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Fabrication and physical characterization of Zn (OH) ₂/PVA and ZnO nanofibers using Electrospinning nanofiber generator

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Abstract: Zinc oxide nanofibers were prepared using the polymer - Zinc acetate solution, by a modest programmable microcontroller aided electro spinning technique. The prepared and calcinated nanofibers were characterized using standard analytical methods. The hexagonal wurtzite structure for calcinated nanofibers of diameters ranging between 10-13 nm were inferred from structural analysis. The Field Emission Scanning Electron Microscope analysis showed that nanofibers sizes are varied from 100 to 500 nm for the prepared and calcinated samples. The optical absorption analysis evidently showed the presence of nanophase Zinc Oxide by means of a strong blue shift (372 nm) in the band edge absorption region. The functional group analysis showed the presence of organic bands related to Polyvinyl Alcohol for uncalcinated nanofiber. This article proposes that an indigenously manufactured electro spinning system can cover the active research area of preparing ceramic and composite nanofiber with various compositions and properties.

Keywords: microcontroller, nanofibers, optical properties, thin films, X-ray diffraction

I. Introduction

Over the past few decades, several methods have been proposed by various researchers for the preparation of nanostructured materials. Enormous efforts have been devoted by their teams to optimize the growth process to achieve uniform and ultrathin one dimensional nanostructure [1, 2]. Vapor Liquid Solid (VLS) method, Chemical Vapor Deposition (CVD) method, Molecular Beam Epitaxial (MBE) method, and Template Assisted Wet Chemical Synthesis method have been widely employed in the production of nanostructures with limitations such as highly expensive, complicated procedures, [3-6]. Electro spinning is a simple, economical and versatile method for generating a rich variety of ultrathin fibrous materials that include polymers, composites, ceramics etc., [7]. The basic principle of electro spinning is non-mechanical, but electrostatically charging the surface of the ejected polymer droplet by a liquid jet through spinneret arrangement (using high voltage electrostatic field) Fig. 1. An electrical potential is applied between the polymer droplet or melt, held at the end of a capillary tube and grounded collector. When the droplet overcomes the surface tension

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by the charged jet of polymer solution ejected. The charged jet is controlled by an externally applied electric field. The jet exhibits bending instabilities caused by repulsive forces between the charged spiraling loops. As the loops increase in diameter, the jet grows longer and thinner fibers, until it solidifies on the collector [8].

Recently, automated equipment's are used in various manufacturing processes that are used in healthcare and industrial companies to develop accurate and high quality products with benefits such as reduced production cost, number of laborers, and minimum time [9-11]. Microcontroller based electro spinning generators are used in nanofiber generation, in order to produce uniform nanofibers with accurate and high aspect ratio. The variety of fibers with different lengths and diameters is electronically controlled by experimental parameters. The electro spinning process is conducted at room temperature under various atmospheric conditions. The nanofibers prepared by this method exhibit very high surface area and porosity. More than 100 types of polymers have been reported, namely, poly vinyl alcohol (PVA), poly acrylic acid (PAA), poly lactic acid (PLA); collagen and organic compounds such as nylon, polyester, peptide and cellulose are the precursors in nanofiber production [12-15].

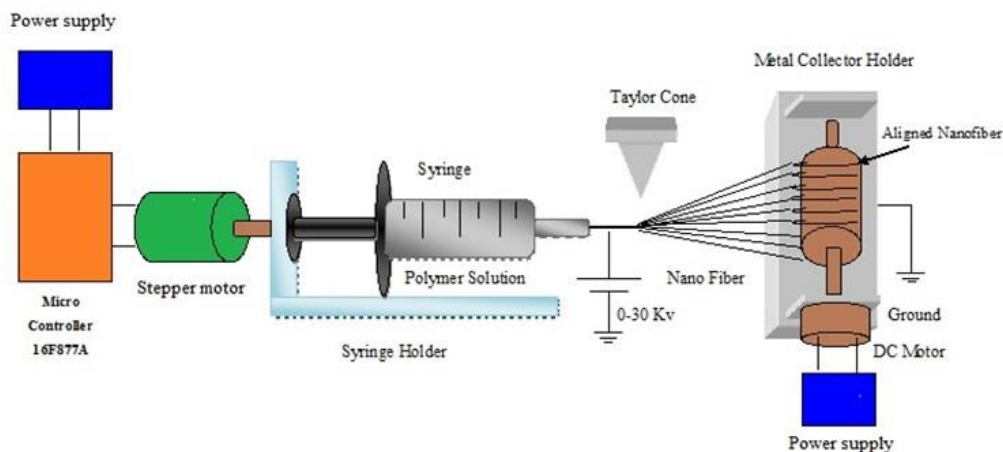


Fig. 1 Schematic diagram of electrospinning nanofiber generator.

Tremendous research works are under way for the development of one dimensional inorganic nanomaterial. Among the various inorganic systems such as III-V, IV, I-III-V and II-VI compound semiconductor, Zinc oxide (ZnO) is considered as one of the best multifunctional semiconductor systems with distinguished potentials that are suitable for electronic, optic, photonics and optoelectronic device oriented industries. It has also served as the best application in the fabrication of solar cells, sensors, varistors and piezoelectric devices. Various methods are available for the preparation of one dimensional ZnO nanostructures - hydrothermal synthesis, sol-gel method, chemical vapor deposition, bio-template assisted method... [16-20].

The combination of sol gel technique with electro spinning was first reported by Larsen et al in the production of nanofibers made from inorganic oxides and hybrid (organic/inorganic) materials with diameters ranging between micrometer and sub micrometer [21]. Yang et al reported that ZnO nanofibers have been prepared by electro spinning set up, using poly vinyl alcohol as the organic system and zinc acetate as the zinc precursor [22].

In the present study, a systematic investigation has been carried out to fabricate highly oriented uniform ZnO nanofibers after 480°C of calcination. The prepared nanofibers were characterized via standard analytical tools: X-ray diffraction (XRD) analysis, field emission scanning electron microscopic method (FESEM), ultra violet (UV) - visible absorption analysis and Fourier transform infrared (FT-IR) absorption spectroscopy methods. Electro spinning is an assured standard method for cost effective, less complicated procedure for the highly uniform fabrication of ZnO nanofibers.

II. Materials and Methods

Well aligned nanofibrous ZnO systems were prepared by microcontroller 16F877A assisted nanofiber generator using PVA dissolved in millipore water as the solvent and zinc acetate dehydrate as Zn precursor. In order to obtain uniformly distributed $\text{Zn}(\text{OH})_2$ / PVA solution, 1.5g zinc acetate dehydrate and 3.0g PVA were added to the 40 ml of millipore water and continuously stirred for 6 hours. The prepared solution was preserved in an air tight container for a 3 hour ageing period, and further used for the generation of $\text{Zn}(\text{OH})_2$ / PVA nanofibers. The electro spun nanofibers were calcinated at 480°C and as a result, well aligned nano ZnO fibers were derived.

The microcontroller based electrospinning nanofiber generator consists of three major units: high voltage variable power supply- 0 to 30 kV, syringe/spinneret-solution feeding unit, and a grounded collector unit. Microcontroller unit energized by a 12 V power supply was used to control the mechanical force that maintained forward and reverse movements of syringe tab via stepper driver and stepper motor. The key component of this circuit is Microcontroller 16F877A, to generate pulse width modulation (PWM), where the PWM is an inbuilt circuit. The frequency of the PWM was adjusted using variable potentiometer, and connected across pin numbers 1, 2, and 10 of the microcontroller. High voltage variable power supply was energized by Alternating Current (AC) main through transformer and its 24 V secondary voltage was rectified by full-wave bridge rectifier followed by a filtering process through

three 1000 μ F electrolytic capacitors which produced ripple free DC output 24 V. The ripple free 24 V was fed to fly-back transformer which was useful in generating high output voltages (0 - 50 kV), alternatively low currents. Syringe pumps, also known as spinnerets, are small pumps precisely operated via "C" language programmed microcontroller 16F877A, automated Direct Current (DC) motors that produce controlled mechanical force or torque to accurately move the syringe tap in forward and reverse direction. Grounded collector system which consists of a rotatable flat plate collector (0-3000 rpm) is made up of aluminum or stainless steel rectangular plates. A high voltage negative potential is connected to this grounded collector terminal. During nanofiber generation, the collector must be grounded or maintained at high negative potential; a positive potential is connected to the tip of the syringe or spinneret.

The final products - Zn (OH) 2/PVA nanofibers and 480 °C calcinated ZnO branched nanofibers were examined for their structural and phase identification using X-ray diffraction analysis. To this, Rigaku-Dmax 2500 diffractometer was used and it was operated with voltage and current settings of 40 kV and 200 mA respectively, and Cu-K α radiation (1.5405 Å) was used. Qualitative study was performed by recording XRD diagrams in an interval of 20°≤2θ≤90° at the rate of scanning 2°/min. The Zn(OH)2/PVA nanofiber and 480 °C calcinated ZnO branched nanofiber samples were subjected to morphological characterization, using field emission scanning electron microscope (FEI – QUANTA – FEG 250), with accelerating voltage, ranging from 200 V to 30 kV, magnification 20X to 106 X, resolution 1 nm. The optical absorption characteristics of Zn(OH)2/PVA nanofiber and 480°C annealed ZnO branched nanofiber for the UV Visible region ranging from 400 to 1100 nm were performed by UV – 1700 series spectrophotometer, with a slit width of 1nm by dispersing the solids in the ethanol medium, for a path length of 1 cm. The samples were investigated by Fourier transform infrared radiation using Shimadzu make FTIR 8400 S series spectrophotometer. For analysis, Zn(OH)2/PVA nanofiber and 480 °C calcinated ZnO branched nanofiber were directly exposed to the infrared radiation range 400 to 4000 cm⁻¹ at a scan rate of 25 scans/min with 4 cm⁻¹ resolution.

III. Results and Discussion

3.1 Structural Analysis

The preparation of different nanostructures use the following parameters which play a crucial role: reaction temperature, nature of precursor, dispersing agent, reactants concentration and addition rate. The structural properties of the prepared (Zn (OH)/PVA microfibers) and calcinated ZnO nanosystems were analyzed using XRD method. The XRD analysis clearly demonstrated the role of temperature on the formation of nano ZnO from Zn (OH)/PVA microfibers. The much broadened and less intense XRD peaks Fig. 2 (b) indicated the poor crystalline state of the product. The impact of temperature on the crystalline structure was confirmed by Fig. 2 (a), which exhibited less broadened and well separated sharp peaks as the signature of a good and highly oriented crystalline state. Various crystalline properties were calculated using standard formulae. The size of the crystallites was calculated using Debye Scherer formula. The particle size calculated from the study was found to be 18 nm. All peaks showed considerable broadening which was the cause of the nanophase formation with less internal stress.

The lattice strain and crystalline size was calculated from the following equation (1)

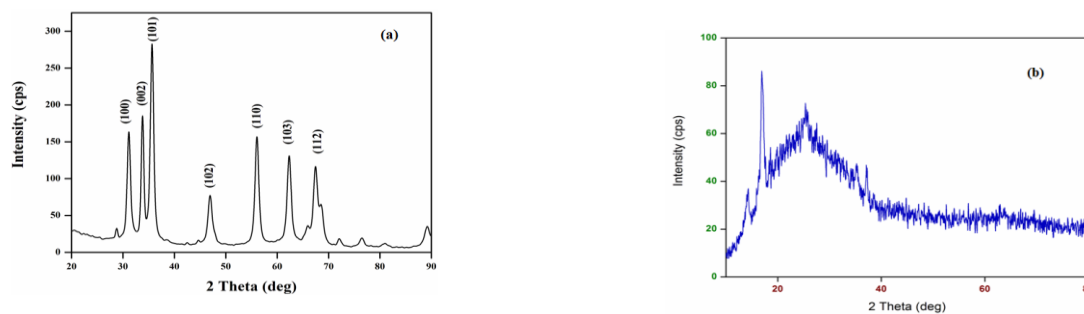


Fig. 2 (a) XRD analysis of annealed branched ZnO nanofibers. Fig. 2 (b) XRD analysis of unannealed Zn(OH)2/PVA nanofibers.

$$\frac{B \cos \theta}{\lambda} = \frac{1}{\varepsilon} + \frac{\tau \sin \theta}{\lambda} \quad (1)$$

where B is the measured full-width at half maximum (FWHM), θ is the Bragg peak angle of the peak in radians, λ is the wavelength of X-ray used for diffraction (1.59 Å), ε is the effective particle size in nm and τ is the effective strain.

All the diffraction peaks were strongly adhered to the JCPDS card no.89-1397. The peaks at various scattering angles were identified at 31.07°, 33.74°, 35.53°, 46.88°, 55.93°, 62.31° and 67.53° and were of the reflection planes (100), (002), (101), (102), (110), (103), and (112) respectively. The crystal structure was identified by calculating the unit cell parameters $a = b = 3.261$ Å and $c = 5.228$ Å and was inferred as hexagonal wurtzite structure with space group (C6V=P63mc). The increase in the values of cell parameters were attributed to the local crystalline defects of the nanofiber. The results inferred from the XRD analysis strongly adhered to that of the electron microscopic data.

3.2 Morphological Analysis

The morphological properties of Zn (OH)₂/PVA nanofibers were analyzed using FESEM method Fig. 3(a). It is inferred that the prepared nanofibers were formed in clustered state and bundled form. The fibers also formed in branched structure, made up of small spheres or faceted particles. The diameters of the fibers were measured using a 5 millimeter scale; the number of fibers within the scale, was estimated using different values of average diameters. The inset picture represents the magnified image selected from Fig. 3 (a) and was measured using a 2 millimeter scale. It was noted that fibers were in branched structure and in free standing state. The sample annealed at 480 °C was also analyzed using FESEM method Fig. 3(b). The surface morphology of the annealed fibers was found in branched structure. It is presumed that the evenly distributed ions in PVA matrices were oxidized during calcination process. The inset picture clearly depicts the clustered state of ZnO particles adhering to each other, and thus forming the branched nanofibrous structure. The aggregation of nanoparticles has been discussed by various authors and theories. The following assumption is made for the aggregation of nanocrystals that lead to the formation of branched ZnO fibers. Reaction under controlled growth regime, at the initial stage of formation of ZnO nanofibers, an excess number of monomers were injected to the growth site to initiate growth process. In this state, the effect of diffusion was limited to large number of monomers, the diffusion process occurred only whenever there was free space in the growing crystal. Hence, the incorporation rate depended only on the number of available sites on the surface of the crystal, which resulted growth of single crystallite. More individual growth occurred and aggregated in further process.

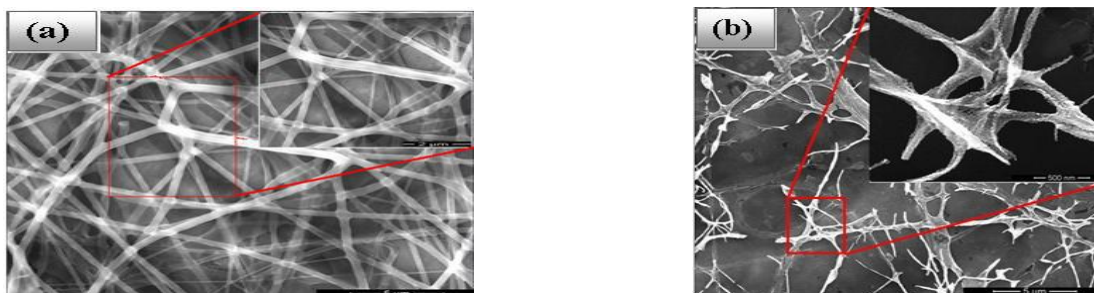


Fig. 3 (a) FESEM images of unannealed Zn (OH)₂/PVA nanofibers. Fig. 3 (b) FESEM images of annealed branched ZnO nanofibers.

The branched structure was reasoned as follows, during growth, monomers were deposited onto the high energy facets of the arms, i.e. On their tips, whereas deposition of monomers onto the lateral facets of the arms was hindered. The main difference in the growth process resided in the nucleation event during the early stage of the growth. The octa twin model further explains the formation mechanism as follows: It describes the branched or tetrapod structure as composed of several domains that are exclusively in wurtzite structure, in which the core is composed of eight wurtzite domains. Such domains have two different types of tetrahedral shape: one type has the basal facet (0 0 0 1) of wurtzite structure and the second, top facet of (0 0 0 1₋). Two different types of tetrahedral are interconnected through a twin plane. This twin structure shows an inverted symmetry. As domains of the first are connected preferentially to domains of the second type and vice versa, the octahedron formed by eight of these domains, exposes an alternating pattern of (0 0 0 1) and (0 0 0 1₋) facets. These facets exhibit hexagonally organized atoms, identical to $\pm (1\ 1\ 1)$ facets of cubic structure [23, 24]. The internal strain of the crystallites created broadening in the XRD pattern and obstructed the completion of cell volume of eight wurtzite domains. In the FESEM micrograph of the sample annealed at 480 °C, the inset picture depicts the agglomerated state of plague-like morphology, which originated from the less negative potential among crystallites that were contributed for the formation of branch-like morphology. The polymer matrices also act as the encapsulating agent for Zn (OH)₂ molecules that hold the above said molecules from individual growth that resulted with agglomerated nano ZnO systems.

3.3 Infrared and Optical Analysis

The functional group analysis of the prepared Zn (OH)₂/PVA nanofiber and 480°C annealed ZnO branched nanofiber were characterized using FT-IR absorption analysis. From Fig. 4(a), it is seen that the unannealed Zn (OH)₂/PVA nanofiber exhibited both the metal oxygen as well as the fundamental functional groups of poly vinyl alcohol polymer. The strong vibrational band observed between 2960 and 3730 cm⁻¹, was attributed to the presence of coordinated water molecules in the sample. The altered medium stretched C-H vibrations were observed from 2280 to 2430 cm⁻¹. The strong stretching vibrational bands belong to C=O and C-O and CH₂. Wagging mode vibrational groups were observed at 1500 - 1770 cm⁻¹ and 1360 -1470 cm⁻¹ respectively. In addition, the out of plane bending vibrations of CH₂ functional group was noted at 960 -1050 cm⁻¹. The characteristic hydrated metal group vibrational bands were observed for the unannealed sample and they were attributed between 470 and 540 cm⁻¹. From the study, it is inferred that the Zn(OH)₂ molecules were strongly encapsulated by PVA polymer, and further presumed that the existence of various functional groups in the IR spectrum may also have originated from Zn precursor (in the present study it is zinc acetate dehydrate). The sample annealed at 480°C was analyzed for functional groups using FT-IR technique Fig. 4(b). The sample

showed that formation of metal oxygen ν M-O bands appearing between 470 and 540 cm^{-1} were attributed to the presence of ZnO in the sample [25]. The additional strong stretching band arising between 3200 and 3600 cm^{-1} was attributed to the presence of superfluous (-OH) vibrations on the formed ZnO branched nanofiber.

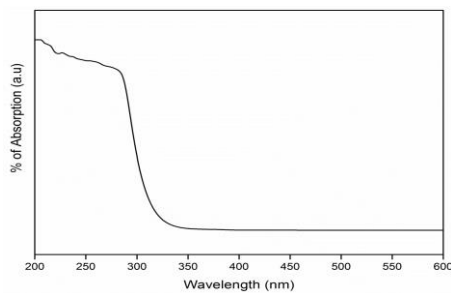


Fig. 4 (a) FT-IR absorption analysis of unannealed Zn (OH) 2/PVA nanofibers.

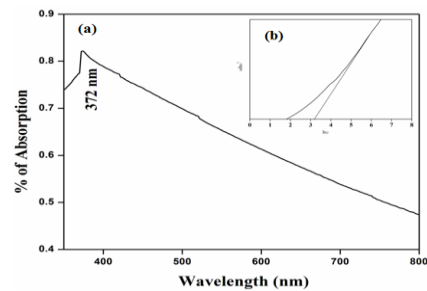
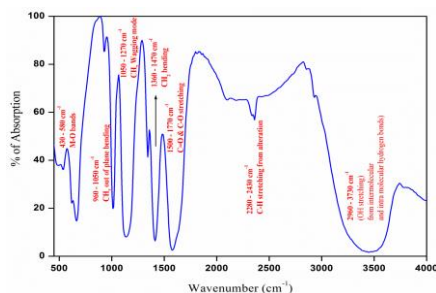


Fig. 4 (b) FT-IR absorption analysis of annealed branched ZnO nanofibers.

In order to investigate the quantum size effect in nanosized materials, optical studies provide excellent support., UV-visible absorption analysis Under optical studies is regarded as an useful tool for the investigation of semiconductor nanostructures that exhibit the quantum size effect caused by photo induced electron – hole pair formation. According to Calandra et al, the UV visible absorption spectrum of the semiconductor nanosystems is the function of their sizes and the absorption maximum decreases upon increasing size of nanoparticles. The unannealed Zn (OH)2/PVA nanofibers were also analyzed using UV visible absorption analysis and it showed an absorption edge at 272 nm Fig. 5 (a). The estimated band gap value is found to be 4.22 eV using the relation $E_g = hc/\lambda$ eV, where h is the Planck's constant (4.135×10^{-15} eV), c is the velocity of light (3×10^8 m/s) and λ is the wavelength of absorption (272 nm). From Fig 4, it is observed that the absorption peak for 480°C annealed ZnO branched nanofiber was seen at 372 nm. The position of absorption edge was found decreased in wavelength and is applicable to the nanodimensional semiconductor systems. This absorption shift was the cause of quantum size effect which originated from the change in band gap along with excision features. It also resembled the particle size and size distribution state [26]. The energy gap of the material is calculated using Tauc plot method; the plot resembles the direct allowed transition process of the electron hole pair. The calculated energy gap value was found to be 3.33 eV, inset picture of Fig. 5 (b). On comparison with the bulk band of ZnO, the estimated value was found to be high and it further confirmed that the annealed ZnO nanofiber was in nanodimensional state.



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