiation (Kumar and Pandey, 2017). The photocatalytic degradation was carried out by adding 1 g of Cu-doped TiO$_2$ into 100 ml of 20 ppm MO solution. 5 ml of the mixed solution was taken out and recorded as blank. Then, the rest of the mixture were exposed to the UV radiation to undergo photodegradation process for 3 h. 5 ml of the mixture was taken out at every 30 min of time interval to be measured under Perkin Elmer UV-vis spectrophotometer. Then absorption spectra were recorded and the percentage degradation was calculated using the formula in Equation 3.2 (Xue et al., 2017).

\[
\text{Degradation (\%)} = \frac{(C_o - C_t)}{C_o} \quad \text{Equation 3.2}
\]

Where $C_o$ is the initial absorption of dye and $C_t$ is the absorption of dye after the reaction at $t$ time.
3.4.6 Water Contact Angle

Water contact angle (WCA) is a measurement which is a convenient way to measure the contact angle in order to determine a surface hydrophobic or hydrophilic (PVA TePla America, 2016). A type of liquid will be drop on the surface. When the liquid spread and has smaller angle (<< 90°) it is hydrophilic and when the liquid do not spread evenly, creates droplet or beading and has larger angle (>> 90°) it is hydrophobic (Bracco and Holst, 2013). Figure 3.6 showed the example of water contact angle on hydrophilic and hydrophobic surfaces. There are a few types of liquid that can be used in this measurement technique such as water, oil (Ozkan and Erbil, 2017), and mercury (Ethington, 1990).

![Water contact angle on hydrophilic and hydrophobic surfaces](image)

Figure 3.10 Water contact angle on hydrophilic and hydrophobic surfaces (Bracco and Holst, 2013).

In this work, WCAs were measured using telescope-goniometer (Rame-hart Model 260, USA) equipped with CCD camera at room temperature (∼27 °C). Deionized water was used as testing liquid in this study. The volume of water droplet selected was ~5 μl and dropped on the tile sample of size of 2 cm x 2 cm. The measurement of contact angles in 3 various points on the surface of each sample.
CHAPTER 4

RESULTS & DISCUSSIONS

4.1 Introduction

This chapter presents the experimental results and comprehensive discussions obtained from the analyses performed on the as-prepared Cu-doped TiO₂ nanotubes by hydrothermal technique followed by the fabrication of superhydrophobic coating on ceramic wall tiles. Basically, the chapter can be divided into two main sections, i) preparation of Cu-doped TiO₂ nanotubes by hydrothermal technique, and ii) development of superhydrophobic coating on different types of ceramic wall tiles.

4.2 Synthesis of Cu-doped TiO₂ nanoparticles by hydrothermal method

In this work, Cu-doped TiO₂ nanotubes was synthesized by hydrothermal method. Commercial TiO₂ was used as the precursor with the addition of cupric nitrate trihydrate (source of Cu²⁺ metal ion) to synthesized Cu-doped TiO₂ nanotubes. The as-synthesized was washed, dried and calcined at 300°C. The as-calcined was then used as the main coating, while the colloidal silica and silane-based were used as the coupling agent for the coating solution. The purpose of the addition of Cu-doped TiO₂ nanotubes is to create surface roughness on the substrate to serve as the self-cleaning and antibacterial agent on the substrate. Two different solvents (colloidal silica and silane-based) were tested in this study as to investigate the effectiveness of this binders to hold Cu-doped TiO₂ nanotubes on the surface of the substrate. Binder which is able to form a strong bonding between the coating materials and surface of the substrate, show no peeling-off or cracks and having the highest water contact angle (WCA) will be the key
measurement criteria in developing a superhydrophobic surfaces on ceramic wall tiles in this study.

4.2.1 XRD analysis

The crystal structure of the TiO\textsubscript{2} precursor and synthesized Cu-doped TiO\textsubscript{2} nanoparticles before and after calcination had been characterized by XRD analysis. Figure 4.1 shows the XRD patterns of the TiO\textsubscript{2} precursor, Cu-doped TiO\textsubscript{2} nanoparticles dried at 80°C and Cu-doped TiO\textsubscript{2} nanoparticles calcined at 300°C. The TiO\textsubscript{2} precursor revealed a series of sharp and narrow crystalline peaks at 2\(\theta\) of 25.87°, 38.33°, 48.54°, 54.38°, 55.55° and 63.16°. These peaks are the characteristic of the crystalline anatase TiO\textsubscript{2} phase structure with tetragonal crystal system (PDF: 98-000-5225).

The TiO\textsubscript{2} precursor was doped with Cu\textsuperscript{2+} metal ion by hydrothermal method. The XRD patterns of the as-dried and as-calcined Cu-doped TiO\textsubscript{2} nanopowder shows rather broad compared to precursor (Figure 4.1(b) and Figure 4.1 (c) respectively). It is because nano particles has less mass atoms which the lattice sum is not be able to converge to a diffraction line but broaden. It was observed that only three peaks appeared at 2\(\theta\) about 24.12°, 28.62° and 48.64° for Cu-doped TiO\textsubscript{2} dried at 80°C. The same trend of the XRD pattern was then observed for as-calcined Cu-doped TiO\textsubscript{2} at 2\(\theta\) of 24.26°, 28.47° and 48.38°. Both Cu-doped TiO\textsubscript{2}, as-dried and as-calcined revealed the characteristic of h-TiO\textsubscript{2} phase structure (PDF: 98-005-5018). The same observation was previously reported by our group (Razali \textit{et al.}, 2014b), indicating this worth is highly repeatable and consistent. From the results obtained, it can be clearly seen that the addition of dopant after the crystal phase of TiO\textsubscript{2} from anatase TiO\textsubscript{2} (tetragonal) for TiO\textsubscript{2} precursor (un-doped TiO\textsubscript{2}) to hexagonal structure for Cu-doped TiO\textsubscript{2}. The lattice parameters of the anatase TiO\textsubscript{2} of the TiO\textsubscript{2} precursor and hexagonal TiO\textsubscript{2} of the Cu-
doped TiO$_2$ nanoparticles were determined based on the XRD pattern were collected and list in Table 4.1.

Figure 4.1 XRD patterns of (a) TiO$_2$ precursor, (b) Cu-doped TiO$_2$ dried at 80°C and (c) Cu-doped TiO$_2$ calcined at 300°C.
Table 4.1 Lattice parameter of Cu-doped TiO$_2$ nanoparticles.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Sample</th>
<th>$a = b$ (Å)</th>
<th>$c$ (Å)</th>
<th>Phase</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precursor</td>
<td>Commercial TiO$_2$</td>
<td>3.78</td>
<td>9.51</td>
<td>Anatase TiO$_2$ (tetragonal)</td>
<td>11.08</td>
</tr>
<tr>
<td>80</td>
<td>Cu-doped TiO$_2$ nanotubes</td>
<td>5.13</td>
<td>6.04</td>
<td>Hexagonal TiO$_2$</td>
<td>6.57</td>
</tr>
<tr>
<td>300</td>
<td>Cu-doped TiO$_2$ nanotubes</td>
<td>5.29</td>
<td>6.13</td>
<td>Hexagonal TiO$_2$</td>
<td>5.51</td>
</tr>
</tbody>
</table>

The commercial TiO$_2$ precursor has lattice parameters of ($a$- and $c$-axes) of 3.78 Å and 9.51 Å, respectively (Table 4.1). The unit cell of this precursor is tetragonal based on the Bravais lattice. While, for the Cu-doped TiO$_2$ nanoparticles, the $a$ and $c$ lattice parameter values were significantly different compared to the TiO$_2$ precursor. The Cu-doped TiO$_2$ dried at 80°C and calcined at 300°C has lattice parameter of $a = 5.13$ Å, $c = 6.04$ Å and $a = 5.39$ Å, $c = 6.13$ Å, respectively. The transformation to the new phase formed probably due to the incorporation of the metal ion into the interstitial positions of the TiO$_2$ lattice (Razali et al., 2014b).

Although the dried and calcined Cu-doped TiO$_2$ nanoparticles have the same phase structure (hexagonal), the crystallite sizes are different. It was found that the as-calcined Cu-doped TiO$_2$ has relatively smaller crystallite size which is 5.51 nm as compared to the dried Cu-doped TiO$_2$ that has about 6.57 nm. By comparing the
crystallite size of the as-prepared and precursor TiO$_2$, the later has larger crystallite size which is approximately 11.08 nm. It is known that smaller crystallite sizes has higher specific surface area and smaller band gap of TiO$_2$ particles. Thus, will lead to better photocatalytic activity of the TiO$_2$ particles (Khairy and Zakaria, 2014).

4.2.2 Morphological analysis

In order to study the surface morphologies of the as-prepared Cu-doped TiO$_2$, FESEM analyses was carried out. The commercial TiO$_2$ powder precursor that was characterized as received without any purification, revealed agglomerated and nearly-spherical shape particles (Figure 4.2(a)) The diameter of the TiO$_2$ precursor particles is roughly about 200 nm measured using Image J software.

Figure 4.2(b) shows the FESEM micrograph of the Cu-doped TiO$_2$ calcined at 300°C. It is revealed that the nanoparticles showed the formation of fibrous-like structures. These fibrous-like structures have an average diameter of about 8 nm and 90 nm in length. The dissolution-recrystallization during the reaction of the TiO$_2$ precursor with sodium hydroxide solution lead to the formation of nanotubes or nanowires (Ge et al., 2017).
Figure 4.2 FESEM micrograph of (a) commercial TiO$_2$ powder precursor and (b) Cu-doped TiO$_2$ calcined at 300°C.
TEM was then used to observe the actual features and particle size of Cu-doped TiO$_2$ calcined at 300°C. The TEM micrograph of the calcined Cu-doped TiO$_2$ is shown in Figure 4.4. The existence of hollow inside the fibrous-like structures indicating the formation of nanotubes structure. The inner and outer diameters of the nanotube were measured using Image J software and found out to be about 4 nm and 8 nm, respectively. It is known that the nanotubular configuration have larger specific surface area due to the internal and external areas of the nanotubes. This will enhance the absorption of organic molecules onto the surface of the photocatalyst. By having this nanotubular architecture, the electrons mobility also can be increased, hence promote one directional electrical channel for photogenerated charge carriers transport (Razali et al., 2014a). These unique features are desirable for the photocatalytic degradation of organic pollutant.
Figure 4.3 TEM micrograph of Cu-doped TiO$_2$ calcined at 300°C.

### 4.2.3 EDX analysis

EDX analysis was performed to investigate the presence of dopant in the sample and its compositions, the elemental analysis of the Cu-doped TiO$_2$ nanotubes. The EDX spectra of the sample is illustrated in Figure 4.5. The presence of copper was detected as a small peak shown in the figure. This result indicates that the TiO$_2$ structure was successfully doped with copper as dopant. Besides copper element, only oxygen and titanium elements were detected. The amount of dopant, titanium and oxygen presence in the sample are tabulated in Table 4.2.

![EDX spectra of TiO$_2$ nanotubes with Cu$^{2+}$ metal ions.](image)

Table 4.2 Average elemental compositions of calcined Cu-doped TiO$_2$ nanotubes obtained from EDX analysis.

<table>
<thead>
<tr>
<th>Element</th>
<th>Ti (wt%)</th>
<th>O (wt%)</th>
<th>Cu (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti L</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O K</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti Kα</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti Kβ</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

52
The band gap of the Cu-doped TiO$_2$ nanotubes was determined using UV-Diffuse Reflectance Spectroscopy (DRS). Graph of $[\ln(R_{\text{max}}-R_{\text{min}}/R-R_{\text{min}})]^2$ versus photon energy (band gap energy, $E_g$) was plotted to determine the band gap energy, where $R_{\text{max}}$ is the maximum reflectance value in the desired wavelength and $R_{\text{min}}$ is the minimum reflectance value in the desired wavelength. The band gap energy was determined based on the intersection of extrapolation straight line of the curve to the y-axis = 0 (Razali et al., 2014a).

In this study, the $E_g$ of TiO$_2$ precursor and Cu-doped TiO$_2$ nanotubes were measured. From Figure 4.5, the band gap of TiO$_2$ precursor that being used in this study was determined to be around 3.3 eV which is similar to the band gap value of pure anatase TiO$_2$ in the literature (Luttrell et al., 2015). While for the calcined Cu-doped TiO$_2$, the band gap was reduce to around 3.2 eV as shown in the Figure 4.6. As one known, a smaller band gap of TiO$_2$ structure will promote better photocatalytic activity. This is because electrons from the conduction band (CB) can be easily excite to the valence band (VB) when they received sufficient energy from the light (i.e. sunlight). By having smaller band gap, these electrons only require lower energy for excitation as the distance between conduction band and valence band had been reduced. The excitation of the electrons will produce electron and hole pairs. Hydroxyl radicals (OH$^*$) (produce from the holes) will combine with the oxygen anions (O$_2^*$) (produce due to reduction of oxygen) to produce reactive oxygen species (ROS) that are harmless to the environment and surrounding (Haider et al., 2017). Thus, this make the material to be potentially serve as self-cleaning applications.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu-doped TiO$_2$</th>
<th>31.52</th>
<th>67.73</th>
<th>0.75</th>
</tr>
</thead>
</table>

4.2.5 UV-DRS analysis
Figure 4.5 Band gap energy of TiO$_2$ precursor.

Figure 4.6 Band gap energy of Cu-doped TiO$_2$. 
4.2.6 Photocatalytic activity study for MO degradation

Figure 4.8 shows the percentage of MO degradation in the presence of Cu-doped TiO$_2$ nanotubes and precursor TiO$_2$. It is thought that degradation of MO was found to be about 75.54% and 97.31% for precursor TiO$_2$ and Cu-doped TiO$_2$ nanotubes after 180 minutes reaction. The Cu-doped TiO$_2$ nanotubes resulted in higher degradation of MO owing to their large surface area compared to the precursor TiO$_2$. Doping with metal ions could prevent the crystal growth and nanotubes agglomeration, thus produce high surface area of doped TiO$_2$ nanotubes. The precursor TiO$_2$ shows about 26.35% degradation after 30 min. By comparing the results, it is clearly shown that Cu-doped TiO$_2$ nanotubes revealed about 62.65% degradation after 30 min. This indicates that doping can accelerate the degradation of MO as it can reduce the recombination rate by acting as electron and hole trapper.

Figure 4.7 Photocatalytic degradation of MO in the presence of Cu-doped TiO$_2$ nanotubes.
4.3 Development of superhydrophobic coating on wall tiles

4.3.1 Colloidal silica coating

In this work, Ludox AS-40 was combined with Cu-doped TiO$_2$ nanotubes as the coating materials. The outer surface of well-cleaned tiles (glazed and unglazed) were dipped in the coating solution for 1, 3 and 5 times, and cured at 80°C in order to study the hydrophobicity of the coated surface.

4.3.1.1 Morphological analysis

In order to study the surface morphology of the colloidal silica coating, FESEM analyses was carried out. Figure 4.8 shows the morphologies of colloidal silica coating after one dipping process, Figure 4.8(a) on a glazed wall tiles, while, Figure 4.8(b) on an unglazed wall tiles. The distribution of the Cu-doped TiO$_2$ nanoparticles were not homogenous after one dip in the colloidal silica for both tiles. The colloidal silica coating on the glazed tile after one dip shows rather smooth surface with only a few spots of Cu-doped TiO$_2$ nanotubes observed. While, the colloidal silica coating on unglazed tile after one dip shows rough surface but only a few spots of Cu-doped TiO$_2$ nanoparticles. This would probably due to the weak bonding between the binder and the surface of substrate. The coating layers was not completely adhered to surface that make it formed cracks or peel-off coating layer after a few dips (Figure 4.8).
Figure 4.8 Image and FESEM morphologies on colloidal silica coating of (a) and (c) glazed tile after one dip, (b) and (d) unglazed tile after one dip.

4.3.1.2 WCA test

The wettability of the colloidal silica coating was being measured by water contact angle measurement. Figure 4.9(a) shows the WCA measurement on a cleaned tiles without any coating revealed to be $57.28^\circ \pm 0.47$ and surface energy of $49.47 \pm 0.28$ J/m$^2$. While, Figure 4.9(b) shows that the WCA measurement of the colloidal silica coating on glazed wall tiles have lower WCA measurement which is $42.73^\circ \pm 0.06$ and higher surface energy with $57.88 \pm 0.03$ J/m$^2$. Based on the result, it is clearly shows that the free coating tile and colloidal silica coating indicates hydrophilic characteristic because the angle obtained was lower than $90^\circ$. It is revealed that colloidal silica coating makes surface become more hydrophilic as the WCA measurements decrease as compared to the free coating tiles.
Figure 4.9 WCA on (a) cleaned glazed tile without any coating and (b) colloidal silica coating on glazed tile after one dip.

The results in the morphological analysis and water contact angle measurement proved that surface roughness and surface energy influenced the formation of the new developed coating. After a few dips, the coating layer started to show cracks and peel-off on both glazed and unglazed tiles (Figure 4.10). Lower surface roughness and high surface energy makes the coating to be hydrophilic. Moreover, the water contact angle of the newly developed coating on tiles became lower than the free coating tile that divert the aim by getting more hydrophilic surfaces instead of hydrophobic. It is clearly shows that coating solution was not completely adhered to the tiles surface and proves that the coating material was not form bonding to the surface. Thus, colloidal silica Ludox AS-40 was not suitable to be used as binder to form superhydrophobic surfaces.
Figure 4.10 Images of colloidal silica coating that peeled-off and cracks on the (a) glazed wall tiles and (b) unglazed wall tiles.

4.3.2 Silane-based coating

In this work, MTCS, toluene and Cu-doped TiO$_2$ nanoparticles were combined as the coating material. The outer surface of well-cleaned tiles (glazed and unglazed) were dip in the coating solution for 1, 3 and 5 times. The coated tiles were cured at 80°C and annealed at 150°C. The coating surface were investigated to study its hydrophobicity.
Figure 4.11 Images of silane-based coating prepared from 1, 3 and 5 dips on glazed wall tiles ((a), (b) and (c) respectively) and unglazed wall tiles ((d), (e) and (f) respectively).

4.3.2.1 XRD analysis

The crystal structure of the coated tiles surfaces had been characterized using XRD in order to evaluate the phase and crystal structure changes between 1, 3, and 5 dips on glazed and unglazed wall tiles. The sharp and narrow crystalline peaks obtained at 2θ of 28.15°, 44.91° and 54.55°. These peaks are the characteristic of rutile TiO₂ with tetragonal crystal system (PDF: 98-003-5191). While, peak obtained at 2θ of 36.78°, 48.76° and 56.67° are the characteristic of hexagonal TiO₂ (PDF: 98-005-5018). The hexagonal phase of Cu-doped TiO₂ nanotubes had transformed to rutile phase of
coating on wall tiles probably through the first-order transformation. The metastable hexagonal converts to rutile may due to several factors including the presence of impurities, feature size, texture and strain which was affected when the hexagonal TiO$_2$ react with the coating materials. Also with annealing, porosity/surface area of the hexagonal TiO$_2$ may reduce that lead to nucleation growth of phase transformation (Grimes and Mor, 2009). These phase transformation will affect its band gap energy. Rutile phases has band gap energy of 3.0 eV based on the literature (Luttrell et al., 2015). Thus, the photocatalytic activity of rutile TiO$_2$ require a bit higher energy for the excitation of electrons from CB to VB compared to the hexagonal TiO$_2$.

![XRD pattern of 1 (a), 3 (b) and 5 (c) dips on glazed wall tiles and 1 (d), 3 (e) and 5 (f) dips on unglazed wall tiles.](image)

Figure 4.12 XRD pattern of 1 (a), 3 (b) and 5 (c) dips on glazed wall tiles and 1 (d), 3 (e) and 5 (f) dips on unglazed wall tiles.
4.3.2.2 Morphological analysis

The surface morphologies of the coating were then analysed using FESEM. Figure 4.11 shows the micrograph of the silica coatings prepared after one, three and five dips, respectively on glazed and unglazed wall tiles. A fairly homogenous distribution of Cu-doped TiO$_2$ nanoparticles was observed to be deposited on the substrate after one dip (Figure 4.11 (a) and (d)). As the dipping cycle increased, more Cu-doped TiO$_2$ nanoparticles deposited on the substrate of wall tiles. As a result, a rough surface morphology was observed after three dips as compared to morphology after a single dip (Figure 4.11 (b) and (e)). By further increasing the cycle of dips, more Cu-doped TiO$_2$ nanoparticles are adhered to the previously deposited nanotubes on the substrate. At 5 dipping cycle, the substrate were almost reach the saturation level of coating deposition as most of the substrates were fully covered by the nanoparticles, resulting in in rougher surface. This surface morphology performing a similar function to the nanostructure of lotus leaf which produce a high water contact angle (>150°) on the surface and causing low surface energy.
Figure 4.13 FESEM images of silica coating prepared from 1, 3 and 5 dips on glazed wall tiles ((a), (b) and (c) respectively) and unglazed wall tiles ((d), (e) and (f) respectively).
4.3.3 WCA Test

The wettability of the newly developed coatings on glazed and unglazed wall tiles were evaluated by water contact angle measurement. The cleaned glazed and unglazed wall tiles demonstrate hydrophilic behaviour with the water contact angle less than 90° which is 57.28° ± 0.47 and high surface energy of 49.47 ± 0.28 J/m² for glazed tile while for unglazed tile, the water droplet was quickly absorbed and spread on the surface, thus could not be measured. However, after the coating procedure, the WCA measurements of the samples increased up to 153.96 ± 0.03 and 0.00 surface energy. It is known that sample with low surface energy reduce contact surface area between liquid drop and coating surface, inducing higher WCA measurements. Figure 4.12 and Figure 4.13 showed the WCA measurement on cleaned tiles without any coating and 1, 3 and 5 dips of silica coating on glazed and unglazed wall tiles respectively.

Figure 4.14 Water contact angle on cleaned glazed tiles without any coating.
Figure 4.15 Water contact angle on silica coated with 1, 3 and 5 dips on glazed ((a), (b) and (c) respectively) and unglazed ((d), (e) and (f) respectively) wall tiles.
Table 4.3 WCA measurement on coated and uncoated tiles.

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<th>Surface Energy (J/m²)</th>
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From the data in Table 4.3, unglazed wall tiles with 5 dips showed the highest WCA measurements followed by unglazed wall tiles with 1 and 3 dips. While, glazed wall tiles showed lower WCA compared to unglazed wall tiles. This is because, glazed tiles has shiny and glossy surface that make it impermeable, and hence the coating solution is difficult to adhere on the tiles surface. The unglazed wall tiles provide better surface for the adherence of the coating materials on the tiles surface as the tiles are rough as compared to glazed tiles. The unglazed tiles are less dense in which they allow higher water/liquid absorption as in contact with their surface. Glazing is not only to enhance the aesthetic value, but it also make the tiles impermeable and denser. Thus, the absence of glazing on the surface of the tiles makes the water or liquid easily absorbed when it touch the tiles surface.

The results in the morphological analysis and water contact angle measurement proved that surface roughness and surface energy influenced the formation of the new
developed coating. The distribution of the Cu-doped TiO₂ nanotubes on the substrate after dip, indicates the surface roughness. With sufficient amount of surface roughness, water droplet able to form bead-like shape when hitting the coating surface. When the water droplet bounce and roll-off, indicates the Cassie-Baxter model where underneath the water droplet has air pocket it represents the superhydrophobic surface. With lower surface energy approaching to zero J/m², the high water contact angle measurement will represents superhydrophobic when more than 150°.

By comparing the silane-based coating with the colloidal silica coating, silane-based coating shows more homogenous deposition of Cu-doped TiO₂ nanotubes on the substrate resulting higher water contact angle and lower surface energy. One dipping for glazed silane-based coating shows WCA of 106.80° ± 0.09 and surface energy of 18.96 ± 0.05 J/m². While, one dipping cycle for colloidal silica coating shows WCA of 42.73° ± 0.06 and surface energy of 57.88 ± 0.03 J/m². It is important for the coating to be transparent because we do not want the beautiful features of the tiles being covered with other colours from the coating.

Based on our finding, at this stage it is clearly shown that the choice of solvent/binder used in preparing the coating materials solution play an important role in determining the nature of the surface produced. It is also crucial to ensure that the Cu-doped TiO₂ nanotubes are well deposited on the substrate. The right combination of solvent used and TiO₂-based materials define the success of the development of superhydrophobic coating on the wall tiles in this study. Therefore, silane-based coating is chosen as the best solvent to deposite TiO₂ on the wall tiles in order to create the superhydrophobic effect, which can be potentially ben used in self-cleaning applications.
CHAPTER 5

CONCLUSIONS & RECOMMENDATION

5.1 Conclusions

In this project, Cu-doped TiO$_2$ nanotubes have been successfully synthesized using hydrothermal method. The XRD characterization shows a good result by obtaining hexagonal TiO$_2$ with crystallite size of 5.51 nm. The FESEM and TEM shows good morphology structure of nanotubes with the inner diameter and outer diameter are 4 nm and 8 nm respectively. The EDX result confirmed the presence of, Cu element in the TiO$_2$ structure. The UV-DRS and UV-Vis shows that the Cu-doped TiO$_2$ has lower band gap energy and good photocatalytic efficiency.

Hydrophobic coating has been designed using Cu-doped TiO$_2$ nanoparticles as the precursor, while colloidal silica and silane base solution as the solvent by sol-gel method. For the first trial, colloidal silica coating formed hydrophilic surface on glazed tiles (1 dip) with WCA of $42.73^\circ \pm 0.06$ and high surface energy of $57.88 \pm 0.03$ J/m$^2$. The FESEM result shows that the distribution of the Cu-doped TiO$_2$ nanoparticles were not distributed homogeneously. The coating layer was also peeled-off from the tiles surface probably due to the incompatible coating solution with the tiles surface. Thus, the coating solution could not adhere to the tiles surface.

For the silane-based coating it is revealed that the Cu-doped TiO$_2$ nanoparticles formed on the surface was rutile tetragonal by using XRD analyses. The characteristics of the Cu-doped TiO$_2$ before mixed with coating materials, it was hexagonal TiO$_2$. This phase transformation from hexagonal TiO$_2$ to rutile TiO$_2$ (tetragonal) is not fully understood at this stage of study. Normally phase transformation occurs with increasing
temperature. Despite the phase transformation, it is revealed that silane-based coating were hydrophobic on the glazed tiles with WCA of 106.80° ± 0.09, 119.83° ± 0.49 and 129.50° ± 0.04 and superhydrophobic on unglazed tiles with WCA of 144.73° ± 0.02, 152.51° ± 0.01 and 152.51° ± 0.01 for 1, 3 and 5 dips respectively. Glazed tiles has lower water contact angle probably due to the glossy and impermeable surface made the coating solution difficult to adhere on it. The unglazed tiles has higher water contact angle probably due to the rough and permeable surface made the coating solution to adhere easily on it. The FESEM analyses shows that coating has homogenous distribution of Cu-doped TiO₂ nanoparticles. It is revealed that by increasing the dipping cycle, the higher the surface roughness. Due to time limitation, photocatalysis and antibacterial tests for the coated surfaces was not conducted.
5.2 Recommendation for future works

The focus on potential application of superhydrophobic in various industries must be explored. Hence, several suggestion and improvement of the current formulation and future developments were proposed as follows:

1. Study the effect of different metal ions such as silver and cobalt into TiO$_2$ structure on the photocatalytic and antibacterial behaviours.
2. Produce doped-TiO$_2$ nanoparticles using other method such as sol-gel, chemical vapor deposition, solvothermal, direct oxidation and electrodeposition.
3. Use other coating method such as spin-coating, spray-coating and micropattern coating to create the superhydrophobic surface on the wall tiles.
5. Investigate the surface roughness, tilt angle and durability (via water immersion with different pH) properties on the coated and uncoated wall tiles.
6. Study on superhydrophilic coating surface using TiO$_2$ based material in different solvents (hydrophilic solvent).
REFERENCES


72


APPENDICES

Name and formula

Reference code: 98-000-5225
Mineral name: Anatase
Chemical name: Titanium Oxide
Common name: Anatase
ICSD name: Titanium Oxide
Chemical formula: \( \text{O}_2\text{Ti}_1 \)
Second chemical formula: \( \text{TiO}_2 \)

Crystallographic parameters

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Space group number: 141

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Subfiles and Quality

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ICSD Pattern

Quality: Calculated (C)

Comments

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Temperature in Kelvin: 298
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Structure type: TiO2(tI12)
Recording date: 1/1/1980
Modification date: 4/1/2006
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ANX formula: AX2
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Calculated density: 3.89
R value: 0.023
Pearson code: tI12
Wyckoff code: e a
PDF code: 00-021-1272
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REMARK Transformed from non-centrosymmetric setting.
Publ. title: Refinement of the structure of anatase at several temperatures

References


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Common name: Titanium Oxide
ICSD name: Titanium Oxide
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Second chemical formula: TiO$_2$

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Space group number: 152
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c (Å): 6.1330
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Beta (°): 90.0000
Gamma (°): 120.0000
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Volume of cell (10$^6$ pm$^3$): 148.69
Z: 3.00
RIR: 5.80

Subfiles and Quality

Subfiles: Inorganic
ICSD Pattern
Quality: Calculated (C)

Comments

Structure: Quartz, low
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Original ICSD space group: P3121
PEG model (polarization-included electron gas)
Hypothetical structure with quartz-type, existence not proven
Origin shift of .3333 along c-axis.
At least one temperature factor missing in the paper.
No R value given in the paper.
X-ray diffraction from single crystal
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Structure calculated theoretically
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Stick Pattern
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