Research Article

WO₃-Doped TiO₂ Coating on Charcoal Activated with Increase Photocatalytic and Antibacterial Properties Synthesized by Microwave-Assisted Sol-Gel Method

Weerachai Sangchay

Faculty of Industrial Technology, Songkhla Rajabhat University, Songkhla, Thailand

Correspondence should be addressed to Weerachai Sangchay; weerachai.sang@yahoo.com

Received 3 October 2016; Revised 21 December 2016; Accepted 11 January 2017; Published 31 January 2017

Academic Editor: Linhua Xu

Copyright © 2017 Weerachai Sangchay. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

WO₃-doped TiO₂ coating on charcoal activated (CA) was prepared by microwave-assisted sol-gel method. The samples calcined at the temperature of 500°C for 2 h with a heating rate of 10°C/min were characterized by XRD, EDS, and SEM. The photocatalytic and antibacterial activities of WO₃-doped TiO₂ coating on CA were investigated by means of degradation of a methylene blue (MB) solution and against the bacteria *E. coli*, respectively. The effects of WO₃ concentration were discussed. The 1% WO₃-doped TiO₂ coated CA seems to exhibit the higher photocatalytic and antibacterial activity than other samples. The WO₃-doped TiO₂ coated on CA are expected to be applied as a photocatalyst for water purification.

1. Introduction

Titanium dioxide (TiO₂) is a semiconductor photocatalyst and exists in three crystalline phases including anatase, rutile, and brookite [1, 2]. TiO₂ is one of the important photocatalysts because of its high activity, chemical stability, robustness against photocorrosion, low toxicity, no-twin pollution, and availability at low cost so far, especially for the detoxification of water and air and antibacterial [3–6]. TiO₂ possesses antibacterial properties due to its strong oxidation activity in the presence of light and the generation of reactive oxygen species such as hydroxyl radicals ([•]OH), hydrogen peroxide (H₂O₂), and superoxide ions (O₂^{•−}) from photocatalytic reaction [7].

The photocatalytic activity of TiO₂ nanoparticles depends not only on the properties of the TiO₂ material itself, but also on the modification of TiO₂ with metal or metal oxide. Previous studies reported that the addition of WO₃ in TiO₂ enhances its photocatalytic efficiency [5, 6]. However, WO₃ nanoparticles have prospective applications including biosensing, biodiagnostics, optical fibers, and antimicrobial and photocatalytic uses. WO₃ ions are known to cause denaturation of proteins present in bacterial cell walls and slow down bacterial growth [6, 7].

In the current work, CA powder was selected as an adsorptive support for TiO₂-doped with WO₃ which was prepared by microwave-assisted sol-gel method and these samples were tested for UV degradation of MB and UV photoinactivation of Gram-negative bacteria *Escherichia coli* (*E. coli*).

2. Experimental and Details

2.1. Materials. The charcoal activated from Laboratory Reagents and Fine Chemicals Co., Ltd., was crushed into small particles of 1.5 mm. Titanium (IV) isopropoxide (C₁₂H₂₈O₄Ti, TTIP) and sodium tungstate dihydrate (Na₂WO₄·2H₂O) were obtained from Aldrich Chemistry Co., Ltd., and Chem-Supply, respectively. The other reagents, such as ethanol (C₂H₅OH) 36.5–38.0% and hydrochloric acid (HCl) 69–70%, were all of analytical grade.

2.2. Materials Preparation. Based on our previous studies [8, 9], WO₃-doped TiO₂ coated CA were prepared by the following method. Firstly, to prepare WO₃-doped TiO₂ sol, Na₂WO₄·2H₂O (1, 3, and 5 mol%), TTIP (10 mL), C₂H₅OH (150 mL), and water (250 mL) were mixed and stirred for

15 min at room temperature. The solution was acidified to pH = 3 by adding few droplets of 3 M HCl into the solution and stirred for 45 min. The treated solution was refluxed at 180 W for 1 h using a domestic microwave oven (Samsung, ME82V) to produce a milky solution. The 10 g CA powder was used as an adsorptive support and immersed into the WO₃-doped TiO₂ sol under ultrasonic assistance. After the sol-coated CA formed a gel, the WO₃-doped TiO₂ gel-coated CA was dried at room temperature for 24 h and then calcined at 500°C for 2 h with a heating rate of 10°C/min. The formation of a TiO₂ anatase phase after the calcination at 500°C has been confirmed in our previous study. Pure TiO₂ coated CA was prepared using the same procedures as described above except for addition of the dopant. All samples were designated as TP, TIW, T3W, and T5W of various mol ratios of WO₃ to TiO₂ were 0, 1, 3, and 5 mol%, respectively.

2.3. Characterizations. Morphology and particle size of the synthesized WO₃-doped TiO₂ coated CA were characterized by a Scanning Electron Microscope (SEM) (Quanta 400) and energy-dispersive X-ray spectroscopy (EDS). The phase composition was characterized using an X-ray diffractometer (XRD) (Phillips X'pert MPD, Cu-K). Samples were scanned from 10° to 70° at a rate of 2°/min (in 2 θ). The crystallite size was calculated by the Scherrer equation as $0.9\lambda/\beta \cos \theta_B$, where k is equal to 0.9, a shape factor for spherical particles, λ is the X-ray wavelength ($\lambda = 0.15405$ nm), θ is the Bragg angle, and $\beta = B - b$, the line broadening. B is the full-width of the diffraction line at half of the maximum intensity and $b = 0.042$ is the instrumental broadening [9].

2.4. Photocatalytic Activity. The photocatalytic activity of the WO₃-doped TiO₂ coated CA was evaluated by MB degradation under UV irradiation (eleven 50 W of black light lamps) for a certain time. The particular photocatalytic course and setup were the same as previously described [10]. The experiment was performed in a 15 mL cylindrical glass reactor, with an UV lamp (356 nm, 3.89 mW/cm²) mounted at its center. The volume of the solution was 10 mL and the input MB concentration was 1×10^{-5} M. The amount of the catalysts was 1.0 g. After adsorption in dark for 1 h (to reach adsorption equilibrium), the sample was kept in a chamber under UV irradiation for 0 to 3 h. After that the supernatant solutions were measured for MB absorption at 665 nm using a UV-Vis spectrophotometer (GENESYS™ 10S). The removal rate (within 3 h) is calculated as $(1 - (C/C_0) \times 100\%)$, where C_0 is the concentration of MB aqueous solution at the beginning (1×10^{-5} M) and C is the concentration of MB aqueous solution after exposure to a light source. The photocatalytic activity of 3 samples was tested and an averaged value was taken for evaluation.

2.5. Antibacterial Activity. In a previous work [10], antibacterial activity of the synthesized the WO₃-doped TiO₂ coated CA against the bacteria *E. coli* was studied. Aliquots of 10 mL *E. coli* conidial suspension (10^3 CFU/mL) were mixed with 1.0 g of the sample. The mixture was then exposed to UV irradiation (eleven 50 W of black light lamps) for 0, 30, 60,

90, and 120 min. After that, 0.1 mL of the mixture suspension was sampled and spread on nutrient agar (NA) plate and incubated at 37°C for 24 h. After incubation, the number of viable colonies of *E. coli* on each NA plate was observed and disinfection efficiency of each test was calculated in comparison with that of the control as $100(N_0 - N)/N_0$, where N_0 and N are the average number of live bacterial cells per milliliter in the flask of the initial or control and powders finishing agent or treated fabrics, respectively. The antibacterial activities of three samples were tested.

3. Results and Discussion

3.1. Characterization. Figure 1 represents XRD curve of WO₃-doped TiO₂ samples with different concentrations of WO₃. All samples exhibited mainly anatase TiO₂ (JCPDS file number 21-1272) [11], whereas in case of hear, WO₃ was not observed by XRD due to its small amount presenting in the samples. It was very interesting to note that only anatase phase is noticed without reflections of rutile and brookite phases. The presence of NaCl on the peak XRD curves is as a result of precursors used for the preparation of WO₃-doped TiO₂.

The crystallite size was calculated using the Scherrer equation with the full-width at half of the maximum intensity. The calculating results were 16.6, 11.8, 12.6, and 13.1 nm for TP, TIW, T3W, and T5W, respectively. It was apparent that WO₃ added in TiO₂ has significant effect on crystallite size. The crystallite size of the anatase phase decreased with an increased WO₃ doping. The smallest crystallite size was observed from TIW sample. As shown in the SEM photographs, the WO₃-doped TiO₂ particulates were uniformly distributed on the surface of CA. The EDS spectrum image taken from the TIW is presented in Figure 2, where the presence of W, Ti, and O atoms derived from WO₃/TiO₂ composite is shown. Figure 3(a) shows the WO₃-doped TiO₂ particles impregnated onto the surface of single activated carbon grain. Figure 3(b) shows cross-sectional morphologies of WO₃-doped TiO₂ coated CA. It was found that the thicknesses of thin films were in the range of 2.5 to 5.0 μ m. Their surfaces are dense and very smooth.

3.2. Photocatalytic Activity. Photocatalytic activity of the WO₃-doped TiO₂ coated CA was performed by means of the degradation of MB with an initial concentration of 1×10^{-5} M under UV for various irradiation times. It could be seen that WO₃ has an effect on the photocatalytic activity of the as-prepared samples and 1% WO₃-doped TiO₂ coated CA (TIW) exhibits an optimum photoactivity (Figure 4). According to the previous report, many factors influenced the photoactivity of TiO₂ photocatalyst such as crystalline phase, grain size, specific surface area, surface morphology, and surface state (surface OH radical) and these were closely related to each other [9, 12].

As seen in Figure 1, TIW exhibits small crystallite size of anatase phase. Moreover, it was testified that WO₃ dispersed on the surface of TiO₂, which could prohibit the recombination of the photogenerated electron-hole pairs and increase

FIGURE 1: The XRD patterns of WO₃-doped TiO₂.

FIGURE 2: EDS spectrum image 1% WO₃-doped TiO₂ coated CA.

photo quantum efficiency. These phenomena promote the photocatalytic activity of the WO₃-doped TiO₂ coated CA and it seems to exhibit the highest performance of approximately 84.93% for degradation of MB solution at 3 h UV irradiation (Figure 5). However, the photocatalytic activity of TP was less than those of T3W and T5W, respectively, due to the effect of WO₃ on hindrance of anatase growth (Figure 4).

3.3. Antibacterial Activity. Figure 6 presents the *E. coli* survival rate of WO₃-doped TiO₂ coated CA after UV irradiation. The results showed that *E. coli* survivals decreased with irradiation time. It was found that T1W exhibited higher antibacterial properties than those TiO₂ doped with 0, 3, and 5% WO₃ coated CA, respectively. The *E. coli* kill percentage of WO₃-doped TiO₂ coated CA under UV

FIGURE 3: WO₃-doped TiO₂ coated CA: (a) WO₃-doped TiO₂ particulates adhered onto CA surface; (b) cross-sectional morphologies.

irradiation is shown in Figure 7. It was found that the *E. coli* were killed under UV irradiation for 120 min being 63.33, 100.00, 98.67, and 96.00% for 0, 1, 3, and 5% WO₃-doped TiO₂ coated CA, respectively. The photo of viable bacterial colonies for the synthesized WO₃-doped TiO₂ coated CA

samples treated with UV irradiation for 0, 30, 60, 90, and 120 min is illustrated in Figure 8. It is very obvious that the cell walls and cell membranes were damaged when microbial cells came into contact with WO₃-doped TiO₂ coated CA under UV irradiation. In this sense, the photogenerated hydroxyl

FIGURE 4: The photocatalytic activity of WO_3 -doped TiO_2 coated CA on degradation of MB.

FIGURE 6: The antibacterial activity of WO_3 -doped TiO_2 coated CA.

FIGURE 5: The degradation percentage of WO_3 -doped TiO_2 coated CA on degradation of MB.

FIGURE 7: The *E. coli* kill percentage of WO_3 -doped TiO_2 coated CA.

($\cdot\text{OH}$) and super oxygen (O_2^-) radicals acted as powerful oxidizing agents which react with peptidoglycan (poly-*N*-acetylglucosamine and *N*-acetylmuramic acid) of bacterial cell wall [12].

4. Conclusion

In this work, WO_3 -doped TiO_2 coated CA was prepared by microwave-assisted sol-gel method. It was found that WO_3 has an effect on hindrance of anatase growth, resulting in reduction photocatalytic and an antibacterial activity of WO_3 -doped TiO_2 coated CA compared to that of pure TiO_2 . The 1% WO_3 -doped TiO_2 coated CA seems to exhibit

FIGURE 8: Photo of viable *E. coli* colonies on synthesized WO_3 -doped TiO_2 coated CA.

the better photocatalytic and an antibacterial activity than other composite films. The WO_3 -doped TiO_2 coated CA are expected to be applied as photocatalyst materials for water purification.

Competing Interests

The author declares that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

The authors would like to acknowledge Institute of Research & Development, Songkhla Rajabhat University, and Faculty of Industrial Technology, Songkhla Rajabhat University, Thailand, for financial support of this research.

References

- [1] M. Lazzeri, A. Vittadini, and A. Selloni, "Structure and energetics of stoichiometric TiO_2 anatase surfaces," *Physical Review B*, vol. 63, no. 15, Article ID 155409, 2001.
- [2] D. Reyes-Coronado, G. Rodríguez-Gattorno, M. E. Espinosa-Pesqueira, C. Cab, R. De Coss, and G. Oskam, "Phase-pure TiO_2 nanoparticles: anatase, brookite and rutile," *Nanotechnology*, vol. 19, no. 14, Article ID 145605, 2008.
- [3] A. Fujishima, T. N. Rao, and D. A. Tryk, "Titanium dioxide photocatalysis," *Journal of Photochemistry and Photobiology C*, vol. 1, no. 1, pp. 1–21, 2000.
- [4] S. Y. Lee and S. J. Park, " TiO_2 photocatalyst for water treatment applications," *Journal of Industrial and Engineering Chemistry*, vol. 19, no. 6, pp. 1761–1769, 2013.
- [5] M. Hussain, S. Tariq, M. Ahmad et al., "Ag- TiO_2 nanocomposite for environmental and sensing applications," *Materials Chemistry and Physics*, vol. 181, pp. 194–203, 2016.
- [6] M. L. Škorić, I. Terzić, N. Milosavljević et al., "Chitosan-based microparticles for immobilization of TiO_2 nanoparticles and their application for photodegradation of textile dyes," *European Polymer Journal*, vol. 82, pp. 57–70, 2016.
- [7] N. Abbas, G. N. Shao, M. S. Haider et al., "Inexpensive sol-gel synthesis of multiwalled carbon nanotube- TiO_2 hybrids for high performance antibacterial materials," *Materials Science and Engineering: C*, vol. 68, pp. 780–788, 2016.
- [8] W. Sangchay and T. Rattanakol, "The efficiency of photocatalytic reaction in degradation methylene blue of TiO_2 powders prepared by microwave-assisted sol-gel method," *Engineering Journal Chiang Mai University*, vol. 22, no. 1, p. 18, 2015.
- [9] W. Sangchay, "Study of the photocatalytic and antibacterial activities of TiO_2 powder synthesized by microwave-assisted sol-gel method," *KKU Research Journal*, vol. 21, no. 1, p. 67, 2016.
- [10] W. Sangchay, "Photocatalytic and antibacterial activity of Ag-doped TiO_2 nanoparticles," *KKU Research Journal*, vol. 18, no. 5, pp. 731–738, 2013.

- [11] Z. Jiang, Y. Liu, T. Jing et al., "Enhancing visible light photocatalytic activity of TiO_2 using a colorless molecule (2-methoxyethanol) due to hydrogen bond effect," *Applied Catalysis B: Environmental*, vol. 200, pp. 230–236, 2017.
- [12] L. Sikong, B. Kongreong, D. Kantachote, and W. Sutthisripok, "Inactivation of *salmonella typhi* using Fe^{3+} doped $\text{TiO}_2/\text{3SnO}_2$ photocatalytic powders and films," *Journal of Nano Research*, vol. 12, pp. 89–97, 2010.