Investigation on Synthesis of Zinc Oxide-Polyethylene Oxide Composite Nano-Fibers by Electrospinning Method

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Abstract: Studying on nano-fibers is an interesting investigation because of their very small diameter and this gives them a very extent surface area in relation to their volume. Surface interaction of nano fibers is greater than different structure of materials because of their extent surface area. Geometrically, nano-fibers arranged in one dimensional materials category. These one dimensional structures have special properties comparing to other materials, because of their high flexibility and inelasticity characteristics. If the core of nano-fiber is filled by nano particles then they will have a nano-fibers structure. In this study electrospinning method has selected for nano fiber and nano composite synthesis, among the different methods. Essentially, electrospinning process is based on tensioning a polymer solution under high voltage. Firstly, nano particles of zinc oxide have processed by chemical method and then these they were used in synthesis of zinc oxide-polymer composite nano-fibers. These synthetic composite nano fibers were studied by Raman scattering, UV-Visible and IR spectroscopy, also by Scanning Electronic Microscopy (SEM) and Transmission Electronic Microscopy (TEM). The results of Raman characterization affirm formation of ZnO nano particles in the form of Poly Vinyl Pyrrolidone (PVP) polymer fibers. SEM images show that the synthesized nano fibers PEO/ZnO have an average diameter of 277 nm. SEM images have shown also, the diameter of these nano fibers is not the same along their length, i.e., they have not the same cross section along the length of nano fiber.

Keywords: Composite nano-fiber, electrospinning, nano particles, raman scattering spectroscopy, SEM

INTRODUCTION

Although, nano-fibers synthesis by electrospinning method is the results of research and evolution of ideas of different researchers in several decades, but electrospinning is a process developed by Formhals (1934) to create polymer fibers via the electrostatic force (Formhals, 1934). Formhals was reported the results of different experiments for polymeric fibers synthesis by using electrostatic forces, in 1934-1944. Vonnegut and Neubauer (1952) were able to produce streams of highly electrified uniform droplets of about 0.1 mm in diameter (Vonnegut and Neubauer, 1952). Drozin investigated the dispersion of a series of liquids into aerosols under high electric potentials (Drozin, 1955). Simons patterned a method for producing of light nano-textiles (simons, 1966). Baumgarten has made a device for electrostatic spinning of acrylic microfibers of about 0.5 to 1.1 μ in diameter (Baumgarten, 1971). Then, during afterward years, particularly in recent years, electrospinning method was developed and extended for producing nano-fibers from different type of polymers (Ramakrish et al., 2005; Huang et al., 2003; Chronakis, 2005).

Nano-fibers have very interesting flexibility and inelasticity characteristics, because they have a high surface area per mass unit. For example, this may be about 10000 to 1000000 (Song et al., 2005). Their large surface area, leads to provide a high capacity for binding to different types of nano particles. Nowadays, synthesis of polymer and composite polymer nano-fibers, because of their considerable applications, is much more desirable. There are many techniques for synthesizing polymer and composite polymer nano-fibers, in this study electrospinning method was used (Huang et al., 2003).

Electrospinning process consists of creating a high voltage between a reservoir containing polymer solution and having a capillary of maximum 0.3 mm in diameter and the target metallic plate where nano-fiber will be collect. High voltage between polymer solution and collecting plate causes an electrical force which creates a stream from inside of capillary to collector. In order that the fluid can flow, electrical force must overcome surface tension of polymer. The fluid in the end of capillary takes the shape of tailor cone, as critical voltage was reached, then the flow of polymer begins from the end of cone. Instability in flexibility cause narrowing of flow and forms nano-fiber over metallic plate.

Zinc oxide is a semiconductor which due to its wide bond gap (3.37 eV) (Morkoc et al., 1994) and interesting optical properties (nonlinear) (Michelotti et al., 2003), has
been the aim of much more investigations consisting semiconductors. A significant characteristic of ZnO is its high electron-cavity dependency energy, which results in extreme stability of electron-cavity dependency (Chen et al., 1998). It is well known that semiconductors of small dimension, because of quantum restrictions, may have very interesting optical properties (Dong et al., 2006; Schwartz et al., 2003). These properties and actual applications of ZnO, results in much more studies for providing nano structures of ZnO, so that synthesis of ZnO nano structures as nanorods and nanowires, nano particles and nano composite fibers are widely reported (Jiang et al., 2005; Müller and Wei, 1994; Kananth and Fu, 2005; Vayssieres, 2003; Sui et al., 2007).

In this approach we have provided nano particles of ZnO and then have synthesized zinc oxide-polymer composite nano-fibers by using Polyethylene Oxide (PEO) as polymer basis. The structure and characteristic of nano composite fibers were studied by Raman scattering, UV-Visible and IR spectroscopy, also by Scanning Electronic Microscopy (SEM) and Transmission Electronic Microscopy (TEM).

**MATERIALS AND METHODS**

This study was performed in Payame Noor University, Tehran, Iran, as a research project on synthesis of polymeric nano-fibers and nano composites in 2010 and 2011.

**Materials:** Polyethylene Oxide (PEO) (Mw = 400000), N, N-Dimethylformamide (DMF), Zinc acetate dihydrate ((CH₃COO)2 Zn.2H₂O) and Tetramethylammonium Hydroxide (TMAH).

**Electrospinning system:** The system which have used in this study consist of following sections: stainless steel rotary cylindrical collector, high voltage system (23 kV, 100 mA, accuracy = 100 V), polymer solution feeding system (using a micro-pump for uniform output of either polymer or polymer composite solution, minimum output flow = 1 mL/h). This system has been placed inside of a hood, for preventing any propagation of nano-fibers in air. This electrospinning system have been designed and mounted in nano-fiber and nano composite laboratory of Tarbiat Modarres University.

**Method of synthesizing ZnO-polyethylene oxide composite nano-fibers:** Synthesis of these composite nano-fibers was performed four stages as following:

- Providing suitable polyethylene oxide solution for electrospinning process, polymer powder was added gradually into DMF solvent and agitation by a stirrer at 25°C for 1 h. Materials properties and electrospinning process conditions were indicated in Table 1.
- Providing ZnO nano particles, firstly we have prepared 0.5 M zinc acetate by dissolving required amount of CH₃COO)2 Zn.2H₂O in DMF solvent. Then we add TMAH solvent within an interval of 20 min, by burette, for hydrolyzing initial solution in proportionality 1 to 1/4 of zinc acetate to TMAH. Note that, this step performs inside a bath of cold water and was agitated by a stirrer throughout the process.
- For preparing polymeric composite solution, obtained solution of ZnO nano particles (stage 2) was added to polyethylene oxide solution (stage 1) in different volume proportions. Then, this composite solution was agitated by a magnetic stirrer for 1 h in order to obtain a homogeny distribution of nano ZnO nano particles in solution.
- Electrospinning process was performed by charging the micro-pump with composite solution (prepared in stage 3).

Injecting this solution by micro-pump and introducing start up voltage for initiating electrospinning process, causes that polymer solution induced by repulsion forces of similar electrical charges via electrode of high voltage source and attractive forces due to grouping of opposite charges over rotary electrode, spout towards rotary cylindrical collector. The spouting composite traversing its pathway towards collector undergoes instability in flexibility, so that, while achieving collector, will traverse a spiral pathway and will collected over stainless steel rotary cylindrical collector. During process, the diameter, length and shape of nano-fibers may be controlled by voltage changes, distance between two electrodes, the rate of polymer solution injection and the velocity of rotary electrode.

**RESULTS AND DISCUSSION**

**Studying raman spectra of ZnO composite nano-fibers synthesized by electrospinning method:** There two types of nano-fibers which were synthesized from different ZnO nano particles solution with different volume proportionality, by electrospinning method in the
Fig. 1: Raman spectra (a), (b) and (c) for ZnO-PEO composite nano-fibers in relation with 15, 17.5 and 20 cm gaps, respectively, for low concentrations of ZnO nano particles

Fig. 2: Raman spectra (d), (e) and (f) for ZnO-PEO composite nano-fibers in relation with 15, 17.5 and 20 cm gaps, respectively, for high concentrations of ZnO nano particles

The spectra of low and high concentration of ZnO nano particles were shown in Fig. 1 and 2.

Because, these are Raman spectra, of composite nano-fibers, we must expect that in addition to polymer Raman peaks, Raman peaks due to ZnO nano particles, also, are present. But in the region where the peaks of ZnO nano particles must appear, there is only a large peak at 325 per cm. This peak was extended asymmetrically towards the upper wave numbers and overlap throughout the region. Thus, due to its high intensity, any sign of vibrating mode of nano particles, even, by increasing in ZnO nano particles concentration the peaks, couldn’t be observed. This may be interpreted as following:

- Considering that ZnO molecules are polar and asymmetric, peak intensity of this compound is essentially weak.

Therefore, because of its low intensity and presence of other impurities, probably, its Raman peak can’t be observed.

- Reference Raman spectra of Aldrich Co., consider much more peaks of vibrating modes, for PEO molecules, in this region. In the other hand, vibrating modes of ZnO lie, also, in the same region, consequently, it may be probable overlap of these vibrating modes results in a large peak which was observed at 325 per cm.

- If matrix spattering curves in a composite polymer is not in accordance with the same one for material which is composed, then the possibility of vibrating phonon propagation occurs only for the substances which have high luminescence. Generally, in such substances, related peaks appear in different regions of spectrum. In the case of our study, eventually, such interpretation may be admissible.

Studying UV-visible spectrometry: Further, we have noted that ZnO is a semiconductor with a wide gap bond (3.37 eV). Considering the fact, we will study UV-visible spectra of ZnO nano particles which have dried in 25 and
180°C. UV-visible spectra of ZnO nano particles are shown in Fig. 3. The spectrum obtained in room temperature, shows a peak at 968 nm which is not present in the spectrum obtained in 180°C. Since ZnO is transparent at visible wave length due to its wide gap bond, therefore, the mentioned peak may be attributed to existent impurities. As it can be observed, after drying in 180°C this peak disappears and not any more present. Adsorption wave length approximatively was placed at 364 nm which predicts a gap energy of about 3.4 eV which is compatible with gap energy of ZnO.

**SEM images of ZnO-PEO nano-fibers:** Studying SEM images of ZnO-PEO nano-fibers, we can confirm formation of fibrous structure of materials obtained from electro spinning method and their nano scales. Synthesis suitable nano fibers with adequate elongation and an average diameter in nano scale, needs much more investigations and experiments, providing different samples with different concentrations and determination of electrospinning conditions. Figure 4 shows SEM images of ZnO-PEO composite nano-fibers which have synthesized in our experimental conditions which are explained above. Figure 5 shows distribution diagram of ZnO-PEO composite nano-fibers in the same conditions discussed above.
CONCLUSION

Raman spectrometry shows that the spectrum of polymer fibers is similar to polymer powder one and the peaks present in both spectra haven’t so differences. This represents that polymer solvent will evaporate during electrospinning process and for this reason there is not any sign in fibers spectra. By Raman spectrometry we have satisfied formation of ZnO nano-fibers composite in PEO polymer matrix. The results obtained from UV-visible spectra show that the range of adsorbed wave lengths, partly is due to electronic transition of polymer molecules and partly is due to inter-bonds transition of semiconductor nano particles in composite.

SEM images show that synthesized nano-fibers of ZnO polymer composite, have an average diameter of 277 nm and show also, the diameter of these fibers varies along its length.

REFERENCES


