ZIBELINE INTERNATIONAL PUBLISHING

Water Conservation and Management (WCM)

DOI: http://doi.org/10.26480/wcm.01.2021.26.29

ISSN: 2523-5664 (Print)
ISSN: 2523-5672 (Online)
CODEN: WCMABD

RESEARCH ARTICLE

DEVELOPMENT OF CARBON NANOTUBE AS HIGHLY ACTIVE PHOTOCATATLYTIC ADSORBENT FOR TREATMENT OF ACID RED 88 DYE

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ARTICLE DETAILS

Article History:

Received 12 January 2021
Accepted 18 February 2021
Available online 08 April 2021

ABSTRACT

In recent years, photocatalysts have been used in various fields, and are particularly attracting attention in the fields of environment, medicine, and agriculture. A large number of catalytic active sites are required to produce a more efficient photocatalyst, and for that purpose, a large specific surface area is desired. Therefore, in this study, in order to develop a highly active photocatalytic material, the outer diameter of titanium oxide nanotubes was controlled by a template synthesis method using carbon nanotubes with different outer diameters to increase the specific surface area. Characterization was carried out by using diffent analytical instruments such as UV-Spectrophotomoter, XRD, SEM, TEM, BET. Results show using titanium oxide nanotubes with a smaller outer diameter tended to have higher photocatalytic activity (almost complete degradation was obtained when 10-20nm was used).

KEYWORDS

Photocatalysts, titanium oxide & carbon nanotubes, template synthesis method, surface area.

1. INTRODUCTION

In recent years, technology for controlling the production of titanium oxide at the nanoscale level has become extremely important. In particular, titanium oxide nanotubes have a high specific surface area, and therefore may have a higher photocatalytic activity than particulate titanium oxide (Guo et al., 2010; Jang et al., 2008; Tian et al., 2015; Liu et al., 2018; Rodriguez et al., 2003). So far, hydrothermal synthesis methods, anodizing methods, and template synthesis methods have been proposed for the production of titanium oxide nanotubes. However, it has been clarified that the titanium oxide nanotubes synthesized by the conventional hydrothermal synthesis method lose their tube shape and become particulate at the firing stage where the crystal layer appears (Weng et al., 2006; Yu and Wang, 2008; Fujishima et al., 2000; Tao et al., 2008; Gong et al., 2001). On the other hand, the template synthesis method has an advantage that the morphology of the titanium oxide nanotubes produced can be controlled (Mor et al., 2003; Huang et al., 2010). Therefore, in this study, carbon nanotubes with different outer diameters were used as templates, and the purpose was to control the outer diameter of titanium oxide nanotubes on a nanoscale. In addition, the prepared titanium oxide nanotubes were applied to the decolorization of the dye (Acid Red 88), and the photocatalytic activity of each was evaluated.

2. EXPERIMENTAL AND METHODS

2.1 Creation of titanium oxide nanotubes

Carbon nanotubes (50 mg) were added to ethanol (1.2 ml). At this time, the outer diameters of the carbon nanotubes were changed to 10-20, 20-40, 40-60, and 60-100 nm. Ultrasonic irradiation was performed for 10 minutes to disperse. Then, the mixture was cooled to 0 ° C., benzyl alcohol (0.39 ml) and water (0.14 ml) were added, then mixture was stirred. A solution prepared by dissolving titanium (IV) tetrabutoxide monomer in ethanol was gradually added then the mixture was stirred for 1 hour. After that mixture was filtered under reduced pressure, the filtrate was washed with ethanol, and dried at room temperature for 24 hours. The obtained substance was calcined at 550 ° C. for 2 hours to obtain titanium oxide nanotubes. In the experiment to examine the influence of sintering temperature, carbon nanotubes with an outer diameter of 10-20 nm were used, and the sintering temperature was changed to 350, 450, 550, and 650 ° C.

2.2 Preparation of dye solution

Acid Red 88 was used as the dye, and it was dissolved in water treated with an ultrapure water device (GSH-2000, Advantech Toyo Co., Ltd.) with stirring for about 1 day to prepare a stock solution with a concentration of 90 ppm. This was diluted to 20 ppm each time and the experiment was conducted.

2.3 Light irradiation experiment

30 ml of Acid Red 88 aqueous solution (20 ppm) and 30 mg of photocatalyst were added to a Pyrex glass reaction vessel. After stirring in a dark place for 30 minutes to reach the absorption / desorption equilibrium, light was irradiated with a xenon lamp (4.5 mW / ㎠). At this

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Cite the Article: Tomoki Sugiyama, Ahmed H. A. Dabwan, Mai Furukawa, ikki Tateishi, Hideyuki Katsumata, Satoshi Kaneco (2021). Development of Carbon Nanotube as Highly Active Photocatatlytic Adsorbent for Treatment of Acid Red 88 Dye. *Water Conservation and Management, 5(1): 26-29.*

time, the reaction vessel was placed in a constant temperature bath (a water tank with a quartz plate window) and the temperature was adjusted to 25 ° C.

2.4 Analysis

2.4.1 Analysis of acid bleaching rate of Acid Red 88

After light irradiation, the reaction solution was filtered through a 0.20 μm membrane filter to remove the photocatalyst, and then the absorbance was measured with a visible ultraviolet spectrophotometer and calculated by the ratio of the absorbance of Acid Red 88, which had been decolorized, to the initial absorbance.

2.4.2 Absorption spectrum of catalyst

Photocatalyst (50mg) was diluted with 3.5 g of barium sulfate, and the absorbance was measured with a visible ultraviolet spectrophotometer.

2.4.3 Observation with an electron microscope

SEM (acceleration voltage 25kV) and TEM (acceleration voltage 80kV) images of the photocatalyst were taken.

2.4.4 X-ray diffraction

SRD measurement of photocatalyst was performed.

2.4.5 BET surface area

Using liquid nitrogen, the BET surface area of the photocatalyst was measured by adsorption and desorption of nitrogen. The BJH method was used as the calculation method.

3. Results and Discussion

3.1 Effect of outer diameter of carbon nanotubes

3.1.1 SEM image and TEM image

The effect of the outer diameter of the carbon nanotube used as a template was examined. Figure 1 shows the SEM image of titanium oxide nanotubes prepared using carbon nanotubes with different outer diameters, and Figure 2 shows the TEM image.

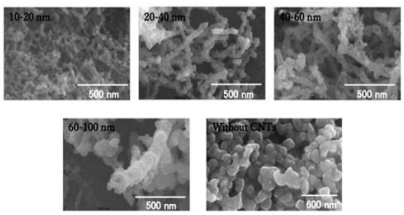

Figure 1: SEM image of titanium oxide nanotubes

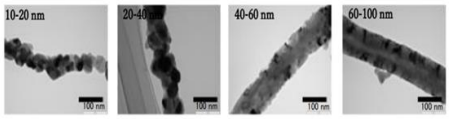

Figure 2: TEM image of titanium oxide nanotubes

Table 1 shows the outer diameter range analyzed from these images and their average. From these results, it is considered that the outer diameter of titanium oxide nanotubes can be controlled by producing titanium oxide nanotubes by changing the outer diameter of carbon nanotubes.

Table 1: Outer diameter range and average of titanium oxide nanotubes

Diameter of CNTs (nm)	Extent (nm)	Average (nm)
10-20	23-33	28
20-40	33-56	43
40-60	46-93	64
60-100	67-150	98

3.1.2 Effect of different outer diameters on photocatalytic activity

Acid Red 88 was decolorized using titanium oxide nanotubes with different outer diameters, and the photocatalytic activity of each was examined. The experimental conditions at this time are shown in Table 2, and the results are shown in Figure 3. The time change of the dye concentration was calculated by measuring the absorbance with a visible ultraviolet spectrophotometer (514 nm) and calculating the ratio of the absorbance of the decolorized Acid red 88 to the initial absorbance.

Table 2: Experimental conditions for light irradiation experiments

Dye	Acid Red 88
Sample concentration	20 mg/L
Temperature	25 ℃
Sample volume	30 mL
Light intensity	4.5 mW/cm²
Catalyst amount	30 mg

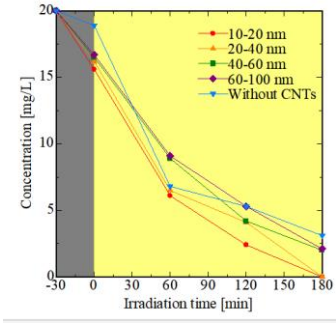

Figure 3: Time change of dye concentration by outer diameter

From these results, the removal rate of all titanium oxide nanotubes after 180 minutes was higher than that of the particulate ones. Furthermore, titanium oxide nanotubes with a smaller outer diameter tended to have higher photocatalytic activity.

3.1.3 Absorbance of catalyst

The visible ultraviolet absorption spectrum of the catalyst was measured. The results are shown in Figure 4. Absorption was observed in the visible light region of the titanium oxide nanotubes with a large outer diameter, but no significant change was observed in the excitation wavelength in any of the photocatalysts.

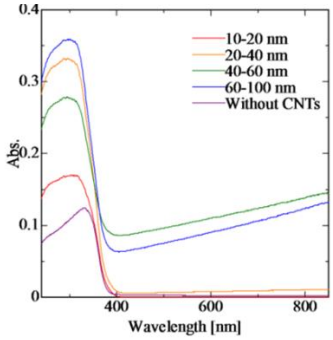

Figure 4: Visible ultraviolet absorption spectrum of titanium oxide nanotubes

3.1.4 BET surface area

The specific surface area of the prepared titanium oxide nanotubes was measured. The results are shown in Table 3. Those with a diameter of 40-60 nm showed a higher specific surface area than the others, but the specific surface area tended to decrease as the outer diameter of the titanium oxide nanotubes increased. From this, it is considered that the surface area is one of the factors affecting the photocatalytic activity. The adsorption isotherms at 10-20 nm (a) and 60-100 nm (b) are shown in Figure 5, and the pore distribution curve is shown in Figure 6.

Table 3: Specific surface area of titanium oxide nanotubes

Diameter of CNTs (nm)	Surface Area (m^2/g)
Without CNTs	17.0
10-20	27.4
20-40	24.0
40-60	34.1
60-100	18.2

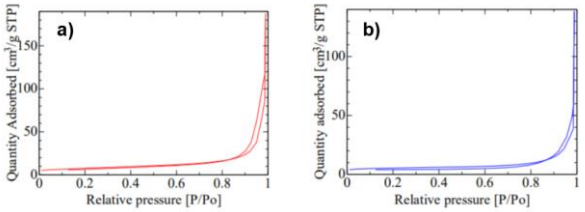

Figure 5: Adsorption isotherm

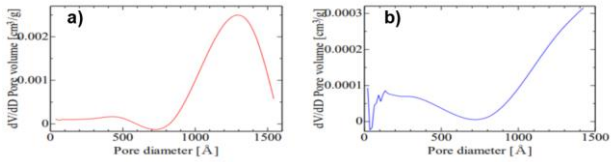

Figure 6: Pore distribution curve

3.2 Examination sintering temperature

3.2.1 *Effect of sintering temperature on photocatalytic activity*

Since the activity of titanium oxide changes depending on the sintering temperature, the effect of the firing temperature was examined. Figure 7 shows the changes in dye concentration over time due to titanium oxide nanotubes with different sintering temperatures. From this result, it is considered that the lower the sintering temperature, the higher the photocatalytic activity.

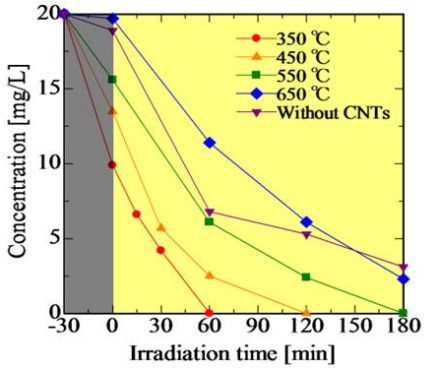

Figure 7: Time change of dye concentration by sintering temperature

3.2.2 *SEM image and TEM image*

Fig. 8 shows an SEM image of titanium oxide nanotubes with different sintering temperatures, and Fig. 9 shows the TEM image.

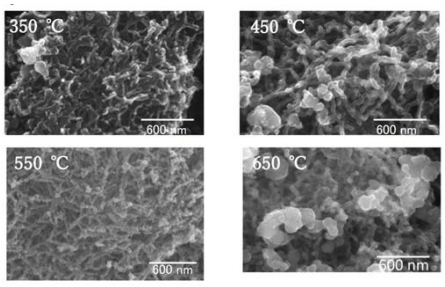

Figure 8: SEM image

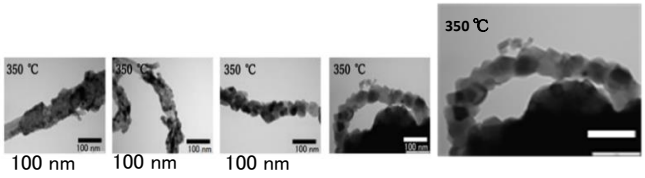

Figure 9: TEM image

According to SEM observation, the yield of nanotubes decreased in those calcined at 650 ° C, and many aggregated parts were observed. TEM observation revealed that carbon nanotubes remained at 350 ° C and 450 ° C without any change.

3.2.3 *Absorbance of catalyst*

The visible ultraviolet spectroscopic spectrum of the catalyst at each sintering temperature was measured. The results are shown in Fig. 10. When the sintering temperature was low, absorption was observed in the visible light region, but the excitation wavelength did not change significantly as before.

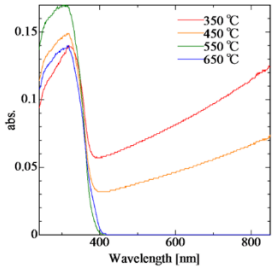

Figure 10: Visible UV absorption spectrum

3.2.4 *X-ray diffraction*

The X-ray diffraction of the catalyst was measured with changes in the firing temperature. It is shown in Fig 11, where A shows anatase peak and B shows rutile peak. At 350 ° C and 450 ° C, carbon nanotubes remained, but the peak of carbon nanotubes was not detected, and the peak was the same as that of titanium oxide prepared without adding carbon nanotubes, so titanium oxide was deposited on the carbon nanotubes. In addition, there was no peak indicating rutile. On the other hand, it was found that anatase and rutile were mixed at 550 ° C and 650 ° C. Table 4 shows the content and crystal size of each crystal phase. As the calcination temperature was raised, the crystal phase of rutile grew, and the crystal size of anatase increased.

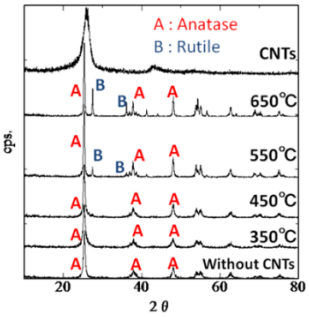

Figure 11: X-ray diffraction

Table 4: Crystal phase content and crystal size

Calcination temperature (°C)	Anatase		Rutile	
	Cristal size, D(101) (nm)	X_A (%)	Cristal size, D(110) (nm)	X_R (%)
Without CNTs	15	100	-	0
350	13	100	-	0
450	17	100	-	0
550	27	85	40	15
650	32	70	40	30

3.2.5 BET surface area

The BET surface area of titanium oxide nanotubes at which the sintering temperature was changed was measured. The results are shown in Table 5. As the sintering temperature increased, the specific surface area of the titanium oxide nanotubes decreased. Therefore, the surface area is considered to be one of the factors affecting the photocatalytic activity. The adsorption isotherm at 350 ° C is shown in Fig. 12, and the pore distribution curve is shown in Fig. 13.

Table 5: Specific surface area of titanium oxide nanotubes

Calcination temperature (°C)	Surface Area (m^2/g)
Without CNTs	17.0
350	81.0
450	79.9
550	27.4
650	11.6

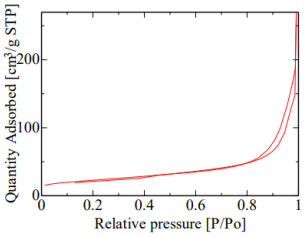

Figure 12: Adsorption isotherm

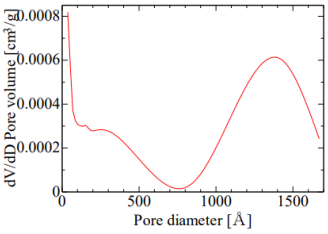

Figure 13: Pore distribution curve

3.2.6 Interaction between titanium oxide and carbon nanotubes

Temperatures 350 °C and 450 °C are considered to be affected by the interaction with carbon nanotubes. Figure 14 shows the reaction pathway. When the titanium oxide is exposed to light, the electrons are excited and separated into electrons and holes. If only titanium oxide is used, recombination will occur here. However, when titanium oxide is present on the carbon nanotubes, the generated electrons move to the carbon nanotube side, so that the recombination of the electrons and holes is suppressed. As a result the photocatalytic activity was enhanced.

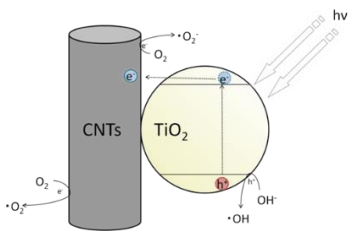

Figure 14: Reaction path of titanium oxide and carbon nanotubes.

4. Conclusions

By using carbon nanotubes with different outer diameters, it was possible to control the outer diameter of titanium oxide nanotubes. The photocatalytic activity of titanium oxide nanotubes tended to be higher than that of sub-μ titanium oxide particles, and the activity tended to be higher when the outer diameter of titanium oxide nanotubes was smaller. Moreover, by sintering at a low temperature, a complex photocatalyst with carbon nanotubes could be produced. By using this complex photocatalyst, the photocatalytic activity could be further improved.

Acknowledgements

Part of this research was carried out in University Collage TATI, GRANT NO. 9001-2011. Any opinions, findings, Conclusions or recommendations expressed in this paper are those of the authors and do not necessarily reflect the view of the supporting organizations.

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