Photocatalytic Degradation of Methylene Blue in Aqueous Solution over Fe－doped and S－doped TiO2 under Visible Light Ir

吳嘉峰、柯雅雯

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

ABSTRACT

The objectives of this work are to prepare Fe-doped and S-doped TiO2 photocatalysts using the sol-gel method, and to investigate the photo-degradation of methylene blue (MB) in aqueous solutions under visible light irradiation. The preparation conditions, including the type and amount of dopants and calcinations temperature were studied the characteristics of the resulting photocatalysts were analyzed. Additionally, the optimum experimental conditions (including pH value and initial dye concentration) were evaluated.

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 38.7~79.4 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 and S-doped TiO2 in the visible light region was strengthened and the phenomena of red-shift was apparent. As for the photocatalytic degradation of MB, the pseudo-first-order rate equation can be used to fit the concentration vs. time data. It also revealed that the prepared photocatalysts had greater reaction rates and could react with MB more effectively under visible light irradiation. The S-doped TiO2, using 0.15 mole thiourea as the dopant, and at the calcination temperature of 500℃ would exhibit the highest catalytic activity with respect to MB in this study. The optimum experimental conditions are found to be pH 3, and at the initial MB concentration of 10ppm. The removal efficiency of MB reached 88% after 60 minutes of visible light irradiation.

Keywords : sol-gel method、photocatalysts、visible light、Fe、S、TiO2、MB

Table of Contents

REFERENCES

?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氧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氧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?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，「WOx摻雜TiO2-xNx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TiO2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 Fe3+ ion doping to TiO2 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 TiO2 thin film for enhancement of indoor air guality ”, 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。?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。?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 TiO2-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 TiO2 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 TiO2-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 TiO2 photocatalyst with Pt-modification:Role of TiO2 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 TiO2 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.,“ TiO2-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 TiO2 thin films by N2 – H2 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 TiOxNy 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。?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 TiO2-xNx and Fe-N co-doped Ti1-yFeyO2-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/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

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/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。?Sano, T., Puzenat, E., Guillard, C., Geantet, C., Matsuzawa, S.,“ Degradation of C2H2 with modified-TiO2 photocatalysts under visible light irradiation ” Journal of Molecular Catalysis A: Chemical, Vol.284, pp.127-133, 2008。?Sato, S.,“ Photocatalytic activity of NOx-doped TiO2 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 (TiO2) ”, 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 TiO2 nanocrystals for photocatalytic H2 production over N-doped TiO2 under visible light irradiation ”, Journal of hydrogen energy, pp.1-11, 2008。?Sun, H., Bai, Y., Jin, W., Xu, N.,“ Visible-light-driven TiO 2 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-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.,“ Photocatalystic 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。