EFFECTS OF FLUORINE MODIFIERS AND GOLD COLLOIDS IN ENHANCING PHOTOCATALYTIC ACTIVITY OF TiO_2 UNDER VISIBLE LIGHT IRRADIATION

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For those who value knowledge.

and even if all the trees on the earth were pens, and the sea (were ink) with seven more seas to increase it, still these could not suffice to record all the words of God.

(31:27)

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And to you reading this, may you find this study worthy and useful.

ABSTRACT

The process where a light-activated catalyst is used to break down organic contaminant is known as photocatalysis. In the class of photocatalyst, titanium dioxide (TiO_2) has isolated itself on top of the list and widely applied in environmental remediation including water treatment. In addition to the worrying release of industrial dye containing organic pollutants that threaten the environment, TiO_2 can be utilized to degrade dyes in the wastewater. To tune TiO_2 into a better photocatalyst with enhanced photocatalytic activity under visible light irradiation, TiO_2 was initially synthesized using peroxotitanic acid (PTA) method using two different solvents of distilled water and Zamzam water. Fluorine was then added into TiO_2 to control the crystal phase and morphology of TiO_2 nanoparticles which are proven by X-Ray Diffractometer (XRD) and Field Emission-Scanning Electron Microscope (FE-SEM) respectively. Fluorine-modified TiO_2 (F-TiO_2) revealed to be in single anatase form with the particle shape directed to ovoid shape. Gold nanoparticles (GNP) was also deposited on TiO_2, producing Au-TiO_2 to enhance the absorption in the visible light region as well to facilitate electron-hole separation. GNP stabilized using *Acacia senegal* and aloe vera were characterized using Ultraviolet-Visible (UV-Vis) spectrophotometer. Stabilization of GNP was found to be better using *Acacia senegal* with 2 : 1 weight ratio of stabilizer to gold precursor as compared to aloe vera. The photocatalytic activity of synthesized TiO_2 was carried out with 0.04 g/L Reactive Blue 19 dye aided with blue light (475 nm) to activate the photocatalyst. Photocatalysts synthesized from distilled water were found to display higher photocatalytic activity than Zamzam samples. Within 120 minutes of reaction, the highest percentage of degradation of 49.23 % was recorded by Au(AS)/F-P-TiO_2 (HF) which was characterized to be anatase, ovoid shape, crystallite size of 30.71 nm and band gap energy of 3.22 eV. The data presented in this study thus recognized the ability of TiO_2 to carry out photodegradation of reactive dye in the visible light region with credits given to the action of fluorine and gold for revamping the photocatalytic properties of TiO_2.

ABSTRAK

Proses di mana mangkin yang diaktifkan menerusi cahaya dan digunakan untuk menguraikan pencemar organik ditermakan sebagai fotopemangkinan. Di kalangan fotopemangkin, titanium dioksida (TiO_2) menduduki carta teratas dan banyak diaplikasikan dalam remediasi alam sekitar termasuk rawatan air. Masalah pelepasan pewarna fabrik yang mengandungi pencemar organik dan membahayakan alam sekitar kian meruncing, justeru, TiO_2 boleh digunapakai untuk merawat air sisa yang mengandungi pewarna fabrik. Untuk menjadikan TiO_2 sebagai fotopemangkin yang berupaya diaktifkan melalui cahaya nampak, TiO_2 dihasilkan menggunakan asid peroksotitanat (PTA), dan dua jenis pelarut digunakan sama ada air suling atau air Zamzam. Florin kemudian diasimilasikan bersama TiO_2 bagi mengawal fasa kristal dan morfologi nano partikel TiO_2 yang dibuktikan melalui Pembelau Sinar-X (XRD) dan Pengimbasan Elektron Pancaran Medan Mikroskopi (FE-SEM). F-TiO_2 telah dikenalpasti berada di dalam fasa anatas dan zarahnya didapati berbentuk bujur telur. Nano partikel emas (GNP) juga ditempelkan ke atas TiO_2 untuk membentuk Au-TiO_2 supaya penjerapan cahaya nampak dapat diperhebat dan juga untuk mendorong perceraian elektron-lubang. GNP distabilkan dengan *Acacia senegal* dan aloe vera telah dicirikan menggunakan Spektroskopi Ultralembayung-Nampak (UV-Vis). Penstabilan GNP menggunakan *Acacia senegal* pada nisbah 2 : 1 (penstabil kepada pelopor emas) adalah lebih baik berbanding aloe vera. Aktiviti fotopemangkinan TiO_2 dijalankan dengan 0.04 g/L Reactive Blue 19 dan dilengkapi cahaya biru (475 nm) untuk mengaktifkan fotopemangkin. Pemangkin dihasilkan dari air suling ternyata lebih baik daripada sampel Zamzam. Dalam masa 120 minit, kadar degradasi yang berjaya direkod adalah 49.23 % iaitu melalui Au(AS)/F-P-TiO_2 (HF) yang telah dicirikan sebagai *anatase*, berbentuk bujur telur, mempunyai diameter sebanyak 30.71 nm berserta tenaga sela jalur 3.22 eV. Data yang dipaparkan di dalam penyelidikan ini ternyata membuktikan kemampuan TiO_2 untuk menjalani proses fotopemangkinan pewarna fabrik di bawah jurang cahaya nampak melalui dwi-aksi florin dan GNP yang menjadikan sifat pemangkin TiO_2 ke suatu tahap yang lebih baik.

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LIST OF SYMBOLS AND ABBREVIATIONS

A	-	Absorbance
AS	-	*Acacia senegal*
Au	-	Gold
AV	-	Aloe vera
BET	-	Brunauer-Emmett-Teller
β	-	Full Width at Half Maximum
C	-	Concentration
CB	-	Conduction Band
D, d	-	Diameter
DR-UV	-	Ultraviolet-Visible Diffuse Reflectance
E_{BG}	-	Band gap energy
F	-	Fluorine
FE-SEM	-	Field Emission-Scanning Electron Microscopy
FTIR	-	Fourier Transform Infrared
GNP	-	Gold nanoparticle
HF	-	Hydrogen fluoride
HOMO	-	Highest occupied molecular orbital
k'	-	First-order-reaction rate
λ	-	Wavelength
LUMO	-	Lowest unoccupied molecular orbital
NBu_4F	-	Tetrabutylammonium fluoride
PTA	-	Peroxotitanic acid
RB19	-	Reactive Blue 19
SPR	-	Surface plasmon resonance
STEM	-	Scanning Transmission Electron Microscopy
TEM	-	Transmission Electron Microscopy

TTIP	-	Titanium isopropoxide
θ	-	Angle of diffraction
t	-	Time
TiO_2	-	Titanium dioxide
UV-Vis	-	Ultraviolet-Visible
VB	-	Valence band
XRD	-	X-Ray Diffraction

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CHAPTER 1

INTRODUCTION

1.1 Overview of Research

The term photocatalysis is no longer unusual in the world of science and technology today. Dated back in 1910, the terms photocatalysis and photocatalyst made their first debut in a Germany textbook on photochemistry [1]. In general, photocatalysis can be defined as the alteration of chemical reaction in the presence of light, where a photocatalyst; a light-activated catalyst by absorbing light photon increases the rate of reaction without itself being altered or consumed at the end of reaction. This process is considered to be an excellent way to degrade organic pollutants [2,3]. Among the potential photocatalysts ever studied, titanium dioxide (TiO_2) has been considered to be more superior than the others and act as an ideal material for environmental remediation. TiO_2 has been widely applied in photocatalysis as coating agent, air purifier, water remediation agent, as well as for cancer treatment [4,5]. Being inexpensive, chemically stable, non-toxic, commercially available, easy to be prepared in the laboratory, and possessing high photocatalytic reactivity made TiO_2 being intensively studied for its photocatalytic properties [6–8].

Titanium dioxide is also known as titania, titanium oxide and titanium (IV) oxide [9]. It appears as white, odourless powder and non-combustible solid [10] . TiO_2 exists in three different mineral forms (polymorphs) with the same chemical formula but different crystalline structures. Those three polymorphs of TiO_2 are anatase, rutile, and brookite [11]. Generally at temperature below 350°C, TiO_2 exist in amorphous form. Above that temperature, anatase phase is formed and when the temperature is elevated to 800°C or greater, rutile phase is formed [12]. While some researchers generally accept that pure phase of anatase TiO_2 demonstrated better photocatalytic properties, some proved that mixed phase of anatase and rutile owns the top [13–15].

TiO_2 is also termed as semiconductor photocatalyst because it exhibits semiconductor properties. Semiconductors as defined in Chemistry 9th Edition (2010) are the substances that have filled bands (valence band) that are slightly below, but do not overlap with empty band (conduction band). Semiconductors do not conduct electricity at low temperatures, but a small increase in temperature is sufficient to excite some of the highest-energy electrons into the empty conduction band. For electrons to be excited, the photon energy of light irradiation must be equal or greater than the band gap energy of the semiconductor [16]. Band gap energy is the energy difference between the two bands. As a semiconductor photocatalyst, when TiO_2 is irradiated by UV light, it absorbs the photon energy; causing the electron in valence band to be excited to conduction band. This left positively charged hole in the valence band. The photogenerated electron-hole pair will react with water and oxygen adsorbed on the surface of photocatalyst to produce radical species. These radical species are able to mineralize organic contaminants adsorbed on the surface. Eventually, repeated attacks by the radicals may result in complete mineralization to carbon dioxide and water [17,18].

To this date, textile industry is among the top contributors of pollution worldwide - with the utilization of synthetic dyes being one of the concerns. Reactive dye is one of the synthetic dyes being used in textile industry. Over 700, 000 tons of dyes are reckoned to be used annually with around 5-50% of these dyes are not fixed to the fiber and goes into the wastewater [19]. Reactive dye is one of the most common used type of dye in textile industry [20]. It is reported that the fixation rate of reactive dye is in the range of 50 – 90 % with 10 – 50 % of these dyes are directed in the wastewater [21]. Dyes in wastewater including reactive dyes consist of hardly biodegradable pollutants including persistent organic compounds, thus threatening the environment and our health [22,23]. Therefore, an effective and environmental friendly technology is very much needed to treat dye wastewater. In literature, TiO_2 has been used successfully to photocatalytically degrade dyes [24–28].

Though the successful application of TiO_2 in breaking down organic contaminants looks empowering, there are some issues that hinder its potential for practical application. Firstly, TiO_2 is only active with the presence of ultraviolet (UV) light because of its large band gap of 3.2 eV for anatase and 3.0 eV for rutile [29]. The dependency on UV light lowers the energy efficiency of TiO_2 because UV light only counters for 4 – 5 % of the solar spectrum while visible light dominated by 40 %. It is wise therefore to widen the absorption edge of TiO_2 from the UV region to the visible light region to increase it photocatalytic potential and make full use of the solar spectrum [30,31].

Secondly, the photogenerated electron-hole pair will recombine at the surface of TiO_2. Their accumulation in bulk at the surface thus reduces the active sites for photocatalysis. This will result in low photocatalytic activity that lowers the potential degradation rate by TiO_2 on the target contaminant [32]. This research is indeed motivated to counter for the drawbacks of TiO_2, enhancing its photocatalytic application under visible light irradiation for degradation of reactive dye.

This study had been conducted following the steps shown in the flowchart attached in Chapter 3 (see Figure 3.1). The study was initiated by synthesizing TiO_2 photocatalyst and modifying the photocatalyst to enhance its photocatalytic properties. Following these was the characterization of the synthesized samples and the study on photocatalytic activity. The conducted studies are briefly explained in the following pages, and a more detailed explanation is available on Chapter 3.

In order to achieve the primary objective of this study in producing visible light active TiO_2 photocatalyst, several experimental parameters had been optimized. First, two types of solvents (distilled water and Zamzam water) were used in the synthetic process to confab and further evaluate the variation in physical and chemical properties of TiO_2 that may arise during the synthesis of TiO_2 photocatalyst. According to Ritonga (2011) Zamzam water was reported to possess the most beautiful crystal molecule compared to other water [33]. Besides, Zamzam water is also believed to have healing power [34,35]. The unique crystal structure together with the healing power of Zamzam water are hoped to be able to improve the morphology of the synthesized TiO_2 and to better degrade the target pollutant.

Second, the addition of different fluorine modifiers (tetrabutylammonium fluoride, NBu_4F and hydrogen fluoride, HF) was aimed to control the size and morphology of TiO_2 particles. According to a study by Jan-Yves (2013), it was reported that modifying TiO_2 with fluorine (F) was able to control the shape of TiO_2 nanoparticles into egg-shaped (ovoid) with the addition of fluorine-containing salts as the surface modifier [36].

Third, the addition of gold nanoparticles (GNP) by either direct or post deposition were carried out to evaluate the shift of band gap of the synthesized photocatalyst. GNP was added as it has plasmonic effect that may lead to strong absorption in the visible light region [37]. This is possible due to the surface plasmon resonance (SPR) effect that allows strong absorption of the visible light. Besides, with GNP loading, charge separation between photo-generated electron and hole pairs are enhanced since the electrons are attracted to the GNP. The shift towards visible light absorption and induced charge separation therefore help to increase the photocatalytic activity of the modified TiO_2 [38,39].

Lastly, optimization of the ratio of two different types of stabilizing agent for gold colloid (Au-colloid) using *Acacia senegal* (arabic gum) and aloe vera with Au precursor (tetrachloroauric acid hydrate; $HAuCl_4$) was carried out to evaluate the effect of the addition of plant-based stabilizer towards hindering Au-colloid aggregation. According to the literature, Arabic gum and aloe vera may act as a stabilizing agent and further impede the aggregation of GNP [40–44].

There are several established methods to synthesize TiO_2 in which, among the well-known are sol-gel method, hydrothermal method and chemical vapor deposition [45,46]. Thermal degradation is another way of synthesizing TiO_2 which is also called as green synthesis because it is simple, cheap and does not incorporate the usage of hazardous chemicals [47]. In this study, TiO_2 samples were synthesized following thermal degradation of peroxotitanic acid (PTA) achieved from the reaction between the precursor; titanium isopropoxide (TTIP), and hydrogen peroxide (H_2O_2). PTA approach control the crystalline phase of TiO_2 by oxidizing amorphous titanium oxide precipitates using hydrogen peroxide, followed by a hydrothermal treatment at low temperature [48].

Successfully synthesized TiO_2 photocatalysts were then characterized by X-ray Diffraction (XRD), Fourier-Transform Infrared Spectroscopy (FTIR), Field Emission – Scanning Electron Microscopy (FE-SEM), Brunauer-Emmet-Teller (BET) analysis, Ultraviolet-Visible Reflectance spectrometry (DR-UV), and Ultraviolet – Visible Spectroscopy (UV-Vis). XRD serves to determine the crystallite phase and to estimate the crystallite size, while FTIR allows the analysis of the functional groups present in the synthesized TiO_2. To evaluate the surface morphology of the synthesized TiO_2, FE-SEM was used, whilst BET gives the surface area of TiO_2 particles. The band gap energy of the samples was determined using DR-UV.

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