

# Degradation of dye pollutants by the modified TiO<sub>2</sub> photocatalysts under visible light irradiation :

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## ABSTRACT

The objectives of this work are to prepare Fe-doped, N-doped and S-doped TiO<sub>2</sub> photocatalysts, respectively, using the sol-gel method, and to investigate the photo-degradation behaviors of different dyes including, MG, AR13 and AR27 in aqueous solutions under visible light irradiation. The preparation conditions, including type and amount of dopants were studied and degradation of dye molecules was analyzed. The physical-chemical characteristics of the prepared photocatalysts were analyzed by ICP-AES, SEM, EDX, XRD, and UV-Vis. Results of the XRD analysis indicated that the major crystalline type of the prepared TiO<sub>2</sub> is anatase. UV-Vis spectra showed that absorption in the visible light region was strengthened and the phenomena of red-shift was apparent. As for the photocatalytic degradation of MG, AR13 and AR27, the pseudo-first-order rate equation can be used to describe the reaction kinetics. Further, the prepared photocatalysts could react with MG, AR13 and AR27 more effectively under visible light irradiation. As for the Fe-doped, N-doped and S-doped TiO<sub>2</sub> photocatalysts, iron nitrate, urea, thiourea were found to be the best dopants, respectively. Among these photocatalysts, the N-doped photocatalysts using urea as the dopant possessed the best reactivity under visible light irradiation.

Keywords : TiO<sub>2</sub>、visible light、N、S、Fe、dye

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## REFERENCES

中文摘要 1. 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。2. 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。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研究所，2005。5. 葉世墉，「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Ag/TiO<sub>2</sub>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TiO<sub>2</sub>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、鎆、鐵改質型TiO<sub>2</sub>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碳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. 方芊涵，「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?Ikan, 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.2007,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., 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。 22. 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。 23. 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。 24. Rane, K.S., Mhalsiker, R., Yin, S., Sato, T., Cho, K., Dunbar, E., Biswas, P., " Visible light-sensitive yellow TiO<sub>2-x</sub>Nx and Fe-N co-doped Ti<sub>1-y</sub>FeyO<sub>2-x</sub>Nx 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 PhotobiologyA: 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.