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Synthesis of Titanium Dioxide Shell-Core Ceramic Nano Fibers by Electrospin Method

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Abstract: In this investigation titanium dioxide nano particles were produced and were used to synthesize polymeric composite nano fibers and also, titanium dioxide - zinc oxide shell-core polymeric composite nano fibers by electrospinning method. Produced nano fibers are studied and characterized by Raman scattering, UV-Visible and IR spectroscopy, also by Scanning Electronic Microscopy (SEM) and Transmission Electronic Microscopy (TEM).The results of Raman specification prove the formation of TiO_2nano particles composite in Poly Vinyl Pyrrolidone (PVP) polymer fibers matrix.SEM images have shown the formation of TiO_2 polymeric composite fibers with an average diameter of 214 nm. TEM images have shown also, the diameter of these fibers vary along their length, in the other words, these composite fibers haven't a uniform cross section.
Keywords: Polymeric composite,electrospinning methodshell-core, nano particles, Raman scattering.

Introduction

Study for nano fiber synthesis by electrospinning method is the results of different researchers' investigations during decades and the progress of this idea, but the first apply of this method was performed by Formhals[1]. He has reported a patent for synthesis of nano fibers by electrostatic forces. Vonnegut et al could produce continuously and uniform stream of drops of 0.1 mm diameter by an electrical field[2]. Drozin has studied sedimentation of some liquids in aerosol suspension under high electric potential[3]. A pattern has been reported for produce of light nano textile by electrospinning method[4]. Baumgarten has constructed a device for electrospining of acrylic fibers of 0.5 to 1.1 micron diameter[5]. In the recent years, development and improvement of electrospin process was performed and composite nano fibers was produced by using this method[6]. Electrospinning process may be arising from electrodynamics effect, which is a physical process and is due to introducing an electrical force on a liquid drop.

It seems that, between different methods for producing nano fibers, electrospining process is the most convenient for producing individual and continuous nano fibers in massive amounts[7-9]. In this study synthesis of shell – core ceramic nano fiber by electrospinning method was investigated as a simple effective method for producing composite nano fibers.

Materials and Methods

Instrument. Electrospining system which was used in this research consists of different parts which was designed and constructed as following: 1. High voltage system, 2. Polymeric solution feeding system, 3. Electrospin system, and 4. Collector (figure 1).

Synthesis of titanium dioxide polymeric composite nano fibers: For producing this polymeric composite, nano particles of TiO_2 was prepared, firstly. The Method is the same as described by Ashrafi et al for synthesis of ZnO nano particles [6]. Then, Polymeric composite solution which is a composition of TiO_2 nano particles solution and polymeric solution by using electrospinning process were produced composite nano fibers. For modifications in morphology of fibers, process parameters as applied voltage, type of collecting electrode, the distance between two electrodes, and composite solution parameters as concentration of TiO_2nano particles in solution may be change. The samples of electrospin fibers and their shell for determination of their length, plot of distribution, direction and orientation and characterization of TiO_2 nano particles in their structure before and after thermal treatment on the shell, were studied by Raman scattering spectroscopy, SEM, TEM, XRD, UV-Visible and IR spectroscopy. The results obtained from microscopic and structural studies show formation of TiO_2 composite nano fibers. SEM and TEM images show that the surface of composite fibers because of polymeric specifications is completely uniform.

Synthesis of ZnO – TiO_2 shell – core ceramic nano fibers by electrospinning method: The process is described as above. Firstly, polymeric composite solution in which TiO_2 nano particles were distributed uniformly has prepared. Then, electrospinning process was followed by applying new arrangement of system for producing co-axial nano fibers (figure 2). In this case polymeric composite solutions of ZnO and TiO_2 were injected into electrostatic field of electrospinning process by two individual pumps and syringes. Certainly one of these solutions considered as shell and other one as the core of nano fiber, which may be considered as two co-axial cables.

Figure 1. Electrospinning system as used in this investigation

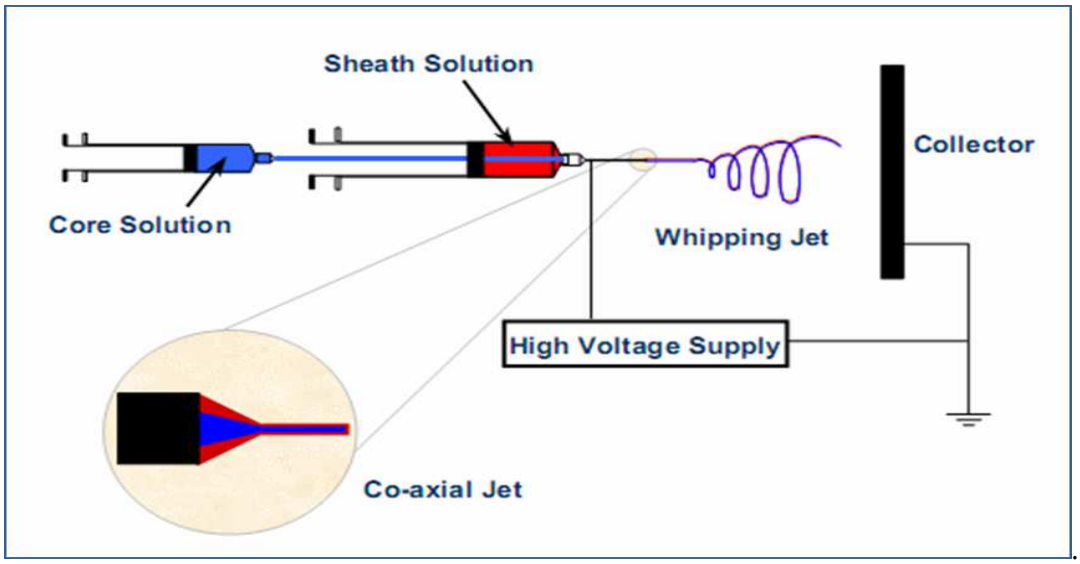

Figure 2. Scheme of electrospin system for producing co-axial nano fibers

For stability of process the flow rate of core solution must be less than shell solution. At the end of the process and collecting ZnO – TiO_2 shell – core ceramic nano fibers, they must be exposing to a calcification for elimination excess polymers and other organic substances, and ZnO – TiO_2 shell – core ceramic nano can be obtain.

Results and discussion

Studying Raman spectra of TiO_2 Nano fibers synthesized by electrospinning: TiO_2 nano particles prepared by sol-gel method have Anatase phase, and were calcified in 450°C. They have a specified Raman spectrum which is shown in figure 3. As it can be seen they show three main modes of TiO_2 nano particles in 399.6 cm^{-1}, 521.8 cm^{-1}, and 643.0 cm^{-1}. Thus, observation these modes in synthesized nano fibers will indicate presence of TiO_2 nano particles.

The spectra of pure PVP polymer powder and fiber are shown in figure 4. This is for observing probably variation due to remaining solvent in the structure of polymer nano fiber.

As it can be seen in these spectra they are almost the same allure and the existent peaks in these two spectra haven't so changes. This shows that polymer's solvent (water or ethanol) during electrospinning process will evaporate and leave polymer, because there isn't any trace due to these solvent in Raman spectra (figure 4).

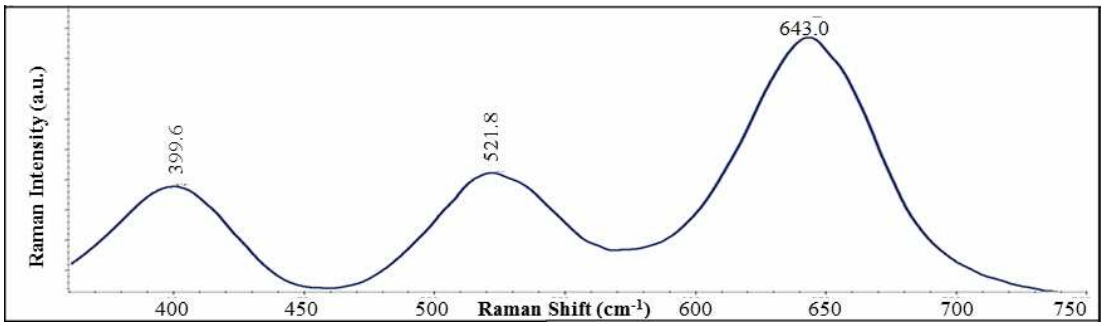

Figure 3. Three main modes of Raman spectrum of nano TiO_2 prepared by sol-gel method

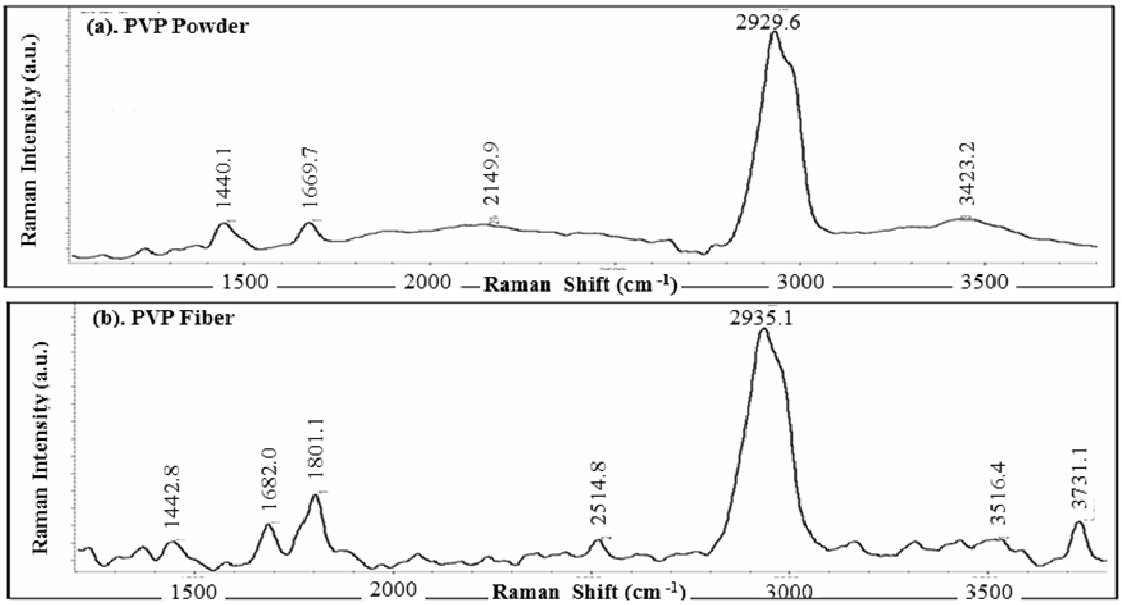

Figure 4.Raman spectra of (a).PVP polymer powder and (b).PVP fiber prepared by electrospinning

Figure 5 shows Raman spectra of TiO_2 nano particles, PVP fibers and PVP/TiO_2 composite fibers in the interval where TiO_2 modes are present. As the spectra show, two peaks in 522.5 cm^{-1} and 643.2 cm^{-1} related with TiO_2 nano particles have appeared by good approximation in 532.2 cm^{-1} and 639.7 cm^{-1}. In fact, the spectrum of PVP/TiO_2 composite nano fibers is the consequent of TiO_2 nano particles and PVP fibers spectra. Thus, formation of TiO_2 nano particles in matrix of PVP polymer nano fibers may be studied by Raman spectroscopy.

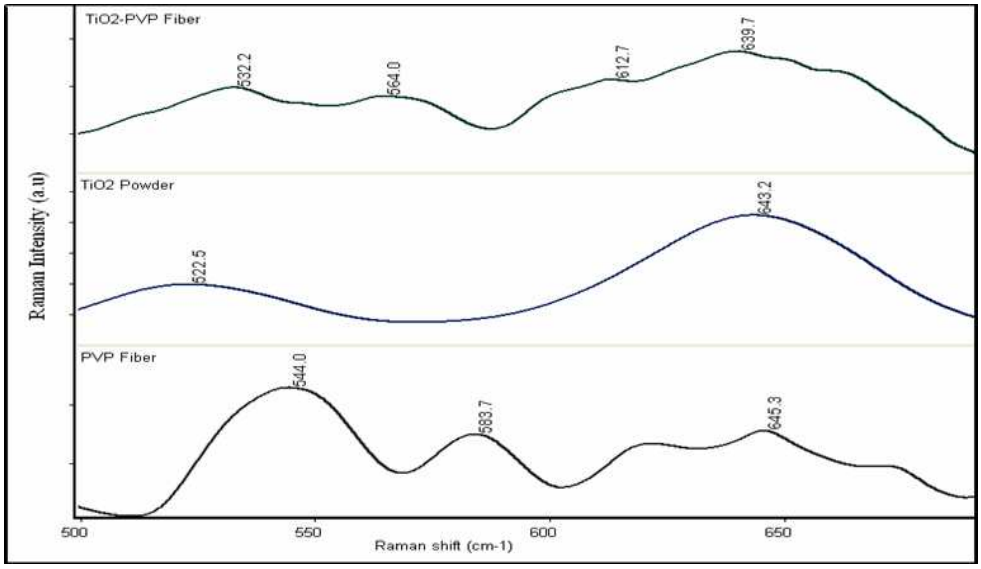

Figure 5. The spectra of PVP/ TiO_2 composite nano fibers comparing with TiO_2 nano particles and PVP polymer nano fibers

Studying the results of UV/Visible/NIR spectra: TiO_2 and ZnO are semi-conductors and their energy band gaps are 3.2 eV and 3.37 eV, respectively. Figure 6 shows UV/Visible/NIR spectrum of nano fiber shell. As it can be seen, adsorption intensity increases with wave length decrease, so that it has a maximum adsorption at about 300 nm. This is in accordance with transparency of polymers in IR region.

Figure 7 shows UV/Visible/NIR spectrum ofTiO_2 nano particles which were composited with polymeric nano fibers. As it can be observing, adsorption wave length in 377 nm is in good accordance with energy bond gap of TiO_2.

UV/Visible/NIR spectrum of ZnO shows a maximum absorbance at 364 nm which approximately gives 3.4 Ev energy gap and in good accordance with the energy gap of ZnO (figure 8).

Comparing UV/Visible/NIR spectra of produced shell-core nano fibers (figure 9) it can be seen that these spectra are not similarly with polymeric nano fibers spectra. In fact, maximum absorbance for composite shell-core nano fibers which was 300 nm in absence of nano particles shifted towards higher wave lengths, i.e. towards the wave lengths which were absorbed by nano particles.

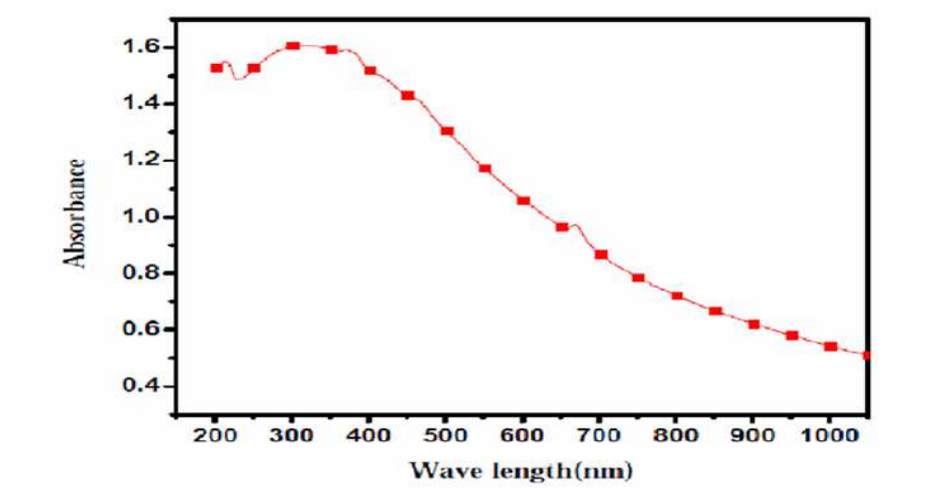

Figure 6. UV/Visible/NIR spectrum of polymeric nano fiber shell

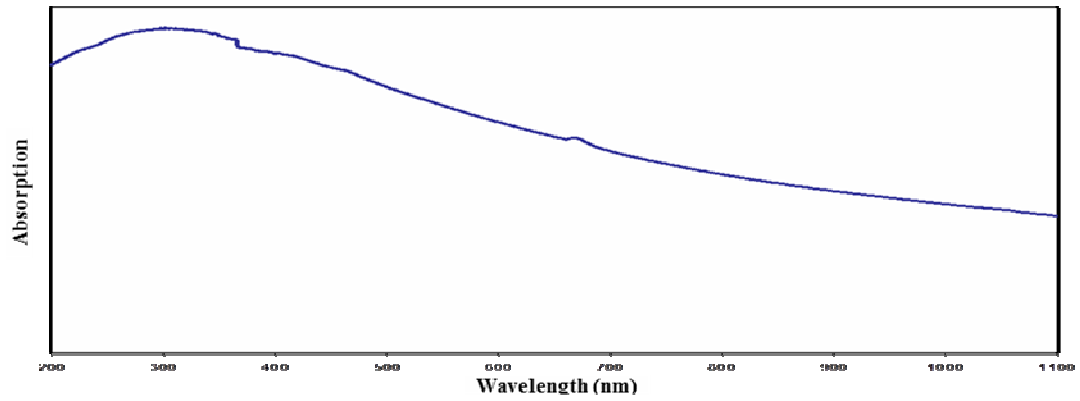

Figure 7.UV/Visible/NIR spectrum of TiO_2 (Anatase) nano fibers produced by electrospinning

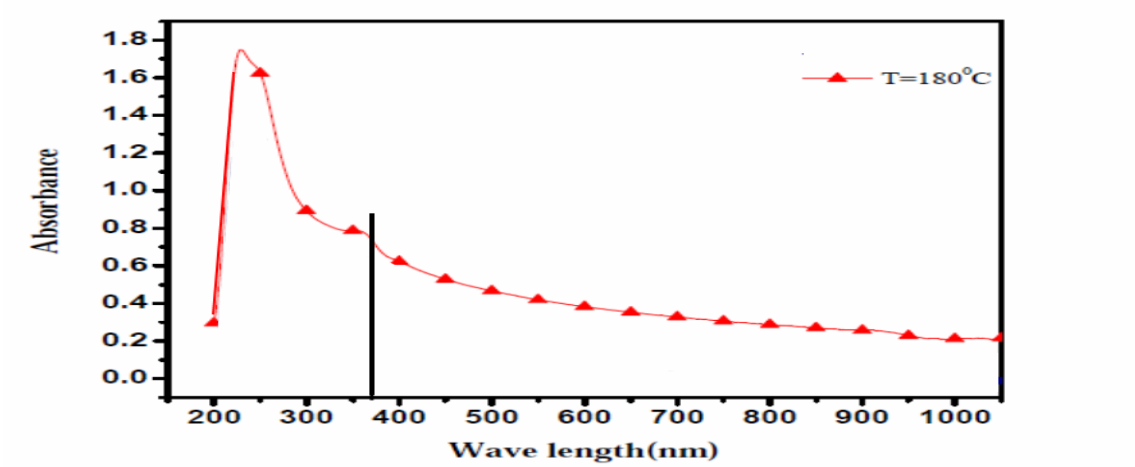

Figure 8. UV/Visible/NIR spectrum of ZnO nano particles after calcification at 180°C

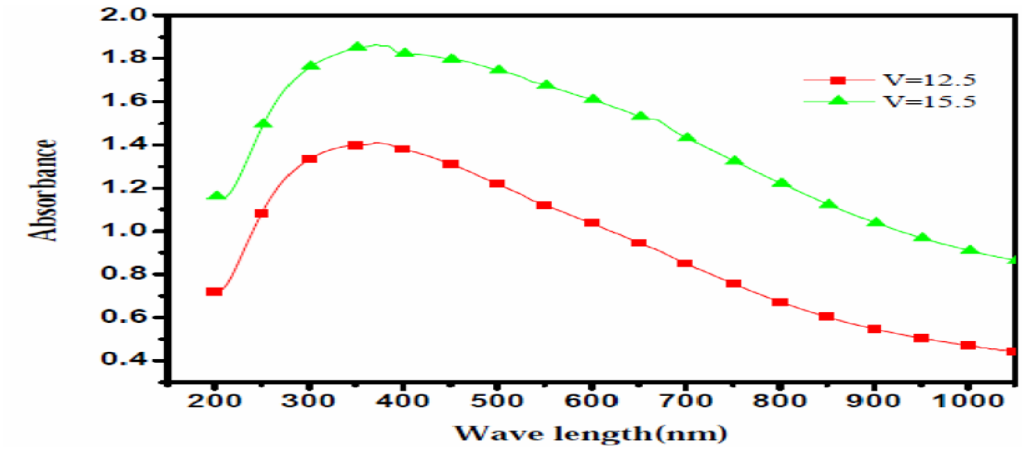

Figure 8. UV/Visible/NIR spectrum of synthesized shell-core nano fibers in different voltages

Generally, it can be deduced from these spectra that,in shell-core composite nano fibers comparing with polymeric nano fibers, wave lengths adsorption range spreads so that, part of adsorbed wave lengths range is related to electronic transitions of polymer molecules and the other part is related to intra-band transitions of composite semi-conductor nano particles. Spectrum spreading, with regard to nano particles and polymeric nano fibers spectra may be interpreted as such, polymer molecules in composite shell-core nano fibers has more contribution in the 300-350 nm wave lengths of adsorption range, and semi-conductor nano particles in composite have more contribution in the 300-400 nm wave lengths of adsorption range.

Results from SEM images: Synthesis of convenient fibers which having suitable length and diameter in nano scale needs a wide research work for obtaining optimized conditions of electro spinning method. Figure 9 shows SEM images of ZnO composite polymeric nano fibers with an average diameter of 277 nm and TiO_2 composite polymeric nano fibers with an average diameter of 214 nm.

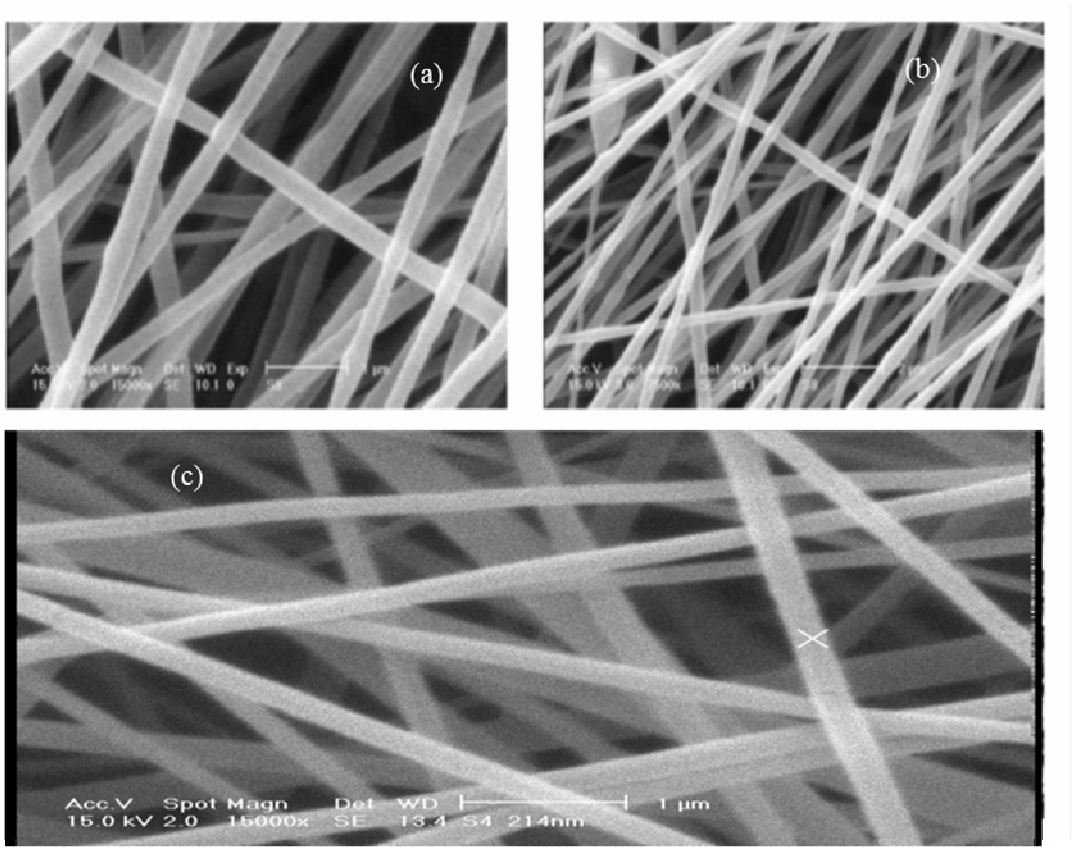

Figure 9.SEM images (a) and (b) ZnO composite polymeric nano fiberswith average diameter of 277 nm, and (c) TiO_2 composite polymeric nano fibers with average diameter of 214 nm.
(gap: 20 cm, Voltage 14 kV, and feeding rate: 0.5 mL h^{-1})

Figure 10 shows SEM images obtained from ZnO/TiO_2 shell-core ceramic nano fibers which were produced by electrospinning co-axial method. As it can be seen from these images, the ceramic co-axial nano fibers at similar condition have an average diameter greater than each of ZnO or TiO_2 polymeric nano fibers.

Results from TEM images: Studying nano fibers TEM images will give an idea of its internal structure. Figure 11 shows TEM images of ZnO/TiO_2 shell-core ceramic nano fibers. Figure 11. a shows that the diameter of these fibers varies along their length, in the other words they haven't the same cross section along their length. Figure 11. b shows a shell-core structure where transparent domains are the shell of nano composite. This structure is more evident in figures 11.c and 11.d. the core of this composite fibers was formed of nano particles which firstly were distributed homogenously in polymeric solution. Then, due to repulsion of induced electrical charges to polymeric solution surface, these particles were directed towards inside of polymeric solution column and were pushed toward co-axial nuzzles.

Conclusion

Raman spectroscopy (R.S.) shows that the spectra of polymeric fibers are nearly similar to the R.S. of polymers powder and existent peaks in these spectra haven't any differences from each other.

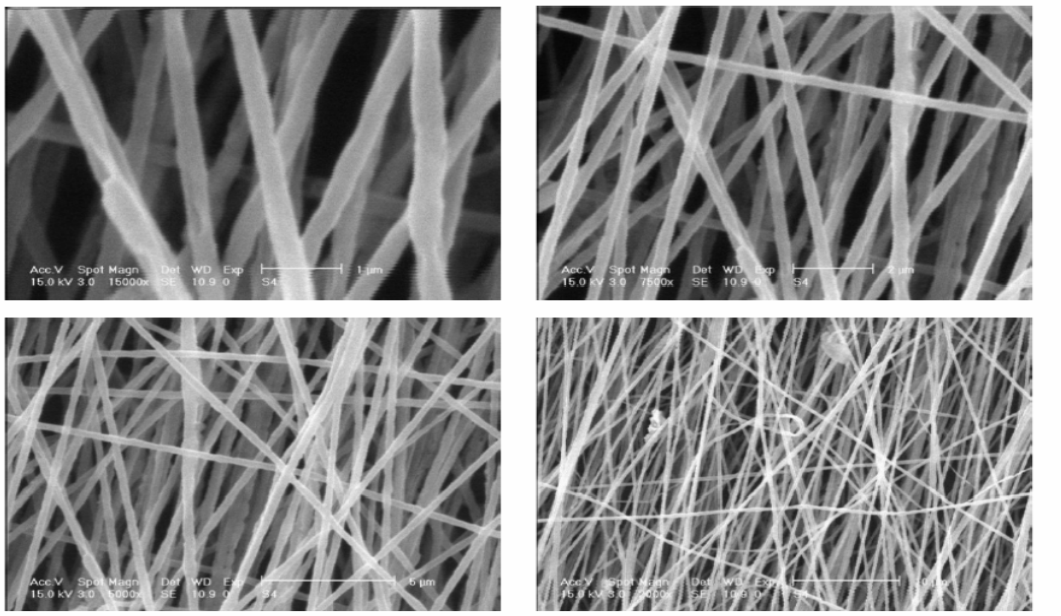

Figure 10.SEM images of ZnO/TiO_2 shell-core ceramic nano fibers with an average diameter of 328 nm (gap: 20 cm, Voltage 14 kV, and feeding rate: 0.5 mL h^{-1})

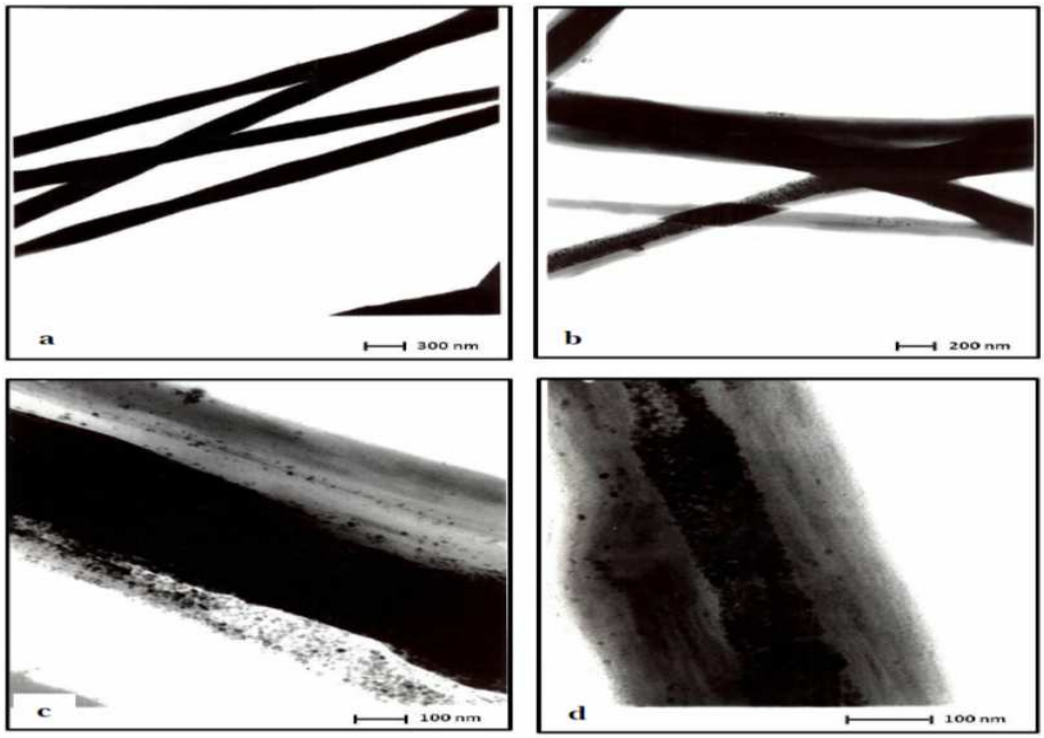

Figure 11. TEM images ofZnO/TiO_2 shell-core ceramic nano fibers (gap: 17.5 cm, Voltage 14 kV, and feeding rate: 0.5 mL h^{-1})

This shows that polymer solvent (water or ethanol) was evaporated during electrospinning process and was separated from polymer. By using Raman spectrometry we were demonstrated formation the composite of TiO_2 nano fibers in the matrix of PVP polymer fibers. Becauseof overlap of Raman spectra of ZnO polymeric composite and TiO_2 nano particles composite, it is not apply to study ZnO/TiO_2 shell-core ceramic nano fibers.

The results of UV/Visible/NIR spectra have shown in shell-core composite nano fibers, only the range of adsorption of wave lengths expands comparing with polymeric nano fibers. Thus, a part of adsorbed wave lengths range is related to electronic transitions of polymer molecules and the other part will be due to intra-banding transitions of composite semi-conductor nano particles.

SEM images were shown that ZnO composite polymeric nano fibers, TiO_2 composite polymeric nano fibers, and ZnO/TiO_2 shell-core ceramic nano fibers have an average diameter of 277, 214 and 328 nm respectively.

TEM images were shown that the diameters of ZnO/TiO2 shell-core ceramic nano fibers vary along their lengths, i.e. they haven't the same cross section.

Acknowledgments

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