

Comparative study on the photocatalytic degradation of dye pollutants over the TiO₂ photocatalyst doped with different s

方芊涵、柯雅雯

E-mail: 321429@mail.dyu.edu.tw

ABSTRACT

The objectives of this work are to prepare N-doped, S-doped and Fe-doped TiO₂ photocatalysts, respectively, using the sol-gel method, and to investigate the photo-degradation behaviors of different dyes including AR27, MG, MO, and AR4 in aqueous solutions under visible light irradiation. The preparation conditions, including the type and amount of dopants and photocatalyst concentration were studied and the degradation of dye molecules were analyzed. The physical-chemical characteristics of the prepared photocatalysts were analyzed by BET, SEM, EDX, XRD, and UV-Vis. Results showed that the specific surface area of the photocatalysts is about 26.86~38.25 m²/g. XRD patterns indicated that the major crystalline type of the prepared TiO₂ is anatase. UV-Vis diffuse reflectance spectra showed that absorption of Fe-doped TiO₂ in the visible light region was strengthened and the phenomena of red-shift was apparent. As for the photocatalytic degradation of AR27, MG, MO and AR4, the pseudo-first-order rate equation can be used to describe the reaction kinetics. The degradation behaviors varied with the photocatalyst concentration and the type of dopants for the prepared photocatalysts. It also revealed that the reaction rate constants for the prepared photocatalysts are greater than those for commercial TiO₂. Further, the prepared photocatalysts could react with AR27, MG, MO and AR4 more effectively under visible light irradiation, especially for the N-doped and S-doped TiO₂.

Keywords : photocatalysts、 visible light、 Fe、 S、 N、 TiO₂、 AR27、 AR4、 MO、 MG

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REFERENCES

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。 陳志賢，「奈米可見光V/TiO₂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。 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所，2005。 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。 林有銘，「奈米光觸媒」，科學發展，408期，2006。 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。 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。 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。 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系，2009。 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系, 2009. Akbal, A. F., Onar, A. N., " Photocatalytic degradation of phenol ", *Environ Monit Assess*, Vol.83, pp.295-302, 2003. Akpan, U.G. , Hameed, B.H. , " Parameters affecting the photocatalytic degradation of dyes using TiO₂-based photocatalysts: A review ", *Journal of Hazardous Materials*, Vol.170, pp.520-529, 2009. Ananpattarachai, J., Kajitvichyanukul, P., Seraphin, S., " Visible light absorption ability and photocatalytic oxidation activity of various interstitial N-doped TiO₂ prepared from different nitrogen dopants ", *Journal of Hazardous Materials*, Vol.168, pp.253-261, 2009. 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. Asilturk, M., Say?lkan, F., Arpac, E., " Effect of Fe³⁺ ion doping to TiO₂ on the photocatalytic degradation of Malachite ", *Journal of Photochemistry and Photobiology A: Chemistry*, Vol.203, pp.64-71, 2009. Behnajady, M.A., Modirshahla, N., Daneshvar, N., Rabbani, M., " Photocatalytic degradation of an azo dye in a tubular continuous-flow photoreactor with immobilized TiO₂ on glass plates ", *Chemical Engineering Journal*, Vol.2007, pp.167-176, 2007. Carp, O., Huisman, C. L., Reller, A., " Photoinduced reactivity of titanium dioxide ", *Progress in Solid State Chemistry*, Vol.32, pp.33-177, 2004. Chatterjee, D., Patnam, V., Sikdar, A., Joshi, P., Misra, R., Rao, N.N., " Kinetics of the decoloration of reactive dyes over visible light-irradiated TiO₂ semiconductor photocatalyst ", *Journal of Hazardous Materials*, Vol.156, pp.435-441, 2008. Ching, W. H., Leung, M., Leung, Y. C., " Solar photocatalytic degradation of gaseous formaldehyde by sol-gel TiO₂ 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 TiO₂ nanoparticles obtained under hydrothermal conditions ", *Materials Chemistry and Physics*, Vol.112, pp.146-153., 2008. Epling, A. E., Chitsan, L., " Photoassisted bleaching of dyes utilizing TiO₂ and visible light ", *Chemosphere*, Vol.46, pp.561-570, 2002. 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 TiO₂ ", *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 FeTiO₃/TiO₂ 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. Janus, M., Choina, J., Morawski, A.W., " Azo dyes decomposition on new nitrogen-modified anatase TiO₂ with high adsorptivity ", *Journal of Hazardous Materials*, Vol.166, pp.1-5, 2009. 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., " TiO₂-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations ", *Applied Catalysis B: Environmental*, Vol.49, pp.1-14, 2004. 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 TiO₂ photocatalyst realized by cationic S-doping and its application for phenol degradation ", *Journal of Hazardous Materials*, Vol.152, pp.48-55, 2008. 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_xN_y films ", *Thin Solid Films*, Vol.468, pp.48-56, 2004. 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. Ohno, T., Akiyoshi, M., Umebayashi, T., Asai, K., Mitsui, T., Matsumura, M., " Preparation of S-doped TiO₂ photocatalysts and their photocatalytic activities under visible light ", *Applied Catalysis A: General*, Vol.265, pp.115 – 121, 2004. 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. Rane, K.S., Mhalsiker, R., Yin, S., Sato, T., Cho, K., Dunbar, E., Biswas, P., " Visible light-sensitive yellow TiO₂-xN_x and Fe-N co-doped Ti_{1-y}FeyO₂-xN_x 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/ TiO₂ 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 Photobiology A: Chemistry*, Vol.86, pp.185-189, 1995b. Ranjit, K. T. and Viswanathan, B., " Photocatalytic reduction of nitrite and nitrate ions to ammonia on M/ TiO₂ 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 TiO₂, " *Applied Catalysis B: Environmental*, Vol.69, pp.138-144, 2007. 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 (TiO₂) ", *J. Korean Ind. Eng. Chem*, Vol.19, pp.1-16, 2008. Sun, J., Qiao, L., Sun, S., Wang, G., " Photocatalytic degradation of Orange G on nitrogen-doped TiO₂ catalysts under visible light and sunlight irradiation ", *Journal of Hazardous Materials*, Vol.155, pp.312-319, 2008. Teoh, W. Y., Amal, R., Madler, L., Pratsinis, S. E., " Flame sprayed visible light-active Fe-TiO₂ 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 Fe³⁺-doped TiO₂ 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 TiO₂ 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 TiO₂ 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 TiO₂-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 TiO₂ 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/TiO₂ catalyst with fine silver clusters ” , Journal of Catalysis, Vol.232, pp.424 – 431, 2005。