Synthesis of ZnO-TiO2/Chitosan Nanorods by Using Precipitation Methods and Studying Their Structures and Optics Properties at Different Precursor Molar Compositions

Y Rilda1*, D Damara1, Syukri1, Y E Putri1, Refinel1, and A Agustien2
1Department of Chemistry, Faculty of Mathematics and Natural Sciences, Andalas University, Indonesia
2Department of Biology, Faculty of Mathematics and Natural Sciences, Andalas University, Indonesia

*yetriarilda@yahoo.com

Abstract. ZnO-TiO2/Chitosan nanorods were synthesized by precipitation method from mixture Zinc nitrate dihydrate (Zn(NO3)2.2H2O) and Titanium Iso Propoxide (TIP) as precursors with different ratio molar composition of ZnO and TiO2 at pH = 11.0. Then, addition of sodium hydroxide (NaOH) and Methyleneamine (C6H12N4) for control pH solution. ZnO-TiO2/Chitosan resulting from the characterization of X-ray diffraction (XRD) show that ZnO-TiO2/Chitosan with hexagonal wurtzite structures. The nanorods size of ZnO-TiO2/Chitosan is (35–42) nm. Surface topographic information investigated by Scanning Electron Microscopy (SEM) shows the distribution of shapes are nanorods. The interactions Zn-O-Ti were studied on the Fourier Transform-Infrared Spectroscopy (FT-IR) analysis on wave numbers 680 cm⁻¹. The optical properties indicated UV-Vis Diffuse Reflectance Spectroscopy (UV-DRS) shows the result of modification of different precursor compositions of ZnO and TiO2 giving a smaller value (Eg = 3.24–3.25 eV) when compared without doped TiO2 (Eg = 3.32 eV) and on any different the composition significantly does not provide different band gap values.

Keyword: ZnO-TiO2, Chitosan, Synthesis

1. Introduction
Zinc oxide (ZnO) is among the most extensively studied II–VI semiconductors for photocatalyst applications, owing to its wide band gap (Eg = 3.37 eV at 300⁰K) and large exciton binding energy (60 meV) [1-3]. In particular, the one-dimensional (1D) ZnO nanostructures display very excellent photocatalyst activity because of possessing effective carrier transport and large surface area. In addition, ZnO has excellent crystalline quality, high electron mobility, wave guiding effect, and the possibility of quantum confinement. The excitation light of ZnO was in ultraviolet region, which means the low utilization of daylight [4]. Moreover, the electron-hole pair has a high recombination rate due to the charge attraction, and all these would reduce the photocatalyst antibacterial performance. Several of strategies have been adopted to improve the charge separation efficiency and then enhance the photocatalyst activity such as the semiconductor doping, decorating, constructing hetero junctions, and catalyst carrier, were usually used to enhance the photocatalyst and antibacterial activity of ZnO nano structure[5-7].

The coupling of other semiconductors to form hetero junctions with ZnO is also interesting because varying interfacial interactions provide new properties, which do not belong to any individual nanomaterial. Semiconductors that can be used such as, TiO2, CuO, CdS, and etc. In the number of various semiconductors, which were used; titanium dioxide (TiO2) was one of the most important photocatalyst for the degradation of environmental contaminants. This is because of its high photocatalyst activity, non-toxicity, chemicals stability under different conditions, non orrosion and relative inexpensiveness. TiO2 can reduce band gap and increase of photoactivity of ZnO because it has smaller band gap. TiO2 carries out this by increasing the charge separation and extending excitation energy range[8]. The TiO2 can also decrease corrosion of ZnO. Currently, a large number of researches have been carried out to investigate the effectiveness of ZnO-TiO2 mixed oxides for degrading several organic pollutants. These mixed oxides can be synthesized by using various methods such as sol-gel and precipitation methods because of simplicity, reproducibility, lower processing temperatures, high purity...
of materials and good control of the size and the shape of the nanoparticles[9-10]. The precipitation process, pH greatly affects the shape of the crystals produced, at different pH it will give different ZnO morphology [11]. Liu (2015) report at pH = 11.0 can be produced of ZnO nanorods with best crystallization, nanosize and good optical properties. The form of nanorods has high photocatalyst activity.

2. Experimental Methods

2.1. Material

The materials used in this study are distillad water, Tetra Ethyl orto Silicate (TEOS) (C₈H₂₀O₄Si) (Merck), Hydrochloric Acid (HCl) (Merck), Acetic Acid (CH₃COOH) (Merck) and Isopropanol (C₃H₈O) (Merck), Cetyl Trimethyl Ammonium Bromide (CTAB) (C₁₈H₃₃N(CH₃)₃Br) (Merck), technical chitosan (C₆H₁₁NO₄)n, Zinc Nitrate Dihydrate (Zn(NO₃)₂.2H₂O) (Merck), Methyleneamine (C₆H₁₂N₄) (Merck), Sodium Hydroxide (NaOH) (Merck), culture of Staphylococcus epidermis. All chemicals were used as received without further purifications.

2.2. Preparation ZnO-TiO₂/chitosan

Zinc nitrate dehydride (2.72 g) was dissolved in distilled water (100 mL) under constant stirring to which a molar solution of NaOH (20 mL) was added at 60 °C. After that, methylenamine was added into the solution. The solution was continuously stirred for 3 h at 60 °C. Suspension of ZnO was obtained. Simultaneously, Suspension of ZnO seed was made by 0.81 g ZnO nanoparticles which dissolved in distillad water. Then, the solution was continuously stirred for 2h. And suspension of TiO₂ was made by sol-gel method from TIP: DEA (1:2) molar ratio. Different composition of Zn and Ti is by molar ratio (3:1) and (1:1)[8]. After that, all of the suspension were mixed. The chitosan and CTAB were added to control growing of nanomaterial. The mixed continuously stirred for 6 h. Finally, ZnO-TiO₂/chitosan were obtained after calcination at 600°C for 6 h. ZnO-TiO₂/chitosan were characterized by XRD, FT-IR, UV-Vis DRS and SEM-EDX.

2.3. Characterization

The crystal structures of the prepared materials were characterized by powder X-ray Diffraction (XRD) using an XPERT MPD_PRO diffractometer with Cu Kα radiation. The accelerating and the applied current were 45 kV and 40 mA, respectively. The determination of the crystalline phases was carried out by applying the Bragg law where λ= 1.5406 Å. Fourier Transform Infra-Red (FT-IR) spectra were obtained as KBr pellets in the 600–4000 cm⁻¹ wavenumber range using an FT-IR spectrometer (type JASCO 4100). The morphologies and elemental analysis of the prepared nanoparticles were determined by SEM (Scanning Electron Microscopy combined with Energy Dispersive X-ray spectroscopy (EDX). Diffuse Reflectance UV–Vis spectra were recorded using a JASCO V-570 spectrophotometer equipped with a Lab sphere DRA-CA-30I integration sphere using BaSO₄ as reference.

3. Result and discussion

3.1. Synthesized ZnO-TiO₂/chitosan

ZnO-TiO₂/chitosan is synthesized by precipitation method. In this synthesis using ZnO nanoparticle as seed for ZnO particle growth. The Zn (NO₃)₂ precursor is ionized to form Zn²⁺ ion as a zinc source. Then it is precipitated with NaOH to form a white precipitate of Zn (OH)₂.

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\begin{align*}
\text{Zn}^{2+} + \text{OH}^- & \leftrightarrow \text{Zn(OH)}_2 \quad (1) \\
\text{C}_8\text{H}_{16}\text{N}_4 + 6\text{H}_2\text{O} & \leftrightarrow 6\text{CH}_2\text{O} + \text{NH}_3 \quad (2) \\
\text{NH}_3 + \text{H}_2\text{O} & \leftrightarrow \text{NH}_4^+ + \text{OH}^- \quad (3) \\
\text{Zn(OH)}_2 + 4\text{NH}_3 & \leftrightarrow \text{Zn(OH)}_2(\text{NH}_3)_4 \quad (4) \\
\text{Zn(OH)}_2(\text{NH}_3)_4 & \leftrightarrow \text{ZnO} + 4\text{NH}_3 + \text{H}_2\text{O} \quad (5) \\
\text{Zn(OH)}_2 + 4\text{NH}_3 & \leftrightarrow [\text{Zn(NH}_3)_4]^{2+} + 2\text{OH}^- \quad (6) \\
[Zn(\text{NH}_3)_4]^{2+} + 2\text{OH}^- & \leftrightarrow \text{ZnO} + 4\text{NH}_3 + \text{H}_2\text{O} \quad (7) \\
\text{Zn(OH)}_2 + 2\text{OH}^- & \leftrightarrow [\text{Zn(OH)}_4]^{2-} \quad (8)
\end{align*}
\]
Addition of methylenamine as a buffer and source of ammonia (NH$_3$). Zn (OH)$_2$ reacts with NH$_3$ to form a complex compound $[\text{Zn (NH}_3)_4\text{]}^{2+}$ or Zn (OH)$_2$(NH$_3$)$_4$. ZnO (ZnO growth) is formed from the decomposition of these two compounds, besides that it is also formed from dehydration of Zn (OH)$_2$. ZnO crystal growth occurs in seed ZnO which begins with crystal nucleus formation. The growth process is controlled by the addition of CTAB and chitosan as well as printing the pores of nanoparticles[10]. In the deposition, the pH of the solution is also considered, because the formation of ZnO nanoparticles depends on pH[13]. In this study the pH is set to 11, where the pH is good. At this pH, ZnO nanoparticles have better crystal. This is in accordance with the XRD pattern in figure 2. The addition of TTIP sol in DEA as the source of Ti by sol-gel method is to form a ZnO-TiO$_2$/chitosan hybrid[14-15].

3.2. Analysis XRD (X-ray diffraction)
In Figure 3.1 shows the X-ray pattern of ZnO/chitosan, ZnO-TiO$_2$/chitosan and ZnO standard (JCPDS no. 36-1451) with wurtzite hexagonal structure. The sample pattern with the standard is almost the same, it can be concluded that ZnO has a hexagonal wurtzite with nine main peaks at (100), (002), (101), (102), (110), (103), (200), (112) and (201)[7]. In this study synthesis of ZnO-TiO$_2$/Chitosan with the difference of molar ratio Zn and Ti aims to see the effect of modification of ZnO nanoparticles with TiO$_2$. The XRD pattern, the more TiO$_2$ that is loaded reduce the crystallinity. That is, TiO$_2$ inhibits crystal growth from ZnO. On the contrasts, the size of the crystal is increasing when the amount of TiO$_2$ composition[16]. Based on calculations, the size of pure ZnO crystals is 35.65 nm. Whereas, ZnO-TiO$_2$/chitosan (3:1) and ZnO-TiO$_2$/ chitosan (1:1) each had a crystal size of 35.8 nm and 41.5 nm.

3.3. Analysis FT-IR (Fouter Transforman Infra Red)
FT-IR analysis was used to study the interaction in ZnO and ZnO-TiO$_2$ particles. In figure 3 shows the characteristic peaks of ZnO-H terminals at 1645 and 3400 cm$^{-1}$. The peaks at 860 cm$^{-1}$ indicated of Zn-OH bonds. The new peak appeared in treated ZnO-TiO$_2$ spectra at 680 cm$^{-1}$ attributed to Zn-O-Ti bonds. At a peak of 2200 cm$^{-1}$ shows the N-O bond, the nitrogen is derived from chitosan that lives after calcination. Based on the above analysis it can be said that the synthesis of ZnO-TiO$_2$/ chitosan has been successful[17]. FT-IR analysis has a correlation with EDX analysis based on semi-qualitative composition.
3.4. Analysis SEM-EDX

The surface morphology of ZnO-TiO$_2$/chitosan with molar ratio is (3:1) shown in Figure 4. Based on the picture, it can be seen that the particles of ZnO-TiO$_2$/chitosan are bars with a length of about 3 micrometers and a diameter of 400 nanometers. The size of the particles obtained is quite large, of course the surface area is smaller.

EDX analysis ZnO-TiO$_2$/chitosan with (1:1 and 3:1) molar ratio shown in Figure 3 has a composition, namely: (1:1) O = 71%, Ti = 15.2% and Zn = 13.8% and (3:1) O = 31.6%, C = 49.7%, Ti = 3.66% and Zn = 15.1%. Based on EDX analysis can calculate the comparison of the composition of Zn and Ti from synthesized powder. The results of the calculation prove that the comparison of the synthesis composition is in accordance with the product obtained, and can be correlation with FT-IR analysis.

Figure 3. The FT-IR pattern of (a) ZnO (b) ZnO-TiO$_2$/chitosan (3:1) and (c) ZnO-TiO$_2$/chitosan (1:1).

Figure 4. SEM image of ZnO-TiO$_2$/chitosan nanorods in molar Zn dan Ti. A. (1 : 1) and pH =11.0 B. Nanorods in molar Zn dan Ti (3:1)
Figure 5. EDX Pattern for the result of qualitative analysis of the composition nanorods Zn-TiO2/chitosan nanorods in molar Zn and Ti (3 : 1) and pH =11.0

Analysis UV-Vis DRS
The UV-Vis DRS results are shown in Figure 5a is ZnO, (5b) ZnO-TiO2/chitosan (1:1) and (5c) ZnO-TiO2/chitosan (3:1) containing 16.7% Ti and 50% Ti, respectively. These results indicate sharp absorption in the UV domain. The prepared ZnO-TiO2 nanomaterial showed new optical properties, which differed from ZnO which showed that the diffusion reflectance spectrum of ZnO-TiO2 nanomaterials was made by precipitation method with red Ti variations when compared with TiO2. Red shift can be caused by the composition of the crystal phase, morphology and particle size.

The previously prepared sample energy gap is calculated by plotting $(\alpha h\nu)^n = A (h\nu - E_g)$, where $A$ is the proportionality constant, $\alpha$ is the linear absorption constant, $h$ is the Planck constant, and $n = 2$ and 0.5 for the band transition - directly and indirectly, each shows a plot of $(\alpha h\nu)$ versus $h\nu$ assuming a direct band-gap transition for all samples [18].

Figure 6. UV-Vis DRS spectrum of (a) ZnO/chitosan (b) ZnO-TiO2/chitosan (1:1), (c) ZnO-TiO2/chitosan (3:1)

The result of the band gap value is a decrease in which the band gap of ZnO is 3.37 eV while that of the research is 3.27 eV. With modification with TiO2 there was also a significant decrease in band gap value. The TiO2 band gap value is 3.2 eV. Based on the results of the modification, it was obtained band gap ZnO-TiO2/chitosan (1:1) and ZnO-TiO2/chitosan (3:1), namely 3.25 and 3.24 eV respectively. The decrease in band gap is caused by TiO2 particles contained in ZnO particles. In addition, the morphology and particle size affect the absorption of light.

4. Conclusion
In this study, the obtained physicochemical characterization results indicated that the crystalline
structure, the optical and the morphological properties of the ZnO-TiO2/chitosan are strongly influenced by the preparation precipitation method as well as the ZnO and TiO2 weight ratio. Analysis XRD and SEM-EDX show that Zinc oxide nanocrystal with wurtzite hexagonal structures. The crystal size of ZnO-TiO2/chitosan is between 35 – 42 nm with distribution of homogeneous and shapes are nanorods. The interactions Zn-O-Ti on wave numbers 680 cm⁻¹ were studied with FT-IR. The UV-Vis-DRS show different compositions Ti giving a smaller value (Eg = 3.24 – 3.25 eV) when compared without doped TiO2 (Eg = 3.32 eV). The ZnO-TiO2/chitosan composite can be used potential as a photocatalyst.

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