VANADIUM OXIDES DOPED POROUS TITANIA PHOTOCATALYST FOR PHENOL PHOTODEGRADATION

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To my beloved parents and family,

respectable supervisor and supportive friends

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ABSTRACT

Two series of new porous photocatalysts of vanadium oxides (1 - 5 wt%) doped porous TiO_2 using tetrabutyl titanate (TBT) and titanium tetraisopropoxide (TTIP) as Ti precursor were successfully synthesized. The photocatalysts were synthesized via sol-gel method using cetyltrimethylammonium bromide (CTAB) as template. X-ray diffraction analysis showed that all the photocatalysts crystallined in anatase phase. There was no CTAB residue in the photocatalyst synthesized after calcination at 773 K. According to diffused reflectance UV-visible spectroscopy analysis, the band gap energy reduced from 3.02 (in TBT-TiO_2) to 2.72 eV (in 5V-TBT-p-TiO_2) for TiO_2 synthesized using TBT as Ti precursor. Similarly, reduction in band gap energy from 3.11 (in TTIP-TiO_2) to 2.66 eV (in 5V-TTIP-p-TiO_2) for TiO_2 synthesized using TTIP as Ti precursor. The nitrogen adsorption-desorption analysis revealed that the surface area of both series increased with the amount of dopant. These materials contained of disorder mesopores with particle size range of 5 – 56 nm. The photocatalytic testing results showed that samples 4V-TBT-p-TiO_2 and 4V-TTIP-p-TiO_2 recorded the highest percentage of phenol degradation under visible light irradiation in their respective series. Sample 4V-TBT-p-TiO_2 photodegraded 62.2% phenol, while 4V-TTIP-p-TiO_2 photodegraded 62.8% phenol after 7 h reaction time. There was no significant difference between the photodegradation performances of two series of vanadium oxide doped TiO_2.

ABSTRAK

Dua siri TiO_2 fotomangkin didopkan vanadium oksida telah berjaya dihasilkan dengan menggunakan tetrabutil titanat (TBT) dan titanium tetraisopropoxida (TTIP) sebagai sumber Ti. Kaedah sol-gel telah digunakan untuk menghasilkan semua fotomangkin dan cetiltrimetilammonium bromida (CTAB) digunakan sebagai templat. Analisis pembelauan sinar-X menunjukkan semua fotomangkin dalam kristal bentuk fasa anatas. Tiada sisa CTAB tertinggal dalam sampel selepas pengkalsinan pada 773 K. Menurut analisis spektroskopi UV-Vis resapan pantulan, jurang tenaga dikurangkan daripada 3.02 (dalam TBT-TiO_2) ke 2.72 eV (dalam 5V-TBT-p-TiO_2) untuk TiO_2 yang dihasilkan dengan TBT sebagai sumber Ti. Manakala, penurunan jurang tenaga daripada 3.11 (dalam TTIP-TiO_2) ke 2.66 eV (dalam 5V-TTIP-p-TiO_2) juga dikesan untuk TiO_2 yang dihasilkan dengan TTIP sebagai sumber Ti. Analisis penjerapan dan pembebasan nitrogen mendedahkan bahawa luas permukaan kedua-dua siri fotomangkin telah meningkat dengan pertambahan jumlah pendopan. Bahan-bahan itu mempunyai mesoliang yang tidak serata dengan saiz zarah berjulat 5 - 56 nm. Keputusan ujikaji pemfotomangkinan telah menunjukkan sampel 4V-TBT-p-TiO_2 dan 4V-TTIP-p-TiO_2 mencatatkan dalam siri masing-masing peratusan fotodegradasi fenol tertinggi di bawah sinaran cahaya nampak. Sampel 4V-TBT-p-TiO_2 memfotodegradasi 62.2% fenol, manakala 4V-TTIP-p-TiO_2 memfotodegradasi 62.8% fenol selepas 7 jam tempoh tindak balas. Aktiviti fotodegradasi fenol antara dua siri TiO_2 didopkan vanadium oksida tidak menunjukkan perbezaan yang ketara.

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using TTIP as Ti precursor.

LIST OF ABBREVIATIONS

AOP	Advanced Oxidation Processes
Å	Angstrom
BET	Brunauer-Emmett-Teller Model
BJH	Barrett-Joyner-Halenda method
cm	Centimeter
CPC	Cetylpyridinium Chloride
CTAB	Cetyltrimethylammonium Bromide
^{o}	Degree
°/s	Degree Per Second
DRUV-VIS	Diffused Reflectance Ultraviolet-Visible Spectroscopy
EISA	Evaporation Induced Self-Assembly Method
EU	European Union
eV	Electronvolt
FESEM	Field Emission Scanning Electron Microscope
FTIR	Fourier Transform Infrared Spectroscopy
g	Gram
K	Kelvin
KV	Kilovolt
L	Liter
m	Meter
M	Molarity
mA	Milliamps
mL	Mililiter
mol	Mole
mol%	Mole Percent
nm	Nanometer

%	Percent
PEO	Polyethylene Oxide
ppm	Part per Million
SDS	Sodium Dodecyl Sulphate
TBT	Tetrabutyl Titanate
TIPO	Titanium Iso-propoxide
TTIP	Titanium Tetraisopropoxide
US EPA	United State Environmental Protection Agency
UV	Ultraviolet
V	Volt
λ	Wavelength
W	Watt
wt%	Weight Percent
XRD	X-ray Diffraction

CHAPTER 1

INTRODUCTION

1.1 Background

Phenol is an organic pollutant which is widely found in many industries wastewater including resins, paint, oil refineries, herbicides, textile, food, flavoring agent, petrochemical, antioxidants and photographic chemicals [1]. The presence of phenol in wastewater cause several environmental problems and harmful to human being. Phenolic compounds are the major component of water pollutant. These compounds react with chlorine to form toxic polychlorinated phenolic compounds [2]. Therefore, a huge conventional biological system is always needed to treat the phenolic wastewater [3]. Traditional or conventional wastewater treatment usually involves usage of activated carbon, specific chemical or solvent to remove the phenolic compounds. However, these methods have resulted higher cost for further treatment of byproducts [4].

Phenol is categorized as refractory organic compound which consists of toxicity of carcinogenesis, mutagenicity and teratogenesis [5]. The water treatment of phenol-containing wastewater has drawn attention of many researchers. Since the traditional phenolic wastewater treatment methods are not able to function effectively, an alternative way with a low cost and high efficient wastewater treatment method is highly desired to solve the problem.

Several new technologies in photocatalytic degradation of organic pollutant, called Advanced Oxidation Processes (AOP), have been developed. AOP provide a route to degrade organic pollutant into carbon dioxide, water and inorganic ions which are environmentally friendly [6-8]. Among AOP, titania-based photocatalytic oxidation has been recognized as an effective method especially in mineralization of many toxic and non-degradable organic pollutants in wastewater treatment [9,10]. TiO_2 is a good heterogeneous photocatalyst because it has high chemical stability, and low cost. Moreover, sunlight can be used as a light source for TiO_2 photocatalyst activity [11].

When the electron in the valance band of TiO_2 absorbs enough light energy, it can be excited to conduction band. This phenomenon will cause a positive vacancy or hole in the valance band. On the surface of catalyst, there are photo-generated electrons and holes which function to convert the water molecule to hydroxide radical. The radicals will then react with organic pollutants. However, the electron and hole pair may also recombine. Thus, the recombination of electrons and holes should be reduced in order to enhance the photoactivity of TiO_2 photocatalysts.

TiO_2 is still not a perfect photocatalyst. The anatase phase of TiO_2 possess 3.2 eV band gap which is too large and causes titania unable to use visible light as irradiation source. Moreover, the fast electron and hole recombinationhas limited the photodegradation activity of TiO_2. Many modifications have been done on TiO_2 such as metal oxides doping [12], dye sensitizer [13] and metal coupling [14] in order to improve the photoactivity of TiO_2. Among the modification methods, metal oxide doping has achieved the best result. Doping of vanadium oxide into TiO_2 is able to delay the recombination of hole and electron pairs [15,16] and boost the adsorption activity [17]. Besides, non-porous TiO_2 also related with the issue of low mass transport rates between the organic pollutant and the active centres of TiO_2 [18]. In order to further enhance the photocatalytic activity of TiO_2, porous TiO_2 was

synthesized. Increasing the porosity of TiO_2 could provide a larger surface area which increased the accessibility of organic pollutant to the active sites on the TiO_2. Thus, photodegradation of organic pollutant would be enhanced.

1.2 Statement of Problem

Phenolic compounds are one of the common organic pollutants found in the industrial wastewater. It pollutes our environmental and it is harmful to human. Compare to the traditional method, AOP have been studied intensively as particularly efficient method to degrade phenolic compounds in the wastewater [19]. Although TiO_2 offers high chemical stability and good particle size distribution properties, it is not yet an effective photocatalyst. There are many reports on the effect of transition metals doping into TiO_2 using sol-gel method. However, there are contradict statements for photocatalytic performance of metal oxide doped TiO_2. Some researchers commented that presence of metal oxide could boost the photoactivity of TiO_2 photocatalyst, but some other researchers denied it. Besides, the problem of low mass transport rate of organic pollutants to the active centres of TiO_2 photocatalyst also always being discussed and related with the porosity of TiO_2. Effect of Ti precursors on the properties and photocatalytic performance of transition metal oxide doped TiO_2 is yet to be explored.

1.3 Research Objectives

The objectives of this research were:

a) To synthesize vanadium oxide doped porous TiO_2 photocatalysts using two different precursors of tetrabutyl titanate and titanium tetraisopropoxide.
b) To characterize the TiO_2 and vanadium oxide doped porous TiO_2 photocatalysts
c) To investigate the effect of Ti precursors and vanadium oxides in TiO_2 and vanadium oxide doped porous TiO_2 for phenol photodegradation.

1.4 Scope of Study

Porous TiO_2 and vanadium oxide doped porous TiO_2 were synthesized via sol-gel method. Titanium tetraisopropoxide and tetrabutyl titanate were utilized as Ti precursors. The synthesized materials were characterized using X-ray diffraction (XRD), diffused reflectance ultraviolet-visible (DRUV-VIS) spectroscopy, nitrogen adsorption-desorption analysis, fourier transform infrared spectroscopy (FTIR), field emission scanning electron microscope (FESEM) and energy dispersive X-ray (EDX) analysis. The photocatalytic activity of vanadium oxide doped porous TiO_2 in photodegradation of phenol was evaluated. The effects of weight percentage of transition metal oxide doped (1 – 5 wt%) and precursor type on the properties and photodegradation of phenol were explored.

1.5 Significance of study

The resulted materials of vanadium oxides doped porous TiO_2 could be potential catalysts to photodegrade the phenol and other organic pollutants. The research findings could contribute to the development of excellent catalyst which is applicable in various fields of water treatment including the petrochemical, textile, dyes, agricultural, plastic, production process of pesticides and paint. Moreover, the resulted photocatalysts could function to protect water resources such as surface and ground water. Besides, they could help to maintain the balance of ecosystem as it help to remove the phenolic pollutant which is toxic to aquatic organisms. In addition, the synthesized photocatalysts help to save cost for water treatment as they utilize sunlight radiation to remove organic pollutants.

REFERENCES

1 Ayodele, O. B., Lim, J. K. and Hameed, B. H. (2012). Degradation of Phenol in Photo-Fenton Process by Phosphoric Acid Modified Kaolin Supported Ferric-Oxalate Catalyst: Optimization and Kinetic Modeling. *Chemical Engineering Journal*. **197**, 181–192.

2 Brown, V. M., Jordan, D. H. M. and Tiller, B.A. (1967). The Effect of Temperature on the Acute Toxicity of Phenol To Rainbow Trout in Hard Water. *Water Research*. **1**, 587–597.

3 Autenrieth, R. L., Bonner, J. S., Akgerman, A. and McCreary, E. M. (1991). Biodegradation of Phenolic Wastes. *Journal of Hazardous Materials*. **28**, 29–53.

4 Hu, C., Wang, Y. Z. and Tang, H. X. (2000). Destruction of Phenol Aqueous Solution by Photocatalysis or Direct Photolysis. *Chemosphere*. **41**, 1205–1209.

5 Matos, J., Laine, J. and Herrmann, J. (1998). Synergy Effect in the Photocatayltic Degradation of Phenol on the Suspended Mixture of Titania and Activated Carbon. *Applied Catalysis B: Environmental*. **18**, 281-291.

6 Ziegmann, M. and Frimmel, F. H. (2010). Photocatalytic Degradation of Clofibric Acid, Carbamazepine and Iomeprol Using Conglomerated TiO_2 and Activated Carbon in Aqueous Suspension. *Water Science & Technology*. **61**, 273–281.

7 Barka, N., Qourzal, S., Assabbane, A., Nounah, A. and Ait-Ichou, Y. (2011). Degradation of Phenol in Water by Titanium Dioxide Photocatalysis. *Oriental Journal of Chemistry*. **29**(3), 1055-1060.

8 Çatalkaya, E. Ç., Bali, U. and Sengül, F. (2003). Photochemical

Degradation and Mineralization of 4-Chlorophenol. *Environmental Science and Pollution Research*. **10**, 113–120.

9 Barka, N., Qourzal, S., Assabbane, A., Nounah, A. and Ait-Ichou, Y. (2010). Photocatalytic Degradation of an Azo Reactive Dye, Reactive Yellow 84, in Water using an Industrial Titanium Dioxide Coated Media. *Arabian Journal of Chemistry*. **3**, 279-283.

10 Abaamrane, A., Qourzal, S., Barka, N, Mançour Billah, S., Assabbane, A. and Ait-Ichou, Y. (2012). Optimal Decolorization Efficiency of Indigo Carmine by TiO_2 /UV Photocatalytic Process Coupled with Response Surface Methodology. *Oriental Journal of Chemistry*, **28**(3), 1091–1098.

11 Phanikrishna Sharma, M. V., Durga Kumari, V. and Subrahmanyam, M. (2008). TiO_2 Supported over SBA-15: An Efficient Photocatalyst for the Pesticide Degradation Using Solar Light. *Chemosphere*. **73**, 1562–1569.

12 Choi, J., Park, H. and Hoffmann, M. R. (2010). Effects of Single Metal-Ion Doping on the Visible-Light Photoreactivity of TiO_2. *Journal of Physical Chemistry C*. **114**, 783-792.

13 Chowdhury, P., Moreira, J., Gomaa, H. and Ray, A. K. (2012). Visible-solar-light-driven Photocatalytic Degradation of Phenol with Dye-Sensitized TiO_2: Parametric and Kinetic Study. *Industrial & Engineering Chemistry Research*. **51**, 4523–4532.

14 Zyoud, A. H., Zaatar, N., Saadeddin, I., Ali, C., Park, D., Campet, G. and Hilal, H. S. (2010). CdS-sensitized TiO_2 in Phenazopyridine Photo-degradation: Catalyst Efficiency, Stability and Feasibility Assessment. *Journal of Hazardous Materials*. **173**, 318–325.

15 Zhang, S., Chen, Y., Yu, Y., Wu, H., Wang, S. Zhu, B., Huang, W. and Wu. S. (2008). Synthesis, Characterization of Cr-doped TiO_2 Nanotubes with High Photocatalytic Activity. *Journal of Nanoparticle Research*. **10**, 871-875.

16 Hamdan, H., Muhid, M. N. M., Lee, S. L. and Tan, Y. Y. (2009). Visible

Light Enabled V and Cr Doped Titania-Silica Aerogel Photocatalyst. *International Journal of Chemical Reactor Engineering*. **7**, Article 54.

17 Liang, X. L., Zhu, S. Y., Zhong, Y. H., Zhu, J. X., Yuan, P., He, H. P. and Zhang. J. (2010). The Remarkable Effect of Vanadium Doping on the Adsorption and Catalytic Activity of Magnetite in the Decolorization of Methylene Blue. *Applied Catalysis B: Environmental*. **97**, 151-159.

18 Wang, X. D. and Caruso, R. A. (2011). Enhancing Photocatalytic Activity of Titania Materials by Using Porous Structures and the Addition of Gold Nanoparticles. *Journal of Material Chemistry*. **21**, 20-28.

19 Bach, A., Shemer, H. and Semiat, R. (2010). Kinetics of Phenol Mineralization by Fenton-Like Oxidation. *Desalination*. **264**, 188–192.

20 Fujishima, A. and Honda, K. (1972). Electrochemical Photolysis of Water at a Semiconductor Electrode. *Nature*. **238**, 37-38.

21 Ye, F., and Ohmori, A. (2002). The Photocatalytic Activity and Photo-absorption of Plasma Sprayed TiO_2-Fe_3O_4 Binary Oxide Coatings. *Surface and Coatings Technology.***160**, 62-67.

22 Saravanan, P., Pakshirajan, K. and Saha, P. (2009). Degradation of Phenol by Tio_2-Based Heterogeneous Photocatalysts in Presence of Sunlight. *Journal of Hydro-environment Research*. **3**, 45-50.

23 Fox, M. and Dulay, M. (1993). Heterogeneous Photocatalysis. *Chemical Reviews*. **93**, 341-357.

24 Herrmann, J., Duchamp, C., Karkmaz, M., Hoai, B., Lachheb, H. and Puzenat, E. G. (2007). Environmental Green Chemistry as Defined by Photocatalysis. *Journal of Hazardous Materials*. **146**, 624-629.

25 Oller, I., Gernjak, W., Maldonado, M. I., Perez-Estrada, L. A., Sanchez-Perez, J. A. and Malato, S. (2006). Solar Photocatalytic Degradation of Some Hazardous Water-Soluble Pesticides at Pilot-Plant Scale. *Journal of Hazardous Materials*. **138** (Part B), 507–517.

26 Garcýa, A., Amat, A. M., Arques, A., Vicente, R., Lopez, M. F., Oller, I.,

Maldonado, M. I. and Gernjak, W. (2007). Increased Biodegradability of Ultracide in Aqueous Solutions with Solar Tio2photocatalysis. *Chemosphere*. **68**, 293–300.

27 Nolan, N. T., Seery, M. K. and Pillai, S. C. (2009). Spectroscopic Investigation of the Anatase-to-Rutile Transformation of Sol-Gel-Synthesisized TiO_2 Photocatalysts. *The Journal of Physical Chemistry C*. **113**, 16151-16157.

28 Hu, Y., Tsai, H. L. and Huang, C. L. (2003). Effect of Brookite Phase on the Anatase-Rutile Transition in Titania Nanoparticles. *Journal of the European Ceramic Society*. **23**(5), 691–696.

29 D. Nicholls, Complexes and First-Row Transition Elements, MacMillan Education, Hong Kong, 1974.

30 Shao, Y. Q., Tang, D. and Ding, Y. D. (2000). Thermal Stability of Nano-Scale Rutile TiO_2 Prepared Under Low Temperatures. *Chinese Journal of Chemistry, Transactions of Nonferrous Metals Society of China*. **10** (Suppl.1), 227-229.

31 Carp, O., Huisman, C. L. and Reller, A. (2004). Photoinduced Reactivity of Titanium Dioxide. Progress in Solid State Chemistry. 32(1–2), 33-177.

32 Chen, X. and Mao, S. S. (2007). Titanium Dioxide Nanomaterials: Synthesis, Properties, Modifications, and Applications. *Chemical Reviews*. **107**, 2891-2959.

33 Gong, X. Q. and Selloni, A. (2007). First-Principles Study of the Structures and Energetics of Stoichiometric Brookite TiO_2 Surfaces. *Physical Review B*. **76**, 2891-2959.

34 Wisitsoraat, A., Tuantranont, A., Comini, E., Sberveglieri, G. and Wlodarski, W. (2009). Characterization of N-type and P-type Semiconductor Gas Sensors Based on NiO_x Doped TiO_2 Thin Films. *Thin Solid Films*. **517**, 2775-2780.

35 Asahi, R., Taga, Y., Mannstadt, W. and Freeman, A. J. (2000). Electronic

and Optical Properties of Anatase TiO_2. *Physical Review B*. **61**, 7459-7465.

36 Amtout, A. and Leonelli, R. (1995). Optical Properties of Rutile Near Its Fundamental Band Gap. *Physical Review B*. **51**, 6842–6851.

37 Koelsch, M., Cassaignon, S., Thanh Minh, C. T., Guillemoles, J. F., and Jolivet, J. P. (2004). Electrochemical Comparative Study of Titania (Anatase, Brookite and Rutile) Nanoparticles Synthesized in Aqueous Medium. *Thin Solid Films*. **451**, 86–92.

38 Hoffmann, M. R., Martin, S. T., Choi W. Y., and Bahnemann, D. W. (1995). Environmental Applications of Semiconductor Photocatalysis. *Chemical Reviews*. **95**, 69-96.

39 Wang, Y., Huang, Y., Ho, W., Zhang, L., Zou, Z. and Lee, S. (2009). Biomolecule-controlled Hydrothermal Synthesis of C-N-S-tridoped TiO_2 Nanocrystalline Photocatalysts for NO Removal under Simulated Solar Light Irradiation. *Journal of Hazardous Materials*.**169**, 77-87.

40 Su, C., Tseng, C. M., Chen, L. F., You, B. H., Hsu, B. C. and Chen, S. S. (2006). Sol-hydrothermal Preparation and Photocatalysis of Titanium Dioxide. *Thin Solid Films*. **498**, 259-265.

41 Fujishima, A. and Honda, K. (1972). Electrochemical Photolysis of Water at a Semiconductor Electrode. *Nature*. **238**, 37-38.

42 Frank, S. N. and Bard, A. J. (1977). Heterogeneous Photocatalytic Oxidation of Cyanide Ion in Aqueous Solution at TiO_2 Powder. *Journal of the American Chemical Society*. **99**, 303-304.

43 Frank, S. N. and Bard, A. J. (1977). Heterogeneous Photocatalytic Oxidation of Cyanide and Sulfite in Aqueous Solutions at Semiconductor Powders. *The Journal of Physical Chemistry*. **81**, 1484-1488.

44 Zhao, J., Wu, T., Wu, K., Oikawa, K., Hidaka, H. and Serpone, N. (1998). Photoassisted Degradation of Dye Pollutants. 3. Degradation of the Cationic Dye Rhodamine B in Aqueous Anionic Surfactant/TiO_2

Dispersions under Visible Light Irradiation: Evidence for the Need of Substrate Adsorption on TiO_2 Particles. *Environmental Science and Technology*. **32**, 2394-2400.

45 Boroski, M., Rodrigues, A. C., Garcia, J. C., Sampaio, L. S., Nozaki, J. and Hioka, N. (2009). Combined Electrocoagulation and TiO_2 Photoassisted Treatment Applied to Wastewater Effluents from Pharmaceutical and Cosmetic Industries. *Journal of Hazardous Materials*. **162**, 448–454.

46 Pirkanniemi, K. and Sillanpaa, M. (2000). Heterogeneous Water Phase Catalysis as an Environmental Application: A Review. *Chemosphere*. **48**, 1047–1060.

47 Chong, M. N., Jin, B., Chow, C. W. K. and Saint, C. (2010). Recent Developments in Photocatalytic Water Treatment Technology: A Review. *Water Resources*. **44**, 2997-3027.

48 Hoffmann, M. R., Martin, S. T., Choi, W. and Bahnemann, D. W. (1995). Environmental Applications of Semiconductor Photocatalysis. *Chemical Reviews*. **95**, 69-96.

49 Herrmann, J. M. (1999). Heterogeneous Photocatalysis: Fundamentals and Applications to the Removal of Various Types of Aqueous Pollutants. *Catalysis Today*. **53**, 115-129.

50 Su, C., Hong, B. Y. and Tseng, C. M. (2004). Sol–Gel Preparation and Photocatalysis of Titanium Dioxide. *Catalysis Today*. **96**, 119– 126.

51 Adel, A. I. and Detlef, W. B. (2011). Mesoporous Titania Photocatalysts: Preparation, Characterization and Reaction Mechanisms. *Journal of Materials Chemistry*. **21**, 11686-11707.

52 Huo, Q. S., Margolese, D. I., Ciesla, U., Feng, P. Y., Gier, T. E., Sieger, P., Leon, R., Petroff, P. M., Schüth, F. and Stucky, G. D. (1994). Generalized Synthesis of Periodic Surfactant/Inorganic Composite Materials. *Nature*. **368**, 317 – 321.

53 Faustinoa, C. M.C., Caladoa, A. R.T. and Garcia-Rio, L. (2011). Mixed Micelle Formation Between Amino Acid-Based Surfactants and Phospholipids. *Journal of Colloid and Interface Science*. **359(2)**, 493–498.

54 Mahoney, L. and Koodali, R. T. (2014). Versatility of Evaporation-Induced Self-Assembly (EISA) Method for Preparation of Mesoporous TiO_2 for Energy and Environmental Applications. *Materials*. **7**, 2697-2746.

55 Tseng, T. K., Lin, Y. S., Chen, Y. J. and Chu, H. (2010). A Review of Photocatalysts Prepared by Sol-Gel Method for VOCs Removal. *International Journal of Molecular Sciences*. **11**, 2336-2361.

56 Dulay, M. T., Quirino, J. P., Bennett, B. D., Zare, R. N. (2002). Bonded–phase Photopolymerized Sol-Gel Monoliths for Reversed Phase Capillary Electrochromatography. *Journal of Separation Science.***25**, 3–9.

57 Brinker, C. J. and Scherer, G. W. Sol–gel Science. Academic Press: Boston, MA, USA, 1990.

58 Brinker, C. J. and Scherer, G. W. (1990). *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing.* San Diego. Academic Press, Inc. 53.

59 Antonelli, D. M. and Ying, J. Y. (1995). Synthesis of Hexagonally-Packed Mesoporous TiO_2 by a Modified Sol-Gel Method. *Angewandte Chemie International Edition*. **34(18)**, 2014-2017.

60 Antonelli, D.M. (1999). Synthesis of Phosphorus-Free Mesoporous Titania via Templating with Amine Surfactants. *Microporous and Mesoporous Materials*. **30(2)**, 315.

61 Wang, Y. Q., Tang, X. H., Yin, L. X., Huang, W. P., Hacohen, Y. R. and Gedanken, A. (2000). Sonochemical Synthesis of Mesoporous Titanium Oxide with Wormhole-like Framework Structures. *Advanced Materials.* **12**, 1183-1186.

62 Beyers, E., Cool, P. and Vansant, E. F. (2007). Stabilisation of Mesoporous TiO_2 By Different Bases Influencing the Photocatalytic Activity. *Microporous and Mesoporous Materials*. **99**, 112–117.

63 Chen, D., Cao, L., Huang, F., Imperia, P., Cheng, Y. and Caruso, R. A. (2010). Synthesis of Monodisperse Mesoporous Titania Beads with Controllable Diameter, High Surface Areas, and Variable Pore Diameters (14-23 nm). *Journal of the American Chemical Society*. **132**, 4438.

64 Yang, P., Zhao, D., Margolese, D. I., Chmelka, B. F. and Stucky, G. D. (1998). Generalized Block Copolymer Syntheses of Large-Pore Mesoporous Metal Oxides with Semicrystalline Frameworks. *Nature*. **396**, 152-155.

65 Crepaldi, E. L., Soler-Illia, G., Grosso, D., Cagnol, F., Ribot, F. and Sanchez, C. (2003). Controlled Formation of Highly Organized Mesoporous Titania Thin Films: from Mesostructured Hybrids to Mesoporous Nanoanatase TiO_2. *Journal of the American Chemical Society*. **125(32)**, 9770–9786.

66 Fan, J., Boettcher, S. W. and Stucky, G. D. (2006). Nanoparticle Assembly of Ordered Multicomponent Mesostructured Metal Oxides via a Versatile Sol-gel Process. *Chemistry of Materials*. **18**, 6391–6396.

67 Zhang, J., Deng, Y., Gu, D., Wang, S., She, L., Che, R., Wang, Z. S., Tu, B., Xie, S. and Zhao, D. (2011). Ligand-assisted Assembly Approach to Synthesize Large-Pore Ordered Mesoporous Titania with Thermally Stable and Crystalline Framework. *Advanced Energy Materials*. **1**, 241–248.

68 Lee, A. C., Lin, R. H., Yang, C. Y., Lin, M. H. and Wang, W. Y. (2008). Preparations and Characterization of Novel Photocatalysts with Mesoporous Titanium Dioxide (TiO_2) via a Sol–Gel Method. *Materials Chemistry and Physics.* **109**, 275–280.

69 Tian, B., Yang, H., Liu, X., Xie, S., Yu, C., Fan, J., Tu, B. and Zhao, D.

(2002). Fast preparation of Highly Ordered Nonsiliceous Mesoporous Materials via Mixed Inorganic Precursors. *Chemical Communications*. **17**, 1824-1825.

70 Jiang, S. T., Zhao, Q., Li, M. and Yin, H. B. (2008). Preparation of Mesoporous Titania Solid Superacid and Its Catalytic Property. *Journal of Hazardous Materials*. **159**, 204–209.

71 Zhang, W. J., Pei X. B. and Chen, J. L. (2015). Sol-gel Preparation of Porous In-Tio$_2$ Photocatalyst using Cetyltrimethylammonium Bromide as Template. *Journal of Chemical and Pharmaceutical Research.* **7(4)**, 405-410.

72 Teoh, W. Y., Amal, R. and Scott, J. (2012). Progress in Heterogeneous Photocatalysis: from Classical Radical Chemistry to Engineering Nanomaterials and Solar Reactors. *The Journal of Physical Chemistry Letters*. **3**, 629–639.

73 Yamashita, H., Harada, M., Misaka, J., Takeuchi, M., Neppolian, B. and Anpo, M. (2003). Photocatalytic Degradation of Organic Compounds Diluted in Water using Visible Light-Responsive Metal Ion-Implanted TiO_2 Catalysts: Fe ion-implanted TiO_2. *Catalysis Today*. **84**, 191-196.

74 Wu, C. G., Chao, C. C. and Kuo, F. T. (2004). Enhancement of the Photo Catalytic Performance of TiO2 Catalysts Via Transition Metal Modification. *Catalysis Today*. **97**, 103-112.

75 Zhu, J., Chen, F., Zhang, J., Chen, H. and Anpo, M. (2006). Fe^{3+}-TiO_2 Photocatalysts Prepared by Combining Sol-Gel Method with Hydrothermal Treatment and Their Characterization. *Journal of Photochemistry and Photobiology A*. **180**, 196-204.

76 Shi, J., Zheng, J., Hu, Y. and Zhao, Y. (2008). Photocatalytic Degradation of Methyl Orange in Water by Samarium-Doped TiO_2. *Environmental Engineering Science.***25**, 489-496.

77 Surolia, P. K., Tayade, R. J. and Jasra, R. V. (2010). Photocatalytic

Degradation of Nitrobenzene in an Aqueous System by Transition-Metal-Exchanged ETS-10 Zeolites. *Industrial & Engineering Chemistry Research*. **49**, 3961-3966.

78 Kamat, P. V. (2007). Graphene-based Nanoarchitectures. Anchoring Semiconductor and Metal Nanoparticles on a Two-Dimensional Carbon Support. *The Journal of Physical Chemistry Letters*. **1**, 520–527.

79 Kato, S., Hirano, Y., Iwata, M., Sano, T., Takeuchi, K. and Matsuzawa, S. Photocatalytic Degradation of Gaseous Sulphur Compounds by Silver-Deposited Titanium Dioxide. *Applied Catalysis B: Environmental*. **57**, 109-115.

80 Klosek, S. and Raftery, D. (2001). Visible light driven V-doped TiO_2 Photocatalyst and Its Photooxidation of Ethanol. *The Journal of Physical Chemistry B*. **105**, 2815-2819.

81 Anpo, M., Dohshi, S., Kitano, M., Hu, Y., Takeuchi, M. and Matsuoke, M. (2005). The Preparation and Characterization of Highly Efficient Titanium Oxide-Based Photofunctional Material. *Annual Review of Materials Research*. **35**, 1.

82 Gu, D. E., Yang, B. C. and Hu, Y. D. (2008). V and N Co-doped Nanocrystalanatase TiO_2 Photocatalysts with Enhanced Photocatalytic Activity under Visible Light Irradiation. *Catalysis Communications*. **9**, 1472-1476.

83 Tian, B., Li, C., Gu, F., Jiang, H., Hu, Y. and Zhang, J. (2009). Flame Sprayed V-doped TiO_2 Nanoparticles with Enhanced Photocatalytic Activity under Visible Light Irradiation. *Chemical Engineering Journal*. **151**, 220–227

84 Zhou, W. F., Liu, Q. J., Zhu, Z. Q. and Zhang, J. (2010). Preparation and Properties of Vanadium-Doped TiO_2 Photocatalysts. *Journal of Physics D: Applied Physics*. **43**,1-6

85 Lin, W. C. and Lin, Y. J. (2012). Effect of Vanadium (IV)-Doping on the

Visible Light-Induced Catalytic Activity of Titanium Dioxide Catalysts for Methylene Blue Degradation. *Environmental Engineering Science*. **29** (6), 447-452.

86 Rodriguez, I., Llompart, M. P. and Cela, R. (2000). Solid Phase Extraction of Phenols. *Journal of Chromatography A*. **885**, 291-304.

87 Bruce, R., Santodonato, J. and NEAL, M. (1987). Summary Review of the Health Effects Associated with Phenol. T*oxicology and Industrial Health*. **3**, 535-568.

88 Guo, Z., Ma, R. and Li, G. (2006). Degradation of Phenol by Nanomaterial TiO_2 in Wastewater. *Chemical Engineering Journal.***119**, 55–59.

89 Yoshio, W., Eiichiro, M. and Kozo. (2011). *X-Ray Diffraction Crystallography: Introduction, Examples and Solved Problems.* New York. Springer-Verlag Berlin Heidelberg. 73.

90 Gómez, R. B., Morales, I. D. H. and Alonso, I. S. (2011). *Design and Applications of Novel Titanium and Copper Containing Mesoporous Organic-Inorganic Hybrid Materials*. Madrid. Los autores. 146.

91 Smith, B. C. (1996). *Fundamentals of Fourier Transform Infrared Spectroscopy*. New York. CRC Press LLC. 1 - 7.

92 Sakka, S. (2005). *Handbook of Sol-Gel Science and Technology: Processing, Characterization and Applications*. New York. Kluwer Academic Publishers. 131-135.

93 Mulder, M. (1991). *Basic Principles of Membrane Technology*. New York. Kluwer Academic Publishers. 123.

94 Amretashis Sengupta and Chandan Kumar (2015). *Introduction to Nano: Basics to Nanoscience and Nanotechnology. New York.* Springer-Verlag Berlin Heidelberg. 132-133.

95 Adel, A. I. and Detlef, W. B. (2011). Mesoporous Titania Photocatalysts: Preparation, Characterization and Reaction Mechanisms. *Journal of Materials Chemistry*. **21**, 11686-11707.

96 Astorino, E., Peri, J. B., Willey, R. J. and Busca, G. (1995). Spectroscopic Characterization of Silicalite-1 and Titanium Silicalite-1. J. Catal. 157: 482- 500.

97 Jeffrey Wu, C. S. and Chen, C. H. (2004). A Visible-Light Response Vanadium-Doped Titania Nanocatalyst By Sol–Gel Method. *Journal of Photochemistry and Photobiology A: Chemistry*. **163**, 509–515.

98 Asahi, R., Morikawa, T., Ohwaki, T., Aoki, K. and Taga. Y. (2001). Visible-Light Photocatalysis in Nitrogen Doped Titanium Oxides. *Science*. **293**, 269-271.

99 Bhattacharyya, K., Varma, S., Tripathi, A. K., Bharadwaj, S. R. and Tyagi, A. K. (2008). Effect of Vanadia Doping and Its Oxidation State on the Photocatalytic Activity of TiO_2 for Gas-Phase Oxidation of Ethane. *The Journal of Physical Chemistry*. **C112** (48), 19102-19112.

100 Nagaveni, K., Hegde, M. S. and Madras. G. (2004). Structure and Photocatalytic Activity of Ti1-xMxO2±ō (M = W, V, Ce, Zr, Fe, and Cu) Synthesized by Solution Combustion Method. *Journal of Physical Chemistry B*. **108** (52), 20204–20212.

101 Manoj, A. L., Shaji, V. and Santhosh, S. N. (2012). Photocatalytic Water Treatment by Titanium Dioxide: Recent Updates. *Catalysts.* **2**, 572-601.

102 Katalin, S. (2010). Influence of Chemical Conditions on the Nanoporous Structure of Silicate Aerogels. *Materials.* **3**, 704-740.

103 Hanaor, D. A. H., Assadi, M. H. N., Li, S., Yu, A. and Sorrell, C. C. (2012). Ab Initio Study of Phase Stability in Doped TiO_2. *Computational Mechanics.* **50**, 185-194.

104 Nguyen, T. B., Hwang, M. J. and Ryu, K. S. (2012).High Adsorption Capacity of V-doped TiO_2 for Decolorization of Methylene Blue. *Applied Surface Science*. **258**, 7299-7305.

105 Donohue, M. D. and Aranovich, G. L. (1999). A New Classification of Isotherms for Gibbs Adsorption of Gases on Solids. *Fluid Phase*

Equilibria. **158–160**, 557–563.

106 Sing, K. S. W., Everett, D. H., Haul, R. A. W., Moscou, L., Pierotti, R. A., Rouquerol, J. and Siemieniewska, T. (1985). Reporting Physisorption Data for Gas/Solid Systems with Special Reference to the Determination of Surface Area and Porosity. *Pure and Apply Chemistry*. **57**(4), 603-619.

107 Halimaton, H., Mohd Nazlan, M. M., Lee, S. L. and Tan, Y. Y. (2009). Visible Light Enable V and Cr Doped Titania-Silica Aerogel Photocatalyst. *International Journal of Chemical Reactor Enginnering*. **7** (A54). 1-22.

108 Lin, W. C. and Lin, Y. J. (2012). Effect of Vanadium (IV)-Doping on the Visible Light-Induced Catalytic Activity of Titanium Dioxide Catalysts for Methylene Blue Degradation. *Environmental Engineering Science.* **29**, 447-452.

109 Li, F. B. and Li, X. Z. (2002). The Enhancement of Photodegradation Efficiency Using Pt-TiO_2 Catalyst. *Chemosphere*. **48**, 1103.