STRUCTURE-PHOTOCATALYTIC ACTIVITY RELATIONSHIP OF CARBON DOPED TITANIUM DIOXIDE ANALYZED BY DENSITY FUNCTIONAL THEORY AND FUZZY LOGIC GRAPH

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DEDICATION

To my beloved husband, Mohammad Lutfi bin Mohd Afandi,
late father, Hj Alias bin Hj Sulaiman, mother, Hjh Normah binti Hj Ab Karim,
mother-in-law, Junaidah Deraman, son, Muhammad Iskandar Zulkarnain bin
Mohammad Lutfi and all family members for their du'a, love, support,
encouragements and advices.

*Al-fatihah to my late father, Hj Alias bin Hj Sulaiman, and my late father-in-law,
Mohd Afandi bin Mohd Noor*

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ABSTRACT

Carbon doping is a promising way to modify the properties of TiO_2 for enhancing its photocatalytic performance. Although there are many publications about the enhancement of photocatalytic activity of TiO_2, the relationship between the structural and physical properties with the photocatalytic activity of TiO_2 is still not clearly understood. A new approach has been proposed to evaluate the structure-photocatalytic activity relationship with the aim to better understand the dominant properties that determine the photocatalytic activities of C-doped TiO_2. Fuzzy logic graph has been used as a new approach in determining the dominant factor for the structure-photocatalytic activity relationship of C-doped TiO_2. Characterization results from experimental study were used in the fuzzy logic graph. For the experimental study, two types of C-doped TiO_2 were successfully synthesized by the sol-gel method with addition of cetyltrimethylammonium bromide (CTAB) surfactant and without the addition of CTAB, at different calcination temperatures, to compare with commercial TiO_2. The synthesized photocatalysts were characterized using several characterization techniques. Photooxidation of styrene with aqueous hydrogen peroxide has been used as the model reaction for organic pollutants to study the structure-photocatalytic activity relationship under UV and visible light irradiation. X-ray photoelectron spectroscopy (XPS) spectra show that C was doped into TiO_2's lattice with the amount of C of about 2.5 at% for CTAB-C/TiO_2-500 samples and about 10.5 at% for C/TiO_2-500 samples at interstitial and substitutional positions of anatase TiO_2. Energy dispersive X-ray spectroscopy (EDX) and XPS results for CTAB-C/TiO_2 samples show a lower amount of C incorporated into TiO_2 as compared to C/TiO_2 without the addition of CTAB, which may be caused by the removal of C impurity by the CTAB surfactant. Furthermore, the effects of calcination temperature from 300 to 700°C on the physicochemical properties of the C-doped TiO_2 were also studied. Calcination temperature affected the phase, morphology, surface area, porosity, crystallite size and amount of C. The surface area of CTAB-C/TiO_2 and C/TiO_2 samples is shown to decrease as the calcination temperature increased. Additionally, the confirmation on the effect of C on the band gap energy of the anatase TiO_2 was investigated using density functional theory (DFT). Total density of states (TDOS) shows that the C affects the band gap energy of TiO_2 by introducing the mid gap states between the band gap. Based on DFT analysis and photocatalytic experiment, six physical properties have been chosen to be used for fuzzy logic graph, i.e. surface area, phase, amount of electron-hole recombine, band gap energy, existence of sub-band gap and amount of C. Fuzzy logic graph analysis shows that surface area is a dominant factor for the photooxidation of styrene under UV and visible light irradiations, followed by phase , amount of C and amount of electron-hole recombine. This study demonstrated that the combination of photocatalytic experiment, DFT and fuzzy logic graph analysis can be used to clarify the structure-photocatalytic activity relationship in TiO_2 photocatalytic systems.

ABSTRAK

Pendopan karbon adalah cara yang menjanjikan dalam pengubahsuaian sifat TiO_2 bagi meningkatkan prestasi fotopemangkinannya. Walaupun terdapat banyak penerbitan tentang peningkatan aktiviti fotopemangkinan TiO_2, hubungan antara sifat-sifat struktur dan fizik dengan aktiviti fotopemangkinan TiO_2 masih belum difahami dengan jelas. Satu pendekatan baharu telah dicadangkan untuk menilai hubungan struktur-aktiviti fotopemangkinan dengan matlamat untuk memahami dengan lebih baik sifat-sifat dominan yang menentukan aktiviti fotopemangkinan TiO_2 didopkan-C. Graf logik kabur telah digunakan sebagai pendekatan baharu dalam menentukan faktor dominan bagi hubungan struktur-aktiviti fotopemangkinan TiO_2 didopkan-C. Keputusan pencirian daripada kajian eksperimen telah digunakan dalam graf logik kabur. Bagi kajian eksperimen, dua jenis TiO_2 didopkan-C telah berjaya disintesis dengan menggunakan kaedah sol-gel dengan penambahan surfaktan setiltrimetilammonium bromida (CTAB) dan tanpa penambahan CTAB, pada suhu pengkalsinan yang berbeza untuk dibandingkan dengan TiO_2 komersial. Fotomangkin yang disintesis telah dicirikan menggunakan beberapa teknik pencirian. Pengoksidaan stirena dengan hidrogen peroksida telah digunakan sebagai model tindak balas bagi bahan pencemar organik untuk mengkaji hubungan struktur-aktiviti fotopemangkinan di bawah sinaran UV dan cahaya nampak. Spektrum spektroskopi fotoelektron sinar-X (XPS) menunjukkan bahawa C telah terdopkan ke dalam kekisi TiO_2 dengan jumlah C kira-kira 2.5 at% bagi sampel CTAB-C/TiO_2-500 dan kira 10.5 at% bagi sampel C/TiO_2-500 pada posisi di antara ruang dan posisi penggantian TiO_2 anatas. Hasil spektroskopi serakan tenaga sinar-X (EDX) dan XPS bagi sampel CTAB-C/TiO_2 menunjukkan jumlah C yang lebih rendah telah digabungkan ke dalam TiO_2 berbanding C/TiO_2 tanpa penambahan CTAB, yang mungkin disebabkan oleh penyingkiran bendasing C oleh surfaktan CTAB. Tambahan pula, kesan suhu pengkalsinan dari 300 hingga 700°C terhadap sifat fizikokimia TiO_2 didopkan-C telah juga dikaji. Suhu pengkalsinan telah memberi kesan kepada fasa, morfologi, luas permukaan, keliangan, saiz hablur dan jumlah C. Luas permukaan sampel CTAB-C/TiO_2 dan C/TiO_2 menunjukkan ia telah berkurang apabila suhu pengkalsinan meningkat. Tambahan lagi, pengesahan kesan C terhadap tenaga luang jalur TiO_2 anatas telah disiasat menggunakan teori ketumpatan berfungsi (DFT). Ketumpatan keadaan keseluruhan (TDOS) menunjukkan bahawa C mempengaruhi tenaga luang jalur TiO_2 dengan memperkenalkan keadaan luang pertengahan di antara luang jalur. Berdasarkan analisis DFT dan eksperimen fotopemangkinan, enam sifat fizik telah dipilih untuk digunakan bagi graf logik kabur, iaitu luas permukaan, fasa, jumlah gabungan semula elektron-lubang, tenaga luang jalur, kewujudan luang sub-jalur dan jumlah C. Analisis graf logik kabur menunjukkan bahawa luas permukaan adalah faktor dominan bagi fotopengoksidaan stirena di bawah sinaran UV dan cahaya nampak, diikuti dengan fasa, jumlah C dan jumlah gabungan semula elektron-lubang. Kajian ini membuktikan bahawa gabungan eksperimen fotopemangkinan, DFT dan analisis graf logik kabur boleh digunakan untuk menjelaskan hubungan struktur-aktiviti fotopemangkinan dalam sistem fotopemangkinan TiO_2.

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λ	-	Wavelength
2θ	-	Bragg angle
Å	-	Angstrom
a.u.	-	Arbitrary unit
ARE	-	Average relative error
AARE	-	Absolute average error
ANA	-	Anatase
BET	-	Brunauer-Emmet-Teller
BG	-	Band gap energy
BJH	-	Barret-Joyner-Halenda
%C	-	Amount of carbon in percent
C	-	Carbon
C/TiO_2	-	C-doped TiO_2 samples without addition of CTAB
CASTEP	-	Cambridge serial total energy package
CB	-	Covalent band
CdS	-	Cadmium sulfide
CTAB	-	Cetyltrimethylammonium bromide
$CTAB\text{-}C/TiO_2$	-	C-doped TiO_2 samples with addition of CTAB
D	-	Debye
DFT	-	Density functional theory
EDX	-	Energy dispersive X-ray spectroscopy
E		Energy
E_c	-	Cohesive energy
E_f	-	Formation energy
E_g	-	Band gap energy
e^-	-	Electron
e-h	-	Amount of electron-hole recombine
FESEM	-	Field emission scanning electron microscope
FTIR	-	Fourier transform infrared
GC	-	Gas chromatography

GGA	-	Gradient approximations
h^+	-	Positive hole
H_2O_2	-	Hydrogen peroxide
HF	-	Hatree fock
m	-	Meters
min	-	Minute(s)
mL	-	Milliliter
MP2	-	2^{nd} order Moller-Plesset perturbation theory
MSE	-	Mean squared normalized error
nm	-	Nanometers
PBE	-	Perdew-Burke-Ernzerhorf
PCA	-	Photocatalytic activity
PDOS	-	Partial density of states
PH	-	Phase
PL	-	Photoluminescence
RMSE	-	Root mean squared error
RUT	-	Rutile
SA	-	Surface area
SBG	-	Sub-band gap energy
SD	-	Standard deviation
TDOS	-	Total density of states
TEM	-	Transmission electron microscope
TGA	-	Thermogravimetric analysis
TiO_2	-	Titanium dioxide
UV-Vis	-	Ultraviolet-visible
UV-Vis DR	-	UV-Visible diffuse reflectance
VASP	-	The Vienna a*b initio* simulation package
VB	-	Valence band
XRD	-	X-ray diffraction
ZnO	-	Zinc oxide

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Major concerns on the rising number of environmental problems have resulted in compulsive development of environmental purification methods. This fundamental advanced environmental solution has drawn attention and gained importance due to its full potential in bringing a significant change in human life. Therefore, a great deal of research efforts have been done on photocatalysis in various areas such as degradation of organic and inorganic pollutants, hydrogen production and organic synthesis [1].

Titanium dioxide, TiO_2 or titania is the most widely studied material due to its superior performance since 1972 when Fujishima and Honda reported water decomposition using TiO_2 electrode as a potential semiconductor photocatalytic material [2,3]. TiO_2 is known as an outstanding and promising material in paints pigments, degradation of water pollutants, electrochromic displays, electrochemical electrodes, capacitors, lithium-ion batteries, sensors and catalysts' support [4–6].

TiO_2 is a commonly used photocatalytic material due to its rather low material cost, high chemical stability, high specific surface area and nontoxicity [7–9]. It is generally believed that a relationship exists between TiO_2 photocatalyst's physicochemical properties and photocatalytic activity. However, the discussion on the relationship between the physicochemical properties of TiO_2 and its photocatalytic activity is limited, and there seems to be no comprehensive approach or tool to discuss this relationship. The discussion has been restricted to several samples synthesized in a similar manner or a small number of commercial samples [10]. Ohtani [11,12] who has made a significant contribution to heterogeneous photocatalysis for more than 30 years and has published over 200 original and review papers on photocatalysis, also remains frustrated with the fact that the structure-photocatalytic activity relationship of photocatalyst has not yet been clarified [11].

Furthermore, the main dominant factor has not been clearly investigated by a comprehensive method. Previous study done by Muniandy [13] reported that the surface area was the main factor which enhanced the photocatalytic activity of TiO_2 photocatalyst. However, previous works [14,15] also found the surface area may be a requirement but cannot be the decisive factor for the enhanced photocatalytic activity. It was found that surface properties (i.e. acidity of the surface and hydroxyl groups content) and synergistic effect of C-doping at interstitial position and surface carbonaceous species, were the main factors that can improve the performance of TiO_2 as a photocatalyst.

Prieto-Mahaney and coworkers [10] are among the sole researchers that studied the comprehensive relationship between the structural and physical properties with the photocatalytic activity of TiO_2 powders using mathematical methods. Statistical multivariable analyses were used with the aim of obtaining the relationship of six properties of 35 commercially available TiO_2 samples in Japan, with five photocatalytic reactions. From the statistical multivariable analyses, it was found that the photocatalytic activities strongly depended on the properties of the TiO_2 powders. However, this method required higher number of samples, which are a major limitation on determining the structure-photocatalytic activity of TiO_2.

Besides that, some of the properties are imprecise or incomplete data have been given in the series of samples [16]. The data also cannot be generalized and analysed using binary logic (1 or 0 / true or false) that are precise and in discrete terms. Therefore, the computational intelligence technique is desperately required that accounts for all complexities and variations of data in investigating the structure-photocatalytic activity relationship of TiO_2 photocatalyst. Recently, the use of computational techniques for various applications, including modeling and problem solving, has attracted considerable interest between researchers, primarily in the science and engineering area. Fuzzy logic is the nearest solution to complex problems which has the potential of combining human thought and experience into computer-assisted decision making.

Zadeh introduced fuzzy logic, which takes into account the complexity of the real world and the uncertainty that everything cannot have absolute values and follow a linear function [17]. Fuzzy logic deal with vague, indecisive ideas and subjective information which depending on "degrees of truth" (0 to 1) instead of the usual "true or false" (1 or 0). It is also possible to calculate exactly the qualitative and quantitative variables with different amounts and meanings[18]. To the best of our knowledge, no study has been reported in the literature on the relationship between TiO_2 photocatalyst's physicochemical properties and its photocatalytic activity using fuzzy logic.

Fuzzy graph is another focus on the implementation of fuzzy theory in its relation to the theory of graphs. Fuzzy graph in the form of a graph describes the relationship between variables, which accurately shows the relationship degree between variables. Therefore, in this study, fuzzy graph in the form of graph is applied to clarify the structure-photocatalytic activity relationship of TiO_2 photocatalyst. Imagine combining the physicochemical properties and photocatalytic activity of all data in current literature to clarify the structure-photocatalytic activity relationship of TiO_2 photocatalyst between them using fuzzy logic.

Carbon doped TiO_2 (C-doped TiO_2) was chosen as the photocatalyst model in explaining the structure-photocatalytic relationship of TiO_2. The addition of carbon, C to TiO_2 semiconductor's lattice are believed to one of the suitable methods to modify TiO_2 to enhance its photocatalytic performance. Furthermore, the preparation of TiO_2 usually contains C impurity, which is difficult to remove, and this C impurity significantly affects the TiO_2 photocatalytic activity. The modification of TiO_2 with carbon can generally change the structure, physicochemical and electronic properties of TiO_2 which enhance its photocatalytic performance by facilitating faster transport to the active sites on TiO_2's surface, narrowing the band gap energy, extending the light absorption to visible range and suppressing the rate of electron-hole recombination [19].

However, in order to clarify the structure-photocatalytic activity relationship of TiO_2 photocatalyst, the experimental approach is not enough. A theoretical approach by DFT calculation is also necessary to be carried out to determine the electronic structure of C-doped TiO_2 photocatalyst. DFT is a computational method that is used to calculate the properties and electronic band structures of molecules using the results of the theoretical quantum chemistry. In this study, the combination of experimental work, DFT calculation and fuzzy graph may well explain the relationship between the C-doped TiO_2 physicochemical properties with its photocatalytic activity. The schematic presentation of the research plan is represented in Figure 1.1.

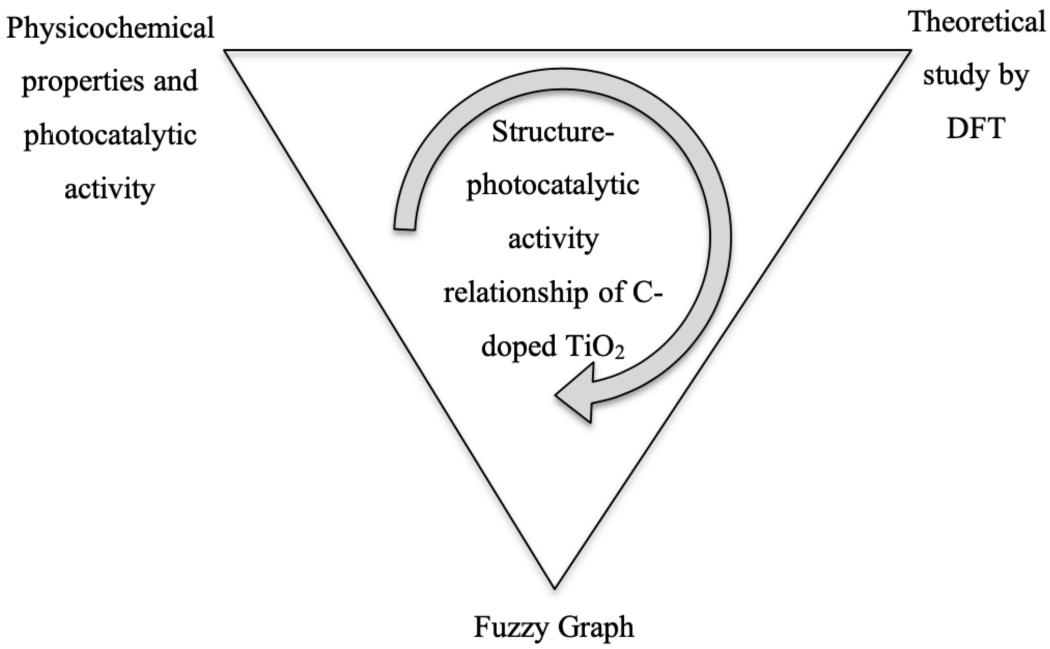

Figure 1.1 Schematic presentation of the research plan

1.2 Problem Statement

TiO_2 photocatalyst has gained significant attention as one of the most promising materials in the removal of various organic pollutants, such as organic dyes and phenolic compounds. It is known that photocatalytic activity is correlated with the structural and physicochemical properties of TiO_2. However, there has been no clear explanation on the relationship between physicochemical properties and photocatalytic reactions. In this research, to solve this problem, a new approach has been proposed to evaluate the structure-photocatalytic activity relationship with the aim to better understand the dominant properties in determining the photocatalytic activities of C-doped TiO_2. The dominant properties found in the fuzzy graph can be used as a future guideline to synthesize the photocatalyst with high photocatalytic activity. Photooxidation of styrene has been used as the model of organic pollutant reaction due to the oxidation of styrene are importance for academics and industry, particularly in the production of fine chemicals including benzaldehyde. Fuzzy logic graph with the combination of fuzzy inference system modelling has been used as a new approach in determining the dominant factor for the structure-photocatalytic activity relationship of C-doped TiO_2. Characterization results from experimental study were used in the fuzzy logic graph and the electronic structure were discussed with the theoretical calculations of C-doped TiO_2 using DFT. The C-doping, structure distortions and oxygen vacancy may affect electronic structure of anatase; that is why in this study further investigation of different C doping positions, and location of C, was necessary.

1.3 Objectives of Study

Several objectives were set to study the structure-photocatalytic activity relationship of C-doped TiO_2 as follows:

(a) To investigate the physicochemical properties of the prepared C-doped TiO_2 photocatalysts at different calcination temperature and their photocatalytic activity of styrene under UV and visible light irradiation.

(b) To investigate the effect of C doping, structure distortion and oxygen vacancy on the band gap energy of anatase TiO_2 by DFT calculation

(c) To clarify the structure-photocatalytic activity relationship of C-doped TiO_2 and the dominant properties that determine the photocatalytic activities of C-doped TiO_2 samples using fuzzy logic graph from experimental work and DFT calculation.

1.4 Scope of Study

This study demonstrated the combination of photocatalytic experiment, DFT and fuzzy logic graph analysis, can be used to clarify the structure-photocatalytic activity relationship in TiO_2 photocatalytic systems. In order to accomplish the research's objectives, the scope of the study is designated into three parts, which are the preparation of C-doped TiO_2 and its photocatalytic activity, theoretical study by DFT and fuzzy logic graph .

This study focussed on the preparation of anatase TiO_2 and C-doped anatase TiO_2 using the sol-gel process, calcined at different temperature of 300 to 700 °C. The synthesized materials were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), energy dispersive X-ray spectroscopy (EDX), field emission electron microscopy (FE-SEM), N_2 adsorption-desorption, UV-Visible diffuse reflectance (UV-Vis DR) spectroscopy, photoluminescence (PL) spectroscopy and X-Ray photoelectron spectroscopy (XPS). The photocatalytic activity of C-doped TiO_2 was evaluated in the photocatalytic oxidation of styrene, as the model reaction for organic pollutants under irradiations of UV and visible light.

DFT theoretical calculation was performed using Gaussian 09 to study the electronic properties of anatase TiO_2 and C-doped anatase TiO_2. The scope of the DFT study were limited to only the anatase structure of TiO_2. The performance of HF and five popular exchange-correlation functionals of DFT including hybrid (B3LYP, B3PW91, PBE1PBE or known as PBE0 and PBEh1PBE), double-hybrid functional (B2PLYP) and MP2 that is available in Gaussian 09 package was investigated in predicting band gap energy. In addition, the structure distortion and effect of C at different amount of C and location of C on the band gap energy of TiO_2 were studied using DFT calculation. The total density of states (TDOS) and partial density of states (PDOS) for C-doped anatase TiO_2 are plotted to further investigates the effect of C on the band gap energy and sub-band gap energy of anatase.

The combination of fuzzy logic graph and fuzzy inference system was used to study the structure-photocatalytic activity relationship of C-doped TiO_2. Fuzzy inference system model was developed by MATLAB software. A sensitivity analysis was carried out from developed fuzzy inference system model to obtain the membership value that represents the dominant properties that determine the photocatalytic activities of C-doped TiO_2 under irradiations of UV and visible light.

1.5 Significance of Study

This research provides an understanding on the structure-photocatalytic activity relationship and the dominant properties that determine the photocatalytic activities of C-doped TiO_2 photocatalytic system. Fuzzy logic graph with the combination of fuzzy inference system modelling has been proposed as a new approach to clarify the structure-photocatalytic activity relationship with the aim to better understand the dominant properties in determining the photocatalytic activities of C-doped TiO_2 supported with DFT calculation. The combination of photocatalytic experiment, DFT, and fuzzy logic graph analysis can be used to clarify the structure-photocatalytic activity relationship in TiO_2 photocatalytic systems. DFT explained the effect of structural distortion, oxygen vacancy, C-doped at different location and amount of C on the electronic structure of anatase TiO_2. From the DFT study, double hybrid functional B2PLYP employing 6-311G(d) has been proposed as the accurate exchange-functional methods in predicting the TiO_2 band gap energy compared to the previous studies such as B3LYP, B3PW91, PBE1PBE, and PBEh1PBE. Furthermore, the dominant properties found in the fuzzy graph can be used as a future guideline to synthesize the photocatalyst with high photocatalytic activity.

1.6 Research Outline

This research was conducted in three parts. The first part, discussed in **Chapter 2**, is the preparation of C-doped TiO_2 using a simple sol-gel method. Various instruments were used to study the physicochemical properties of prepared C-doped TiO_2 photocatalyst. Five physicochemical properties of C-doped TiO_2 samples were analyzed in detail, including the crystal structure and crystallinity, functional groups, chemical composition, morphology structure, surface area, porosity, and band gaps. Besides, to study the photocatalytic activity of C-doped TiO_2 samples, the photooxidation of styrene with aqueous hydrogen peroxide was tested as the model of organic pollutant reaction under UV and visible light irradiations.

The second part in **Chapter 3** discusses the electronic structure of C-doped TiO_2 by DFT calculation. For this section, the performance of the theoretical DFT methods in determining the anatase cluster's band gap energy was investigated to find the accurate methods for predicting TiO_2's band gap energy using Gaussian 09. Furthermore, the effect of structural distortion, oxygen vacancy, C-doped TiO_2 on the anatase TiO_2 band gap energy will be clarified.

The last part of the research in **Chapter 4**, involves the structure-photocatalytic activity relationship of C-doped TiO_2 samples and the dominant properties that determine the photocatalytic activities of the C-doped TiO_2 photocatalytic system using the fuzzy logic graph.

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LIST OF PUBLICATIONS

1. Siti Hajar Alias, Nurul Najidah Mohamed, Leaw Wai Loon and Sheela Chandren (2019). Synthesis of carbon-doped titanium dioxide and its activity in the photocatalytic oxidation of styrene under visible light irradiation, *Malaysian Journal of Fundamental and Applied Sciences, 15*(1), 291-297. **(Indexed by Clarivate Analytics).**