PREPARATION AND CHARACTERIZATION OF ZIF-67/TiO_2 THIN FILM

LENNY KHOO

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SIGNATURE

1. **DR. MOH PAK YAN**
   (SUPERVISOR)

2. **PROF. DR. BABA BIN MUSTA**
   (DEAN)

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ABSTRACT

Titanium dioxide (TiO_2) is one of the most widely used photocatalyst due to its non-toxic, low cost, good chemical stability, elemental abundance, and photocatalytic properties. But there are some problems faced by TiO_2, first is that if TiO_2 used is in the powder form an additional separation process is needed to separate the TiO_2 particles from the wastewater after the treatment. TiO_2 has a high bandgap which requires UV-A light to activate it. The high recombination rate of electron hole pair occurs before the photocatalytic process starts. ZIF-67 is well known for its porosity properties. It is used in this study to act as an adsorbent to adsorb organic dye on the surface of TiO_2 to allow photodegradation to occur and at the same time forming synergetic effect with TiO_2 to reduce its band gap from UV region to visible light region. ZIF-67/TiO_2 thin film is form by using dip-coating method. The morphology of ZIF-67/TiO_2 is observed by using SEM. A square-like shape of ZIF-67 is observed on the surface of TiO_2 thin film. The photodegradation result obtained show that ZIF-67/TiO_2 (43.63%) has a lower photodegradation efficiency than un-doped TiO_2 (58.81%) under the irradiation of UV-A light. This shows that ZIF-67 does not enhance the photocatalytic ability of TiO_2 under irradiation of UV-A light. This may cause by the combination of ZIF-67 with the Co-doped TiO_2 thin film does not show a synergetic effect in photodegradation. Besides that, ZIF-67 does not overcome the high recombination rate of electron hole pair of TiO_2 by adsorbing MB longer on the surface. But from this study shows that cobalt can act as a dopant to enhance the photocatalytic properties of TiO_2 in the visible light region. Co-doped TiO_2 shows a photodegradation efficiency of 25.27 % compared to un-doped TiO_2 which is only 14.36 %.

PENYEDIAAN DAN PENCIRIAN FILEM NIPIS ZIF-67/TiO_2

ABSTRAK

Titanium dioksida (TiO_2) adalah salah satu fotomangkin yang paling banyak digunakan. Ia digunakan kerana tidak beracun, kos yang rendah, kestabilan kimia yang baik, mudah didapati, dan mempunyai sifat fotopemangkinan yang baik. Tetapi terdapat beberapa masalah yang dihadapi oleh TiO_2, pertama adalah bahawa jika TiO_2 digunakan adalah dalam serbuk ini menubuhkan satu proses pemisahan ini adalah untuk memisahkan zarah TiO_2 dari air sisa selepas rawatan. Di samping itu, TiO_2 mempunyai bandgap yang tinggi yang memerlukan UV-A cahaya untuk mengaktifkannya. Tambahan pula, kadar penggabungan semula yang tinggi untuk lubang dan elektron berlaku sebelum proses fotopemangkinan bermula.ZIF-67 terkenal dengan sifat keliangan. Ia digunakan dalam kajian ini untuk bertindak sebagai adsorben untuk menjerap pewarna organik di permukaan TiO_2 untuk membolehkan fotodegradasi berlaku dan pada masa yang sama membentuk kesan sinergis dengan TiO_2 untuk mengaktifkan TiO_2 dari rantau UV kepada rantau cahaya visible. ZIF-67/TiO_2 filem nipis dibentukkan dengan menggunakan kaedah kemiringan lapisan. Morfologi ZIF-67/TiO_2 didapati dengan menggunakan SEM. Satu bentuk persegi daripada ZIF-67 dipelihara pada permukaan TiO_2 filem nipis. Kaedah fotodegradasi diperolehi bahawa ZIF-67/TiO2 (43,63%) mempunyai kaedah yang lebih rendah daripada TiO_2 sendiri (58,81%) di bawah sinaran UV-A cahaya. Ini menunjukkan bahawa ZIF-67 tidak meningkatkan keupayaan fotopemangkinan daripada TiO_2 di bawah sinaran UV-A cahaya. Ini boleh menyebabkan oleh gabungan ZIF-67 dengan TiO_2 filem nipis tidak menunjukkan kesan sinergis dalam Pemfotorosotaan. Di samping itu, ZIF-67 tidak mengatasi masalah kadar penggabungan semula yang tinggi untuk lubang dan elektron TiO_2 dengan adsorbing MB di permukaan TiO_2 lebih lama. Tetapi daripada kajian ini menunjukkan bahawa kobalt boleh bertindak sebagai pendopan untuk meningkatkan sifat-sifat fotopemangkinan daripada TiO_2 di rantau cahaya visible. Co-doped TiO_2 menunjukkan kecekapan Pemfotorosotaan yang lebih baik daripada 25,27% berbanding un-doped TiO_2 yang hanya 14,36%. Ini adalah kerana dengan doping kobalt ke TiO_2 boleh beralih kelebihan penyerapan optik dari UV ke dalam julat cahaya visible.

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LIST OF SYMBOLS AND ABBREVIATIONS

λ_{max}	Base peak length
e^-	Conductive band electron
h^+	Valence band hole
K_α	Kappa alpha
A	Acceptor molecule
AB	Anatase and brookite
ANA	Analcime
AR	Anatase and rutile
BCT	Body centered tetragonal
BDC	1,4-benzenedicarboxylic acid
BET	Brunaur-Emmett-Teller
CVD	Chemical vapour deposition
D	Donor molecule
D_{abs}	Photodegradation efficiency
DI	Deionized
E_g	Band gap
GIS	Gismondine
GME	Gmelinite
HKUST	Hong Kong University Science and Technology
LED	Light-emitting diode
LTA	Linde type A
MB	Methylene blue
MBE	Molecular beam epitaxy
MER	Merlinoite
MIL	Material Institute Lavoisier
MOF	Metal organic framework
MW	Microwave
PEG	Polyethylene glycol
PL	Photo luminescence
PXRD	Powder x-ray diffractometer
RE^{3+}	Rare earth ions

RHO	Rhodonite
SEM	Scanning electron microscope
SOD	Sodalite
TBOT	Titanium (IV) butoxide
US	Ultrasound
UV	Ultraviolet
UV-Vis	Ultraviolet-Visible
Vis	Visible
ZIF	Zeolitic imidazolate framework

CHAPTER 1

INTRODUCTION

1.1 PHOTOCATALYSIS IN WASTEWATER TREATMENT

In present years, environmental pollution is one of the most serious issues that causes a huge impact to the world. This is due to the increasing living standards and growth of population in the world as well as the unreasonable energy usage that have aggravated the pollution of environment. Many research activities are devoted in order to solve these problems (Li *et al.*, 2014). Among the researches, photocatalysis shows the most promising solutions towards elimination of environmental contaminants (Pichat, 2013).

In photocatalysis reaction either the catalyst molecule or the substrate molecule, are in an electronically excited state during the catalytic step. The absorption of photon by the catalyst causes the electron to be promoted from the valence band to the conduction band leaving a hole, h^+ behind. Excited state of electrons in the conduction band and the holes in the valence band can cause a recombination process and dissipate the energy as heat or react with electron donors and electron acceptors adsorbed on the semiconductor surface (Hoffmann *et al.*, 1995). The efficiency of catalytic reaction is highly dependent on the concentration of the electronically excited catalyst species. It is non-catalytic in the absence of photons, therefore to maintain the catalytic cycle, a continuous irradiation is required (Oppenlander, 2003).

Titanium dioxide (TiO_2) is one of the most widely used photocatalyst due to its non-toxic, low cost, good chemical stability, elemental abundance, excellent physicochemical properties for the applications in scope of energy and environmental science (Chen *et al.*, 2014). In nature it can exist in three crystal form which are rutile, anatase and brookite (Othmer, 1996). The form of TiO_2 is temperature dependent, to obtained anatase form during the calcination process of TiO_2, the temperature is required to rise around 500 °C. (López-Muñoz *et al.*, 2014). TiO_2 is insoluble in water and in diluted acids, but it dissolves slowly in hot sulphuric acid (Oppenlander, 2003). From the past research, anatase form shows a band gap of 3.21 eV (López-Muñoz *et al.*, 2014). The photocatalytic activity of TiO_2 is strongly affected by its crystallinity and particle size (Pecchi *et al.*, 2001). Anatase shows more photocatalytic activity than rutile TiO_2 due to its larger charge carrier diffusion rates and lower recombination rates compared to rutile (Heather, 2002). Although rutile shows lower photocatalytic activity than anatase, the combination of anatase and rutile to form Degussa P-25 TiO_2 shows greater photocatalytic activity than anatase alone. This material consists of about 80 % of anatase 20 % of rutile and has a BET specific surface area of ca. 55 $m^2\ g^{-1}$. The diameter of its particles usually lies between 25 nm and 35 nm (Oppenlander, 2003).

Despite of all the advantages in the usage of TiO_2, there are some challenges faced in this material. First of all, the separation of TiO_2 particles from its aqueous suspensions represents a serious problem for practical use. Besides that, the high recombination rate of e^-/h^+ impeded TiO_2 from practical application. The reactivity of a TiO_2 is dependent on the recombination rate of e^-/h^+ at the surface. In order to increase the efficiency of the photocatalyst, the photogenerated holes and electrons must have a long lifespan, since recombination process shows a direct competition with the surface charge transfer to the adsorbed species. Hence, the recombination rate must be minimized to achieve optimum efficiency. Various experiments had been done such as doping, to extend the lifespan of the photogenerated holes and electrons. For example, the photocatalytic degradation of rhodamine B by TiO_2 was highly enhanced when doped with lanthanide metals such as Eu^{3+}, La^{3+}, Nd^{3+}, and Pr^{3+}. These dopants create a potential gradient at the surface, separating the photogenerated e^-/h^+ pairs by trapping them as well as by facilitating their faster movement along the surface of TiO_2 (Magesh *et al.*, 2009). Lastly, the large band gap of TiO_2 (3.2 eV for anatase polymorph) which falls in the range of UV region, only shows photo-response to UV light, making it more costly due to the need of UV light source (Bagwasi *et al.*, 2013).

In this study, TiO_2 thin film in anatase phase is used to overcome the separation problem caused by TiO_2 particles. Furthermore, Metal Organic Framework (MOF) is introduced in this study to overcome the high recombination rate of electron-hole pair and large band gap faced by TiO_2 photocatalyst. MOF is a material consist of metal centres which is bound to each other by organic molecules ligands, instead of binding to a single metal centre, it is bind with several metal centres to form coordination polymers. By altering the types of metal nodes and bridging ligands, desirable framework topologies can be prepared (Schroder, 2010). In this study, ZIF-67 was used as the MOF to form ZIF-67/TiO_2 composite. The low band gap of ZIF-67 (1.98 eV) is highly possible to reduce the band gap of TiO_2 (3.2 eV) and alter the absorption spectrum from UV region towards visible light region. Besides that, the porous properties of ZIF-67 can also help to overcome the electron recombination problem of TiO_2 by elongating the time of adsorption between the pollutants and the surface of TiO_2.

1.2 OBJECTIVES OF STUDY

The objectives of this study are:

i) to prepare ZIF-67/TiO_2 thin film,
ii) to characterize ZIF-67/TiO_2 thin film,
iii) to determine the photocatalytic activity of ZIF-67/TiO_2 thin film towards the degradation of methylene blue, and
iv) to determine the adsorption ability of ZIF-67/TiO_2 thin film towards methylene blue.

1.3 SCOPE OF STUDY

This study focuses on the synthesis and characterization of ZIF-67/TiO_2 thin film. The Co-doped TiO_2 thin film was synthesized using the sol-gel method where TiO_2 precursor sol-gel was prepared from mixture of isopropyl alcohol (IPA) and titanium

(IV) butoxide (TBOT). Then $CoCl_2 \bullet 6H_2O$ and isopropyl alcohol (IPA) are added to the sol-gel to form the precursor sol-gel of Co-doped TiO_2. Then a glass slide was dipped in the sol-gel followed by drying and calcination. ZIF-67 precursor was prepared from $CoCl_2 \bullet 6H_2O$ and 2-methylimidazole. ZIF-67/TiO_2 composite was formed by dip-coating method.

The surface morphology of ZIF-67/TiO_2 was determined using scanning electron microscope (SEM). Lastly, the photocatalytic activity was determined using UV-VIS spectrophotometer in the degradation of methylene blue solution.

CHAPTER 2

LITERATURE REVIEW

2.1 TITANIUM DIOXIDE

Titanium dioxide, TiO_2 also known as titania is a natural occurring oxide of titanium. The main advantages of TiO_2 are its high chemical stability when exposed to acidic and basic compounds, its nontoxicity, its relatively low cost and its highly oxidizing power, which make it a competitive candidate for many photocatalytical applications (Ohama *et al.*, 2011). In nature titanium dioxide can exist in three crystal form which are rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic) (Othmer, 1996). Figure 2.1 shows the crystal structures of anatase, brookite and rutile.

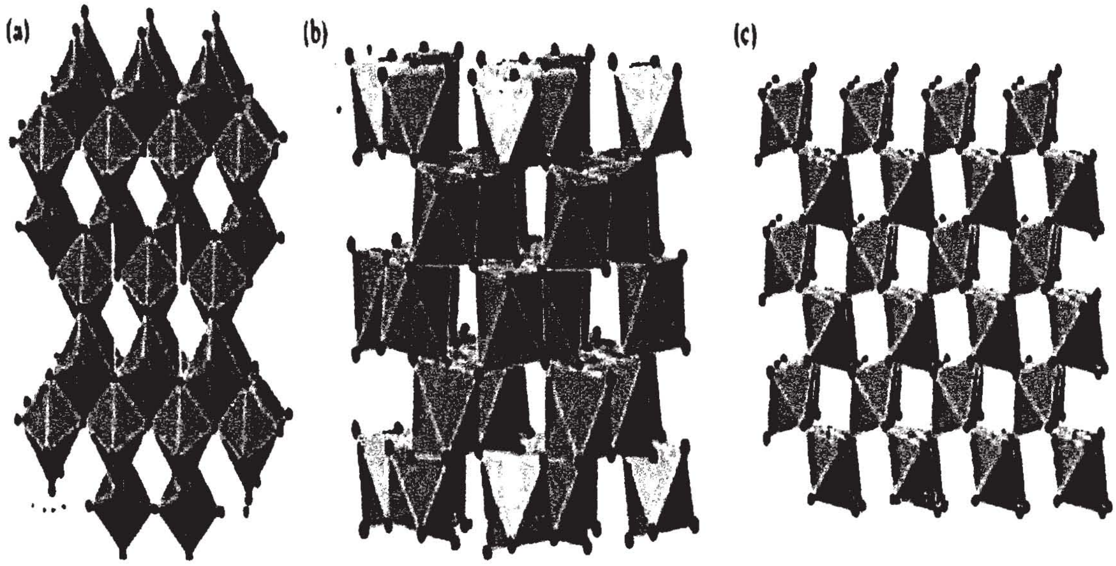

Figure 2.1: Crystal structures of titanium dioxide (a) anatase (b) brookite and (c) rutile. [Figure adapted from Štengl *et al.* (2007)]

Among the three crystal forms, brookite is the most unstable form and rutile is the most thermally stable form found most in the crystal growth (Štengl *et al.*, 2007). Therefore the form of TiO_2 is temperature dependent. Calcination process at higher temperature (>600 °C) for rutile phase with higher crystallinity and smaller specific surface, while at 500 °C form anatase phase with lower crystallinity and larger crystallinity and larger specific surface area, at temperature 200 °C brookite is form (López-Muñoz *et al.*, 2014; Oppenlander, 2003). Most photocatalytic studies have focused on the rutile (3.0 eV) and anatase (3.2 eV) (Heather, 2002). Although, anatase is less thermally stable compared to rutile, but anatase has better photocatalytic activity than rutile (Shinde *et al.*, 2008). Table 2.1 shows the basic physical properties of anatase (Ohama & Gemert, 2011).

Table 2.1: Basic physical properties for anatase form of titanium dioxide. [Table modified from Ohama and Gemert (2011)]

Crystal form	Tetragonal system
Density (g/cm^3)	3.90
Refractive index	2.52
Permittivity	31
Thermal stability	Change to rutile form at high temperature

TiO_2 containing both anatase and rutile (AR) or anatase and brookite (AB) TiO_2 crystals shows better photocatalytic activity than single phase TiO_2. The presence of more than one polymorph of TiO_2 reduces the recombination effect to enhance the photocatalytic performance of the resulting sample than in pure single phase TiO_2 (Boppella *et al.*, 2012). It is thought that the existence of the different phases of the same semiconductor offer a synergetic junction effect property. For instance, biphasic TiO_2 with an AR mixture such as found in Degussa P25 is a good photocatalyst due to the presence of this junction effect that enhances its electron hole separation (Carneiro *et al.*, 2011). Hiroaki and coworkers postulated that the high photocatalytic activity of an AR mixture is due to interfacial electron transfer from anatase to rutile that increases the charge separation efficiency (Kawahara *et al.*, 2002). Ohno and coworkers suggested that the large band bending in rutile is responsible for the high reactivity of Degussa P25 (AR titania mixture) powders in the photocatalytic oxidation of naphthalene in air (Ohno *et al.*, 2001).

Recently, Ismail and coworker had shown that the brookite phase is a potentially good photocatalyst due to its lower symmetry and its band gap that is close to that of anatase (Ismail *et al.*, 2010). Therefore, biphasic TiO_2 with either (AB) or (AR) mixture has the potential to become a better heterogeneous photocatalyst than pure anatase due to the enhanced charge carrier separation (Ardizzone *et al.*; 2007). Generally TiO_2 with brookite phase or a mixture of TiO_2 polymorphs are obtained hydrothermally at high temperature and pressure conditions (Moonoosawmy *et al.*, 2012). Additionally, a fine control of the parameters such as temperature, the nature of the precursor, water content, pH, catalyst, ionic strength and the nature of chelating agent is greatly required to promote phase selectivity (Stengl *et al.*, 2011)

There are some general applications of titanium dioxide. Titanium dioxide is used in heterogeneous catalysis, as a photocatalyst, and in electric devices in solar cells for production of hydrogen and electric energy. Besides that TiO_2 can be used as gas sensor and white pigment (e.g. in paints and cosmetic products). Furthermore TiO_2 can be used as coating for different purposes such as a corrosion-protective coating, as an optical coating in ceramics (Diebold, 2003).

2.1.1 Photocatalytic Reaction of TiO_2

TiO_2 is a semiconductive material that can acts as a strong oxidizing agent to decompose organic and inorganic compounds during the illumination of UV-A light. The illumination of the surface of the TiO_2 induces the separation of two types of carriers: (1) an electron (e^-) and (2) a hole (h^+). To produce these two carriers, sufficient energy must be supplied by a photon to promote an electron (e^-) from the valence band to the conduction band, leaving a hole (h^+) behind in the valence band. The recombination of holes and electrons is relatively slow in TiO_2 compared to electrically conducting materials such as metals where the recombination occurs immediately (Ohama & Gemert, 2011).

$TiO_2 + hv \rightarrow h^+ + e^-$ (2.1)

The required energy that has to be supplied by the photons for the promotion of the electrons depends on the band gap for the specific material. The band gap is the difference in energy between the highest permitted energy level for the electron in the valence band and the lowest permitted energy level in the conduction band. The band gap is the minimum energy of light required to make the material electrically conductive. The band gap energy, E_g of TiO_2 (anatase) is 3.2 eV, which corresponds to photons with a wave length of 388 nm (Ohama & Gemert, 2011).

The photoinduced hole can oxidize a donor molecule (D) adsorbed on the TiO_2 surface.

$D + h^+ \rightarrow \bullet D^+$ (2.2)

The electron in the conduction band can reduce an acceptor molecule (A).

$A + e^- \rightarrow \bullet A^-$ (2.3)

The strong oxidation power of the hole enables a one-electron oxidation step by reacting with water to produce a hydroxyl radical ($\bullet$ OH).

$H_2O + h^+ \rightarrow \bullet OH + H^+$ (2.4)

Oxygen can act as an electron acceptor, and be reduced by the promoted electron in the conduction band to form a superoxide ion ($\bullet O_2^-$). The superoxide ions are highly reactive particles, which are able to oxidize organic materials. Besides that, oxygen also plays an important role in reducing the electron-hole recombination rate, which increases the lifetime of the excited state and thus yield of the photocatalytic reaction (Ohama & Gemert, 2011). The oxidation-reduction process is shown in Figure 2.2.

$O_2 + e^- \rightarrow \bullet O_2^-$ (2.5)

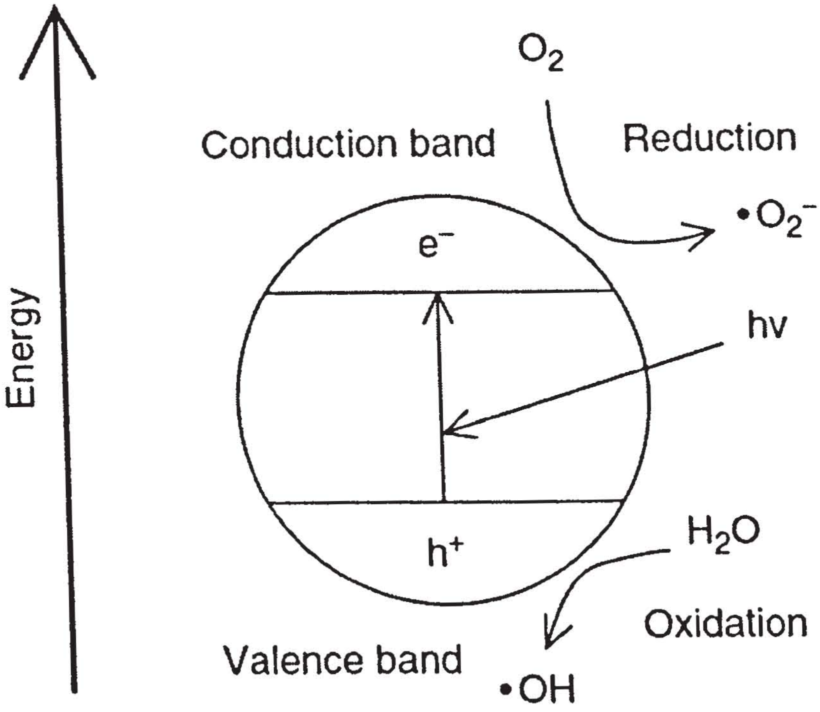

Figure 2.2: Photochemical mechanism of TiO_2. [Figure adapted from Ohama and Gemert (2011)]

2.1.2 Challenges Encountered by TiO_2

Recent years, the applications of TiO_2 had been widely spreaded due to its superior properties such as high chemical stability, good photocatalytic properties and nontoxicity. Despite of all the advantages in TiO_2, there are some challenges faced in this material. First of all, the separation of TiO_2 particles from its aqueous suspensions represents a serious problem for practical use (Fujishima *et al.*, 2000). Besides that, the high electron-hole recombination rate of TiO_2 reduces its photocatalylic ability. Lastly, the large band gap of TiO_2 (3.2 eV for anatase polymorph) which falls in the range of UV region, only shows photo-response to UV light. This limits the usage of TiO_2 as a photocatalyst, because only a small fraction of suns's energy (< 10 %) consists of UV light. This makes TiO_2 more costly because it requires a UV light source to irradiate sufficient energy for it to undergo photocatalytic degradation process (Chen *et al.*, 2007). Several researches had been done to improve the performance of TiO_2 such as modification of TiO_2 into thin films, nanotube, and nanorod, forming composites with other elements or alter the properties by doping TiO_2 material with other elements (Chen & Mao, 2007).

REFERENCES

Al-Qaradawi, S., & Salman, S. R. 2002. Photocatalytic degradation of methyl orange as a model compound. *Journal of Photochemistry and Photobiology A: Chemistry,* **148**(1-3): 161-168.

Alvaro, M., Carbonell, E., Ferrer, B., FX, L. i. X., & Garcia, H. 2007. Semiconductor behavior of a metal-organic framework (MOF). *Chemistry* **13**(18): 5106-5112.

Ardizzone, S., Bianchi, C. L., Cappelletti, G., Gialanella, S., Pirola, C., & Ragaini, V. 2007. Tailored anatase/brookite nanocrystalline TiO_2. The optimal particle features for liquird-and gas-phase photocatalytic reactions. *The Journal of Physical Chemistry,* **111**(35): 13222-13231.

Bagwasi, S., Tian, B., Zhang, J., & Nasir, M. 2013. Synthesis, characterization and application of bismuth and boron Co-doped TiO2: A visible light active photocatalyst. *Chemical Engineering Journal,* **217**(0): 108-118.

Batten, S. R., Champness, N. R., Chen, X.-M., Garcia-Martinez, J., Kitagawa, S., Ohrstrom, L., O'Keeffe, M., Suh, M. P., & Reedijk, J. 2013. Terminology of metal-organic frameworks and coordination polymers. *Pure Applied Chemistry,* **85**(8): 1715-1724.

Bessekhouad, Y., Rober, D., Weber, J. V., & J, C. N. 2004. Effect of alkaline-doped TiO_2 on photocatalytic efficiency. *Journal of Photochemistry and Photobiology A,* **167**: 49.

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

Bhattcharjee, S., Jang, M.-S., Kwon, H.-J., & Ahn, W.-S. 2014. Zeolitic Imidazolate Frameworks: Synthesis, Functionalization, and Catalytic/Adsorption Applications. *Catalysis Surveys from Asia,* **18**: 101-127.

Boppella, R., Basak, P., & Manorama, S. V. 2012. Viable method for the synthesis of biphasic TiO_2 nanocrystals with tunable phase composition and enabled visible-light photocatalytic performance *ACS applied materials & interfaces,* **4**(3): 1239-1246.

Burrows, A. D., Frost, C. G., Mahon, M. F., & Richardson, C. 2008. The post-synthetic modification of tagged metal-organic framework. *Angewandte Chemie International Edition,* **47**: 8482-8486.

Carneiro, J. T., Savenijie, T. J., Moulijn, J. A., & Mul, G. 2011. How phase composition influence opto-electronic and photocatalytic properties of TiO_2. *Journal of Physical Chemistry C,* **115**: 2211-2217.

Chen, E.-X., Yang, H., & Zhang, J. 2014. Zeolitic Imidazolate Framework as Formaldehyde Gas Sensor. *Inorganic Chemistry,* **53**: 5411-5413.

Chen, K., Jiang, Z., Qin, J., Jiang, Y., Li, R., Tang, H., & Yang, X. 2014. Synthesis and improved photocatalytic activity of ultrathin TiO_2 nanosheets with nearly 100% exposed (001) facets. *Ceramics International,* **40**(10, Part B): 16817-16823.

Chen, S. F., Chen, L., Gao, S., & Cao, G. Y. 2005. The preparation of nitrogen-doped photocatalyst $TiO_{2-x}N_x$ by ball milling. *Chemical Physics Letters,* **413**: 404-409.

Chen, S. W., Lee, J. M., Lu, K. T., Pao, C. W., Lee, J. F., Chan, T. S., & Chen, J. M. 2010. Bang-gap Narrowing of TiO_2 Doped with Ce Probed with X-ray Absorption Spectroscopy. *Applied Physics Letters,* **97**: 12104.

Chen, X., & Mao, S. S. 2007. Titanium Dioxide Nanomaterials: Synthesis, Properties, Modifications, and Applications. *Chemical Review,* **107**: 2891-2959.

Cho, W., Park, S., & Oh, M. 2011. Coordination polymer nanorods of Fe-MIL-88B and their utilization for selective preparation of hematite and magnetite nanorods. *Chemical Communications,* **47**: 4138-4140.

Choi, W., Termin, A., & Hoffmann, M. R. 1994. The Role of Metal Ion Dopants in Quantum-Sized TiO_2: Correlation between Photoreactivity and Charge Carrier Recombination Dynamics. *Journal of Physical Chemistry* **98**: 13669-13679.

deKrafft, K. E., Wang, C., & Lin, W. 2012. Metal-Organic Framework Templated Synthesis of Fe_2O_3/TiO_2 Nanocomposite for Photocatalytic Hydrogen Production. *Advanced Materials,* **24**: 2014-2018.

Diebold, U. 2003. The surface science of titanium dioxide. *Surface Science Reports,* **48**(5–8): 53-229.

Djaoued, Y., Bruning, R., Bersani, D., Lottici, P. P., & Badilescu, S. 2004. Sol-gel Nanocrstalline brookite-rich titania films. *Materials Letters,* **58**(21): 2618-2622.

Du, Y. K., Gan, Y. Q., Yang, P., P, H. N., & L, J. 2005. Improvement in th heat-induce hydrophilicity of TiO_2 thin films by doping Mo (VI) ions. *Thin Solid Films,* **491**: 133-136.

Ertl, G., Knozinger, H., Schuth, F., & Weitkamp, J. (2008). *Handbook of Heterogeneous Catalysis* (Vol. 1). Weinheim: Wiley-VCH.

Ferey, G. 2008. Hybrid porous solids: past, present, future. *Chemical Society Review,* **37**(1): 191-214.

Fu, Y., Sun, D., Chen, Y., Huang, R., Ding, D. Z., Fu, P. D. X., & Li, P. D. Z. 2012. An Amine-Functionalized Titanium Metal-Organic Framework Phoocatalyst with Visible-Light-Induced Activity for CO$_2$ Reduction. *Angewandte Chemie International Edition,* **51**(14): 3364-3367.

Fu, Y., Sun, D., Chen, Y., Huang, R., Ding, Z., Fu, X., & Li, Z. 2012. An Amine-Functionalized Titanium Metal-Organic Framework Photocatlyst with Visible-Light-Induced Activity for CO$_2$ Reduction. *Angewandte Chemie International Edition,* **124**(14): 3420-3423.

Fujishima, A., Rao, T. N., & Tryk, D. A. 2000. Titanium dioxide photocatalysis. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews,* **1**(1): 1-21.

Gascon, J., Hernandez-Alonso, M. D., Almeida, A. R., Klink, G. P. M. v., Kapteijn, F., & Mul, G. 2008. Isoreticular MOFs as Efficient Photocatalysts with Tunable Band Gap: An Operando FTIR Study of the Photoinduced Oxidation of Propylene. *ChemSusChem,* **1**: 981-983.

Goh, T. W., Xiao, C., Maligal-Ganesh, R. V., Li, X., & Huang, W. 2015. Utilizing mixed-linker zirconium based metal-organic frameworks to enhance the visible light photocatalytic oxidation of alcohol. *Chemical Engineering Science.*

Gomes, C., Luz, I., Llabres, F., Corma, A., & Garcia, H. 2010. Water stable Zr-benzenedicarboxlate metal-organic frameworks as photocatalyst for hydrogen generation. *Chemical- A European Journal,* **16**(36): 11133-11138.

Hamadanian, M., Vanani, A. R., & Majedi, A. 2010. Sol-Gel Preparation and Characterization of Co/TiO$_2$ Nanoparticles: Application to the Degradation of Methyl Orange. *Journal of the Iranian Chemical Society,* **7**: 52-58.

Heather, A. B. (2002). TiO2 Nanoparticles for Photocatalysis *Interfacial Applications in Environmental Engineering.* CRC Press.

Hitosugi, T., Kamisaka, H., Tamashita, K., Nogawa, H., & Furubayashi, Y. 2008. Electronic band structure of transparent conductor: Nb-doped anatase TiO$_2$. *Applied Physics* **1**(11): 111203.

Hoffmann, M. R., Martin, S. T., Choi, W., & Bahnemann, D. W. 1995. Environmental Applications of Semiconductor Photocatalysis. *Chemistry Review,* **95**: 69-96.

Hou, D. X., Goei, R., Wang, X., Wang, P., & Lim, T. T. 2012. Preparation of carbon-sensitized and Fe-Er codoped TiO$_2$ with response surface methodology for bisphenol A photocatalytic degradation under visible-light irradiation. *Applied Catalysis B: Environmental,* **126**: 121-133.

Ismail, A. A., Kandiel, T. A., & Bahnemann, D. W. 2010. Titania-Based Photocatalysts: Brookite Nanorods and Mesoporous Structures. *Journal of Photochemistry and Photobiology A,* **216**: 183-193.

Jhung, S. H., Lee, J.-H., & Chang, J.-S. 2005. Microwave Synthesis of a Nanoporous Hybrid Material, Chromium Trimesate. *Bulletin of the Korean Chemical Society,* **26**(6): 880-881.

Jimmy, C. Y., Yu, J., & Zhao, J. 2002. Enhanced photocatalytic activity of mesoporous and ordinary TiO_2 thin films by sulfuric acid treatment. *Applied Catalysis B: Environmental,* **36**: 31-43.

Jung, S., Cho, W., Lee, H. J., & Oh, M. 2009. Self-template-directed formation of coordinationpolymer hexagonal tubes and rings. and their calcination to ZnO rings. *Angewandte Chemie International Edition,* **48**: 1459-1462.

Kawahara, T., Konishi, Y., Tada, H., Tohge, N., Nishii, J., & Ito, S. 2002. A Patterned TiO2(Anatase)/TiO2(Rutile) Bilayer-Type Photocatalyst: Effect of the Anatase/Rutile Junction on the Photocatalytic Activity. *Angewandte Chemie International Edition,* **41**(15): 2811-2813.

Khan, S. U., Al-Shahry, M., & Ingler, W. B. 2002. Efficient photochemical water spliting by a chemically modified n-TiO_2. *Journal of Science,* **297**(5590): 2243-2245.

Knowles, J. P., Elliott, L. D., & B, M. K. I. 2012. Flow photochemistry: Old light through new windows. *Bellstein Journal of Organic Chemistry,* **8**: 2025-2052.

Li, F. B., Li, X. Z., Hou, M. F., Cheah, K. W., & Choy, W. C. H. 2005. Enhanced photocatalytic activity of Ce^{3+}-TiO_2 for 2 mercaptobenzothiazole degradation in aqueous suspension for odour control. *Applied Catalysis A,* **285**: 181-189.

Li, Y., Li, S., Li, Y., Guo, Y., & Wang, J. 2014. Visible-light driven photocatalyst (Er3+:YAlO3/Pt–NaTaO3) for hydrogen production from water splitting. *International Journal of Hydrogen Energy,* **39**(31): 17608-17616.

Liu, H. L., & Chiou, Y. R. 2005. Optimal decolorization efficiency of Reactive Red 239 by UV/TiO_2 photo catalytic process coupled with response surface methodology. *Chemical Engineering Journal,* **112**: 173-179.

López-Muñoz, M. J., Revilla, A., & Alcalde, G. 2014. Brookite TiO2-based materials: Synthesis and photocatalytic performance in oxidation of methyl orange and As(III) in aqueous suspensions. *Catalysis Today,* **240**: 138-145.

Lu, G. Q., & Zhao, X. S. (2004). *Nanoporous Materials: Science and Engineering* (Vol. 4). United Kingdom: Imperial College Press.

Magesh, G., Viswanathan, B., Viswanath, R. P., & Varadarajan, T. K. 2009. Photocatalytic behavior of CeO_2-TiO_2 system for the degradation of methylene blue. *Indian Journal of Chemistry,* **48A**: 480-488.

Masuda, T., & Kato, K. 2009. Iridescent Stand-Alone TiO_2 Films Crystallized from Aqueous Solutions. *Journal of Nanoscience and Nanotechnology,* **9**: 439-444.

Moonoosawmy, K. R., Katzke, H., Es-Souni, M., & Dietze, M. 2012. Mesoporous and Macroporous Brookite Thin Films Having a LargeThermal Stability Range. *Langmuir,* **28**(16): 6706-6713.

Moret, M. P., Zallen, R., Vijay, D. P., & Desu, S. B. 2000. Brookite-rich titania films made by pulsed laser deposition. *Thin Solid Films,* **366**: 8-10.

Nasalevich, M. A., Goesten, M. G., Savenije, T. J., Kapteijn, F., & Gascon, J. 2013. Enhancing opical absorption of metal-organic framework for improved visible light photocatalysis. *Chemical Communications,* **49**(90): 10575-10577.

Nasalevich, M. A., Veen, M. v. d., Kapteijn, F., & Gascon, J. 2014. Metal-organic frameworks as heterogeneous photocatalysts: advantages and challenges. *CrystEngComm,* **16**: 4919-4926.

Obregon, S., Kubacka, A., Fernandez-Garcia, M., & Colon, G. 2013. High-performance Er^{3+}-TiO_2 system: dual up-conversion electronic role of the lanthanide. *Journal of Catalysis,* **299**: 298-306.

Ohama, Y., & Gemert, D. V. (2011). *Photocatalysis to Construction Materials.* New York: Springer Dordrecht Heildelberg.

Ohno, T., Sarukawa, K., Tokieda, K., & Matsumura, M. 2001. Morphology of a TiO_2 Photocatalyst (Degussa, P-25) Consisting of Anatase and Rutile Crystalline Phases. *Journal of Catalysis,* **203**(1): 82-86.

Oppenlander, T. (2003). *Photochemical Purification of Water and Air.* Germany: WILEY-VCH Verlag GmbH & Co. KGaA.

Othmer, K. (1996). Encyclopedia of Chemical Technology (4th ed., Vol. 19). New York: John Wiley & Sons.

Parida, K. M., & Sahu, N. 2008. Visible light induced photocatalytic activity of rare earth titania nanocomposites. *Journal of Molecular Catalysis A: Chemical,* **287**: 151-158.

Park, K. S., Ni, Z., P, C. A., Y, C. J., R, H., J, U.-R. F., K, C. H., O'Keeffe, M., & Yaghi, O. M. 2006. Exceptional chemical and thermal stability of zeolitic imidazolate frameworks. *Proceedings of the National Academy of Sciences,* **103**(27): 10186-10191.

Pecchi, G., Reyes, P., Sanhueza, P., & Villasenor, J. 2001. Photocatalytic Degradation of Pentachlorophenol on TiO_2 Sol-Gel Catalyst. *Chemosphere,* **43**: 141-146.

Phan, A., Doonan, C. J., Uribe-Romo, F. J., Knobler, C. B., O'Keeffe, M., & Yaghi, O. M. 2010. Synthesis, Structure, and Carbon Dioxide Capture Properties of Zeolitic Imidazolate Frameworks. *Accounts of Chemical Research,* **43**(1): 58-67.

Pichat, P. (2013). *Photocatalysis and Water Purification From Fundamentals to Recent Applications.* Germany: WILEY-VCH Verlag GmbH & Co. KGaA.

Qian, J., Sun, F., & Qin, L. 2012. Hydrothermal synthesis of zeolitic imidazolate framework-67 (ZIF-67) nanocrystals. *Materials Letters,* **82**: 220-223.

Qiu, L. G., Li, Z. Q., Wu, Y., Wang, W., Xu, T., & Jiang, X. 2008. Facile synthesis of nanocrystals of a microporous metal-organic framework by an ultrasonic method and selevtive sensing of organoamines. *Chemical Communications,* **31**: 3642-3644.

Qiu, S., & Zhu, G. 2009. Molecular enginering for synthesizing novel structure of metal-organic frameworks with multifunctional properties. *Coordination Chemistry Reviews,* **253**(23-24): 2891-2911.

Reszczynska, J., Grzyb, T., Sobczak, J. W., Lisowski, W., Gazda, M., Ohtani, B., & Zaleska, A. 2014. Lanthanide co-doped TiO_2: The effect of metal type and amount on surface properties and photocatalytic activity. *Aplied Surface Science,* **307**: 333-345.

Reszczynska, J., Iwulska, A., Sliwinski, G., & Zaleska, A. 2012. Characterization and Photocatalytic Activity of Rare Earth Metal-Doped Titanium Dioxide. *Physicochemical Problems of Mineral Processing,* **48**(1): 201-208.

Rowsell, J. L. C., & Yaghi, O. M. 2004. Metal-organic frameworks: a new class of porous materials. *Microporous and Mesoporous Materials,* **73**: 3-14.

Santara, B., Pal, B., & Giri, P. K. 2011. Signature of strong ferromagnetism and optical properties of Co doped TiO_2 nanoparticles. *Journal of Applied Physics,* **110**: 1-7.

Santiago, A. G., Mayen, S. A., Delgado, G. T., Perez, R. C., Maldonado, A., & Olvera, L. 2010. Photocatalytic degradation of methylene blue using undoped and Ag-doped TiO_2 thin films deposited by a sol-gel process: Effect of the ageing time of the starting solution and the film thickness. *Materials Science and Engineering B,* **174**: 84-87.

Schroder, M. (2010). *Functional Metal-Organic Frameworks: Gas Storage, Separation and Catalysis.* New York: Springer Heidelberg Dordrecht.

Shinde, P. S., Sadale, S. B., Patil, P. S., Bhosale, P. N., Brüger, A., Neumann-Spallart, M., & Bhosale, C. H. 2008. Properties of spray deposited titanium dioxide thin films and their application in photoelectrocatalysis. *Solar Energy Materials and Solar Cells,* **92**(3): 283-290.

Štengl, V., Bakardjieva, S., Murafa, N., Šubrt, J., Měšťánková, H., & Jirkovský, J. 2007. Preparation, characterization and photocatalytic activity of optically transparent titanium dioxide particles. *Materials Chemistry and Physics,* **105**(1): 38-46.

Stengl, V., & Králová, D. 2011. Photoactivity of brookite-rutile TiO_2 nanocystalline mixtures obtained by heat treatment of hydrothermally prepared brookite. *Materials Chemistry and Physics,* **129**: 794-801.

Stock, N., & Biswas, S. 2011. Synthesis of Metal-Organic Frameworks (MOFs): Routes to Various MOF Topologies, Morphologies, and Composites. *Chemical Reviews,* **112**(2): 933-969.

Tagliabue, M., Farrusseng, D., Valencia, S., Aguado, S., Ravon, U., Rizzo, C., Corma, A., & Mirodatos, C. 2009. Natural gas treating by selective adsorption: material science and chemical engineering interplay. *Chemical Engineering Journal,* **155**: 553.

Wang, C., Xie, Z., deKrafft, K. E., & Lin, W. 2011. Doping metal-organic frameworks for water oxidation, carbon dioxide reduction, and organic photocatalysis. *Journal of American Chemical Society,* **133**(34): 13445-13454.

Wang, J.-L., Wang, C., & Lin, W. 2012. Metal-Organic Frameworks for Light Harvesting and Photocatalysis. *ACS Catalysis,* **2**(12): 2630-2640.

Wang, Y., Cheng, H., Hao, Y., Ma, J., Li, W., & Cai, S. 1999. Characterization and photo-electri behaviors of Fe (III) diped TiO_2 nanoparticels. *Journal of Materials Science,* **34**: 3721-3729.

Wang, Z., & Cohen, S. M. 2009. Postsynthetic Modification of Metal-Organic Frameworks. *Chemical Society Review,* **38**: 1315-1329.

Wen, T., Gao, J., & Shen, J. 2001. Preparation and characterization of TiO_2 thin films by the sol-gel process. *Journal of Materials Science,* **36**: 5923-5926.

Wu, X., Bao, Z., Yuan, B., Wang, J., Sun, Y., Luo, H., & Deng, S. 2013. Microwave synthesis and characterization of MOF-74 (M = Ni, Mg) for gas separation. *Microporous and Mesoporous Materials,* **180**: 114-122.

Yaghi, O. M., O'Keeffe, M., Ockwig, N. W., Chae, H. K., Eddaoudi, M., & Kim, J. 2003. Reticular synthesis and the design of new materials. *Nature,* **423**: 705.

Yang, H., He, X.-W., Wang, F., Kang, Y., & Zhang, J. 2012. Doping copper into ZIF-67 for enhancing gas uptake capacity and visible-light-driven photocatalytic degradation of organic dye. *Journal of Materials Chemistry,* **22**: 21849-21851.

Yilmaz, B., Trukhan, N., & Muller, U. 2012. Industrial Outlook on Zeolites and Metal Organic Frameworks. *Chinese Journal of Catalysis,* **33**(1): 3-10.

Zhang, C. Y., Ma, W. X., Wang, M. Y., Yang, X. J., & Xu, X. Y. 2014. Structure, photoluminescent properties and photocatalytic activities of a new Cd)II_ metal-organic framework. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy,* **118**: 657-662.

Zhou, W., Zhong, X., Wu, X., Yuan, L., Shu, Q., & Xia, Y. 2006. Structural and Optical Properties of Titanium Oxide Thin Films Deposited on Unheated Substrate at Different Total Pressures by Reactive dc Magnetron Sputtering with a Substrate Bias. *Journal of the Korean Physical Society,* **49**(5): 2168-2175.

Zhu, J., Zhu, K., & Chen, L. 2006. Influence of gold nanoparticles on the upconversion fluorescence in Sm^{3+}. *Journal of Non-Crystalline Solids,* **352**(2): 150-154.