

FLUORESCENT CDSE NANOPARTICLES IN ELECTROSPUN POLYETHYLENE OXIDE (PEO) NANOFIBRES: PREPARATION AND CHARACTERIZATION

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ABSTRACT

Polyethyleneoxide/CdSe composites nanofibres were fabricated using electrospinning technique. The composites were prepared by dissolving 2, 5 and 6 % (with respect to PEO) CdSe in PEO polymer solution with the concentration of 3 wt %. The effect of CdSe loading on the fibre diameters, morphology, optical and thermal properties was evaluated using SEM, UV-Visible, photoluminescence, TGA. The diameters of the fibres were found to increase with CdSe loading while their morphology also changes. The UV-visible and photoluminescence showed the absorption and the emission properties of characteristic CdSe nanoparticles with a stable emission at all CdSe loadings. The XRD showed a decrease in crystallinity of the polymer upon addition of CdSe nanoparticles. The stability of the composite fibres was evaluated with TGA which showed that the concentration had no significant effect of the stability of the polymer.

Keywords: *Nanocomposite, nanofibres, quantum dots, cadmium selenide, polyethylene oxide.*

1. INTRODUCTION

Electrospinning technique has drawn a lot of attention as a useful method for fabricating polymer fibres. This technique produces fibres with large surface area and small diameters [1]. The discovery of the technique has attracted interests in the production of polymer nanocomposites (PNCs) materials apart from the original pure fibres [2-5]. PNCs are materials in which inorganic materials are dispersed in organic polymers [6]. Despite the applications of pure electrospun fibres the addition of inorganic materials into fibres creates new properties to the composite material which make it useful for other applications. The recent endeavours have involved the dispersion of fluorescent quantum dots in polymers for the production of optical fibres [7-9]. These materials are very promising for the fabrication of photonic devices [10]. Quantum confinement effect that is a characteristic of quantum dots result in unique optical properties which can be tuned across the visible spectrum. This property allows the same material to emit light of different colours at different wavelengths [11]. Despite the growing demand in the use of composite polymers containing fluorescent materials little work has been done on electrospun polymer/quantum dots nanocomposites. These fibres are important for applications of optical fibres [12]. Electrospun fibres have found applications in sensors, electronics and medicine [13-15]. The shortage of such information results in limitations in applications. Advancements in applications require intensive studies and understanding of the behaviour and properties of such electrospun composite materials.

As part of the exciting attempts on the electrospun polymer/quantum dots we herein report the properties of the PEO electrospun fibres incorporated with CdSe. CdSe belong to the group II-VI semiconductor nanoparticles which are well known by their unique optical properties and a wide range of applications which includes for example solar cells, light emitting diodes and bio-labeling [16-19]. The reported PEO/CdSe fibres could be useful for a wide range optical and electronic applications. The properties of the composite fibres such as morphology, structure, optical and thermal have been investigated.

2. EXPERIMENTAL SECTION

2.1. Materials

All chemicals were used without any further purification. Trioctylphosphine (TOP) and hexadecylamine (HDA) (90%), Cadmium chloride, selenium powder, polyethylene oxide (PEO) ($M_w = 200,000$ g/mol) were purchased from Sigma Aldrich. The solvents, tetrahydrofuran (THF), N, N-dimethylformamide (DMF), toluene and methanol were also obtained from Sigma Aldrich.

2.2. Characterisation

2.2.1. Infrared Spectrometer

FT-IR spectra were recorded on a Bruker Tensor 27 spectrometer with 32 scans from 600–4000 cm^{-1} IR region. The powder complex and the polymers fibres were placed on the instrument sample holder and subjected to analysis.

2.2.2. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis was performed using a Perkin Elmer TGA 4000 thermogravimetric analyzer under nitrogen with a flow rate of 20 $^{\circ}\text{C}/\text{min}$. The fibre samples and the dithiocarbamate complex were heated from 30 $^{\circ}\text{C}$ to 800 $^{\circ}\text{C}$ at a scanning rate of 10 $^{\circ}\text{C}/\text{min}$.

2.2.3. Optical Characterization

The optical measurements were carried out using Analytikjena Specord 50 UV-VIS spectrophotometer. CdSe nanoparticles were dissolved in toluene and placed in glass cuvettes (1 cm path length) for analysis. The PEO composite samples were dissolved in DMF (heated slowly to dissolve the polymer) and analyzed in glass cuvettes as the quantum dots. A Perkin Elmer LS 45 Fluorimeter was used to measure the photoluminescence of the dissolved samples.

2.2.4. Transmission electron microscopy (TEM)

The TEM images were obtained using Jem-100S transmission microscope operated at 80 kV. CdSe nanoparticles were prepared by first diluting with toluene, placing a drop of diluted sample on a copper grid and drying at room temperature.

2.2.5. Electron scanning microscopy (SEM)

The FE-SEM (Leo, Zeiss) scanning electron microscopy operated at 1.00 kV electron potential difference was used to study the fibre morphologies and diameters. The polymer fibre samples were prepared by placing in the instruments sample holders, coated with a carbon tape and dried at room temperature.

2.2.6. X-Ray Diffraction (XRD)

The X-ray diffraction analysis were done on a Phillip's X'Pert materials research diffractometer at 40 kV/50 mA using secondary graphite monochromated Cu $K\alpha$ radiation ($= 1.5406 \text{ \AA}$). Measurements were taken at high angle 2θ range of 5° - 90° .

2.3. Synthesis of CdSe nanoparticles

In the preparation of CdSe nanoparticles selenium powder (0.5g, 6.3 mmol) was dissolved in (TOP) (5 mL) to prepare the solution of TOPSe. The prepared TOPSe solution was then injected into a hot mixture of HDA and cadmium chloride salt (0.5 g, 3.4 mmol) at a specific reaction temperature under the flow of nitrogen. The reaction was allowed to stand for 1 hour and it was then cooled to room temperature and the CdSe nanoparticles were precipitated with methanol and then separated by centrifugation.

2.4. Preparation of PEO/CdSe nanofibres

The PEO polymer solutions of different concentrations were prepared by dissolving the polymer in a mixture of THF and DMF (50:50) and stirred for 12 hours with slight heating to dissolve the PEO, then CdSe nanoparticles were dispersed into the prepared solutions and mixtures were stirred for 30 minutes at 60 $^{\circ}\text{C}$ to form composite solutions. The composite mixtures were subjected to electrospinning to produce fibres

3. RESULTS AND DISCUSSION

3.1. Morphology and structure of the composite nanofibres

The morphologies of the PEO and composite fibres were studied on the SEM to evaluate the effect of the addition of CdSe (**Fig. 1**). It can be noted that even though the addition of quantum dots increased the concentration, there was no major whipping motion experienced because of the low concentrations of the polymer that were used. The jet went a lot of axisymmetric Rayleigh and bending instabilities but little spiralling was observed at higher loadings as the viscosity increased. The jet inconsistencies due to the low viscosity used resulted in irregular fibre surfaces being formed. The fibre diameters were also affected by the loading of the QDs and as show by the histograms in **Fig. 1e** the diameters increased with an increased loading of either CdSe nanoparticles.

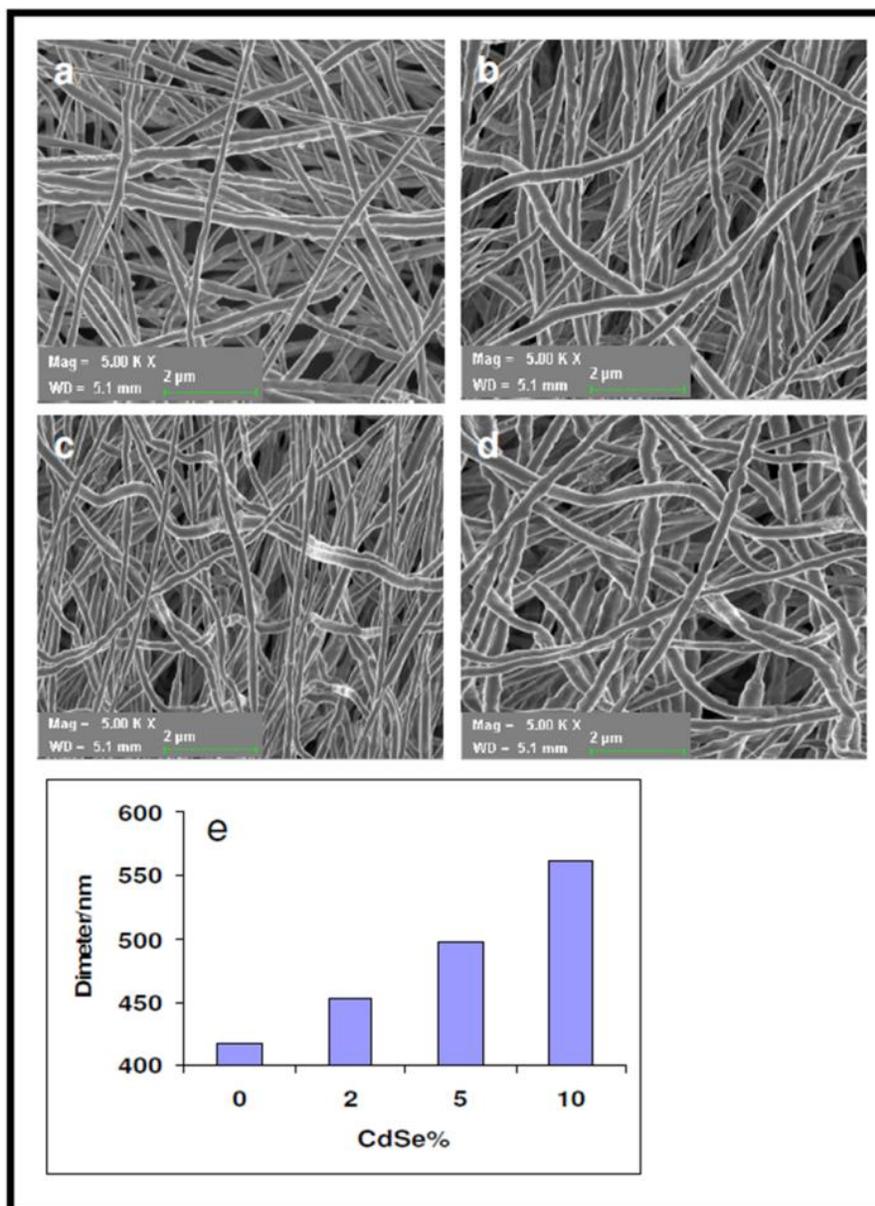


Figure 1: SEM images of 3 wt% PEO with (a) 0%, (b) 2 %, (C) 5 %, (d) 10 % of CdSe, (e) Histogram showing comparison between fibre diameter and the % of CdSe.

The histograms were obtained from the diameters which were estimated from the SEM images. For the given electrospinning conditions the diameters of the PEO fibres increased from the range of 491 to 559 nm for solutions spun with 3 wt% concentration of the pure polymer to 10% CdSe loading. The results obtained show that the addition of CdSe increased the concentration of the solution and alter the spinnability, morphology and diameter of electrospun fibres.

The presence of CdSe nanoparticles in the polymer, PEO was confirmed using EDX on SEM by the presence of Cd and Se on the spectrum (Fig. 2). The presence of the highly intense aluminium peak is due to the aluminium foil on which the fibres were deposited. The carbon and oxygen peaks were due to the PEO. The inserted image shows the distribution of the pure CdSe nanoparticles before incorporation. The CdSe nanoparticles gave size distribution of short rods ranging from 8 to 14 nm in diameter and uniform lengths of 12 – 14 nm.

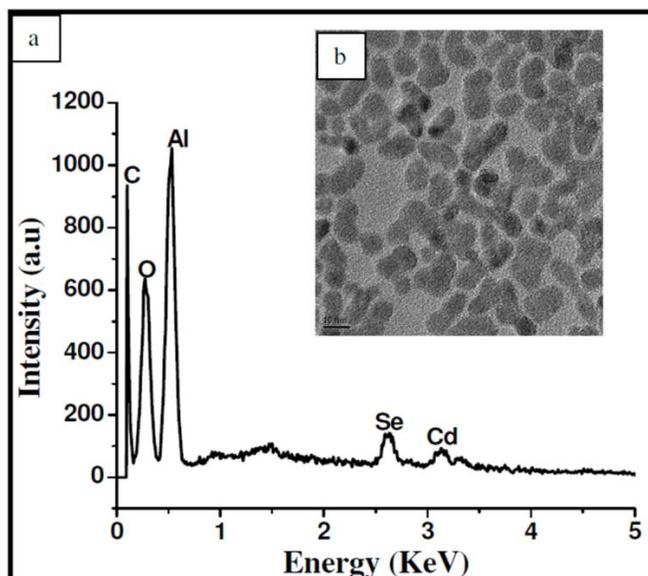


Figure 2: (a) EDX spectrum of PEO/CdSe composite fibres and (b) TEM image of CdSe nanoparticles before incorporation into fibres.

The XRD patterns of PEO/CdS and PEO/CdSe are illustrated in **Fig. 5.12** below. The presence of the two prominent peaks between 19° and 25° (2θ) indicate the presence of crystalline PEO. The XRD peaks of the free polymer and the composites appear at almost the same position although a peak shift was observed for the 5 wt% CdSe loading due to error caused by the height difference on the packed XRD samples. The XRD patterns show a decrease in the intensity as they become broader with increase in QD loading. This could be due to a disruption of a crystalline phase of the PEO as the quantum dots enter the voids of the polymer chains during complexation. This shows a loss of crystallinity of the polymer.

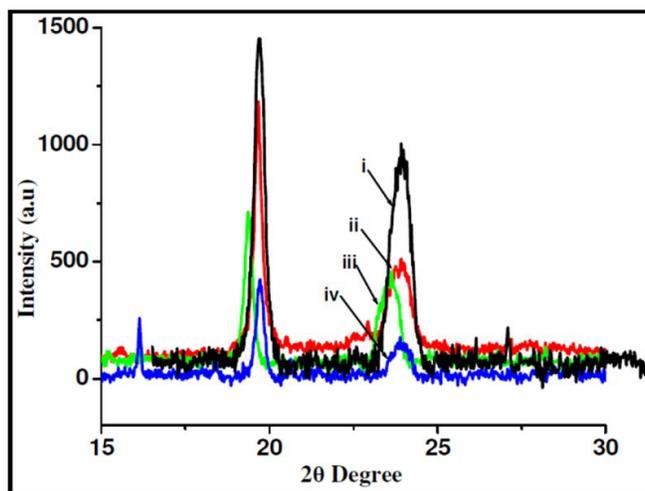


Figure 3: X-ray diffraction patterns of the composite fibres of PEO /CdSe; (i) 0 %, (ii) 2 %, (iii) 5 % and (iv) 10 % CdSe.

3.2. Optical properties of the composite fibres

The UV-visible and photoluminescence spectra of the prepared composite fibres are shown in **Fig. 4**. The excitonic peaks in the absorption spectra show the quantum confinement features of the incorporated QD, which were also featured in the polymer fibres. The absorption and emission peaks of PEO/CdSe composite fibre (**Fig. 4**) show red shifts of about 7 and 6 nm respectively from the free CdSe nanoparticles. This shift might have been a result of re-absorption as a result of the overlap between the absorption and emission spectra which promote exciton trapping and result in a red shift [20, 21]. Varying the amounts of the quantum dots had no effect on the peak positions of both absorption and emission spectra (**Figs. 4 c & d**). This indicated that the growth was not affected by the concentration during the electrospinning process. This indicate that the good quantum confinement properties of the

quantum dots. The emission peaks became narrower as the QD increases indicating a better interaction and distribution at higher loading. All the obtained absorption and emission spectra are blue shifted from the conventional bulk materials showing quantum confinement in the incorporated nanoparticles.

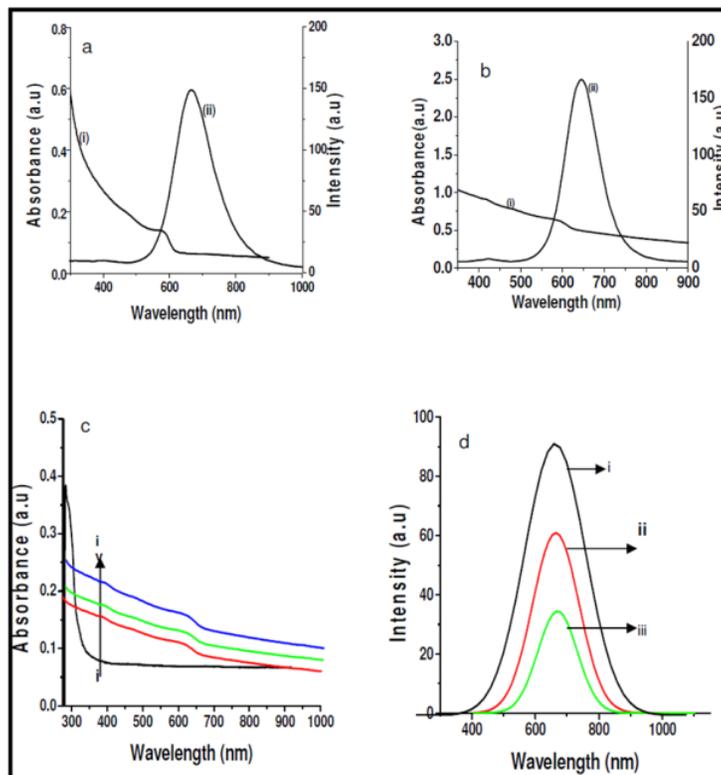


Figure 4: Optical absorption (i) and photoluminescence (ii) spectra of (a) HDA-capped CdSe, and (b) PEO/CdSe, as well as the absorption (c) and emission (d) spectra of PEO/CdSe composite fibres with (i) 0%, (ii) 2%, (iii) 5% and (iv) 10% of CdSe QD's

3.3. Thermogravimetric analysis (TGA) of the composite fibres

The TGA graphs of PEO/QDs in Fig. 5 depict a negligible change in thermal stability with loading of CdSe. The polymer chains begin decomposing at an onset of about 366 °C with the final decomposition at 433 to 435 °C as the QD loading changed from zero to 10 wt%. The thermograms show residues of quantum dots of about 4% (2 & 5 wt% loadings) to 16% (10 wt% loading). This shows the CdSe remainder after the decomposition of the polymer which does not show in the pure polymer. This is in contrast to the same interactions observed for CdSe and CdS QD's incorporated into polymer, poly methylmethacrylate, PMMA [22].

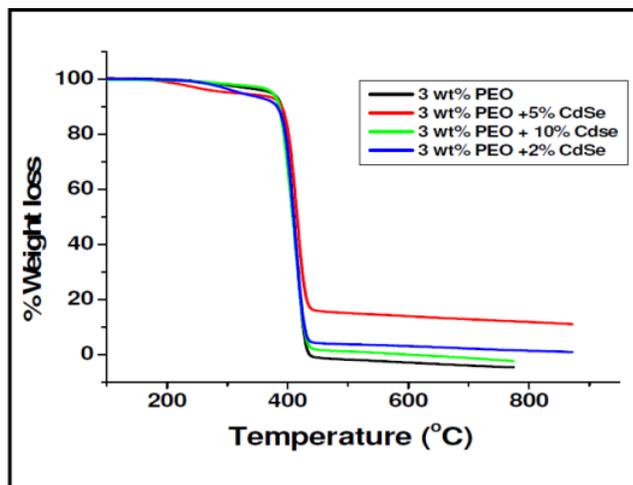


Figure 5: TGA of PEO/CdSe composite fibres.

4. CONCLUSIONS

CdSe nanoparticles were incorporated into PEO nanofibres using electrospinning technique. The loading of CdSe altered the concentration of the electrospinning solution thus the resulted in changes in morphology and an increase in fibre diameters. The incorporated CdSe nanoparticles exhibit good electronic properties after electrospinning. However the concentration had no significant effect on the thermal stability of the electrospun polymer.

5. ACKNOWLEDGEMENTS

This work was supported by the National Research Foundation (NRF) and was carried in the Department of Chemical Technology, University of Johannesburg. Dr P S Mdluli from Mintek (NIC), is also thanked for making the electrospinning technique accessible for the work.

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