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Bulletin of Chemical Reaction Engineering & Catalysis, 11 (1), 2016, 40-47

Research Article

Visible Light Photocatalytic Properties of Modified Titanium Dioxide Nanoparticles via Aluminium Treatment

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Received: 10th November 2015; Revised: 7th January 2016; Accepted: 7th January 2016

Abstract

Titanium dioxide (TiO_2) has gained much attentions for the last few decades due to its remarkable performance in photocatalysis and some other related properties. However, its wide bandgap (~3.2 eV) can only absorb UV energy which is only ~5% of solar light spectrum. The objective of this research was to improve the photocatalytic activity of TiO_2 by improving the optical absorption to the visible light range. Here, colored TiO_2 nanoparticles range from light to dark grey were prepared via aluminium treatment at the temperatures ranging from 400 to 600 °C. The modified TiO_2 is able to absorb up to 50% of visible light (400-700 nm) and shows a relatively good photocatalytic activity in organic dye (Rhodamine B) degradation under visible light irradiation compared with the commercial TiO_2. Copyright © 2016 BCREC GROUP. All rights reserved

Keywords: Colored Titania; Photocatalysis; Photodegradation; TiO_2; Visible Light Absorption

How to Cite: Ariyanti, D., Dong, J.Z., Dong, J.Y., Gao, W. (2016). Visible Light Photocatalytic Properties of Modified Titanium Dioxide Nanoparticles via Aluminium Treatment. *Bulletin of Chemical Reaction Engineering & Catalysis*, 11 (1): 40-47. (doi:10.9767/bcrec.11.1.414.40-47)

Permalink/DOI: http://dx.doi.org/10.9767/bcrec.11.1.414.40-47

1. Introduction

Fujishima and Honda reported water splitting breakthrough using TiO_2 semiconductor in 1972 [1]. Since then, TiO_2 has been extensively investigated as a promising material used in broad range of research areas, especially in environmental and energy-related fields [2-4]. The absorption of photons by a semiconductor provokes photocatalytic reactions at its surface such as water splitting or the degradation of organic compounds. Compared to other semiconductor photocatalyst, TiO_2 shows higher chemical stability, nontoxicity, and photoreactivity [5]. Its capability in harvesting photon can be used to oxidize or to produce hydrogen and hydrocarbons, decompose organic compounds, and remove pollutants from various media.

Photocatalytic activity of TiO_2 nanomaterial is related to their optical absorption properties, crystallinity, defect structure and surface area [6]. In terms of the optical absorption properties, larger optical absorption can increase the amount of light absorbed, and generate more electrons and holes [7]. Common crystal phases of TiO_2 (anatase, rutile and brookite) were reported to have large bandgap of ~3.2 eV which limits their optical absorption only in the ultraviolet region (290-400 nm) of solar light spec-

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trum [8]. It is a common knowledge that UV spectra only accounts ~5% from full spectrum of solar energy. Even if TiO_2 is very efficient in utilizing energy from UV light, its overall photocatalytic activity in solar light is relatively limited [4].

Various synthetic methods such as hydrogen thermal treatment, hydrogen plasma, chemical reduction, chemical oxidation, and electrochemical reduction have been developed to make engineered TiO_2 with different shapes, particle sizes, morphologies, and extend the light absorption towards the visible light region [4]. The result of those methods still varied in terms of optical properties and rate of recombination. Al reduction has been reported as one of the method that can enhance the optical absorption of TiO_2. It is more technically feasible for the visible light TiO_2 production compared to other processes. The basic principle is the reduction of oxide by other metal has been known for years as a method to produce transition metal alloy including Ti-Al Alloy [9]. Reduction of oxide can be accomplished by the removal of lattice oxygen and/or dissolution of reductant into the lattice structure. Here we present the result of a study in development of modified TiO_2 via Al treatment at atmospheric pressure, including its structure, morphology, optical properties and photocatalytic activity.

2. Experimental Section

2.1. Preparation of modified TiO_2

TiO_2 nanopowder (ECP Ltd, 20-30 nm in size) were mixed with Al powder (ECP Ltd, 30 micron) with weight ratio of 1:1. The mixture was put in ceramic crucible and heated to 400, 500, and 600 ^oC in a furnace for 3 hours. After cooling, the samples were treated with HCl (ECP Ltd., 10% in concentration) for 2 h and then dried overnight in oven at temperature 30 ^oC. Another HCl treatment was needed to remove excess of Al.

2.2. Sample Characterizations

The prepared samples were characterized by X-ray diffraction (XRD). Scanning Electron Microscope with Energy Dispersive X-ray Spectrometer (SEM-EDS, Philips XL30S FEG) was used to examine the microstructure and surface composition of modified TiO_2. UV-Vis-NIR Spectrophotometer (Shimadzu UV-3600) equipped with an integrating sphere was used to measure the light absorbance on the samples.

2.3. Photocatalytic Degradation

Photocatalytic activity was evaluated by monitoring the decomposition of Rhodamine B (RhB) in an aqueous solution under UV and visible light irradiation. Photocatalyst (50 mg) was mixed with RhB solution (50 mL, 5 ppm). After stirring for 60 min in the dark to reach the adsorption equilibrium, the solution was illuminated with UV light (Spectroline ENF-260C 6W SW BLE-6254S) or blue light (Dulux S BL 9W/71) for visible light irradiation. Sample (2 mL) was taken every 20 minutes and filtered by 0.2 μm PVDF syringe filter prior analysis. The concentration of aqueous RhB was determined with a UV-Vis spectrophotometer (Perkin Elmer Instrument) by measuring the peak intensity at 553 nm.

3. Results and Discussion

3.1. Structure features and physical properties

The color of commercial TiO_2 changed to light and dark grey respectively after Al treatment at 400 and 500 °C (samples T400 and T500), as shown in Figure 1A. However, the samples were not very stable since color changes were observed after one week at room temperature in ambient atmosphere. As reported, oxygen deficiencies in TiO_2 are reflected in a pronounced color change from transparent to light, and dark blue, which introduce changes in electronic structure (in particular a bandgap feature at ~0.8 eV below EFermi) [10]. However, upon exposure to molecular oxygen gas even at room temperature, the oxygen defect stated disappears [11, 12] due to dissociation of the gaseous oxygen and filling of the oxygen vacancies [6]. In the case of modified TiO_2 via Al treatment, oxygen deficiencies was appeared after the process with the color change from white to grayish; and then after a week placed in the open air, the oxygen gas from its surrounding started to enter the oxygen vacancies (color changes were observed).

Meanwhile, X-ray diffraction patterns illustrated in Figure 1B shows strong diffraction peaks in both commercial TiO_2 and modified TiO_2 which indicate that all the samples were highly crystalline. The patterns also reveal no evident of change in the XRD peak position and directions of T400 and T500, which means both have the same phase as commercial TiO_2 (anatase). On the other hands, the remains of Al still detected in T600 after two sequences of HCl treatment. A major difference between the commercial TiO_2 and modified TiO_2 was that the peak intensity (T400 < T500 < commercial TiO_2 < T600).

Scanning electron microscopy (SEM) was used to investigate the morphology and microstructure of modified TiO_2 (Figure 2). Similar shapes of nanoparticles were observed in T400, T500 and T600 compared to commercial TiO_2. Aluminium treatment are subjected to reduce the surface of TiO_2 which means to assist the formation of oxygen vacancies and keeping the similar morphology to the TiO_2 prior Al treatment. Some of the Al particles also found in T600 sample (Figure 2D), confirming the XRD pattern result.

3.2. UV-Vis diffuse reflectance spectra

Optical absorption properties of the commercial TiO_2 and modified TiO_2 were measured by UV-Vis spectrophotometry equipped with diffuse reflectance accessory. As displayed in Figure 3A, red-shift were imposed onto the cut-off edge of the absorption spectrum of T400 and T500, which extended the absorption from near 400 nm to 800 nm.

The absorbance intensity in the wavelength range from near 400 nm to 800 nm increased as the Al treatment temperature increased. Such light absorbance enhancement in the visible light range was consistent with the grayish color characteristic of the modified TiO_2 via Al treatment samples. Only T600 possesses low light absorption in UV region, as the presence of Al in the sample may contribute to the decreased light absorption behavior. The relation of colored TiO_2 with the enhancement of light absorption properties in visible light range in different methods and morphologies were also reported in several papers [9, 13-16].

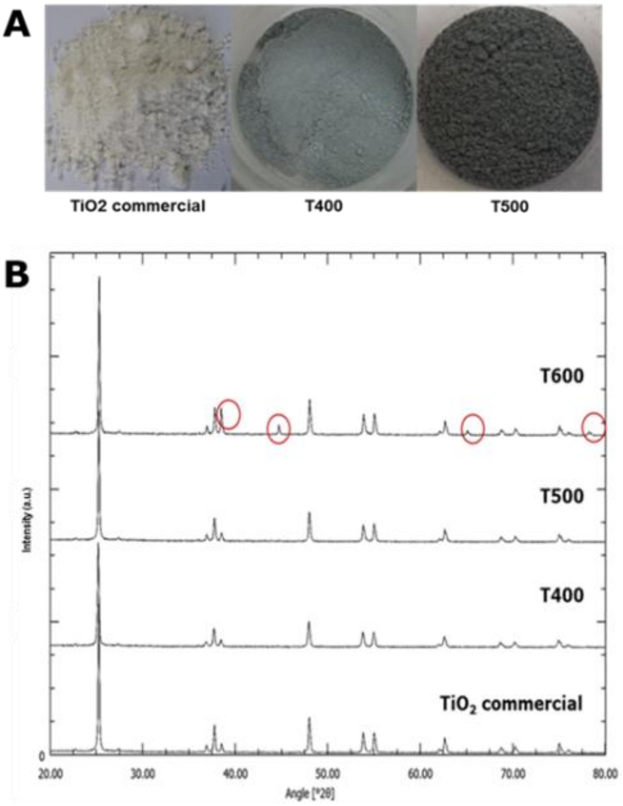

Figure 1. Photographs (A) and XRD patterns (B) of commercial TiO_2 and modified TiO_2 in different temperature

The broadening of the light absorption range from the UV to the visible light arises maybe because of the contributions of the oxygen vacancies in the lattice due to Al reduction or Al atom attachment. The Al atoms induced the local states near the valence band edge and the oxygen vacancies give rise to the local states below the conduction edge. The oxygen vacancies can act as the color centre. The color centre is the electrons vacancy that tend to absorb light in the visible spectrum and material that is usually transparent becomes colored. In addition, the electrons left in the oxygen vacancies can also interact with adjacent Ti^{4+} to give the Ti^{3+} color centre. The presence of these colour centres in TiO_2 also contributes to the visible light absorption [13, 17].

In line with the optical absorption properties, indirect bandgap energy (Eg) of commercial TiO_2 and modified TiO_2 (T400; T500; T600) can be estimated by employing Kubelka-Munk equation (Equation 1).

$$F(R) = \frac{(1-R)^2}{2R} \tag{1}$$

Reflectance data of UV-Vis spectra was converted to the absorption coefficient $F(R)$; plotted in ordinate as $(h\nu F(R))^{1/2}$ with photon energy ($h\nu$) values as the axis and determine the extrapolation of the linear portions of curves to energy axis [18]. Using the Kubelka–Munk function, the variation of $(h\nu F(R))^{1/2}$ versus hv for all samples were plotted in Figure 3B. The calculated bandgap for commercial TiO_2, T400, T500 and T600 were 3.31, 3.17, 3.24 and 3.19 eV, respectively, with 99.7% of confidence interval. Narrowed bandgap were observed within the results, compared to the commercial TiO_2. The bandgap narrowing is dictated by the synergistic presence of oxygen vacancies and surface disorder [19]. However, we still could not confirm the presence of stable oxygen vacancies and also surface disorder in the modified TiO_2.

3.3. Photocatalytic activity

The photocatalytic activities of modified TiO_2 samples were evaluated by the decomposition of RhB under UV (254 nm) and visible light (400-500 nm) irradiation. Direct decomposition of RhB solution in the absence of photocatalyst is not detected under light irradiation in a control experiment. Figure 4A shows the degradation curves of 5 ppm RhB solution catalyzed by T500 with 60 minutes of stirring in dark prior UV irradiation. The concentration of RhB decreased almost 35% after 90 minutes as monitored at 553 nm over time. Compared to TiO_2 commercial (Figures 4B and 4C), modified TiO_2 exhibited lower photocatalytic activity (T600 < T400 = T500 < commercial TiO_2), although it has higher UV light absorption as shown in UV-Vis diffuse reflectance and absorbance spectrum result.

The following photocatalytic activity was measured by the degradation of RhB solution in visible light (400-500 nm) irradiation employing the same concentration of photocatalyst and the concentration of solution. As illustrated in Figure 4D, T500 photocatalyst was able to decompose almost 40% of 5 ppm RhB solution in 90 minutes. Plotted with TiO_2 commercial (Figures 4E and 4F), modified TiO_2 (T400, T500) possess higher photocatalytic activity.

Based on the experimental data, the rate of RhB solution degradation using commercial and modified TiO_2 was calculated as illustrated in Figures 4C and 4F. The photocatalytic degradation is following pseudo first-order reaction kinetics. The reaction kinetics has often been described and widely used in terms of Langmuir-Hinshelwood model as the concentration of adsorption in the dark condition is relatively small (negligible). The kinetics equation can be described as Equation (2) where C is concentration of RhB at the stated time; C_o is initial concentration of RhB; k is kinetics rate constant; and t is time [20].

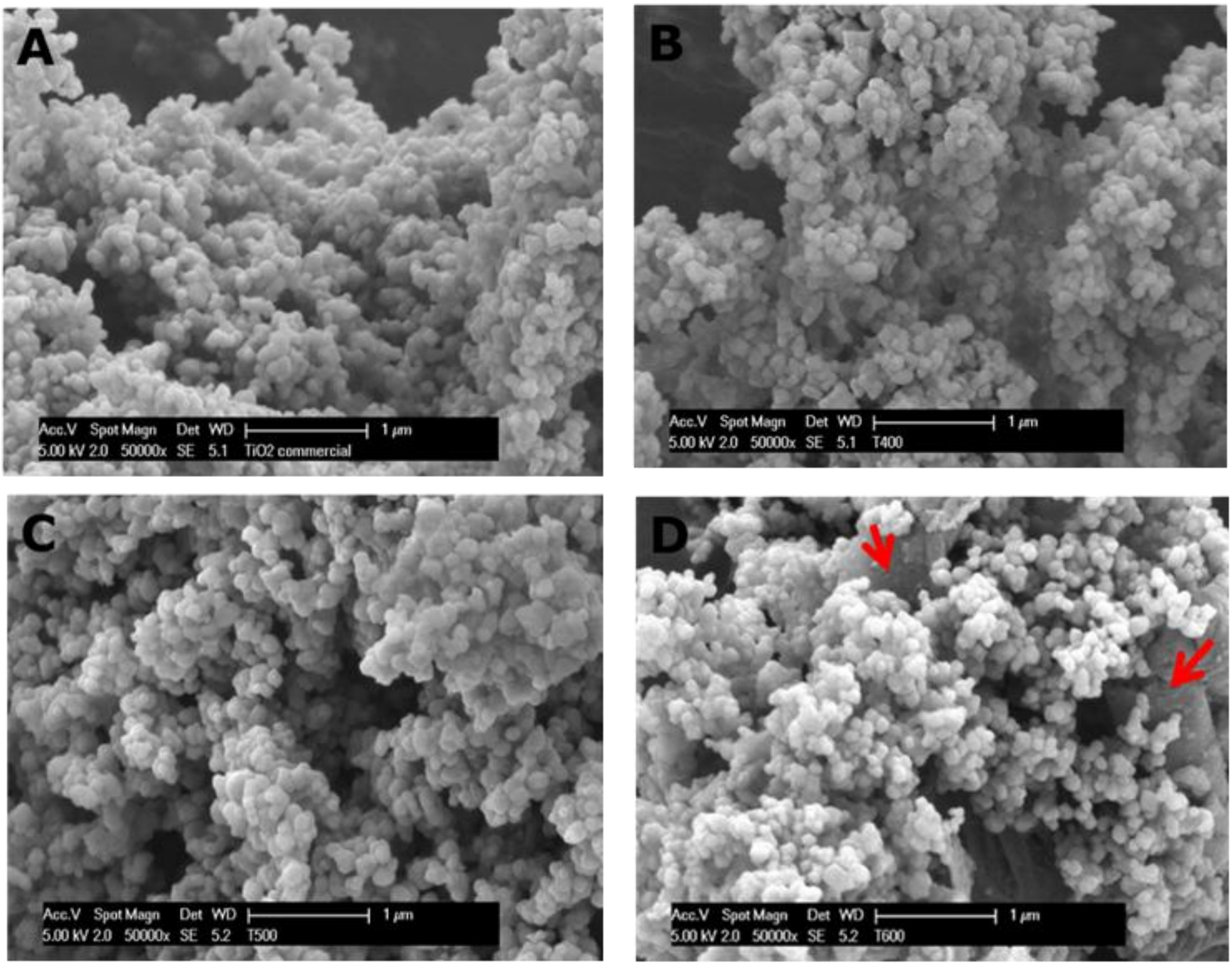

Figure 2. SEM images of commercial TiO_2 (A) and modified TiO_2 in different temperature (B = T400; C = T500; D = T600)

$$ln\left(\frac{C_0}{C}\right) = kt \qquad (2)$$

In UV light irradiation, the degradation rate constant of commercial TiO_2, T400, T500 and T600 is 0.0265, 0.004, 0.004 and 0.0021 min^{-1} respectively with the 95-99% of confidence interval. While in visible light irradiation, the degradation rate constant is 0.0017, 0.0025, 0.0047 and 0.0007 min^{-1} in the same sequence.

When the energy of an incident light exceeds the bandgap of the semiconductor photocatalyst during the photocatalysis process, electrons in the valence band will be excited into the conduction band, leaving holes in the valence band. Some of the electrons and holes will be further transferred to the photocatalyst surface and the charge carriers can form superoxide anions (electrons combine with adsorbed oxygen) and hydroxyl radicals (holes react with OH^-). The charge carriers will react with reactants [13]. However, not all electrons and holes can be transferred to the surface of photocatalyst, some of them will recombine each other, such the photocatalytic activities of TiO_2 photocatalysts are usually limited by the fast recombination of the photogenerated electron and hole pairs [5].

In the case of the modified TiO_2 via Al treatment, our speculation is that Al not only assist the creation of oxygen vacancies (temporary defect) but also attach to the structure as a dopant. Oxygen vacancies caused by Al reduction contribute to the colour change in modified TiO_2 and enhancement in the optical absorption properties which lead to the increased amount of excited electrons and holes. The presence of oxygen vacancies were also reported to cause trapped states in the forbidden bandgap, 0.75-1.18 eV away from the conduction band minimum (CBM) [12, 21, 22]. On the other hand, Al is also found in the samples and it may attached as a dopant. Doping with transition metals such as Fe(III), Ru(III), V(IV), Mo(V), Os(III), Re(V), Rh(III) ions substantially increased photocatalytic activity under UV irradiation, whereas doping with Co(III) and Al(III) decreased the photoactivity [2]. The presence of Al in the samples acts as a centre of recombination, leading to the decreasing photocatalytic activity. Even there were enhancement in the amount of excited electrons and holes due to oxygen vacancies, the amount of working electrons and holes that transferred to the surface is limited due to the presence of Al. In addition, excessive oxygen vacancies reported to become e-h recombination centres and harm photocatalysis [9]. That might be the explanation why the modified TiO_2 (T400 and T500) do not have a good photocatalytic activity in UV region.

4. Conclusions

Aluminium treatment in ambient atmosphere and pressure is used to create defect at the surface of TiO_2 nanoparticles. However Al seems to not only create temporary defect (color change) but also attached to the structure as a dopant. The modified TiO_2 at 500 °C

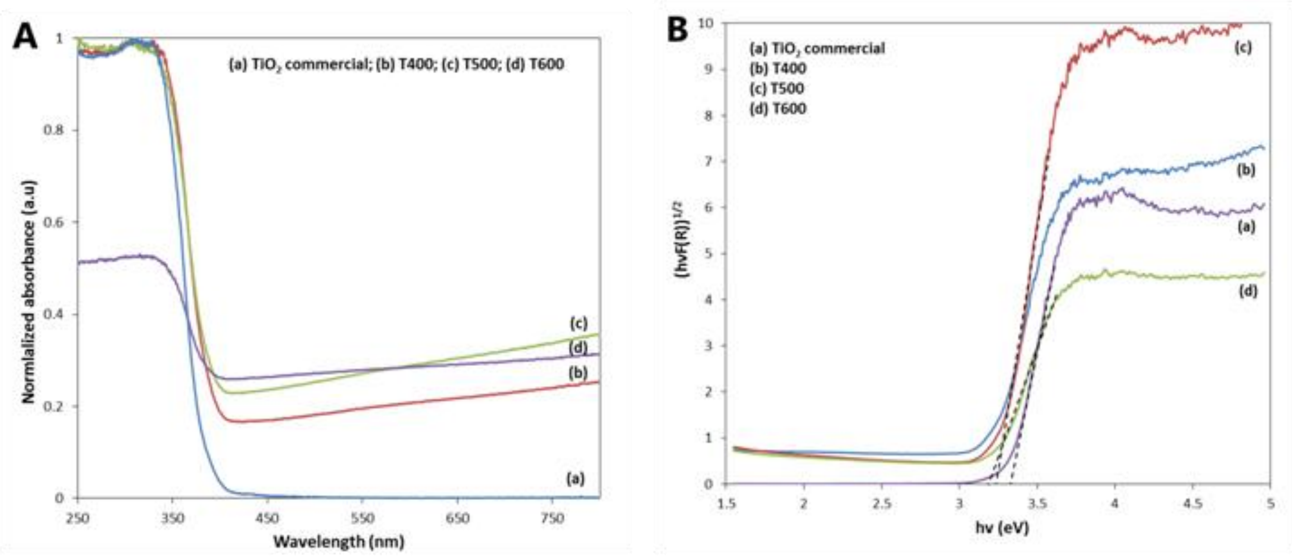

Figure 3. (A) UV-Vis diffuse reflectance and absorbance spectrum; (B) the plots [$h\upsilon F(R)^{1/2}$] vs photon energy of samples

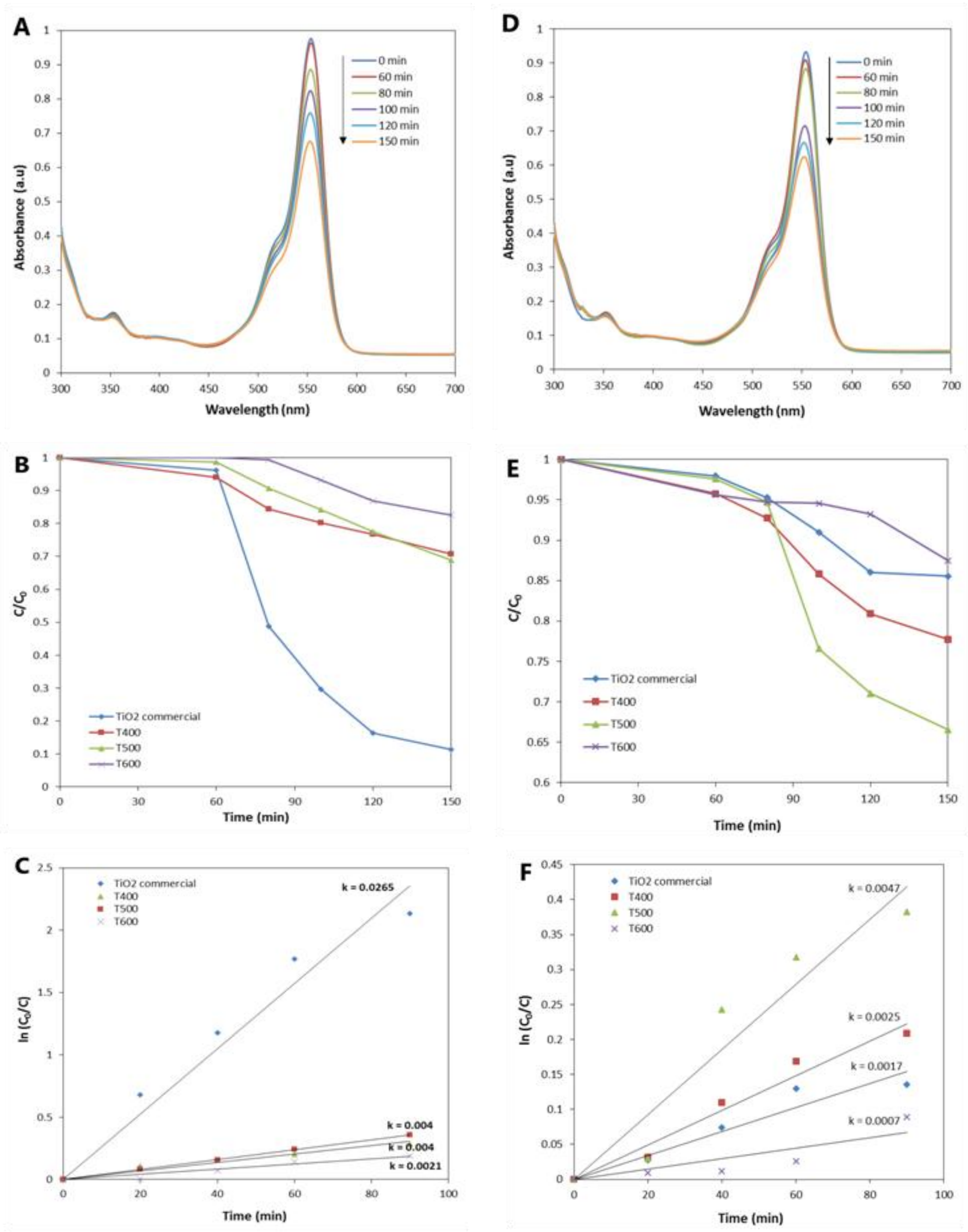

Figure 4. (A-C) under UV light irradiation: (A) RhB decomposition by sample T500; (B) Comparison of photocatalytic activities of samples and standard commercial TiO_2; (C) First order kinetics of photocatalytic RhB degradation of samples; (D-F) under Blue light irradiation: (D) RhB decomposition by sample T500; (E) Comparison of photocatalytic activities of samples and standard commercial TiO_2 under Blue light irradiation; (F) First order kinetics of photocatalytic RhB degradation of samples (per min)

possesses the visible light absorption up to 40% and relatively increase the photocatalytic activity by 20% compared to the commercial TiO_2. However, at the same time the Al treatment influence its photocatalytic activity in UV region to become lower than commercial TiO_2 as the attachment of Al to the structure tend to increase the centre of recombination for electrons and holes excited after photon absorption. Further work should be conducted to reduce the Al content on the treated samples, and the examination of the photocatalytic behavior of Al modified TiO_2 needs to be proved. Furthermore, the approach of using Al treatment at ambient pressure does not work well to enhance its photocatalytic activity in overall spectrum of solar light.

Acknowledgement

The authors thank the group of Advanced Materials and Department of Chemical and Materials Engineering, the University of Auckland for their assistances. The authors also thank Directorate General of Higher Education, Ministry of Education and Culture of Indonesia for the scholarship support.

References

[1] Fujishima, A., Honda, K. (1972). Electrochemical Photolysis of Water at a Semiconductor Electrode. *Nature*, 238: 37-38.

[2] Park, H., Park, Y., Kim, W., Choi, W. (2013). Surface modification of TiO_2 photocatalyst for environmental applications. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews,* 15: 1-20.

[3] Liu, L., Chen, X. (2014). Titanium Dioxide Nanomaterials: Self-Structural Modifications. *Chemical Reviews*, 114: 9890-9918.

[4] Chen, X., Liu, L., Huang, F. (2015). Black titanium dioxide (TiO_2) nanomaterials. *Chemical Society Reviews*, 44: 1861-1885.

[5] Schneider, J., Matsuoka, M., Takeuchi, M., Zhang, J., Horiuchi, Y., Anpo, M., Bahnemann, D.W. (2014). Understanding TiO_2 Photocatalysis: Mechanisms and Materials. *Chemical Rev*iews, 114: 9919-9986.

[6] Xia, T., Zhang, Y., Murowchick, J., Chen, X. (2014). Vacuum-treated titanium dioxide nanocrystals: Optical properties, surface disorder, oxygen vacancy, and photocatalytic activities. *Catalysis Today*, 225: 2-9.

[7] Zhuang, J., Dai, W., Tian, Q., Li, Z., Xie, L., Wang, J., Liu, P., Shi, X., Wang, D. (2010). Photocatalytic Degradation of RhB over TiO2 Bilayer Films: Effect of Defects and Their Location. *Langmuir*, 26: 9686-9694.

[8] Wang, Z., Helmersson, U., Käll, P. (2002). Optical properties of anatase TiO2 thin films prepared by aqueous sol–gel process at low temperature. *Thin Solid Films*, 405: 50-54.

[9] Wang, H., Lin, T., Zhu, G., Yin, H., Lü, X., Li, Y., Huang, F. (2015). Colored titania nanocrystals and excellent photocatalysis for water cleaning. *Catalysis Communications*, 60: 55-59.

[10] Diebold, U. (2003). The surface science of titanium dioxide. *Surface Science Reports*, 48: 53-229.

[11] Pan, J., Maschhoff, B.L., Diebold, U., Madey, T.E. (1992). Interaction of water, oxygen, and hydrogen with TiO_2 (110) surfaces having different defect densities. *Journal of Vacuum Science & Technology A* 10(4): 2470-2476.

[12] Henderson, M.A., Epling, W.S., Perkins, C.L., Peden, C.H.F., Diebold, U. (1999). Interaction of Molecular Oxygen with the Vacuum-Annealed TiO_2 (110) Surface: Molecular and Dissociative Channels. *The Journal of Physical Chemistry B*, 103: 5328-5337.

[13] Wang, J., Tafen, D.N., Lewis, J.P., Hong, Z., Manivannan, A., Zhi, M., Li, M., Wu, N. (2009). Origin of Photocatalytic Activity of Nitrogen-Doped TiO_2 Nanobelts. *Journal of the American Chemical Society*, 131: 12290-12297.

[14] Dong, J., Han, J., Liu, Y., Nakajima, A., Matsushita, S., Wei, S., Gao, W. (2014). Defective Black TiO_2 Synthesized via Anodization for Visible-Light Photocatalysis. *ACS Applied Materials & Interfaces*, 6: 1385-1388.

[15] Lin, T., Yang, C., Wang, Z., Yin, H., Lu, X., Huang, F., Lin, J., Xie, X., Jiang, M. (2014). Effective nonmetal incorporation in black titania with enhanced solar energy utilization. *Energy & Environmental Science*, 7: 967-972.

[16] Zhu, G., Yin, H., Yang, C., Cui, H., Wang, Z., Xu, J., Lin, T., Huang, F. (2015). Black Titania for Superior Photocatalytic Hydrogen Production and Photoelectrochemical Water Splitting. *ChemCatChem*, 7: 2614-2619.

[17] Serpone, N. (2006). Is the Band Gap of Pristine TiO2 Narrowed by Anion- and Cation-Doping of Titanium Dioxide in Second-Generation Photocatalysts? *The Journal of Physical Chemistry B*, 110: 24287-24293.

[18] Hamdam Momen, M., Amadeh, A., Heydarzadeh Sohi, M., Moghanlou, Y. (2014). Photocatalytic properties of ZnO nanostructures grown via a novel atmospheric pressure solution evaporation method. *Materials Science and Engineering: B*, 190: 66-74.

[19] Naldoni, A., Allieta, M., Santangelo, S., Marelli, M., Fabbri, F., Cappelli, S., Bianchi, C. L., Psaro, R., Dal Santo, V. (2012). Effect of Nature and Location of Defects on Bandgap Narrowing in Black TiO_2 Nanoparticles. *Journal of the American Chemical Society*, 134: 7600-7603.

[20] Yan, C., Yi, W., Yuan, H., Wu, X., Li, F. (2014). A highly photoactive S, Cu-codoped nano-TiO2 photocatalyst: Synthesis and characterization for enhanced photocatalytic degradation of neutral red. *Environmental Progress & Sustainable Energy*, 33: 419-429.

[21] Kurtz, R.L., Stock-Bauer, R., Msdey, T.E., Román, E., De Segovia, J. (1989). Synchrotron radiation studies of H_2O adsorption on TiO_2 (110). *Surface Science*, 218: 178-200.

[22] Henderson, M.A., Epling, W.S., Peden, C.H. F., Perkins, C.L. (2003). Insights into Photoexcited Electron Scavenging Processes on TiO_2 Obtained from Studies of the Reaction of O_2 with OH Groups Adsorbed at Electronic Defects on TiO_2 (110). *The Journal of Physical Chemistry B*, 107: 534-545

Selected and Revised Papers from The 2nd International Conference on Chemical and Material Engineering 2015 (ICCME 2015) (29-20 September, 2015, Semarang, Indonesia) (http://econference.undip.ac.id/index.php/iccme/2015) after Peer-reviewed by ICCME 2015 and BCREC Reviewers