

PREPARATION AND PHOTOCATALYTIC PROPERTY OF NANO-TiO₂ LOADED ACTIVATED CARBON FIBERS FROM LIQUEFUED WOOD

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ABSTRACT

Nano-TiO₂ loaded wooden Activated Carbon Fibers (TiO₂/WACFs) was prepared by sol-gel method and with WACFs as the support which was obtained after phenol liquefaction, melt spinning, and curing treatment from the phenolated Chinese Fir (*Cunninghamia lanceolata*) by CO₂ activation. The surface morphology, loading rate of nano-TiO₂, and photocatalytic property of TiO₂/WACFs were studied. The results showed that TiO₂ was deposited on almost each WCAFS with a coating thickness of about 10nm. With increased heating rate and calcination time, the degradation rate of methylene blue of TiO₂/WACFs gradually increases, but calcination time has little effect on degradation rate of methylene blue of TiO₂/WACFs. When calcination temperature is 450°C, the loading quantity of nano-TiO₂ and the degradation rate of methylene blue reach the maximal values of 74.47 mg.g⁻¹ and 25.61 %, respectively.

KEYWORDS: Wood, activated carbon fibers, nano-TiO₂, loading rate, photocatalyst.

INTRODUCTION

Nano-TiO₂ has numerous excellent characteristics, including high oxidative property, good stability, low cost, and non-toxicity. Nano-TiO₂ is one of the most promising photocatalyst materials. However, suspension system powder-type TiO₂ photocatalyst degrades more slowly when the target pollutant content is lower (Morooka et al. 1989, Vinodgopal et al. 1994). Thus, much research has been devoted to immobilizing TiO₂ photocatalyst on porous supporting matrices, such as silica, alumina, zeolites, and activated carbon (Torimoto et al. 1996, Ding et al. 2001, Hsien et al. 2001, Anandan and Yoon 2003, Huang and Saka 2003). But most of the supports are still in the form of granules, and the problem of separation and recovery of the photocatalyst from the reaction media still exists. Activated carbon fibers (ACF_s), with good

adsorption and uniform pore structure, has been used as a catalyst support for different purposes (Fu et al. 2004a, b, Liu et al. 2006, Mo and Ye 2009, Yao et al. 2010).

ACFs as the support are mainly prepared from fossil resource and are adverse to sustainable use of carrier materials. Over the last few decades, some scientists have paid attention to the wooden activated carbon fibers (Uraki et al. 2001, Asakura et al. 2004, Okabe et al. 2005 Satoshi et al. 2007). However, in these studies, some component of wood must be separated and wood utilization was lower. In recent years, many techniques have been developed for using wood effectively. Wood liquefaction is one of those techniques for converting wood into useful liquid materials (Alma et al. 1995, Lin et al. 1995, Alma et al. 1996, 1998). In our previous work, carbon fiber was successfully prepared from *Cunninghamia lanceolata* by liquefied, spun, cured, carbonized and so on, and achieved a tensile strength of 1.5 GPa (Ma and Zhao 2010).

In this paper, the objective of this study was to prepare TiO₂ loaded Activated Carbon Fibers from liquefied wood (TiO₂/WACFs). The surface morphology, loading rate of nano-TiO₂, and photocatalytic property of TiO₂/WACFs were studied by SEM and UV-vis adsorption spectroscopy. This study provides reference for preparing biomass photocatalytic composite material.

MATERIAL AND METHODS

The raw material was Chinese fir (*Cunninghamia lanceolata*). Debarked chips were ground and the power of 20-80 mesh size was dried in an oven at 105°C for 24 h prior to being used. All other chemicals in the study were reagent grade and they were used without further purification.

A mixture composed of dried Chinese Fir powder (20-80 mesh) and phenol at a mass ratio of 1:6 was liquefied for 2.5 h at 160°C with 8 % phosphoric acid (based on the mass ratio of phenol). The as-prepared liquefied wood was placed into a reaction tube with 5 % hexamethylenetetramine (based on the mass ratio of liquefied wood) as the synthetic material. The mixture was heated from room temperature to 130°C in 40 min to prepare the spinning solution. The spinning solution was placed into a spinning machine (Fig. 1), and the initial fibers were prepared by melt-spinning (Fig. 2a).

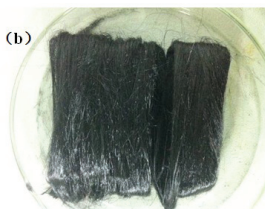
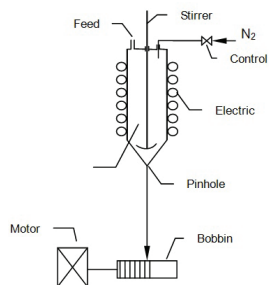


Fig. 1: Schemes of spinning equipment. Fig. 2: Fibers (a) and WACFs (b) from the phenolated Chinese fir.

After melt-spinning, the spun filaments were cured by soaking in an acid solution HCHO and HCl as main components at 95°C for 4h, washed with demonized water and finally dried at 90°C for 2 h the precursors were activated for 40 min by heating from room temperature to

different activation temperature at a heating rate of $5^{\circ}\text{C}\cdot\text{min}^{-1}$ in a $100\text{ ml}\cdot\text{min}^{-1}$ stream of N_2 and $500\text{ ml}\cdot\text{min}^{-1}$ flow rate of CO_2 . WACFs from liquefied wood were prepared (Fig. 2b).

Adding 10 mL of $(\text{TiOC}_4\text{H}_9)_4$ dropwisely into 2/3 ethyl alcohol, solution A was obtained after stirring for 1 h with a magnetic stirring apparatus. Glacial acetic acid was added dropwise into the remaining 1/3 ethyl alcohol, which was mixed with a certain quantity of deionized water to obtain solution B. Then, solution B was slowly added to solution A and stirred for 1 h until it became transparent. The mixture was placed in a thermostatic water bath at 35°C for 2 h aging to obtain a milky white colloidal solution. The measured WACFs were put into the solution and vibrated for 30 min. After a certain time of still dipping, the fibers were weighed after drying at 105°C for 2 h, and calcined for several hours in a $100\text{ ml}\cdot\text{min}^{-1}$ stream of N_2 , and then naturally cooled. WACFs supported nano- TiO_2 photocatalytic material was prepared.

Scanning electron microscope (SEM) images of composite material was taken by a microscope (JSM-7500F, JEOL) with an acceleration voltage of 10 keV.

The loading rate of nano- TiO_2 is measured by ash method, TiO_2 is a non-combustible material. While carrier-WACFs become ash after calcining for 2 h at 800°C . Its assay method is based on the GB/T 12496-1999 Test Methods for Wooden Activated Carbon-Determination of Ash Content. Composite materials with the same mass and under different calcinations temperatures, as well as WACFs, were placed in a weighed crucible to be calcined in a carbonization furnace for 2 h. the samples were removed and weighed after cooling for 30 min. The formula is as follows:

$$X = \frac{m_2 - m_1}{m} \times 100 (\%) \quad (1)$$

where: X - ash content (%),
 m_2 - mass of ash and crucible (g),
 m_1 - mass of the crucible (g),
 m - mass of sample (g).

The ash content of WACFs were very low, so the difference between ash content of composite material and ash content of WACFs was used as the loading rate of nano- TiO_2 for simplified calculation.

The photocatalytic property of composite material is determined by a self-made photocatalytic reaction device (darkroom with ultraviolet lamp and magnetic stirring apparatus). We used 100 mL of methylene blue solution with a certain content (the maximal absorption wavelength was 665 nm) as the target degradation product. Up to 0.1 g of shredded composite material were poured into the solution to be degraded and stirred for 15 min in a darkroom to reach adsorption equilibrium. Then, the 254 nm ultraviolet lamp was turned on. After a period of illumination, the absorbance of the sample was measured at 665 nm by ultraviolet-visible spectrophotometry. The degradation rate of methylene blue was calculated using the following equation:

$$\alpha = \frac{A_0 - A}{A_0} \times 100 (\%) \quad (2)$$

where: A_0 - the solution content before illumination and,
 A - the solution content after illumination at a moment.

RESULTS AND DISCUSSION

The SEM image of $\text{TiO}_2/\text{WACFs}$ is showed in Fig. 3. Figs. 3 a), b), and c) show that TiO_2 was deposited on almost each WCAFs with a coating thickness of about 10 nm. Thus, the sample has better composite structure and the same film thickness. However, the cracking and spalling of the formed film are observed on the surface of $\text{TiO}_2/\text{WACFs}$. This is due to not firmly loaded of the formed TiO_2 film on the surface of WACFs before calcination and the shrinkage of the formed TiO_2 film during calcination. Fig. 3d shows that some particles are present on the surface of $\text{TiO}_2/\text{WACFs}$. It is found that the granular TiO_2 was deposited onto on the surface of $\text{TiO}_2/\text{WACFs}$ during reacting.

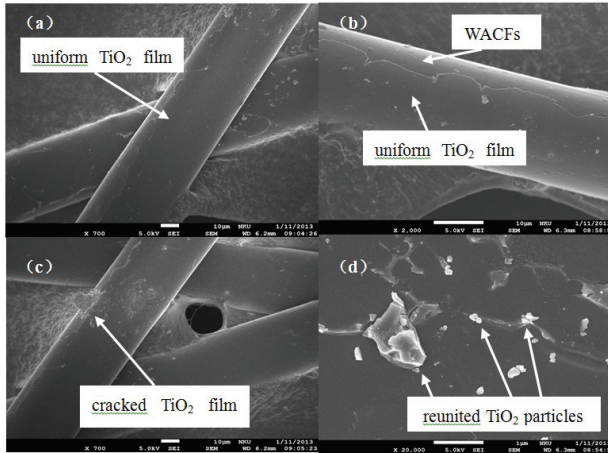


Fig. 3: SEM of $\text{TiO}_2/\text{WACFs}$ a),b),c),d)- Surface.

Fig. 4 shows loading rate of $\text{TiO}_2/\text{WACFs}$ at various calcination temperatures. With increased calcination temperature, the loading rate of nano- TiO_2 gradually increases and then decreases. The temperature increases from 400 to 550°C, the loading rate of nano- TiO_2 increase (decrease) by 15.50, 37.71, and 12.47 %, respectively. When calcinations temperature ranged from 450 to 500°C, the curve variation is larger. This is mainly because that with increased calcination temperature, the load firmness of nano- TiO_2 is enhanced due to the changes of the surface fabric property of WACFs, and the growth of the crystal structure of TiO_2 , resulting in an increasingly

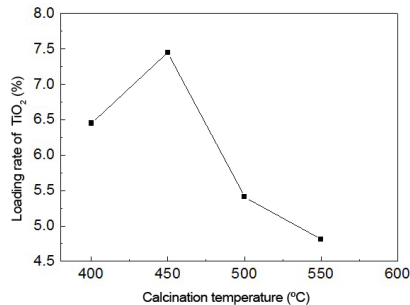


Fig. 4: Loading rate of $\text{TiO}_2/\text{WACFs}$ at various calcination temperatures.

high content of TiO_2 . However, when the calcination temperature is too high, the sintering of the TiO_2 particle causes the film to the shrinking and cracking, or even peel off, resulting in the decrease of TiO_2 content and the loading rate of $\text{TiO}_2/\text{WACFs}$.

Fig. 5 shows degradation rate of methylene blue of $\text{TiO}_2/\text{WACFs}$ at various calcination temperatures. With increased calcination temperature, degradation rate of methylene blue of $\text{TiO}_2/\text{WACFs}$ increases and then decreases, and reaches the maximum at 450°C . The temperature increases from 400 to 550°C , the degradation rate of methylene blue of $\text{TiO}_2/\text{WACFs}$ increase (decrease) by 20.63, 9.54, 13.88 %, respectively. This is due to the more firmly loaded and the change from amorphous without photocatalysis to anatase with superior photocatalysis of TiO_2 with increased calcination temperature, resulting in the increase of the degradation rate of methylene blue of $\text{TiO}_2/\text{WACFs}$. Because of the part change from anatase to rutile with poor photocatalytic property of TiO_2 , degradation rate of methylene blue of $\text{TiO}_2/\text{WACFs}$ declines when the calcination temperature exceeds 450°C .

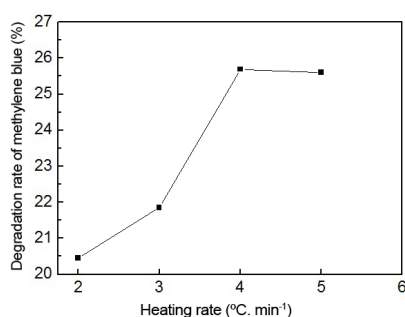
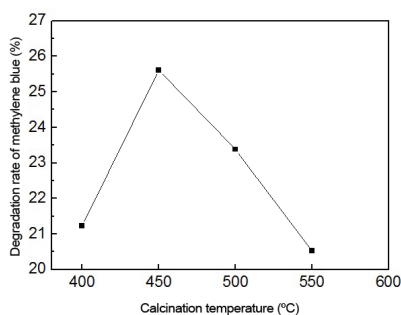


Fig. 5: Degradation rate of methylene blue at various calcination temperatures (heating rate of $5^\circ\text{C}\cdot\text{min}^{-1}$, calcination time of 60 min).

Fig. 6: Degradation rate of methylene blue at various heating rates (calcination temperature of 450°C , calcination time of 60 min).

Fig. 6 shows degradation rate of methylene blue of $\text{TiO}_2/\text{WACFs}$ at various heating rates. Heating rate has minimal effect on crystal formation of nano- TiO_2 powder and only affects particle size. With increased heating rate, the degradation rate of methylene blue of $\text{TiO}_2/\text{WACFs}$ gradually increases, and stabilizes after $4^\circ\text{C}\cdot\text{min}^{-1}$ heating rate. The heating rate increases

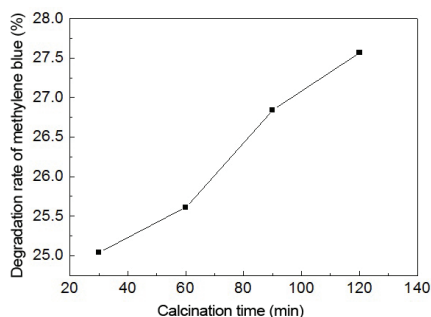


Fig. 7: Degradation rate of methylene blue at various calcination times (calcination temperature of 450°C , heating rate of $5^\circ\text{C}\cdot\text{min}^{-1}$).

from 2 to 5°C.min⁻¹, the degradation rate of methylene blue of TiO₂/WACFs increase (decrease) by 6.85, 17.57, 0.31 %, respectively. It is found that slow heating rate and long sintering time cause large nano-TiO₂ crystal particle supported on the surface of WACFs, which affect its photocatalytic property. On the other hand, the symmetrical distributing of Nano-TiO₂ obtained by increasing heating rate and shortening sintering time enhances the photocatalytic property of TiO₂/WACFs.

Fig. 7 shows degradation rate of methylene blue of TiO₂/WACFs at various calcination times. With increased calcination time, the degradation rate of methylene blue of TiO₂/WACFs gradually increases. This is mainly because with increased calcination time, nano-TiO₂ is supported firmly on the surface of WACFs and gradually realizes crystallization. The partial organic group in the system is fully removed and the crystal formation of TiO₂ completely changes from amorphous to anatase, causing enhance photocatalytic property of TiO₂/WACFs. When calcination time increases from 30 to 120 min, the degradation rate of methylene blue increases by 9.18 %. Based on calcination temperature and heating rate, calcination time has little effect on degradation rate of methylene blue of TiO₂/WACFs.

CONCLUSIONS

Nano-TiO₂ loaded wooden Activated Carbon Fibers (TiO₂/WACFs) was prepared by sol-gel method and with WACFs as the support which was obtained after phenol liquefaction, melt spinning, and curing treatment from the phenolated Chinese Fir (*Cunninghamia lanceolata*) by CO₂ activation. The following conclusions were obtained:

1. TiO₂ was deposited on almost each WCAFS with a coating thickness of about 10nm. However, cracks or some particles are observed in some films.
2. With increased calcination temperature, the loading rate of nano-TiO₂ gradually increases and then decreases. When calcination temperature is 450°C, the loading quantity of TiO₂/WACFs reach the maximal values of 74.47 mg.g⁻¹.
3. With increased heating rate, the degradation rate of methylene blue of TiO₂/WACFs gradually increases, and stabilizes after 4°C.min⁻¹ heating rate. With increased calcination temperature, degradation rate of methylene blue of TiO₂/WACFs initially increases and then decreases. With increased calcination time, the degradation rate of methylene blue of TiO₂/WACFs gradually increases, but calcination time has little effect on degradation rate of methylene blue of TiO₂/WACFs.

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REFERENCES

1. Alma, M.H., Yoshioka, M., Yao, Y., Shiraishi, N., 1995: Some characterizations of hydrochloric acid catalyzed phenolated wood-based materials. *Mokuzai Gakkaishi* 41(8): 741-748.

2. Alma, M.H., Yoshioka, M., Yao, Y., Shiraishi, N., 1996: The preparation and flow properties of HCl catalyzed phenolated wood and its blends with commercial novolak. *Holzforschung* 50(1): 85-90.
3. Alma, M.H., Yoshioka, M., Yao, Y., Shiraishi, N., 1998: Preparation of sulfuric acid-catalyzed phenolated wood resi. *Wood Science and Technology* 32(4): 297-308.
4. Anandan, S., Yoon, M., 2003: Photocatalytic activities of the nano-sized TiO₂-supported Y-zeolites. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews* 4(1): 5-18.
5. Asakura, R., Morita, M., Hatori, H., Yamada, Y., 2004: Preparation of fibrous activated carbons from wood fiber. *Journal of Materials Science* 39(1): 201-206.
6. Ding, Z., Hu, X J., Yue, P.L., Lu, G.Q., Greenfield, P.F., 2001: Synthesis of anatase TiO₂ supported on porous solids by chemical vapor deposition. *Catalysis Today* 68(1-3): 173-182.
7. Fu, P., Luan, Y., Dai, X., 2004a: Preparation of TiO₂ photocatalyst anchored on activated carbon fibers and its photodegradation of methylene blue. *China Particuology* 2(2): 76-80.
8. Fu, P., Luan, Y., Dai, X., 2004b: Preparation of activated carbon fibers supported TiO₂ photocatalyst and evaluation of its photocatalytic reactivity. *Journal of Molecular Catalysis A: Chemical* 221(1-2): 81-88.
9. Hsien, Y.H., Chang, C.J., Chen, Y.H., Cheng, S., 2001: Photo degradation of aromatic pollutants in water over TiO₂ supported on molecular sieves. *Applied Catalysis B: Environmental* 31(4): 241-249.
10. Huang, B., Saka, S., 2003: Photocatalytic activity of TiO₂ crystallite-activated carbon composites prepared in supercritical isopropanol for the decomposition of formaldehyde. *Journal of Wood Science* 49(1): 79-85.
11. Kubo, S., Yoshida, T., Kadla, J.F., 2007: Surface porosity of lignin/PP blend carbon fibers. *Journal of Wood Chemistry and Technology* 27(3-4): 257-271.
12. Lin, L., Yoshioka, M., Yao, Y., Shiraishi, N., 1995: Physical properties of moldings from liquefied wood resins. *Journal Applied Polymer Science* 55(11): 1563-1571.
13. Liu, J.H., Yang, R., Li, S.M., 2006: Preparation and application of efficient TiO₂/ACFs photocatalyst. *Journal of Environmental Science* 18(5): 979-982.
14. Ma, X., Zhao, G., 2010: Preparation of carbon fibers from liquefied wood. [J]. *Wood Science and Technology* 44(1): 3-11.
15. Mo, D., Daiqi, Ye, D., 2009: Surface study of composite photocatalyst based on plasma modified activated carbon fibers with TiO₂. *Surface and Coatings Technology* 203(9): 1154-1160.
16. Morooka, S., Yasutake, T., Kobata, A., Ikemizu, K., Kato, Y., 1989: A mechanism for the production of ultrafine particles of TiO₂ by a gas phase reaction. *International Chemical Engineering* 29(1): 119-126.
17. Okabe, K., Yao, T., Shiraishi, N., Oya, A., 2005: Preparation of thin carbon fibers from waste wood-derived phenolic resin. *Journal of materials science* 40(14): 3847-3848.
18. Yao, S., Li, J., Shi, Z., 2010: Immobilization of TiO₂ nanoparticles on activated carbon fiber and its photodegradation performance for organic pollutants. *Particuology* 8(3): 272-278.
19. Torimoto, T., Ito, S., Kuwabata, S., Yoneyama, H., 1996: Effects of adsorbents used as supports for titanium dioxide loading on photocatalytic degradation of propylamide. *Environmental Science and Technology* 30(4): 1275-1281.

20. Uraki, Y., Nakatani, A., Kubo, S., Sano, Y., 2001: Preparation of activated carbon fibers with large specific surface area from softwood acetic acid lignin. *Journal of Wood Science* 47(6): 465-469.
21. Vinodgopal, K., Stafford, U., Gray, K.A., Kamat, P.V., 1994: Electrochemically assisted photocatalysis. 2. The role of oxygen and reaction intermediates in the degradation of 4-chlorophenol on immobilized TiO₂ particulate films. *Journal of Physical Chemistry* 98(23): 6797-6803.

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