

Materials science communication

Electrospun polymeric nanofibrous composites containing TiO₂ short nanofibers

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HIGHLIGHTS

- Polymeric nanofibrous composites containing anatase TiO₂ short nanofibers (TiO₂-SNF) were produced via electrospinning.
- PMMA, PAN, PET and PC electrospun nanofibers containing TiO₂-SNF were obtained.
- The nanofibrous composites containing TiO₂-SNF has shown photocatalytic activity.

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ABSTRACT

In this study, polymeric nanofibrous composites containing anatase TiO₂ short nanofibers (TiO₂-SNF) were successfully produced via electrospinning. The fabrication of the nanofibrous composite structure includes two steps. First, anatase TiO₂ nanofibers were obtained by calcination of electrospun PVP/TiO₂ nanofibers and then crushed into short nanofibers ranging from few microns in length. Second, these TiO₂-SNF were dispersed into polymer solutions and then electrospun into nanofibrous composites. We obtained nanofibers containing TiO₂-SNF from different polymer types including PMMA, PAN, PET and PC. The SEM and TEM imaging indicated that some of the TiO₂-SNF were fully covered by the polymeric matrix whereas some TiO₂-SNF were partially covered and/or stick on the surface of the fibers. The photocatalytic activity of nanofibrous composites containing TiO₂-SNF was evaluated by monitoring the photocatalytic decomposition of a model dye (rhodamine-6G) under UV irradiation.

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1. Introduction

Functional nanofibers can be easily produced from various polymers, polymer blends, sol–gels, composites and metal oxides via electrospinning technique [1–8]. Electrospun nanofibers/nanowebs have several remarkable characteristics such as a very large surface area to volume ratio and nanoporous features along with physical, chemical and surface functionalization [1–8]. In addition, it is fairly easy to improve the functionality of the electrospun nanofibers by electrospinning of polymer matrix containing functional additives (e.g. nanoparticles) [2,3,9]. For instance, the incorporation of metaloxide nanoparticles such as TiO₂ into electrospun polymeric nanofibers were reported and it was shown that these functional nanofibrous composites have potentials to be used in filtration since TiO₂ nanoparticles show photocatalytic activity and are very effective for degradation of organic pollutants and/or killing bacteria [10–13]. Yet, the leaching of nanoparticles from these polymeric composites and their recov-

ery is always an environmental issue [14,15]. Recently, it has also been reported that electrospun TiO₂ short nanofibers having few micrometers in length have shown better photocatalytic activity compared to TiO₂ nanoparticles [16].

In this study, we used TiO₂ short nanofibers (TiO₂-SNF) for producing polymeric nanofibrous composite structures. These polymeric nanofibers containing TiO₂-SNF were successfully produced via electrospinning with the goal to develop functional nanofiltration materials since TiO₂ is known to be very effective for degradation of organic pollutants due to its photocatalytic activity. We electrospun nanofibers containing TiO₂-SNF from different polymer types which are commonly used as filtration materials such as poly(methyl methacrylate) (PMMA), polyacrylonitrile (PAN), polyethylene terephthalate (PET) and polycarbonate (PC). As a preliminary study, the photocatalytic activity of PET nanofibers containing TiO₂-SNF was investigated for photocatalytic decomposition of rhodamine-6G under UV irradiation. To the best of our knowledge, this is the very first report showing that metal oxide short 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.

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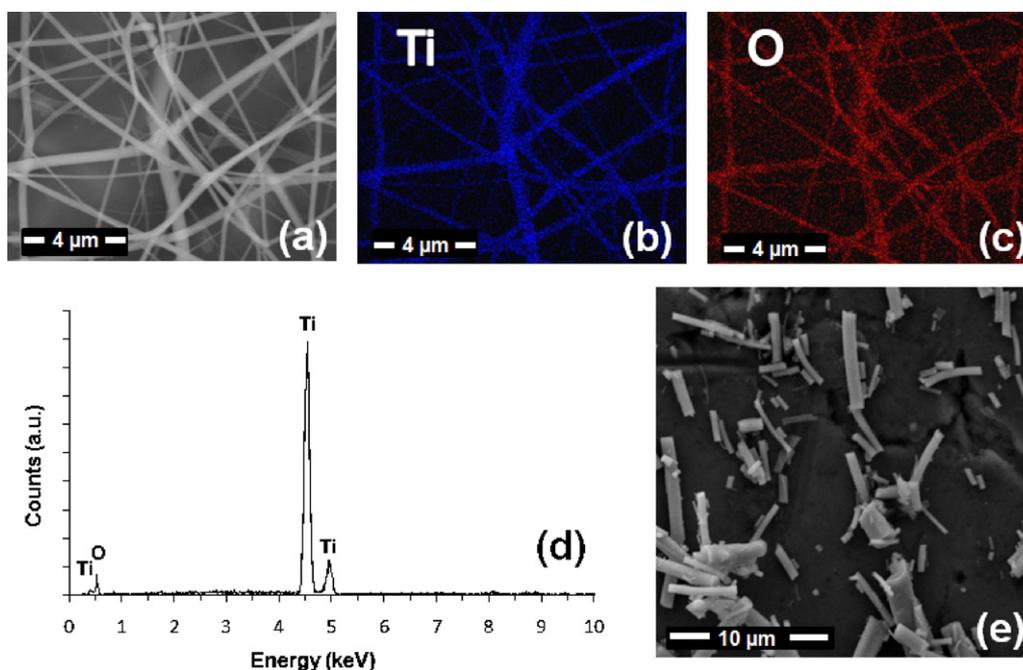


Fig. 1. (a) Representative SEM image, (b) and (c) EDX elemental maps and (d) EDX spectrum of electrospun TiO_2 nanofibers, (e) SEM image of TiO_2 -SNF obtained after crushing the electrospun TiO_2 nanofibers.

2. Experimental details

2.1. 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, Mw $\sim 1,300,000$, Aldrich), poly(methyl methacrylate) (PMMA) (Mw $\sim 350,000$, Aldrich), polyacrylonitrile (PAN) (donated by AKSA Co., Turkey), polyethylene terephthalate (PET) (donated by Korteks Co., Turkey), polycarbonate (PC) (Mw $\sim 64,000$, Aldrich) were used as-received.

2.2. Preparation of TiO_2 nanofibers

Titanium (IV)-isopropoxide (2.88 ml) precursor was mixed with glacial acetic acid (2 ml) and ethanol (2 ml) solvent system. After stirring for 10 min, PVP (0.6 g) dissolved in ethanol (3 ml) was added to this solution. The resulting mixture was constantly stirred for 12 h, and the yellowish sol-gel was obtained. The PVP/ TiO_2 sol precursor was placed into a 1 ml syringe having metallic needle tip (inner diameter = 0.4 mm) for electrospinning. The solution was fed by a syringe pump horizontally (Model: SP 101IZ, WPI). Electric field was comprised by the high voltage power supply (Matusada Precision, AU Series, Japan). The electrospinning parameters were as follows: applied voltage = 15 kV, feed rate = 0.5 ml h^{-1} , tip-to-collector distance = 10 cm. 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 23°C at 26% relative humidity. The electrospun nanofibers were dried overnight under the hood and then calcinated at 500°C for 3 h in an oven in order to obtain pure TiO_2 nanofibers.

2.3. Preparation of polymeric nanofibers containing TiO_2 short nanofibers

TiO_2 short nanofibers (TiO_2 -SNF) ranging from ~ 1 to $\sim 10 \mu\text{m}$ in length were obtained by crushing the electrospun TiO_2 nanofibers in a mortar. 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. Then, 6% TiO_2 -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 % 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 with the following parameters: applied voltage = 15 kV, tip-to-collector distance = 10 cm and feed rate = 1 ml h^{-1} . For PMMA

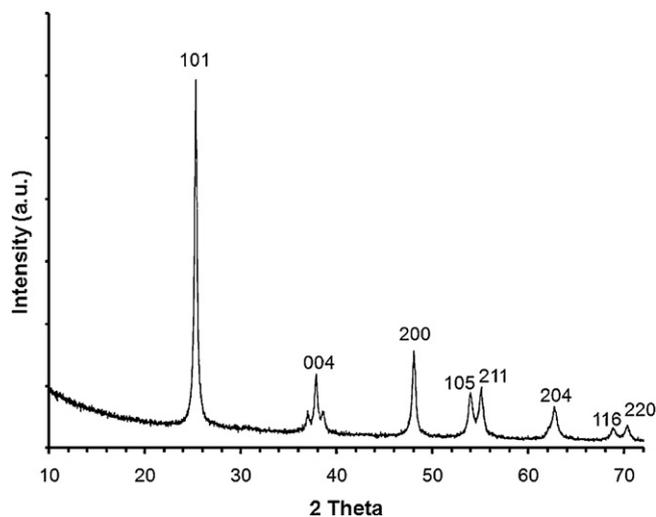


Fig. 2. XRD pattern of TiO_2 -SNF.

solution the parameters were as follows: applied voltage = 10 kV, tip-to-collector distance = 15 cm and feed rate = 1 ml h^{-1} .

2.4. Photocatalytic activity of polymeric nanofibers containing TiO_2 short nanofibers

The photocatalytic activity was analyzed by photodegradation of rhodamine-6G (Rh-6G) ($2 \times 10^{-5} \text{ M}$) in aqueous medium. Electrospun PET nanoweb containing TiO_2 -SNF (PET-NF/ TiO_2 -SNF) (weight of nanoweb: 2 mg, dimension of the nanoweb: $1.0 \text{ cm} \times 1.0 \text{ cm}$) was put into quartz cuvette (width: 1 cm, length: 1 cm, and height: 5 cm, Hellma) filled with rhodamine-6G solution. The cuvette was placed with a distance of 5 cm from the UV source (8 W, UVLMS-38 EL) and kept under UV irradiation at 254 nm wavelength. At known time intervals, the dye concentration was measured by using UV-vis spectrophotometer. During the UV-vis measurement, the PET-NF/ TiO_2 -SNF nanoweb was floating on the top of the dye solution and therefore the nanoweb did not interfere with the UV-vis measurement.

2.5. Measurement and characterization

Scanning electron microscope (SEM) (FEI - Quanta 200 FEG) and transmission electron microscope (TEM) (FEI - Tecnai G2F30) were used for the

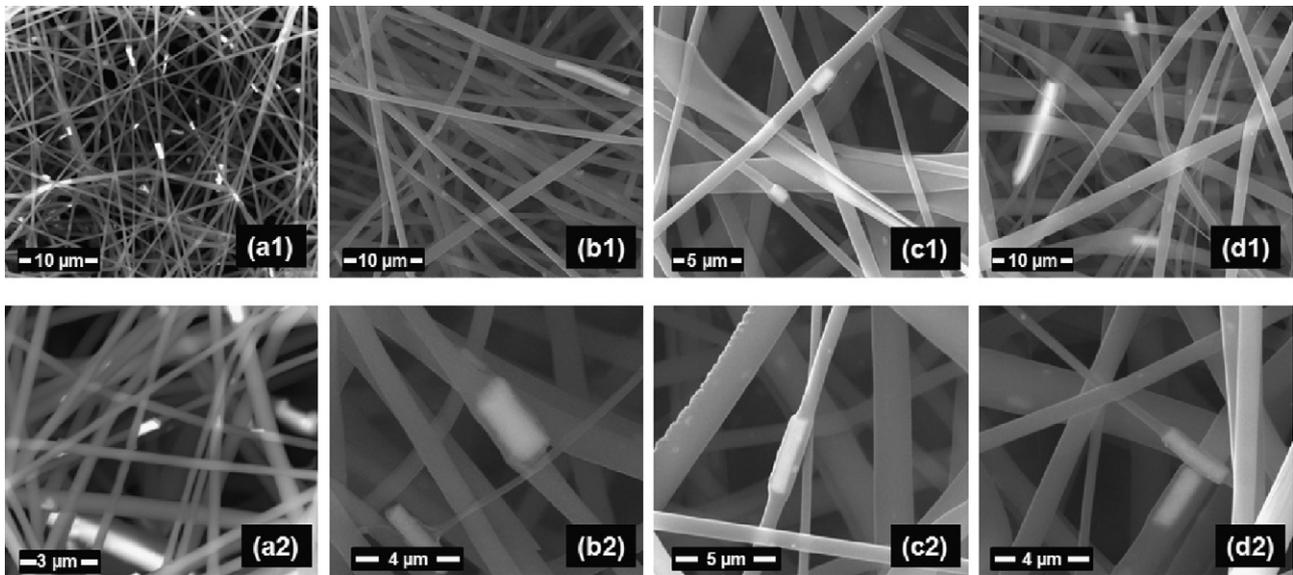


Fig. 3. SEM images of nanofibrous composites with (1) low magnification and (2) high magnification: (a1) and (a2) PMMA-NF/TiO₂-SNF, (b1) and (b2) PAN-NF/TiO₂-SNF, (c1) and (c2) PET-NF/TiO₂-SNF and (d1) and (d2) PC-NF/TiO₂-SNF.

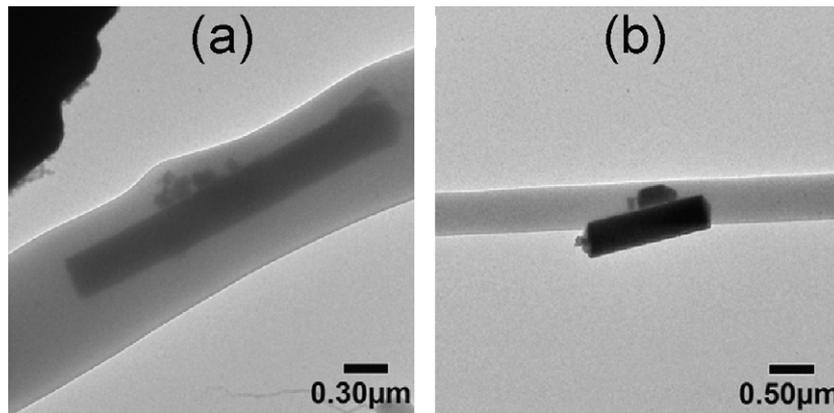


Fig. 4. TEM images of the PMMA-NF/TiO₂-SNF from two different fibers showing that (a) the TiO₂-SNF was embedded in the PMMA fiber matrix and (b) the small TiO₂-SNF was embedded and the large TiO₂-SNF was sticking out from the PMMA fiber matrix. TiO₂-SNF was visualized as a dark object in the TEM image.

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 nanofibers. The X-ray diffraction (XRD) pattern for TiO₂ nanofibers were obtained by using PAN analytical X'Pert Powder diffractometer with Cu K α radiation in a range $2\theta = 10\text{--}75^\circ$. UV-vis-NIR spectrophotometer (Varian Cary 5000) was used at the range 400–600 nm wavelength to monitor the photocatalytic degradation of rhodamine-6G dye solution.

3. Results and discussion

Pure TiO₂ nanofibers were produced via electrospinning of PVP/TiO₂ sol precursor followed by removal of organic component (PVP) by calcination at 500 °C for 3 h. During the calcination process of PVP/TiO₂, the material maintained its fibrous structures and brittle TiO₂ nanofibers were obtained. The scanning

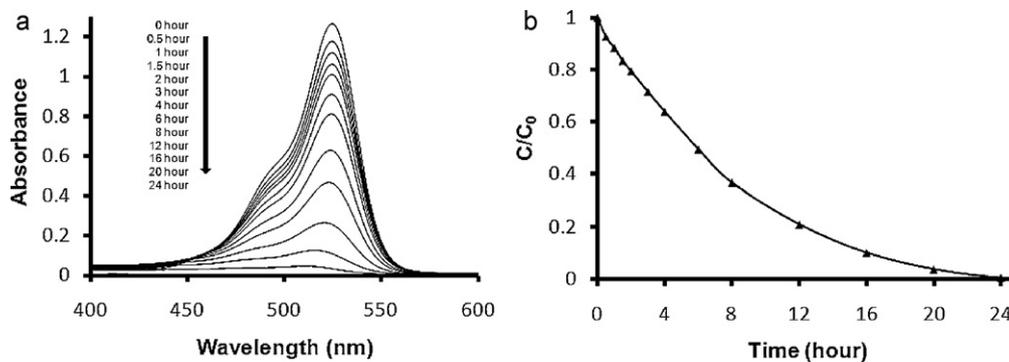


Fig. 5. The UV-vis spectrum of the Rh-6G solution containing PET-NF/TiO₂-SNF (a) as a function of the UV irradiation time, (b) the rate (C/C_0) of Rh-6G degradation. The absorption peak point of Rh-6G at 526 nm was used for calculating the rate (C/C_0).

electron microscopy (SEM) and the energy dispersive X-ray (EDX) spectroscopy analyses of TiO₂ nanofibers were performed (Fig. 1). Bead-free TiO₂ nanofibers having diameters in the range of 40–500 nm with average fiber diameter of 200 ± 120 nm were obtained. The elemental mapping of TiO₂ nanofibers by EDX showed that titanium and oxygen are the main elements of the nanofibers (Fig. 1(b)–(d)). Electrospun TiO₂ nanofibers were crushed into short nanofibers (TiO₂-SNF) ranging from ~1 to ~10 μm in length (Fig. 1(e)).

The crystalline structure of TiO₂-SNF was identified by X-ray diffraction (XRD). Fig. 2 has shown the XRD of TiO₂-SNF with series of diffraction peaks corresponding to anatase phase which is known for its photocatalytic activity [17–19]. The salient peak at 2θ = 25.4° corresponds to the (1 0 1) plane of the anatase TiO₂ structure and the other peaks at 2θ = 38.1°, 48.4°, 54.3°, 55.3°, 63.0°, 69.1°, 70.3° correspond to the diffraction of (0 0 4), (2 0 0), (1 0 5), (2 1 1), (2 0 4), (1 1 6), and (2 2 0) planes, respectively [20]. XRD pattern of the TiO₂-SNF has no diffraction peak at 2θ = 27.5° which is characteristic for the rutile phase signifying that calcination process yielded TiO₂ nanofibers having pure anatase structure.

The fabrication of electrospun polymeric nanofibers containing TiO₂-SNF includes two steps. In the first step, PVP/TiO₂ electrospun nanofibers were calcinated in order to obtain pure anatase TiO₂ nanofibers and then they were crushed into short nanofibers ranging from ~1 to ~10 μm in length (Fig. 1(e)). These TiO₂-SNF were blended with polymer solution and then electrospun into nanofibrous composite structures. In this study, we electrospun nanofibers from several different polymer types including poly(methyl methacrylate) (PMMA), polyacrylonitrile (PAN), polyethylene terephthalate (PET) and polycarbonate (PC) containing TiO₂-SNF. These electrospun nanofibrous composites were abbreviated as: PMMA-NF/TiO₂-SNF, PAN-NF/TiO₂-SNF, PET-NF/TiO₂-SNF and PC-NF/TiO₂-SNF. The representative SEM images of these nanofibrous composites are depicted in Fig. 3. We observed that the incorporation of TiO₂-SNF did not affect the electrospinning of these polymers and bead-free nanofibers were obtained in all cases. We further analyzed these nanofibrous composites by transmission electron microscopy (TEM). The representative TEM images of the PMMA-NF/TiO₂-SNF composite nanofibers are given in Fig. 4. SEM and TEM analyses revealed that some of the TiO₂-SNF were fully covered by the polymeric matrix whereas some TiO₂-SNF were present on the surface of the polymeric matrix and/or sticking out from the polymeric matrix. As mentioned above, TiO₂-SNF has anatase structure which is known for its photocatalytic activity. As a preliminary study, we also investigated the photocatalytic activity of PET-NF/TiO₂-SNF.

The photocatalytic degradation of rhodamine-6G (Rh-6G) dye solution was used as a model photoreaction, and its degradation was followed by the UV–vis measurement of the solution containing PET-NF/TiO₂-SNF. The change in the absorbance on the UV–vis spectrum of the Rh-6G solution containing PET-NF/TiO₂-SNF as a function of the UV irradiation time is shown in Fig. 5. The change of the absorption peak point of Rh-6G at 526 nm was used for calculating 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. As the photodegradation of Rh-6G

occurred with respect to UV irradiation time, the absorbance of the Rh-6G solution in the UV–vis spectrum decreased gradually, and the red color of the solution disappeared totally after 24 h of UV irradiation indicating that almost 100% of the Rh-6G was decomposed. This result confirmed the photocatalytic degradation of Rh-6G by PET-NF/TiO₂-SNF nanofibrous composite.

4. Conclusion

Here, we summarized the production of polymeric nanofibrous composites containing anatase TiO₂ short nanofibers (TiO₂-SNF) via electrospinning technique. We have shown that nanofibrous composites containing TiO₂-SNF from different polymers such as PMMA, PAN, PET and PC can easily be obtained via electrospinning. The SEM and TEM studies revealed that some TiO₂-SNF were fully inside the polymeric matrix whereas some TiO₂-SNF were partially covered and stick on the fiber surface. The photocatalytic activity of these nanofibrous composites containing TiO₂-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. Moreover, such nanofibrous composite structures can also be applicable in other areas depending on the polymer type and the function of metal oxides.

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