

NANOFIBROUS NANOCOMPOSITES VIA
ELECTROSPINNING

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MASTER OF SCIENCE

By

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August, 2011

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ABSTRACT

NANOFIBROUS NANOCOMPOSITES VIA ELECTROSPINNING

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August, 2011

In recent years, numerous studies have been reported for fabrication of composite nanofibers from polymeric and inorganic materials by using electrospinning method. In the first part of this study, TiO_2 and ZnO inorganic nanofibers were produced by electrospinning from their precursors by using polymeric carrier matrix and their photocatalytic activity of these metal oxide nanofibers were studied. Moreover, electrospun TiO_2 nanofibers were crushed into short nanofibers (TiO_2 -SNF) and embedded in electrospun polymeric nanofiber matrixes such as poly(methyl methacrylate) (PMMA), polyacrylonitrile (PAN), polyethylene terephthalate (PET), polycarbonate (PC) and polyvinylidene fluoride (PVDF). Different weight loading of TiO_2 -SNF ranging from 2% to 8% (w/w, respect to polymer) incorporated into PVDF nanofibrous matrix was applied and the structural and morphological changes along with their photocatalytic activities were also examined.

In the second part, metallic nanoparticles produced by laser ablation method were incorporated into nanofibrous polymeric matrix by using electrospinning technique. For example, gold (Au) and silver (Ag) nanoparticles (NPs) were produced from their metallic sources by laser ablation method directly in the polymer solutions. The NPs/polymer mixtures were electrospun and surface plasmon resonance effect of Au-NPs and Ag-NPs on optical properties of the nanofibers was studied. In addition, germanium nanocrystals produced by means of laser ablation were mixed with PVDF polymer solution and consequently electrospun into composite polymeric nanofiber matrix.

Keywords: Electrospinning, nanofibers, TiO₂, ZnO, photocatalytic activity, laser ablation, germanium nanocrystals, gold nanoparticles, silver nanoparticles, nanocomposites.

ÖZET

ELEKTROEĞİRME İLE NANOFİBRİL YAPILI NANOKOMPOZİTLER

Ali Ekrem Deniz

Malzeme Bilimi ve Nanoteknoloji Programı, Yüksek Lisans

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Son yıllarda yapılan birçok çalışmada elektroegirme tekniği kullanılarak polimerik ve anorganik malzemelerden kompozit nanofiberler üretildiği bildirilmektedir. Bu çalışmada, titanyum dioksit (TiO_2) ve çinko oksit (ZnO) anorganik nanofiberler, kimyasal başlangıç maddelerinden polimerik taşıyıcı matriks kullanılarak üretilmiş ve fotokatalitik aktiviteleri çalışılmıştır. Bundan başka, TiO_2 nanolifleri TiO_2 kısa nanoliflerine (TiO_2 -SNF) parçalanarak poli(metil metakrilat) (PMMA), poliakrilonitril (PAN), poli(etilen teraftalat) (PET), polikaprolakton (PC) ve poli(viniliden florür) (PVDF) gibi elektroegirilmiş polimerik nanolif matrikslerine yerleştirilmiştir. %2 den %8'e (ağırlıkça polimere oranla) değişen TiO_2 -SNF farklı ağırlıklarda PVDF nanolif matriksine eklenmiştir ve fotokatalitik aktivitelerinin yanında yapısal ve morfolojik değişiklikler de gözlemlenmiştir.

İkinci kısımda ise lazer ablasyon metoduyla üretilen metal nano parçacıklar polimerik nanolif matrikslerine elektroëirme teknięi ile yerleřtirilmiřtir. Buna örneđ olarak, altın (Au) ve gümüş (Ag) nano parçacıklar (NPs) metal kaynaklarından direk polimer solüsyonlarında lazer ablasyon sayesinde üretilmiřtir. Bu NPs/polimer karışımları elektroëirilmiř, Au-NPs ve Ag-NPs'nin yüzey plazmon rezonanslarının, polimerlerin optik özelliklerine etkisi çalışılmıřtır. Buna ek olarak, germanyum nano kristalleri lazer ablasyon sayesinde üretilmiř, PVDF polimer solüsyonuyla karıştırılmıř ve sonu olarak kompozit polimer nanolif matriksi elektroëirme ile elde edilmiřtir.

Anahtar Kelimeler: Elektroëirme, nanolif, TiO₂, ZnO, fotokatalitik aktivite, lazer ablasyon, germanyum nano kristalleri, altın nano parçacık, gümüş nano parçacık, nanokompozit.

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PART 1

INTRODUCTION

1.1. Electrospinning

Electrospinning is a versatile and cost-effective technique for the production of multi-functional nanofibers from various polymers, polymer blends, composites, sol-gels, ceramics, etc. [1]. The basic principle of this technique is based on generating the direct movement of charged molecules by applying high voltage to supply the ejection of a liquid jet through spinneret from polymer solution droplet [2].

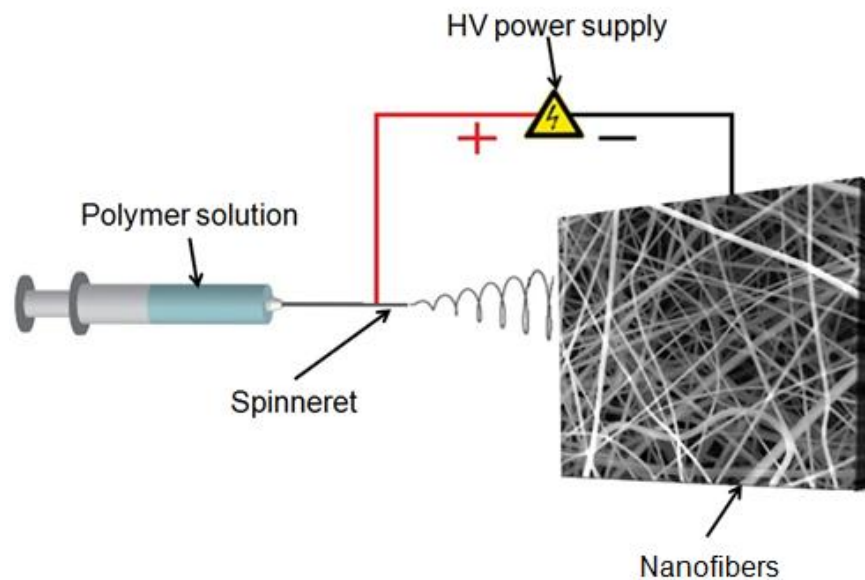


Figure 1 Schematic view of electrospinning

Electrospinning setup consists of three main components; high voltage power supplier, syringe pump and collector. Figure 1 shows the schematic view of electrospinning for polyacrylonitrile (PAN) nanofibers. When the electric field is created between the droplet of solution and the grounded collector, it overcomes the surface tension of solution and the polymer jet is formed for the fiber formation. The Taylor cone shape starts to be observed at the tip of the needle during the injection of this jet (Figure 2) [3]. The route of this charged jet is controlled by the electric field and bending instabilities which occur because of the repulsive forces existing in the jet. The bended jet extends through the collector hence it gets longer and thinner along with the evaporation of solvent by the collection of nanofiber structure [4].

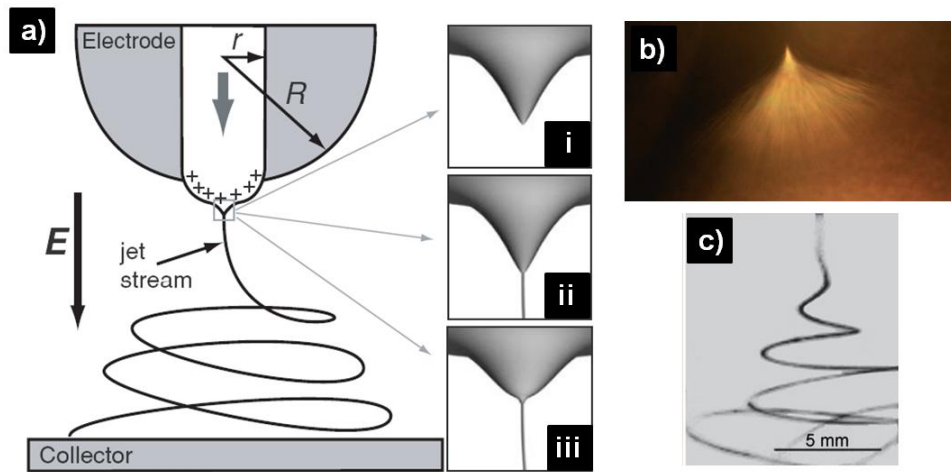


Figure 2 (a) Schematic representation of an electrospinning apparatus (r , radius of the capillary; R , curvature radius of the electrode used) and Taylor cones. (i) Formation of Taylor cone in an applied electric field. (ii) Taylor cone ejects fluid jet. (iii) Surface tension causes cone shape to relax [4]. (b) Photograph of a jet of PEO solution during electrospinning, (c) High-speed

photograph of jet instabilities [5]. These figures were adapted from [4,5] with permission.

1.2. Parameters of electrospinning

In electrospinning process, the morphology and uniformity of nanofibers are determined by considering a number of parameters which are investigated under two main parts: a) polymer/solution properties such as molecular weight, molecular weight distribution, viscosity, conductivity, dielectric constant, surface tension; and b) set-up parameters such as the electric field, the flow rate of solution, tip-to-collector distance. Moreover, the ambient parameters (temperature, humidity and air velocity in the chamber) may affect the formation of nanofibers.

The polymer/solution properties have the most important influence on the electrospinning process. For instance, the molecular weight of polymer type and the concentration of polymer solution should be high enough to provide the viscosity that is required for the curicial point of electrospinning; chain entanglement. It supplies the resistance also continuity of jet not to break into droplets and so prevents the bead formation during the process.

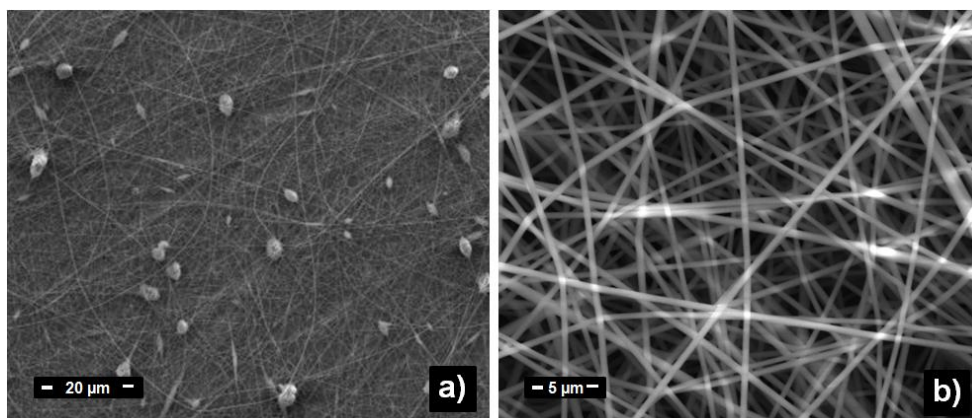


Figure 3 Representative SEM images of PAN nanofibers obtained from a) 15%, and b) 20% polymer concentrations. With increasing concentration, the bead structures are eliminated and bead-free, uniform PAN nanofibers are obtained.

Figure 3 shows the morphology tendency of electrospun PAN nanofibers in the increasing regime of concentrations. The beads structures are eliminated at higher concentration due to the adequate viscosity finally chain entanglement in the solution. Surface tension of polymer solution is another significant parameter that is taken into account. To obtain continuous fiber structures, the surface tension should be overcome by electrical charge of solution. The higher viscosity yields into more interaction between solvent molecules and polymer chains hence it restricts the gathering of solvent molecules to form the surface tension in the spherical shape on the polymer jet.

The set-up parameters are the second important issue that has certain effect on the fiber morphology. One of them is the tip-to-collector distance. As the distance gets further, the thinner fibers can be obtained owing to more

stretching time during the collecting of nanofibers. Otherwise, the closer distance between needle and collector causes coarse fiber formation or collapsing problem with the insufficient solvent evaporation. The other most decisive parameter of electrospinning process is applied voltage. The increasing voltage leads to decreasing at fiber diameter because fibers are exposed to more stretching under high electrical field. However, in the case of higher voltage, the fiber diameter indicates increasing because of the higher amount of pumped polymer solution [1, 2, 6].

1.3. Electrospun nanofibers and their applications

The electrospinning process can be carried with any soluble synthetic or natural polymer type having enough molecular weight. Electrospun nanofibers are easily obtained from synthetic polymer types like; nylon, polyesters, polyurethane etc. and also from natural polymers such as; collagen, silk, chitosan, alginate, cellulose etc. [3]. Moreover, metal oxide nanofibers are acquired by using suitable precursors in the polymer matrix. Nanofibers are not only produced from unique structures. To attain from the multifunctional properties of composite materials, they can also be performed so as to be in blend form or can be combined with additives such as; nanoparticles, drugs and different kinds of chemical components [1].

Nowadays, nanofibers have received considerable attention of materials science due to their exclusive properties that can be implemented in specific areas such as catalysis, filtration, nanocomposites, nanofibrous structures,

protective textiles, tissue scaffolds, drug delivery systems, etc. (Figure 4) [7].

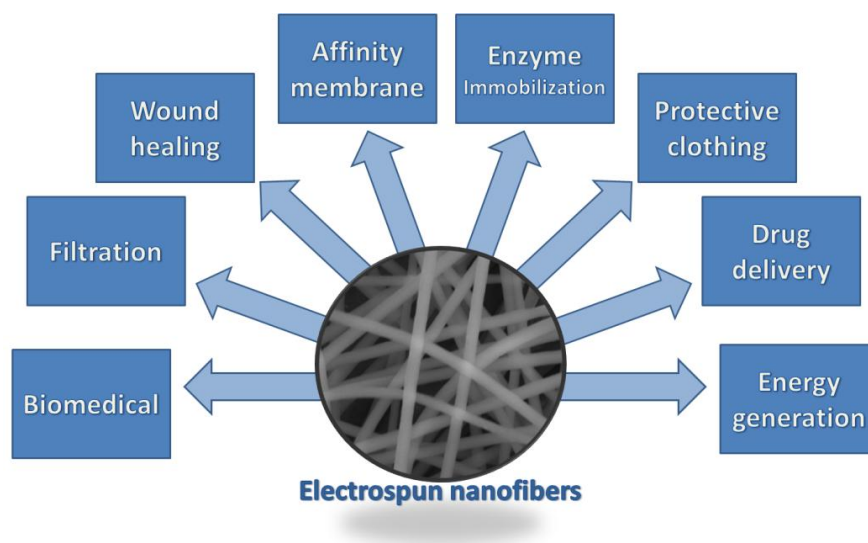


Figure 4 General application areas of electrospun nanofibers

Nanomaterials are of great interest as catalyst substrates owing to their large surface area and high catalyst loading capacity [7]. Nanofibrous catalysts could replace catalytic nanoparticles in order to transcend the issue of catalyst recovery. They have several advantages, such as flexibility in shape and low resistance to the flow of gases and liquids [8]. The activity of the catalyst supported on a substrate mainly depends on its large active surface area. Nonporous substrates can be coated with a high surface area material like nanofibers in order to increase the surface area, thus improving reactivity [8]. For instance, carbon nanofiber supports loaded with iron particles have demonstrated high conversion of hydrocarbons in comparison with active carbon and γ -alumina. It has been observed that the intrinsic

catalyst effect is more evident when loaded in smaller diameter fibers such as nanofibers [7].

Filtration is another area where nanofibers have been implemented. Polymeric nanofibers have been utilized in air filtration applications for more than a decade [8]. The small fiber diameters cause slip flows at fiber surfaces, causing an increase in the interception and inertial impaction efficiencies of these composite filter media. The enhanced filtration efficiency at the same pressure drop becomes feasible with fibers having diameters less than 0.5 micron. The implementation of nanofiber networks as a filtering medium holds promising potential. Keeping in mind that the essential features of protective clothing are high atmospheric moisture transport, increased fabric breathability, and enhanced toxic chemical resistance, electrospun nanofiber membranes stand as good candidates for these applications. The highly porous electrospun membrane surfaces aid in moisture vapor transport [7].

Moreover, tissue scaffolds and drug delivery are other well-known application areas of nanofibers. Nanofibers with high surface area and porosity have enormous potential for applications in engineering mechanically stable and biologically functional tissue scaffolds. The tissue scaffolding material must be selected carefully to ascertain its biocompatibility with the body cells. The biocompatibility depends on the surface chemistry of the scaffolds, which is dictated by the material properties [9]. The high surface to volume ratio of the nanofiber provides

more space for the cell attachment than the regular fibers. The dimensions of these engineered scaffolds were in the comparable scale with those of the natural extra cellular matrix. Electrospun biodegradable polymers are considered as suitable scaffolds for tissue engineering, with their big pore diameter and volume. The high porosity of the electrospun nanofiber scaffolds provides enough space for the cell accommodation and an easy passage for the nutrients and metabolic waste excretion. Mechanical properties like elasticity modulus and strain at failure are important for the application of electrospun nanofibers as tissue scaffolds [7, 9]. Moreover, nanofiber mats with their unique functional characteristics find application as drug carriers for the drug delivery system. Controlled delivery of drugs at a defined rate over a span of treatment is possible with biocompatible delivery matrices of either biodegradable or nonbiodegradable polymers [10].

In addition, electrospun nanofiber membranes also stand as potential candidates for protective clothing applications, because of their light weight, large surface area, high porosity, great filtration efficiency, effective resistance to penetration of harmful chemical agents in aerosol form and their ability to neutralize the chemical agents without impedance of the air and humidity permeability. Many methods for modification of nanofiber surfaces have been tried in order to achieve improvement in protection against toxins and one of the protection methods that has been used includes chemical surface modification and attachment of reactive moieties such as oximes, cyclodextrins, and chloramines [3].

Polymeric conductive membranes have enormous potential for applications such as, photovoltaic devices, electrostatic dissipation, corrosion protection, electromagnetic interference shielding, fabrication of electronic devices and sensors. Conductive membranes comprised of nanofibers can also be implemented for use as porous electrodes in developing high performance batteries and polymer electrolyte membrane fuel cells, due to their high porosity and inherent large surface area. Conductive nanofibers offer valuable properties of polymer batteries, for instance, reduced electrolyte leakage, high dimension flexibility, and high energy density per unit mass [3].

As is evident from the aforementioned brief discussion on the applications of nanofibers, the potential of nanostructured materials in advanced applications is highly promising (Figure 4). Researchers are constantly making efforts to exploit the high surface area and porosity properties to develop sophisticated state of art materials.

PART 2

CHAPTER I. INORGANIC NANOFIBERS

2.1. Inorganic nanofibers

Inorganic nanomaterials exhibit extraordinary chemical and physical features such as magnetic, electrical, optical and catalytic properties. There are numerous methods including; deposition, ball milling technique, synthesis in reversed micelles, Langmuir–Blodgett film, and self-assembled monolayers. In addition to these methods, combining the sol-gel processing and electrospinning technique enables us to produce inorganic nanofibers in a very practical manner. That method can be summarized with three steps; Firstly, a sol with suitable inorganic precursor and polymer system were prepared. Secondly, electrospinning procedure was applied with suitable parameters. Finally, inorganic nanofibers were obtained by calcinating the polymeric carrier matrix. For instance, titanium dioxide (TiO_2), silicon dioxide (SiO_2), zinc oxide (ZnO), aluminum oxide (Al_2O_3) and zirconium dioxide (ZrO_2) are the most commonly known metal oxide nanofiber types obtained by this method. Due to their high specific surface area, more active sites, abundant inner spaces and heterogeneous interfaces, inorganic nanofibers show superiority according to their bulk form in terms of electrical, optical and catalytic properties. Especially TiO_2 nanofibers can be more efficiently employed as photoanodes for dye-sensitized solar cells,

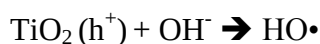
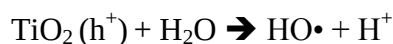
anode material for lithium-ion batteries and photocatalysts for filtration membranes [11, 12, 43].

2.2. Photocatalytic activity

The acceleration of photoreaction with the help of catalyst is called as photocatalysis. During the reaction, a substrate absorbs light and creates electron hole pairs that have ability to generate free radicals. The materials having photocatalytic property can be used for the destruction of organic pollutants in the water. Over the years, a large number of metal oxides have been utilized as photocatalysts for this purpose. The most commonly studied ones are TiO₂ and ZnO because of their high photosensitivity, nontoxic nature and large band gap. Due to their properties, both of them have the availability to be used for the detoxification of water from organic pollutants. When aqueous solution of TiO₂ is irradiated with photons whose energy is equal to or greater than its band gap energy (E_g = 3.2 eV) i.e., with $\lambda < 380$ nm, electron-hole pairs are developed (Figure 5).



Then, the hole produced by UV-light reacts with H₂O or surface-bound hydroxyl ion to produce OH• radicals which is the most oxidizing species in this process.



On the other hand, electrons released by irradiation of photocatalyst combines with dissolved molecular oxygen to form superoxide anion radical $O_2^{\bullet-}$. Then, these superoxide radicals generate peroxides which are able to combine with electron and form $OH^{\bullet}$ radicals in the medium.



Finally, hydroxyl radicals decompose by oxidizing the organic pollutants (OP) into non-toxic materials such as CO_2 and water.

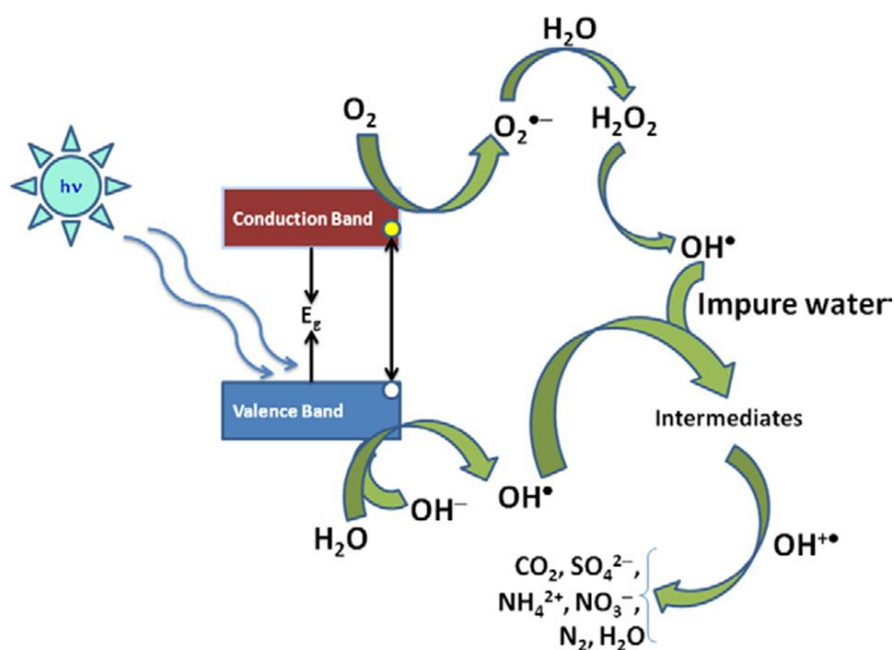
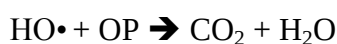


Figure 5 Mechanism of metaloxide photocatalysis. Picture is adapted with permission from [13]. The oxidizing species, $OH^{\bullet}$ radicals are produced by the reaction between electron-hole pairs and H_2O or surface-bound hydroxyl ion.

ZnO is also considered as a suitable photocatalytic agent due to its similar mechanism and bandgap energy with TiO₂. Moreover, it is one-up owing to its low cost, absorption ability of larger fraction at UV spectrum and availability to be used in commercial range in higher efficiency especially for herbicides and pesticides [10-12].

2.3. Materials

Titanium (IV)-isopropoxide (97%, Aldrich), zinc acetate dihydrate (reagent grade, Aldrich), glacial acetic acid (% 100, Merck), ethanol ($\geq$ 99.8%, Sigma-Aldrich), dimethylformamide (DMF) (Riedel, Pestenal), polyvinylpyrrolidone (PVP, Mw~1300000, Aldrich) were used as-received without any further purification.

2.4. Electrospinning unit at UNAM

Electrospinning unit at UNAM consists of syringe pump, high voltage supply, and a collector (Figure 6). Syringe pump (Model: SP 101IZ, WPI) is situated horizontally, and electric field was comprised by the high voltage power supply (Matsusada Precision, AU Series, Japan). Mostly, electrospun nanofibers were deposited on a grounded stationary cylindrical metal collector covered by a piece of aluminum foil. The electrospinning was carried out in enclosed Plexiglas box. That box is suctioned by portative hood for protection from hazardous solvents. Inside temperature and relative humidity are monitored by scientific wireless thermo-hygrometer (Honeywell, TM0005-X).

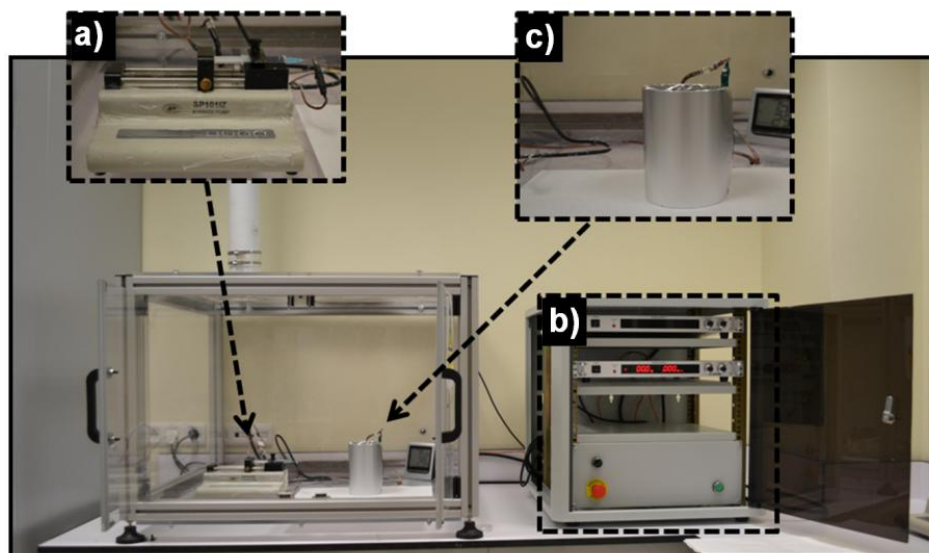


Figure 6 Electrospinning unit at UNAM consists of a) syringe pump, b) high voltage supply, and c) collector.

2.5. Fabrication of titanium dioxide (TiO₂) nanofibers via electrospinning

Firstly, solvent system was prepared by mixed with glacial acetic acid (2 ml) and ethanol (2 ml). Then, titanium (IV)-isopropoxide (2.88 ml) as a precursor was added into this solvent system. After stirring for 10 min, carrier polymer in electrospinning process which is PVP (0.6 g) dissolved in ethanol (3 ml) was added to this solution. Finally, the mixture was constantly stirred for 12 hours until the yellowish sol-gel was obtained.

For electrospinning process, the PVP solution which contains TiO₂ sol precursor was placed into a 1 ml syringe having metallic needle tip (inner diameter=0.4 mm). The syringe pump was used horizontally to feed the polymeric solution. The electrical field was generated by using high voltage

power supply. The electrospinning parameters were adjusted by applied voltage = 15 kV, feed rate = 0.5 ml/h, tip-to-collector distance = 10 cm. Finally, electrospun nanofibers were deposited on a grounded stationary cylindrical metal collector covered by a piece of aluminum foil (Figure 7).

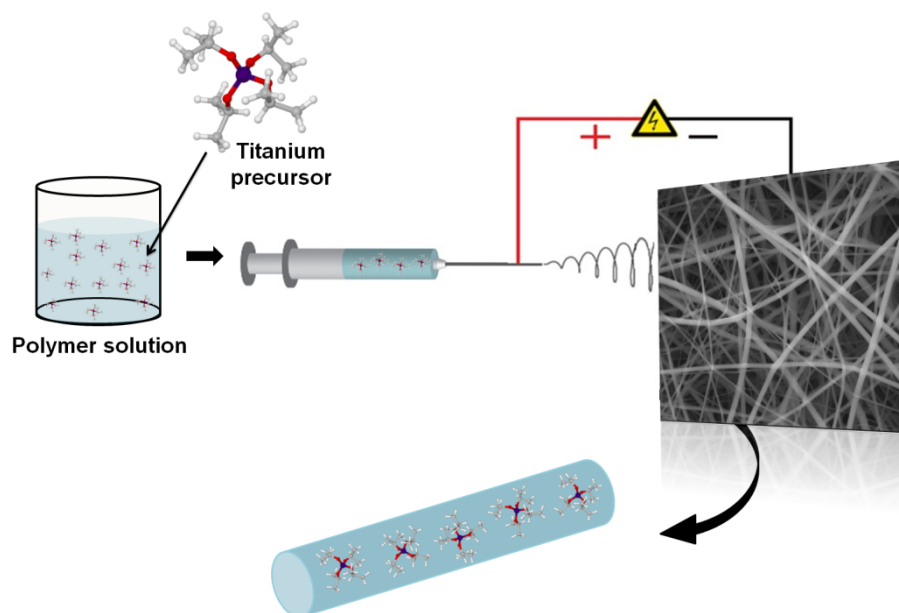


Figure 7 Schematic view of electrospun PVP nanofibers containing TiO_2 sol precursor from sol-gel polymer solution by applied voltage = 15 kV, feed rate = 0.5 ml/h, tip-to-collector distance = 10 cm.

The experiments were carried out in the closed Plexiglass box in order to provide protection from hazardous volatile solvents of process. Temperature and relative humidity were recorded as 23 °C and 26 %. After the electrospinning process, nanofibers were dried overnight under the hood and then calcinated at 500 °C for 3 hours in an industrial oven in order to obtain pure TiO_2 nanofibers.

2.6. Characterization techniques

Scanning electron microscope (SEM) (FEI - Quanta 200 FEG) and transmission electron microscope (TEM) (FEI - Tecnai G2F30) were used for the morphological investigation of the nanofibers. The fiber diameter range and the average fiber diameter were determined from the SEM images and around 100 fibers were analyzed. Energy dispersive X-ray (EDX) was performed for the elemental analysis of the TiO₂ and ZnO nanofibers. The X-ray diffraction (XRD) patterns for these metal oxide nanofibers were obtained by using PAN analytical X'Pert Powder diffractometer with Cu K α radiation in a range $2\theta=10^{\circ}$ - 70° . UV-Vis-NIR spectrophotometer (Varian Cary 5000) was used to analyze photocatalytic degradation of Rhodamine-6G and methylene blue dye solutions including TiO₂ and ZnO nanofibers, respectively.

2.7. Characterization of TiO₂ nanofibers

The representative SEM images and fiber diameter distributions of the electrospun nanofibers of PVP/precursor and TiO₂ are shown in Figure 8. Bead-free nanofibers of PVP/precursor (Figure 8-a) and TiO₂ (Figure 8-c) were obtained with diameters in the range of 60-850 nm (Figure 8-b) and 40-500 nm (Figure 8-d) having average fiber diameter of 300 ± 130 nm and 200 ± 120 nm, respectively.

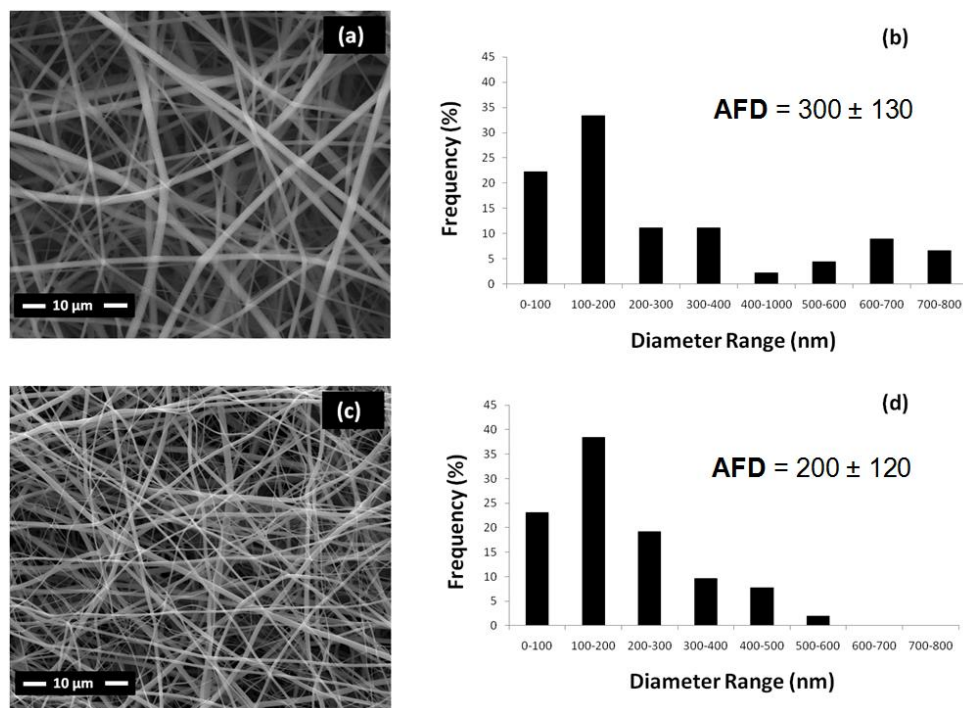


Figure 8 SEM images of the electrospun nanofibers of (a) PVP/precursor and (c) TiO₂ nanofibers and diameter ranges of (b) PVP/precursor and (d) TiO₂ nanofibers.

SEM findings suggest that diameter of composite materials decreases by removal of organic component (PVP) by calcination at 500 °C for 3 hours. During the calcination process of PVP/titanium precursor, the material maintained its fibrous structures and brittle TiO₂ nanofibers were obtained and the energy dispersive X-ray spectroscopy (EDX) analyses of TiO₂ nanofibers were performed (Figure 9). The elemental mapping of TiO₂ nanofibers by EDX showed that titanium and oxygen are the main elements of the nanofibers.

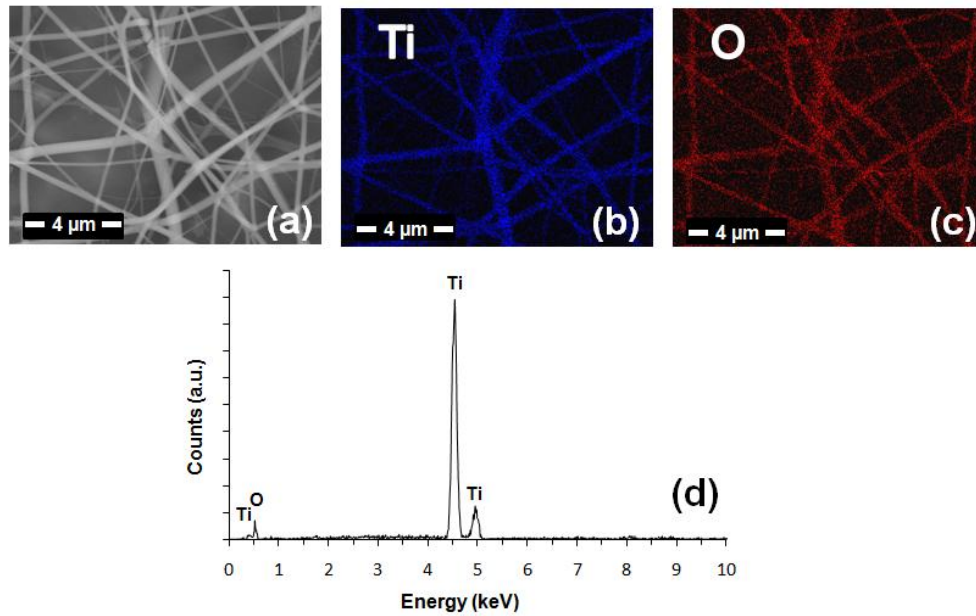


Figure 9 (a) SEM image, (b)-(c) elemental maps and (d) EDX spectrum of TiO_2 nanofibers showing that titanium and oxygen are the main elements of the nanofibers.

The crystalline structure of TiO_2 nanofibers was identified by X-ray diffraction (XRD). Figure 10 has shown the XRD of TiO_2 nanofibers with series of diffraction peaks corresponding to anatase phase which is known for its photocatalytic activity. The salient peak at $2\theta=25.4^\circ$ corresponds to the (101) plane of the anatase TiO_2 structure and the other peaks at $2\theta=38.1^\circ$, 48.4° , 54.3° , 55.3° , 63.0° , 69.1° , correspond to the diffraction of (004), (200), (105), (211), (204), (116), and (220) planes, respectively [16]. XRD pattern of the TiO_2 nanofibers has no diffraction peak at $2\theta=27.5^\circ$ which is characteristic for the rutile phase signifying that calcination process yielded TiO_2 nanofibers having pure anatase structure.

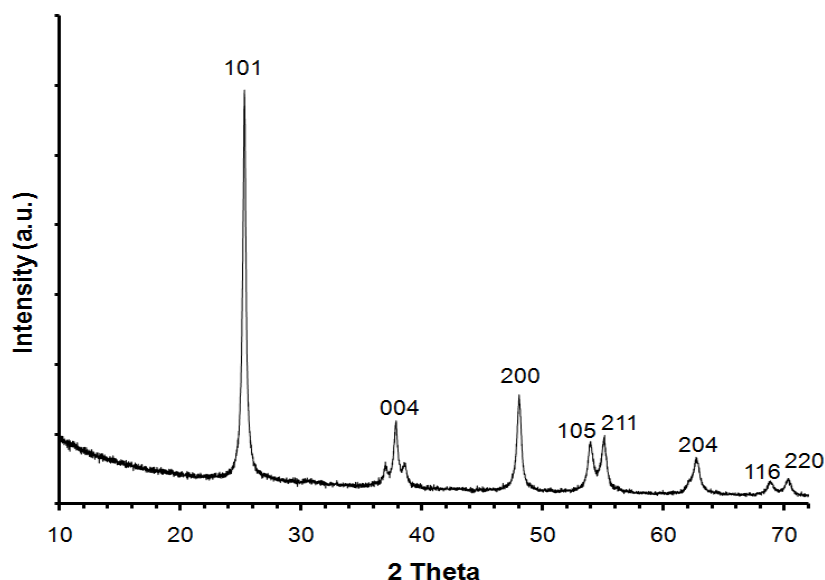


Figure 10 XRD pattern of TiO₂ nanofibers having pure anatase structure

2.8. Photocatalytic activity of TiO₂ nanofibers

The photocatalytic degradation of rhodamine-6G dye solution was used as a model photoreaction and its degradation was followed by the UV-Vis absorption measurement of the solution containing TiO₂ nanofibers by using UV treatment with 254 nm wavelength for 14 hours. They are placed into quartz cuvettes (10.00 mm, Hellma) with a distance of 5 cm from the UV source (8 W, UVLMS-38 EL). At known time intervals, the dye concentration was measured by using UV-Vis-NIR spectrophotometer.

When rhodamine 6G solution containing TiO₂ nanofibers was exposed to UV light, we observed that the solution turned colorless. The change in the absorbance on the UV-Vis spectrum of the Rh-6G solution containing TiO₂ nanofibers as a function of the UV irradiation time is shown in Figure 11-a.

Rhodamine 6G with TiO₂ nanofibers as a catalyst decomposed completely after 14 hours under UV. Figure 11-b shows the rate (C/C_0) of Rhodamine 6G degradation where C_0 and C indicate the initial concentration of rhodamine 6G before UV irradiation and after UV irradiation at time t , respectively.

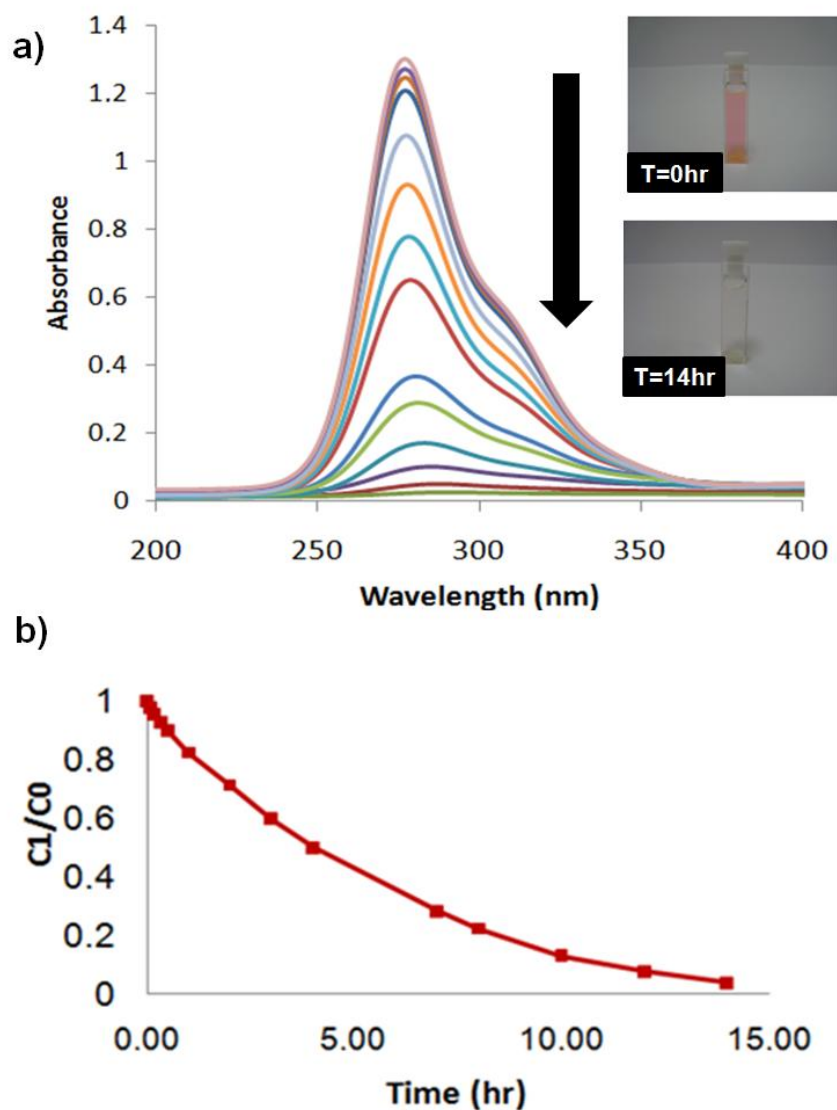


Figure 11 (a) UV-Vis spectrum of Rhodamine 6G solution containing TiO₂ nanofibers, (b) the rate (C/C_0) of Rhodamine 6G degradation by TiO₂ nanofibers by exposing UV light with 254 nm wavelength for 14 hours.

2.9. Fabrication of zinc oxide (ZnO) nanofibers via electrospinning

Firstly, PVP; carrier polymer (0.400 g) was dissolved in a solvent system consisting of ethanol (2 ml) and DMF (2 ml). Then, zinc acetate (1.400 g) was added into this polymeric solution. Finally, the mixture was constantly stirred for one hour until the transparent solution was obtained.

For electrospinning process, the PVP solution containing zinc acetate was placed into a 3 ml syringe having metallic needle tip (inner diameter=0.6 mm). The syringe pump and high voltage power supply are the same with previous experiments. The electrospinning parameters were adjusted as applied voltage = 15 kV, feed rate = 0.5 ml/h, tip-to-collector distance = 13 cm. Finally, electrospun nanofibers were deposited on a grounded stationary cylindrical metal collector covered by a piece of aluminum foil. The electrospinning was carried out in enclosed plexiglass box and at 20 °C at 33 % relative humidity (Figure 12). The electrospun nanofibers were dried overnight under the hood and then calcinated at 450 °C for 4 h in an oven in order to obtain pure ZnO nanofibers.

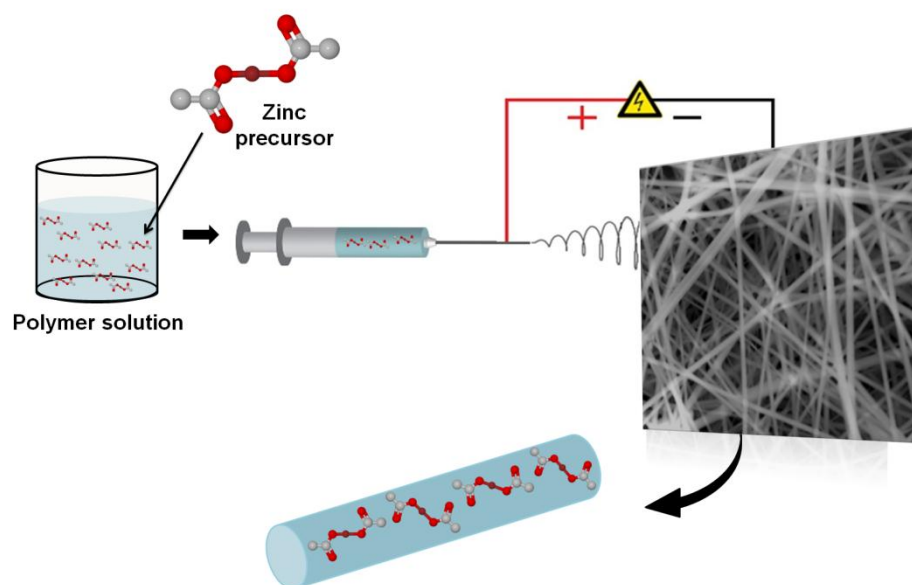


Figure 12 Schematic view of electrospun PVP nanofibers containing zinc acetate by applied voltage = 15 kV, feed rate = 0.5 ml/h, tip-to-collector distance = 13 cm.

2.10. Characterization of ZnO nanofibers

ZnO nanofibers are analyzed by SEM and EDX to investigate the nanostructure and chemical composition. SEM images revealed that ZnO nanofibers are obtained in grains morphology after the calcination of PVP/zinc acetate composites web (Figure 13).

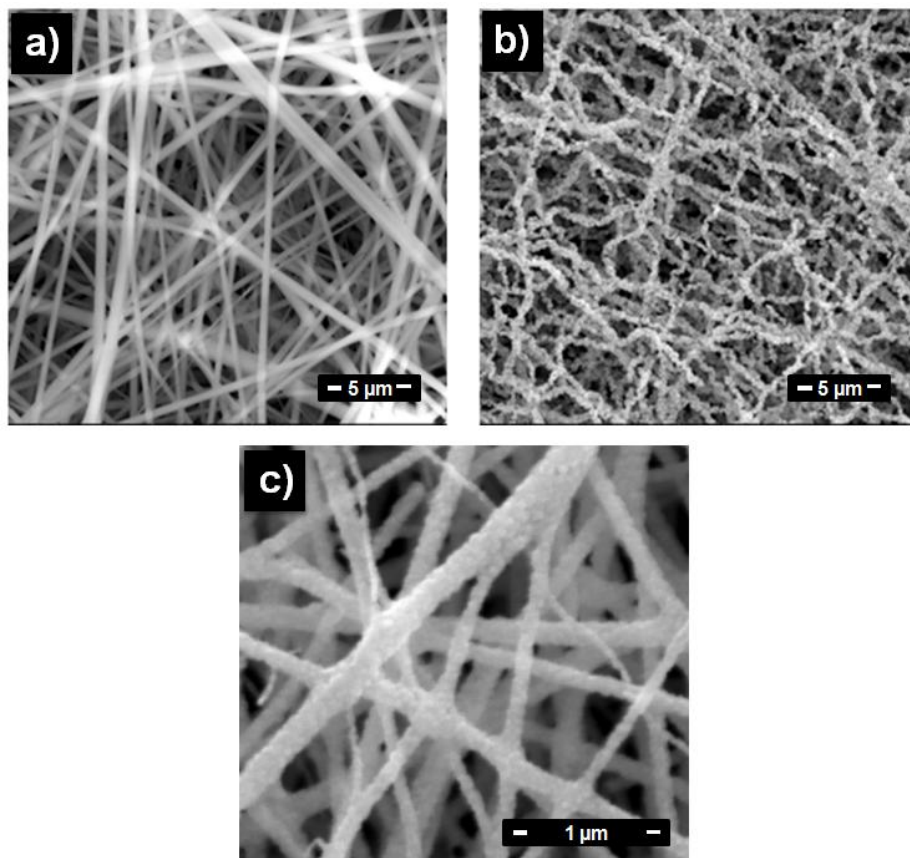


Figure 13 The SEM images of a) PVP nanofibers containing zinc acetate, ZnO nanofibers after calcination at 450 °C for 4 h. Magnification: b) 15000x, c) 100000x

Elemental maps of ZnO nanofibers show that zinc and oxygen are the main elements of the nanofibers. ZnO nanofibers having diameters in the range of 20-1100 nm with average fiber diameter of 200 ± 180 nm were obtained (Figure 14).

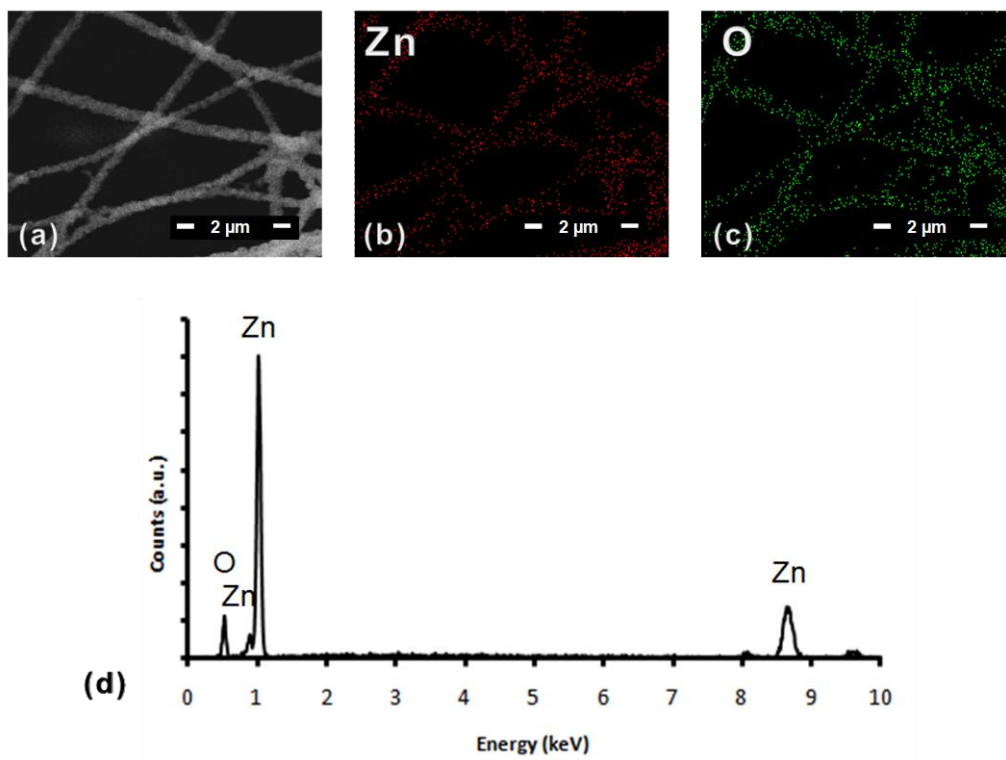


Figure 14 (a) SEM image, (b)-(c) elemental maps and (d) EDX spectrum of ZnO nanofibers showing that zinc and oxygen are the main elements.

2.11. Photocatalytic activity of ZnO nanofibers

Photocatalytic activity of the ZnO nanofibers was evaluated by measuring the photocatalytic degradation of methylene blue solution by using UV treatment with 254 nm wavelength for 4 hours. They are placed into quartz cuvettes with a distance of 5 cm from the UV source. At known time intervals, the dye concentration was measured by using UV-Vis-NIR spectrophotometer. After the UV treatment, the methylene blue solution containing ZnO nanofibers become colorless (Figure 15-a). Changes in the concentration of methylene blue with respect to time were examined by UV-

Vis-NIR spectrophotometer at the wavelength of 665 nm which is the maximal absorption. Methylene blue solution containing ZnO nanofibers decomposed completely after 4 hours under UV. Figure 15-b shows the rate (C/C_0) of methylene blue degradation where C_0 and C indicate the initial concentration of methylene blue before UV irradiation and after UV irradiation at time t , respectively.

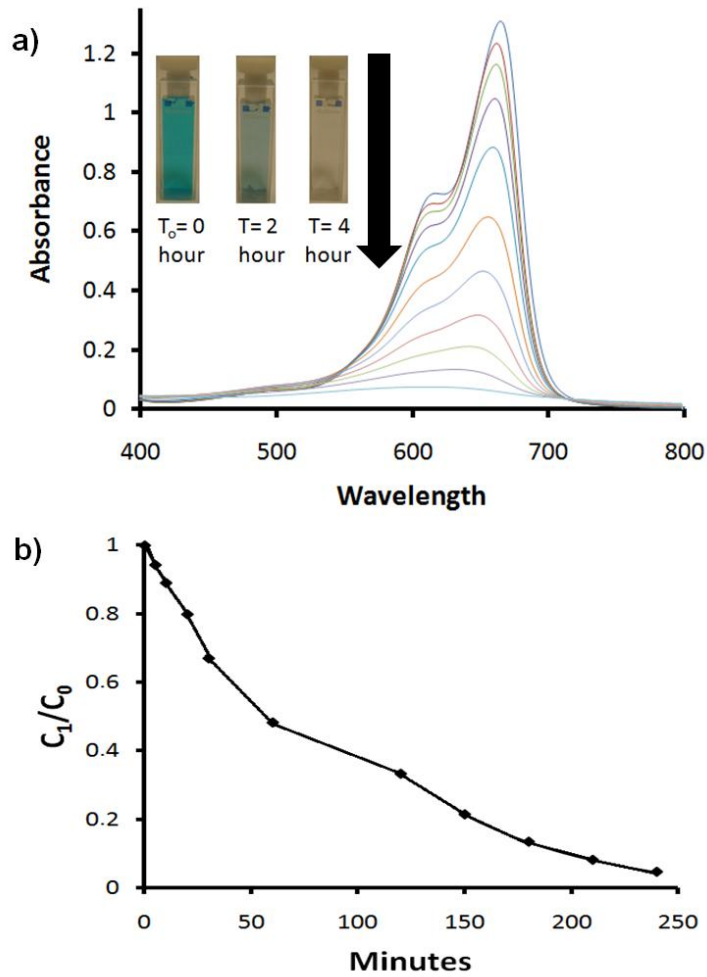


Figure 15 (a) UV-Vis spectrum of methylene blue solution containing ZnO nanofibers, (b) the rate (C/C_0) of methylene blue degradation by ZnO nanofibers by using UV treatment with 254 nm wavelength for 4 hours

CHAPTER II. NANOCOMPOSITE NANOFIBERS

3.1. Nanocomposite nanofibers

Composites are prominent materials with their multifunctional properties originated from the combination of two or more constituent materials with their distinct physical and/or chemical features. These composite structures generally have advantages in terms of mechanical, thermal, electrical, optical, electrochemical and catalytic properties [45]. In the case of nanocomposite production, the mentioned properties are significantly improved due to the exceptional high surface to volume ratio. Polymeric matrix supplies the enhancement at the performance of composite materials by capitalizing the properties of nanofillers so they are generally considered as an excellent carrier for nanocomposite materials. However, to attain the high performance composites, the good dispersion of nanofillers is required in the polymeric media [46]. From this point of view, electrospun nanofibers can be accepted as a great candidate to constitute carrier matrix that supplies the homogenous dispersion of nanofillers. For instance, TiO_2 nanoparticles were incorporated into PVP nanofiber matrices via coupling sol–gel method and electrospinning technique to achieve the production of photoluminescent (PL), electroluminescent (EL) and non-linear optical devices [47]. On the other hand, TiO_2 can be produced in the form of both nanoparticles and nanofiber but it was investigated that TiO_2 nanofibers show higher photocatalytic activity when it is compared to nanoparticle types so the adding type of TiO_2 was determined as short nanofibers because of the

effects of mesoporosity and interparticle charge transfer (Figure 16) [19]. For this purpose, we obtained pure anatase TiO_2 short nanofibers (TiO_2 -SNF) by crushing the nanofiber structure and they were used to produce polymeric nanofibrous composite structures. We obtained electrospun nanofibers from different polymer types such as poly(methyl methacrylate) (PMMA), polyacrylonitrile (PAN), polyethylene terephthalate (PET), polycarbonate (PC) and polyvinylidene fluoride (PVDF) containing TiO_2 -SNF.

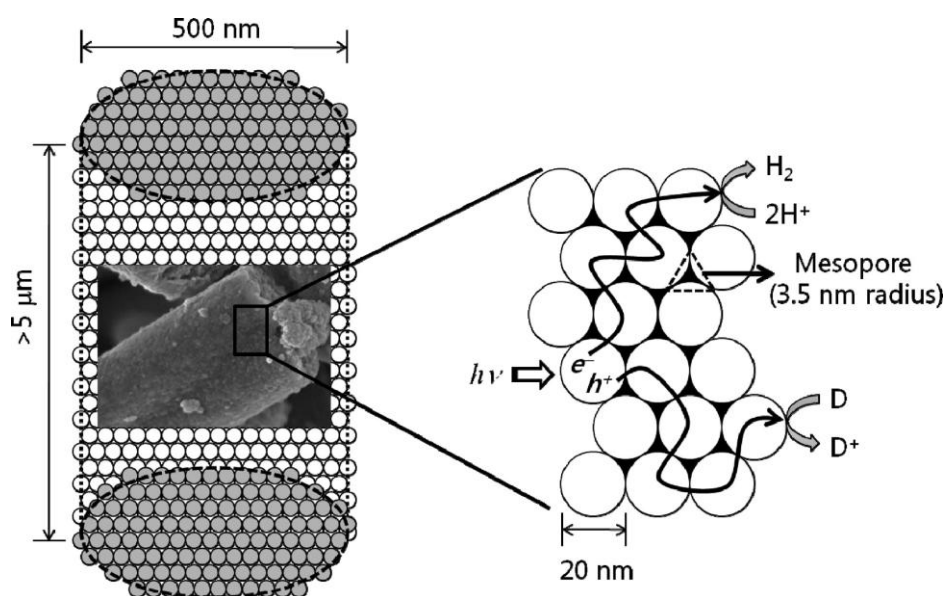


Figure 16 Schematic illustration for a mesoporous TiO_2 nanofiber and its photocatalytic reaction mechanisms. Picture is adapted with permission from [19].

As a preliminary study, the photocatalytic activity of PET nanofibers containing TiO_2 -SNF was investigated for photocatalytic decomposition of rhodamine-6G under UV irradiation. Additionally, the different loading effect of TiO_2 -SNF on photocatalytic activity was studied in PVDF

nanofiber matrix which has the unique properties of nanofiber/nanoweb systems. These examples are the very first reports showing that short metal oxide nanofibers can be incorporated into polymeric nanofibers via electrospinning. Such nanofibrous composite structures can be obtained from different polymer types and will be applicable in various areas depending on the polymer type and the function of metal oxides.

3.2. Materials

Titanium (IV)-isopropoxide (97%, Aldrich), glacial acetic acid (% 100, Merck), ethanol ($\geq 99.8\%$, Sigma-Aldrich), dimethylformamide (DMF) (Riedel, Pestenal), tetrahydrofuran (THF) ($\geq \% 99.5$, Sigma), dichloromethane (DCM) ($\geq \%99$, Sigma), trifluoroacetic acid (TFA) (% 99, Sigma-Aldrich), polyvinylpyrrolidone (PVP, $M_w \sim 1300000$, Aldrich), poly(methyl methacrylate) (PMMA) ($M_w \sim 350000$, Aldrich), polyacrylonitrile (PAN) (donated by AKSA Co., Turkey), polyethylene terephthalate (PET) (donated by Korteks Co., Turkey), polycarbonate (PC) ($M_w \sim 64000$, Aldrich), polyvinylidene fluoride (PVDF) (Kynar 761, donated by Elf Atochem North America Inc.) were used as-received without any further purification. The water was used from Millipore Milli-Q Ultrapure Water System.

3.3. Electrospun polymeric nanofibrous composites containing TiO₂ short nanofibers (TiO₂-SNF)

Firstly, TiO₂ short nanofibers (TiO₂-SNF) ranging 1 micron to several microns in length were obtained by crushing the electrospun TiO₂ nanofibers in a mortar (Figure 17). Then, the concentration of the polymer solutions and the electrospinning parameters were optimized in order to get bead-free uniform fibers. The polymer solutions were prepared as follows: PMMA and PAN were dissolved in DMF using 12.5% (w/v) and 20% (w/v) polymer concentration, respectively. In addition, 20% (w/v) PET was dissolved in TFA:DCM (1:1, v/v), while 25% (w/v) PC was dissolved in THF:DMF (3:2, v/v) solvent system.

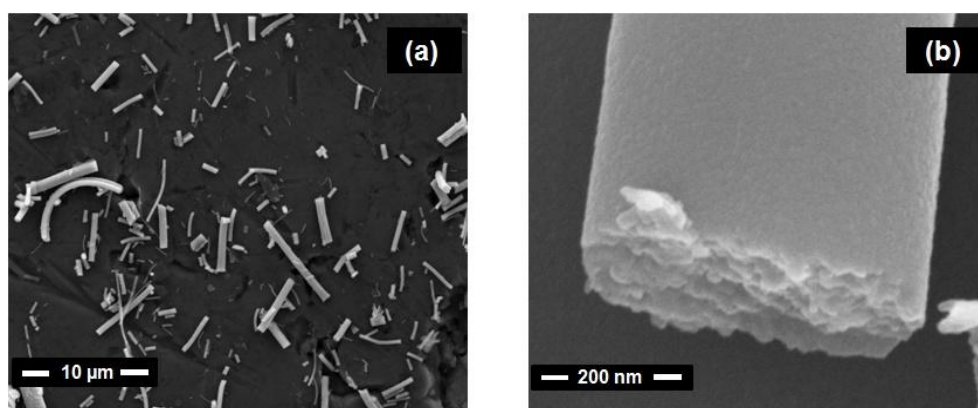


Figure 17 SEM images (a) low-magnification and (b) high magnification of TiO₂ nanofibers ranging 1 micron to several microns in length were obtained by crushing in an agar mortar

Afterwards, previously prepared TiO₂-SNFs were blended with polymer solution. In detail, 6% TiO₂-SNF (w/w, with respect to polymer) in PMMA

and 2% TiO_2 -SNF (w/w, with respect to polymer) in PAN, PET and PC solutions were dispersed by stirring for 1 h. The percentage loading of TiO_2 -SNF was affecting the electrospinning, therefore, TiO_2 -SNF loading was chosen for each polymer solution that did not affect the electrospinning of bead-free nanofibers. Subsequently, PAN, PET and PC solutions were electrospun into nanofibers in order to produce nanofibrous composite structures with the following parameters: applied voltage = 15 kV, tip-to-collector distance = 10 cm and feed rate = 1 ml/h. For PMMA solution the parameters were as follows: applied voltage = 10 kV, tip-to-collector distance = 15 cm and feed rate = 1 ml/h. These electrospun nanofibrous composites were abbreviated as; PMMA/ TiO_2 -SNF, PAN/ TiO_2 -SNF, PET/ TiO_2 -SNF and PC/ TiO_2 -SNF (Figure 18).

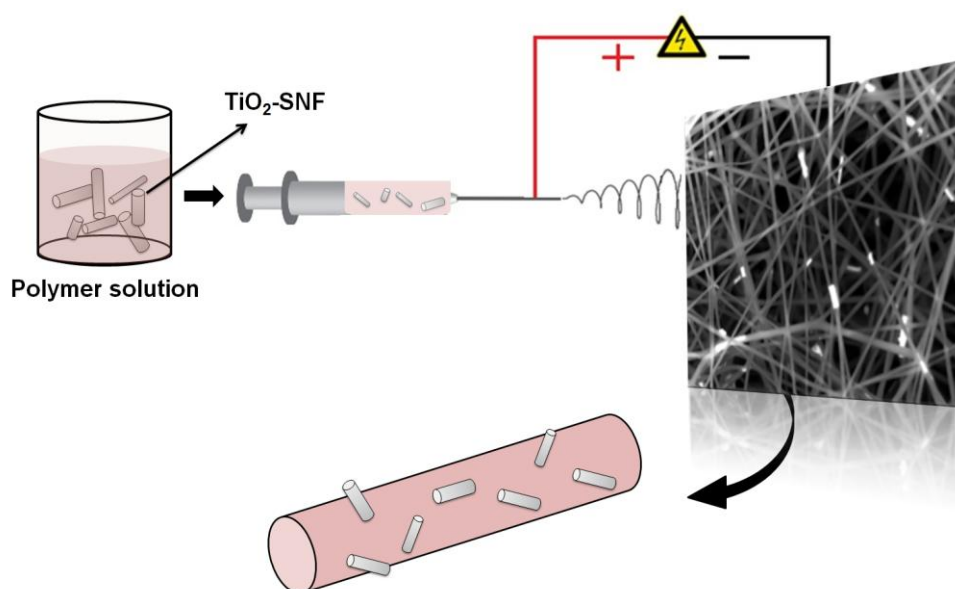


Figure 18 Schematic view of electrospun polymeric nanofibers containing TiO_2 -SNF by applied voltage = 15 kV, tip-to-collector distance = 10 cm and feed rate = 1 ml/h.

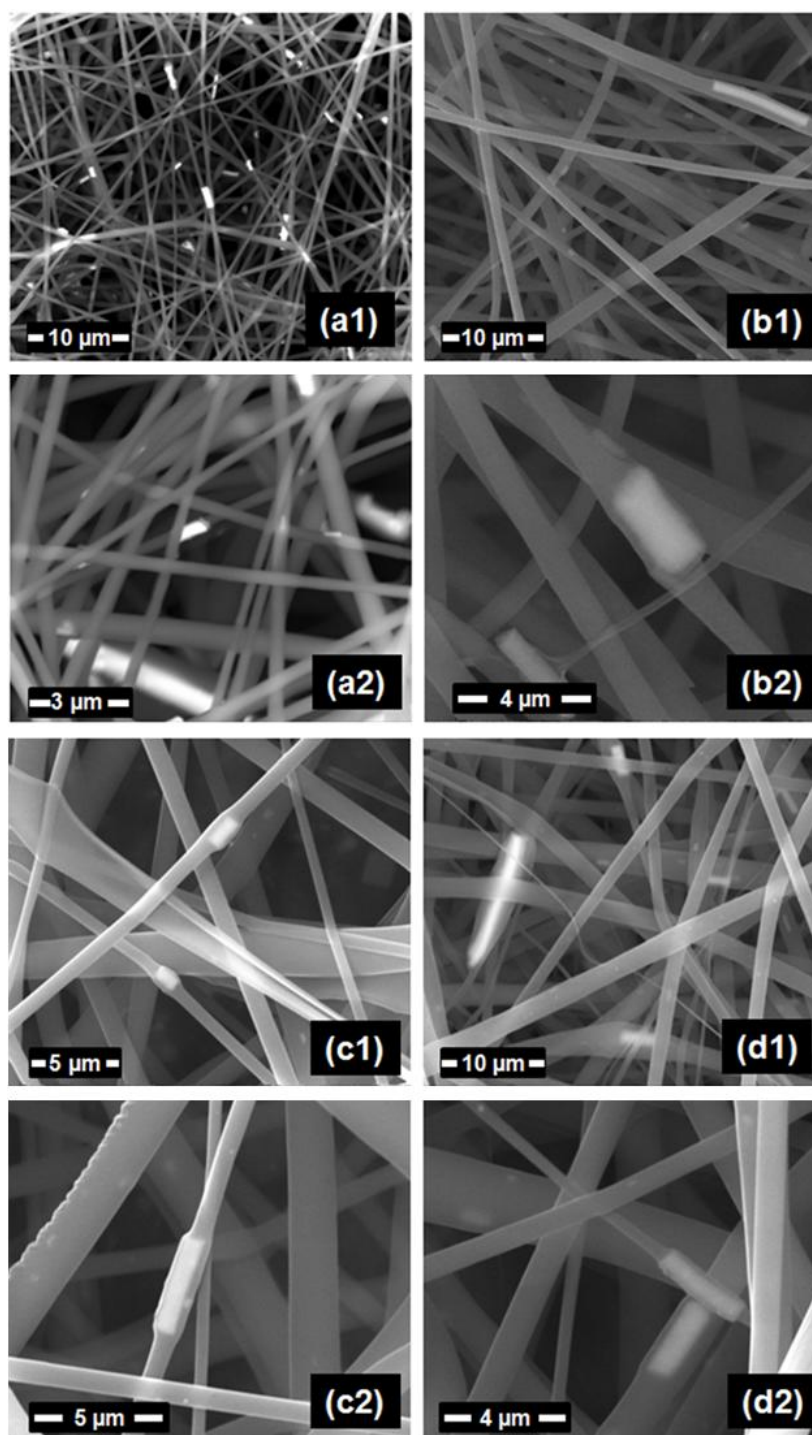


Figure 19 SEM images of nanofibrous composites with (1) low magnification and (2) high magnification: (a1)-(a2) PMMA/TiO₂-SNF, (b1)-(b2) PAN/TiO₂-SNF, (c1)-(c2) PET/TiO₂-SNF and (d1)-(d2) PC/TiO₂-SNF.

The representative SEM images of these nanofibrous composites are depicted in Figure 19. We observed that the incorporation of TiO_2 -SNF did not affect the electrospinning of these polymers and bead-free nanofibers were obtained in all cases.

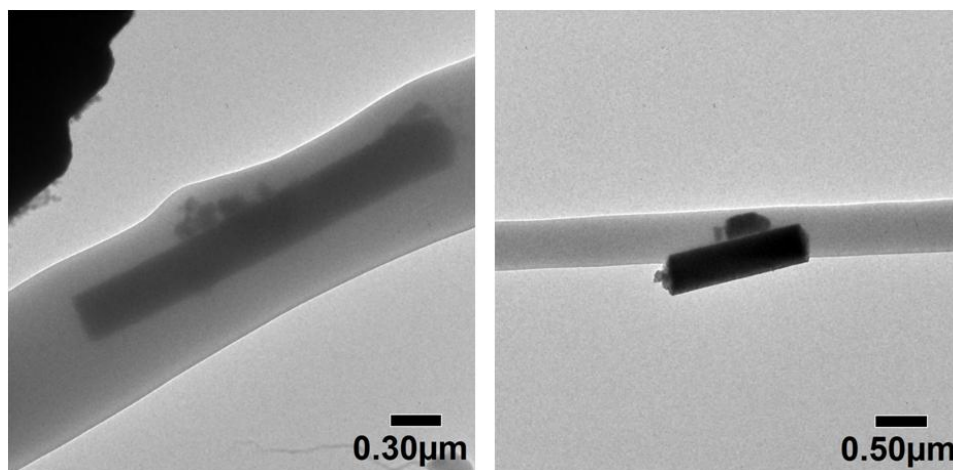


Figure 20 TEM images of the PMMA/ TiO_2 -SNF composite nanofibers showing that some of the TiO_2 -SNF were fully covered by the polymeric matrix whereas some TiO_2 -SNF were present on the surface of the polymeric matrix.

We further analyzed these nanofibrous composites by TEM. The representative TEM images of the PMMA/ TiO_2 -SNF composite nanofibers are given in Figure 20. SEM and TEM analyses revealed that some of the TiO_2 -SNF were fully covered by the polymeric matrix whereas some TiO_2 -SNF were present on the surface of the polymeric matrix and/or sticking out from the polymeric matrix.

3.4. Photocatalytic activity of polyethylene terephthalate (PET) nanofibers containing TiO₂-SNF

As mentioned above, TiO₂-SNF have anatase structure which is known for its photocatalytic activity. As a preliminary study, we also investigated the photocatalytic activity of PET/TiO₂-SNF nanofibers. The photocatalytic activity was analyzed by photodegradation of rhodamine-6G (2×10^{-5} M) in aqueous medium. PET nanofibers containing crushed TiO₂ nanofibers (2 mg, 1.0 cm x 1.0 cm) were put into quartz cuvette filled with rhodamine-6G solution. The cuvette was placed with a distance of 5 cm from the UV source and kept under UV irradiation at 254 nm wavelength. At known time intervals, the dye concentration was measured by using UV-Vis-NIR spectrophotometer. The change in the absorbance on the UV-Vis absorption spectrum of the Rh-6G solution containing PET/TiO₂-SNF nanofibers as a function of the UV irradiation time is shown in Figure 21. This figure also shows the rate (C/C_0) of Rh-6G degradation where C_0 and C indicate the initial concentration of Rh-6G before UV irradiation and after UV irradiation at time t , respectively.

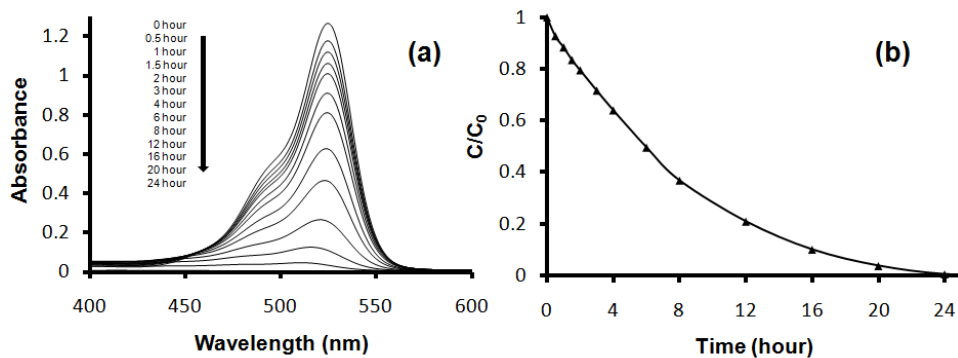


Figure 21 (a) The UV-Vis absorption spectrum of the Rh-6G solution containing PET/TiO₂-SNF nanofibers as a function of the UV irradiation time, and (b) the rate (C/C_0) of Rh-6G degradation under UV irradiation at 254 nm wavelength for 24 hours.

As the photodegradation of Rh-6G occurred with respect to UV irradiation time, the absorbance of the Rh-6G solution in the UV-Vis absorption spectrum decreased gradually, and the red color of the solution disappeared totally after 24 hours of UV irradiation indicating that almost 100% of the Rh-6G was decomposed. This result confirmed the photocatalytic degradation of Rh-6G by nanofibrous composites.

3.5. Polyvinylidene fluoride (PVDF) nanofibers with varying TiO₂-SNF concentrations

Firstly, polymer solution was prepared as follows: 20 % (w/v) PVDF dissolved in DMAc: Acetone (1:1, v/v). Then TiO₂-SNF were added in PVDF solution were dispersed by stirring for one hour with the ratios 2%, 4%, and 8% (w/w) (with respect to polymer). Finally, PVDF solution was

electrospun with following parameters: applied voltage = 20 kV, tip-to-collector distance =10 cm and feed rate = 1 ml/h.

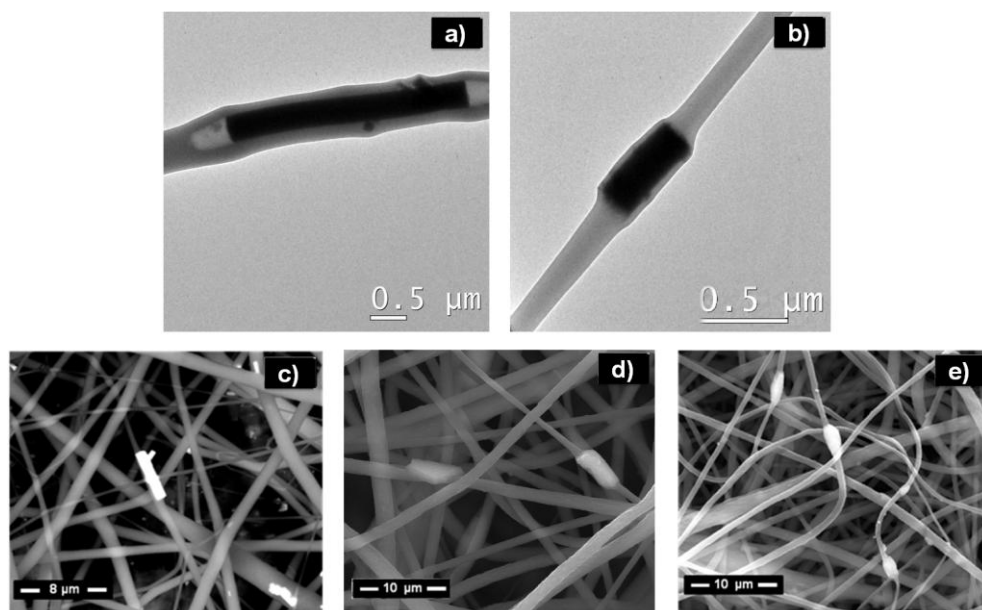


Figure 22 TEM images of the (a), (b) 2% (w/w) and SEM images of (c) 2% (d) 4% and (e) 8% (w/w) PVDF/TiO₂-SNF nanofibers.

TEM and SEM images showed that nanofibers were detected as black and white segments, respectively and it was observed that they preserved their original structure (Figure 22). The elemental mapping of PVDF nanofibers containing TiO₂-SNF by EDX showed that carbon, oxygen, fluorine, and titanium are the main elements of the nanofibers (Figure 23).

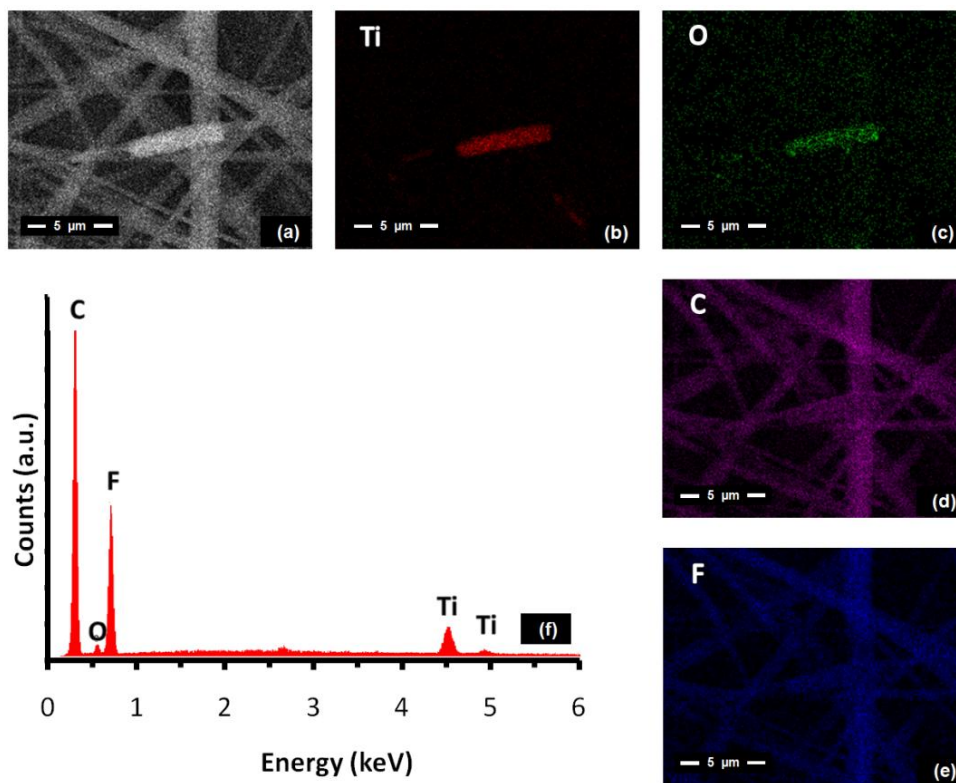


Figure 23 (a) SEM image, (b)-(c)-(d)-(e) elemental maps and (f) EDX spectra of PVDF/TiO₂-SNF nanofibers showing that carbon, oxygen, fluorine, and titanium are the main elements of the nanofibers.

According to literature, three main crystalline forms of PVDF have distinct molecular conformations; which are all trans structure (β - phase), trans-gauche structure (α -phase), and an intermediate conformation, consisting in sequences of three trans bonds separated by a gauche bond, is found in the case of γ - phase [21].

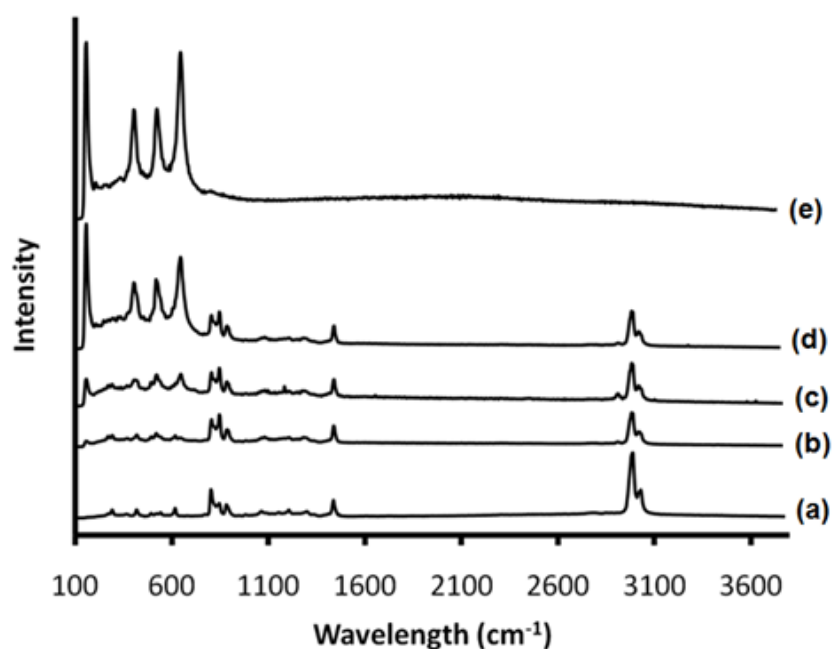


Figure 24 Raman spectrum of (a) neat PVDF nanofibers, (b) 2%, (c) 4%, and (d) 8% (w/w) PVDF/TiO₂-SNF, and (e) crushed TiO₂ nanofibers.

Figure 24 shows the Raman spectra of pure PVDF, TiO₂ nanofibers and PVDF nanofibers including TiO₂ – SNF in 2%, 4%, 8% (w/w) concentrations. The PVDF nanofiber spectrum presents absorption peaks in 1426 (CH₂ bending), 836 (CH₂ rocking), 2969 and 2986 (CH₂ symmetric stretching) wavenumber. Moreover, 795 cm⁻¹ is the characteristic of the alpha-phase (CH₂ rocking). These peaks are fitted with our data [22] which are 1430, 839 and 795 cm⁻¹ and two peaks around 3000 cm⁻¹, respectively. 839 cm⁻¹ is common to both forms I and III but is very strong only in the first case, while the 811 cm⁻¹ band is only characteristic of form III, which shows that PVDF nanofibers have a crystalline form of β - phase inspite of γ - phase. Moreover, the band at 795 cm⁻¹ characteristic of the alpha-phase

(form 2) and assigned to CH₂ rocking [23]. Raman indicates the crystalline forms of PVDF which is mixture of α -phase and β - phase.

On the other hand, The TiO₂ nanofibers spectrum shows absorptions in the 151, 401, 516 and 639 cm⁻¹ wavenumbers. According to literature [24] anatase TiO₂ has the Raman lines at 151, 409, 515 and 633 cm⁻¹ can be assigned as the Eg, B1g, A1g or B1g, showing excellent agreement with the literature. Moreover, it is clearly observed that while TiO₂-SNF was added occurred ascendings in the absorption spectrum in the 151, 409, 515 and 633 cm⁻¹, however the band at 795 cm⁻¹ characteristic of the alpha-phase (form 2) and assigned to CH₂ rocking appears regardless the amount of TiO₂-SNF. [22] On the other hand, band at 840 cm⁻¹ that designates the polar β -phase of the polymer decreases. This conformational change of the polymer has also been observed for other PVDF/TiO₂-SNF nanocomposite nanofibers which obviously says that $\beta \rightarrow \alpha$ transition in all membranes regardless the amount of TiO₂-SNF.

Figure 25 indicates the X-ray patterns of pure PVDF, TiO₂ nanofibers and PVDF nanofibers including TiO₂-SNF in 2%, 4%, 8% (w/w) concentrations. Crystalline structure of PVDF polymers show α -, β -, γ -phase and each phase have specific diffraction peaks in 2θ Bragg angle during XRD measurement. The electrospun PVDF nanofibers can be determined as the combination of two crystalline type because while the 18.4° (020), 27.8° (111) correspond to the α -phase, 20.8° (110), 20.7° (200), and 36.6° (020) stand for β -phase crystalline structure. Also pure TiO₂

nanofibers show characteristic peak at 25.3° , 38.6° , 48.1° and 55.0° corresponds to anatase type of TiO_2 and its intensity increase distinctly as its amount is increased at the sample. To the contrary, the specific peak of PVDF show decline in intensity because of more dominant crystalline structure of TiO_2 -SNF additive.

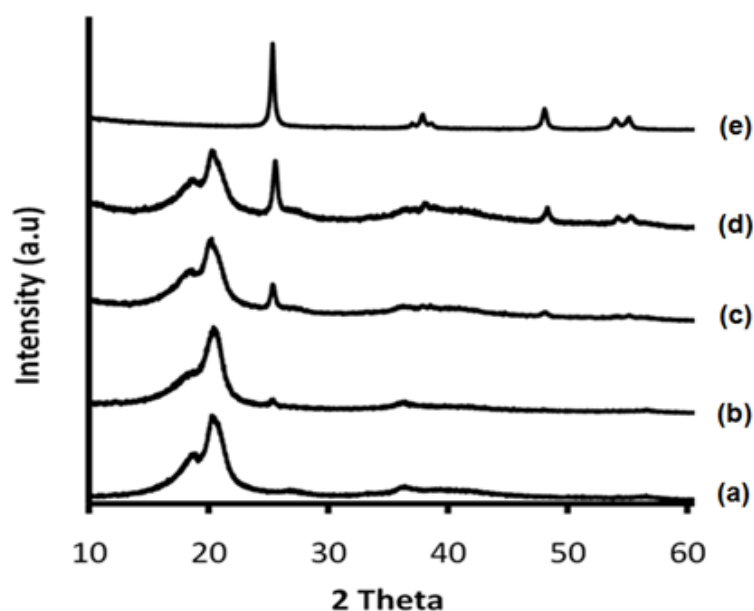


Figure 25 XRD patterns of (a) neat PVDF nanofibers, (b) 2%, (c) 4%, and (d) 8% (w/w) PVDF/ TiO_2 -SNF, and (e) crushed TiO_2 nanofibers show characteristic peak at 25.3° , 38.6° , 48.1° and 55.0° corresponds to anatase type of TiO_2 and its intensity increase distinctly as its amount is increased at the sample.

Differential scanning calorimeter (DSC) and thermogravimetric (TGA) methods were carried out in increasing concentration of TiO_2 -SNF to observe the TiO_2 -SNF effect on the thermal behavior of PVDF nanofibers. Figure 26 shows TGA thermograms of samples in increasing TiO_2 -SNF

content. For pure PVDF nanofibers, strong one-step degradation was observed above 450 °C. On the other hand, composite PVDF nanofibers indicate decomposition behavior at around 350 °C that is lower than pure PVDF. This can be originated from the catalytic property of the TiO₂ causing oxidative and earlier decomposition of samples during the process [20].

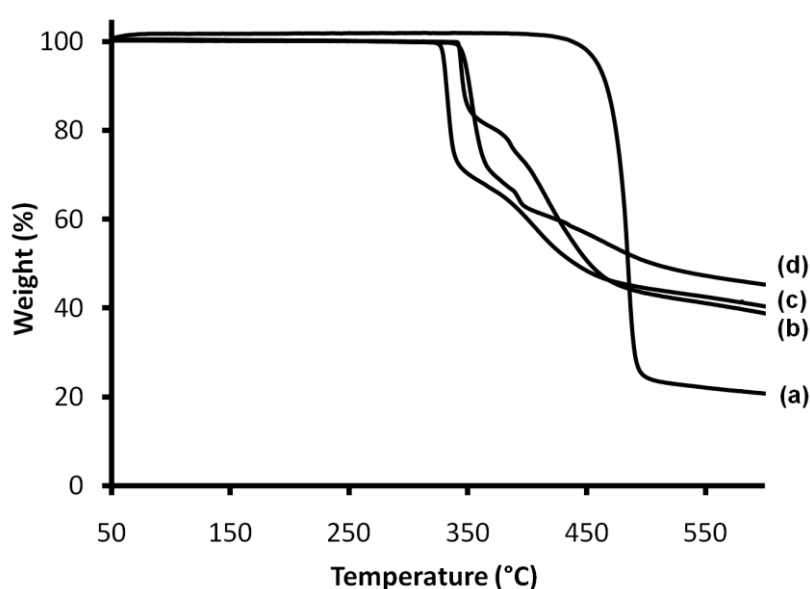


Figure 26 Thermal gravimetric analysis of (a) neat PVDF, (b) 2%, (c) 4%, and (d) 8% (w/w) PVDF/TiO₂-SNF nanofibers decompose at around 350 °C that is lower than pure PVDF because of the catalytic property of the TiO₂ nanofibers.

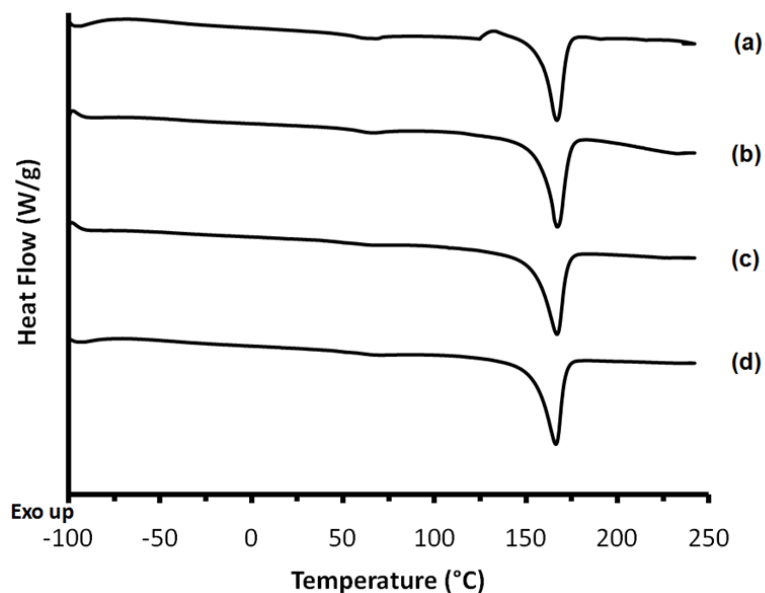


Figure 27 DSC thermograms of (a) 2%, (b) 4%, and (c) 8% (w/w) PVDF/TiO₂-SNF and (d) neat PVDF nanofibers showing that PVDF nanofibers and composites have a melting peak around 166 °C

Figure 27 shows the graph of heat flow versus temperature for PVDF nanofibers and PVDF/ TiO₂-SNF composites samples. It is observed that PVDF nanofibers and composites show an endothermic melting peak around 166 °C, this behavior is characteristic of the PVDF alpha phase [20]. It slightly changes depending on the concentration of TiO₂-SNF.

Sample	Melting temperature (°C)	Melting enthalpy (J/g)	Crystallinity (%)	
			XRD	DSC
Pure PVDF	166.3	78.8	74.1	75.2
PVDF + 2% TiO ₂ - SNF	166.7	86.9	81.5	82.9
PVDF + 4% TiO ₂ - SNF	166.2	79.7	74.3	76.1
PVDF + 8% TiO ₂ - SNF	165.4	75.2	70.2	71.8

Table 1 Thermal properties and crystallinity of PVDF/TiO₂-SNF composite nanofibers with different TiO₂-SNF contents

Table 1 indicates the crystalline percentages that were calculated from the DSC data with the following formula.

$$\text{Crystallinity (\%)} = \frac{\Delta H_m^{\text{sample}}}{\Delta H_m^*} \times 100$$

Where ΔH_m^* is the melting enthalpy for totally crystalline PVDF. Assuming the same melting enthalpy for all crystalline forms of PVDF, the melting enthalpy of 100% crystalline was given as 104.7 J/g [41]. However it is not definite regime because, while the concentration of TiO₂-SNF at 2%, the crystallinity percentage increases to 82.9%. On the other hand, as the content percentage is increased to 4% and 8%, it is observed that the crystallinity decrease significantly to 76.1% and 71.8%, respectively. This case can be based on the fact that, TiO₂-SNF enhance the crystalline nucleation of PVDF at the 2% concentration but behaves as anti-nucleating agent at the 4% and 8% concentrations [20]. The crystallinity percentages were also calculated from XRD patterns of samples according to following

formula and as it is observed from table 1 results are correlated with DSC calculations.

$$\text{Crystallinity (\%)} = \frac{A_c}{A_c + A_a} \times 100$$

Where A_c is the area of the crystalline phase and A_a is the area of amorphous phase.

3.6. Photocatalytic activity of PVDF nanofibers containing TiO₂-SNF

The photocatalytic activity test was carried out by observing the photodegradation of rhodamine-6G (Rh-6G) (2×10^{-5} M) dye in aqueous medium. PVDF/TiO₂-SNF composite nanofibers (2 mg, 1.0 cm x 1.0 cm) containing the 2-4-8 % TiO₂-SNF (w/w, with respect to polymer) were put into quartz cuvettes filled with rhodamine-6G solution. Then these cuvettes were exposed UV irradiation at 254 nm wavelength by placing at a distance of 5 cm from the UV source and the dye concentrations were determined by measuring absorbance of samples with UV-Vis-NIR spectrophotometer in a known time intervals.

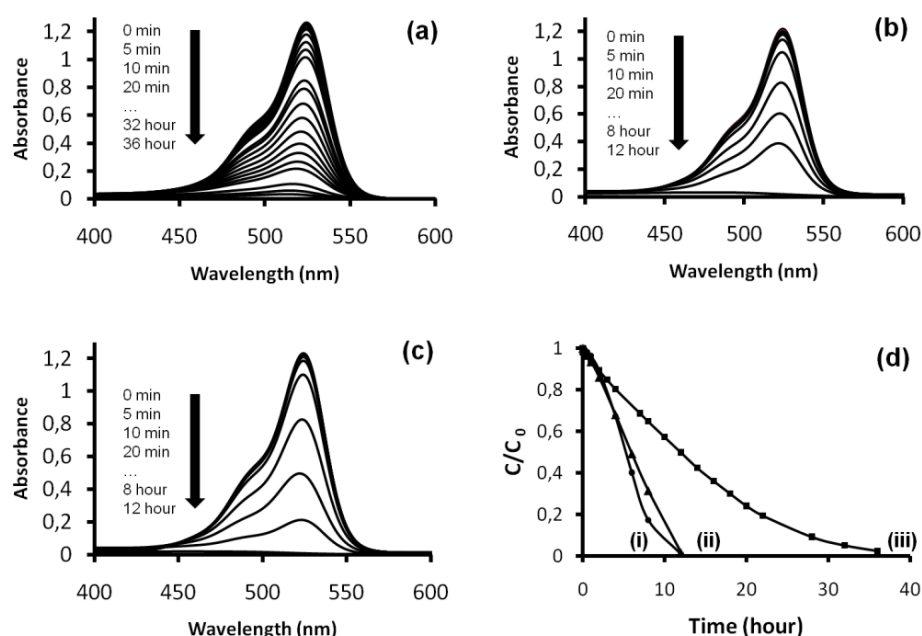


Figure 28 The UV-Vis absorption spectrum of the Rh-6G solution containing PVDF/TiO₂-SNF composite nanofibers including TiO₂-SNF a) 2%, (b) 4%, and (c) 8% (w/w) as a function of the UV irradiation time, and (d) the rate (C/C_0) of Rh-6G degradation by PVDF/TiO₂-SNF composite nanofibers including TiO₂-SNF i) 2%, (ii) 4%, and (iii) 8% (w/w)

As it is observed from graphs, absorbance values are decreased gradually and the pink color of the solutions disappear totally after 36 hours for 2%, 12 hours for 4% and 8% concentrations. So we can say that, as the content of TiO₂-SNF increases the photocatalytic activity of composite materials increases too. However, there is not a distinct difference between 4% and 8% concentrations. Figure 28 indicates the rate (C/C_0) of Rh-6G degradation where C_0 and C indicate the initial concentration of Rh-6G before UV irradiation and after UV irradiation at time t , respectively. This result also proves the content ratio effect on the degradation rate of dye agent in the

progressing time intervals. Moreover, figure 29 shows the SEM images of composite photocatalyst nanofibers which were exposed to degradation. We can say that they were not destroyed from this measurement and protect their initial morphology.

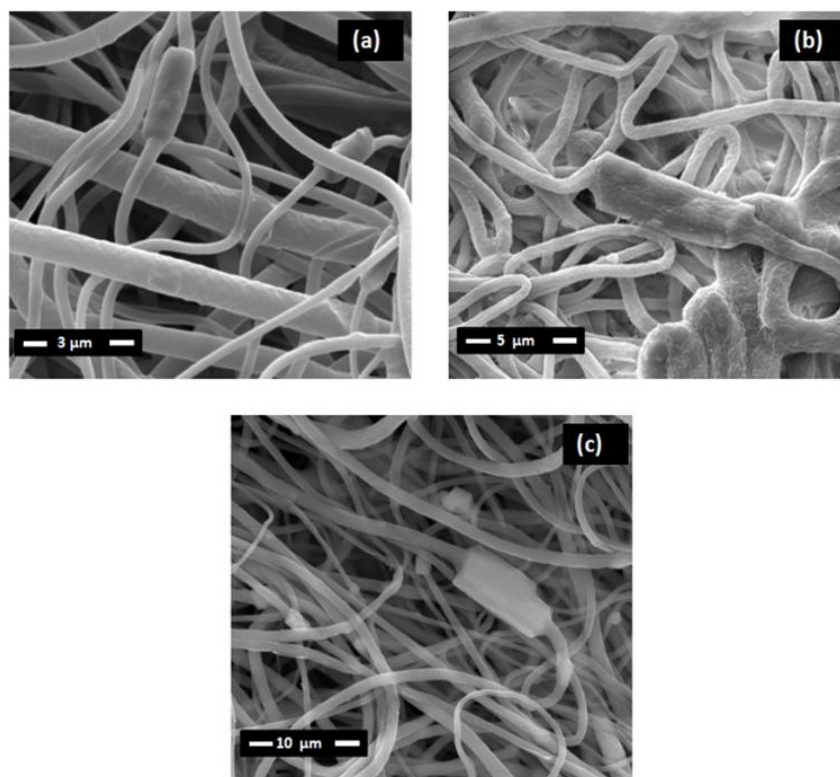


Figure 29 SEM images of the (a) 2%, (b) 4%, and (c) 8% (w/w) PVDF/TiO₂-SNF composite nanofibers after UV-Treatment in fiber morphology.

CHAPTER III. FUNCTIONAL NANOFIBERS CONTAINING NANOPARTICLES

4.1. Functional nanofibers

In the last decade, the electrospinning of functional nanofibers has received great deal of attention since the electrospun nanofibers and their nanowebs have distinct characteristic such as very high surface area to volume ratio [4, 25]. In addition, it is rather easy to improve the functionality of the electrospun nanofibers by incorporating functional additives such as nanoparticles (NPs) [26-29]. NPs have unique optical, electronic, magnetic, and catalytic properties; hence, the incorporation of NPs into electrospun nanofibers is quite attractive for the development of functional nanofibrous composites having promising physical, chemical, optical, and catalytical properties [26-29]. The very interesting properties and the multifunctionality nature of these nanofibers are therefore quite applicable in many areas including biotechnology, sensors, photonics, optoelectronics, energy, etc. [25-31].

Two different approaches are mainly applied for the electrospinning of polymeric nanofibers containing NPs [27, 32]. In most cases, NPs are first obtained by chemical and/or thermal treatment, and these NPs are dispersed in polymer solutions and then electrospun, yet, non-homogenous dispersion of the NPs in the polymer matrix and their aggregation is always a problem, therefore, certain precautions should be taken for obtaining uniform composite structures [32]. The other common approach is dissolving

metallic precursor together with the polymer and then electrospun into nanofibers, yet again, the reducing agents are used to obtain metal ions in the form of NPs [27]. These two approaches mentioned above involve several optimized processes for each material and require the use of reducing agents and stabilizer or protecting agent which are usually toxic chemicals. In this chapter, we describe for the first time the use of a laser ablation and electrospinning together for the fabrication of polymer/metal nanoparticle nanofibrous composites. Compared to other methods, laser ablation carried out directly in a polymer solution has a number of advantages such as chemical safety, clean process, less time consumption, and applicability for the production of various NPs [29, 30]. Here we report, direct synthesis of gold (Au-NPs) and silver nanoparticles (Ag-NPs) obtained in the poly(vinylpyrrolidone) (PVP) polymer solution by using laser ablation which are further electrospun to form uniform composite nanofibers.

PVP was chosen for a couple of reasons; (i) the electrospinning of the PVP nanofibers is very easy, and PVP has been shown to be a good fibrous matrix for incorporation of metal NPs. (ii) PVP is a water soluble polymer having a hydrophilic nature and it is widely used as a stabilizer and capping agent for nanoparticles and therefore protect the NPs from agglomeration in the medium. [35-37].

4.2. Materials

Silver, gold, and germanium nanoparticles were prepared by Bülend Ortaç research group via laser ablation method at UNAM. Polyvinylpyrrolidone (PVP, Mw~1300000, Aldrich), poly(vinylidene fluoride) (PVDF) (Kynar 761, donated by Elf Atochem North America Inc.) dimethylacetamide (DMAc) (>99%, Sigma-Aldrich) ethanol (%99, Aldrich), and acetone (>99%, Sigma-Aldrich), were purchased commercially. The water was used from Millipore Milli-Q Ultrapure Water System. The materials were used without any purification.

4.3. Fabrication of PVP nanofibers containing Au and Ag nanoparticles by laser ablation method

PVP was dissolved in ethanol:water (1:1, v/v) solvent system at 15 % (w/v) polymer concentration then gold and silver nanoparticles were generated by laser ablation method in this polymeric media. The PVP solutions containing Au-NPs (PVP/Au-NPs) and Ag-NPs (PVP/Ag-NPs) were electrospun with the following parameters: applied voltage = 15 kV, tip-to-collector distance =12 cm and feed rate = 0.5 ml/h. Electrospun nanofibers were deposited on a grounded stationary cylindrical metal collector covered by a piece of aluminum foil. The electrospinning apparatus was enclosed in Plexiglas box and the electrospinning was carried out at 23 °C at 20 % relative humidity (Figure 30). For comparison, the electrospinning of 15 % (w/v) PVP in ethanol:water (1:1, v/v) was also

performed under the same conditions without subjected to laser ablation of NPs.

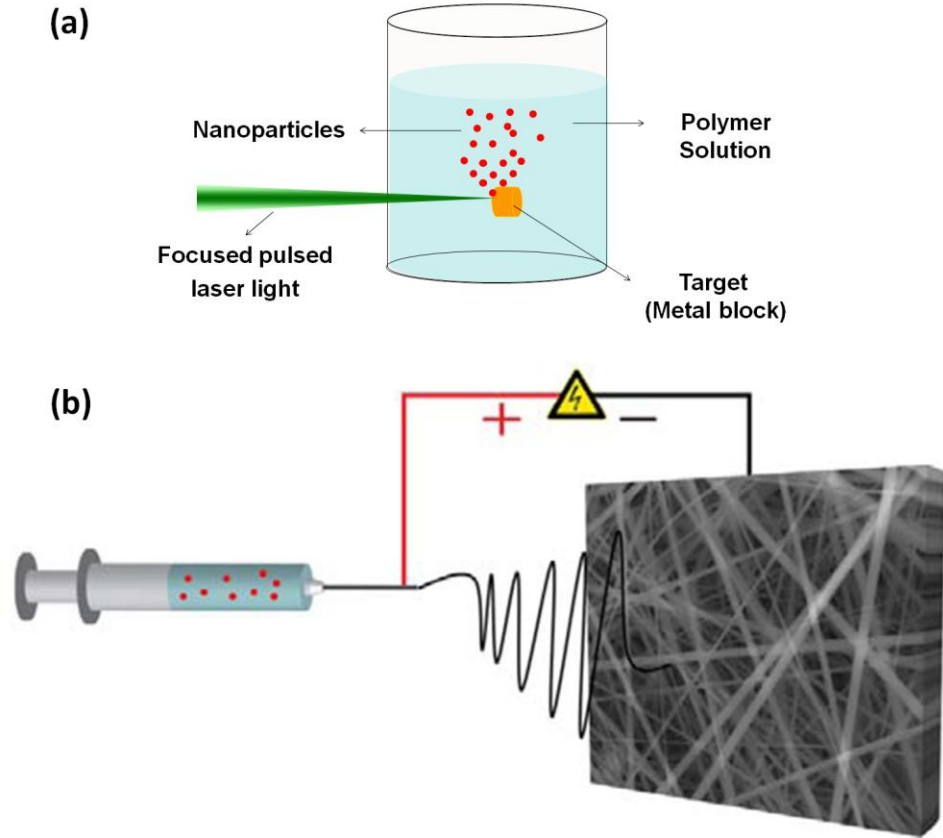


Figure 30 Schematic view of (a) formation nanoparticles in polymer solutions by laser ablation method by Bülend Ortaç research group, and (b) electrospinning process of them.

4.4. Characterization of PVP nanofibers containing Au and Ag nanoparticles by laser ablation method

The morphology and the diameter of the nanofibers were investigated by SEM and TEM. The AFDs were calculated by analyzing around 100 fibers from the SEM images. EDX was performed for the elemental analysis of the PVP nanofibers containing Au-NPs and Ag-NPs. The infrared spectra of nanofibers were obtained by using FTIR spectrometer. The samples were mixed with KBr and pressed as pellets. The scans (64 scans) were recorded between 4000 and 400 cm^{-1} at a resolution of 4 cm^{-1} . UV-Vis-NIR spectrophotometer was used at the range 350 - 750 nm wavelength to analyze the PVP/Au-NPs and PVP/Ag-NPs nanofibrous web at the solid state. Finally, photoluminescence measurements were evaluated by JobinYvon-Horiba Fluorolog spectrometer fitted with a detector (FL-1073) working at 950 V with a Xenon source.

After the laser treatment, color of PVP solutions including Au NPs and Ag NPs becomes dark purple and deep yellow, respectively. Also, the electrospun nanoweb structures show the shade of these colors lightly.

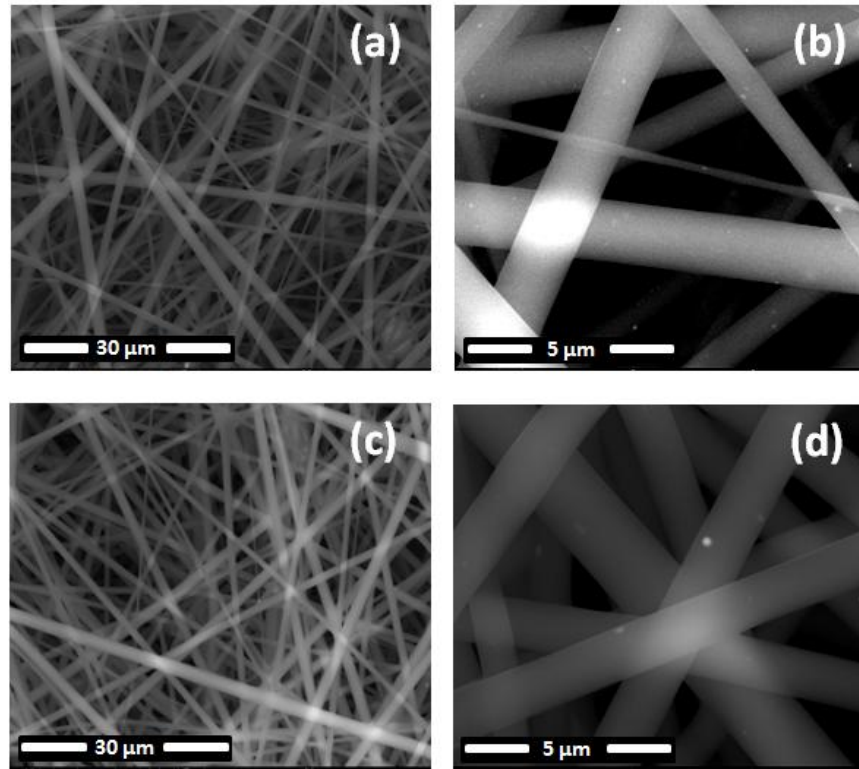


Figure 31 The representative (a), (b) SEM images of PVP/Au-NPs; (c), (d) Sem images of PVP/Ag-NPs nanofibers. Magnification: 5000x, 30000x

The representative SEM images of PVP nanofibers including Au-NPs and Ag-NPs were indicated in Figure 31. We observed that the incorporation of Au-NPs and Ag-NPs did not affect the electrospinning and bead-free nanofibers having average fiber diameter of 810 ± 480 nm and 815 ± 445 were obtained for PVP/Au-NPs and PVP/Ag-NPs nanofibers, respectively.

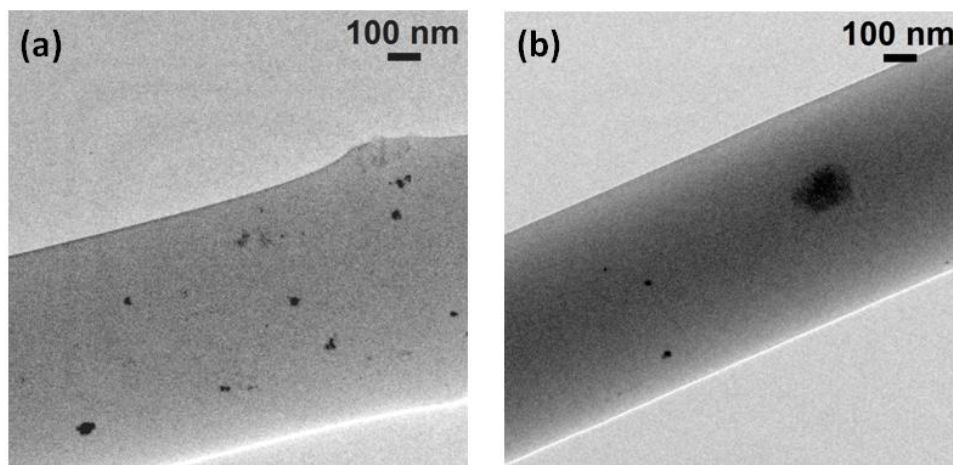


Figure 32 TEM images of (a) PVP/Au-Nps, and (b) PVP/Ag-Nps nanofibers

Moreover, the presence of nanoparticles and their distribution in the PVP nanofibers were further visualized by TEM imaging (Figure 32). The Au NPs and Ag NPs were mostly dispersed in a spherical form homogeneously in the PVP matrix, yet, some aggregations especially of the Ag-NPs were also observed and exhibit a narrow size distribution with the average diameter of 17 nm and 31 nm and in the range of 5 to 20 nm, 4 to 120 nm, respectively.

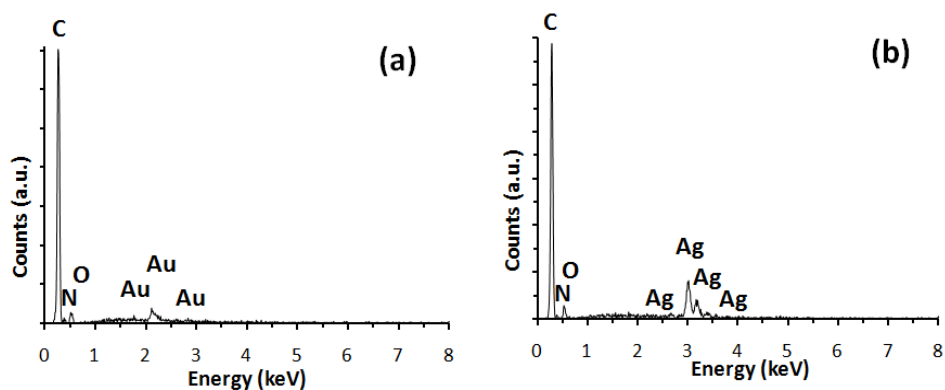


Figure 33 EDX spectrums of (a) PVP/Au-Nps, and (b) PVP/Ag-Nps nanofibers

The elemental analyses performed by EDX showed that carbon, nitrogen, oxygen, gold and silver are the main elements of the nanofibers (Figure 33). Then FTIR spectrometer was used to determine if any interaction between the polymeric part and the metallic NPs. Characteristic peaks of PVP are 1290 cm^{-1} for the amide ($-\text{C}\equiv\text{N}$) stretching, 1440 cm^{-1} for the carboxylic ($\text{O}-\text{H}$) bending, and 1372 cm^{-1} for the ($\text{C}-\text{H}$) vibrations which are not changed by laser ablation method except at 1660 cm^{-1} for the ($\text{C}=\text{O}$) carbonyl stretching vibration. The blue shifts were observed for PVP/Au-NPs and PVP/Ag-NPs to the around 1670 cm^{-1} due to the interaction of carbonyl ($\text{C}=\text{O}$) with the NPs (Figure 34) [30, 31, 33].

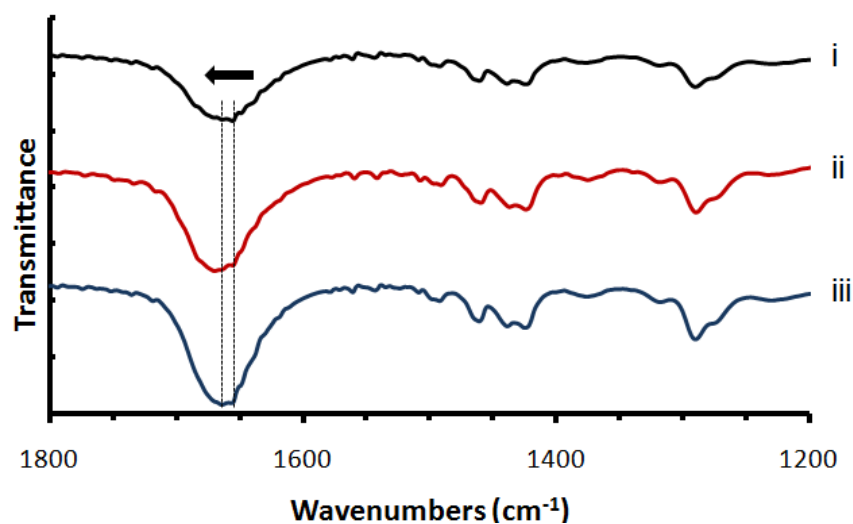


Figure 34 The FTIR spectrums of (i) pure PVP, (ii) PVP/Au-NPs, and (iii) PVP/Ag-NPs nanofibers.

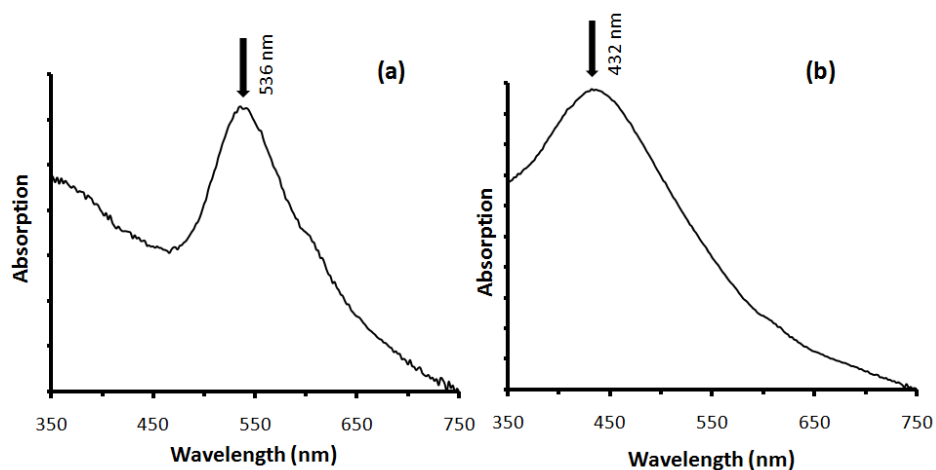


Figure 35 The solid-state UV-Vis absorption spectrums of the (a) PVP/Au-NPs, and (b) PVP/Ag-NPs nanofibers.

Moreover, PVP has a characteristic of dielectric properties [38] when the Au-NPs and Ag-NPs are doped into dielectric matrices, the materials will show specific optical absorption property owing to discrete energy levels

and specific states of nanoparticles. So, UV-Vis spectroscopy can be considered as a useful characterization technique for metal NPs [39-40]. Figure 35 shows the UV-Vis absorption spectrums of PVP nanofibers containing Au and Ag nanoparticles in solid state by background correcting with pure PVP nanofibers in the range of wavelength from 350 – 750 nm at room temperature. The absorption peaks at 536 nm and 432 nm are due to the surface plasma resonances (SPRs) of Au and Ag NPs, respectively. These results indicate the formation of Au-NPs and Ag-NPs via laser ablation method was very successful and the electrospun PVP/Au-NPs and PVP/Ag-NPs nanowebs have shown enhanced optical properties.

4.5. Fabrication of PVDF nanofibers contains Ge nanocrystals (Ge-NCs) by laser ablation method

Ge nanoparticles (Ge-NPs) have interesting applications in optoelectronic devices such as; photodetectors, field-effect transistors and multijunction solar cells etc. due to its optical and electronic properties. Moreover, they have low toxicity and exhibit size-dependent photoluminescence properties. Colloidally stable Ge-NPs can be produced by different processing techniques which are required annealing treatment [42]. However, by using the reactive pulsed laser deposition methods, it was achieved to synthesize Ge-NPs in the controllable size and photoluminescent property without applying any annealing process [43]. This approach was utilized in germanium nanocrystal (Ge-NCs) synthesis in acetone. After the laser ablation, the color of solution becomes brown-yellow presenting of

colloidal Ge-NCs. Then DMAc and PVDF were added to obtain 20 % (w/v) PVDF in DMAc: acetone solution contained Ge-NCs (1:1) solvent system for electrospinning process. The resulting mixture was constantly stirred for 6 hours and sonicated for 1 hour to obtain homogenous solution.

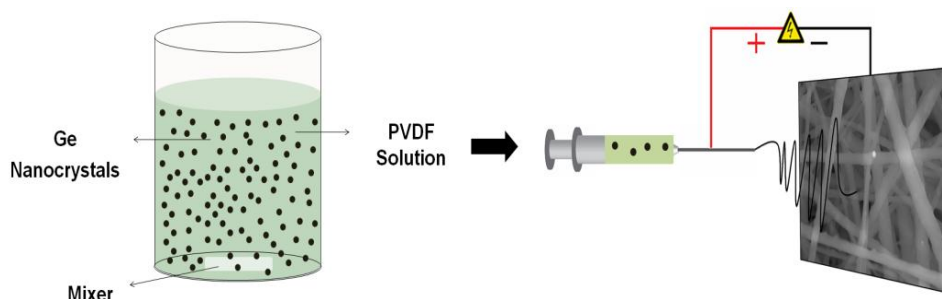


Figure 36 Schematic view of electrospun PVDF nanofibers containing Ge-NCs

The solution was placed into a 3 ml syringe having metallic needle tip (inner diameter=0.8 mm). Afterward, it was fed by a syringe pump horizontally. Electric field was comprised by the high voltage power supply and the electrospinning parameters were as follows: applied voltage = 15 kV, feed rate = 0.5 ml/h, tip-to-collector distance = 13 cm. Electrospun PVDF nanofibers containing Ge-NCs (PVDF/Ge-NCs) were deposited on a grounded stationary cylindrical metal collector covered by a piece of aluminum foil. The electrospinning of PVDF/Ge-NCs solution was carried out in enclosed Plexiglas box and at 22 °C at 24 % relative humidity. Finally, the electrospun nanofibers were dried overnight under the hood (Figure 36).

4.6. Characterization of PVDF nanofibrous composites containing Ge-NCs by laser ablation method

The morphology, the microstructure, the elemental analysis and diameters of the composite nanofibers were evaluated by using SEM, EDX and TEM techniques. The SEM sample was prepared by collecting the PVDF/Ge-NCs nanofibers composite on a silicon substrate.

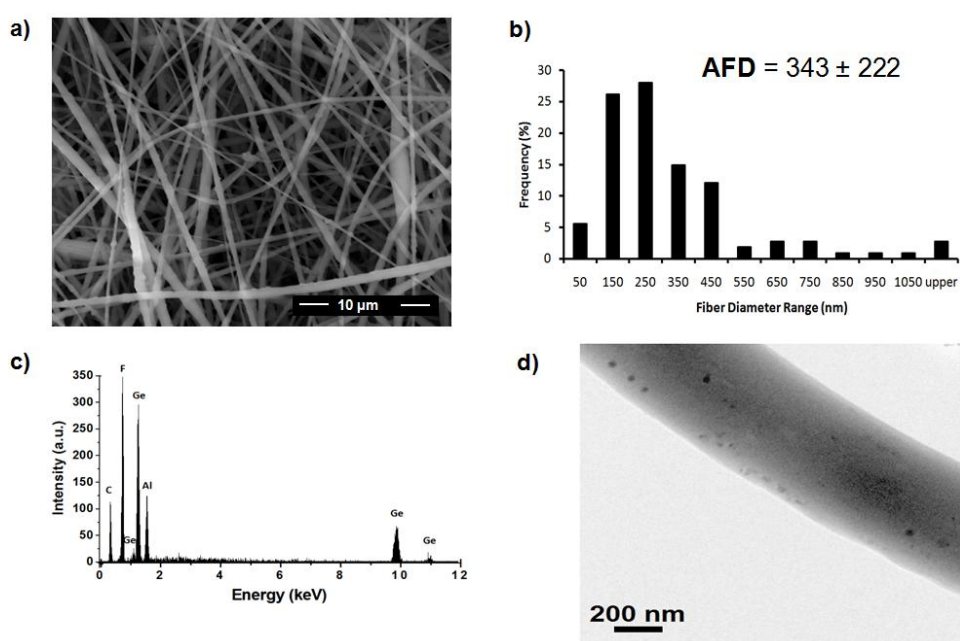


Figure 37 (a) SEM image, (b) The fiber diameter distribution histogram, (c) EDX spectrum, and (d) TEM image of PVDF/Ge-NCs composite nanofibers.

Figure 37-a represents the SEM image for the electrospun PVDF/Ge-NCs nanofibers. The SEM image clearly showed that the incorporation of Ge-NCs into PVDF structure did not affect the electrospinning with smooth surface morphology and straight nanofiber structure. The average diameter of bead-free PVDF/Ge-NCs nanofibers was determined by analyzing around

100 fibers from the SEM images and diameters of the electrospun PVDF/Ge-NCs nanofibers were 50-3000 nm, and average fiber diameter is 343 ± 222 nm. The histogram of the fiber diameter distribution is shown in Figure 37-b. Figure 37-c represents the EDX spectrum of PVDF/Ge-NCs composite nanofibers. The elemental spectrum of EDX results confirms the incorporation of Ge-NCs in the PVDF nanofibers indicating the presence of the Germanium peaks. Carbon, nitrogen and oxygen peaks in the obtained EDX spectra correspond to the characteristics peaks of the PVDF. No other characteristic peaks of the nanocomposite from any impurity are observed. We further studied the PVDF/Ge-NCs nanofibers by TEM analysis. The TEM sample was prepared by placing the composite on a holey carbon-coated TEM grid. TEM image demonstrates that small spherical Ge-NCs are homogeneously distributed in the PVDF nanofiber matrix (Figure 37-d).

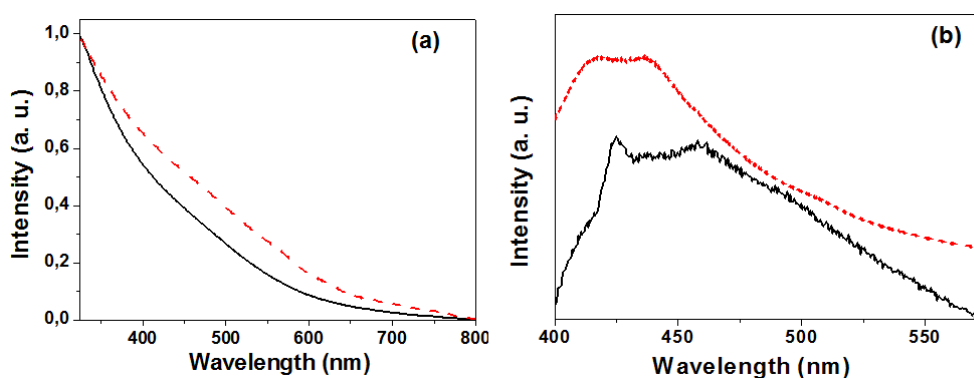


Figure 38 (a) UV-Vis absorption spectrums of Ge-NCs in acetone (black solid line) and Ge-NCs/PVDF nanofibers (red dashed line) and (b) PL spectra of Ge-NCs in acetone (black solid line) and Ge-NCs/PVDF nanofibers (red dashed line)

Moreover, UV-Vis absorption and photoluminescence measurements of Ge-NCs in acetone (black solid line) and Ge-NCs/PVDF nanofibers (red dashed line) were carried out (Figure 38). As it is observed from the graphs, the optical properties of Ge-NCs are supplied in the solid-state PVDF nanofibers with the approximate characteristic values.

CHAPTER 4

CONCLUSION

In this thesis, we focus on three different studies. In the first part, we obtained inorganic nanofibers (TiO_2 and ZnO) from their precursor solutions by using polymeric materials as a carrier matrix then photocatalytic activity of these inorganic nanofibers was studied. In the second part, we report the production of polymeric nanofibrous composites containing anatase TiO_2 -SNF via electrospinning technique. We have shown that nanofibrous composites containing TiO_2 -SNF from different polymers such as PMMA, PAN, PET, PC, and PVDF can easily be obtained via electrospinning. The SEM and TEM studies revealed that some TiO_2 -SNF were fully inside the polymeric matrix whereas some TiO_2 -SNF were partially covered and stucked on the fiber surface. The photocatalytic activity of these nanofibrous composites containing TiO_2 -SNF was evaluated by the photocatalytic decomposition of rhodamine-6G under UV irradiation. Our preliminary results indicated that these nanofibrous composites have photocatalytic activity and could be useful for treatment of organic pollutants. In the last part, we report novel synthesis method of PVP nanofibers incorporating silver and gold nanoparticles. Composite nanofibers are produced by combination of laser ablation and electrospinning techniques. The presence of Ag-NPs and Au-NPs in the PVP nanofibers was confirmed by SEM, TEM

and EDX analyses. The FTIR study suggested the presence of molecular interactions between PVP matrix and the NPs in the nanofibrous composites. The UV-Vis absorption and photoluminescence measurements confirmed the enhancement of the optical properties of the PVP/Ag-NPs and PVP/Au-NPs nanofibers in the solid state due to the surface plasma resonance effect of NPs. On top of that, we demonstrated the synthesis of stable colloidal Ge-NCs by pulsed laser ablation method in acetone to fabricate PVDF nanofibers containing highly pure Ge-NCs.

As a conclusion, we have shown two facile routes to produce multifunctional nanofibrous nanocomposites. The first one is based on merging of inorganic short nanofibers (SNF) into polymeric nanofiber matrix. The second route combines laser ablation and electrospinning to fabricate polymer/nanoparticle nanofibrous composites. Hence, we have demonstrated that; different type of NPs or inorganic SNF can be incorporated into the polymeric nanofiber matrix to develop multifunctional nanocomposites for certain applications.

FUTURE PROSPECTS

In addition to our present study, our nanocomposite materials can be enhanced and so their application opportunities may be extended by applying more advanced process types or by using various chemical components. For instance, coaxial electrospinning method enables the production of hollow and core-shell nanofiber structures hence the surface area of materials can be improved enormously or the polymers/inorganic agents which are difficult to process can be co-electrospun due to this technique. We have achieved the fabrication of nanocomposites by combining polymeric matrix with nanoparticles in the same way; inorganic nanofibers may be an alternative matrix structure for the nanoparticles that are obtained by laser ablation method. This can provides the improvement in the optical and catalytical properties of ultimate nanocomposites owing to synergic effect of more than one inorganic component. Moreover, we have observed in our study that, the short inorganic nanofibers can be fully or partially covered by polymeric matrix. To enhance the photocatalytic property, two different polymer types can be used during the electrospinning and one of them can be removed chemically so as to attain porous surface that will supply the utilization from the inner inorganic short nanofibers. These all approaches can lead the production of more functional nanocomposites in company with more extended application areas.

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