

# 改質二氧化鈦光觸媒在可見光下對染料溶質反應之研究

張孟儒、柯雅雯

E-mail: 343877@mail.dyu.edu.tw

## 摘要

本研究以溶膠凝膠法 (sol-gel method) 製備不同的二氧化鈦光觸媒, 以不同鐵、氮、硫摻雜物的方式進行改質二氧化鈦光觸媒, 並摻雜於基材 $\text{Al}_2\text{O}_3$ 上, 包括 $\text{Fe}/\text{TiO}_2/\text{Al}_2\text{O}_3$  (硝酸鐵、硫酸亞鐵)、 $\text{N}/\text{TiO}_2/\text{Al}_2\text{O}_3$  (尿素、硝酸銨)、 $\text{S}/\text{TiO}_2/\text{Al}_2\text{O}_3$  (硫?、硫酸), 在可見光下進行MG、AR13、AR27染料的降解實驗; 並探討最佳的操作條件。本實驗先利用ICP-AES、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鐵與非金屬氮、硫摻雜於 $\text{TiO}_2/\text{Al}_2\text{O}_3$ 上, XRD結果顯示晶型以銳鈦礦為主, 在UV-vis結果顯示整體上各種改質光觸媒吸收可見光能力皆往可見光區增加。若觀察MG、AR13、AR27染料降解情形, 並以擬一階反應速率方程式來描述實驗結果, 可發現改質後的二氧化鈦光觸媒, 在可見光下具有較佳的光降解效果, 且各種元素最佳摻雜物為硝酸鐵、尿素、硫?, 其中尿素為最佳改質摻雜物。

關鍵詞: 二氧化鈦、可見光、氮、硫、鐵、染料

## 目錄

第一章 前言 1.1 研究緣起 1.2 研究目的 1.3 研究內容 第二章 文獻回顧 2.1 光觸媒的簡介 2.1.1 二氧化鈦基本特性 2.1.2 二氧化鈦光觸媒的應用 2.1.3 二氧化鈦光觸媒的製備 2.2 二氧化鈦光觸媒反應機制 2.2.1 光催化氧化機制 2.2.2 光敏化氧化機制 2.2.3 光催化反應動力模式 2.3 以不同元素與摻雜物改質的二氧化鈦光觸媒 2.3.1 以不同元素改質的二氧化鈦光觸媒 2.3.2 以不同摻雜物改質的二氧化鈦光觸媒 2.4 影響光催化反應的因素 2.4.1 摻雜劑量 2.4.2 觸媒添加量 2.4.3 其他影響反應因素 第三章 實驗材料與研究方法 3.1 研究流程 3.2 實驗設備與材料 3.2.1 實驗裝置與儀器 3.2.2 實驗藥品與耗材 3.3 二氧化鈦光觸媒的製備 3.4 光觸媒的特性鑑定與分析 3.4.1 成份分析 - ICP-AES 3.4.2 表面形貌及表面元素分析 - SEM/ED 3.4.3 晶相分析 - XRD 3.4.4 觸媒吸收光譜分析 - 紫外光-可見光光譜儀 UV-vis 3.4.5 觸媒紅外線光譜分析 - 傅氏轉換紅外線光譜儀FT-IR 3.5 實驗設計與步驟 3.6 分析方法 3.6.1 光能強度測定分析 3.6.2 染料濃度的分析 第四章 結果與討論 4.1 改質二氧化鈦光觸媒之特性分析 4.1.1 改質光觸媒之成分分析- ICP-AES 4.1.2 改質光觸媒之元素鑑定- SEM/EDX 4.1.3 改質光觸媒之晶相鑑定-XRD 4.1.4 改質光觸媒之吸收光譜分析-UV-vis 4.1.5 改質光觸媒之FT-IR 4.2 以改質光觸媒對染料進行光催化之反應 4.2.1 改質光觸媒在可見光下的反應結果 4.2.2 改質光觸媒對不同染料的光催化效果 4.3 以不同元素與摻雜物改質的光觸媒對染料光催化之影響 4.3.1 含Fe摻雜物的改質光觸媒 4.3.2 含N摻雜物的改質光觸媒 4.3.3 含S摻雜物的改質光觸媒 4.4 改質光觸媒的最佳反應條件 4.4.1 最佳摻雜劑量 4.4.2 最佳觸媒添加量 4.4.3 最佳染料初始濃度 第五章 結論與建議 5.1 結論 5.2 建議 參考文獻

## 參考文獻

中文摘要 1. 陳重男、杜玫芬、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。 2. 陳志賢, 「奈米可見光 $\text{V}/\text{TiO}_2$  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。 3. 游智宏, 「可見光二氧化鈦奈米管製備、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。 4. 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炭在液-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研究所, 2005。 5. 葉世壙, 「二氧化鈦的合成與光催化性質的研究」, 碩士論文, 中央大學化學工程與材料工程研究所, 2005。 6. 劉全得, 「偶氮染料之二氧化鈦光催化?色反應特性研究」, 碩士論文, 國立高雄第一科技大學環境與安全衛生工程學研究所, 2005。 7. 鄭千芳, 「以溶膠凝膠法製備複合奈米 $\text{Ag}/\text{TiO}_2$ 光觸媒之研究」, 碩士論文, 國立雲林科技大學化學工程學研究所, 2005。 8. 林有銘, 「奈米光觸媒」, 科學發展, 408 期, 2006。 9. 陳凱文, 「具可見光吸收之金屬改質型 $\text{TiO}_2$ 奈米光觸媒」, 碩士論文, 東海大學環境科學與工程系研究所, 2006。 10. 鄭森源, 「以高級氧化法處理水中染料之研究」, 碩士論文, 崑山科技大學環境工程學研究所, 2006。 11. 謝嘉鴻, 「新型光觸媒之製備及光催化染料廢水之研究」, 碩士論文, 國立雲林科技大學環境與安全衛生工程系, 2006。 12. 張碩修, 「具可見光吸收之銅、銻、鐵改質型 $\text{TiO}_2$  奈米光觸媒」, 碩士論文, 東海大學環境科學與工程系研究所, 2008。 13. 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。 14. 林廣山, 羅又寧, 徐寶崇, 陳孝行, 「製備含氮、鐵二氧化鈦披覆粒狀活性炭應用連續式流體化床光催化處理偶氮染料之研究」, 中華民國環境工程學會廢水處理技術研討會, 2009。 15. 林佑珍, 王皓, 林文崇, 林聰樂, 「可見光光觸媒之製備及其應用於水中染料之光催化分解」, 中華民國環境工程學會廢水處理技術研討會, 2009。 16. 吳嘉峰, 「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」, 碩士論文,

大葉大學環境工程學研究所, 2009. 17. 賴佑昌, 「以改質光觸媒結合臭氧化程序處理染料廢水之反應行為研究」, 碩士論文, 大葉大學環境工程學研究所, 2009. 18. 方芋涵, 「比較不同鑲嵌元素之二氧化鈦光觸媒在可見光下對染料溶液的反應行為之研究」, 碩士論文, 大葉大學環境工程學研究所, 2010. 英文摘要 1. Akbal, A. F., Onar, A. N., " Photocatalytic degradation of phenol ", *Environ Monit Assess*, Vol.83, pp.295-302, 2003. 2. Akpan, U.G. , Hameed, B.H. , " Parameters affecting the photocatalytic degradation of dyes using TiO<sub>2</sub>-based photocatalysts: A review ", *Journal of Hazardous Materials*, Vol.170, pp.520-529, 2009. 3. Ananpattarachai, J., Kajitvichyanukul, P., Seraphin, S., " Visible light absorption ability and photocatalytic oxidation activity of various interstitial N-doped TiO<sub>2</sub> prepared from different nitrogen dopants ", *Journal of Hazardous Materials*, Vol.168, pp.253-261, 2009. 4. 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. 5. Asilturk, 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. 6. Behnajady, M.A., Modirshahla, N., Daneshvar, N., Rabbani, M., " Photocatalytic degradation of an azo dye in a tubular continuous-flow photoreactor with immobilized TiO<sub>2</sub> on glass plates ", *Chemical Engineering Journal*, Vol.207, pp.167-176, 2007. 7. Carp, O., Huisman, C. L., Reller, A., " Photoinduced reactivity of titanium dioxide ", *Progress in Solid State Chemistry*, Vol.32, pp.33-177, 2004. 8. Chatterjee, D., Patnam, V., Sikdar, A., Joshi, P., Misra, R., Rao, N.N., " Kinetics of the decoloration of reactive dyes over visible light-irradiated TiO<sub>2</sub> semiconductor photocatalyst ", *Journal of Hazardous Materials*, Vol.156, pp.435-441, 2008. 9. 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. 10. 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. 11. 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. 12. 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. 13. 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. 14. Janus, M., Choina, J., Morawski, A.W., " Azo dyes decomposition on new nitrogen-modified anatase TiO<sub>2</sub> with high adsorptivity ", *Journal of Hazardous Materials*, Vol.166, pp.1-5, 2009. 15. 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. 16. 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. 17. 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. 18. 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. 19. 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. 20. 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. 21. Mozia, S., Tomaszewska, 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. 22. Ohno, T., Akiyoshi, M., Umabayashi, 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. 23. Poullos, 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. 24. 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. 25. 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. 26. Ranjit, K. T., Krishnamoorthy, R., Varadarajan, T. K., Viswanathan, B., " Photocatalytic reduction of nitrite on CdS ", *Journal of Photochemistry and Photobiology A: Chemistry*, Vol.86, pp.185-189, 1995b. 27. 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. 28. 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. 29. 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. 30. Sun, J., Qiao, L., Sun, S., Wang, G., " Photocatalytic degradation of Orange G on nitrogen-doped TiO<sub>2</sub> catalysts under visible light and sunlight irradiation ", *Journal of Hazardous Materials*, Vol.155, pp.312-319, 2008. 31. 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. 32. 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. 33. 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. 34. 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. 35. 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. 36. 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. 37. 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. 38. 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. 39. 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. 40. 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. 41. Yanmin, Liu., Jingze, Liu., Yulong, Lin., Yanfeng, Zhang., “ Simple fabrication and photocatalytic activity of S-doped TiO<sub>2</sub> under low power LED visible light irradiation ” , *Ceramics International* 35,pp.3061 – 3065, 2009. 42. 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.