

Coaxial nanofibers containing TiO₂ in the shell for water treatment applications

N Kizildag^{1,2}, J Geltmeyer¹, N Ucar², K De Buysser³ and K De Clerck¹

¹Ghent University, Department of Materials, Textiles and Chemical Engineering, Technologiepark 907, 9052 Zwijnaarde, Ghent, Belgium

²Istanbul Technical University, Department of Textile Engineering, Inonu Cad. 65, Gumussuyu, Istanbul, Turkey

³Ghent University, Department of Inorganic and Physical Chemistry, Campus Sterre, S3, Krijgslaan 281, B-9000 Ghent, Belgium

E-mail: kizildagn@itu.edu.tr

Abstract. In recent years, the basic electrospinning setup has undergone many modifications carried out to enhance the quality and improve the functionality of the resulting nanofibers. Being one of these modifications, coaxial electrospinning has attracted great attention. It enables to use different materials in nanofiber production and produce multi-layered and functional nanofibers in one step. In this study, TiO₂ has been added to the shell layer of coaxial nanofibers to develop functional nanofibers which may be used in water treatment applications. The coaxial nanofibers containing TiO₂ in the shell layer are compared to uniaxial nanofibers containing TiO₂ in bulk fiber structure, regarding their morphology and photocatalytic activity. Uniform uniaxial and coaxial nanofibers with TiO₂ were obtained. The average nanofiber diameter of coaxial nanofibers were higher. Coaxial nanofibers, which contained lower amount of TiO₂, displayed similar performance to uniaxial nanofibers with TiO₂ in terms of photocatalytic degradation ability against isoproturon.

1. Introduction

The well-known electrospinning technique is recently expanded to produce a novel class of nanofibers with core-shell structure which are either called core-shell or coaxial nanofibers. Coaxial electrospinning attracts great attention as it makes it possible to use different materials in nanofiber production and produce multi-layered and functional nanofibers in one step [1]. It was first reported by Sun et al. They successfully created coaxial fibers made of combinations of different materials: polyethyleneoxide (PEO)-poly (dodecylthiophene), polylacticacid (PLA)-palladium, and PEO-polysulfone, and a composition of identical polymers (PEO-PEO) [2]. Since then many researchers have been using coaxial electrospinning. Unspinnable materials such as drugs, enzymes, etc. could be electrospun as the core of a fiber-forming polymer [3-6]. Nanofibers encapsulating epoxy within a polymeric shell were found to be suitable for self-healing applications [7]. Biocompatible nanofibers with improved mechanical properties [8], hollow nanofibers [9], nanofibers from unspinnable polymers [5,10] could be electrospun. Coaxial nanofibers encapsulating bio-based phase change material (bio-PCM) exhibited balanced thermal storage and releasing properties for thermo-regulating functions [11]. It could be possible to attach composite nanofibers onto a textile substrate by coaxially spinning PU (shell)/ Nylon-6 (core) nanofibers [12].



Coaxial nanofiber structure is also expected to bring advantages in the photocatalyst immobilization. The incorporation of the photocatalysts into the shell layer of the coaxial nanofibers may result in decreased diffusion length, increased accessible surface area and more active sites, all of which are expected to improve the photocatalyst activity. In addition, another advantage is regarding the mechanical properties. Incorporation of high amount of additives to the nanofiber structure affects the mechanical properties negatively. When the additives are added to the shell and pure polymer is used as the core the sacrifice regarding the mechanical properties will not be that much. Furthermore, it may provide cost reduction especially when working with expensive additives. When the additive is only added to the shell instead of the bulk fiber structure, the additive amount used will be less and the costs regarding the additive will be lower. In this study, TiO_2 was selected as the photocatalyst and used in the production of coaxial nanofibers containing TiO_2 in the shell. For comparison, uniaxial nanofibers with TiO_2 were also produced. Coaxial nanofibers were compared to uniaxial nanofibers in terms of morphology and photocatalytic activity.

2. Experimental

2.1. Materials

Polyamide (PA6) (Sigma Aldrich, 181110), titanium (IV) dioxide (TiO_2) (Sigma Aldrich, 718467, Aeroxide® P25), formic acid (Sigma Aldrich, F0507), acetic acid (Sigma Aldrich, 33209) were used as received. Isoproturon (Dr. Ehrenstorfer GmbH) and distilled water were used in photocatalytic activity tests.

2.2. Methods

18 wt% PA6 solution and 5 wt% PA6 solution with 200 wt% TiO_2 (with respect to the polymer weight) were used as the core and the shell solutions respectively to obtain coaxial nanofibers with an actual TiO_2 content of 8.4 wt%. Coaxial needle (Raméhart Custom Needle, 100-10-COAXIAL-2016, outer needle: 1.7 mm OD, inner needle: 0.9 mm OD) was placed on the needle holder of the electrospinning setup. Two pumps (KD Scientific Pump Series 100) were used to feed the core and shell solutions respectively. A high voltage power supply (Glassman High Voltage Series) was used to apply high voltage to the outer needle. The distance between the tip of the needle and the collector, the flow rates of the solutions and the voltage were adjusted to obtain stable electrospinning. In order to see whether the shell solution was electrospinnable, it was used as the electrospinning solution on the basic setup using uniaxial needle. Uniaxial PA6 nanofibers containing 50 wt% TiO_2 were also produced for comparison. For uniaxial nanofiber production, a uniaxial needle (Sigma Aldrich, Z261351-1EA, Stainless steel 316 syringe needle, pipetting blunt 90 tip, 18 gauge, 6 inch) was placed on the needle holder. The electrospinning solution was fed to this needle by a pump (KD Scientific Pump Series 100). A high voltage power supply (Glassman High Voltage Series) was used to apply high voltage to the solution. Using a syringe of 10 mL, electrospinning solutions, were fed using PTFE tubing (OD=1/16''=1.6mm OD) through the needle. The distance between the tip of the needle and the collector, the flow rates of the solutions and the voltage were adjusted to obtain stable electrospinning. Large homogeneous nanofiber webs were obtained using the in-house developed electrospinning machine, which contained a moving needle support and a moving collector [13]. Nanowebs with the same specific weight (10 g/m²) were produced. The speed of the aluminium foil was adjusted to obtain nanowebs with the same weight.

2.3. Characterization

The functionalised nanofibers were characterized in terms of morphology and photocatalytic activity against isoproturon. The morphologies of the nanofibers were analysed using scanning electron microscope (SEM, Jeol Quanta 200 FESEM). SEM images were taken at an accelerating voltage of 20 kV. Before SEM analysis, the samples were coated with gold using a sputter coater (Baljes Union SKD 030). The fiber diameters were measured using Image J. The average nanofiber diameters and

the standard deviations were based 80 measurements per sample. Average nanofiber diameters were expressed as the mean $\pm$ standard deviation. Photocatalytic activities of the functionalised nanofibers against isoproturon were assessed under UV irradiation. Samples with diameters of 8 cm were immersed in 100 ml isoproturon solutions (5 mg/l) and illuminated from a 20 cm distance by a 300 W Osram Ultra-Vitalux lamp. Sampling was done after 1, 2, 4 and 6 h of illumination after which the concentration of the isoproturon was measured by recording its absorbance at 247 nm with a UV-Vis spectrophotometer. The percentage of degradation efficiency was calculated as C/C_0 where C is the isoproturon concentration after the illumination for a certain period of time and C_0 is the isoproturon concentration before the illumination. Non-functionalised electrospun nanofiber membranes were considered as a reference. UV-Vis absorption spectra of the isoproturon solutions were taken by Perkin-Elmer Lambda 900 spectrophotometer in the 300-1100 nm region.

3. Results and Discussion

3.1. Morphology

SEM image of the web electrospun from 5 wt% PA6 solution with 200 wt% TiO_2 , which was prepared to be used as the shell solution in coaxial electrospinning, can be seen in Figure 1. The web produced on the basic electrospinning setup using uniaxial needle, consisted mainly of large TiO_2 agglomerates with some nonuniform, very fine fibrous structures in between. It was not possible to obtain uniform composite nanofibers from the solution which is used as the shell solution in coaxial nanofibers. It was an unelectrospinnable solution.

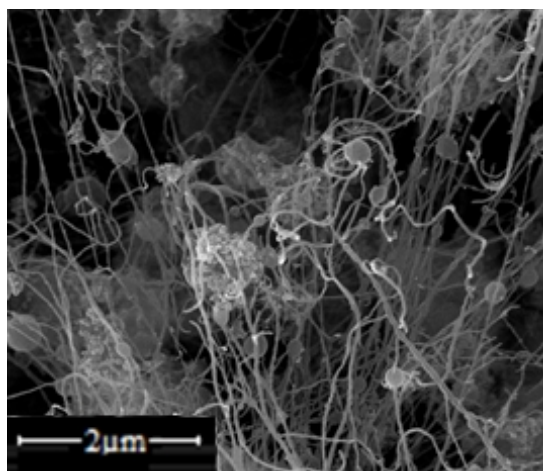


Figure 1. SEM images of the web electrospun from shell solution (5 wt% PA6 solution with 200 wt% TiO_2) using uniaxial needle.

SEM images of coaxial nanofibers with TiO_2 in the shell and the uniaxial nanofibers with TiO_2 in the bulk fiber structure can be seen Figure 2. The nanofibers were uniform in structure without any beads.

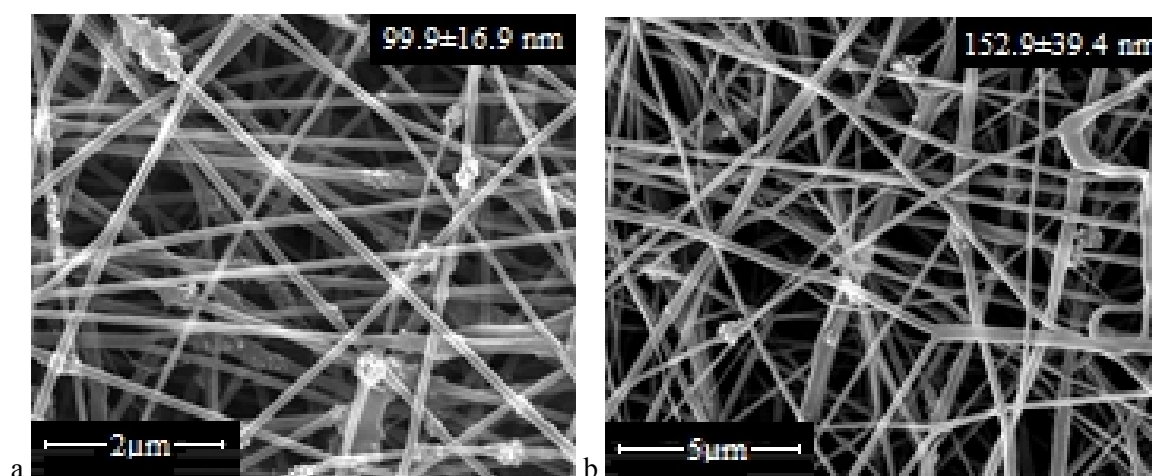


Figure 2. SEM images of a. PA6/50%TiO₂ uniaxial; b. PA6/8.4%TiO₂ coaxial nanofibers

TiO₂ agglomerates were visible on the SEM images. The coaxial electrospinning resulted in thicker nanofiber formation due to the higher total flow rate used in coaxial electrospinning and larger diameter of the coaxial needle compared to the uniaxial needle. While the shell solution was not electrospinnable on its own (Figure 1), it could be used as the shell solution in coaxial electrospinning.

3.2. Photocatalytic degradation

When TiO₂ nanoparticles are exposed to UV light, electrons reaching the sufficient energy pass from the valence band to the conduction band, leaving holes in the valence band. While the holes react with water to produce hydroxyl radicals, the electrons react with molecular oxygen molecules producing superoxide radical anions. These two reactive species react with the organic contaminants and decompose them [14-17]. The photocatalytic activity of TiO₂ is widely studied in literature. Im et al. (2007) prepared electrospun PAN-based nanofiber webs containing 100 wt % TiO₂. They showed that the TiO₂ containing nanowebs suspending on the dye solution had a dye removal efficiency of 60% [18]. Daels et al. (2014) produced polyamide-6 (PA-6) nanowebs containing TiO₂ nanoparticles by electrospinning. They tested different types of TiO₂ functionalization methods (inline functionalization and post-functionalization) with two types of TiO₂ nanoparticles. The results of photodegradation with methylene blue in aqueous solution demonstrated excellent photocatalytic activity of TiO₂ nanoparticles immobilized in and on the nanowebs. After 2 h of UV irradiation, a degradation up to 84% methylene blue was observed which further increased and resulted in a degradation up to 99% methylene blue after 6 h of illumination. They suggested that electrospun nanowebs functionalized with TiO₂ nanoparticles could be used as a water filter medium [14]. Jeun et al. (2011) reported the production of composite of PAN nanoweb containing 100 wt % of sol-gel-derived nanometer size TiO₂ and the effect of the e-beam irradiation on the photocatalytic ability of the nanowebs. While the nonirradiated PAN/ TiO₂ nanofibers degraded methylene blue at the low rate of 58.6% for 3 h, e-beam irradiation resulted in a significant increase in the photodegradation ability (72.5%) of the nanowebs [19]. Jo et al. prepared polyacrylonitrile (PAN)-supported titania (PAN-TiO₂) fibers with different TiO₂ to PAN ratios and investigated their feasibility for indoor air cleaning applications. The TiO₂ content was changed as 5, 10, 50 and 100 wt % (with respect to the weight of PAN). The composite nanowebs were tested for their degradation efficiency against four different target compounds of benzene, toluene, ethyl benzene, and xylene. For all target aromatic compounds, the decomposition efficiencies of PAN-TiO₂ fibers increased as the TiO₂ content increased. For the highest TiO₂ of 100 w%, the decomposition efficiencies of the PAN- TiO₂ fibers were close to 100% for the target compounds over the 3h photocatalytic process [20]. Cossich et al. (2015) produced TiO₂ containing polyamide-12 nanofibers. TiO₂ content was varied as 0, 10 and 20 wt % of TiO₂. The photocatalytic

performance of the samples was measured against methylene blue (MB). PA12 with 20 wt % TiO_2 removed nearly all the MB from the solution in 100 min [21].

In this study, the photocatalytic activity of coaxial nanofibers containing TiO_2 in the shell layer was tested against isoproturon, which is one of the pollutants detected in surface and groundwater above permissible levels, and compared to that of uniaxial nanofibers containing TiO_2 in bulk structure. Isoproturon photolysis was determined. Pure PA6 nanofibers were also tested as reference.

The photocatalytic activity of the nanofibers in comparison with isoproturon photolysis, and photodegradation activity of PA6 of the nanofibers can be seen in Figure 3.

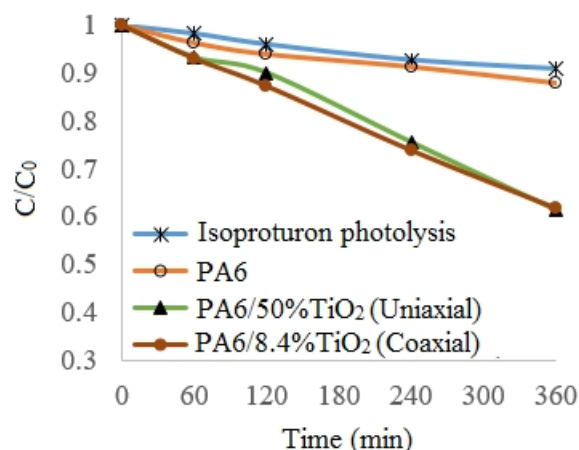


Figure 3. Photodegradation activity of uniaxial and coaxial nanofibers.

When isoproturon solution is exposed to UV-light for 6 hours without any nanoweb in it, 9.1 % of isoproturon is degraded as a result of photolysis. 12 % reduction is observed in isoproturon concentration when the isoproturon solution is exposed to UV-light with PA6 nanoweb in it which means that around 3 % isoproturon is absorbed by the nanoweb. Both coaxial nanofibers containing TiO_2 in the shell layer and the composite uniaxial nanofibers with TiO_2 were found to be effective in the degradation of isoproturon under UV irradiation. PA6/50% TiO_2 uniaxial nanofibers and PA6/8.4% TiO_2 coaxial nanofibers displayed around 38% photocatalytic activity. The photocatalytic activity of TiO_2 is reported to be dependent on its content [22]. While uniaxial nanofibers contained 50 wt% TiO_2 , coaxial nanofibers contained 8.4 wt% TiO_2 in their shell layer. Coaxial nanofibers displayed similar performance to uniaxial nanofibers in terms of isoproturon photodegradation but with lower TiO_2 content. This is attributed to the presence of TiO_2 closer to the surface in coaxial nanofibers.

4. Conclusions

Uniform uniaxial and coaxial nanofibers functionalized with TiO_2 were obtained. While the shell solution was not electrospinnable on its own using uniaxial needle, it could be used as the shell solution in the production of the coaxial nanofibers. Uniaxial nanofibers with 50 wt% TiO_2 and coaxial nanofibers containing 8.4 wt% TiO_2 closer to the surface of the nanofibers both displayed around 38% photocatalytic activity against isoproturon in 6 hours. Coaxial nanofibers can be suggested as an economical way of functionalization, which may be important especially when working with expensive additives.

Acknowledgments

Nuray Kizildag would like to thank The Scientific and Technological Research Council of Turkey (TUBITAK) for the scholarship (2214-A/1059B141500560) she received for her research study at Ghent University.

References

- [1] Elahi M F, Lu W, Guoping F and Khan F 2013 *Bioengineering & Biomedical Sciences* **3(1)** 1.
- [2] Sun Z C, Zussman E, Yarin A L, Wendorff J H and Greiner A 2003 *Adv. Mater.* **15** 1929.
- [3] Wang J, Naguib H E and Bazylak A 2012 Electrospun porous conductive polymer membranes *Behavior and Mechanics of Multifunctional Materials and Composites* vol 8342, ed N C Goulbourne and Z Ounaies, Proc. of SPIE.
- [4] Díaz J E, Nieves A F, Barrero A, Márquez M and Loscertales I G 2008 *Journal of Physics: Conference Series* **127** 012008.
- [5] Ojha S S, Stevens D R, Hoffman T J, Stano K, Klossner R, Scott M C, Krause W, Clarke L I and Gorga R E 2008 *Biomacromolecules* **9** 2523.
- [6] Diaz J E, Lallave M, Galan D, Marquez M, Barrero A and Loscertales I G 2005 *Fiber Society Spring 2005 Conf. St. Gallen Switzerland*.
- [7] J Mitchell T and Keller M W 2013 *Polym. Int.* **62** 860.
- [8] Merkle V M, Zeng L, Slepian M J and Wu X 2014 *Biopolymers* **101** 336.
- [9] Li D and Xia Y 2004 *Nano Lett.* **4** 933.
- [10] Pakravan M, Heuzey M C and Ajji A 2012 *Biomacromolecules* **13** 412.
- [11] Hu W and Yu X 2012 *RSC Adv.* **2** 5580.
- [12] Han X J, Huang Z, He C and Liu L 2007 *High Perform. Polym.* **19** 147.
- [13] Westbroek P, Van Camp T, De Vrieze S and De Clerck K 2008 *Production and Use of Laminated Nanofibrous Structures. Patent 2687563*.
- [14] Daels N, Radoicic M, Radetic M, Van Hulle S W H and De Clerck K 2014 *Sep. Purif. Technol.* **133** 282.
- [15] Bedford N Ma nd Steckl AJ 2010 *ACS Appl. Mater. Inter.* **2(8)** 2448.
- [16] Deveau P A, Arsac F, Thivel P X, Ferronato C, Delpech F, Chovelon J M, Kaluzny P and Monnet C 2007 *J. Hazard. Mater.* **144** 692.
- [17] Yang J, Chen C, Ji H, Ma W and Zhao J 2005 *J. Phys. Chem. B* **109** 21900.
- [18] Im J S, Kim M I and Lee Y S 2008 *Mater Lett* **62** 3652.
- [19] Jeun J P, Park D W, Seo D K, Kim H B, Nho Y C and Kang P H 2011 *Rev. Adv. Mater. Sci.* **28** 26.
- [20] Jo W K and Kang H J 2013 *Ind. Eng. Chem. Res.* **52(12)** 4475.
- [21] Cossich E, Bergamasco R, Pessoa de Amorim M T, Martins P M, Marques J, Tavares C J, Lanceros Méndez S and Sencadas V 2015 *Mater. Chem. Phys.* **164** 91.
- [22] Sharma M V P, Kumari V D and Subrahmanyam M 2008 *Chemosphere* **72** 644.