GREEN SYNTHESIS OF TiO_2 – Ag NANOCOMPOSITES FOR SELF-CLEANING AND ANTIMICROBIAL PROPERTIES ON COTTON FABRIC

SUNDERISHWARY S. MUNIANDY

UNIVERSITI SAINS MALAYSIA
2018

GREEN SYNTHESIS OF TiO_2 – Ag NANOCOMPOSITES FOR SELF-CLEANING AND ANTIMICROBIAL PROPERTIES ON COTTON FABRIC

by

SUNDERISHWARY S. MUNIANDY

Thesis submitted in fulfilment of the requirements
for the degree of
Master of Science

May 2018

ACKNOWLEDGEMENT

Foremost, I would like to express my sincere gratitude to the School of Chemical Sciences, Universiti Sains Malaysia (USM) for giving me the opportunity to conduct my research work in fulfillment of my Masters degree. My sincere appreciation to my supervisor Dr. Lee Hooi Ling for the continuous support, patience, motivation, enthusiasm and immense knowledge. Her guidance has helped me in all the time of research and writing of this thesis. I would like to acknowledge the financial support provided by USM Research University Individual Grant (RUI: 1001/PKimia/811265).

My special thanks to my co-supervisor Dr Noor Haida Mohd for her encouragement. I would also like to thank Dr. Sasidharan from INFORMM for his insightful comments, guidance and helping me to understand and interpret the results obtained for the antimicrobial test. Not forgetting, the technical staff from School of Chemical Sciences especially Mr. Sujeyndran, Mr. Zamri, Mr. Ali and Mr. Siva, for the kind assistance and excellent services. Besides, that I would like to thank my lab members and friends especially Vicky, Ruzaina, Loges, Jaga, Johnny, Azia and Mimi for their views and useful discussions. My acknowledgement also goes to respective staff from INFORMM and Institute of Postgraduate Studies (IPS) for their kind assistance and guidance.

Last but not least, my sincere gratitude to my parents, Mr. and Mrs. Muniandy Thanalaxmi, my siblings, VimThinsAgesh, my husband, Dhaarshan Rao and my in-laws, Mr. and Mrs. Sivarao Seetha family for their love, trust and unconditional support throughout my study.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SCHEMATIC DIAGRAMS

LIST OF SYMBOLS AND ABBREVIATIONS

Å	Angstrom (= 10^{-10} meters)
Ag	Silver
$AgNO_3$	Silver (I) nitrate
BET	Brunauer-Emmet-Teller
BJH	Barret-Joyner-Halenda
eV	Photon energy
FESEM	Field emission scanning electron microscopy
FTIR	Fourier transform infrared
FWHM	Full-width at half maximum
GOF	Goodness of fitness
hr	Hour(s)
IEP	Isoelectronic point
M	Molarity
MB	Methylene blue
min	Minute(s)
mm	Millimeter(s)
MO	Methyl orange
N_2	Nitrogen
NAA	Nitrogen adsorption analysis
NaH_2PO_4	Sodium hypophosphite
NCs	Nanocomposites
NH_4OH	Ammonium hydroxide
nm	Nanometer(s)
NPs	Nanoparticles

NR	Neutral red
ppm	Parts per million
PVP	Polyvinylpyrrolidone
R	Molar ratio
SHP	Sodium hypophosphite
TiO_2	Titanium (IV) dioxide
TOC	Total organic carbon
TTIP	Titanium (IV) tetraisopropoxide
XRD	X-ray diffraction
XPS	X-ray photoelectron spectroscopy
ZOI	Zon of inhibition

SINTESIS NANOKOMPOSIT TiO_2 – Ag MENGGUNAKAN PENDEKATAN KIMIA HIJAU BAGI APLIKASI PEMBERSIHAN SENDIRI DAN CIRI – CIRI ANTIMIKROB PADA KAIN KAPAS

ABSTRAK

Pendekatan kimia hijau merupakan pendekatan terbaharu yang dijangka mempunyai implikasi yang luas di semua bidang sains dan teknologi. Walaupun kimia hijau masih lagi di peringkat awal, ia sudah terbukti bahawa ia telah menjadi sebuah aset yang penting dalam meningkatkan prestasi bahan nano serta menarik minat para saintis dari seluruh pelusuk dunia. Nanopartikel titanium dioksida (TiO_2 NP), nanopartikel argentum (AgNP) dan nanokomposit titanium dioksida-argentum (TiO_2 - Ag NK) telah berjaya disintesis menggunakan pendekatan kimia hijau. Bahan - bahan yang disintesis telah diuji dalam aktiviti pemangkinan cahaya dan antimikrob yang dipamerkan oleh TiO_2 NP dan AgNP. Mesoliang anatase TiO_2 NP yang terdop sendiri (Ti^{3+}) telah disintesis dengan menggunakan kaedah pemendakan mudah pada suhu yang rendah telah menyumbangkan peranan penting dalam aktiviti pemangkinan cahaya. Luas permukaan spesifik TiO_2 NP adalah 87.2 m^2 g^{-1} dan purata saiz liang meso adalah 8.7 nm, manakala bagi liang makro adalah 50 hingga 70.2 nm. Kehadiran liang meso dan makro meningkatkan proses fotodegradasi metilena biru (MB) di bawah cahaya matahari. Kesan parameter tindak balas terhadap aktiviti pemangkinan cahaya oleh TiO_2 NP yang disintesis menggunakan 0.01 mol titanium isopropoksida (TTIP) pada pH beralkali telah dikaji dan ia menunjukkan bahawa 0.1 g TiO_2 NP berfungsi dengan lebih baik dalam pewarna kationik (MB). TiO_2 NP yang disintesis mempamerkan ciri – ciri aktiviti pemangkinan cahaya yang tinggi untuk sekurang-kurangnya sepuluh kitaran

penggunaan berpanjangan tanpa kehilangan kecekapannya. Nanopartikel argentum yang seragam (AgNPs) dengan saiz kristal 19.3 nm telah berjaya disintesis dengan menggunakan kaedah hidrotermal yang mudah. Kajian pengoptimuman untuk sintesis AgNP telah ditentukan melalui ujian antimikrob iaitu ujian cakera penyebaran. AgNP yang disintesis dengan menggunakan nisbah molar $AgNO_3$: PVP (1:5) pada suhu 160 °C selama 24 jam menunjukkan ciri-ciri antimikrob yang kuat terhadap bakteria Gram negatif (14.3 ± 0.57 mm) daripada bakteria Gram positif (12.3 ± 0.57 mm). Apabila Ag digabungkan dengan TiO_2, didapati bahawa sifat kedua-dua elemen dalam suatu bahan tunggal (TiO_2-Ag NK) telah bertambah baik. TiO_2-Ag NK telah disintesis menggunakan kaedah hidrotermal menggunakan pelbagai muatan asal TiO_2 (TTIP). Kajian telah mengesahkan bahawa saiz Ag dalam TiO_2 – Ag NK yang berkurang secara mendadak sehingga 5 nm telah mendorong kesan sinergi dan secara tidak langsung mendorong aktiviti antimikrob TiO_2-Ag NK. TiO_2-Ag NK yang disintesis telah disalut pada kain kapas untuk menghasilkan kain pintar yang mempunyai ciri – ciri pembersihan sendiri dan antimikrob. TiO_2-Ag NK telah berjaya disalut pada kain dengan bantuan ejen pemautan silang (asid suksinik) dan juga pemangkin (natrium hipofosfit) melalui kaedah hidroterma. Kain kapas yang disalut TiO_2-Ag NK telah terbukti mempunyai ciri – ciri pembersihan sendiri yang berkesan walaupun selepas empat basuhan.

GREEN SYNTHESIS OF TiO_2 – Ag NANOCOMPOSITES FOR SELF-CLEANING AND ANTIMICROBIAL PROPERTIES ON COTTON FABRIC

ABSTRACT

Green chemistry approach is an emerging interdisciplinary area that is expected to have wide ranging implications in all fields of science and technology. Although green chemistry is still in its infancy, it is already proving to be a useful tool in improving the performance of nanomaterial and generating worldwide interest. Titanium (IV) dioxide nanoparticles (TiO_2 NPs), silver nanoparticles (AgNPs) and titanium dioxide – silver nanocomposites (TiO_2 – NCs) have been successfully synthesised using hydrothermal green chemistry approaches. The synthesised TiO_2 NPs and AgNPs materials were tested in the photocatalytic and antimicrobial studies respectively. A self - doped (Ti^{3+}) mesoporous anatase TiO_2 NPs were synthesised using simple precipitation method under low temperature and their significant role in photocatlytic activities was revealed. The surface area of TiO_2 NPs is 87.2 m^2 g^{-1} and the average pore size of mesopore is 8.7 nm, meanwhile for macropores are 50 to 70.2 nm. The presence of meso and macropores enhance the photodegradation process of methylene blue (MB) solution under sunlight. The reaction parameters of photocatalytic activities by the TiO_2 NPs synthesised using 0.01 mol of titanium isopropoxide (TTIP) under basic condition showed that 0.1 g of TiO_2 NPs worked effectively in the photodegradation of cationic dye (MB). Synthesised TiO_2 NPs maintained high photocatalytic activities for at least ten cycles of extended usage without losing their efficiency. Uniform silver nanoparticles (AgNPs) with crystallite size 19.3 nm were successfully synthesised using facile

hydrothermal method. Optimisation studies for synthesis of AgNPs were determined using disc diffusion assay for antimicrobial test. AgNPs were synthesised using molar ratio $AgNO_3$: PVP (1:5) at 160 °C for 24 hr showed stronger antimicrobial properties against Gram negative (14.3 ± 0.57 mm) bacteria than Gram positive (12.3 ± 0.57 mm) bacteria. When Ag is incorporated with the TiO_2, it was found that the dual properties of both elements in single material (TiO_2 – Ag NCs) were improved. TiO_2 – Ag NCs were synthesised *via* one- pot hydrothermal method using various loading of TiO_2 precursor (TTIP). Studies confirmed that the size of Ag in TiO_2 NCs reduced drastically to 5 nm which induce the synergy effect and indirectly boost the antimicrobial activities of TiO_2 – Ag NCs. Synthesised TiO_2 – Ag NCs were further coated on cotton fabric in order to produce a smart material with self – cleaning and antimicrobial properties. The TiO_2 – Ag NCs were successfully coated on fabric with the aid of cross – linking agent (succinic acid) and also catalyst (sodium hypophosphite) using hydrothermal method. TiO_2 – Ag NCs coated cotton fabric has been proven to have a promising self – cleaning properties even after four washings.

CHAPTER 1

INTRODUCTION

1.1 Overview

Nanotechnology is still progressive and largely in the "discovery phase" since twenty first century. In general, nanotechnology can be defined as employment of materials at the atomic level by a combination of engineering, chemical, and biological approaches. The modern concept of nanotechnology, which is now considered to be the most widely studied field in science has been attracting a great deal of attention for a variety applications ranging from automotive, biomedical, electrical and so on because of the attractive mechanical, chemical and physical properties offered by the nanoparticles (Suresh, 2013). It is therefore now possible to modify the use of nanostructures in the coating industry to the specific needs of the various applications. In that case, nano-based coatings are widely used today to produce smart materials, for instance, to functionalise surfaces, to provide protection against corrosion and dirt, and to generate attractive designs by special colour effects (Kalangutkar, 2015).

Smart materials obtained through deposition of photoactive nanoparticles on fabrics have gained increasingly more interest on the market due to their multifunctional properties. Typically, new properties can be added on to various fabrics (e.g cotton, polyester, wool, etc.) by incorporating functional agents onto their fibres using chemical or physical procedures. Noble metals and metallic oxide nanoparticles (NPs) are mostly used in developing multifunctional textiles with special properties such as antibacterial activities (against *Escherichia coli*, *Staphylococcus aureus*, and *Klebsiella pneumoniae*) (Samal, Jeyaraman, & Vishwakarma, 2010) and self-cleaning properties on fabric by employing the photocatalytic process on the

fabric with photocatalyst such as titanium dioxide (TiO_2). This smart fabric with enhanced dual functionalities also has enormous potential for improvement of in health industries in order to save the time, energy, material, and subsequently the production cost. Moreover, this technology embraces environmental friendly properties as it efficiently reduces the cleaning efforts and save a significant amount of water and energy (El-Khatib, 2012).

Incorporating noble metals with metal oxides and noble metals have been reported in previous studies (Viana et al., 2013). The use of nanostructured noble metals with antibacterial properties has drawn considerable attention due to their high heat resistance, low decomposability, and long life expectancy. Among noble metals, metallic silver (Ag) has been known as effective antimicrobial agent because Ag is a noble metal that does not corrode during self-cleaning or photocatalytic activity (Yang, 2017). In general, titanium (IV) dioxide (TiO_2) is the most common photocatalyst selected to be incorporated with Ag in order to produce a dual functionalised material, TiO_2-Ag nanocomposites (TiO_2-Ag NCs). TiO_2 can be an ideal candidate for integration with Ag since the chemical and physical properties of both metal and metal oxide can be enhanced. TiO_2, a binary metal oxide with a bandgap of 3.2 eV for anatase has received large attention due to its biological and chemical inertness, cost-effectiveness, low toxicity and ease of preparation in bulk or nanostructured forms.

Abundant conventional methods such as sol-gel technique, chemical precipitation and chemical vapour depositions are applied to synthesize metal oxides (TiO_2 NPs) and noble metals (AgNPs). However, most of the traditional methods employ harmful reagents, long reaction time and required complicated process involving more than one step process as carried by the other reported researchers (Thein, Pung, Aziz, & Itoh, 2015). Therefore, modifying the existing methods for

synthesis of nanomaterials by applying green chemistry principles is considered better as it is eco-friendly, sustainable, and relatively reproducible and the end products are often more stable.

1.2 Problems statement

The production of nanoparticles through expensive conventional physical and chemical methods such as sol-gel, solvothermal and electrochemistry methods resulted in lethal by-products which are hazardous to environment. Although these conventional methods can provide various improvement in nanomaterial for another several hundred years, continuous reliance on them will cause severe problems to our economy and environment. Economic problems are predicted to arise from a steady increase of harmful chemical reagents because of continuous demand but restricted supply. Excessive use of solvents or chemicals and conducting synthesis under high energy for long term may lead to devastation in our ecosystem. Multiple conventional methods has been applied to synthesis TiO_2 and AgNPs in large amounts with well-defined sizes and shapes in a short period of time. However, these techniques use hazardous chemicals, such as organic solvents, reducing agents and stabilisers that are used to prevent unwanted agglomeration of the nanoparticles. Therefore, all these factors can be potentially controlled by synthesis nanomaterials using *via* green chemistry approaches. As a result, the nanoparticles synthesised using green technique have diverse natures and greater colloidal stability. Even though green chemistry has been introduced decades ago, but most of the methods developed to synthesis TiO_2 and AgNPs are two step methods such as two-step sol-gel method or microwave assisted solvothermal method. One potential way to meet these challenges is to synthesis nanoparticle without organic solvents or chemicals, using water as synthesis media and carried out an inexpensive one step reaction.

1.3 Research objectives

The objectives of this research are as follows:

i. To develop green chemistry techniques in synthesising titanium oxide (TiO_2), silver (Ag) nanoparticles (NPs) and titanium oxide-silver (TiO_2-Ag) nanocomposites (NCs).
ii. To evaluate the photocatalytic and antimicrobial performance of TiO_2 NPs, AgNPs and TiO_2-Ag NCs under various conditions.
iii. To deposit TiO_2-Ag NCs on cotton fabrics and compare their antibacterial and photocatalytic properties.

1.4 Outline of the thesis

The thesis consists of seven chapters:

Chapter 1 is the introduction of the thesis. It emphasises on the problem statements, research objectives and outlines of the content.

Chapter 2 is a detailed literature review on some basic knowledge of photocatalysis and antibacterial activities, green chemistry principle and properties of TiO_2 and Ag nanoparticles.

Chapter 3 outlines the general experimental techniques and procedures for synthesising TiO_2 NPs, AgNPs and TiO_2 – Ag NCs using green chemistry approaches. The principles of the instrumental characterisations methods by field emission scanning electron microscope (FESEM), X-ray diffraction (XRD), nitrogen adsorption analysis (NAA), Fourier transform infrared (FTIR) analysis, Zeta potential analysis and X-ray photoelectron spectroscopy (XPS) are briefly discussed.

Chapter 4 summaries the green synthesis and characterisations of TiO_2 NPs under different concentrations of precursor and initial solution pH as reported. Optimisation studies for photocatalytic activity of synthesised TiO_2 NPs were also stated.

Chapter 5 outlines the green synthesis AgNPs *via* hydrothermal route and their antimicrobial studies were investigated and reported. Optimisation parameters for molar ratio of precursors and colloid stabiliser, reaction time and temperature of reaction were described.

Chapter 6 describes the synthesis of TiO_2 – Ag NCs under different concentrations of precursor. The TiO_2 – Ag NCs were then deposited on cotton fabric and tested in both photocatalytic and antimicrobial analyses.

Chapter 7 abstracts a conclusion of the thesis and recommendations for future research.

CHAPTER 2

LITERATURE REVIEW

2.1 Solar-driven photocatalysis

Solar energy is a great and renewable energy source and it is estimated that around 0.01% of the energy of sunlight irradiation is sufficient to supply all the energy that human activities required (Reza Gholipour, Dinh, Béland, & Do, 2015). Most of the solar energy is extensively used in the photochemical process such as photosynthesis. Photochemical process is an economically feasible and environmentally attractive because solar photons can be directly absorbed by catalysts to initiate the reactions. For example, solar photochemical detoxification technologies are extensively applied in the environmental waste management industry by using abundant energy from the sun to degrade the wastes (Kubacka, Fernández-García, & Colón, 2012).

Metal oxide-mediated photocatalysis is expected to be a vital revolution in the employment of solar processes. A metal oxide photocatalyst speeds up the action of light by first absorbing photon and producing electrons and holes. With the abundance of costless solar radiations, a low cost catalyst may be useful for numerous applications (Zyoud et al., 2015). It shows a possible number of promising applications to this environmental technology, because with natural sunlight complete mineralisation of persistent contaminants seems to be the most practical process. Hence, no doubt that detoxifying pollutants by solar-driven photocatalysis using metal oxides as catalysts is full of potential (Robert & Malato, 2002).

2.2 Concept of a heterogenous photocatalysis

The word photocatalysis includes the combination of photochemistry with catalysis. It is a chemical process catalysed by a solid with strong oxidising agent (usually dissolved oxygen) under the energy source which is an electromagnetic field with wavenumbers in the UV visible-infrared range (Robert & Malato, 2002). Photocatalysis may also define as the acceleration of a photoreaction in the presence of a catalyst (Ibhadon & Fitzpatrick, 2013). Photocatalysis generally can be divided into two systems: heterogeneous and homogeneous photocatalysis. Heterogeneous system involve different state of photocatalyst slurries for catalysis, whereas homogeneous photocatalysis is used in a single-phase system (Kubacka et al., 2012). Heterogeneous catalysts have numerous benefits compared to other catalytic processes because they avoid formation of inorganic salts and the recovery of photocatalyst is inexepensive. Heterogeneous photocatalysts are also safe to handle, easy to store and have long life time (Atalay & Ersöz, 2016).

As photocatalyst, the metal oxides must consist of the following properties: (i) capable to absorb visible and/or UV light, (ii) chemically and biologically inert and photo stable, (iii) inexpensive and (iv) non-hazardous (Kubacka et al., 2012). In this case, photo stable means metal oxide which is resistant to change under the influence of radiant energy, especially light. Besides, a semiconductor is different from insulator because semiconductors possess an empty energy region in between highest occupied energy band (valance band (VB)), and the lowest unoccupied band (conduction band (CB)). The empty energy region between the VB and CB is called bandgap (Nyankson et al., 2013).

Generally, photocatalytic activity on semiconductors consists of five basic steps; (1) reactants diffused to the surface of semiconductor, (2) adsorption of reactants onto the surface of solid, (3) reaction on the surface of semiconductor, (4) desorption of products from the surface of the semiconductor and (5) diffusion of products from the surface of the semiconductor (Ibhadon & Fitzpatrick, 2013). The initial process for heterogeneous photocatalysis of organic and inorganic compounds by semiconductors initiates with the absorption of photons with energy equivalent to or greater than the bandgap of the semiconductor. This produces electron-hole (e^-/h^+) pairs which leads to the redox reaction on the surface of semiconductor (Figure 2.1).

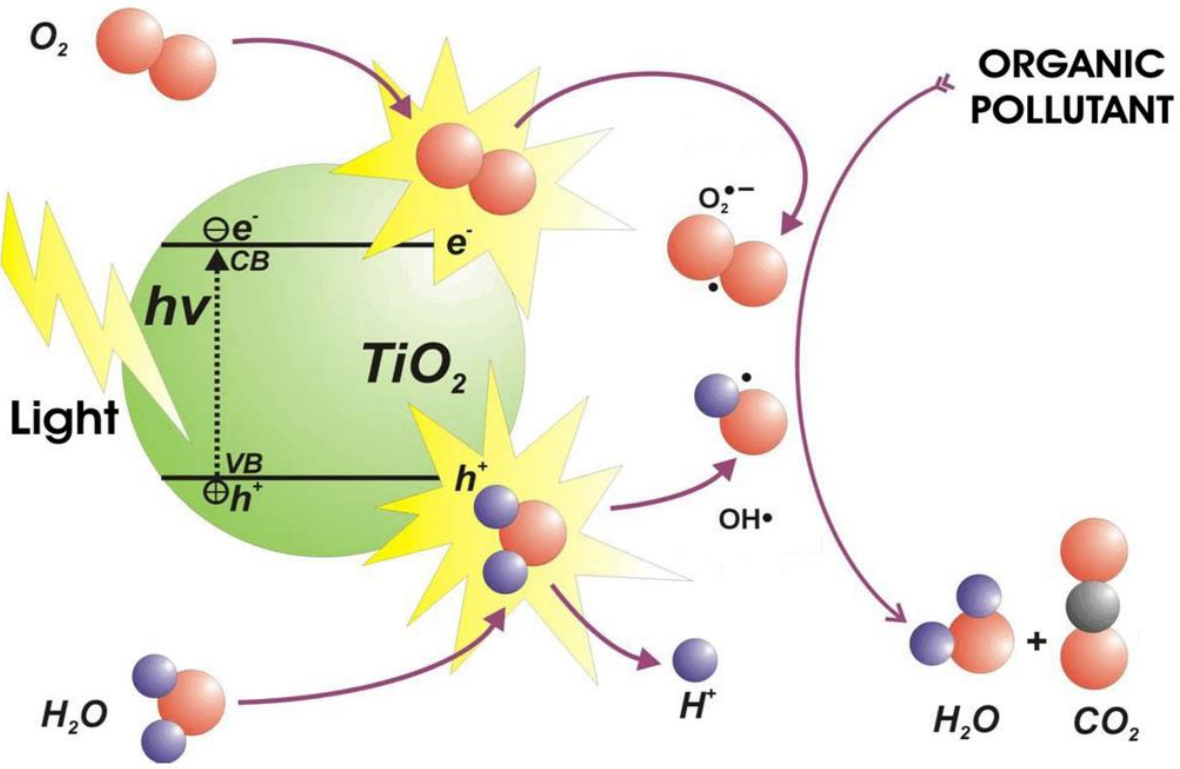

Figure 2.1: Schematic illustration of photocatalytic mechanism of activated semiconductor photocatalyst (Ibhadon & Fitzpatrick, 2013).

Participation of excited electron and the hole in redox reactions with water, hydroxide ion (OH^-), oxygen and organic compounds leading to mineralisation of the pollutant into H_2O and CO_2. It is also observed that in the absence of H_2O,

heterogeneous photocatalytic activity could not occur because hydroxyl radicals cannot be created. Subsequently, oxidation of water or OH^- by the hole produces the hydroxyl radical (•OH), a powerful oxidant. •OH radicals, which are known as the most main radicals are form in semiconductor photocatalysis and they are able to attack the pollutants rapidly on the semiconductor surface. Reduction of adsorbed oxygen to oxygen radicals is a substantial reaction in the conduction band and this stops the electron from recombining with the hole. Hence, the oxygen radicals are accumulated at the conduction bands which can also contribute in degrading waste product in solution (Pelaez et al., 2012). This heterogeneous photocatalytic property of semiconductors provides its self-cleaning property and potentially used in environmental cleaning.

2.3 Kinetics of photocatalytic activity

2.3.1 Rate constants

Chemical kinetics are related with reaction rate and are concerned with both disappearance and appearance of chemical substances. In chemical equilibrium, the reactants and the products are in dynamic state of balance. Generally, for photocatalysis they deal with two types of chemical kinetics; first-order kinetics and Langmuir-Hinshelwood kinetics (Gaya, 2014).

Rate constants, k, are precise for a specific reaction at certain temperatures. The activation energy, Ea ,of a reaction is calculated using the temperature dependence rate constants. Subsequently, rate constants are commonly given in a general form as a function of T (the absolute temperature). Thus, if environmental temperatures and reactant concentrations are known, the rates of reactions under various conditions can be evaluated. The units associated with a rate constant depend on the molecularity

(order) of the reaction. This can be proven by rearranging the differential rate equation to isolate k (Wang et al., 2010).

Integrated law for first-order processes:

$$r = \frac{-d[A]}{dt} = k[A] \tag{2.1}$$

$$ln\frac{[A]_t}{[A]_0} = -kt \tag{2.2}$$

For second-order processes:

$$r = \frac{-d\,[A]}{dt} = k[A]^2 \tag{2.3}$$

$$-\frac{1}{[A]_t} + \frac{1}{[A]_0} = -kt \tag{2.4}$$

However, first-order kinetics is generally employed for reactions proceeding in homogeneous solution or gaseous phase. The rate of a monomolecular reaction obeys a first-order rate expression that is explained by that proportion (number) of molecules having kinetic energy larger than the activation energy is estimated only by temperature of the reaction. Basically, the first-order kinetics has often been used for discussion of time courses of photocatalytic reactions, meanwhile (pseudo) first-order model is extensively used to determine the adsorption capacity of catalyst in which the experiment for kinetic studies are carried out in dark condition (Vezzoli, 2012; Ayanda, Adeyi, Durojaiye, & Olafisoye, 2012). When an adsorption of products on catalyst was considered, a modified pseudo first-order rate expression is used.

Adsorption capacity at equilibrium needs to be calculated before continuing to pseudo-first-order rate expression:

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{2.5}$$

Where C_0 is the initial dye concentration (mg L^{-1}), C_e is the dye concentration at equilibrium (mg L^{-1}), V is the volume of dye solution used (L) and m is the mass of the catalyst used (mg). The integrated pseudo-first-order model is generally expressed as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_l}{2.303} t \tag{2.6}$$

Where q_e (mg g^{-1}) and q_t (mg g^{-1}) are adsorption capacity at equilibrium and time *t*, respectively, while k_l (min^{-1}) is the pseudo-first-order rate constant.

On the other hand, kinetics of reactions occurring on a solid catalyst or photocatalyst surface, are different because monomolecular reaction cannot proceed on the solid surface. Thus for heterogenous catalysis Langmuir-Hinshelwood type of mechanism in the lower concentration region is more appropriate.

2.3.2 Langmuir-Hinshelwood kinetics

In many cases, the Langmuir-Hinshelwood (L-H) kinetic model is widely applied to describe the kinetics of the heterogeneous catalysis system. Most researchers have claimed that a photocatalytic reaction is a surface reaction and it proceeds *via* the L-H mechanism when a linear reciprocal relation is observed between the reaction rate and the concentration of reaction substrate in a solution. A general integrated rate law for L-H model is given below:

$$-\frac{dC}{dt} = k_{LH}\frac{K_L C}{1 + K_L C} \quad (2.7)$$

where, K_L = Langmuir adsorption constant (L mg^{-1}) and k_{LH} = Langmuir-Hinshelwood reaction rate constant (mg $L^{-1}min^{-1}$)

In most photocatalytic kinetic studies it is assumed that the low concentration of substrate, (mol L^{-1}) < 10^{-3} (Lazar, Varghese, & Nair, 2012; Ferreira, Asenjo, Santamarı, & Mene, 2017), the term K_L becomes < 1, when the denominator on equation (2.7) is neglected and the equation (2.7) can be reduced to an apparent integrated first order reaction:

$$\ln\frac{C_0}{C_t} = k't \quad (2.8)$$

However, if K_L >> 1 (at high concentration of substrate) then equation (2.7) becomes a zero order expression (Eng et al., 2013), indicating a broad coverage of the active centers by the organic molecules:

$$\ln\frac{C_0}{C_t} = k'' \quad (2.9)$$

Where, C_t is the concentration of methylene blue (MB) at *t* time(min), and *k'*, *k''* are the rate constants for L-H first-order and zero-model, respectively.

According to numerous evaluations on L-H kinetic model, the first-order kinetic expression has been proved to be compatible with most of the photocatalytic activities of semiconductors (Joonwichien, Yamasue, Okumura, & Ishihara, 2011). Besides, in order to determine the superiority of new photocatalysts over commercialised photocatalysts in market such as P25 Degussa TiO_2 (Acros Organics, New Jersey, USA), many physicochemical characteristics of the

photocatalysts such as the crystallinity, size, surface defects, specific surface area and aggregation of particles are investigated and compared (Rochkind, Pasternak, & Paz, 2015; Ibhadon & Fitzpatrick, 2013).

2.4 Metal oxides in photocatalytic activities

Different semiconducting materials with various bandgap energies have been evaluated as photocatalysts in the literatures (Nagaveni, Hegde, Ravishankar, & Subbanna, 2004; Genuino, Huang, Njagi, Stafford, & Suib, 2012). An ideal photocatalyst is expected to have certain advantages such as easy to produce and use, cost effective, photostable, non-hazardous for humans and the environment, efficiently activated by solar light and able to catalyse the chemical reaction proficiently (Kubacka et al., 2012).

The semiconductors such as TiO_2, ZnO, $SrTiO_3$, CeO_2, WO_3, Fe_2O_3 and CuO have shown promising redox or charge-transfer processes because of their electronic structures which are characterised by a filled valence band and an empty conduction band. However, most of the reported photocatalysts possess disadvantages. They are not appropriately used in catalysis in aqueous media as they readily undergo photo-corrosion problems upon excitation in solution. ZnO is still unfavourable when compared to TiO_2 because it is readily dissolved in water to produce $Zn(OH)_2$ on the ZnO particle surface, which deactivates the catalyst after being used for several times. Fe_2O_3, on the other hand, is well-known for its low cost and narrow bandgap for harnessing solar energy. However the only disadvantage for using Fe_2O_3 is that it suffers from rapid charge recombination and a short charge carrier diffusion length (Ibhadon & Fitzpatrick, 2013). Meanwhile, SnO_2 and WO_3 possess a conduction band edge at an energy level below the reversible hydrogen potential where these materials

need an aid of an exterior electrical bias to complete the photocatalytic process (Gupta & Tripathi, 2011).

TiO_2 is the most commonly used photocatalyst for degradation of a wide range of pollutants because it fulfills all of the above requirements as well as displaying sufficient conversion values (Kubacka et al., 2012). TiO_2 in its anatase form is effective, photochemically stable, non-toxic in nature and inexpensive. Moreover, due to its strongly oxidised holes and highly redox selective, several novel heterogeneous photocatalytic reactions and self-cleaning properties have been explored extensively for environmental cleanup applications.

2.5 Titanium (IV) dioxide (TiO_2)

2.5.1 General

Titanium dioxide (TiO_2) belongs to the family of transition metal oxides. It is a naturally occurring oxide of Titanium (Ti). The unique properties of TiO_2 is directly connected to its crystal structure which is also related to its processing method (Nyankson et al., 2013). As n-type semiconductor, TiO_2 is photoactive, biologically and chemically inert, resistant to photo and chemical corrosion, low cost, long durability and low toxicity (Vadlapudi & Behara, 2013). Due to its excellent pigmentary properties, high ultraviolet absorption and high thermal stability, TiO_2 is has been used in diverse applications such as electro-ceramics, glass, paints, sunscreen, self-cleaning surfaces, air and water purification, water splitting and photoelectrochemical conversion (Pelaez et al., 2012).

2.5.2 Chemical structures and properties of TiO_2

The unique properties of TiO_2 is directly related to its crystal structure. It is also reported as one of the factors affecting its activity. TiO_2 generally occurs in nature in three crystallographic phases (Figure 2.2):

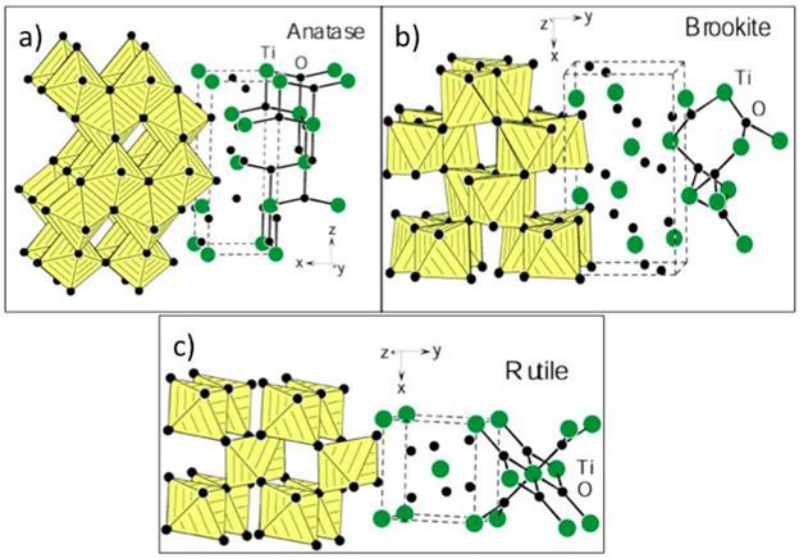

Figure 2.2: Crystalline structures of (a) anatase, (b) brookite and (c) rutile TiO_2 (Reza Gholipour et al., 2015).

1) Anatase: It has the distortion of the TiO_6 octahedron and is slightly larger compared to rutile phase. Anatase is made up of corner (vertice) sharing octahedra which form (001) planes resulting in a tetragonal structure.

2) Rutile: It is the primary source and the most stable form of TiO_2 at most pressures and temperatures. In rutile, the octahedra share edges at (001) planes to give a tetragonal structure.

3) Brookite : It has an orthorhombic crystal system. Its unit cell is composed of 8 formula units of TiO_2 and is formed by edge and corners sharing TiO_6 octahedra.

TiO_2 is a large band semiconductor, with bandgaps of 3.2, 3.0, and ~3.2 eV for the anatase, rutile and brookite phases, respectively. Even though, rutile exhibits the lowest bandgap, the anatase structure is preferred over other polymorphs because of its higher electron mobility and lower density (Kandiel, Robben, Alkaim, & Bahnemann, 2013). Brookite known as the least active phase of TiO_2 due to its more complicated crystalline structure with larger cell volume. It is also the least dense compared to anatase and rutile (Gupta & Tripathi, 2011).

Normally, when anatase and brookite TiO_2 are introduced with temperatures exceeding 600 °C, they will be transformed into more thermodynamically stable rutile which has a very poor photocatalytic activities. The transformation is also influenced by other factors such as synthesis conditions, types of precursors used, impurities, oxygen vacancies and the primary particle size of the anatase phase (Reza Gholipour et al., 2015).

2.6 Modification of TiO_2 into TiO_2 nanocomposites

Nanocomposite is a combination of matrix, in which different materials combine to develop new properties ensuring that one of the materials has size in the range of 1-100 nm. Various researches have been exploited to modify TiO_2 into nanocomposites using numerous approaches to improve the performance TiO_2 nanomaterials and to produce an end product with dual functionalities. Although the use of pure TiO_2 as a UV absorber is possible, it has become clear that this is less feasible for utilising photoelectrochemical properties of TiO_2 alone into the biological applications. Thus, more researches have been dedicated to the construction of nanoscale TiO_2 composite materials (Dastjerdi, Montazer, & Shahsavan, 2010). In addition, there have been great efforts to incorporate additional components including

polymers, transition metals, metal oxides and noble metals to develop the properties of TiO_2 or to provide multi-functioned TiO_2.

Many polymer nanocomposites have been manufactured using polyester, polypropylene, polyethylene, nylon with TiO_2 as fillers to improve the surface area to volume ratio, and to develop system energy and structure of TiO_2 (Chaudhari, 2015). Polymers are also incorporated with TiO_2 to immobilise the TiO_2 powders which improve the reusability efficiency of the photocatalyst. Moreover, instead of using a single semiconductor (TiO_2), uniting the TiO_2 with other semiconductors or metals would lead to the development of a heterojunction structure between them. Besides, coupling collective oscillations of the electrons were found to improve the performance of several devices such as solar cells (Reza Gholipour et al., 2015; Chen & Mao, 2007).

Since TiO_2 is known to have a broader range of applications in healthcare, environmental, cosmetic and food industries, modified TiO_2 with noble metals are considered to be more effective due to different physicochemical properties in comparison to their fine particles. Modified TiO_2 with noble metals are also used significantly in environmental applications like water and air purification, dye removal and solar water splitting. In addition, TiO_2-noble metal composites have also been explored extensively in biomedical applications such as in photodynamic therapy (PDT) for cancer, drug delivery system, cell imaging, biosensors for biological assay, and as endonucleases in genetic engineering (Ghosh & Das, 2015). Thus, the synthesis of numerous nanocomposites of TiO_2 semiconductor with several noble metals will be further discussed in the following section. These composites are considered to have unique dual properties that is yielding the greatest benefits in diverse applications.

2.7 Combination of TiO_2 with noble metals

Several strategies have been employed for modification of TiO_2 nanoparticles. However, incorporation of noble metals to TiO_2 has received the utmost attention compared to polymer/ceramic based nanocomposites because of its hybridisation of two or more materials with distinctive properties. This acts synergistically to develop new functionalities and hence improving their properties. One of the reasons semiconductor NPs coupled to noble metals co-catalyst is to increase the effectiveness of photocatalytic reaction by enhancing the quantum yield of the electron transfer processes. The electron transfer process occurred during the charge separation route in the semiconductor where photogenerated electrons were discharged across the interface and providing a redox pathway with low over-potential. Thus, when the metal nanoparticles are introduced to semiconductor nanoparticles, they able to accept and transport electrons to an acceptor molecules easily (Ibhadon & Fitzpatrick, 2013).

TiO_2 composite systems have been analysed from the starting point of the photocatalysis research field. Fine noble metals that have been investigated are Ag, Pt, Pd and gold Au (Kubacka et al., 2012). Among metal nanomaterials, metallic Ag has been known as effective composite material to be merged with TiO_2 because Ag is a noble metal that does not corrode under photocatalytic conditions. For economical and resourceful use of Ag, composite materials incorporating Ag nanoparticles have been developed and verified in diverse applications.

Generally, TiO and metal incorporated based on two main models which correspond to phase-coupled or coreshell geometries. In addition to the improvement of photocatalysis, composite structures can yield other benefits. For example, addition of Ag noble metal to TiO_2 can yield a product consist of self-cleaning and antimicrobial

properties. Further, composites can be of great use to create highly porous materials, hollow shells and hierarchical structures by templating methods (Dahl, Liu, & Yin, 2014).

2.8 AgNPs

2.8.1 Properties AgNPs

AgNPs material has been studied and exploited in large extent to obtain a complete and organized perspective of AgNPs. In fact, it was reported that nanosilver had a history of approximately 120 years of usage, mainly under the term ‘colloidal silver’ (Yang, 2017). Any noble metals employed in optical detection are usually to obtain the surface plasmon resonance (SPR) effect and Ag shows the highest SPR band intensity than any other NPs like copper and gold. Since Ag NPs show sharper and stronger peaks of plasmon resonance than gold NPs at the equal concentration of particles. This phenomenon proves that the AgNPs have higher plasmon efficiency compared to gold NPs. For this reason Ag NPs show better sensitivity for applications like surface enhanced Raman scattering and localised SPR surface plasmon resonance (Nurani, Saha, Rahman Khan, & Sunny, 2015).

Moreover, nano-sized Ag has distinctive physical, chemical and biological properties compared to their micro-scaled counterparts. AgNPs have unique physico-chemical properties, surface-enhanced Raman scattering, high chemical stability, non-linear optical behaviors and high catalytic activity. These properties induce them to display wide spectrum bactericidal and fungicidal activities (Srikar, Giri, Pal, Mishra, & Upadhyay, 2016) that have made them tremendously popular in a various range of consumer products, including textiles, food, plastics, soaps and pastes. To date, nanosilver technologies have appeared in a variety of manufacturing processes and end products (Tran, Nguyen, & Le, 2013). The following sections will cover the

antimicrobial effects of AgNPs and their mechanisms involved in antimicrobial activity.

2.8.2 Concept of antimicrobial activities of AgNPs towards bacteria

AgNPs have received great attention due to its strong toxicity to a widespread range of microorganisms, including Gram-positive and Gram-negative bacteria. The highest antibacterial activities has been found against *Streptococcus pyogenes, Staphylococcus aureus* and *Staphylococcus epidermidis* and moderate sensitivity against *Klebsiella pneumonia* and *Salmonella typhi* (Nurani et al., 2015). The properties such as shape, size, morphology, aggregation level of AgNPs play an important role in the nanoparticles antibacterial activities. Properties of AgNPs normally can be affected by a number of factors such as the type of stabiliser employed and the techniques used for synthesis of nanoparticles (Zewde, Ambaye, Iii, & Dharmara, 2016). For example, many studies claimed that small Ag particles synthesised using numerous techniques have higher antibacterial activities than the big Ag particles because the antibacterial activities are largely depended on the penetrating ability and the surface to volume ratio of particles. (Renaud, Renaud, Sarantopoulos, & Maury, 2010).

Various mechanisms of the inhibitory effect of AgNPs on bacteria have been suggested. The AgNPs show efficient antimicrobial properties compared to other salts due to their extremely large surface area, which provides better contact with microorganisms. Both Gram positive and Gram negative bacteria hold the same mechanism. Generally, antibacterial activities of AgNPs ranging from (a) formation of pits in cell wall, (b) interference of cell membrane and (c) binding of AgNPs with basic residues within the cell components.

AgNPs have high affinity towards phosphorus and sulphur, and hence it exhibits an efficient antibacterial effect. AgNPs react with the sulphur-containing amino acids outside or inside the cell membrane *via* free radical formation by AgNPs and indirectly inhibit the respiratory enzymes of the microorganism. When AgNPs enter the bacterial cell the Ag^+ ions are released from the AgNPs forming a low molecular weight region in the centre. However, the bacteria conglomerates, protecting the DNA from the Ag^+ ions. In that case, the AgNPs or Ag^+ ions attack the respiratory chain, cell division which results the stoppage of DNA replication and finally, leading to cell death of the bacteria. (Rai, Yadav, & Gade, 2009)

2.9 Green chemistry principles

Green Chemistry, which is also named as sustainable chemistry, is defined as the design of chemical products and processes to decrease or remove the use and generation of toxic substances. (Atalay & Ersöz, 2016). This definition and the concept of Green Chemistry were first formulated at the beginning of the 1990s. Green Chemistry is also well-known for its practice of chemical science and manufacturing by taking into account the important rules such as non-polluting and consuming minimum amounts of materials and energy while producing little to no waste materials. It includes novelty, planning and systematic conception too (Malik, Shankar, Malik, Sharma, & Mukherjee, 2014); (Hutchison, 2007). The field of Green Chemistry has revealed how chemists can design next generation products and processes to ensure that they are profitable while being safe to the environment and human health. The design of environmentally benign chemicals and processes are guided by the 12 Principles of Green Chemistry developed by Anastas and Warner summarised (Figure 2.3).

Furthermore, green nanoscience/nanotechnology involves the application of green chemistry principles to the design of nanoscale products, the expansion of nanomaterial production techniques and the application of nanomaterials. It focuses on the discovery of synthesis and production of nanomaterials that eliminate the use of harmful reagents while providing the compulsory volume of pure material in economically practicable manner. It also provides practical designation to ensure the nanomaterials produced are biologically and ecologically safe. Finally, the application of nanomaterials synthesised must take into account where it provides maximum social advantage while reducing the effect on the ecosystem (Anastas & Eghbali, 2010); (Pattanayak, Basak, & Nayak, 2014).

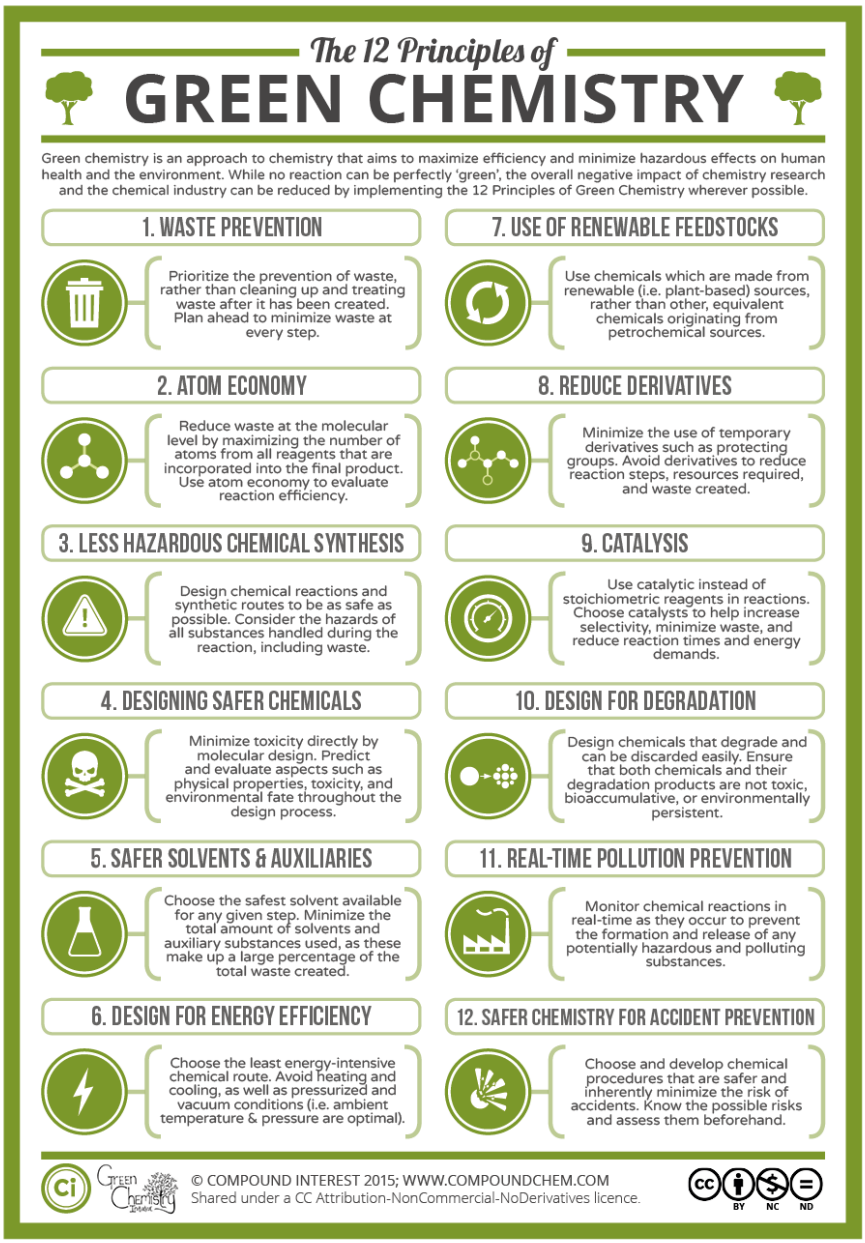

Figure 2.3: The Twelve Principle of Green Chemistry (Source: http://www.compoundchem.com/2015/09/24/green-chemistry/)

2.10 Smart textile with self-functioning capabilities

Textile products play an important role in our basic need. They are commonly produced and used in clothing industry. Textiles or fabrics are also vital in other industries such as agricultural industry, transportation, building material and also health industry. Therefore, the technological advances of textiles are improved in order

to meet the need of various industries. Smart textiles, which are textiles with innovative and mechanical applications, can receive and give responses to the external stimuli in order to adapt to the technological changes in surrounding. ‘Self-functioning’ is an ability of a matter to perform a specific process or response automatically towards a corresponding requirement. In latest decades, implementation of smart textile with different 'self-functioning' competencies have been opened up progressively. Self-functional fabrics are widely acknowledged of bringing great benefits to the sustainable growth of society and to stimulate the quality of life as well (Morais, Guedes, & Lopes, 2016)

A fabric with self-cleaning function is known to be capable of decomposing or removing dirt automatically that can reduce human effort, detergents and water required in cleaning. The functions for self-cleaning include dirt and organic substances decomposition, pollutant degradation, deodorisation, anti-mould, and anti-bacteria. In recent years, photocatalytic coating is a popular approach for developing self-cleaning textiles. Photocatalysts, which are able to absorb light energy and decompose the organic matters during the process of photo catalysis, had been utilised for the invention of new self-cleaning textiles. Titanium dioxide (TiO_2), zinc oxide (ZnO) and porphyrins are the significant examples of photocatalysts.

The study of titanium dioxide (TiO_2) coatings on fabric surfaces had been reported in current years. Nano-crystalline TiO_2 finishing on cotton fabrics’ surface by dip-pad–dry-cure process had been produced. ‘Self-cleaning’ degradation of the organic materials such as colorant, red wine, coffee stains and bacteria under ultra-violet (UV) irradiation was successfully reported in previous study (Ambika & Sundrarajan, 2014). Although the substantial performance of degrading organic