THE EFFECT OF CALCINATION TEMPERATURE ON THE STRUCTURE AND PHOTOCATALYTIC ACTIVITY OF CARBON-DOPED TITANIUM DIOXIDE PREPARED VIA SOL-GEL ROUTE

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Specially dedicated to my beloved
MOM, Miskiah
DAD, Sean
SISTERS, Kartini and Tumirah
BROTHER, Mohd Khairul
Thank you very much for the prayer, love and support.

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ABSTRACT

The outstanding accomplishment by Fujishima and Honda (1972) on the discovery of photocatalytic water splitting by titanium dioxide (TiO_2) electrodes results in the extensive study of TiO_2 for air and water purification for environmental applications. Despite all the advantages provided from TiO_2 compared to other semiconductor photocatalysts, its two main concern issues, which are large band gap energy (E_g) and high recombination rate of photogenerated electrons (ē) and holes (h^+) pairs, restraint its usage in practical applications. Therefore, the development of visible light active TiO_2 become the challenge of researchers in the field of semiconductors photocatalysis. This study has been designated to the development of modified TiO_2 photocatalyst to enhance its photocatalytic activity into visible range and increase the charge carrier separation for more beneficial applications by carbon doping modification. Carbon-doped TiO_2 (C-TiO_2) nanoparticles with amorphous, anatase and mixed anatase/rutile phase were successfully synthesized via a simple and low-cost sol-gel route based on the self-assembly technique exploiting polyoxyethylenesorbitan monooleate (Tween 80) as a carbon source and calcined at 300-600 ^oC. The as-prepared powders were characterized by attenuated total reflectance spectra Fourier transform infrared spectroscopy (ATR-FTIR), diffuse reflectance ultraviolet-visible spectroscopy (DR UV-Vis), X-ray diffraction (XRD), scanning electron microscopy (SEM), photoluminescence (PL), and UV-Visible spectrophotometry (UV-Vis). With prolonged calcination temperature, the crystallite size and E_g were increased and the level of carbon doping decreased. All the nanoparticles showed high absorption in UV and visible light region. This is due to the reduction of E_g and the formation of sub-band observed by UV-Vis and PL spectrum, respectively. The formation of sub-band widens the absorption towards the visible light region. The potential of using the synthesized C-TiO_2 nanoparticles for photocatalytic environment remediation was demonstrated by the degradation of phenolphthalein (PHP) under UV and visible light irradiation. These photocatalytic activities were attributed to the level of carbon doping and crystallite structure. Carbon acts as an electron-trapping agent and causes structural defects as observed by PL spectrum. Obviously, it produces a low rate of recombination of e^-/h^+ as observed by PL spectroscopy which will have high separation of charge carrier and better performance of the photocatalytic activity. It was revealed that the amorphous C-TiO_2 is inert and the samples calcined from 400 ^oC to 600 ^oC have a decreasing trend of photocatalytic activity with the increased in size of nanoparticles. Among all, C-TiO_2 photocatalyst calcined at 400^oC was found to be more effective with an ideal amount of carbon, the presence of hydroxyl group, better crystallinity of amorphous-anatase mixture, and the existence of sub-band which reduces the band gap energy. Thus, exhibits high degradation percentage of PHP under UV and visible light irradiations, leading to as much as 3.7 and 11.89 % respectively. As a result, carbon doping modification is an appropriate strategy to enhance the photocatalytic activity by improving visible-light absorption and e^-/h^+ separation.

ABSTRAK

Pencapaian cemerlang yang diperolehi oleh Fujishima dan Honda (1972) mengenai penemuan fotomangkin pembahagi air pada elektrod titanium dioksida (TiO_2) telah menyebabkan banyak kajian mengenai TiO_2 dalam aktiviti pembersihan udara dan air untuk aplikasi alam sekitar. Walaupun TiO_2 memberikan banyak kelebihan berbanding fotomangkin semikonduktor yang lain, dua permasalahan utamanya iaitu tenaga jurang jalur (E_g) yang besar dan kadar penggabungan semula pasangan elektron yang terhasil (ē) dan lubang ($h^{+)}$ yang tinggi telah menyebabkan penggunaannya di dalam aplikasi praktikal terhad . Oleh itu, penghasilan TiO_2 yang aktif di bawah sinaran cahaya nampak menjadi cabaran kepada para penyelidik di dalam bidang fotopemangkinan semikonduktor. Kajian tersebut meliputi penghasilan fotomangkin TiO_2 yang diubahsuai untuk meningkatkan aktiviti fotopemangkinan di bawah sinaran cahaya nampak dan meningkatkan kadar pemisahan pembawa cas untuk aplikasi yang lebih bermanfaat melalui pendopan karbon. Nanopartikel TiO_2 yang didopkan dengan karbon (C-TiO_2) yang berfasa amorfus, anatase dan campuran fasa anatase/rutil telah berjaya disintesis melalui kaedah sol-gel yang mudah dan berkos rendah berdasarkan teknik pemasangan diri dengan mengeksploitasi polioxietilenasorbitan monooleate (Tween 80) sebagai sumber karbon dan dikalsin pada suhu 300-600 ^oC. Serbuk yang terhasil dicirikan dengan menggunakan spektroskopi infra-merah transformasi Fourier (FTIR), spektroskopi pantulan serakan ultralembayung (DR-UV), pembelauan X-Ray (XRD), mikroskopi pengimbas elektron (SEM) spektroskopi foropendarcahaya (PL), dan juga spektroskopi ultralembayung-cahaya nampak (UV-Vis). Dengan suhu pengkalsinan yang berpanjangan, saiz kristal dan Eg telah meningkat dan tahap karbon yang didopkan berkurangan. Kebanyakan nanopartikel menunjukkan penyerapan yang tinggi di bawah sinaran UV dan cahaya nampak. Ini adalah disebabkan oleh pengurangan E_g dan pembentukan beberapa jalur tambahan sepertimana yang dapat dilihat pada keputusan spektrum UV-Vis dan PL. Potensi nanopartikel C-TiO_2 dalam pemulihan alam sekitar dengan menggunakan fotomangkin telah dibuktikan melalui degradasi fenoftalein (PHP) di bawah sinaran UV dan cahaya nampak. Aktiviti fotopemangkinan yang bertambah baik telah dikaitkan dengan tahap karbon yang didopkan dan struktur kristal itu sendiri. Karbon bertindak sebagai agen pemerangkap elektron dan menyebabkan kecacatan struktur seperti yang diperhatikan di dalam spektrum PL. Jelas sekali, ia menghasilkan kadar penggabungan semula ē/h^+ yang rendah seperti yang diperhatikan di dalam spektroskopi PL yang mempunyai kadar pemisahan pembawa cas yang tinggi dan aktiviti fotopemangkinan yang lebih baik. Ia telah membuktikan bahawa amorfus C-TiO_2 adalah lengai dan sampel yang dikalsin dari suhu 400 ^oC sehingga 600 ^oC mempunyai penurunan aktiviti fotopemangkinan dengan peningkatan dalam saiz nanopartikel. Antara semua, fotomangkin C-TiO_2 yang dikalsin pada 400 ^oC didapati lebih berkesan dengan jumlah yang ideal bagi karbon, kehadiran kumpulan hidroksil, penghabluran yang lebih baik, dan kewujudan jalur tambahan yang mengurangkan tenaga jurang jalur. Oleh itu, mempamerkan peratusan kemerosotan PHP yang tinggi di bawah sinaran UV dan cahaya nampak, yang membawa kepada sebanyak 3.7 dan 11.89 % masing-masing. Kesimpulannya, pengubahsuaian pengdopan karbon adalah salah satu strategi yang sesuai bagi meningkatkan aktiviti fotopemangkinan dengan menggalakkan penyerapan cahaya nampak dan pemisahan e^-/h^+.

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LIST OF ABBREVIATION

%D	-	Percent of degradation
ATR	-	Attenuated total reflectance
C	-	Carbon
CB	-	Conduction band
DFT	-	Density functional theory
DR	-	Diffuse reflectance
e^-	-	Electron
E_g	-	Band gap energy
FTIR	-	Fourier transform infrared spectroscopy
h^+	-	Positive hole
nm	-	Nanometre
OH	-	Hydroxyl
OV	-	Oxygen vacancies
P	-	Pollutant
PHP	-	Phenolphthalein
PL	-	Photoluminescence
POPs	-	Persistent organic pollutants
SEM	-	Scanning electron microscope
TiO_2	-	Titanium dioxide
TTIP	-	Titanium tetraisopropoxide
Tween 80	-	Polyoxyethylenesorbitan monooleate
UV-Vis	-	Ultraviolet-visible
VB	-	Valence band
XRD	-	X-ray diffraction

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Nowadays, the crisis brought by 'greenhouse effect' has become a great issue in many countries. This is due to the combustion of the toxic organic pollutants released from industries into water, air, and soil. Since the first discovery of photocatalytic water splitting on titanium dioxide (TiO_2) electrodes in 1972 by Fujishima and Honda, scientists have done many studies on the photocatalytic activity of TiO_2 to deal with these challenges (Fujishima and Honda, 1972).

TiO_2, which is among the most basic materials in our daily life, represents an effective photocatalyst for water and air purification (Fujishima *et al*., 2000). Additionally, it is also associated with self-cleaning technology that is responsible for the development of green living environment (Zhang Li, 2013). The photocatalyst is the substance which can absorb light quanta of appropriate wavelengths depending on the band structure (Banerjee *et al*., 2015). The process in which this substance is being utilized in the chemical reaction is called photocatalysis (Etacheri *et al*., 2015). In order to develop an efficient photocatalyst, the catalyst should satisfy high stability in extreme environment, photoactive, photo-stable and low cost (Mills *et al*., 1993; Pelaez *et al*., 2012a).

The most commonly used photocatalysts are metal oxides such as TiO_2, ZnO, Fe_2O_3, WO_3, and SnO_2 (Etacheri *et al*., 2015; Fujishima and Honda, 1972; Santhi *et* *al*., 2016; Tayyebi *et al*., 2016; Uddin *et al*., 2016; Wang *et al*., 2016). Among all, TiO_2 is a widely used semiconductor since it provides all the special characteristics in all the aspects mentioned above.

However, despite all the advantages provided by TiO_2 compared to other semiconductor photocatalysts, there are two main concern issues that restrain its usage in practical applications. Firstly, TiO_2 has a large band gap, which is 3.2 eV, and require UV light for the excitation of electrons to take place. This has limited its photocatalytic activity under solar energy or visible light, which is the most abundant light in the electromagnetic spectrum. Figure 1.1 shows the solar spectrum in different spectral irradiance. Secondly, TiO_2 possesses fast electrons (e^-) and holes (h^+) recombination that will decrease the photocatalytic activity. Therefore, for more beneficial photocatalytic applications, it is essential to develop a system that producing TiO_2 with high efficiency under visible light region.

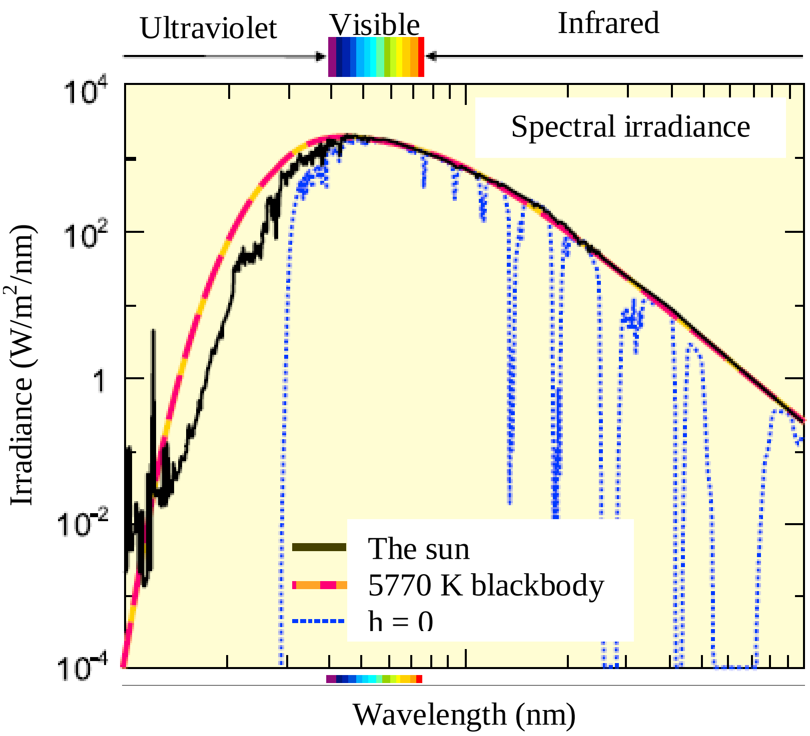

Figure 1.1: Spectrum of solar irradiance, I, compared with that of a 5770 K blackbody radiator. The blue dotted line shows the spectrum of radiation reaching the surface of the Earth (Gray *et al*., 2010; Lean, 1991).

Many studies have been designated to improve the production of highly reactive TiO_2 under visible light. Visible light activated TiO_2 photocatalyst can be prepared by using dye sensitization (Saien and Mesgari, 2016), noble metal loading (Kmetyko *et al*., 2016), transition metal addition (Yadav *et al*., 2016) and non-metal doping (Wang *et al*., 2012). Noble metals such as Ag, Au, Pt and Pd or the combinations of these metals with TiO_2 were of the particular interest due to its well-known properties of improving the photocatalytic efficiency of TiO_2 under visible light irradiation. They can act as an electron trap and delay the recombination of the e^-/h^+ pair through the promotion of the interfacial charge transfer (Fagan *et al*., 2016). However, due to some problems associated with metal doping, which the metals introduced were not incorporated into the TiO_2 framework, and block the reaction sites on the TiO_2 surface, non-metal elements such as carbon and nitrogen were studied comprehensively (Zhu *et al*., 2006).

The use of non-metal as doping material such as nitrogen (Than *et al*., 2017), sulfur (Seo *et al*., 2016), fluorine (Zhang *et al*., 2016), iodine (Wang *et al*., 2016) and carbon (Zhang *et al*., 2016) is able to control the stability of the TiO_2 and also enhance the visible light irradiation. Carbon was found to be more efficient compared to most of the non-metal elements due to its useful properties. Carbon has high electrical and thermal conductivity, high chemical stability, low thermal expansion coefficient, high lubricity, light weight, possibility to have various pores, non-toxic and radiation resistant (Zaleska, 2008).

Since the first report on carbon-modified TiO_2 reported by Kisch and co-workers, many physical and chemical investigations were done for the synthesis of carbon-doped titanium dioxide (Sakthivel and Kisch, 2003). Its ability to narrow down the band gap of TiO_2 significantly increases the photocatalytic activity towards visible light irradiation compared to pure anatase TiO_2 (Zhang *et al*., 2016).

Previously, it has been reported that the use of self-assembly surfactant-based sol-gel methods is effective ways to design the structural properties of TiO_2 from molecular precursors (Choi *et al*., 2006; Zhu *et al*., 2006). Hydrocarbon surfactants were added to act as carbon doping precursor to enhance the photocatalytic activity of TiO_2 under visible light.

Regardless of the numerous studies based on visible light active carbon-doped TiO_2 photocatalyst, the relationship between the synthesis method, optical properties, structural properties and the efficiency of the visible light photocatalytic activity remain controversial and still need to be investigated. Thus, in this research, a simple and low-cost process was established for the synthesis of visible light active C-TiO_2 photocatalysts via the sol-gel route of precursor titanium tetraisopropoxide (TTIP), at different calcination temperature of 300 ^{o}C to 600 ^{o}C for 3 hours.

1.2 Statement of Problem

The utilization of TiO_2 photocatalyst in air and water treatment promises better views as it provides high efficiency in the degradation of organic pollutants (Zaleska, 2008). However, its wide scale of practical application is limited by its large band gap energy (3.2 eV), which allows the only small amount of solar energy to be used. Also, the high recombination rate of photogenerated e^- and h^+ that occurs reduces its photocatalytic activity efficiency, which resulting in low degradation percentage of organic pollutants. Previously, these problems had been solved by developing an effective TiO_2 photocatalyst with a reduced band gap and make it reactive under visible light region. However, most of the techniques used to synthesize the material are expensive, hard to control and chemically unstable (Pelaez *et al.*, 2012). In order to overcome all these problems, a mild and easily controlled sol-gel technique had been chosen to be the promising way to develop highly reactive C-doped TiO_2 under visible light irradiation, with the utilization of polyoxyethylenesorbitan monooleate (Tween 80) surfactant as a carbon source, and titanium tetraisopropoxide (TTIP) as the TiO_2 precursor.

Tween 80 was selected as carbon source material since it contain high number of carbon, easy to obtain, cheap, and highly miscible in aqueous solution compared to other carbon source material, such as carbon nanotube (CNT) (Wongaree *et al.*, 2015), regenerated cellulose membrane (RCM) (M.A. Mohamed *et al.*, 2016), and resorcinol-furfural (Shao *et al.*, 2013). Besides that, C-doping promises a high number of photogenerated electrons and defect sites, which able to trap mobile electrons and lower the recombination rate of e^-/h^+, thereby resulted in the high photocatalytic activity of TiO_2 photocatalysts.

The effect of calcination temperature towards the synthesized C-TiO_2 was characterized by several analytical instruments. The surface bonding of C-TiO_2 was first studied using attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), while the morphological and physical properties were characterized by scanning electron microscope (SEM), and X-ray diffraction (XRD) spectrometer. The optical properties were characterized using diffuse reflectance ultraviolet-visible (DR UV-Vis) spectrometer and photoluminescence (PL) spectrometer.

1.3 Objectives of Study

The objectives of this study are:

- To synthesize carbon-doped TiO_2 photocatalyst by the self-assembly surfactant sol-gel method at different calcination temperature.
- To study the effect of calcination temperature of the prepared carbon-doped TiO_2 by using ATR-FTIR, DR UV-Vis, SEM, XRD, and PL.
- To evaluate the photocatalytic performance of carbon-doped TiO_2 under UV and visible light irradiances by using DR UV-Vis spectroscopy for phenolphthalein degradation.

1.4 Scope of Study

The research covered the synthesis of C-TiO_2 photocatalyst via self-assembly surfactant-based sol-gel method at different calcination temperature. The non-ionic surfactant (Tween 80) was used as the source of carbon material. The photocatalyst was characterized further using XRD, SEM, DR-UV spectrophotometer, ATR-FTIR, and PL. The photodegradation of phenolphthalein was carried out in the presence of UV and visible light and was monitored using diffuse reflectance ultraviolet-visible (DR UV-Vis) spectrometer.

1.5 Hypothesis of Study

Non-metal doping has proved to be an efficient way in modifying the structure of TiO_2 photocatalysts so that it can easily absorb visible light which is abundant in the solar irradiation. It is also responsible for reducing the band gap energy by the formation of sub-band between the valence band and conduction band. In addition, through this doping modification, the rate of recombination of e^-/h^+ has been reported to decrease as the defect sites created by the carbon-doping act as electron trapping agent that delay the rate of e^-/h^+ recombination. This is useful for the oxidation of organic pollutants in the environment. Therefore, non-metal doping seems to be an effective way in enhancing photocatalytic activity of TiO_2 photocatalysts.

1.6 Significant of Study

The development of TiO_2 photocatalysts has led to its usage in many fields including in the degradation of organic pollutants in waste and wastewater treatment. Despite all the advantages provided by TiO_2 photocatalysts, some modifications have been made to increase its efficiency on the photocatalytic activity and the most prominent method to be used is by carbon-doping. Therefore, this research will provide an understanding of the synthetic method used to develop C-doped TiO_2 photocatalyst which relates to their optical and structural properties. This photocatalyst will ultimately reduce the band gap of TiO_2 as well as the rate of e^-/h^+ recombination. As a consequence, this would drive the use of photocatalyst which only use the sunlight for any reaction to occur without the use of any conventional method that is hard to control and time-consuming.

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