Synthesis and Characterisation of ZnS-PVA and ZnS-PVAc Nanofibers with Potential Application in Wastewater Treatment

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Abstract

ZnS nanoparticles were synthesised from pyrolysis of two different ligands of dithiocarbamate at a temperature of 350 ºC. The as-prepared nanoparticles were electro-spun with two different polymer matrices of polyvinyl alcohol (PVA) and polyvinyl acetate (PVAc) to form nanocomposites (nanofibers). The nanofibers were used differently as catalyst in the photodegradation of methylene blue dye in aqueous solution. ZnS/PVAc nanofiber was observed to have more catalytic effect on the dye photodegradation than ZnS/PVA nanofiber composite. ZnS nanoparticles were characterized with UV-vis spectroscopy while the electrospun nanofibers were characterized using fouriertansform infrared (FTIR), scanning electron microscope (SEM) and thermogravimetric (TGA) analyses.

Keywords: Dithiocarbamate; Nanofibers; Nanoparticles; Methylene blue; Thermal stability.

Introduction

Dithiocarbamates are useful mono-anionic chelating ligands, and are able to form stable complexes with all the transition elements and the majority of lanthanide and actinide elements[1]. The compounds can act as monodentate, bidentate chelating or bidentate bridging ligands. The necessary properties determine the structural arrangement of the resultant metal complexes[2].

Change in the size or surface of the nanoparticles' composition can change their physical and chemical properties. The shapes of nanoparticles depend on their interaction with stabilizers and the inductors around them and also their preparation method. It is also known that reaction rate is influenced by the shape of synthesized nanoparticles. Nanoparticles are widely used in different areas which include: advanced materials, electronics, biomedicine, pharmaceuticals, cosmetics, energy, catalytic and environmental detection and monitoring. Furthermore, nanoparticles can also be used in environmental research and health care associated industries[3,4].

Polymers are remarkably used in the synthesis and modification of nanoparticles. The properties of most polymers such as having lightweight constituents which allow easy processing and could be shaped into thin layers by numerous techniques have made them suitable for the application. The incorporation of inorganic nanoparticles into a polymer matrix allows properties from inorganic nanoparticles and polymer to be combined and thus advancing the roles that can be generated by polymer–inorganic nanocomposites[5,6].

Nano fibers can be made from different methods which are: electro spinning, interfacial polymerization, electrostatic spinning and melt processing[6]. Nanofibers are widely used in different areas such as medical, pharmaceutical and cosmetic industries[7]. The use of ZnS- polymer nanofibers is advantageous because of their light-weight, low cost, and mechanical elasticity. Moreover, ZnS are abundant, stable, and environmentally friendly.

Water is the most vital substance for all life on earth and a valuable resource for human refinement. It is one of the basic requirements of life. About 70% of human body is composed of water. Increasing demand and shortage of clean water sources due to the growth of industries, population and droughts have become a concern worldwide.

Practical approaches and solutions have been approved to produce more feasible water resources. Due to small pore sizes, high specific surface areas and high porosity, nanofibers can be used for waste water treatment[8]. Photocatalytic properties of nanofibers have been used to reduce the waste water problem.

In this study we report the synthesis of ZnS/PVA and ZnS/PVAc nanocomposites made from electrospining techniques and the application of the electrospun nanofiber as catalyst in photodegradation of methylene blue.

Materials and Methods

Materials: Carbon disulphide, polyvinyl alcohol polyvinyl acetate, N-methyl aniline and methylene blue, zinc chloride, ethanol, dimethylformamide, ammonium hydroxide and zinc sulphate were obtained from *Sigma-Aldrich.*

Synthesis of ligands: Ammonium *N*-methyl-*N*-phenyl dithiocarbamate, NH₄L¹: A solution of *N*-methyl-aniline (0.1 mol) was added to concentrated aqueous ammonia (30mL) in ice and the mixture was stirred for 10 minutes. An ice-cold carbon disulphide (0.1mol) was thereafter added to *N*-methyl aniline and concentrated ammonia mixture. The solution was stirred for 6-7 hours. The yellowish solid product formed, was then filtered by suction, rinsed 3 times with cold ethanol (5mL) and stored in the refrigerator[9].

Ammonium *N*-ethyl-*N*-phenyl dithiocarbamate NH₄L²: A solution of *N*-ethyl aniline (0.1mol) was added to concentrated aqueous ammonia (30mL) in ice and the mixture was stirred for 10 minutes. An iced cold carbon disulphide (0.1mol) was added to the *N*-methyl aniline and concentrated ammonia mixture. The mixture was stirred for 7 hours. The yellowish solid product formed was then filtered by suction, rinsed 3 times with cold ethanol (5mL) and stored in a refrigerator[9].

Synthesis of complexes: Zinc(II) complexes: [ZnL¹] and [ZnL²]: Ammonium *N*-methyl-*N*-phenyl dithiocarbamate (0.25 g) and ammonium *N*-ethyl-*N*-phenyl dithiocarbamate (0.25g) were each separately dissolved in water (20mL) and stirred for 5 minutes. Zinc chloride (0.170g) dissolved in water was added to each of the two ligands solution. White precipitate was formed immediately in each solution, and was vigorously stirred for 1 hour at room temperature. The products obtained were filtered off and rinsed thoroughly with small quantities of water[9].

Zinc(II) complex [ZnL₁L₂]: About 0.25g of Ammonium *N*-methyl-*N*-phenyl dithiocarbamate and 0.30g of ammonium *N*-ethyl-*N*-phenyl dithiocarbamate were dissolved separately in water (20mL). The ligands solutions were mixed together and stirred for 5 minutes, then zinc chloride (0.170g) dissolved in water was added to the ligand solution. There was an immediate formation of a white precipitate which was vigorously stirred for 1 h at ambient temperature. The product was filtered off and rinsed thoroughly with small quantities of water[10].

Synthesis of ZnS nanoparticles in a furnace: Zn complex (1.5 g) was weighed into a quartz boat and placed in a tube furnace. The temperature was gradually increased at 10°C/min to 350°C and stabilized for 2 h. After cooling, the residue in the quartz boat was reweighed to about 0.12g.

Synthesis of nanofiber: Four (4) solutions were prepared; each containing PAN (1 g) dissolved in 2mL of DMF, and stirred for 1h to attain homogeneity. Varying amounts of the nanopaeticles: 5, 10, and 20mg (represented as ZnS -180, ZnS -220, and ZnS– 260 respectively) were added to PAN/DMF mixtures and stirred for 12h. Different colloidal solutions designated as 10, 13 and 20% were obtained. The electro spinning solutions were loaded in a syringe to which a capillary wire needle was attached. A voltage of 20 kV was connected to the needle tip. On the passage of a high voltage, the polymer samples on crossing the electric fields produced fibres accumulating on the collector. Moreover, the solvent became evaporated rapidly. The collector (the aluminium foil) covered with the electro-spun fiber was dried at 50 °Cto allow the complete evaporation of the solvent[11].

Photocatalytic degradation: As-prepared ZnS-PVA, ZnS-PVAc composites, and ZnS nanoparticle were tested for their photocatalytic properties on aqueous solution containing methylene blue dye under UV light (irradiation = 260nm). Photocatalytic degradation of pure PVA and PVAc were used as control in the experiment. Methylene blue dye (10mg/L) was mixed separately with the nanocomposites (20 mg each of ZnS-PVA, ZnS-PVAc, ZnS nanoparticle, pure PVA and PVAc polymers. The suspensions were agitated with magnetic stirrer in the absence of light to ensure adsorption equilibrium on the surface of the catalysts and proper dispersion of the nanoparticles in the dye solution. An aliquot (2mL) of each sample was taken after 1h of reaction time and centrifuged at 3500 rpm for 15 min in order to remove the nanocomposites and the control samples. The reaction was monitored using UV-visible spectroscopy[12].

Yield: 8.4 (72%)
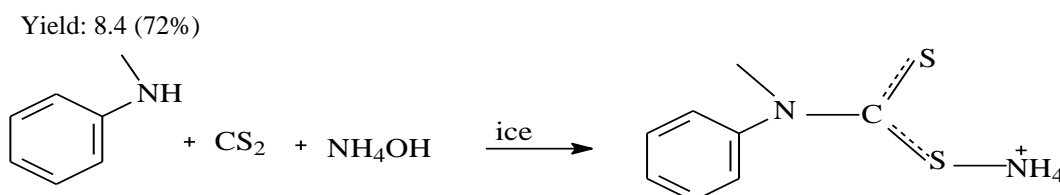
Scheme-1: Synthesis of NH₄L¹

Yield: 6.9g (56%)
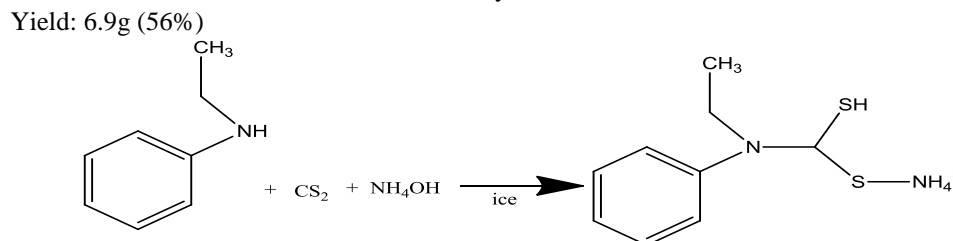
Scheme-2: Synthesis of NH₄L².

Results and Discussion

FTIR studies: The FTIR spectra of the samples are shown in Figures-1(a) and (b). PVA and ZnS-PVA exhibits a broad band at 3301 cm^{-1} which is assigned to O-H stretching frequency of the hydroxyl group. The absorption bands of pure PVA samples at 2927cm^{-1} and 1732cm^{-1} are assigned to C-H and C=O stretching vibrations respectively. However, in the ZnS/PVA sample, the bands are shifted to 2926 cm^{-1} and 1713 cm^{-1} for the C-H and C=O vibrations respectively. There was also a shift in the absorption band at 1582 cm^{-1} due to C=C stretching in the PVA sample to 1566 cm^{-1} in ZnS/PVA nanofiber. The observed changes in characteristic bands show that there was interaction between these semiconductor inorganic nanoparticles and PVA[13]. Figure-1(b) and (c) are the absorption bands of pure PVAc and ZnS–PVAcelectrospun nanofiber. The peak at C=O stretching band is observed at 1733cm^{-1}, and C-O stretching bands are observed at 1237cm^{-1} and 1028cm^{-1}. The peak at 1369cm^{-1} is assigned to CH$_3$ vibration mode. The ZnS–

PVAcelectrospun nanofiber also showed the same pattern as the pure PVAcelectrospun nanofiber with some reduced intensity[13].

UV-vis ZnS nanoparticles: The absorption spectrum of the ZnS nanoparticle is presented in Figure-2. It consists of a long wavelength tail, absorption band at about 350 nm and an absorption maximum at 240 nm. By increasing the time, the absorption tail decreases and the position of the absorption maximum does not change. For an Ostwald-ripening mechanism, larger particles would grow for increasing times due to the dissolution of smaller ones. As a result, the particle sizes would increase continuously during growth. Discontinuous cluster growth was observed, reflected by the occurrence of a well-defined absorption maximum appearing reproduciblyat approximately the same wavelength. The surfactant has the ability to control the size and shape of the growing particles through charge transfer and lowering of surface tension[14].
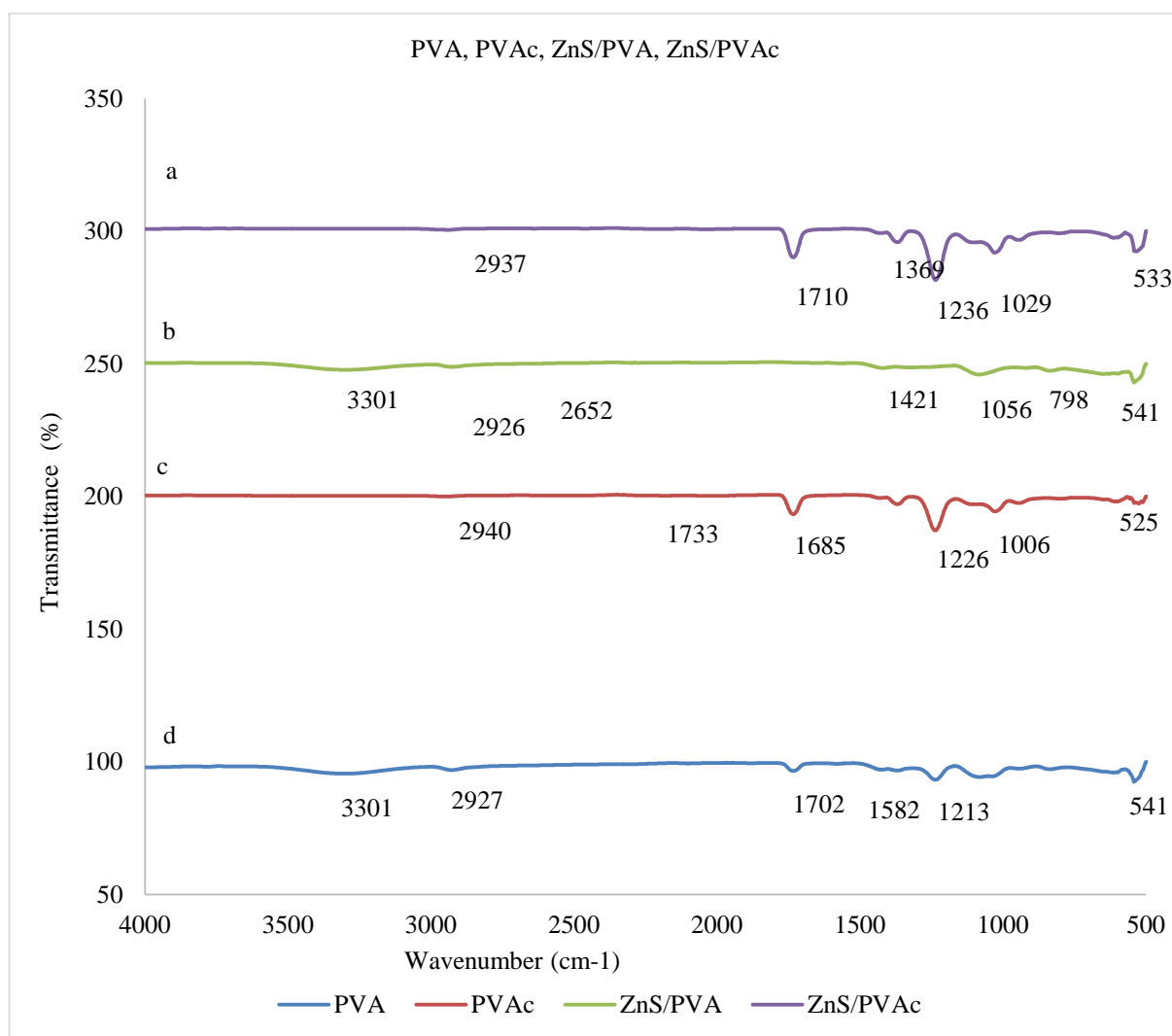

Figure-1: FTIR spectra of (a) pure PVA, (b) ZnS/PVA, (c) pure PVAc, (d) ZnS/PVA.c

SEM studies: The SEM images of the samples are shown in Figure-3 a-d. The images in figures 3a and c of the nanofibers have defects of balls morphology with an average diameter of 88.0µm (PVAc), 100µm (ZnS-PVAc). Figure-3b and 3d demonstrate uniform and randomly oriented fibers with an average diameter of 88µm (PVA) and 92µm (ZnS-PVA). These showed that there is increase in the average fibre diameter from the polymers to the nanofiber. The temperature of the reaction influences the development of particles and affects the shape of the nanofiber. On the other hand, non-equilibrium kinetics conditions are favoured by low reaction temperatures with a relatively high flux of monomers, yielding anisotropic growth e.g., rod-like structures[15].
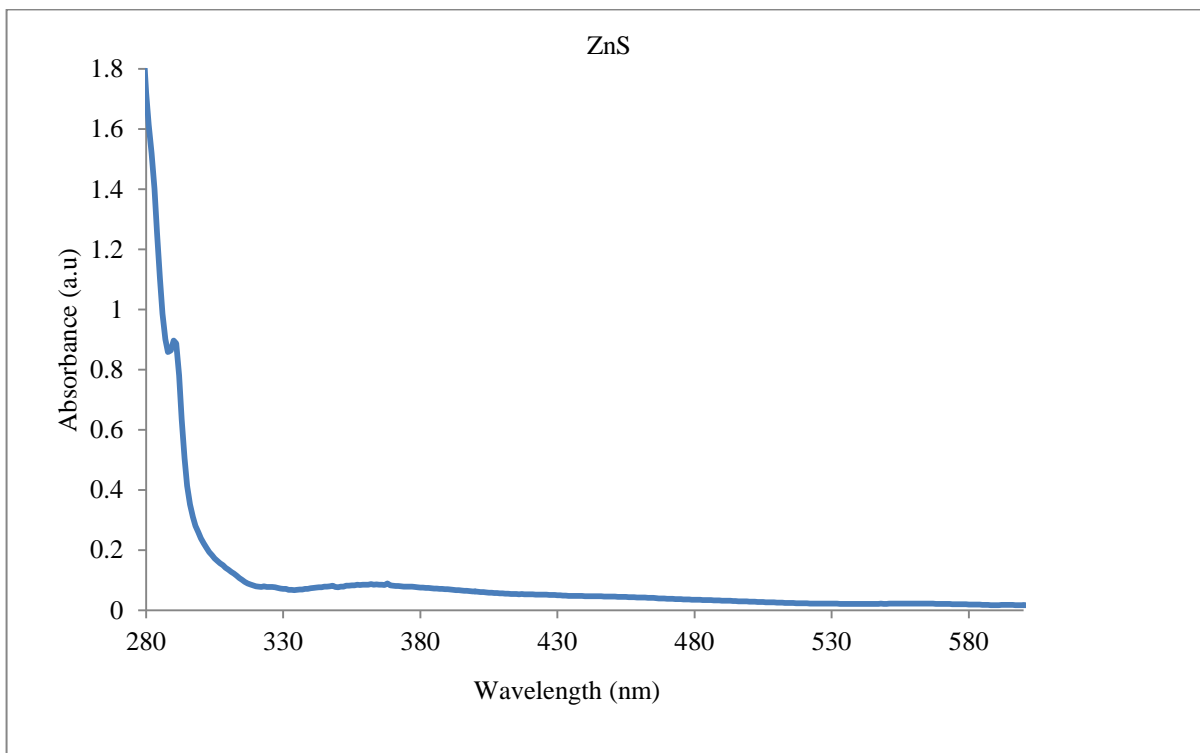

Figure-2: UV-vis of ZnS nanoparticles.
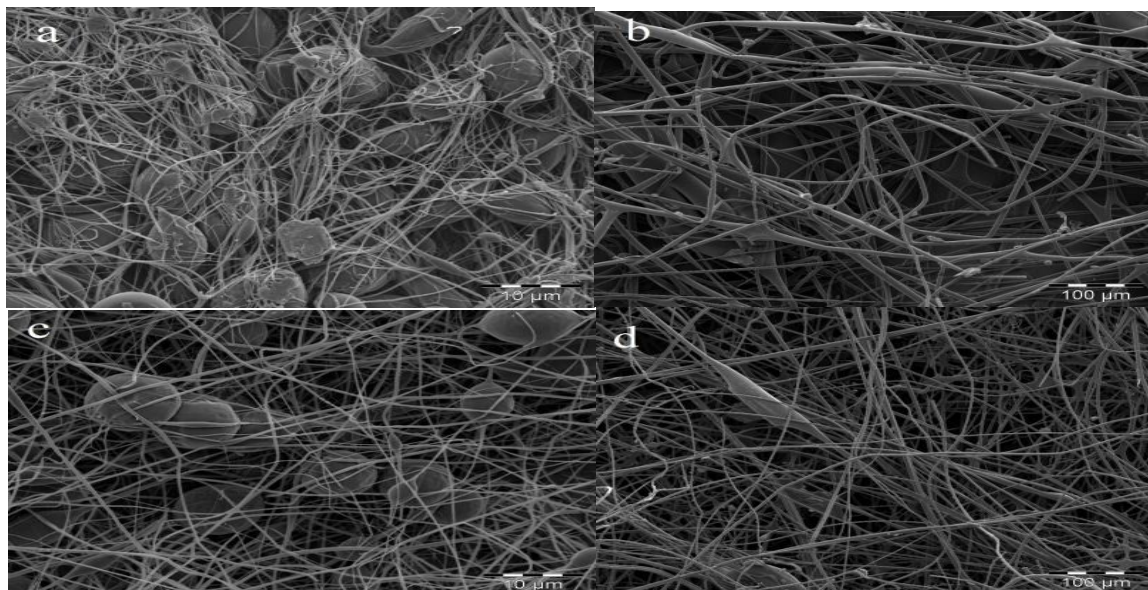
Figure-3: SEM image of (a) PVAc (b) PVA (c) ZnS-PVAc (d) ZnS-PVA nanofibers.

TGA studies: The thermal analysis curves are represented in Figure-4. It is generally observed that the weight loss of the nanofibers varies at different temperatures and the percentage of weight lost[16]. The onset of decomposition of composite nanofibers was found to be around 250°C and at a higher temperature than the pure polymers. This can be explained as an impressive increase in thermal stability that results from the surface interaction of the polymer surface and the inorganic matrix. The interaction may be from the strong interaction between the strong electronegative –CN groups in the ZnS nanofibers[17].
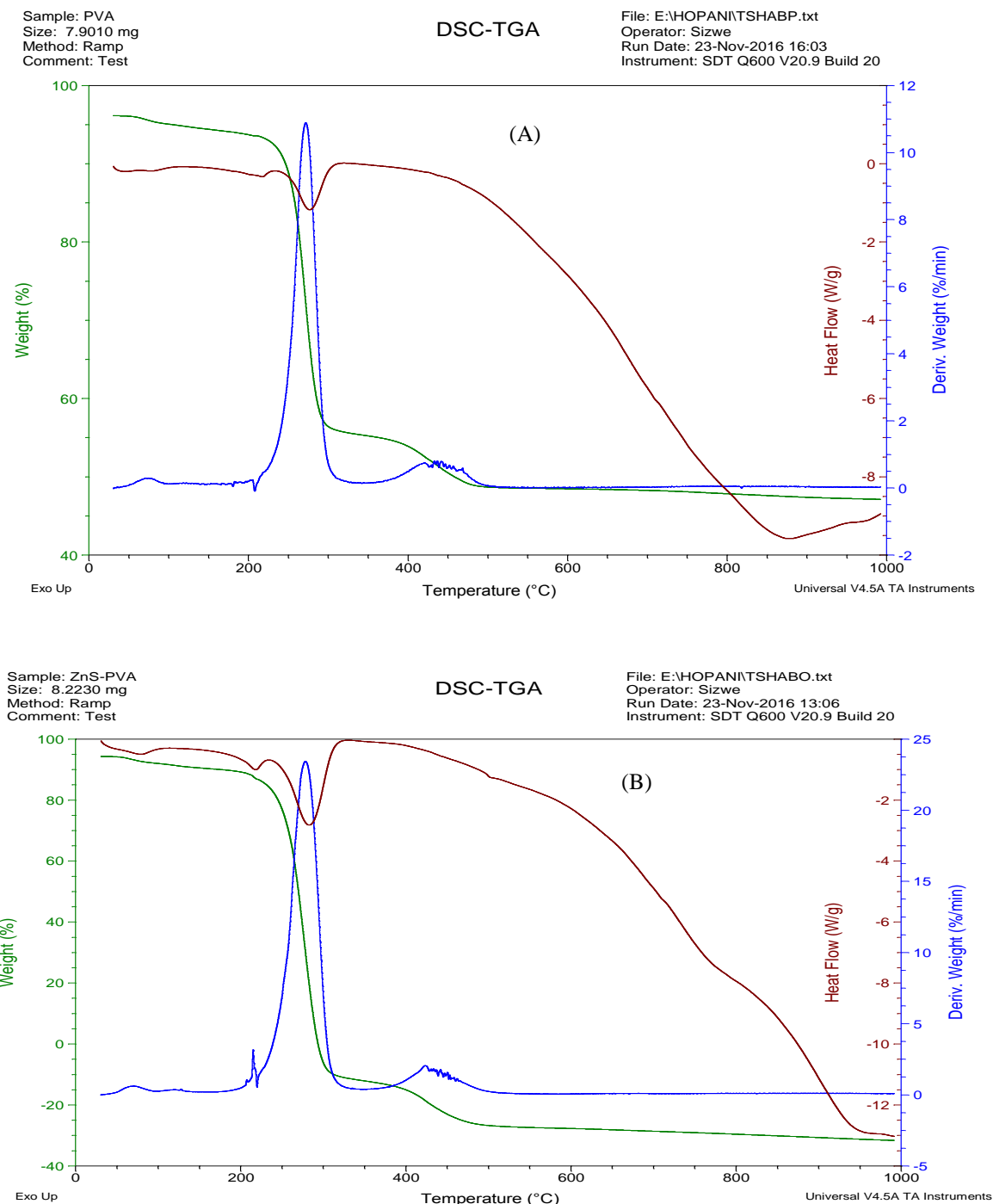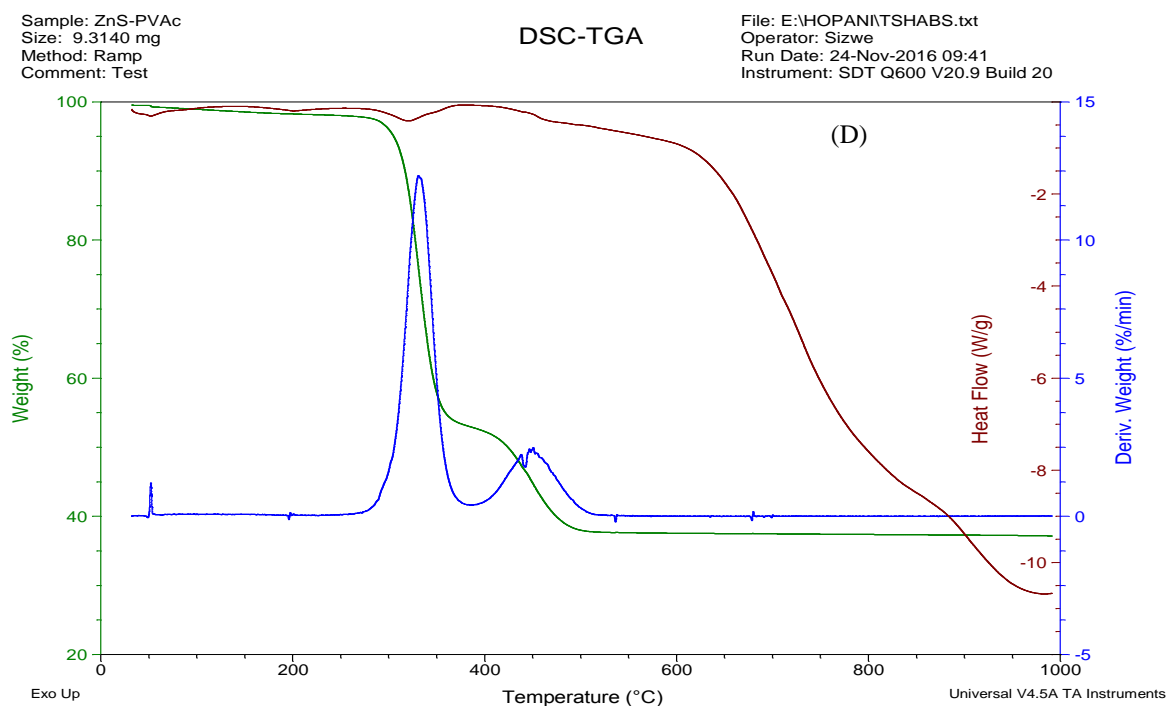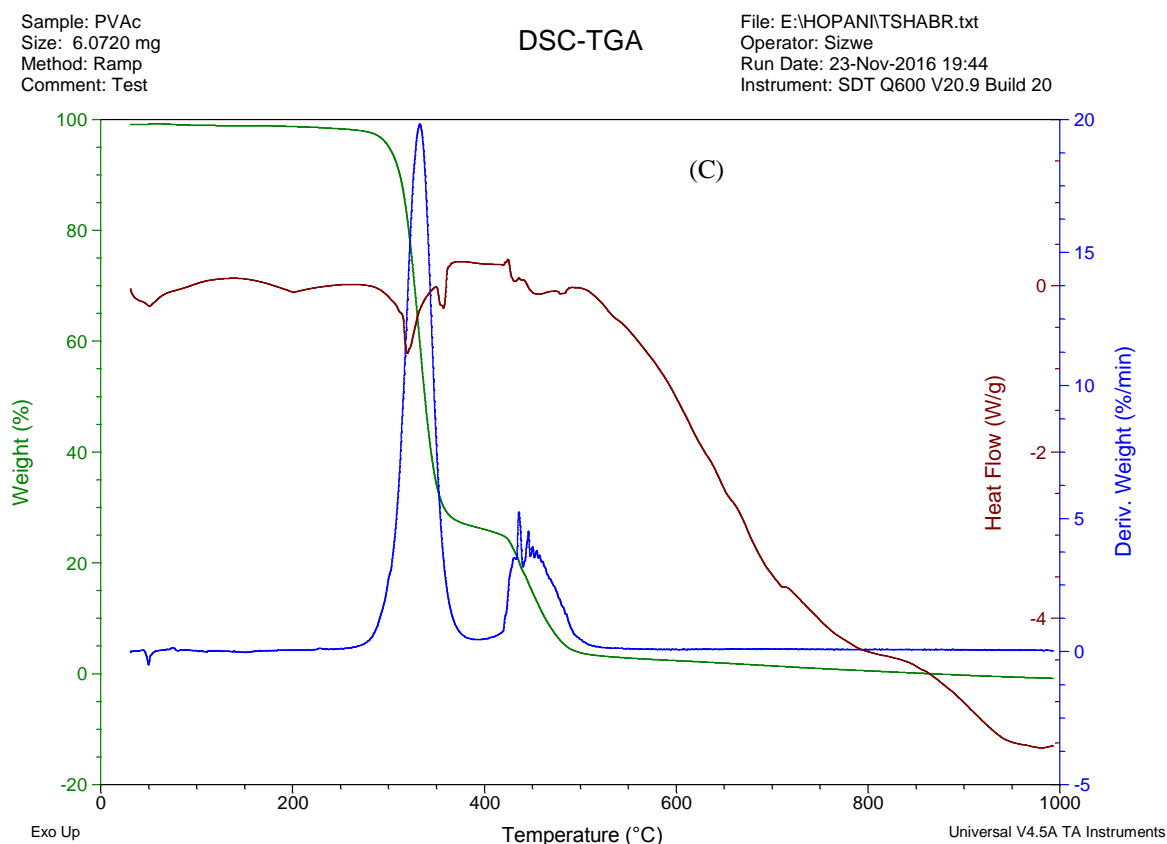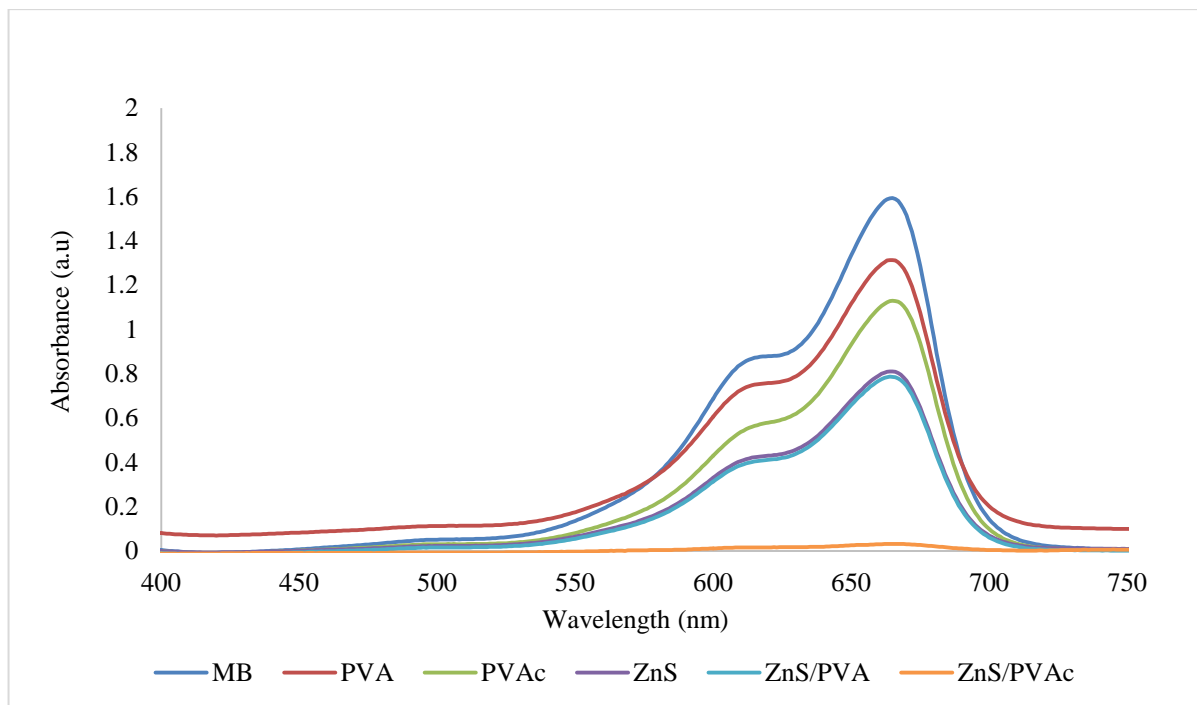
Figure-4: TGA analysis curves of (a) PVA (b) ZnS -PVA (c) PVAc (d) ZnS-PVAc nanofibers.

Figure-5: Photocatalytic degradation of PVA, PVAc, ZnS, ZnS/PVA and ZnS/PVAc.

Photocatalytic degradation of methylene blue: The photocatalytic degradation activities of different nanocomposites were studied. The dye degradation process was monitored at an absorption band of 666 nm which is the maximum absorption wavelength of methylene blue [18]. Pure PVA and PVAc and the ZnS nanoparticle and ZnS/PVA nanocomposite all gave a reduced absorption peak as compared to the methylene blue, with ZnS/PVAc having the highest effect of photodegradation of methylene blue. The absorption peak from the ZnS/PVAc is the lowest when compared with to methylene blue and the other samples. Moreover, there was a complete decolarization of the dye when ZnS/PVAc was used as the catalyst. The photocatalytic activity of the components can be arranged in the following ascending order: PVA<PVAc<ZnS<ZnS/PVA<ZnS/PVAc.

Conclusion

Zn(II) complexes were synthesized from two dithiocarbamate ligands: Ammonium *N*-methyl-*N*-phenyl dithiocarbamate and Ammonium *N*-ethyl-*N*-phenyl dithiocarbamate. The complexes formed served as single source precursors for the preparation nanoparticles (ZnS). The UV-visible spectroscopy have confirmed a blue shift in the absorption band. PVA and PVAc were used to encapsulate the ZnS nanoparticles produced. Among all the nanocomposites samples used in this experiment, ZnS/PVAc exhibited the best photodegradation of the methylene blue dye in aqueous system. FTIR spectra supported the formation of ZnS-PVA and ZnS-PVAcnanocomposites. Thermogravimetric analysis showed that the nanocomposites are stable and with enhanced stability compared to the pure polymers. Scanning electron and transmission electron micrographs confirmed the formation of different morphologies of the nanofibers.

Acknowledgement

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