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TOPO-capped silver selenide nanoparticles and their incorporation into polymer nanofibers using electrospinning technique

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ABSTRACT

Electrospinning is the most common technique for fabricating polymer fibers as well as nanoparticles embedded polymer fibers. Silver selenide nanoparticles were synthesized using tri-*n*-octylphosphine (TOP) as solvent and tri-*n*-octylphosphine oxide (TOPO) as capping environment. Silver selenide was prepared by reacting silver nitrate and selenium with tri-*n*-octylphosphine (TOP) to form TOP–Ag and TOP–Se solutions. Both absorption and emission spectra signify the formation of nanoparticles as well as the TEM which revealed spherical particles with an average particle size of 22 nm. The polymer, PVP used was prepared at concentrations ranging from (35 to 45 wt%) and the TOPO-capped silver selenide nanoparticles (0.2 and 0.6 wt%) were incorporated into them and electrospun by varying the voltage from 11 to 20 kV. The SEM images of the Ag_2Se/PVP composite fibers revealed the fibers of diameters with average values of 425 and 461 nm. The X-ray diffraction results show peaks which were identified due to α-Ag_2Se body centered cubic compound. The sharp peak observed for all the samples at $2\theta = 44.5$ suggest the presence of Ag in the face centered cubic which can be attributed to higher concentration of silver nitrate used with molar ratio of selenium to silver and the abundance of silver in the silver selenide crystal. Fourier transform infrared spectroscopy, thermogravimetric analysis (TGA) and ultraviolet–visible spectroscopy were used to characterize the structure of the PVP/Ag_2Se composite fibers.

1. Introduction

With the emergence of nanotechnology, researchers became more interested in studying the unique properties of nanoscale materials. Electrospinning is an electrostatic fiber fabrication technique that has brought more attention to many researchers due to its versatility and potential for application in many fields. According to previous report, fibers produced by electrospinning have high surface area to volume ratio and have found application in filtration, tissue engineering scaffolding drug delivery and wound dressing [1]. Unlike other conventional spinning techniques (e.g., solution and melt spinning) which are capable of producing fibers with diameters in micro-meter scale, electrospinning is capable of producing fibers with diameters in nanometer range. The incorporation of inorganic nanoparticles into polymer nanofibers can be achieved using either electrospinning polymer solution containing metal nanoparticles or by reducing the metal salts or complexes in the electrospun polymer nanofibers [2–5]. The obtained polymer nanofibers might exhibit improved optical, electrical, catalytic, magnetic and thermal properties. These properties of polymer nanofibers depend on the type of incorporated nanoparticles, their size, shape, their concentration and interaction with polymer matrix. Semiconducting nanoparticles have been material of great interest when it comes to polymer reinforcement due to their exciting properties especially their unusual size-dependent optical properties [6]. Different methods were used for the preparation of semiconducting nanoparticles which are micelle route, sol gel route, chemical precipitation route, colloidal route and metal organic route. In many semiconductors, decreasing the size of the material can provide a way to tune the physical properties and observe new phenomena. In particular, colloidal semiconductor nanocrystals provide strongly size specific optical and optoelectronic properties. These have been investigated for potential applications in solar cells, [7] light emitting diodes, [8,9] and biological imaging [10,11]. Among semiconducting nanoparticles Ag_2Se has been extensively reported in literature due to its interesting and useful properties [12]. Its high-temperature phase (β-Ag_2Se, >133 °C) is a superionic

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conductor that has been used as a solid electrolyte in photochargeable secondary batteries. The low-temperature phase (α-Ag_2Se, <133 °C) is a narrow band gap semiconductor with an energy gap of 1.2 eV. It has been widely used as a thermochromic materials and as well as photosensitizer in photographic films. The low temperature phase of silver selenide is also a promising candidate for thermoelectric applications because of its relatively high Seebeck coefficient ($-150\,\mu V\,K^{-1}$ at 300 K), low thermal conductivity and high electrical conductivity [13]. Jeong and Xia have shown that the reversible phase transition associated with Ag_2Se provides a new platform for the fabrication of photonic crystals with thermally switchable stop bands [14]. All these exciting properties of Ag_2Se nanoparticles could be introduced into polymers by incorporating these nanocrystals into polymers to form composite materials. In our study the PVP (Poly vinyl pyrrolidone) polymer was chosen for the production of polymer fibers. It has drawn a special attention amongst the conjugated polymers because of its good environmental stability, easy processability and excellent transparency. It is also a potential material having a good charge storage capacity and dopant-dependent electrical and optical properties. Chemically it has been bound to be inert, non-toxic and interestingly it displays a wide variety of smaller molecules. The prepared silver selenide nanoparticles were incorporated into PVP polymer to produce polymer nanofibers. The effect of applied voltage and polymer concentration were investigated. Furthermore, the effect of nanoparticles loading on the morphology, diameter and properties of the polymer nanofibers was investigated. The study is based on the principles of established silver nanoparticles with their antibacterial activity applied in different forms. One of the synthetic challenges for silver nanoparticles is their solubility and yield, in which case the introduction of selenide to silver is studied to alleviate such shortcomings of silver nanoparticles and also for possible improved properties, chemical stability and increased activity against bacteria. The selenide group on the metal also provides stronger chemical interaction between the nanoparticles and the polymer.

2. Experimental

2.1. Materials

All chemicals were purchased from Sigma–Aldrich. These are silver nitrate (99%), selenium powder (99.5%, 100 mesh), tri-*n*-octylphosphine (TOP), hexadecylamine (90%) (HDA) and triotylphosphine oxide (TOPO) (90% technical grade), poly (vinyl pyrrolidone) (PVP, M_w = 40,000), ethanol and *N*,*N*- dimethylformamide (DMF). Analytical grades of methanol and toluene were obtained from CC Immelman. All The chemicals were used as received.

2.2. Instrumentation

2.2.1. Optical characterization

The optical measurements were carried out using PerkinElmer Lambda 25 UV/VIS spectrophotometer (ELICO-SL-150). The samples were placed in quarts cuvettes (1 cm path length) using toluene as a reference solvent. A PerkinElmer LS 45 was used to measure the photoluminescence of the particles at the excitation wavelength of 200 nm. The samples were placed in glass cuvettes (1 cm path length).

2.2.2. Transmission electron microscopy (TEM)

The TEM images were recorded using HITACHI JEOL 100S transmission microscope operated at 80 kV. The nanoparticles were diluted in toluene and a droplet of a solution was placed on a carbon-coated copper grid. The sample was dried at room temperature prior to analysis.

2.2.3. X-ray diffraction (XRD)

The powder X-ray diffraction patterns were recorded by a BRUKER D2 diffractometer at 40 kV/50 mA using secondary graphite monochromated Co Kα radiation (λ = 1.7902). Measurements were taken at high angle 2θ range of 5–90° with a scan speed of 0.01 °q s^{-1}.

2.2.4. Scanning electron microscopy (SEM)

The FE-SEM (Leo Zeiss) scanning electron microscopy operated at 1.00 kV electron potential difference was used to study the morphology and diameter of the fibers. The fibers were carbon-coated prior to analysis.

2.2.5. Infrared spectrometer

Infrared spectra of the nanoparticles were recorded on PerkinElmer spectrum 400 FT-IR spectrometer ranging from 650 to 4000 cm^{-1}. The samples were placed onto the universal ATR sample holder and pressed on top by gauge force arm.

2.2.6. Thermogravimetry analysis (TGA)

Thermogravimetric analysis of the fibers and the composite fibers were performed using PerkinElmer STA 6000 simultaneous thermal analyzer under nitrogen with a flow rate of 20 °C/min. The samples were heated from 30 to 800 °C at a heating rate of 10 °C/min.

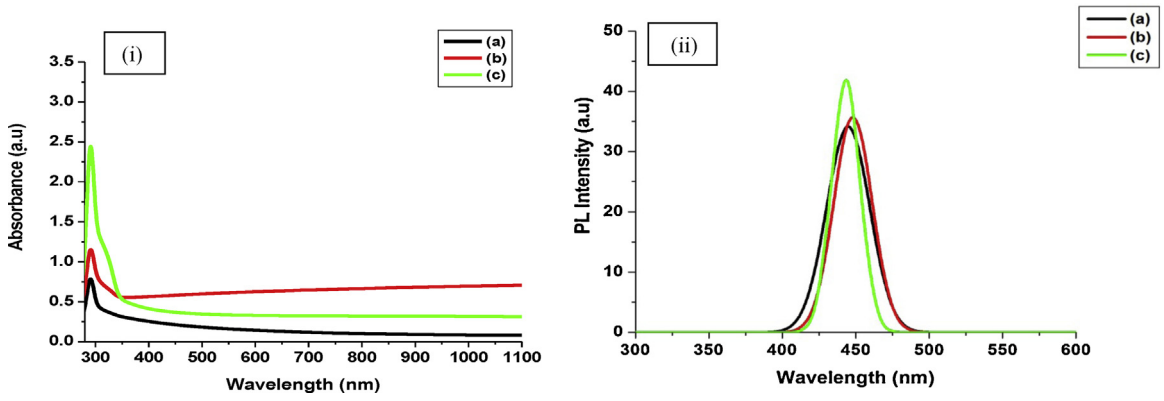

Fig. 1. (i) Absorption and (ii) Emission spectra of TOPO-capped Ag_2Se nanoparticles prepared at different temperatures (a) 180 °C (b) 200 °C and (c) 250 °C.