

# 在可見光照射下以鐵、硫改質之二氧化鈦光觸媒進行亞甲基藍溶液的光催化降解研究

吳嘉峰、柯雅雯

E-mail: 9806244@mail.dyu.edu.tw

## 摘要

本研究以溶膠凝膠法(sol-gel)製備不同的二氧化鈦光觸媒，以鑲嵌Fe與S的方式進行改質二氧化鈦光觸媒，包括FeT-S、FeT-SL、ST-S，在可見光下進行MB染料的降解實驗；並探討其最佳的改質條件(鑲嵌量與鍛燒溫度)與最佳的操作條件(pH值與MB初始濃度)。

本實驗使用BET、SEM/EDX、XRD與UV-vis等儀器鑑定光觸媒之物化特性。實驗結果顯示，以本實驗的改質方法確實能成功將金屬Fe與非金屬S鑲嵌於TiO<sub>2</sub>上，比表面積大約為38.7~79.4 m<sup>2</sup>/g；XRD分析結果顯示其多為銳鈦礦晶相；UV-vis分析顯示改質過後的光觸媒其可見光吸收能力增強，並有明顯的紅位移現象。若觀察MB染料濃度的降解情形，與以擬一階反應速率方程式來描述實驗結果，可以發現改質過後的二氧化鈦光觸媒，在可見光下可具有較佳的光降解效果；最佳的改質觸媒為ST-S在鑲嵌劑量為硫0.15 mole和鍛燒溫度為500°C；最佳的操作條件為pH=11、初始濃度=10ppm。綜合實驗結果，本研究在反應60分鐘後MB的降解率最高可達88%。

關鍵詞：溶膠凝膠法、光觸媒、可見光、Fe、S、TiO<sub>2</sub>、MB染料

## 目錄

封面內頁

簽名頁

授權書 iii

中文摘要 iv

英文摘要 v

誌謝 vi

目錄 vii

圖目錄 x

表目錄 xiii

第一章 前言 01

1.1 研究緣起 01

1.2 研究目的 02

1.3 研究內容 02

第二章 文獻回顧 03

2.1 光催化反應的原理與應用 03

2.1.1 光催化反應原理 03

2.1.2 光觸媒的材料簡介 04

2.1.3 光催化反應的應用 05

2.2 二氧化鈦光觸媒降解有機污染物的機制 07

2.2.1 二氧化鈦的基本特性 07

2.2.2 有機污染物的光降解機制 07

2.2.3 光催化反應動?模式 09

2.3 二氧化鈦光觸媒的製備與改質 11

2.3.1 二氧化鈦製備方法 11

2.3.2 二氧化鈦光觸媒的改質 13

2.3.3 光觸媒鍛燒溫度 18

2.3.4 鑲嵌量 19

2.4 影響光催化反應效能之因子 21

2.4.1 光觸媒添加量 21

2.4.2 反應物初始濃度 22

2.4.3 pH值 23

### 第三章 實驗材料與研究方法 24

3.1 實驗設備與材料 24

3.1.1 實驗裝置與儀器 24

3.1.2 實驗藥品與耗材 26

3.2 研究流程 27

3.3 二氧化鈦光觸媒的製備 29

3.4 光觸媒的特性鑑定與分析 31

3.4.1 比表面積分析 - BET 31

3.4.2 表面形貌及表面元素分析 - SEM/EDX 31

3.4.3 晶相分析 - XRD 32

3.4.4 觸媒吸收光譜分析 - 紫外光-可見光光譜儀 32

3.5 實驗設計與步驟 33

3.6 實驗分析方法 34

3.6.1 光能強度測定分析 34

3.6.3 亞甲基藍濃度的分析 35

### 第四章 結果與討論 37

4.1 改質二氧化鈦光觸媒之特性分析 37

4.1.1 改質光觸媒比表面積分析-BET 37

4.1.2 改質光觸媒之表面形貌與元素鑑定-SEM/EDX 38

4.1.3 改質光觸媒晶相鑑定-XRD 46

4.1.4 改質光觸媒吸收光譜分析 49

4.2 二氧化鈦之改質條件對光催化效果的影響 51

4.2.1 觸媒之鑲嵌劑量對MB的光催化效果 51

4.2.2 觸媒之鍛燒溫度對MB的光催化效果 54

4.3 反應條件對改質光觸媒的MB之降解效果 59

4.3.1 背景實驗與改質光觸媒對MB溶液的降解效果比較 60

4.3.2 pH值對染料的去除效果影響 61

4.3.3 MB初始濃度對去除效果的影響 63

### 第五章 結論與建議 68

5.1 結論 68

5.2 建議 69

參考文獻 70

### 參考文獻

?王順輝，「濺鍍製備硼與碳鑲嵌二氧化鈦薄膜的可見光光觸媒之研究」，碩士論文，東華大學材料科學與工程學研究所，2005。?何淑珠，「以紫外光/二氧化鈦光還原程序回收二氣化碳反應行為之研究」，第二十二屆廢水處理技術研究研討會，2007。?吳怡真，「利用真空濺鍍法製備可見光奈米光觸媒進行丙酮分解之研究」，碩士論文，中山大學環境工程研究所，2007。?周佳樂，「在一氧化碳和氧氣的混合氣體下利用脈衝雷射沉積法製備二氧化鈦可見光光觸媒」，碩士論文，東華大學材料科學與工程研究所，2008。?林有銘，「奈米光觸媒」，科學發展，408期，2006。?林聖凱，「以微波電漿火炬製備可見光化光觸媒之研究」，碩士論文，中原大學化學工程學系，2005。?李彥志、徐寶崇、陳孝行，「奈米級含氮、鐵二氧化鈦之可見光光催化活性機制探討」，廢水處理技術研討會論文集，高雄大學，2007。?范國瑄，「在可見光照射下利用含鐵酸鋅/二氧化鈦光觸媒之粒狀活性碳在液-固流體化床內去除酸性染料之研究」，碩士論文，大同大學化學工程學所，2005。?洪雨利，「溶膠凝膠法製備奈米二氧化鈦觸媒進行光催化還原二氣化碳之批次反應研究」，碩士論文，中山大學環境工程研究所，2003。?陳信宏，「改良型二氧化鈦光觸媒複合材料去除水溶液之染料之研究」，碩士論文，大葉大學環境工程學系，2007。?陳重男、杜致芬、盧明俊，「安丹在二氧化鈦懸浮溶液中之催化光分解反應」，第二十屆廢水處理技術研討會論文集，1995。?陳志賢，「奈米可見光V/TiO<sub>2</sub>觸媒之合成與物性分析」，碩士論文，臺灣大學化學工程學研究所，2003。?游智宏，「可?光二氧化鈦?米管製備、改質及光觸媒性質之研究」，碩士論文，中原大學化學工程學系，2005。?曾郁茗，「以含氮氣體於常溫常壓電漿輔助程序製造可見光及紫外光觸媒研究」，碩士論文，交通大學環境工程研究所，2005。?曾嘉賢，「可?光應答之含氮二氧化鈦光觸媒之合成及其結構鑑定」，碩士論文，彰化師範大學化學系，2007。?蔣庭耀，「WO<sub>x</sub>摻雜TiO<sub>2-x</sub>N<sub>x</sub>光觸媒之結構分析與性質」，碩士論文，東華大學材料科學與工程研究所，2005。?謝欣媛，「溶液燃燒合成法制備可見光光觸媒TiO<sub>2</sub>之製程開發」，碩士論文，成功大學化學工程研究所，2005。?簡宗興，「改良型二氧化鈦光觸媒還原水中硝酸鹽之研究」，碩士論文，大葉大學環境工程學系，2008。?顧洋、馬志明，「以紫外線/二氧化鈦程序處理氣相三氯乙烯污染物反應行為」，第十五屆空氣污染技術研討會論文集

, 1998。?Akbal, A. F., Onar, A. N., “ Photocatalytic degradation of phenol ” , Environ Monit Assess, Vol.83, pp.295-302, 2003。?Asahi, R., Morikawa, T., Ohwaki, T., Aoki, K., and Taga, Y., “ Visible-light photocatalysis in nitrogen-doped titanium oxides ” , Science, Vol.293, pp.269-271, 2001。?Asilt?rk, M., Say?lkan, F., Arpac, E., “ Effect of Fe<sup>3+</sup> ion doping to TiO<sub>2</sub> on the photocatalytic degradation of Malachite ” , Journal of Photochemistry and Photobiology A: Chemistry, Vol.203, pp.64-71, 2009。?Bhatkhande, D. S., Kamble, S. P., Sawant, S. B., Pangarkar, V. G., “ Photocatalytic and photochemical degradation of nitrobenzene using artificial ultraviolet light ” , Vol.102, pp.283-290, 2004 。?Carp, O., Huisman, C. L., Reller, A., “ Photoinduced reactivity of titanium dioxide ” , Progress in Solid State Chemistry, Vol.32, pp.33-177, 2004。?Ching, W. H., Leung, M., Leung, Y. C., “ Solar photocatalytic degradation of gaseous formaldehyde by sol-gel TiO<sub>2</sub> thin film for enhancement of indoor air quality ” , Energy, Vol.77, pp.129-135, 2004。?Diamandescu, L., Vasiliu, F., Mihaila, D. T., Feder, M., Vlaicu, A. M., Teodorescu, C. M., Macovei, D., Enculescu, I., Parvulescu, V., Vasile, E., “ Structural and photocatalytic properties of iron- and europium-doped TiO<sub>2</sub> nanoparticles obtained under hydrothermal conditions ” , Materials Chemistry and Physics, Vol.112, pp.146-153., 2008。?Fan, X., Chen, X., Zhu, S., Li, Z., Yu, T., Ye, J., Zou, Z., “ The structural, physical and photocatalytic properties of the mesoporous Cr-doped TiO<sub>2</sub> ” , Journal of Molecular Catalysis A: Chemical, Vol.284, pp.155-160, 2008。?Gao, B., Kim, Y. J., Chakraborty, A. K., Lee, W. I., “ Efficient decomposition of organic compounds with FeTiO<sub>3</sub>/TiO<sub>2</sub> heterojunction under visible light irradiation ” , Applied Catalysis B: Environmental, Vol.83, pp.202-207, 2008。?Gaya, U. I., Abdullah, A. H., “ Heterogeneous photocatalytic degradation of organic contaminants over titanium dioxide: A review of fundamentals, progress and problems ” , Journal of Photochemistry and Photobiology C: Photochemistry Reviews, Vol.54, pp.1-12, 2008 。?Li, D., Haneda, H., “ Enhancement of photocatalytic activity of sprayed nitrogen-containing ZnO powders by coupling with metal oxides during the acetaldehyde decomposition ” , Chemosphere, Vol.54, pp.1099-1110, 2004。?Li, D., Huang, H., Chen, X., Chen, Z., Li, W., Ye, D., Fu, X., “ New synthesis of excellent visible-light TiO<sub>2</sub>-xNx photocatalyst using a very simple method ” , Journal of Solid State Chemistry, Vol.180, pp.2630-2634, 2007。?Ling, Q., Sun, J., Zhou, Q., “ Preparation and characterization of visible-light-driven titania photocatalyst co-doped with boron and nitrogen ” , Applied Surface Science, Vol.254, pp.3236-3241, 2008。?Liu, S. and Chen, X., “ A visible light response TiO<sub>2</sub> photocatalyst realized by cationic S-doping and its application for phenol degradation ” , Journal of Hazardous Materials, Vol.152, pp.48-55, 2008 。?Houas, A., Lachheb, H., Ksibi, M., Elaloui, E., Guillard, C., Herrmann, J. M., “ Photocatalytic degradation pathway of methylene blue in water ” , Applied Catalysis B: Environmental, Vol.31, pp.145-157, 2001。?Hsu, B.C., Chen, S. S., Su, C., Liu, Y. T., “ Preparation and Characterization of Nitrogen-Doped Titanium Dioxide, ” Journal of Nanoscience and Nanotechnology, Vol.7, pp.1-7, 2007。?Ihara, T., Miyoshi, M., Iriyama, Y., Matsumoto, O., Sugihara, S., “ Visible-light-active titanium oxide photocatalyst realized by an oxygen-deficient structure and nitrogen doping ” , Appl. Catal. B: Environ. Vol.42, pp.403-409, 2003。?Irie, H., Watanabe, Y., Hashimoto, K., “ Nitrogen-concentration dependence on photocatalytic activity of TiO<sub>2</sub>-xNx powders ” , J. Phys. Chem. B, Vol.107, pp.5483-5486, 2003。?Ishibai, Y., Sato, J., Nishikawa, T., Miyagishi, S., “ Synthesis of visible-light active TiO<sub>2</sub> photocatalyst with Pt-modification:Role of TiO<sub>2</sub> substrate for high photocatalytic activity ” , Applied Catalysis B: Environmental, Vol.79, pp.117-121, 2008。?Jang, J. S., Kim, H. G., Joshi, U. A., Jang, J. W., Lee, J. S., “ Fabrication of CdS nanowires decorated with TiO<sub>2</sub> nanoparticles for photocatalytic hydrogen production under visible light irradiation ” , International journal of hydrogen energy, pp.1-6, 2008。?Khana, M. A., Woob, S. I., Yanga, O., “ Hydrothermally stabilized Fe(III) doped titania active under visible light for water splitting reaction ” , international journal of hydrogen energy, pp.1-7, 2008。?Kim, H. R., Eom, Y., Lee, T. G., Shul, Y. G., “ Preparation and photocatalytic properties of Cr/Ti hollow spheres ” , Materials Chemistry and Physics, Vol.108, pp.154-159, 2008 。?Konstantinou, I. K., Albanis, T. A., “ TiO<sub>2</sub>-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations ” , Applied Catalysis B: Environmental, Vol.49, pp.1-14, 2004。?Miao, L., Tanemura, S., Watanabe, H., Mori, Y., Kaneko, K., Toh, S., “ The improvement of optical reactivity for TiO<sub>2</sub> thin films by N<sub>2</sub> – H<sub>2</sub> plasma surface-treatment ” , Journal of Crystal Growth, Vol.260, pp.118-124, 2004。?Mohamed, S.H., Kappertz, O., Niemeier, T., Drese, R., Wakkad, M.M., Wutting, M., “ Effect of heat treatment on structural, optical and mechanical properties of sputtered TiO<sub>x</sub>Ny films ” , Thin Solid Films , Vol.468, pp.48-56, 2004。?Mozia, S., Tomaszevska, M., Kosowska, B., Grzmil, B., Morawski, A. W., Kalucki, K., “ Decomposition of nonionic surfactant on a nitrogen-doped photocatalyst under visible-light irradiation ” , Applied Catalysis B: Environmental, Vol.55, pp.195-200, 2005。?Ohno, T., Akiyoshi, M., Umebayashi, T., Asai, K., Mitsui, T., Matsumura, M., “ Preparation of S-doped TiO<sub>2</sub> photocatalysts and their photocatalytic activities under visible light ” , Applied Catalysis A: General, Vol.265, pp.115 – 121, 2004。?Poulios, I., Tsachpinis, I., “ Photodegradation of the textile dye Reactive Black 5 in the presence of semiconducting oxides ” , J Chem Technol Biotechnol, Vol.74, pp.349-357, 1999。?Rane, K.S., Mhalsiker, R., Yin, S., Sato, T., Cho, K., Dunbar, E., Biswas, P., “ Visible light-sensitive yellow TiO<sub>2</sub>-xNx and Fe-N co-doped Ti<sub>1-y</sub>FeyO<sub>2</sub>-xNx anatase photocatalysts, ” Journal of Solid State Chemistry, Vol.179, pp.3033-3044, 2006。?Ranjit, K. T., Varadarajan, T. K., Viswanathan, B., “ Photocatalytic reduction of nitrite and nitrate ions on Ru/TiO<sub>2</sub> catalysts ” , Journal of Photochemistry and Photobiology A: Chemistry, Vol.89, pp.67-68, 1995a。?Ranjit, K. T., Krishnamoorthy, R., Varadarajan, T. K., Viswanathan, B., “ Photocatalytic reduction of nitrite on CdS ” , Journal of Photochemistry and PhotobiologyA: Chemistry, Vol.86, pp.185-189, 1995b。?Ranjit, K. T. and Viswanathan, B., “ Photocatalytic reduction of nitrite and nitrate ions to ammonia on M/TiO<sub>2</sub> catalysts ” , Journal of Photochemistry and Photobiology A:Chemistry, Vol.108, pp.73-78, 1997a。?Ren, W., Ai, Z., Jia, F., Zhang, L., Fan, X., Zou, Z., “ Low temperature preparation and visible light photocatalytic activity of mesoporous carbon-doped crystalline TiO<sub>2</sub> ” , Applied Catalysis B: Environmental, Vol.69, pp.138-144, 2007。?Sano, T., Puzenat, E., Guillard, C., Geantet, C., Matsuzawa, S., “ Degradation of C<sub>2</sub>H<sub>2</sub> with modified-TiO<sub>2</sub> photocatalysts under visible light irradiation ” Journal of Molecular Catalysis A: Chemical, Vol.284, pp.127-133, 2008。?Sato, S., “ Photocatalytic activity of NO<sub>x</sub>-doped TiO<sub>2</sub> in the visible light region ” , Chemical Physics Letters, Vol.123,

pp.126-128, 1986. ?Sclafani, A., Herrmann, J. H., " Comparison of the Photoelectronic and Photo-catalytic Activities of Various Anatase and Rutile Forms of Titania in Pure Liquid Organic Phases and in Aqueous Solutions ", J. Phys. Chem, Vol.100, pp.13655, 1996. ?Shon, H., Phuntsho, S., Okour, Y., Cho, D. L., Kim, K. S., Li, H. J., Na, S., Kim, J. B., Kim, J. H., " Visible Light Responsive Titanium Dioxide (TiO<sub>2</sub>) ", J. Korean Ind. Eng. Chem, Vol.19, pp.1-16, 2008. ?Sreethawong, T., Laehsalee, S., Chavadej, S., " Comparative investigation of mesoporous- and non-mesoporous- assembled TiO<sub>2</sub> nanocrystals for photocatalytic H<sub>2</sub> production over N-doped TiO<sub>2</sub> under visible light irradiation ", Journal of hydrogen energy, pp.1-11, 2008. ?Sun, H., Bai, Y., Jin, W., Xu, N., " Visible-light-driven TiO<sub>2</sub> catalysts doped with low-concentration nitrogen species ", Solar Energy Materials & Solar Cells, Vol.92, pp.76-83, 2008. ?Teoh, W. Y., Amal, R., Madler, L., Pratsinis, S. E., " Flame sprayed visible light-active Fe-TiO<sub>2</sub> for photomineralisation of oxalic acid ", Catalysis Today, Vol.120, pp.203-213, 2007. ?Tong, T., Zhang, J., Tian, B., Chen, F., He, D., " Preparation of Fe<sup>3+</sup>-doped TiO<sub>2</sub> catalysts by controlled hydrolysis of titanium alkoxide and study on their photocatalytic activity for methyl orange degradation ", Journal of Hazardous Materials, Vol.155, pp.572-579, 2008. ?Uddin, M. M., Hasnat, M. A., Samed, A. J. F., Majumdar, R. K., " Influence of TiO<sub>2</sub> and ZnO photocatalysts on adsorption and degradation behaviour of Erythrosine Dyes and Pigments ", Dyes and Pigments, Vol.75, pp.207-212, 2007. ?Wang, K. H., Hsieh, Y. H., Chen, L. J., " The heterogeneous photocatalytic degradation, intermediates and mineralization for the aqueous solution of cresols and nitrophenols ", Journal of Hazardous Materials, Vol.59, pp.251-260, 1998. ?Wang, Z. P., Cai, W. M., Hong, X. T., Zhao, X. L., Xu, F., Cai, C. G., " Photocatalytic degradation of phenol in aqueous nitrogen-doped TiO<sub>2</sub> suspensions with various light sources ", Appl. Catal. B: Environ, Vol.57, pp.223-231, 2005. ?Wang, Y.Q., Yu, X. J., Sun, D. Z., " Synthesis, characterization, and photocatalytic activity of TiO<sub>2</sub>-xNx nanocatalyst ", Journal of Hazardous Materials, Vol.144, pp.328-333, 2007. ?Xie, Y. and Zhao, X., " The effects of synthesis temperature on the structure and visible-light-induced catalytic activity of F-N-codoped and S-N-codoped titania ", Journal of Molecular Catalysis A: Chemical, Vol.285, pp.142-149, 2008. ?Xu, J. H., Li, J., Dai, W. L., Cao, Y., Li, H., Fan, K., " Simple fabrication of twist-like helix N,S-codoped titania photocatalyst with visible-light response ", Applied Catalysis B: Environmental, Vol.79, pp.72-80, 2008. ?Xu, J. H., Dai, W. L., Li, J., Cao, Y., Li, H., He, H., Fan, K., " Simple fabrication of thermally stable apertured N-doped TiO<sub>2</sub> microtubes as a highly efficient photocatalyst under visible light irradiation ", Catalysis Communications, Vol.9, pp. 146-152, 2008. ?Yu, J., Xiang, Q., Zhou, M., " Preparation, characterization and visible-light-driven photocatalytic activity of Fe-doped titania nanorods and first-principles study for electronic structures ", Applied Catalysis B: Environmental, 2009. ?Zhang, F., Zhang, Jin, R., Chen, J., Shao, C., Gao, W., Li, L., Guan, N., " High photocatalytic activity and selectivity for nitrogen in nitrate reduction on Ag/TiO<sub>2</sub> catalyst with fine silver clusters ", Journal of Catalysis, Vol.232, pp.424 – 431, 2005.