SYNTHESIS AND CHARACTERIZATION OF MOF-5/TiO_2 THIN FILM

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ABSTRACT

The major drawbacks of photocatalytic degradation of organic pollutants by TiO_2 are the wide band gap energy of TiO_2 and the rapid recombination between the charge carriers (e^-/h^+ pairs). These limit the photocatalytic activity of TiO_2 as large amount of solar is still unable to excite the photocatalyst. The MOF-5/TiO_2 thin film was fabricated by dip-coating a TiO_2-coated pyrex tube into a MOF-5 mother solution. XRD analysis of the MOF-5/TiO_2 thin film confirmed the crystalline structures of anatase TiO_2 and MOF-5 respectively. This study utilised MOF-5/TiO_2/UV-A system in the photocatalytic degradation of methyl orange. The MOF-5/TiO_2/UV-A system was capable of degrading 34.3 % of 5 ppm of aqueous methyl orange solution after 2 hours compared to 32.2 % by the TiO_2/UV-A system under the same reaction conditions. This shows that the presence of MOF-5 is able to increase the photocatalytic activity of TiO_2. However, the photodegradation efficiency starts to decrease after irradiation time of 3 hours. This could be due to the competition between methyl orange and its intermediate species during the photodegradation process.

SINTESIS DAN PENCIRIAN FILEM NIPIS MOF-5/TIO_2

ABSTRAK

Kelemahan utama degradasi pemangkinanfoto bahan pencemar organik oleh TiO_2 adalah jurang jalur tenaga TiO_2 yang luas dan penggabungan semula yang cepat antara pembawa cas (e^-/ h^+ pasangan). Ini menghadkan aktiviti pemangkinanfoto TiO_2 kerana jumlah cahaya yang besar masih tidak dapat merangsangkan fotomangkin tersebut. Filem nipis MOF-5/TiO_2 telah difabrikasi dengan mencelup tiub pyrex lapisan TiO_2 ke dalam larutan MOF-5. Analisis XRD saput nipis MOF-5/TiO_2 telah mengesahkan struktur hablur "anatase" TiO_2 dan MOF-5 masing-masing. Kajian ini telah menggunakan sistem MOF-5/TiO_2/UV-A dalam degradasi pemangkinanfoto metil jingga. Sistem MOF-5/TiO_2/UV-A didapati boleh menyingkirkan 34.3 % daripada 5 ppm akueus metil jingga selepas 2 jam berbanding dengan 32.2 % oleh sistem TiO_2/UV-A di bawah keadaan tindak balas yang sama. Ini menunjukkan bahawa kehadiran MOF-5 dapat meningkatkan aktiviti pemangkinanfoto TiO_2. Walau bagaimanapun, kecekapan fotodegradasi tersebut mula berkurangan selepas 3 jam masa penyinaran. Ini mungkin disebabkan oleh persaingan antara metil jingga dengan spesies perantaraannya dalam proses fotodegradasi tersebut.

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LIST OF SYMBOLS AND ABBREVIATIONS

A_0	Initial absorbance at t=0 min
A_t	Absorbance at t min
Abs	Absorbance
AOP	Advanced oxidation process
BDC	1,4-benzyldicarboxylic Acid
BSE	Backscattered electron
CVD	Chemical vapour deposition
D_{abs}	Photodegradation efficiency
DMF	N,N-dimethylformamide
EDC	Endocrine disrupting chemical
MO	Methyl orange
MOF	Metal-Organic Framework
PSM	Postsynthetic modification
PVD	Physical vapour deposition
SE	Secondary electrons
SEM	Scanning electron microscope
TBOT	Tetrabutyl titanate
TTIP	Titanium tetraisopropoxide
TEA	Triethylamine
UV	Ultraviolet

UV-Vis	Ultraviolet-visible
PXRD	Powder X-ray diffraction
λ_{max}	Maximum wavelength
e^-	Conductive band electron
h^+	Valence band hole

CHAPTER 1

INTRODUCTION

1.1 Photocatalytic degradation of organic pollutants by TiO_2

Photocatalytic degradation technique with titanium dioxide (TiO_2) is generally applied for treating wastewater containing organic contaminants due to its ability to achieve complete mineralization of the organic contaminants under mild conditions such as ambient temperature and ambient pressure. Photocatalysis studies using titanium dioxide have been conducted for the degradation of persistent organic pollutants and other organic chemicals which are known to be endocrine disruptors (Thiruvenkatachari *et al.*, 2008). TiO_2-based photocatalysis has been demonstrated to effectively decompose endocrine disrupting chemicals (EDCs) within a short reaction period (Chang *et al.*, 2009). TiO_2 photocatalytic process is receiving more attention because of its low cost when using sunlight as the source of irradiation (Konstantinou & Albanis, 2004).

This semiconductor photocatalysis relies on the use of metal chalcogenides to create oxidized holes, which directly react with adsorbed molecules (Hathway, 2009). Semiconducting oxide photocatalysts have been more focused in recent years due to their potential applications in solar energy conversion and environmental purification. A number of solids can be referred to as photocatalysts and metal oxide semiconductors are considered to be the most suitable photocatalysts due to their photocorrosion resistance and wide band gap energies (Umar & Aziz, 2013). Several semiconductors (TiO_2, ZnO, Fe_2O_3, CdS, ZnS) can act as photocatalysts but titanium dioxide (TiO_2) has been the most commonly studied. This is not only due to its ability to break down organic pollutants and achieve complete mineralization under ultraviolet exposure, (Umar & Aziz, 2013) but also because TiO_2 has a high degradation efficiency with almost any organic molecules making it an excellent and effective photocatalyst for the photocatalytic degradation of various organic pollutants (Hathway, 2009; Uddin *et al.*, 2013).

TiO_2 photocatalyst is also largely available, inexpensive and non-toxic. It does not involve mass transfer and can be carried out under ambient conditions (atmospheric oxygen is used as oxidant) (Konstantinou & Albanis, 2004). Photocatalytic and hydrophilic properties of TiO_2 makes it close to an ideal catalyst due its high reactivity and relatively high chemical stability (Umar & Aziz, 2013). TiO_2 plays an important role as a photocatalyst in many applications, such as fog proof and self-cleaning textiles, antibacterial textiles, antiviral textiles, self-cleaning glass, and water treatment, including dye removal from industrial wastewater (Uddin *et al.*, 2013). The semiconducting property of TiO_2 is responsible for the removal of different organic pollutants through excitation of TiO_2 semiconductor with a light energy greater than its band gap, which could generate electron hole pairs (Mansoori *et al.*, 2008).

However, there are a few problems that have arisen which hampered the full potential of the photocatalytic TiO_2 material (Wang & Caruso, 2011) and thus, limiting the application of the photocatalysis process. The main issues that restrict the photoactivity of TiO_2 materials are the rapid recombination between the photo-induced electron and hole pairs (e^-/h^+ pairs) which results in low quantum yield (~ 10%) (Mansoori *et al.*, 2008) and the wide band gap energy of TiO_2 (3.2 eV for anatase and 3.0 eV for rutile) that requires high energy UV light (achievable from only 5% of sunlight) to induce the excitation (Wang & Caruso, 2011). The other problems associated with the TiO_2 materials include non-selectivity of the systems (Mansoori *et al.*, 2008), the low mass transport rates between the active centres of TiO_2 photocatalyst and the organic pollutant and lastly the associated issues of nanoparticle separation (generally nanoparticle samples are required to achieve high surface areas) (Wang & Caruso, 2011).

To enchance the photocatalyst efficiency, much effort has been devoted to the modification of the TiO_2 materials by both physical and chemical means. The addition of porosity in TiO_2 based photocatalysts is an important means of enhancing the photocatalytic activity by improving mass transfer within the system, as compared to a bulk material. Incorporating porosity within the titania material affords large surface areas without associated nanoparticulate separation issues, and increased accessibility for the organic pollutant to the active sites on the titania. The increased surface accessibility leads to increased photocatalytic reaction centres within the porous materials, thereby enhancing the photocatalytic activity and resulting in higher adsorption of the organic pollutants (Wang & Caruso, 2011).

Porous materials, ranging from zeolites to metal-organic frameworks (MOFs), offer considerable internal surface areas for the separation, manipulation and catalytic transformation of guest molecules. A porous structure can provide more single sites and special passages for charge transport. Thus, the introduction of a porous structure into a photocatalyst may result in markedly enhanced photocatalytic reactivity, providing a promising strategy for the design and fabrication of novel photocatalysts with high performances (Wei *et al.*, 2012).

1.2 Metal-Organic Frameworks (MOFs)

MOFs are hybrid organic-inorganic microporous crystalline materials in which a metal-containing inorganic cluster is linked throughout space by a poly-dentate organic ligand to form a three-dimensional framework (Civalleri *et al.*, 2006). MOFs have a structure composing of metal-oxide units or transition metal ions (or clusters) joined by organic linkers through strong covalent bonds (Yaghi, 2007; Britt *et al.*, 2008). They are self-assemblies of metal ions which act as coordination centers and organic ligands which act as linkers between metal centers. Metal-organic frameworks (MOFs) can be considered as a relatively new member in the vast field of crystalline nanoporous materials (Britt *et al.*, 2008). Nevertheless, MOFs are the fastest growing class of the novel organic-inorganic materials. (Gustafsson, 2012) resulting in the increasing number of publications related with MOFs in the past decade (Seda, 2011).

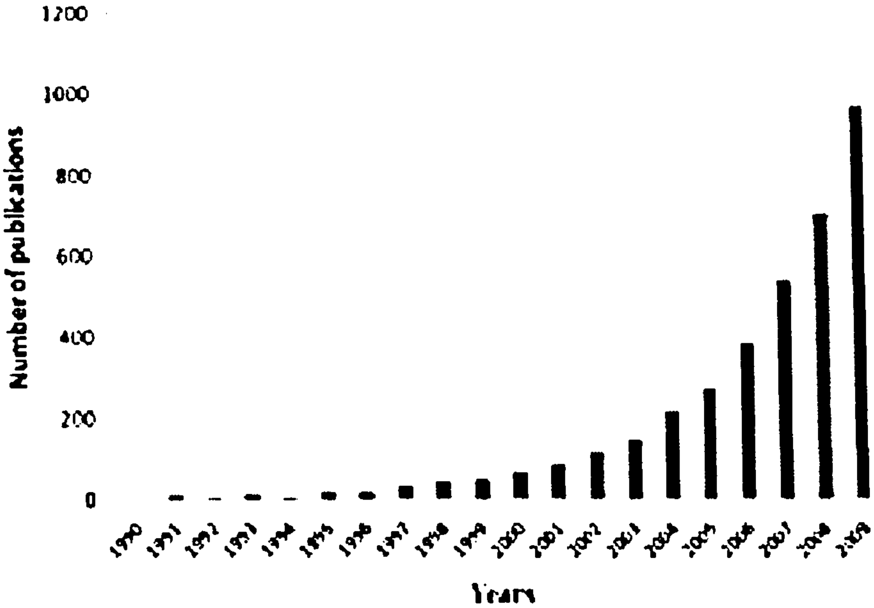

Figure 1.1. Number of publications featuring the term "metal organic frameworks" in their topics (Seda, 2011).

These microporous metal-organic frameworks (MOFs) that display permanent porosity have attracted a great deal of attention because of their high adsorption affinity, diverse structures and pore topologies and accessible functionalization of tunnels (Lu *et al.*, 2012). Their ordered porous constructions with high surface areas and porosities, together with the possibility to functionalize the hybrid frameworks are the main reasons why MOFs have gained a tremendous interest during the last decade. The research area of MOFs have merged the two often separated disciplines; organic chemistry and inorganic chemistry (Gustafsson, 2012). These remarkable properties of porous MOFs make them attractive for an extremely wide range of potential applications such as luminescence, magnetism, catalysis, chemical sensing and gas (hydrogen, methane and carbon dioxide) storage, adsorption and separation (Yaghi, 2007; Sang *et al.*, 2009; Tong *et al.*, 2013).

MOF-5 which is also known as isoreticular metal-organic framework-1 (IRMOF-1), is the simplest and most well studied MOF. The structure of MOF-5 consists of clusters or units of $Zn_4O(CO_2)_6$ that are joined together by benzene links. Each individual unit is composed of four ZnO_4 tetrahedra with a common vertex and six carboxylate C atoms that form the octahedral unit (Yaghi, 2007). This forms a three dimensional cubic framework with the octahedral units at its vertices and the benzene links as the edges. This open framework leads to some exceptional properties that have increased the interest in studying this new material for potential applications on adsorption, separation and storage. As one of the most stable MOFs, MOF-5 also has the ability to tune its structure and functionality directly during synthesis making it possible to tune the organic linker as well as incorporate reactive groups within a MOF. Hence, it is now possible to develop new type of composite materials with improved properties (Li *et al.*, 1999; Seda, 2011). In this study, MOF-5/TiO_2 composite thin film was synthesised and its photocatalytic activity was studied.

1.3 Objectives of the study

The objectives of this study are:

i. to synthesize MOF-5/TiO_2 thin film,
ii. to characterize MOF-5/TiO_2 thin film using XRD and SEM, and
iii. to determine the photocatalytic activity of MOF-5/TiO_2 thin film towards the degradation of methyl orange using UV-VIS spectrometer.

1.4 Scope of the study

Titanium dioxide, TiO_2 thin film was synthesized using the sol-gel method as suggested by Lee *et al.* (2001). It involves dip-coating the pyrex tube in TiO_2 sol gel followed by calcination at 500 °C to obtain TiO_2 in anatase phase. MOF-5 was synthesized at room temperature based on the method suggested by Tranchemontagne *et al.* (2008). It involves the deprotonation of the organic linker, 1,4-benzyldicarboxylic Acid (BDC) by triethylamine (TEA) followed by addition of base, zinc nitrate hexahydrate, $Zn(NO_3)2{\cdot}6H_2O$. The MOF-5/TiO_2 thin film was then prepared by dipping the TiO_2 coated pyrex tube into the MOF-5 mother solution at room temperature. The crystallinity and surface morphology of the nanomaterials were characterized using PXRD and SEM respectively. The photocatalytic activity of the MOF-5/TiO_2 thin film towards the degradation of methyl orange was studied using UV-VIS spectrometer.

CHAPTER 2

LITERATURE REVIEW

2.1 Advanced Oxidation Process (AOP)

Advanced oxidation processes (AOPs) have emerged as an important class of technology for accelerating the oxidation and destruction of a wide range of organic contaminants in polluted water (Goi, 2005). Thus, AOPs are used for application in many wastewater treatment areas such as groundwater remediation pump-and-treat systems, manufacturing facilities, and domestic wastewater treatment plants due to their efficiency in mineralizing a great variety of recalcitrant compounds, through the oxidation of generated hydroxyl radicals. Recently, AOPs using UV irradiation and photocatalyst titanium dioxide (TiO_2) have been gaining growing acceptance as a more effective wastewater treatment method (Thiruvenkatachari *et al.*, 2008).

AOPs have been broadly defined as near ambient temperature and pressure treatment processes based on the in situ generation of highly reactive radicals, especially the hydroxyl radical (•OH) as the primary chemical oxidant (Goi, 2005). The aim of AOP is to destroy even the recalcitrant organic pollutants by the generation of free hydroxyl radicals (•OH). It utilize the very strong oxidizing power of hydroxyl radicals to oxidize organic compounds to the preferred end products of carbon dioxide and water. The hydroxyl radicals in the AOPs are very reactive but short-lived. They are non-selective chemical oxidants which act very rapidly with most organic compounds. The radicals need to be produced on site, in a reactor where they can be in contact with the organics in the wastewater (Munter, 2001).

The generation of •OH radicals can be accelerated by combining ozone (O_3), hydrogen peroxide (H_2O_2), titanium dioxide (TiO_2), UV radiation, ultrasound and (or) high electron beam irradiation. Hence, the various systems of AOPs, in which the hydroxyl radicals may be produced, are ultraviolet radiation/hydrogen peroxide (UV/H2O2), ozone/hydrogen peroxide (Ozone/H_2O_2), ultraviolet radiation/ozone (UV/Ozone), Fenton's reagent (ferrous iron and hydrogen peroxide) (H_2O_2/Fe^{2+}), and titanium dioxide/ultraviolet radiation (TiO_2/UV) (Zhou & Smith, 2002). Once generated, the hydroxyl radicals aggressively attack virtually all organic compounds. Depending upon the nature of the organic species, two types of initial attack are possible: the hydroxyl radical can abstract a hydrogen atom from water, as with alkanes or alcohols, or it can add itself to the contaminant, as in the case of olefins or aromatic compounds (Munter, 2001).

AOPs involve the two stages of oxidation which are the formation of strong oxidants such as hydroxyl radicals, and reaction of these oxidants with organic contaminants in water. However, the term advanced oxidation processes refers specifically to processes in which oxidation of organic contaminants occurs primarily through reactions with hydroxyl radicals. Unlike air stripping and adsorption, which are phase-transfer processes, AOPs are destructive processes. AOPs destroy organic contaminants directly in the water through chemical transformation, as opposed to simply transferring them from the liquid phase into a gas phase (in the case of air stripping) or solid phase (in the case of GAC and resins). AOPs are divided into homogenous and heterogenous systems in which hydroxyl radicals are generated with or without UV irradiation (Goi, 2005; Thiruvenkatachari *et al.*, 2008).

2.1.1 Heterogeneous photocatalysis

Among AOPs, heterogeneous photocatalysis have been proven to be of interest due to its efficiency in degrading recalcitrant organic compounds (Umar & Aziz, 2013). Heterogeneous photocatalysis can be defined as a "catalytic reaction involving the production of a catalyst by absorption of light." (Lazar & Varghese, 2012). Developed in the 1970s, the interest in heterogeneous photocatalysis started with the discovery of photochemical splitting of water into hydrogen and oxygen with TiO_2 and has since been given considerable attention for the past two decades in studies of the applications of heterogeneous photocatalytic oxidation process with a view to decompose and mineralize recalcitrant organic compounds (Ibhadon & Fitzpatrick, 2013; Umar & Aziz, 2013).

In recent years, interest has been focused on the use of semiconductor materials as photocatalysts for the removal of organic and inorganic species from aqueous or gas phase. This method has become an important environmental decontamination method suitable for treatment of water, aqueous wastes and wastewater due to its ability to oxidise the organic and inorganic substrates (Laoufi *et al.*, 2013). Heterogeneous photocatalysis is a favorable combination of charge transport features, electronic structures, excited-state life spans, and light absorption effects (Tan *et al.*, 2011). Heterogeneous photocatalytic processes use certain metal oxides that can readily generate hydroxyl radicals on the surface of particles when absorbing UV light but the most common heterogeneous photocatalytic processes are TiO_2/UV and TiO_2/H_2O_2/UV.

The TiO_2-based photocatalysis process is initiated through photo-activation of the TiO_2 semiconductor. When TiO_2 is irradiated with ultraviolet (UV) light, (Tan *et al.*, 2011) the semiconductor is activated by the absorption of photons with energy equal to, or greater than that of the band gap, which induces electron transitions from the valence band to the conduction band, generating a hole at the valence band and forming electron–hole pairs (e^-/h^+ pair) (a super reductant and oxidant, respectively) (Chang *et al.*, 2009; Wang & Caruso, 2011).

$$TiO_2 + hv \rightarrow e_{cb}^- (TiO_2) + h_{vb}^+ (TiO_2) \qquad (2.1)$$

where cb is conduction band and vb is valence band.

Consequently, following irradiation, the TiO_2 particle can act as either an electron donor or acceptor for molecules in the surrounding medium (Ibhadon & Fitzpatrick, 2013). In the absence of an electron acceptor or donor in the medium, recombination of electron/hole pair occurs, hindering the photodegradation process. The electron and hole can recombine, releasing the absorbed light energy as heat, with no chemical effect. Otherwise, the charges can move to "trap" sites at slightly lower

REFERENCES

Al-Qaradawi, S. & Salman, S. R. 2002. Photocatalytic degradation of methyl orange as a model compound. *J. Photochem. Photobiol. A,* **148** (1–3): 161-168.

Akpan, U. G. & Hameed, B. H. 2010. The advancements in sol–gel method of doped-TiO_2 photocatalysts. *Appl. Catal., A: General,* **375** (1): 1-11.

Baranyai, R., Detrich, A., Volentiru, E. & Horvolgui, Z. 2009. Preparation and characterization of ZnO and TiO_2 sol-gel thin films deposited by dip coating. *Hung. J. Ind. Chem.,* **37** (2): 131-137.

Behera, S., S., G., Ahmad, F., S., S. & Banerjee, S. 2012. UV-Visible spectrophotometric method development and validation of assay of paracetamol tablet formulation. *J. Anal. Bioanal. Tech.,* **3** (6): 1-6.

Bétard, A. & Fischer, R. A. 2011. Metal–organic framework thin films: From fundamentals to applications. *Chemical Rev.,* **112** (2): 1055-1083.

Britt, D., Tranchemontagne, D. J. & Yaghi, O. M. 2008. Metal-organic frameworks with high capacity and selectivity for harmful gases. *Proc. National Academy of Sciences,* **105** (33): 11623-11627.

Chang, S. M., Lo, P. H. & Chang, C. T. 2009. Photocatalytic behavior of TOPO-capped TiO_2 nanocrystals for degradation of endocrine disrupting chemicals. *Appl. Catal., B: Environ.,* **91** (3–4): 619-627.

Choi, J., Park, H. & Hoffmann, M. R. 2010. Combinatorial doping of TiO_2 with Pt, Cr, V, and Ni to acheive enhanced photocatalytic activity with visible light irradiation *J. of Mater. Res.,* **25** (1): 149-158.

Civalleri, B., Napoli, F., Noel, Y., Roetti, C. & Dovesi, R. 2006. Ab-initio prediction of materials properties with crystal: MOF-5 as a case study. *Cryst Eng Comm,* **8** (5): 364-371.

Cranswick, L. 2009. *Principles and Applications of Powder Diffraction: An overview of powder diffraction.* John Wiley & Sons, Ltd.: 1-72.

Dakka, A., Lafait, J., Abd-Lefdil, M. & Sella, C. 2011. Optical study of titanium dioxide thin films prepared by R.F. sputtering. *Moroccan J. of Condens. Matter,* **2** (1): 153-156.

Daneshvar, N., Salari, D. & Khataee, A. R. 2003. Photocatalytic degradation of azo dye acid red 14 in water: investigation of the effect of operational parameters. *J. Photochem. Photobiol., A,* **157** (1): 111-116.

Davis, M. E. 2002. Ordered porous materials for emerging applications. *Nature,* **417** (6891).

Eddaoudi, M. & Eubank, J. F. 2010. *Metal-Organic Frameworks: Insight into the development of metal-organic materials (MOMs): at zeolite-like metal-organic frameworks (ZMOFs).* John Wiley & Sons, Inc.: 37-89.

Eddaoudi, M., Kim, J., Rosi, N., Vodak, D., Wachter, J., O'Keeffe, M. & Yaghi, O. M. 2002. Systematic design of pore size and functionality in isoreticular MOFs and their application in methane storage. *Science,* **295** (5554): 469-472.

Eshaghi, A., Pakshir, M. & Mozaffarinia, R. 2010. Photoinduced properties of nanocrystalline TiO_2 sol-gel derived thin films. *Bull. Mater. Sci.,* **33** (4): 365-369.

Förster, H. 2004. *Characterization I: UV/VIS spectroscopy.* Springer Berlin Heidelberg: 337-426.

Fujita, M. 2010. *From Hofmann Complexes To Organic Coordination Networks*. Metal-Organic Frameworks, John Wiley & Sons, Inc.: 1-35.

Furukawa, H., Cordova, K. E., O'Keeffe, M. & Yaghi, O. M. 2013. The chemistry and applications of metal-organic frameworks. *Science,* **341** (6149).

Goi, A. 2005. Advanced oxidation processes for water purification and soil remediation. Doctor of Philosophy in Engineering, Talinn Umiversity of Technology.

Gonzalez, J., Nandini Devi, R., Tunstall, D. P., Cox, P. A. & Wright, P. A. 2005. Deuterium NMR studies of framework and guest mobility in the metal–organic framework compound MOF-5. *Microporous Mesoporous Mater.,* **84** (1–3): 97-104.

Guettaï, N. & Ait Amar, H. 2005. Photocatalytic oxidation of methyl orange in presence of titanium dioxide in aqueous suspension. Part I: Parametric study. *Desalination,* **185** (1–3): 427-437.

Gustafsson, M. 2012. Metal-organic frameworks (MOFs) for heterogeneous catalysis: synthesis and characterization. Doctor of Philosophy Doctoral thesis, Stockholm University.

Hathway, T. L. 2009. Titanium dioxide photocatalysis: studies of the degradation of organic molecules and characterization of photocatalysts using mechanistic organic chemistry. Doctor of Philosophy Graduate Theses and Dissertations, Iowa State University.

Hermes, S., Schröder, F., Chelmowski, R., Wöll, C. & Fischer, R. A. 2005. Selective nucleation and growth of metal-organic open framework thin films on patterned COOH/CF_3-Terminated self-assembled monolayers on Au (111). *J. Amer. Chem. Soc.,* **127** (40): 13744-13745.

Hosseinnia, A., Keyanpour-Rad, M. & Pazouki, M. 2010. Photo-catalytic degradation of organic dyes with different chromophores by synthesized nanosize TiO_2 particles. *World Appl. Sci. J.,* **8** (11): 1327-1332.

Hu, Y. T., Sun, S. Q., Xi, Z. Y., Duan, C. Y. & Meng, Y. 2006. TiO_2 thin films prepared from aqueous solution and their sterilizing capability. *J. of Ceram. Processing,* **7** (1): 49-52.

Huang, B. L., McGaughey, A. J. H. & Kaviany, M. 2007. Thermal conductivity of metal-organic framework 5 (MOF-5): part I. molecular dynamics simulations. *Int. J. Heat Mass Transfer,* **50** (3–4): 393-404.

Huang, X. H., Tang, Y. C., Hu, C., Yu, H. Q. & Chen, C. S. 2005. Preparation and characterization of visible-light-active nitrogen-doped TiO_2 photocatalyst. *J Environ Sci (China),* **17** (4): 562-565.

Hummel, D. 2002. *Atlas of Plastics Additives: Spectrometry in the ultraviolet and visible regions.* Springer Berlin Heidelberg: 65-69.

Ibhadon, A. & Fitzpatrick, P. 2013. Heterogeneous photocatalysis: recent advances and applications. *Catalysts,* **3** (1): 189-218.

Knowles, J. P., Elliott, L. D. & Milburn, K. I. B. 2012. Flow photochemistry: Old light through new windows. *Beilstein J. Org. Chem.,* **8**: 2025-2052.

Konstantinou, I. K. & Albanis, T. A. 2004. TiO_2-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations: a review. *Appl Catal., B,* **49** (1): 1-14.

Kuppler, R. J., Timmons, D. J., Fang, Q. R., Li, J. R., Makal, T. A., Young, M. D., Yuan, D., Zhao, D., Zhuang, W. & Zhou, H. C. 2009. Potential applications of metal-organic frameworks. *Coord. Chem. Rev.,* **253** (23–24): 3042-3066.

Lamvik, M. K. 2006. *Encyclopedia of Analytical Chemistry: Scanning electron microscopy in analysis of surfaces.* John Wiley & Sons, Ltd.

Laoufi, N. A., Hout, S., Tassalit, D., Ounnar, A., Djouadi, A., Chekir, N. & Bentahar, F. 2013. Removal of a persistent pharmaceutical micropollutant by UV/TiO_2 process using an immobilized titanium dioxide catalyst: parametric study. *Chem. Eng.,* **32**: 1951-1956.

Lazar, M. A., Varghese, S. & Nair, S. S. 2012 Photocatalytic Water Treatment by Titanium Dioxide: Recent Updates. *Catalysts,* **2**: 572-601.

Lee, J. Y., Farha, O. K., Roberts, J., Scheidt, K. A., Nguyen, S. B. T. & Hupp, J. T. 2009. Metal-organic framework materials as catalysts. *Chem. Soc. Rev.,* **38** (5): 1450-1459.

Lee, S., Kang, M., Cho S. M., Han, G. Y., Kim, B., Yoon, K. J. & Chung, C. 2001. Synthesis of TiO_2 photocatalyst thin film by solvothermal method with a small amount of water and its photocatalytic performance. *J. Photochem. Photobiol. A,* **146**: 121-128.

Li, J., Cheng, S., Zhao, Q., Long, P. & Dong, J. 2009. Synthesis and hydrogen-storage behavior of metal–organic framework MOF-5. *Int. J. of Hydrogen Energy,* **34** (3): 1377-1382.

Li, H., Eddaoudi, M., O'Keeffe, M. & Yaghi, O. M. 1999. Design and synthesis of an exceptionally stable and highly porous metal-organic framework. *Nature,* **402** (6759): 276-279.

Li, Y., Li, X., Li, J. & Yin, J. 2006. Photocatalytic degradation of methyl orange by TiO_2-coated activated carbon and kinetic study. *Water Res.,* **40** (6): 1119-1126.

Li, Y., Peng, S., Jiang, F., Lu, G. & Li, S. 2007. Effect of doping TiO_2 with alkaline-earth metal ions on its photocatalytic activity. *J. Serbian Chem. Soc.,* **72** (4): 393-402.

Liu, H. L. & Chiou, Y.-R. 2005. Optimal decolorization efficiency of Reactive Red 239 by UV/TiO2 photocatalytic process coupled with response surface methodology. *Chem. Eng. J.,* **112** (1–3): 173-179.

Liu G., Li, X., Zhao, J., Horikoshi, S. & Hidaka, H. 2000. Photooxidative mechanism of dye alirain red in TiO_2 dispersions under visible illumination: an experimental and theoretical examination. *J. Mol. Catal. A: Chem.*, **153**: 221-229.

Lu, G., Li, S., Guo, Z., Farha, O. K., Hauser, B. G., Qi, X., Wang, Y., Wang, X., Han, S., Liu, X., DuChene, J. S., Zhang, H., Zhang, Q., Chen, X., Ma, J., Loo, S. C., Wei, W. D., Yang, Y., Hupp, J. T. & Huo, F. 2012. Imparting functionality to a metal-organic framework material by controlled nanoparticle encapsulation. *Nat Chem,* **4** (4): 310-316.

Lu, G. Q. & Zhao, X. S. 2004. Nanoporous materials - An overview. *Nanoporous Materials Science and Engineering*. United Kingdom, Imperial College Press: 873.

Mansoori, G. A., Bastami, T. R., Ahmadpour, A. & Eshaghi, Z. 2008. Environmental applications of nanotechnology. Annu. Rev. Nano Research, World Scientific Pub. Co., **2:** 1-73.

Mills, A., Hill, G., Bhopal, S., Parkin, I. P. & O'Neill, S. A. 2003. Thick titanium dioxide films for semiconductor photocatalysis. *J. Photochem. Photobiol., A,* **160** (3): 185-194.

Munter, R. 2001. Advanced oxidation processes - current status and prospects. *Proc. Estonian Acad. Sci. Chem.*, **50** (2): 59-80.

Nashera, M. R., Neisiani, S. M. H. H., Badiib, K. & Adhamia, F. 2012. Preparation and antifog behavior of Fe^{3+}-doped TiO_2 nanometer thin films on soda–lime glass pre-coated with a SiO_2 layer. Proc. 4th International Conference on Nanostructures (ICNS), Sharif University of Technology, Kish Island, I.R. Iran.

Nguyen, V. N., Nguyen, N. K. T. & Nguyen, P. H. 2011. Hydrothermal synthesis of Fe-doped TiO_2 nanostructure photocatalyst. *Adv. Nat. Sci: Nanosci. Nanotechnol.,* **2** (3): 1-4.

Rauf, M. A., Meetani, M. A. & Hisaindee, S. 2011. An overview on the photocatalytic degradation of azo dyes in the presence of TiO_2 doped with selective transition metals. *Desalination,* **276** (1–3): 13-27.

Rosi, N. L., Eddaoudi, M., Kim, J., O'Keeffe, M. & Yaghi, O. M. 2002. Advances in the chemistry of metal-organic frameworks. *Cryst Eng Comm,* **4** (68): 401-404.

Saha, D., Deng, S. & Yang, Z. 2009. Hydrogen adsorption on metal-organic framework (MOF-5) synthesized by DMF approach. *J. Porous Mater.,* **16** (2): 141-149.

Sang, Y. B., David, D., Andrew, N., Krista, S. W., Joseph, T. H. & Randall, Q. S. 2009. Strategies for characterization of large-pore metal-organic frameworks by combined experimental and computational methods. *Chem Mater,* **21** (20): 4768-4777.

Seda, K. 2011. Biomedical applications of metal organic frameworks. *Ind. Eng. Chem. Res.,* **50** (4): 1799-1812.

Sonawane, R. S., Kale, B. B. & Dongare, M. K. 2004. Preparation and photo-catalytic activity of Fe-TiO_2 thin films prepared by sol–gel dip coating. *Mater. Chem. Phys.,* **85** (1): 52-57.

Su, C., Hong, B. Y. & Tseng, C. M. 2004. Sol–gel preparation and photocatalysis of titanium dioxide. *Catal. Today,* **96** (3): 119-126.

Suryanarayana, C. & Norton, M. G. 1998. *X-ray diffraction.* USA, Springer US.

Snyder, R. L. 2007. *X-ray Characterization of Materials: X-Ray diffraction.* Wiley-VCH Verlag GmbH: 1-103.

Tan, Y. N., Wong, C. L. & Mohamed, A. R. 2011. An overview on the photocatalytic activity of nano-doped-TiO_2 in the degradation of organic pollutants. *ISRN Mater. Sci.,* **2011**: 18.

Thiruvenkatachari, R., Vigneswaran, S. & Moon, I. 2008. A review on UV/TiO_2 photocatalytic oxidation process. *Korean J. Chem. Eng.,* **25** (1): 64-72.

Tranchemontagne, D. J., Cortes, M. J. L., O'Keeffe, M. & Yaghi, O. M. 2009. Secondary building units, nets and bonding in the chemistry of metal-organic frameworks. *Chem. Soc. Rev.,* **38** (5): 1257-1283.

Tranchemontagne, D. J., Hunt, J. R. & Yaghi, O. M. 2008. Room temperature synthesis of metal-organic frameworks: MOF-5, MOF-74, MOF-177, MOF-199, and IRMOF-0. *Tetrahedron,* **64** (36): 8553-8557.

Tong, X. L., Lin, H. L., Xin, J. H., Liu, F., Li, M. & Zhu, X. P. 2013. Recent advances as materials of functional metal-organic frameworks. *J. Nanomaterials,* **2013**: 11.

Uddin, M. J., Alam, M. M., Islam, M. A., Snigda, S. R., Das, S., Rahman, M. M., Uddin, M. N., Morris, C. A., Gonzalez, R., Diebold, U., Dickens, T. J. & Okoli, O. 2013. Tailoring the photocatalytic reaction rate of a nanostructured TiO_2 matrix using additional gas phase oxygen. *Int. Nano Lett.,* **3** (1): 1-10.

Umar, M. & Aziz, H. A. 2013. *Organic Pollutants – Monitiring, Risk and Treatment: Photocatalytic degradation of organic pollutants in water.* InTech: 195-208.

Valencia, S., Vargas, X., Rios, L., Restrepo, G. & Marín, J. M. 2013. Sol–gel and low-temperature solvothermal synthesis of photoactive nano-titanium dioxide. *J. Photochem. Photobiol., A,* **251** (0): 175-181.

Van, N. & Ngan, P. 2013. Use of co-spray pyrolysis for synthesizing nitrogen-doped TiO_2 films. *Bull. Mater. Sci.,* **36** (5): 827-831.

Viana, M. M., Mohallem, T. D. S., Nascimento, G. L. T. & Mohallem, N. D. S. 2006. Nanocrystalline titanium oxide thin films prepared by sol-gel process. *Brazilian J. Phys.,* **36**: 1081-1083.

Von Dreele, R. B. & Toby, B. H. 2002. *Characterization of Materials: X-Ray powder diffraction.* John Wiley & Sons, Inc.

Vu, A. T., Nguyen, Q. T., Linh Bui, T. H., Tran, M. C., Dang, T. P. & K., H. T. T. 2010. Synthesis and characterization of TiO_2 photocatalyst doped with transition metal ions. *Adv. Nat. Sci.: Nanoscience and Nanotechnology,* **1** (1).

Wang, X. & Caruso, R. A. 2011. Enhancing photocatalytic activity of titania materials by using porous structures and the addition of gold nanoparticles. *J. Mater. Chem.,* **21** (1): 20-28.

Wang, X., Wu, G., Zhou, B. & Shen, J. 2013. Optical constants of crystallized TiO_2 coatings prepared by sol-gel process. *Materials,* **6** (7): 2819-2830.

Waseda, Y., Matsubara, E. & Shinoda, K. 2011. *X-Ray Diffraction Crystallography.* Japan, Springer Berlin Heidelberg.

Wei, X., Wang, K. X., Guo, X. X. & Chen, J. S. 2012. Single-site photocatalysts with a porous structure. *Proc. R. Soc. A: Math., Phys. and Eng. Sci.,* **468** (2143): 2099-2112.

Wells, O. C. & Joy, D. C. 2006. The early history and future of the SEM. *Surf. Interface Anal.,* **38** (12-13): 1738-1742.

Wongkalasin, P., Chavadej, S. & Sreethawong, T. 2011. Photocatalytic degradation of mixed azo dyes in aqueous wastewater using mesoporous-assembled TiO2 nanocrystal synthesized by a modified sol–gel process. *Colloids Surf., A,* **384** (1–3): 519-528.

Wu, C., Li, H., Fong, H. H., Pozdin, V. A., Estroff, L. A. & Malliaras, G. G. 2011. Room-temperature preparation of crystalline TiO_2 thin films and their applications in polymer/TiO_2 hybrid optoelectronic devices. *Org. Electron.*, **12**: 1073-1079.

Xu, T. H., Song, C. L., Liu, Y. & Han, G. R. 2006. Band structures of TiO_2 doped with N, C and B. *J. Zhejiang University Sci. B,* **7** (4): 299-303.

Yaghi, O. M. 2007. Metal-organic frameworks: a tale of two entanglements. *Nat Mater,* **6** (2): 92-93.

Zacher, D., Shekhah, O., Woll, C. & Fischer, R. A. 2009. Thin films of metal-organic frameworks. *Chem. Soc. Rev.,* **38** (5): 1418-1429.

Zaleska, A. 2008. Doped-TiO_2: a review. *Recent Patents on Engineering,* **2** (3): 157-164.

Zhang, H., Dong, F., Zhai, S., Kang, X. & Fang, S. 2012. Preparation of ordered TiO_2 macroporous membrane using PBMA colloid crystal as template. *Adv. Mater. Res.,* **399-401**: 677-682.

Zhang, Z., Wu, H., Yuan, Y., Fang, Y. & Jin, L. 2012. Development of a novel capillary array photocatalytic reactor and application for degradation of azo dye. *Chem. Eng. J.,* **184** (0): 9-15.

Zhao, Z., Li, Z. Q. & Lin, Y. S. 2009. Adsorption and diffusion of carbon dioxide on metal-organic framework (MOF-5). *Ind. Eng. Chem. Res.,* **48** (22): 10015-10020.

Zhou, H. C., Long, J. R. & Yaghi, O. M. 2012. Introduction to metal-organic frameworks. *Chem Rev,* **112** (2): 673-674.

Zhou, H. & Smith, D. W. 2002. Advanced technologies in water and wastewater treatment. *J. Environ. Eng. Sci.,* **1**: 247-264.