HIBRID MULTILAYER OF ZnO-SiO₂/CHITOSAN NANORODS BY POLY(DIALLYLDIMETHYLAMMONIUM CHLORIDE) (PDDA) AND POLY(SODIUM 4-STYRENESULFONATE) (PSS)

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ABSTRACT

The core-shell synthesis of SiO₂ (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-SiO₂/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 SiO₂ 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 SiO₂ covering on the surface of ZnO (core-shell ZnO-SiO₂). This was indicated by a relatively smaller crystal size of 30.08 nm, with hexagonal wurtzite structure at $2\theta = 3^\circ, 34^\circ, 36^\circ$, and hkl [1 0 0] [0 0 2] and [1 0 1], based on JCPDS36-1451 standards. Furthermore, dinalysis 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 m²/g).

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

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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. SiO₂ is amorphous, adsorptive, exhibits high thermal properties, and possesses good mechanical attributes; using these features to modify ZnO properties, including reducing crystal size,¹⁴ and also to prevent clusters between the nanoparticles.¹⁵ On the other hand, adding silica to photocatalytic applications controls the duration of the catalytic process in sunscreens.⁹ Xue et al., (2011), reported SiO₂ 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.¹⁶ Previous research by Xue et al., (2013), revealed PDDA and PSS cross-links have been used in the comparison (1: 1), resulting in layers (hybrid multilayer) to form a core-shell, and is, therefore, effective in facilitating the photocatalytic activity of ZnO under UV light.¹⁸ The composition of Poly (diallyldimethylammonium chloride) (PDDA) and Poly (sodium 4-styrenesulfonate) (PSS) compounds were modified in the ratio (1: 1, 1: 2 and 2: 1) to form a more stable core-shell. However, this formation was carried out in stages. The stage begins with O-Zn-O coated with a poly (*diallyldimethylammonium chloride*) (PDDA) compound providing a positive charge (+), saturated with a Poly (sodium 4-styrenesulfonate) (PSS) charge, and results in a negative charge (-). SiO₂ in the form of O-Si-O was bonded to form a ZnO-SiO₂ core-shell.¹⁶

EXPERIMENTAL

Material

The materials used in this study were zinc nitrate tetrahydrate (Zn (NO₃)₂·4H₂O), zinc oxide (ZnO), hexamethylenetetramine (TEOS) (C₈H₂₀O₄Si), hydrochloric acid (HCl), sodium hydroxide (NaOH), Heksamethylenetetramine (C₆H₁₂N₄), Isopropanol (C₃H₈O), Ethanol (C₂H₅OH), Poly(diallyldimethylammonium chloride) (PDDA), Poly(sodium 4-styrene sulfonate) (PSS), Commercial chitosan (C₄H₁₁NO₄)_n, and Cetyltrimethyl ammonium bromide (CTAB) (C₁₃H₃₃N(CH₃)₃Br).

Preparation of ZnO-SiO₂/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 SiO₂ 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-SiO₂/Chitosan powder was obtained after calcination at 600°C for 4 hours.

Characterization

Morphological and elemental analysis of ZnO-SiO₂/Chitosan was carried out with SEM-EDX (Scanning electron microscopy-dispersive X-ray spectroscopy). TEM (Transmission Electron Microscope) for observing three-dimensional morphology of the ZnO-SiO₂/Chitosan nanostructure. The crystal structure is determined using XRD (X-ray diffraction). Crystal phase determination was done by applying the Bragg law where $\lambda = 1.5406 \text{ \AA}$. 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 BaSO₄ 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-SiO₂/Chitosan patterned nanorods can be identified from the Scherrer equation based on JCPDS36-1451:

$$1029$$

$$t = \frac{k \times \lambda}{\beta \times \cos \theta}$$

Where: t is the size of the crystal, k (constant: 0.89), λ (wavelength of X-rays), β (FWHM value), and θ (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° , and 36° (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-SiO₂/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 Si⁴⁺ bonding.¹⁶ Thus, more Si attached to the core reveals a reduction in crystal size. The mirage Si from SiO₂ can reduce the intensity and size of crystallization from ZnO to form an active site for Si⁴⁺ bonding.¹⁶ In the PDDA/PSS composition (2:1), with a crystal size of 30.08 nm¹⁴, the effects of SiO₂ 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-SiO₂/Chitosan, without PDDA/PSS, (c) ZnO-SiO₂/Chitosan (PDDA/PSS) (1:1), (d) ZnO-SiO₂/Chitosan (PDDA/PSS) (1:2), (e) ZnO-SiO₂/Chitosan (PDDA/PSS) (2:1)

Table-1: Size ZnO-SiO₂/Chitosan Based on the Difference in Composition of PDDA and PSS

Sample Composition	Crystal Size (nm)			Average (nm)
	hkl 100	hkl 002	hkl 101	
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 hexamethylenetetraamine bases and Chitosan compounds. However, in the ZnO-SiO₂/Chitosan powder sample, there was an interaction in the wavenumber of about 1085 cm⁻¹, that is, Si-O-Si.²⁰ A wavenumber of around 950 cm⁻¹ showed the Zn-

O-Si interaction.²² Moreover, there are -OH groups originating from Zn-OH and Si-OH hydrolyzed at wave number 3360-4000 cm^{-1} .

Fig.-2: FT-IR Pattern of (a) ZnO/Chitosan powder, (b) ZnO-SiO₂/Chitosan, PDDA/PSS (1:1), (c) ZnO-SiO₂/Chitosan, PDDA/PSS (1:2), (d) ZnO-SiO₂/Chitosan, PDDA/PSS (2:1)

Diffuse Reflectance Spectrum Analysis (UV-DRS) Analysis

UV-Vis DRS analysis provides information about the absorbance, width, or value of the energy gap (E_g) 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.²¹ 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-SiO₂ is (2.96 - 3.13) eV, while for ZnO, the value is 3.37 eV according to the literature.² This occurred as a result of introducing SiO₂ 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.¹⁹ The effect of the differences in the composition of PDDA and PSS does not significantly influence changes in the gap values obtained.

Fig.-3: UV-Vis DRS Spectrum of (a) ZnO-SiO₂/Chitosan without PDDA/PSS, (b) ZnO-SiO₂/Chitosan, PDDA/PSS (1:1), (c) ZnO-SiO₂/Chitosan, PDDA/PSS (1:2)

Scanning Electron Microscopy Energy-dispersive X-ray Spectroscopy (SEM-EDX) Analysis

SEM analysis also describes the surface morphology of ZnO-SiO₂/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-SiO₂ compound, EDX analysis was deployed. The analysis also shows the percentage of ZnO, SiO₂ 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.

Fig.-4: SEM Pattern of ZnO-SiO₂/Chitosan Core-shell with PDDA/PSS composition (1:2) at magnification (a)40,000 times (b) 80,000 times.

Fig.-5: EDX Analysis of ZnO-SiO₂/Chitosan Core-shell with PDDA/PDS Composition (1:2)

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 (N₂ adsorption-desorption at 77.3 K) was calculated using the BET equation. Meanwhile, the average pore diameter is obtained through the BJH method.¹⁷ Figure-6 shows ZnO-SiO₂/Chitosan curve of JH pore size distribution and nitrogen isotherms. According to IUPAC²⁴, 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 m²/g, respectively. However, the large surface area observed indicates PDDA/PSS composition (2:1) had more coated SiO₂, 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-SiO₂/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.^{23,25} Figure-7 shows the TEM image of ZnO-SiO₂/Chitosan with a comparison of PDDA/PSS composition (1:1), featuring the coating of particles with polyelectrolytes and SiO₂, 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 SiO₂, while the SAED pattern shows an even distribution.

Table-2: BET/BJH Analysis of Core-shell ZnO-SiO₂/Chitosan Against PDDA and PSS Compositions

Sample Composition	Surface Area (m ² /g)	Pore Diameter(⁰ A)
ZnO-SiO ₂ /Chitosan, without PDDA/PSS	42.697	33.394
ZnO-SiO ₂ /Chitosan, PDDA/PSS (1:1) (P3)	54.565	36.407
ZnO-SiO ₂ /Chitosan, PDDA/PSS (1:2) (P4)	75.433	41.776
ZnO-SiO ₂ /Chitosan, PDDA/PSS (2:1)	113.716	56.047

Fig.-6: Nitrogen Adsorption-desorption Isotherms from (a) ZnO-SiO₂/Chitosan, PDDA/PSS (1:2), (b) ZnO-SiO₂/Chitosan, PDDA/PSS (2:1) Fig.-7: TEM (a), and SAED (b) of Core-shell of ZnO-SiO₂/Chitosan with composition PDDA/PSS (1:1)

CONCLUSION

This research features the optimal synthesis of shell ZnO-SiO₂/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 m²/g, featuring a wurtzite structure pattern with hexagonal geometry. The morphological analysis of SEM-EDX and TEM-SAED showed the successful formation of ZnO-SiO₂/Chitosan patterned nanorods core-shell, using ZnO cores and SiO₂ 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.

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