FUZZY LOGIC GRAPH APPROACH TO ELUCIDATE STRUCTURE-PHOTOCATALYTIC ACTIVITY RELATIONSHIP OF CARBON-DOPED TITANIUM DIOXIDE

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DEDICATION

This thesis is dedicated to my father, who taught me that the best kind of knowledge to have is that which is learned for its own sake. It is also dedicated to my mother, who taught me that even the largest task can be accomplished if it is done one step at a time.

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ABSTRACT

The discovery of photocatalytic water splitting of titanium dioxide (TiO_2) electrodes by Fujishima and Honda (1972) trigger the extensive study of the structure and the improvement in the performance of TiO_2 as photocatalyst in synthetic chemistry and 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 and high recombination rate of photogenerated electrons and holes pairs, restraint its usage in practical applications. Hence, doping TiO_2 with non-metal such as carbon is a promising way to modify the properties of TiO_2 for the enhancement the photocatalytic performance of TiO_2. Although there are many reports about the improvement of TiO_2's photocatalytic activity, the relationship between the structural and physical properties with the photocatalytic activity of carbon-doped TiO_2 is still not well evaluated. In this study, a new approach has been proposed to elucidate the structure-photocatalytic activity relationship to better understand the dominant properties that determine the photocatalytic activities of carbon-doped TiO_2 which is focusing under UV light system only. 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 carbon-doped TiO_2. The logic of expertise and from repetition of promising data were used. Fuzzy Inference System contains three fundamental steps including fuzzification, rule evaluation and defuzzification. This study includes four main stages which were data collection, development of Fuzzy Logic Controller, construction of Fuzzy Inference System and assessment of the results by sensitivity analysis. Experimental data that was used in this study was collected from experimental results obtained by our research group. To unveil the structure and physical properties-activity relationship, the type of crystalline phases, surface area, crystallite size and electron-hole recombination were chosen as the factors to be analyzed. Fuzzy Logic Graph analysis shows that surface area is a dominant factor for photocatalytic activity of carbon-doped TiO_2, it is followed by rate of electron-hole recombination, phase and crystallite size. To summarize, with the help of Fuzzy Logic Controller, the structure physical properties activity relationship of carbon-doped TiO_2 can be evaluated to show which factors that were responsible for the photocatalytic activity of carbon-doped TiO_2. Although we used the limited source of experimental data to elucidate the physicochemical-photocatalytic properties relationship of carbon-doped $TiO_{2,}$ the correlation was successfully described in detail using Fuzzy Logic Graph.

ABSTRAK

Penemuan cemerlang fotomangkin pembelahan air pada elektrod titanium dioksida (TiO_2) oleh Fujishima dan Honda (1972) telah menyebabkan banyak kajian struktural dan penambahbaikkan dalam prestasi fotopemangkin TiO_2 sebagai fotopemangkin dalam kimia sintetik dan aplikasi alam sekitar. Walaupun TiO_2 memberikan banyak kelebihan berbanding fotomangkin semikonduktor yang lain, dua masalah utamanya iaitu tenaga jurang jalur yang besar dan penggabungan semula pasangan elektron dan lubang yang tinggi telah menyebabkan penggunaannya di dalam aplikasi praktikal terhad. Oleh itu, pendopan TiO_2 dengan bukan logam seperti karbon adalah cara yang menjanjikan untuk mengubahsuai sifat-sifat TiO_2 untuk meningkatkan prestasi fotopemangkin TiO_2. Walaupun terdapat banyak laporan tentang peningkatan aktiviti fotopemangkinan TiO_2, hubungan antara sifat-sifat struktural dan fizikal dengan aktiviti fotopemangkinan karbon-terdop TiO_2 dan nampak masih tidak dinilai dengan baik. Dalam kajian ini, satu kaedah baru telah dicadangkan untuk menjelaskan hubungan struktur – aktiviti fotopemangkinan dengan matlamat pemahaman yang lebih baik terhadap sifat-sifat utama yang menentukan aktiviti fotopemangkinan karbon-terdop TiO_2 yang memfokus di bawah sistem cahaya UV sahaja. Graf Logik Kabur dengan gabungan pemodelan Sistem Inferensi Kabur telah digunakan sebagai pendekatan baru dalam menentukan faktor dominan untuk mengenalpasti hubungan aktiviti fotopemangkinan karbon-terdop TiO_2 .Logik kepakaran dan dari pengulangan data yang menjanjikan telah digunakan. Sistem Inferensi Kabur mengandungi tiga langkah asas termasuk fuzzifikasi, penilaian peraturan dan defuzzifikasi. Kajian ini merangkumi empat peringkat utama seperti pengumpulan data, pembangunan Pengawal Logik Kabur, pembinaan Sistem Inferensi Kabur dan penilaian hasil analisis sensitiviti. Data eksperimental yang digunakan dalam kajian ini telah dikumpulkan dari keputusan eksperimental dari kumpulan penyelidikan kami. Untuk merungkai struktur dan hubungan sifat-sifat fizikal, fasa-fasa kristal yang berbeza, luas permukaan, saiz kristal, dan kadar rekombinasi lubang-elektron, akan dijelaskan menggunakan Graf Logik Kabur. Analisis Graf Logik Kabur menunjukkan bahawa kawasan permukaan adalah faktor dominan bagi aktiviti fotopemangkinan karbon terdop TiO_2, diikuti dengan kadar rekombinasi lubang-elektron, fasa dan saiz Kristal. Untuk merumuskan, dengan bantuan Pemodelan Logik Kabur, sifat-sifat struktural dan fizikal dengan aktiviti fotopemangkinan karbon-terdop TiO_2 dapat dinilai untuk menunjukkan faktor-faktor yang bertanggungjawab terhadap aktiviti fotopemangkinan karbon-terdop $TiO_{2.}$ Walaupun kami menggunakan keputusan eksperimental data dari sumber data yang terhad untuk menjelaskan hubungan sifat fizikokimia-fotopemangkin karbon-terdop $TiO_{2,}$ korelasi telah berjaya dibincangkan dengan terperinci oleh Graf Logik.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATION

%	-	Percentage
BET	-	Brunauer-Emmet-Teller
◦ C	-	Degree Celcius
C/TiO_2	-	Carbon doped TiO_2
CB	-	Conduction Band
CdS	-	Cadmiun Sulfide
CTAB	-	cetyltrimethylammonium bromide
CRYS	-	Crystallite Size
Eg	-	Band Gap Energy
e-	-	Electron
e/h	-	Rate of Electron-hole recombine
eV	-	Electron Volt
FESEM	-	Field emission scanning electron microscope
h+	-	Positive hole
H_2O_2	-	Hydrogen peroxide
nm	-	Nanometers
PH	-	Phase
PL	-	Photoluminescence
PCA	-	Photocatalytic Activity
SA	-	Surface area
TEMP	-	Temperature
TiO_2	-	Titanium Dioxide
UV	-	Ultraviolet-visible
UV-Vis DR	-	UV-Visible diffuse reflectance
VB	-	Valance Band
XRD	-	X-ray diffraction
ZnO	-	Zinc Oxide

LIST OF APPENDIX

CHAPTER 1

INTRODUCTION

1.1 Background of Study

A significant problem faced by modern societies and threatening humankind's health is air and water pollution. It is due to the industrial and civil activities that create an enormous amount of organic and inorganic pollutants that unavoidably end up in our seas, soil, rivers, and air (Haider *et al.*, 2017). Nowadays, the rising number of environmental problems has resulted in the compulsive development of environmental purification method. This fundamental advanced environmental solution has drawn attention and gained importance over the past years due to its full potential in bringing a significant change in human life. Therefore, new alternatives, environmentally friendly, and sustainable efforts have been done on photocatalysis in various areas, including dye-sensitized solar cells, hydrogen production, removal of organic and inorganic pollutants, organic synthesis, and disinfection of pathogenic organisms (Lazar *et al.*, 2012).

The field of photocatalysis is one of the fastest growing areas both in research and commercial field. Titanium dioxide (TiO_2) has been given maximum attention due to its superior performance since 1972 when Fujishima and Honda reported water decomposition using TiO_2 electrode as a potential semiconductor photocatalytic material (Paulauskas et al., 2013; Taga, 2009). TiO_2 is one of the most promising material because of their applicability in degradation of water pollutants, paint pigments, air purification, electrochemical electrodes, capacitors and dye-sensitized solar cell (DSSC) electrodes (Abdullah et al., 2016; Wong et al., 2011).

Titanium dioxide (TiO_2) was reported showing the best photostability and highest photocatalytic activity (Fox and Dulay, 1993). Besides, TiO_2 have strong oxidizing abilities for decomposition of organic pollutants, low cost and environmentally friendly (Janczyk et al., 2006; Mital & Manoj, 2011; Yoshio et al., 2004). TiO_2 mainly act as heterogeneous photocatalysts, because of its favourable combination of electronic structures which is characterized by a filled valence band and an empty conduction band, light absorption properties, charge transport characteristics and excited states lifetime (Konstantinou and Albanis, 2004; Nakata and Fujishima, 2012; Khan, 2015).

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. Secondly, TiO_2 possesses fast electrons (e^-) and holes (h^+) recombination that will decrease the photocatalytic activity.

Many strategies and approaches has been proposed to improve the photocatalytic efficiency of TiO_2, which is known as the most active and suitable semiconductor photocatalyst (Dozzi and Selli, 2013). Various strategies, including using dye sensitization (Saien and Mesgari, 2016), noble metal loading (Kmetykó 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 (Di Valentin *et al.*, 2005).

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) can control the stability of the TiO_2. Carbon was found to be more efficient compared to most of the non-metal elements due to its useful properties. Carbon materials exist in various forms, such as diamond, graphite, and carbines (Derjaguin et al., 1977). It has been used in photocatalytic applications due to their excellent properties, including high chemical stability, high electrical and thermal conductivity, light weight, non-toxicity and radiation resistant (Zaleska, 2008).The modification of TiO_2 with carbon has generally changed the structure, physical, and electronic properties of TiO_2. The photocatalytic performance enhanced by facilitating faster transport to the active sites on the TiO_2 surface, narrowing the bandgap energy, extending the light absorption to visible range, and suppressing the rate of the recombination of photo-induced electrons and holes (Palanivelu et al., 2008).

Upon comprehensive review, there is no firm conclusion on the factors that affect the photocatalytic activity. Many studies have been carried out to modify the surface area (Nikhil et al., 2015; Kominami et al., 2003; Kowalska et al., 2012; Kowalska et al., 2015) pore structure in terms of size, volume and shape (He et al., 2015), band gap energy (Wajid Shah et al., 2015) and crystalline phase (Kominami et al., 2003; Ouzzine et al., 2014) of TiO_2. These factors remain the focus in the field of TiO_2 photocatalyst to enhance photocatalytic activity (Nakata and Fujishima, 2012).

The relationship between structural and physical properties of photocatalytic activity also have been studied by Prieto-Mahaney and coworkers (2009). In this study, statistical multivariable analyses were used with the aim of obtaining the structure-photocatalytic properties relationship of six properties of 35 commercially available TiO_2 samples with five photocatalytic reactions. The six properties included are specific surface area, density of lattice defects, primary and secondary particle size and existence of anatase and rutile phase. 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 constitute a significant limitation on determining the structure-photocatalytic activity of TiO_2. In this case, the statistical method have been implemented but it is time-consuming and also money wasting due to usage of chemicals and it needs a lot of data (Murakami et al., 2009).

The predominant factor that affects the photocatalytic activity of TiO_2 still remained unclear and becomes the grand challenge in the research field of TiO_2 (Ohtani, 2017). Therefore, the conventional analytical method is desperately required that accounts for all complexities and variations of data in investigating the structure-photocatalytic activity relationship of TiO_2 photocatalyst. Fuzzy Logic is the nearest solution to complex problems which has the potential of combining human thought and experience into computer-assisted decision making. Fuzzy Set Theory has been studied extensively over the past 30 years. Most of the early interest in Fuzzy Set Theory pertained to representing uncertainty in human cognitive processes (Zadeh, 1965). It is now applied to problems in engineering, business, medical and related health sciences, and the natural sciences (Taylor and Yue, 2010). The use of the Fuzzy Logic Graph is a new approach to correlate the structure and photocatalytic activities. As mentioned above, there are many factors that affect the photocatalytic activity. However, none of the tools have yet been used to elucidate the dominant factors that affect the photocatalytic activity.

As reported, Fuzzy Graph is one of many approaches to solve various problems involving relations and networks (Ore, 1962). The Fuzzy Graph was another focus on the implementation of fuzzy theory in its relation to the theory of graphs. The Fuzzy Graph in the form of graph represents the relationship between the variables precisely indicating the level of the relationship between the variables. Hence, through elucidation using the Fuzzy Graph tool, determination of structure and physical properties-activity can be done.

Regardless of the numerous studies based on the relationship between structural and physical properties of photocatalytic activity remain controversial and still need to be investigated. Thus, in this research, the combination of Fuzzy Logic Graph and Fuzzy Interference System was used to determine the structural-photocatalytic activity relationship of carbon-doped TiO_2.

1.2 Statement of Problem

The utilization of TiO_2 photocatalyst has gained significant attention in air and water treatment as it provides high efficiency in degradation of organic pollutants (Zaleska, 2008). It has been concluded that the photocatalytic activity depends on structural and physicochemical properties of TiO_2. Since then, it is believed that there is a relationship between the structural properties and photocatalytic activity of TiO_2. However, comprehensive research on the correlation between the factors and the photocatalytic performance were not done comprehensively with proof. Many speculations have done to correlate the predominant factor that affects photocatalytic activity of TiO_2.

Furthermore, the dominant factor influencing photocatalytic activity for TiO_2 also have not been clearly clarified. In this study, the 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 carbon-doped TiO_2.

1.3 Objectives of Study

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

- To study the usage of Fuzzy Inference System for photocatalytic activity of carbon-doped TiO_2.
- To evaluate the relationship between structural and physicochemical properties and photocatalytic activity of carbon-doped TiO_2.
- To determine the dominant factor of carbon-doped TiO_2 towards photocatalytic activity through sensitivity analysis.

1.4 Scope of Study

This study focuses on the elucidation of the physicochemical properties-photocatalytic activity relationship of carbon-doped TiO_2 via Fuzzy Logic Controller. This study used a data collection on the physicochemical properties and photocatalytic activity from our research group. The data are the physicochemical properties of carbon-doped TiO_2 characterized using various instruments techniques such as X-ray diffraction (XRD), Scanning Electron Microscope (SEM), UV-visible diffuse reflectance (UV- Vis DR) and Photoluminescence (PL) spectroscopy. The structure and the physical properties-activity relationship was elucidated using the Fuzzy Graph. Four factors, i.e., crystalline phases, surface area, crystallite size, and rate of electron-hole recombination, are chosen as the parameters. In more specific, this study includes four main stages, such as (1) data collection, (2) development of Fuzzy Logic Controller, (3) construction of Fuzzy Inference System and, (4) assessment of the results by sensitivity analysis. In order to predict the dominant factor of physicochemical properties upon determining photocatalytic UV-vis light irradiations, a sensitivity analysis was carried out in the fuzzy model. Sensitivity analysis is the study of how the uncertainty in the output of a mathematical model or system can be divided and allocated to different sources of uncertainty in its inputs.

In this study, data collection on the physicochemical properties and photocatalytic activity were extracted from our research group only to ensure that all data comes in one source and same instrument which is identical system. By using same instruments during characterization, the consistency of data can be maintain. Hence, only four factors, i.e., crystalline phases, surface area, crystallite size and rate of electron-hole recombination, are chosen as the parameters due to the limitation of data from our research group. Therefore, this study will analyze the efficiency of Fuzzy Logic Graph in order to determine the dominant physiochemical properties of carbon-doped TiO_2 towards photocatalytic activity by using existing data only.

1.5 Hypothesis of Study

Fuzzy Logic Controller is one of the simplest methods to clarify the structure-photocatalytic activity relationship of carbon-doped TiO_2 photocatalyst. One hypothesized combining the physicochemical properties and photocatalytic activity of all data in current literature can determine the structure-photocatalytic activity relationship of carbon-doped TiO_2 photocatalyst between them using Fuzzy Logic.

1.6 Significance 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 physicochemical properties that influence photocatalytic activity of carbon-doped TiO_2, the question arises what the dominant factors influencing photocatalytic activity of carbon-doped TiO_2 are. Therefore, this research highlighted one main significance which is a new approach in photocatalysis to find the structure and physical properties-activity relationship using Fuzzy Graph. This research will be a guideline for future research that other photocatalyst can be precisely enhanced depending on the reaction.

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