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Photocatalytic Performance of Zn Doped-TiO_2 Nanotube Particles for Methylene Blue Degradation

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Abstract

TiO_2 nanotube (TiO_2-NT) is one of the promising materials for photocatalytic water remediation. Zn doped -TiO_2-NT (Zn/TiO_2-NT) is synthesized from P25 Degussa via one step hydrothermal method. The XRD and UV-DRS analysis results showed that Zn as a doping material led to decrease band gap energy and decrease the crystal size. The best results obtained was Zn/TiO_2-NT with a crystal size of 7.14 nm, and band gap energy value of 3.18 eV. Photocatalytic performance of Zn/TiO_2-NT samples for textile dye (methylene blue) degradation was examined. Photocatalytic performance was examined under UV mercury lamp for 240 minutes in a photoreactor chamber. During the photocatalytic degradation of methylene blue, the Zn/TiO_2-NT shows considerably higher activity (95.88%) than the non-doped sample (87.72%). This result proved that a smaller crystal size and lower band gap energy led to higher photocatalytic activity.

Keywords: TiO_2 nanotube; Zn doping; one-step hydrothermal; photocatalytic activity; methylene-blue degradation

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INTRODUCTION

Recently, case of environmental aquatic pollution that caused by wastewater generated from various industries has been increasing. One of the industries that produces large quantity of liquid waste is the textile industries (Handojo et al., 2019). They use a lot of dyes in their production process. If the wastewater is not treated properly, it will cause serious contamination to the water system and lead to aquatic pollution. In addition to the changes in color and turbidity, the release of unpleasant odor are the common signs of contamination in the water (Belekbir et al., 2020; Alulema et al, 2021; Hashemi et al, 2021). These conditions will lead to environmental damage and disrupt the survival of the living inhabitants, such as animals, plants and human. Therefore, it is urgent to implement an efficient and economical wastewater treatment.

Photocatalyst using semiconductors is considered the most effective method to be applied in wastewater

treatment because it is relatively inexpensive and practical (Alulema et al, 2021; Eidsvåg et al., 2021; Wang et al., 2022). The commonly used semiconductors in the photocatalyst preparation include titanium dioxide (TiO_2), zinc oxide (ZnO), and cadmium sulfide (Sudha and Sidakumar, 2015) Titanium dioxide (TiO_2) is a type of semiconductor that is most widely used as a photocatalyst material, because it provides several advantages, such as corrosion resistant, abundantly available in nature, and cheaper than other semiconductor materials (Nursanto et al., 2014; Nursanto et al., 2019). However, TiO_2 has a wide bandgap energy value of 3.2 eV that potentially affects the excitation of electrons from the valence band to the conduction band (Huang et al., 2016; Yu et al., 2014).

In order to increase the efficiency of TiO_2 as a photocatalyst, addition of metal materials as doping into the crystal structure of TiO_2 that allows active sites enhancement can be a smart alternative. The improvement of TiO_2 surface area can be carried out by changing the shape of TiO_2 from nanoparticles to TiO_2 nanotubes (TiO_2-NT). Metals doping on TiO_2 led to an increase in its ability to capture charge carriers and reduce recombination rate between e^- and h^+. In previous studies, various metal doping materials, such as cobalt (Co), barium (Ba), manganese (Mn), nickel (Ni), copper (Cu), zinc (Zn), and iron (Fe) had been evaluated for their ability to improve photocatalytic performance (Aritonang et al, 2018; Zakir et al, 2023; Hashemi et al., 2021). Previous research proved that metals as doping materials were able to reduce the crystal size of TiO_2 (Nursanto et.al, 2023). The addition of metal doping led to suppress the crystal size of TiO_2 by inserting metal into the octahedral lattice structure of TiO_2, that subsequently affects into physicochemical properties of TiO_2. Theoretically, smaller crystal size will exhibit higher photocatalytic activity because it can reduce photo-generating charge carrier recombination activity.

Zn doped TiO_2 and TiO_2 nanotubes have been synthesized through several methods, such as hydrothermal, sol-gel, template formation, and electrochemical anodization (Mao et al, 2021; Song et al., 2024). In this research, we combined TiO_2 nanotubes fabrication and Zn doping into one-step hydrothermal synthesis. Zn doping on TiO_2-NT is expected to reduce the bandgap energy and crystal size, by which increases photocatalytic activity of the resulting composites for methylene blue degradation.

RESEARCH METHOD

Synthesis of Zn doped TiO_2 nanotubes

Zn doped TiO_2 nanotubes (Zn/TiO_2-NT) samples were fabricated from mixture of TiO_2 *(*P25 Degussa*)* and Zn $(CH_3COO)_2.2H_2O$ (Sigma Aldrich) according to molar ratios tabulated in Table 1. Sixty millilitres of 10 M NaOH solution (Sigma Aldrich) was added to the mixture of Zn and TiO_2 precursors and vigorously stirred for 1 hour. Then, the resulting solutions were introduced into a hydrothermal reactor (autoclave) and heated at 120°C for 24 hours. After hydrothermal reaction, the solutions were washed with 0.1 M HCl (Sigma Aldrich) solution until their pH value reached about 1-2. Afterward, the samples were centrifuged until neutral pH solutions were formed. The separated solids from centrifuge were dried in an oven at a temperature of 80°C for 6 hours. After drying for 4 h, the samples were further annealed in a furnace at 450^{o}C for 2 hours.

Table 1. The molar ratio between TiO_2 and Zn precursors

Samples	TiO_2 (P25) : $Zn(CH_3COO)_2.2H_2O$
A	20 : 0
B	20 : 0.5
C	20 : 1
D	20 : 1.5
E	20 : 2

Materials characterization

The X-Ray Diffraction and UV-Vis Reflectance Spectrophotometer were employed for materials characterization. X-Ray Diffraction (XRD, Olympus BTX II, Benchtop) analysis was used to investigate the crystal properties of the resulting Zn/TiO_2-NT. Meanwhile, the UV-Vis Diffuse Reflectance (UV-Vis DRS, Shimadzu) Spectrophotometer was used to determine the value of the band gap energy of the Zn/TiO_2-NT formed**.**

Photocatalytic performance evaluation

Photocatalytic degradation performance of the Zn/TiO_2-NT samples was assayed in a photoreactor chamber. Samples weighed as much as 0.1 grams were transferred to 100 ml beaker glass containers, which were covered with aluminum foil. Then, 20-ppm methylene blue solution was added into each beaker glass. Accordingly, approximately 2 ml of the mixture was pipetted then transferred to a centrifuge tube for initial methylene blue concentration test. This sample was recorded as a 0-minute sample. The rest of the mixture was stirred for 1 hour to allow photocatalytic degradation. During photocatalytic performance examination, 2 ml samples were withdrawn at 15, 30, 60, 120, 150, 180, and 240 minutes for methylene blue concentration analysis using a UV-Vis spectrophotometer. The sample solution was centrifuged at 7000 rpm for 10 minutes.

RESULT AND DISCUSSION

Figure 1 presents X-ray diffraction pattern of Zn doped-TiO_2 nanotubes samples (Zn/TiO_2-NT). The anatase phase of TiO_2 is detected on all samples. Based on data obtained and compared with data from JCPDS, sample A (only TiO_2-NT) has an anatase phase at 2θ angles of 25.32^o and 37.38^o. Sample B has an anatase phase at 2θ angles of 25.19^o and 37.87^o.

Meanwhile, sample C has an anatase phase at 2θ angles of 25.09º and 37.78º. Accordingly, sample D has an anatase phase at 2θ angles 25.25º and 37.78º, and finally, sample E has an anatase phase at 2θ angles 25.25º. and 37.89º. No rutile phase was detected on all samples due to the low calcination temperature during annealing process (T < 700ºC).

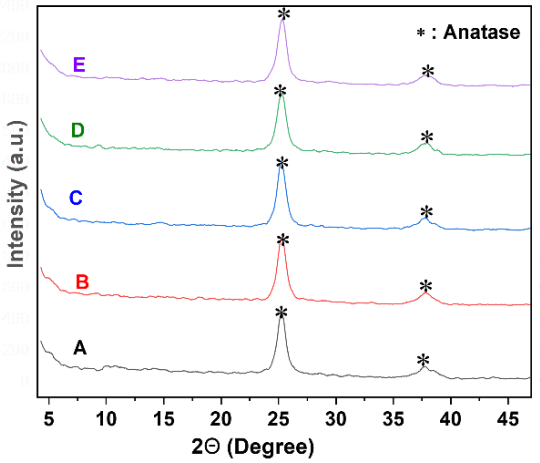

Figure 1. Diffractogram results of Zn/TiO_2-NT samples

Crystal size of each sample was examined using XRD analysis, which was calculated based on crystal peak in XRD result using Scherrer equation. The results are summarized in Table 2.

Table 2. The crystal size of Zn/TiO_2-NT samples

Samples	2θ angle (degree)	crystal size (nm)
A	25.32	8.47
B	25.19	7.27
C	25.09	7.14
D	25.11	7.17
E	25.25	7.42

Table 2 proves that the addition of Zn doping is able to reduce crystal size of TiO_2-NT. Based on previous research conducted by Song et al. (2024), addition of metals doping led to reduce TiO_2-NT crystal size. Furthermore, a smaller crystal size can be expected to increase redox ability of TiO_2-NT (Wang et al, 2022). As a consequence, an increase in redox ability will enhance photocatalytic activity of the resulting TiO_2-NT.

Figure 2 displays SEM analysis of top view images of sample A (TiO_2-NT) and sample C (Zn/TiO_2-NT). The top view SEM images from A and C samples confirm the existence of nanotube structure.

Figure 3 demonstrates the diffuse reflectance spectroscopy of Zn/TiO_2-NT samples at a wavelength of 200 to 800 nm. The result presents an increase in absorbance at a wavelength of 400 nm for all samples.

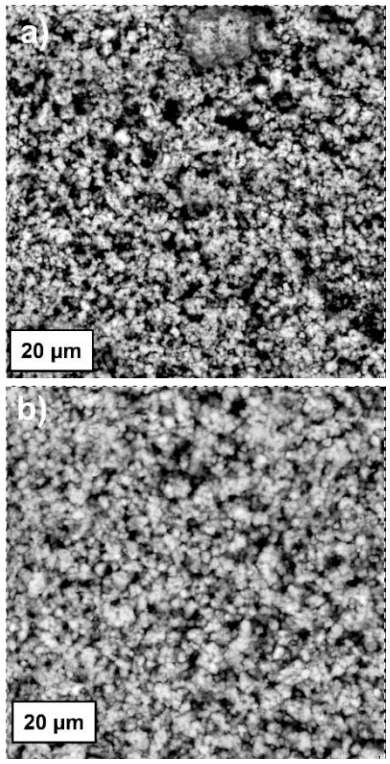

Figure 2. Top SEM images of (a) TiO_2-NT and (b) Zn/TiO_2-NT samples

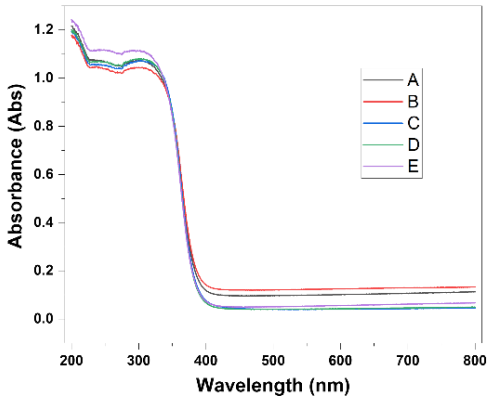

Figure 3. Diffuse Reflectance Spectroscopy (DRS) of Zn/TiO_2-NT samples

Based on Figure 3, the Zn/TiO_2-NT sample has a higher absorbance than only TiO_2-NT (sample A). This indicates that samples with a higher doping ratio have better absorption rate in visible light. In addition to observing the electronic tendency of semiconductor material, the DRS spectrophotometer is also used to determine the energy required for electrons to excite from the valence band to the conduction band of Zn/TiO_2-NT samples. The amount of band gap energy can influence the performance of the semiconductor which can cause inhibition of excitation of electrons from the valence band to the conduction band. The calculation is carried out using the Kubelka Munk method, namely the band gap energy obtained from the graph of the relationship between hv (eV) and

$(F(R')\ hv)^{1/2}$ (Nursanto et al., 2023). The calculated bad gap energy of each sample is presented in Table 3.

Table 3. Band gap energy of samples

Samples	Band gap energy (eV)
A	3.21
B	3.20
C	3.18
D	3.19
E	3.20

The addition of Zn metal as a doping material is very effective in increasing the performance of TiO_2-NT due to a lower fermi level of Zn than TiO_2. As a result of this activity, the performance of the TiO_2 photocatalyst increases by reducing the formation of electrons and holes. From Table 3, sample A only (TiO_2-NT) has a band gap energy value of 3.21 eV, while the other samples (Zn/TiO_2-NT) have lower band gap energies of TiO_2-NT.

The photocatalytic activity of Zn/TiO_2-NT samples are analyzed based on their ability to degrade the selected model pollutant found in textile wastewater, which was methylene blue/MB ($C_{16}H_{18}N_3SCl$). The ability of TiO_2-NT and Zn/TiO_2-NT in degrading pollutants is influenced by several factors including dye concentration, pH, photocatalyst structure or morphology, the ratio between photocatalyst and pollutant, and irradiation time. The photocatalytic reaction process begins with formation of OH^- radical from H_2O. Then, light is absorbed by Zn/TiO_2-NT followed by holes formation. If the semiconductor catalyst is exposed to light that has higher energy, the electrons (e^-) in the valence band will excite towards the conduction band and will leave holes (h^+) in the valence band. Then, the hole (h^+) reacts with H_2O and OH^-, which act as strong oxidizing agents. Furthermore, electrons (e^-) reacts with O_2 in the catalyst to form superoxide radicals ($\bullet O_2^-$), which act as reducing agents.

The mechanism of the Zn/TiO_2-NT photocatalyst in degrading methylene blue (MB) is described in the following equations:

$$TiO_2 + h\nu \longrightarrow h^+ + e^- \quad (1)$$

$$Zn^{2+} + h\nu \longrightarrow Zn^+ + h+ \quad (2)$$

$$MB + h^+ \longrightarrow OH\bullet \quad (3)$$

$$OH\bullet + MB \longrightarrow \text{Degradation product} \quad (4)$$

The photocatalytic activity of TiO_2-NT and Zn/ TiO_2-NT in degrading methylene blue in a photoreactor was carried out using 100 ml of methylene blue solution with a concentration of 20 ppm. Firstly, the mixture of Zn/TiO_2-NT samples and methylene blue solutions were stirred for 1 hour under conditions without light before being irradiated by a mercury lamp. No degradation of methylene blue was observed, when the solution was stirred for 1 hour without light. This evidence shows that methylene blue is not degraded when the mixture is placed in a dark place, since Zn/ TiO_2-NT is only active when sufficient amount of energy is provided by light.

Secondly, Zn/TiO_2-NT samples and methylene blue were stirred and irradiated under a UV mercury lamp for 240 minutes. Changes in color intensity was used as indicator for methylene blue degradation. As seen in Figure 4, methylene blue contained in the solution was degraded by Zn/TiO_2-NT (samples A to E) at 0,15, 30, 60, 120, 150, 180 and 240 minutes.

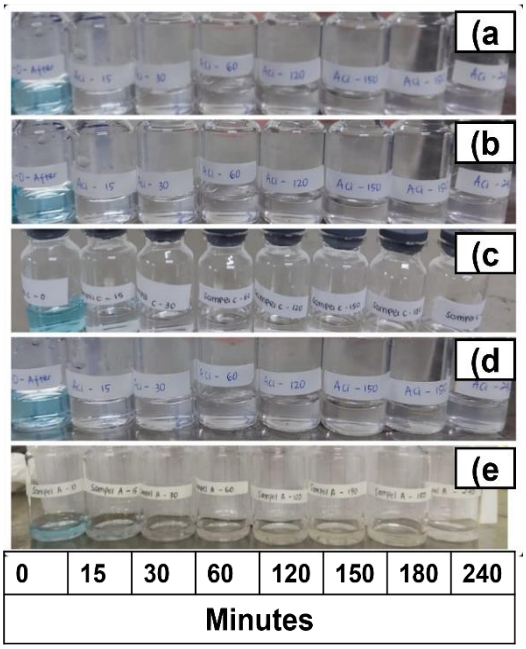

Figure 4. Methylene blue samples after photocatalytic treatment at 0 until 240 minutes by using Zn/ TiO_2-NT (Zn/ TiO_2-NT A to E)

Figure 5 exhibits % degradation of methylene blue by photocatalytic reaction with TiO_2-NT and Zn/TiO_2-NT samples at 0, 15, 30, 60, 120, 150, 180 and 240 minutes. It is clearly shown in Figure 5 that the % degradation of methylene blue is almost stable after 150 minutes photocatalytic reaction.

Table 4 shows the results for % degradation of each sample after 240 minutes photocatalytic process. From Table 4, samples C and D have a higher % degradation compared to samples A, and P25. This is because samples C, and D have a lower particle size and band gap energy than sample A. This is following the theory according to Zakir group (Zakir et.al., 2023), where the addition of metal in the form of Zn as doping can increase the photocatalytic activity of TiO_2-NT. Addition of metal doping can reduce the particle size and a band gap energy from TiO_2-NT.

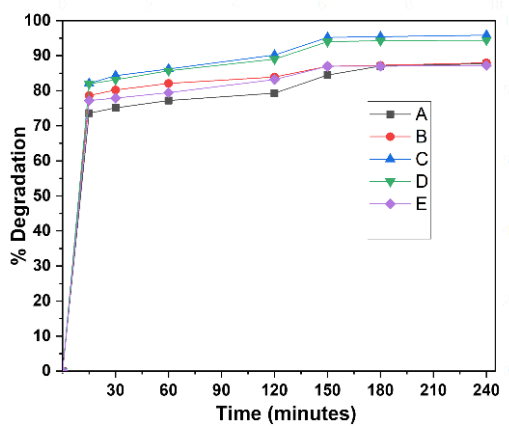

Figure 5. The photocatalytic activity of Zn/TiO_2-NT samples for methylene blue degradation

Table 4. The Degradation of methylene blue for each sample after 240 minutes

Samples	% Degradation of Methylene Blue
P25	84.13
A	87.72
B	87.97
C	95.88
D	94.42
E	87.24

CONCLUSION

TiO_2 nanotubes (TiO_2-NT) and Zn doped TiO_2 nanotubes (Zn/TiO_2-NT) have been successfully synthesized using commercial TiO_2 (P25 Degussa) and Zn $(CH_3COO)_2.2H_2O$ using the hydrothermal method in an autoclave at a temperature of 120°C for 24 hours. Based on the XRD result, the crystal size of TiO_2 nanotubes (TiO_2-NT) was 8.47 nm and sample C displayed smallest crystal size of 7.14 nm. Sample C also exhibited lower band gap value (3.18 eV) compared to band gap of TiO_2-NT (3.21 eV). Smaller crystal size and lower band gap value for Zn/TiO_2-NT led to higher photocatalytic activity for methylene blue degradation. This is proven by high % degradation of methylene blue on Zn/TiO_2-NT (95.88%) compared to TiO_2-NT (87.72 %).

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