Superhydrophobic Electrospun Nanocomposite Fibers for Training Engineering Students

Md. Nizam Uddin[1], Fenil Desai[1], Arvind Raj Murali[1], Andrew Swindle[2], and Eylem Asmatulu[1,*]

[1]Department of Mechanical Engineering, Wichita State University, 1845 Fairmount Street, Wichita, Kansas 67260-0133
[2]Department of Geology, Wichita State University, 1845 Fairmount, Wichita, KS 67260-0133
*Email: e.asmatulu@wichita.edu

Abstract

To address the global water scarcity issue, efficient water collecting surface with fast capturing, and easy drainage is essential. This paper presents a facile method for the fabrication of permanent electrospun superhydrophobic polyacrylonitrile (PAN) and Poly (methyl methacrylate) (PMMA) nanocomposite fibers. The superhydrophobic nanocomposite fibers are fabricated with various proportion of titanium dioxide (TiO_2) nano, and Al microparticles using the facile electrospinning technique followed by stabilization and carbonization to remove all non-carbonaceous material from the fibers. The fibers morphology, surface hydrophobicity, crystal structure of the nanocomposite fibers were investigated by scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and water contact angle. The test results showed that the inclusion of nanoparticles in the carbonized nanocomposite fibers ameliorate the surface roughness as well as surface hydrophobicity. Besides, the degree of crystallization is also improved. A water contact angle of 154.8° was achieved by addition of 10% inclusion of the combination of micro and nanoparticles. Thus, the electrospun carbonized superhydrophobic nanocomposite fibers have various industrial applications; including water collection, water filtration, tissue engineering, composites, and so forth.

Keywords: Electrospinning, Nanocomposite Fibers, Stabilization, Carbonization, Water Contact Angle, Superhydrophobic Surfaces.

1. Introduction

The global water shortage issue leads to the development of water capturing technology since the 20th century, especially countries with arid and semi-arid regions. The rainfalls in such area are limited, so animals and plants get water from atmospheric fog, moisture, etc. However, atmospheric fog represents a substantial fresh water source. Approximately one billion peoples are suffering to access clean water source in the globe [1]. Besides, industrial growth, population growth, urbanization, depleting water resources, deforestation, and many other factors increase this water crisis issue. Therefore, engineers and scientists are challenged with finding the economically feasible and viable water resources to solve this problem. In some Asian, African and Latin American countries alternative methods such as rain and groundwater harvesting, cloud seeding, and desalination are already being used to produce pure water for drinking, agriculture, gardening, medical, industrial, and other purposes [2]. In some parts of Europe and the Middle East, desalination is the only tool for reclaiming fresh water. However, these methods are pricey, with a high operational cost. In the Namib Desert, Stenocara beetle harvest water directly from the fog, mist, and drops into its mouth. This beetle’s carapace has a combination of hydrophilic bumps and a hydrophobic surface that facilitate the water collection from fog [3]. When the fog droplet carried by wind meets the hydrophilic bumps, it captures the droplet and coalescence while hydrophobic surface drains the water directly to its mouth. Cribellate spiders use silks with spindle-knots and joints that provide wettability and curvature gradients to collect water from the atmosphere [4]. In the past decade, extensive research has been done on mimicking nature to develop a cleaner and efficient way for capturing atmospheric water in managing the pure water scarcity issue. For efficient fog harvesting, hydrophobicity, and hydrophilicity of the collector materials for fast water capturing, and easy drainage properties have a significant effect. Moreover, superhydrophobic surfaces have other advantages such as self-cleaning, stain-resisting, drag-reducing, and oil spillage separating [7-9].

Very few studies focused on the fabrication of permanent superhydrophobic nanocomposite fibers using nanotechnology. Almasian et al., 2018 fabricated the fluorinated super-hydrophobic PAN nanofibers for investigating their fog harvesting properties [10]. The synthesis process was optimized by varying the temperature, time, and the amount of fluoroamine compound. The synthesized PAN nanofibers have a water contact angle of 159° and low surface energy of 17.1 mN/m. Alarifi et al., 2015 fabricated multifunctional electrospun PAN fibers structural health monitoring and studied its thermal, electrical, and surface hydrophobic properties [11]. Their experimental results showed that the prepared PAN nanofibers have superior physical properties, and surface hydrophobic properties are in the superhydrophobic range. Qiao et al., 2014 prepared high capacity electrospun hybrid fibers are containing PAN and polystyrene for oil sorption [12]. They studied the influences of the processing parameters on the morphology, and oil sorption capacity of the prepared hybrid fibers. The maximum sorption capacities of the hybrid fibers for pump oil, peanut oil, diesel, and gasoline are 194.85, 131.7, 66.75, and 43.38 g/g, respectively. Yar and his co-workers analyzed the photocatalytic activity of electrospun PAN nanofiber, which was incorporated with TiO_2 nano and ZnO micro particles [13]. The fabricated fibers embedded with nanoparticles were exhibited excellent photocatalytic efficiency as compared with the PAN fibers only. This photo-catalytically active fibers could be used for filtering wastewater without the need for post-processing stages for separating catalysts from the liquid medium.

In this work, TiO_2 nano and Al microparticles were encapsulated with PAN and PMMA, and superhydrophobic nanocomposite fibers were synthesized. The fibers morphology, surface hydrophobicity, degree of crystallinity was investigated. These fibers find application including air, water, and oil filtration, fog harvesting, advanced composites, thermal insulators, battery and supercapacitor separators, and other infrastructures.

2.0 Experiment

2.1 Materials

PAN (molecular weight, Mw 150,000 g/mole) and PMMA (Mw 120,000, Tg 99.0°C) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Dimethylformamide (DMF) (99.8%) was purchased from Fisher Scientific. TiO_2 nano-powder of average particle size of 40nm (anatase, 99.5%) was purchased from US Research Nanomaterials Inc, TX, USA. Aluminum micro-particles (99.7%, 10µm) was also purchased from US Research Nanomaterials Inc., TX, U.S.A. All the materials used in this study were original without any modifications to the supplier specifications.

2.2 Electrospinning of PAN+PMMA Nanocomposite Fibers

The electrospun nanocomposite fiber was developed using electrospinning. Along with PAN and PMMA polymers, micro and nanoparticles of Al, and TiO_2 were respectively sonicated by a probe sonicator to produce a homogeneous composite. Different concentration of nanoparticles was added (0, 2.5, 5, and 10 wt%.). As shown in Figure 1 to prepare a homogeneous solution, PAN was dissolved in solvent dimethylformamide (DMF) with a ratio of 80:20 using a hot plate magnetic stirrer at 45 °C for 4 hours. Subsequently, the micro- and nano-particles of Al and TiO_2 were stirred on a hot plate and then followed by 20 minutes of probe sonication. The prepared nanocomposite was electrospun and then dried for 24 hours to developed fibers. The technical criteria for electrospun were developed in earlier articles and are as shown in Table 1. The developed fiber was then stabilized and carbonized at 250 °C and 850 °C respectively for an hour.

Table 1: Electrospinning parameters used in the present study.

Parameters	Conditions
Power source	25 kV DC
Size of a copper electrode to supply power to syringe	0.25mm
Feed rate	1 ml/hr
Distance to target	25 cm

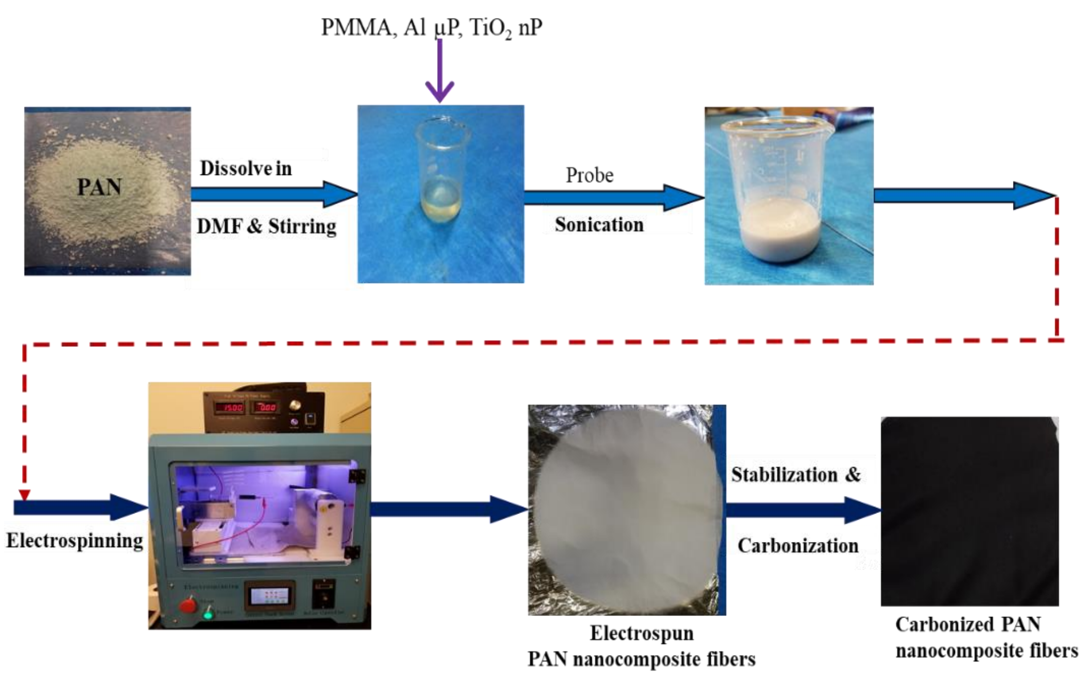

Figure 1: Illustration of the fabrication process of electrospun PAN nanocomposite fibers.

2.3. Characterization of Nanocomposite Fibers

The morphology of the prepared nanocomposite fibers was characterized by SEM device (FEI Nova Nano SEM 450). Using the SEM, several areas were imaged to inspect the uniformity of fibers and the diameters of the fibers were measured by image analysis software (ImageJ v 1.34). A Mitutoyo 178-561-02A Surftest SJ-210 Surface Roughness Tester was used to measure the roughness of the fibers. The surface chemistry and chemical interaction of the nanocomposite fibers were achieved by FTIR (Thermo Scientific™ Nicolet™ iN10 infrared microscope) over a range of 3500−500 cm^{-1}. The structural properties of the nanocomposite fibers were evaluated by the XRD. Cu Kα (λ = 0.15418 nm) radiation over the 2θ range of 10–70° was used for this analysis. A water contact angle goniometer (KSV Instruments Ltd., Model #CAM 100) was used to evaluate the water contact angle of the nanocomposite fibers.

3.0 Results and Discussion

3.1 Characteristics of Nanocomposite Fibers

Fiber roughness plays an important role to capture the fog. Fiber roughness studied for the developed fibers are discussed in Table 2. The results clearly indicate that PAN and PMMA composite fibers have less average roughness compared to PAN+PMMA with nano- and micro-particles. Also, the higher concentrations have the best average roughness in the fiber. It could be concluded by this observation is the surface roughness of the surface is strongly influenced by hydrophobicity of a material.

Table 2: Roughness values with the statistical information for the prepared nanocomposite fibers.

Nanocomposite Fibers	Average Roughness (Ra, µm)	Root Mean Square (Rq, µm)
PAN+PMMA	0.34±0.02	0.44±0.02
PAN+PMMA+2.5 wt%NP	0.49±0.03	0.67±0.04
PAN+PMMA+5 wt% NP	0.94±0.05	1.21±0.02
PAN+PMMA+10 wt% NP	1.77±0.04	2.33±0.05

The FTIR spectra of untreated PAN+PMMA fibers are shown in Figure 2. In the spectrum of untreated fiber, the absorption peaks of C-O groups were reflected at the vibrational stretch of 1130-1150 cm^{-1} and weaken gradually with the addition of Al micro particles and TiO_2 nanoparticles. Moreover, the band range of 1400-1450 cm^{-1} is related to -C-H group but not changed with the addition of Al micro and TiO_2 nanoparticles. The absorption peak at 1700-1720 cm^{-1} of C=O weaken gradually with the addition of Al micro and TiO_2 nanoparticles. After that, PAN+PMMA fibers were carbonized at 850°C for 1hr in an argon atmosphere, and then the FTIR analysis was performed on the samples (Figure 2b). The intensity bands at all peaks were disappeared compared to untreated PAN+PMMA fiber spectrum.

The carbonized nanocomposite fibers with various nanoparticles inclusion were tested using the XRD analysis method. For the carbonized samples, the peaks shifted up with 5 wt.% of the nanoparticles from 21.85º to 25.45º, which approaches the graphite peak position, and diffraction increased. This shows that the atoms of carbon were rearranged in order and improves the crystalline structure in the fiber. The structure parameters determined by XRD for carbonized PAN/PMMA nanocomposite fibers are summarized in

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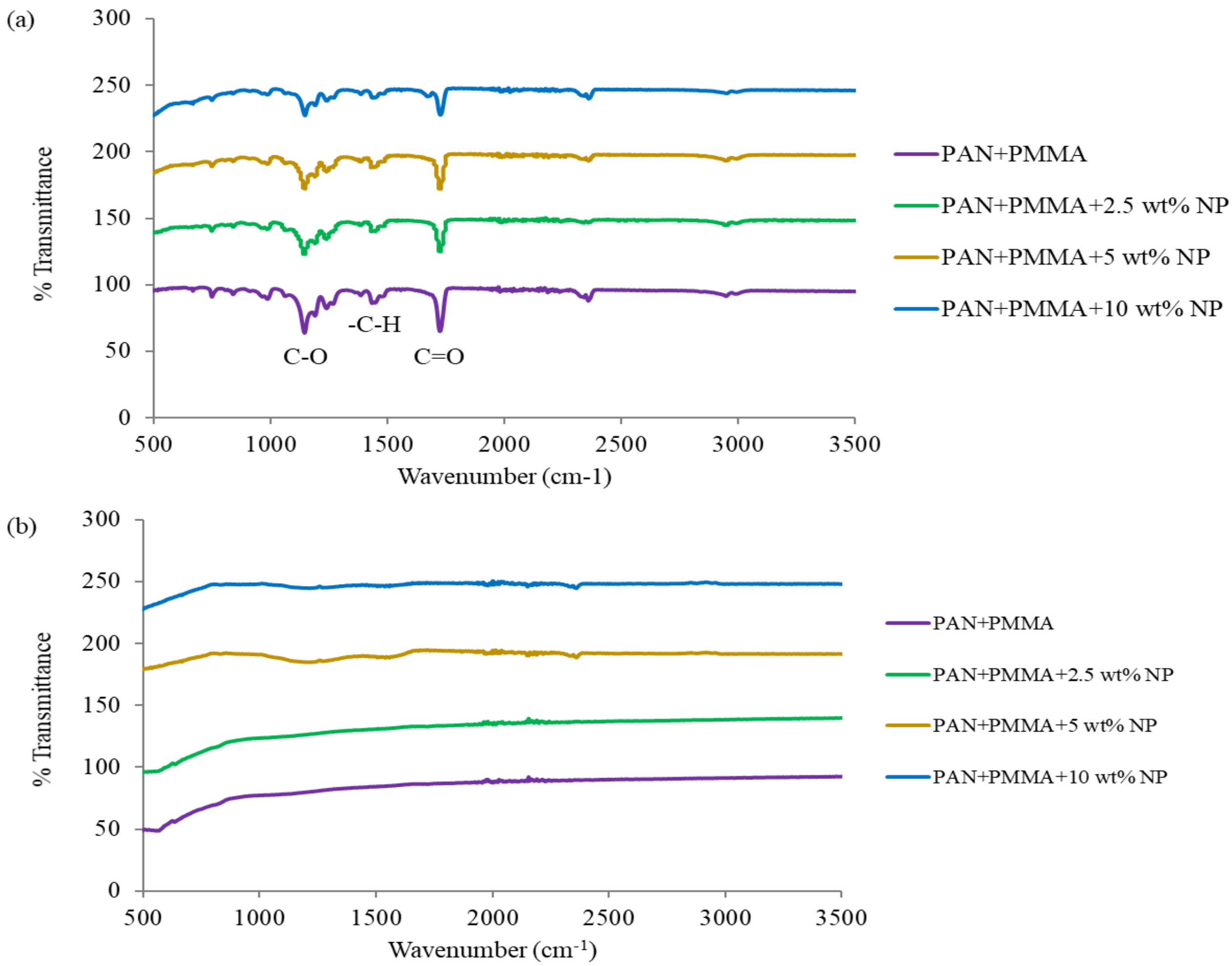

Figure 2: FTIR spectra of the nanocomposite fibers: (a) as prepared; and (b) after carbonization.

Table 3: Structure parameters of XRD for carbonized nanocomposite fibers with various nanoparticles inclusion.

Nanocomposite Fibers	$d_{(002)}$ (nm)	L_c (nm)	$L_c/d_{(002)}$
PAN+PMMA	0.35	1.01	0.027
PAN+PMMA+2.5 wt% NP	0.36	4.83	13.80
PAN+PMMA+5 wt% NP	0.35	7.46	21.31
PAN+PMMA+10 wt% NP	0.36	10.80	30.0

Figure 3 shows the SEM images of carbonized nanocomposite fibers. The nanocomposite fibers were prepared from the different concentration of nano and microparticles of Al and TiO_2 respectively along with PAN and PMMA via electrospinning to prepare uniform fibers suitable for fog harvesting Figure 3(a) shows uniform diameters with a porous surface, but the beading was not significant of the nanocomposite fiber of PAN and PMMA. Figure 3(b) shows the nanocomposite prepared with a 2.5 wt.% of Al and TiO_2 the beading and agglomeration were significant. Fibers with nanoparticles had a uniform diameter, and rough surface and beading were not significant. The solution properties such as viscosity, elasticity, conductivity, and surface tension greatly influence the transformation of polymer solution into nanofibers.

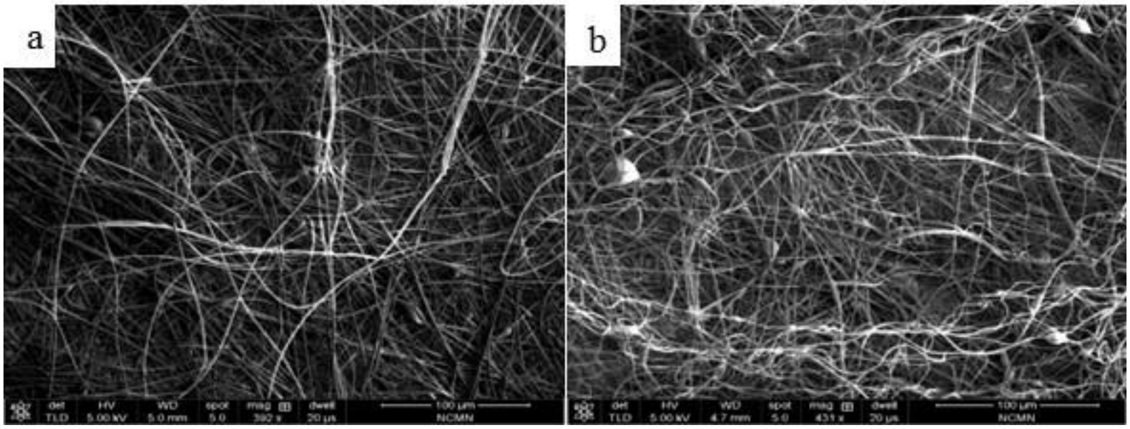

Figure 3: SEM image of electrospun PAN nanocomposite fibers: (a) PAN+PMMA, and (b) PAN+PMMA+2.5 wt % NP.

3.2 Hydrophobic Characteristics of Nanocomposite Fibers

The chemical structure, surface geometrical structure, and consistency stimulate the characteristics of hydrophobicity of a solid surface. The water contact angle of a surface measures the wettability of a material which could be hydrophilic (<90º), hydrophobic (> 90 º) or superhydrophobic (> 150º but < 180º). Due to the superhydrophobic nature of a surface, water droplets have less surface energy and that cause self-cleaning and anticontamination characteristics. [14-15]. The water contact angle of nanocomposites without and with carbonizing was about 130.86°and 154.8° respectively, as shown in Figure 4. So, the carbonized materials with 10wt% of nano- and micro-particles shows the superhydrophobic nature. Also, the composites were tested using 15 wt% of TiO_2 and Al particles, but due to the higher viscosity, it could not use for electrospinning process.

The PAN+PMMA nanocomposite fibers were stabilized at 280°C in an oxygen environment that form the ladder-like structure of PAN [16]. The stabilization process produces physically, chemically, and thermally stable nanocomposite fibers. Besides, during the stabilization process, the nanocomposite fibers are transformed from thermoplastic to thermosetting, reduction in diameters, and change color as well. Then the nanocomposite fibers were converted into carbon fibers by carbonizing at 850°C in an argon atmosphere. This process significantly modifies the morphology, surface chemistry, and structure of the fibers. During this process, PMMA is burned out, making porous fibers and other non-carbonaceous compounds are released and eliminate the polarity by releasing the radicals attached to the main chain of the nanocomposite fibers. The surface roughness, along with porosity, produces heterogeneous wetting state where the air is entrapped by water in the surface cavities [17]. Thereby reducing the contact area between the water and the solid surface while the contact area between water and air is increased. Therefore, the wettability of the solid surface is increased.

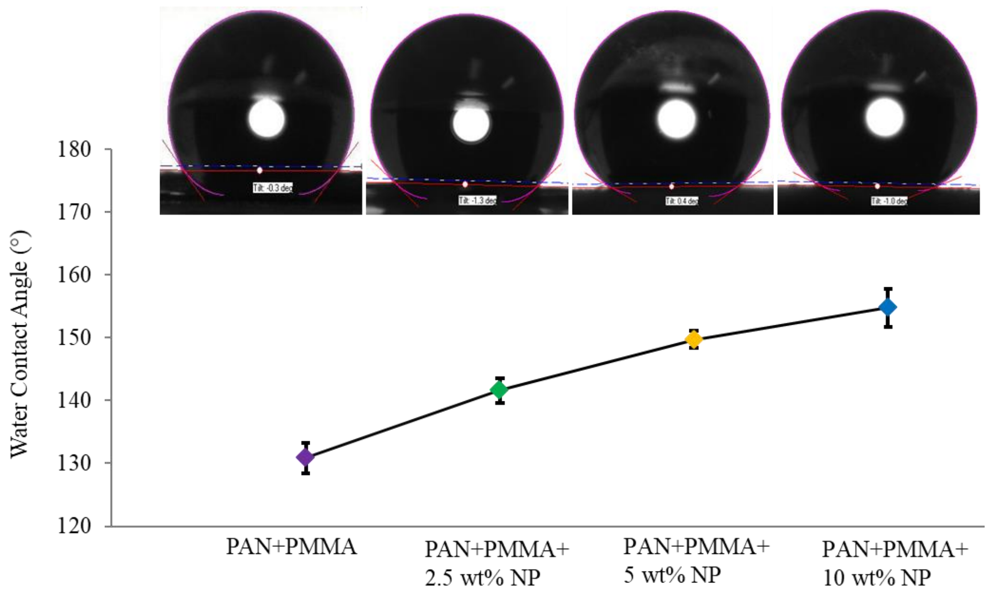

Figure 4: The water contact angle of carbonized electro-spun nanocomposite fibers with various nanoparticles inclusion.

3.3 Training of Engineering Students

Sustainability of engineering education will be the drawing force for the technological development not only in Midwest, but also in the U.S.A. Nanotechnology is one of the leading technology in number of different industries, including transpiration, energy, medicine, defense, electronics and other manufacturing industries, and this technology can address some of the major concerns in global water issues. Department of Mechanical Engineering at WSU has nearly 500 undergraduate and 120 graduate students, and a big portion of these students consider sustainability research projects on environmental issues. During this study, two WSU faculty members (Dr. Eylem Asmatulu and Dr. Andrew Swindle) guided one undergraduate student (Mr. Arvind Raj Murali) and two PhD students (Mr. Md. Nizam Uddin and Mr. Fenil Desai) from the Department of Mechanical Engineering to complete this project. In the present study, these students learned many new techniques and gained a lot of new experiences and knowledge about water, environmental issues, nanotechnology, nanofibers, superhydrophobicity and their properties. The undergraduate students involved in these activities used for the completion of their requirements (Engineer 2020) in the College of Engineering at WSU. The students involved in this study are also co-authors of the study and contributed a lot through the experiments, writing and presentation. It is believed that hands-on experiences on nanotechnology, sustainability and environment will significantly improve the knowledge of the engineering students to accomplish more detail studies in their future academic studies.

4. Conclusions

The permanent superhydrophobic electrospun nanocomposite fibers were fabricated via electrospinning followed by stabilization and carbonization process. The combination of TiO_2 nano and Al microparticles were included in the fibers to produce roughness. The surface roughness significantly alters the water contact angle along with morphology of the surface. The carbonized fibers with 10wt% nanoparticles inclusion exhibit a water contact angle of 154.8° that is in superhydrophobic range. The lower temperature stabilization and higher temperature carbonization process produce high-quality carbon fibers and enhance the surface wettability as well. The process parameters of the stabilization and carbonization process and the nature of precursor fibers influence the properties of the carbon fibers. The experimental results reveal that uniform diameter fibers were produced, and the addition of nanomaterials increase the degree of crystallization of the fibers. Overall the prepared nanofibers can be employed for diverse industrial applications, such as fog harvesting, filtration, transportation, energy, defense, and so on.

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References

1. K. Onda, J. LoBuglio, and J. Bartram, Global access to safe water: Accounting for water quality and the resulting impact on MDG Progress, Int J Environ Res Public Health, 9, 880–894 (2012).
2. M. N. Uddin, M. Alamir, H. Muppalla, M. M. Rahman and R. Asmatulu, Nanomembranes for Sustainable Fresh Water Production, International Conference on Mechanical, Industrial and Energy Engineering, December 23-24, Khulna, Bangladesh (2018).
3. A. R. Parker, C. R. Lawrence, Water capture by a desert beetle, Nature, 414, 33-34 (2001).
4. Y. M. Zheng, H. Bai, Z.B. Huang, X. L. Tian, F. Q. Nie, Y. Zhao, J. Zhai, L. Jiang, Directional water collection on wetted spider silk, Nature, 463, 640-643 (2010).
5. H. G. Andrews, E.A. Eccles, W.C. E. Schofield, J. P. S Badyal, Three-Dimensional Hierarchical Structures for Fog Harvesting, Langmuir, 27, 3798-3802 (2011)
6. J. Ju, H. Bai, Y. M. Zheng, T. Y. Zhao, R.C. Fang, L. A. Jiang, Multi-structural and multi-functional integrated fog collection system in cactus, Nat Commun, 3, 1247 (2012).
7. A. Khadak, M. N. Uddin, M.M. Rahman, and R. Asmatulu, Enhancing the De-icing Capabilities of Carbon Fiber-reinforced Composite Aircraft via Super-hydrophobic Coatings, The Composites and Advanced Materials Expo (CAMX), October 16-18, Dallas, TX, (2018).
8. M. Salahuddin, M. N. Uddin, G. Hwang, R. Asmatulu, Super hydrophobic PAN Nanofibers for Gas Diffusion Layers of Proton Exchange Membrane Fuel Cells for Cathodic Water Management, Int J Hydrogen Energy, 43(25), 11530-11538 (2018).
9. M.N Uddin, H.T.N. Gandy, M.M. Rahman, and R. Asmatulu, Adhesiveless Honeycomb Sandwich Structures of Pre-preg Carbon Fiber Composites for Primary Structural Applications. Advanced Composites and Hybrid Materials 2 (2), 339-350, 2019
10. A. Almasian, G. C. Fard, M. Mirjalili, M. P. Gashti, Fluorinated-PAN nanofibers: Preparation, optimization, characterization and fog harvesting property, J Ind Eng Chem, 62, 146–155 (2018).
11. I. M. Alarifi, A. Alharbi, W.S. Khan, A. Swindle and R. Asmatulu, Thermal, Electrical and Surface Hydrophobic Properties of Electrospun Polyacrylonitrile Nanofibers for Structural Health Monitoring, Materials 8, 7017–7031 (2015).
12. Y. Qiao, L. Zhao, P. Li, Haixiang Sun and Shuo Li, Electrospun polystyrene/polyacrylonitrile fiber with high oil sorption capacity, J Reinf Plast Comp, 33(20), 1-10 (2014).
13. A. Yar, B. Haspulat, T. Ustun, V. Eskizeybek, A. Avc, H. Kamıs¸ and S. Achour, Electrospun TiO2/ZnO/PAN hybrid nanofiber membranes with efficient photocatalytic activity, RSC Adv., 7, 29806–29814 (2017).
14. W.S. Khan, R. Asmatulu, S. Davuluri, V. K. Dandin, Improving the Economic Values of the Recycled Plastics Using Nanotechnology Associated Studies, J Mater Sci Technol, 30(9), 854-859. (2014).

15. S.S.A. Kumar, Uddin, Uddin, M. M. Rahman, and R. Asmatulu, Introducing Graphene Thin Films into Carbon Fiber Composite Structures for Lightning Strike Protection, Polym Compos, 40 (S1), E517-E525, (2019).
16. Ko, T.-H.; Day, T.-C.; Perng, J.-A.; Lin, M.-F. The characterization of pan-based carbon fibers developed by two-stage continuous carbonization. Carbon 1993, 31, 765–771.
17. I. Sas, R. E. Gorga, J. A. Joines and K. A. Thoney, Literature review on superhydrophobic self-cleaning surfaces produced by electrospinning, J. Polym. Sci., Part B: Polym. Phys., 50, 824–845 (2012).