ABSTRACT
The core-shell synthesis of SiO$_2$ (shell) and ZnO (core) carried out in a system, involves the use of Poly(diallyldimethylammonium chloride) (PDDA) and Poly(sodium 4-styrenesulfonate) (PSS) compounds as a crosslinker. Also, ZnO-SiO$_2$-Chitosan core-shell was synthesized, using the hydrothermal method at a temperature of 180°C, for 24 hours. This study is aimed at optimizing the coating of SiO$_2$ on the surface of ZnO, using the varied composition of PDDA and PSS in the ratio (1:1, 1:2 and 2:1), to the ZnO precursor composition ratio of (1:1). However, the multilayer hybrid process is carried out in stages: O-Zn-O/PDDA/PSS/O-Si-O. This method resulted in a corresponding increase in layer formation due to a higher PDDA composition ratio of (2:1), thus leading to greater SiO$_2$ covering on the surface of ZnO (core-shell ZnO-SiO$_2$). This was indicated by a relatively smaller crystal size of 30.08 nm, with hexagonal wurtzite structure at 2θ = 3˚, 34˚, 36˚, and hkl [1 0 0] [0 0 2] and [1 0 1], based on JCPDS36-1451 standards. Furthermore, density analysis nanorod pattern evaluated using SEM-EDX morphology shows the following composition elements: N, O, Si and Zn with the relative mass percentage of 11.40%, 47.93%, 0.67%, and 40%, respectively. Subsequently, BET/BJH analysis identified a correlation between the smaller crystal sizes and the greater surface area (126.271 m$^2$/g).

Keywords: Surface, Multilayers, Chemical Synthesis, Transmission Electron Microscopy (TEM).

INTRODUCTION
Recently, numerous investigations have focused on the use of ZnO compounds as photocatalysts for the degradation of some organic pollutants. This is due to the high photocatalytic activity, alongside the economic and environmentally-friendly features. Meanwhile, ZnO is a semiconductor metal oxide material belonging to groups II-VI, with gap energy of 3.37 eV, characterized by a large excitation binding energy of 60 meV at room temperature.1,2 This nanomaterial, known as one of the multifunctional inorganic substances with effective antibacterial activity, is been applied across several fields including biosensors, pharmacy3, agriculture4, biomedical5, and textile industry.6 Therefore, the photocatalytic activity of ZnO is strongly influenced by morphology, measurement, and surface properties.7 The ZnO exists in form of nanoparticles8, nanowire9 and nanorods.7 As nanorods, they exhibit morphological features with specifications of length (140-400) nm and diameter (20-150) nm.7 Several synthetic ZnO preparation methods have been used to improve the resulting photocatalytic activity, including pyrolysis,7 sol-gel,10 CVD (Chemical Vapor Deposition),11 solvothermal,12 and hydrothermal.2 However, the hydrothermal process is relatively simple, because of the comparably low temperatures required, alongside higher crystal growth uniformity, and easier control of growth parameters.13 These characteristics make it popular for adoption during the nanorods development. Silica, an inert material, is used to modify the surface of ZnO, thus shows the ability to increase the stability and...
photocatalytic activity of the compound. SiO$_2$ is amorphous, adsorptive, exhibits high thermal properties, and possesses good mechanical attributes; using these features to modify ZnO properties, including reducing crystal size, and also to prevent clusters between the nanoparticles. On the other hand, adding silica to photocatalytic applications controls the duration of the catalytic process in sunscreens. Previous research by Xue et al., (2013), revealed SiO$_2$ coating on ZnO could form a core-shell. Meanwhile, after coating on PET fibers (Polyethylene terephthalate), nanorod crystals accumulate on the surface by hydrothermal means. This procedure is difficult as ZnO is an unstable oxide. Previous research by Xue et al., (2011), reported SiO$_2$ coating on ZnO could form a core-shell. Meanwhile, after coating on PET fibers (Polyethylene terephthalate), nanorod crystals accumulate on the surface by hydrothermal means. This procedure is difficult as ZnO is an unstable oxide.

**EXPERIMENTAL**

**Material**

The materials used in this study were zinc nitrate tetrahydrate (Zn(NO$_3$)$_2$.4H$_2$O), zinc oxide (ZnO), hexamethyleneetetramine (TEOS) (C$_8$H$_20$O$_4$Si), hydrochloric acid (HCl), sodium hydroxide (NaOH), Heksamethylenetetramine (C$_6$H$_12$N$_4$), Isopropanol (C$_3$H$_8$O), Ethanol (C$_2$H$_5$OH), Poly(diallyldimethylammonium chloride) (PDDA), Poly(sodium 4-styrene sulfonate) (PSS), Commercial chitosan (C$_4$H$_11$NO$_4$) and Cetyltrimethyl ammonium bromide (CTAB) (C$_{13}$H$_{33}$N(CH$_3$)$_3$Br).

**Preparation of ZnO-SiO$_2$/Chitosan Powder**

ZnO seeds are prepared by dissolving 0.813 g of ZnO in 10 mL of ethanol and 0.25 mL of aquabides. The solution was stirred for 2 hours, then deposited (Section-1). Then to the ZnO suspension hexamethylenetetramine (HMT) was added in a ratio (1:1), and adjusted pH= 13 with the addition of NaOH. The solution was stirred for 4 hours by heating 60°C (Section-2). To the mixture is added 0.1M PDDA and PSS 0.1M containing 0.5M NaCl, with variations in composition (PDDA and PSS) in variations (1:1, 1:2 and 2:1) (Section-3). Subsequently, the SiO$_2$ suspension of 0.886 mL TEOS in 0.1 M HCl was dissolved in ethanol, homogenized for 8 hours at room temperature (Section-4). Then added to the mixture chitosan and CTAB, (5:1). The mixture is homogenized for 12 hours. Then placed on the autoclave temperature of 180°C for 24 hours. ZnO-SiO$_2$/Chitosan powder was obtained after calcination at 600°C for 4 hours.

**Characterization**

Morphological and elemental analysis of ZnO-SiO$_2$/Chitosan was carried out with SEM-EDX (Scanning electron microscopy-dispersive X-ray spectscopy). TEM (Transmission Electron Microscope) for observing three-dimensional morphology of the ZnO-SiO$_2$/Chitosan nanostructure. The crystal structure is determined using XRD (X-ray diffraction). Crystal phase determination was done by applying the Bragg law where $\lambda= 1.5406$ Å. FT-IR (Fourier transform infrared) spectra were obtained as KBr pellets in the range of 400-4000 cm$^{-1}$ wavenumbers using FT-IR spectrophotometer (JASCO 4100 type). (BET/BJH (Brunauer-Emmett-Teller and Barrett-Joyner-Halenda) analysis based on nitrogen absorption was carried out at 77 K using Belsorp mini II to measure a particular surface area distribution and pore size. The UV-DRS (Diffuse Reflectance Spectrum) was recorded using the JASCO V-570 Spectrophotometer equipped with the Sphere Lab scope of integration of the DRA-CA-301 using BaSO$_4$ as a reference.

RESULTS AND DISCUSSION

**X-ray Diffraction (XRD) Analysis**

XRD analysis provides information about the crystal structure and the crystal size of a material. The formation of multilayer hybrid compounds from ZnO-SiO$_2$/Chitosan patterned nanorods can be identified from the Scherrer equation based on JCPDS36-1451:
Where: $t$ is the size of the crystal, $k$ (constant: 0.89), $\lambda$ (wavelength of X-rays), $\sigma$ (FWHM value), and $\theta$ (diffraction angle). Table-1 of Fig.-1 shows the crystallite size of the hybrid layer influenced by PDDA and PSS cross-linker composition. Essentially, the XRD structure shows the crystal structure of ZnO, wurtzite, and hexagonal geometry with intensity at three highest peaks of $2\theta = 31^\circ$, $34^\circ$, and $36^\circ$ (JCPDS36-1451). Table-1 also indicates the crystal size gets smaller when doped. Note, a greater ratio of PDDA composition in respect to PSS, ZnO-SiO$_2$/Chitosan core-shell (2:1), reflects a smaller crystal size than the ratio (1:1 and 1:2). Furthermore, positive charge contribution from PDDA-distributed on ZnO surface is saturated by negative charges from the PSS, forming an active site for Si$^{4+}$ bonding. Thus, more Si attached to the core reveals a reduction in crystal size. The mirage Si from SiO$_2$ can reduce the intensity and size of crystallization from ZnO to form an active site for Si$^{4+}$ bonding. In the PDDA/PSS composition (2:1), with a crystal size of 30.08 nm, the effects of SiO$_2$ when compared to its undoped state, resulted in a crystal size of 39.91 nm.

![Fig.-1: The XRD Pattern of (a) ZnO/Chitosan, (b) ZnO-SiO$_2$/Chitosan, without PDDA/PSS, (c) ZnO-SiO$_2$/Chitosan (PDDA/PSS) (1:1), (d) ZnO-SiO$_2$/Chitosan (PDDA/PSS) (1:2), (e) ZnO-SiO$_2$/Chitosan (PDDA/PSS) (2:1)](image)

### Table-1: Size ZnO-SiO$_2$/Chitosan Based on the Difference in Composition of PDDA and PSS

| Sample Composition                        | Crystal Size (nm) | Average (nm) |
|-------------------------------------------|-------------------|--------------|
| ZnO/Chitosan                              | 39.44 39.66 40.63 | 39.91        |
| ZnO-SiO$_2$/Chitosan, PDDA:PSS (1:1)     | 41.29 38.68 37.71 | 39.22        |
| ZnO-SiO$_2$/Chitosan, PDDA:PSS (1:2)     | 41.90 36.32 39.00 | 39.07        |
| ZnO-SiO$_2$/Chitosan, PDDA:PSS (2:1)     | 24.89 32.49 33.28 | 30.08        |

### Fourier Transform Infrared (FT-IR) Analysis

However, FT-IR analysis in Fig.-2 of ZnO/Chitosan powder, comparing PDDA and PSS composition (1:1), (1:2), and (2:1), shows the intensity at 400-4000 cm$^{-1}$ wavenumbers, OH stretching in the wavenumber 400-450 cm$^{-1}$, and interaction between Zn-O. Also, with a wave number of around 550 cm$^{-1}$, N-Zn interface and N sources are predicted to come from hexamethylenetetramine bases and Chitosan compounds. However, in the ZnO-SiO$_2$/Chitosan powder sample, there was an interaction in the wavenumber of about 1085 cm$^{-1}$, that is, Si-O-Si. A wavenumber of around 950 cm$^{-1}$ showed the Zn-
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Moreover, there are -OH groups originating from Zn-OH and Si-OH hydrolyzed at wave number 3360-4000 cm$^{-1}$.

![FT-IR Pattern](image)

**Diffuse Reflectance Spectrum Analysis (UV-DRS) Analysis**

UV-Vis DRS analysis provides information about the absorbance, width, or value of the energy gap (Eg) of a synthesized compound. The energy gap is the bandgap energy between the valence band, with the saturation of electrons, and the empty conduction band of electrons. Semiconductor performance required photon sources to excite the electrons and holes. Hence, the UV-Vis DRS results shown in Fig.-3, indicated absorption in the UV range. However, from this figure, the energy gap value of ZnO-SiO$_2$ is (2.96 - 3.13) eV, while for ZnO, the value is 3.37 eV according to the literature. This occurred as a result of introducing SiO$_2$ dopant to the ZnO surface causing a new energy band to form between the valence band and the shorter conduction band, thereby resulting in a decreased energy value. The effect of the differences in the composition of PDDA and PSS does not significantly influence changes in the gap values obtained.

![UV-Vis DRS Spectrum](image)
Scanning Electron Microscopy Energy-dispersive X-ray Spectroscopy (SEM-EDX) Analysis
SEM analysis also describes the surface morphology of ZnO-SiO$_2$/Chitosan with nanorods pattern. Also, Fig.-4 investigates the composition and distribution of the elements in a semi-quantitative manner. This evaluation was carried out with two magnifications, including 40,000 and 80,000. Meanwhile, from Fig.-5, to ascertain the composition and distribution of the elements contained in the ZnO-SiO$_2$ compound, EDX analysis was deployed. The analysis also shows the percentage of ZnO, SiO$_2$ and elements with the following composition: N, O, Si and Zn with relative mass percentages of 11.40%, 47.93%, 0.67%, and 40%, respectively.

Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) Analysis
Furthermore, BET/BJH analysis is generally used to evaluate the external specific surface area, and the value for nitrogen isotherms (N$_2$ adsorption-desorption at 77.3 K) was calculated using the BET equation. Meanwhile, the average pore diameter is obtained through the BJH method. Figure-6 shows ZnO-SiO$_2$/Chitosan curve of JH pore size distribution and nitrogen isotherms. According to IUPAC, the results obtained are classified as type IV, noting an extensive pore presence with the average diameter and material area range of 33.394 – 56.047 nm and 42.697 – 113.716 m$^2$/g, respectively. However, the large surface area observed indicates PDDA/PSS composition (2:1) had more coated SiO$_2$, whereby negative charges (-) were moved to attract more positive (+) charges, and as a result, smaller crystal sizes were formed.

Transmission Electron Microscope (TEM) and Selected Area Diffraction (SAED) Analysis
The formation process of a ZnO-SiO$_2$/Chitosan core-shell in a multilayer hybrid is used by, 1) TEM, by showing internal morphology, and 2) SAED, which demonstrates possibly uniform or amorphous crystal composition patterns, compared to the observed particles. Figure-7 shows the TEM image of ZnO-SiO$_2$/Chitosan with a comparison of PDDA/PSS composition (1:1), featuring the coating of particles with polyelectrolytes and SiO$_2$, shell present on the surface of ZnO, affiliated with the core/shell structure formation. Furthermore, the nanoparticle core is surrounded by shadows assumed to mark the shell of SiO$_2$, while the SAED pattern shows an even distribution.
Table-2: BET/BJH Analysis of Core-shell ZnO-SiO$_2$/Chitosan Against PDDA and PSS Compositions

| Sample Composition                          | Surface Area (m$^2$/g) | Pore Diameter(Å) |
|--------------------------------------------|------------------------|------------------|
| ZnO-SiO$_2$/Chitosan, without PDDA/PSS    | 42.697                 | 33.394           |
| ZnO-SiO$_2$/Chitosan, PDDA/PSS (1:1)      | 54.565                 | 36.407           |
| ZnO-SiO$_2$/Chitosan, PDDA/PSS (1:2)      | 75.433                 | 41.776           |
| ZnO-SiO$_2$/Chitosan, PDDA/PSS (2:1)      | 113.716                | 56.047           |

CONCLUSION

This research features the optimal synthesis of shell ZnO-SiO$_2$/Chitosan nanorods by multilayer hybrid, using a hydrothermal process. The process was performed at pH= 13.0, with a crosslinker of PDDA and PSS in a ratio (2:1). Also, the product comprised of a crystal with size 56.047 nm, and a surface area of 113.716 m$^2$/g, featuring a wurtzite structure pattern with hexagonal geometry. The morphological analysis of SEM-EDX and TEM-SAED showed the successful formation of ZnO-SiO$_2$/Chitosan patterned nanorods core-shell, using ZnO cores and SiO$_2$ Cells. Meanwhile, there was also an increase in Zn-O-Si interactions at higher numbers of PDDA, evidenced by the wavenumber 950 cm$^{-1}$, and a decline in the energy gap to 3.26 eV.

ACKNOWLEDGMENT

This research was supported by the Andalas University, Primary Research Scheme of Publication Research Cluster of Andalas University Professor in Research Contracts: T/1/UN.16.17/PP.KO-KRPIGB/LPPM/2020.
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[RJC-6210/2020]