

Carbon Nanofibers Containing Ag/TiO₂ Composites as a Preliminary Stage for CDI Technology

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Received November 2013

ABSTRACT

Silver/titanium dioxide composite nanoparticles imbedded in polyacrylonitrile (PAN) nanofibers and converted into carbon nanofibers by stabilization and calcination was obtained and tested for capacitive deionization technology. First, the silver ions were converted to metallic silver nanoparticles, through reduction of silver nitrate with dilute solution of PAN. Second, the TiO₂ precursor (Titanium Isopropoxide) was added to the solution to form Ag/TiO₂ composites imbedded in the PAN polymer solution. Last step involves electrospinning of viscous PAN solution containing silver/TiO₂ nanoparticles, thus obtaining PAN nanofibers containing silver/TiO₂ nanoparticles. Scanning electron microscopy (SEM) revealed that the diameter of the nanofibers ranged between 50 and 300 nm. Transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS) showed silver/TiO₂ nanoparticles dispersed on the surface of the carbon nanofibers. The obtained fiber was fully characterized by measuring and comparing the FTIR spectra and thermogravimetric analysis (TGA) diagrams of PAN nanofiber with and without imbedded nanoparticles, in order to show the effect of silver/TiO₂ nanoparticles on the electrospun fiber properties.

KEYWORDS

Polyacrylonitrile (PAN) Nanofibers; Carbon Nanofibers; Electrospinning; Silver/TiO₂ Nanoparticles

1. Introduction

Polyacrylonitrile (PAN) and preferably its copolymers are the most common precursors for the production of carbon nanofibers as well as activated carbon nanofibers and fabrics. They are established as the primary precursor used in commercial carbon fiber production. The production of Polyacrylonitrile based carbon nanofibers has grown significantly [1].

Adding metal nanoparticles to polymer nanofiber matrix (metal-polymer nanocomposites) has attracted a great attention due to synergic combinations of the unique optical, electrical, and catalytic properties of metal nanoparticles and excellent specific surface area of polymer nanofibers [2-9]. The incorporation of Ag and/or TiO₂ nanoparticles into polyacrylonitrile (PAN) fibers exhibits excellent catalytic activity, surface-enhanced Raman scattering activity, electrical conductivity, and antimicrobial activity [3,6,7]. D. Lee *et al.* [10] re-

ported that Silver (Ag) nanoparticles were prepared in polyacrylonitrile nanofibrous film by a sol-gel derived electrospinning and subsequent chemical reduction for 30 min in hydrazine hydroxide (N₂H₄OH) aqueous solution. The Ag/PAN nanocomposite film was characterized by XRD, TEM and UV absorption spectrophotometer. N. Pimpha *et al.* [11] reported that Titanium dioxide nanofibers were fabricated by electrospinning technique. The titania solutions were obtained from adding various types of Ti precursor (Ti (OⁱBu)₄, Ti (OⁱPr)₄, and Ti(OPr)₄ to an ethanol solution containing polyvinyl pyrrolidone (PVP). A photocatalytic activity testing shows that the electrospun nanofibers had stronger efficiency to remove NO_x. J. Bai *et al.* [12] reported a novel composite nanofibers consisting of Ag nanoparticles and polyacrylonitrile (PAN) were fabricated successfully and we treated at low temperatures. T. Amna *et al.* [13] reported a biological evaluation of antimicrobial activity using Zn-doped titania nanofibers, which prepared by the electrospinning of a sol-gel. The bacterial cells following the treatment with

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nanofibers solutions. M. A. Kanjwal *et al.* [14] investigated the influence of the silver content and the morphology of nanofibers on the photocatalytic activity of silver-grafted titanium dioxide. Titanium dioxide containing different weight percentages of silver was prepared in nanofibrous and nanoparticulate forms. Silver-grafted titanium dioxide nanofibers were synthesized by the electro spinning process. The prepared nanostructures were utilized as a photocatalyst to degrade two dyes. The obtained results endorse the use of this composite in a nanofibrous form. Y. Li *et al.* reported a Ag-TiO₂ nanoparticles were prepared by a miniemulsion method using Ti(OBu)₄ and Ag(NO₃) as starting materials. The results show that Ag doping showed a controlling effect on the transformation of titania from anatase to rutile. The specific surface area increased with the Ag-doped amount to reach a maximum (86.3 m²·g⁻¹) at Ag/Ti molar ratio of 0.8% and then decreased with further increase of the Ag-doped amount. The applications of nanoparticulate in waste water treatment, for example; Ag (I) and silver compounds have been used as antimicrobial compounds for coliform found in waste water. Nanoscale silver particles are typically 1 - 40 nanometers (nm) with an average particle size of 2 - 10 micron range with a specific surface area of approximately 1 m²·g⁻¹. Applications for silver nanocrystals include as an anti-microbial, antibiotic and anti-fungal agent when incorporated in coatings, nanofibers, first aid bandages, plastics, soap and textiles, in treatment of certain viruses, in self cleaning fabrics, as conductive filler and in nanowire and certain catalyst applications. It has been reported that Ag nanoparticles were active biocides against Gram-positive Gram-negative bacteria [15]. H. Bai *et al.* [16] reported a novel kind of multifunctional membrane was fabricated via integrating the advantages of conventional polymer membrane as supporting layer like hierarchically structured TiO₂/ZnO nanomaterial as functional layer. This novel membrane possesses the common advantages of polymer membrane and multifunctional properties of the hierarchical TiO₂ nanofibers/ZnO nanorod materials, which demonstrated to be able to produce clean water at a constant high flux with no membrane fouling problem and energy saving manner.

In this paper, polyacrylonitrile solution containing Ag/TiO₂ was directly electrospun to obtain nanofibers films containing Ag Ag/TiO₂, and the Ag/TiO₂ of rsuling composite nanofibers were reduced to Ag/TiO₂ nnoparticles. Then, we treated PAN/Ag/TiO₂ composite nanofibers at different temperatures. The PAN/ Ag/TiO₂ nanocomposite film was characterized by scanning eletron microscopy (SEM), X-ray diffraction (XRD) patterns and surface-enhanced Raman scattering (SERS) spectroscopy.

2. Experimental Work

PANNF film was prepared by electrospinning. PAN (7 wt.%) was dissolved in DMF, and stirred until homogenous at room temperature. 0.03 gm AgNO₃ was dissolved in 70 ml DMF with stirring at 30 min (UV/vis spectrometer used to obtain the optimum weight percentage and the time of reduction for AgNO₃), then 0.01 gm of polyethylene glycol was added as stabilizer and reduction agent. This solution was stirred for 30 min before analyze using UV spectra. 0.5 ml of acetic acid and 2 ml of titanium is opropoxide were added into 20 ml DMF. The solution was stirred for 15 min, then 5 wt% PAN was added to the solution. The two solutions were mixed together by adding the first (TIP/PAN) to the second one (Ag/PAN) gradually with continuous stirring until homogenous. The solution containing silver and titanium isopropoxide salt with PAN were stirred for 24 h at room temperature. After that, the solution obtained was added into a plastic syringe, the internal diameter of plastic was 20 cm, the pinhead was connected to a (20-kV) high-voltage, and aluminum foil served as counter electrode. TCD was (21 cm), the feed rate of the solution was adjusted to (0.1 ml/h) through a syringe pump. The electrospinning was performed at room temperature. The nanofibers were stabilized in an air atmosphere at 270°C for 2 h (at a heating rate of 2°C/min) and followed by carbonization at 1000°C for 1 h (at a heating rate of 4.5°C/min) under an inert nitrogen atmosphere to yield carbonized. The resulting carbon nanofibres were cooled down to room temperature in an inert gas atmosphere before they were taken out of the furnace. Full-stained ultra-thin sections were examined using the field emission transmission electron microscope (JEOL-JEM-2100F, Japan). Thermal properties of electrospinning nanofibers were examined using thermogravimetric analysis (TGA) carried on TA-Q500 System of TA; samples of 5 - 10 mg were heated in the temperature range 30°C - 800°C at a scanning rate of 10°C·min⁻¹ under nitrogen atmosphere, and by using TG-DTA: NETZSCH Germany(Model: STA 449 F3). The bonding configurations of the samples of carbon nanofibers were recorded by Fourier-transformer infrared (FT-IR) Spectra using TENSOR 27. Tube furnace (Model: T2F-16/610, carbolite-England) was used in treatment nanofibers to convert them into carbon nanofibers. Thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of sample and reference is measured as a function of temperature. (DSC Q 20-TA National scientific company USA). Counter ions are stored in the electrical double layers which form at the solution interface inside the porous electrodes, with the ions of cations stored in the negatively charged electrode, and anions stored in the positively charged electrode (anode). Plimmer test unit.

3. Results and Discussions

Titanium dioxide (TiO_2) has been the focus of numerous studies in recent years, because of its photocatalytic effects which decompose organic chemicals and kill bacteria [17]. Most of the work carried out focused on the use of TiO_2 powders suspended in the water as a catalyst [18]. It has been applied to a variety of environmental problems in addition to water and air purification [19]. Polymers are a common material used in the fabrication of the membranes. However, it is readily contaminated by proteins and other impurities during water and wastewater treatment, which leads to a sharp drop in the membrane flux [20]. Chemical modification methods could be employed to improve the hydrophilicity of the membrane, but the main chain of polymer molecule would be changed and the advantages of the polymer membrane may be decreased [21,22]. Usually, physical modification method such as mixing was used, and the mixture materials were macromolecules [23-25]. When TiO_2 nanoparticles are dispersed in the polymer membranes, the addition of nanoparticles not only improves the hydrophilicity of polymer membranes but also mitigates the biofouling problem of polymer membrane and membrane bioreactor (MBR) systems [26,27] and the microbial biofouling of RO membranes [28]. In addition, the TiO_2 /polymer membrane could significantly increase the de-

gradation rate of the phenyl urea herbicide known as isoproturon.

One-dimensional (1D) Ag/TiO_2 -carbon composite nanofibers were fabricated via electrospinning of a homogenous mixture of PAN and AgNO_3 /TIP salt precursors at different ratios followed by heat treatments. The 1D nanostructures of the composite material were characterized by field-emission scanning electron microscopy (FE-SEM), powder X-ray diffraction (XRD). **Figure 1** shows the SEM image of the PAN/ Ag/TiO_2 nanofibers web prepared by the electrospinning method in the form of the thin mat. It is seen that the fibers are dispersed randomly but densely covering the whole substrate face. The diameters of the PAN/ Ag/TiO_2 nanofiber diameters lie in the region between 200 and 500 nm. Surprisingly, the PAN/ Ag/TiO_2 web embodied a relatively high degree of adhesion to the substrate. The optimized annealing ramp carried out under nitrogen atmosphere yielded transformation of PAN/ Ag/TiO_2 nanofibers to the desired carbon Ag/TiO_2 nanofibrous form without losing their web structure.

The energy dispersive spectrum (EDS) collected on the PAN/ Ag/TiO_2 NPs sample (whose microstructure is illustrated in **Figure 1** distinctly identifies Ag, Ti as the elemental component in the fiber and is shown in **Figure 2**. The other peaks belonging to carbon are generated from the PAN. Elementary analysis of PAN / Ag/TiO_2

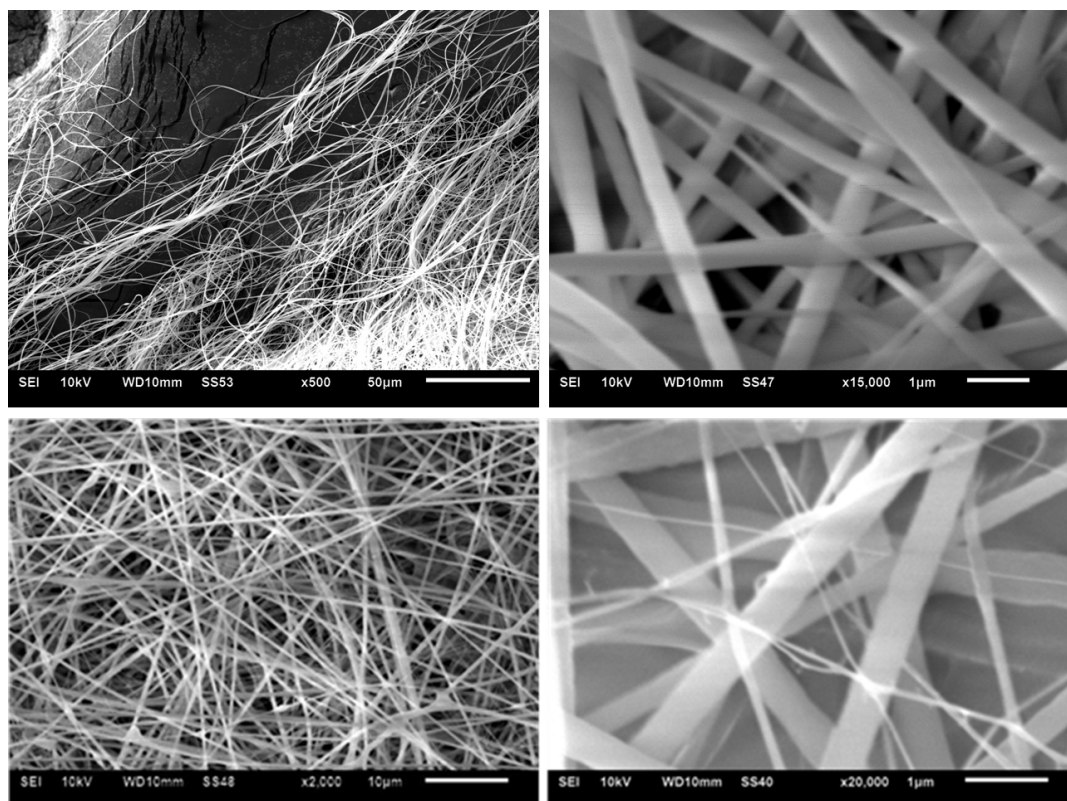


Figure 1. SEM image 0.02 gm of AgNO_3 with 1ml TIP/PAN Nanofibers.

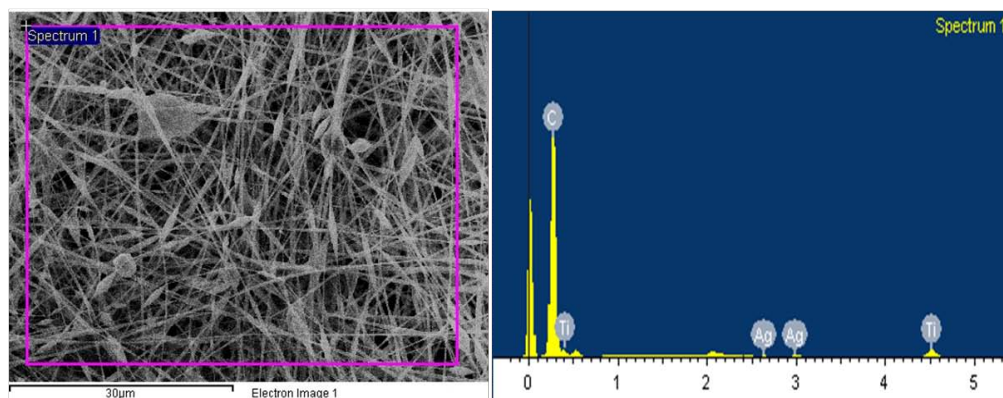


Figure 2. EDS analysis of nanofibers confirms the presence of Ti and Ag in PAN matrix.

NPs nanocomposite was carried out by using SEM-EDS. The results show that carbon and Ag/TiO₂ were the principal element of PAN/Ag/TiO₂ NPs nanocomposite. EDS analysis thus provides direct evidence that Ag/TiO₂ ions embedded in the PAN/ silver/TiO₂ nanocomposite. It is indicated that silver/TiO₂ nanoparticles were well loaded without any chemical and structural modifications into PAN polymer matrix to form an organic-inorganic nanocomposite. The energy dispersive spectrum (EDS) collected on the PAN/Ag/TiO₂ NPs sample distinctly identifies Ag/TiO₂ as the elemental component in the fiber and is shown in **Figure 3**. The other peaks belonging to carbon are generated from the PAN. Elementary analysis of PAN/Ag/TiO₂ NPs nanocomposite was carried out by using SEM-EDS. The results show that Ag and TiO₂ were the principal element of PAN/Ag/TiO₂ NPs nanocomposite. EDS analysis thus provides direct evidence that Ag and TiO₂ ions embedded in the PAN/Ag/TiO₂ nanocomposite. It is indicated that silver and TiO₂ nanoparticles were well loaded without any chemical and structural modifications into PAN polymer matrix to form an organic-inorganic nanocomposite. **Figure 4** shows the X-ray diffraction pattern of a bundle of PAN/Ag/TiO₂ electrospun nanofibers. The nanofibers exhibited two equatorial peaks with a diffuse meridian peak and four sharp peaks. The primary equatorial (1010) peak at $2\theta = 16.88^\circ$ corresponds to a spacing of $d = 5.25 \text{ \AA}$ while the weaker reflection (1120) at $2\theta = 29.5^\circ$ corresponds to a spacing of $d = 3.05 \text{ \AA}$ (note Miller indices (hkl) are used for identification of planes in hexagonal crystals). The TiO₂ peaks were observed at $2\theta = 38^\circ, 45^\circ, 65^\circ, 78^\circ$ as shown in the XRD in **Figure 4**.

Generally PAN begins to degrade when heated near its melting point. The degradation reaction of PAN is so exothermic that it tends to obscure its melting endotherm in ordinary DSC traces. Therefore, the melting endotherm is normally not observed in PAN. In this study, DSC and DTA were conducted in N₂ atmosphere as shown in **Figure 5**.

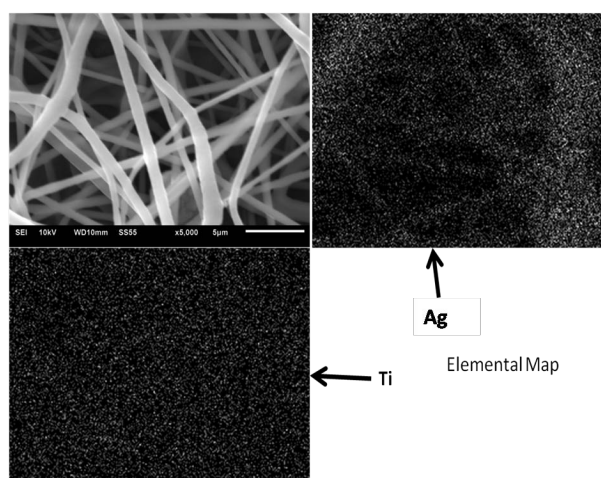


Figure 3. EDS analysis mapping of nanofiber confirms the presence Ti vs C in PAN matrix.

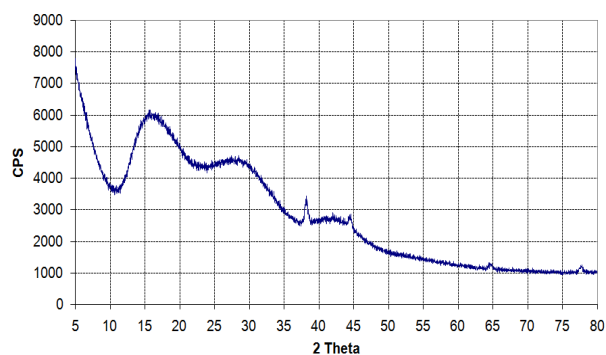


Figure 4. XRD of PAN/Ag/TiO₂ nanofibers.

TEM analysis is used to investigate the crystal structure. **Figure 6** shows the TEM of the obtained Ag/TiO₂ doped nanofibers. As shown in these figures, there are some black dots in both formulations which can be considered as the TiO₂ nanoparticles as these dots have different crystal structures compared to the carbon matrices. Both formulations have good crystallinity as shown in **Figure 6**.

The SEM images of PAN/TiO₂ electrospun nanofibers after stabilization at 270°C for 2 h in air share similar characters of smooth and uniform surfaces with occasional bead-like structures indicating the presence of attached metal oxides (**Figure 7**). There is no significant difference in the diameters of nanofibers with the previous nanofibers. As could be seen, the long duration and high temperature of the stabilization process spoil the fiber morphology.

The stabilized PAN/ TiO₂/Ag nanofiber was subsequently carbonized at a relatively low temperature of 1000°C in an inert (high purity nitrogen gas) environment with the heating rate set at 4.5°C/min as shown in **Figures 8**. All of the carbonized PAN nanofiber bundles were held at the respective final temperatures for 1.5 h to allow the carbonization to complete. The average diameters of the 1000°C carbonized PAN nanofibers were reduced to 250 nm and 220 nm, respectively. During car-

bonization, a variety of gases (e.g., H₂O, N₂, HCN, and others) were evolved and the carbon content increased to 90 wt.% or higher; the process therefore led to the reduction of fiber diameter and the formation of three-dimensional carbonaceous structures.

4. Conclusion

The results showed that, electrically conducting carbon nanofiber (CNF) mats were produced by using polyacrylonitrile (PAN) via electrospinning. The CNF showed high capacitance and energy/power density values due to the formation of ultra-micropores and the introduction of high surface area. Furthermore, this project reports on research conducted on Capacitive Deionization as an alternative to the more conventional membrane desalination technologies like reverse osmosis and electrodialysis. The simultaneous one-pot synthesis of PAN/Ag/TiO₂

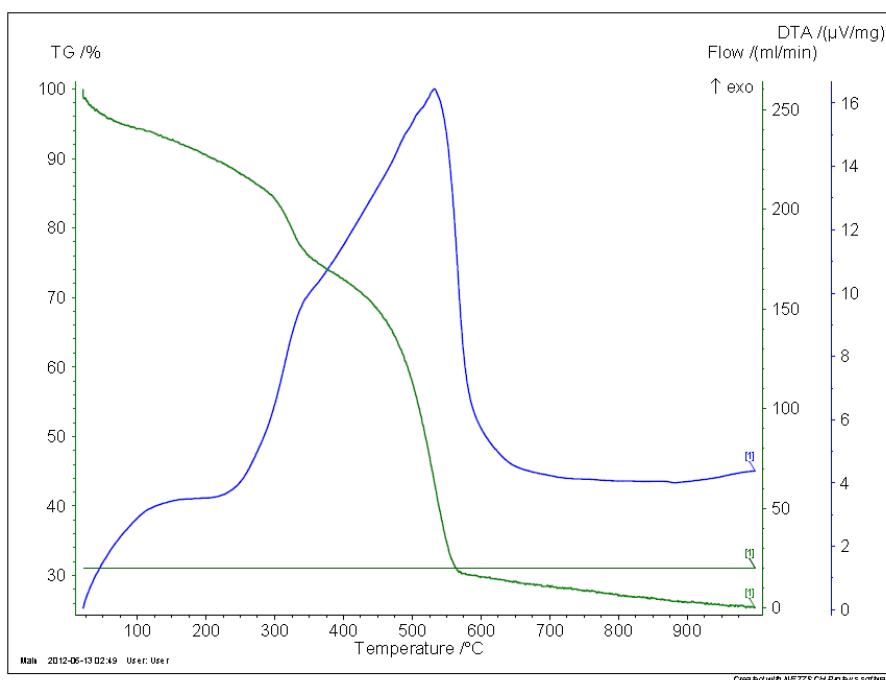


Figure 5. DSC of Ag/TiO₂ composite PAN nanofibers.

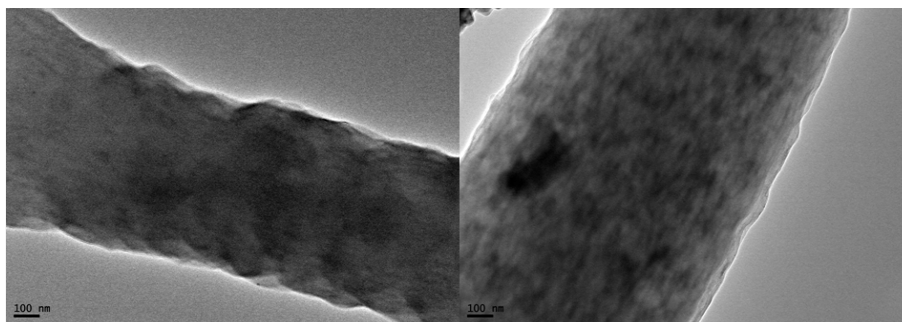


Figure 6. TEM results for Ti/PAN nanofibers.

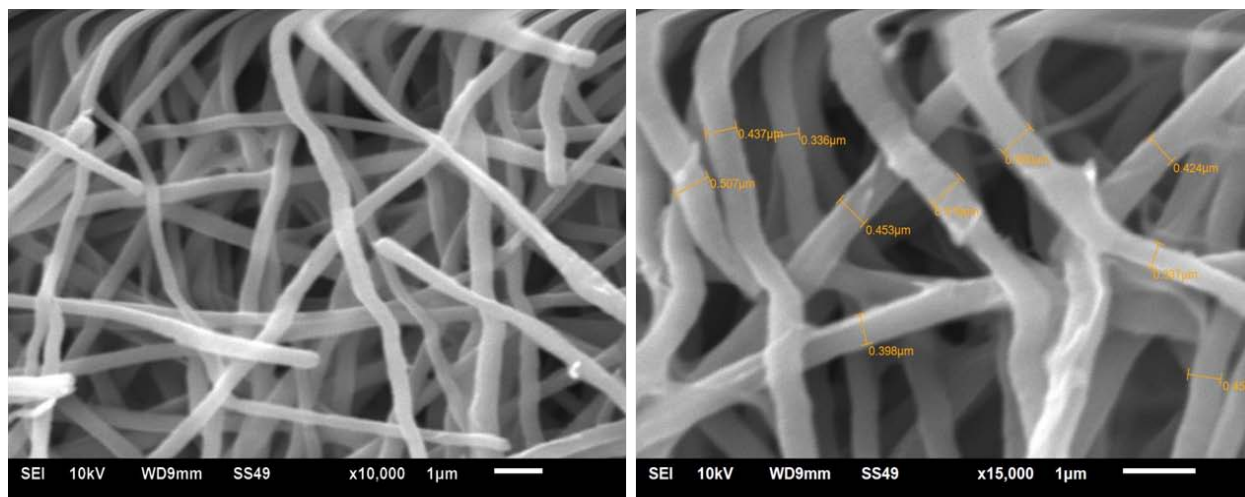


Figure 7. SEM image stabilizations of PAN/Ag/TiO₂ Nanofibers at 270 °C.

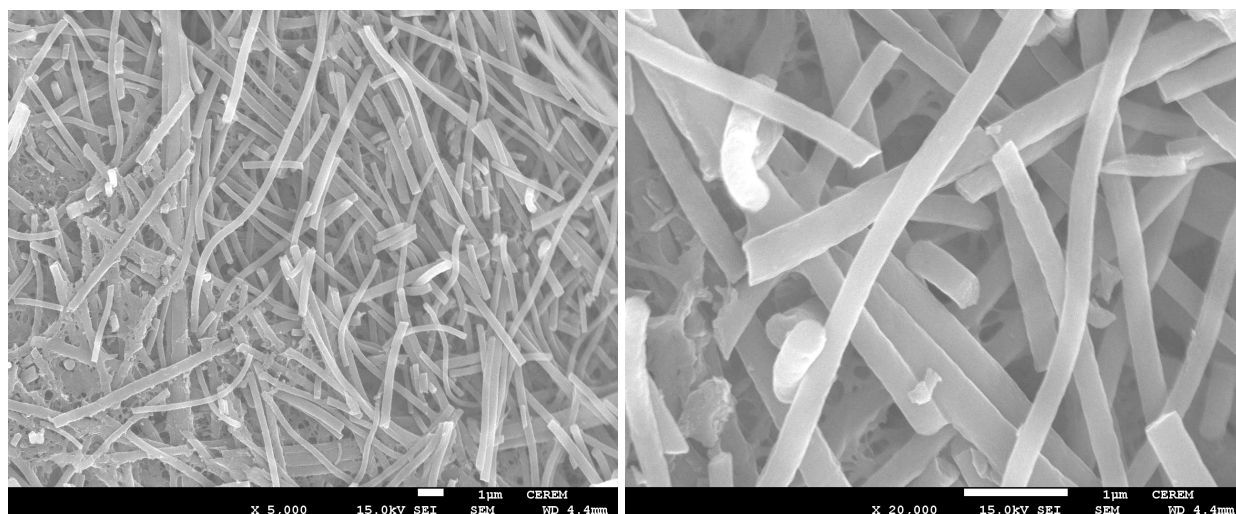


Figure 8. SEM image carbonization of PAN/Ag/TiO₂ Nanofibers at 1000 °C.

composites has several advantages in terms of controlling particle size and fiber diameter. In addition, the FTIR spectroscopy, thermal gravimetry analysis (TGA) proved the presence of silver and titanium dioxide nanoparticles in the PAN fiber. The SEM micrographs clarified that there are random orientation for nanofiber. N,N Dimethylformamide (DMF) was used as both the solvent for PAN and reducing agent for Ag ions. Furthermore, this project reports on research conducted on Capacitive Deionization as an alternative to the more conventional membrane desalination technologies like reverse osmosis and electrodialysis.

Acknowledgements

This work was financially supported by the National Plan for Science & Technology (NPST), King Saud University Project No. 11-NAN1460-02.

REFERENCES

- [1] T. Yuanjian, W. Xiaoqian, S. Hua and X. Lianghua, *Corrosion Science*, Vol. 53, 2011, pp. 2484-2488. <http://dx.doi.org/10.1016/j.corsci.2011.04.004>
- [2] D. Y. Lee, K.-H. Lee, B.-Y. Kim and N.-I. Cho, *Journal of Sol-Gel Science and Technology*, Vol. 54, 2010, pp. 63-68. <http://dx.doi.org/10.1007/s10971-010-2158-0>
- [3] C. Q. Zhang, Q. B. Yang, N. Q. Zhan, L. Sun, H. G. Wang, Y. Song and Y. X. Li, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, Vol. 362, 2010, pp. 58-64. <http://dx.doi.org/10.1016/j.colsurfa.2010.03.038>
- [4] Y. Z. Wang, Q. B. Yang, G. Y. Shan, C. Wang, J. S. Du, S. G. Wang, Y. X. Li, X. S. Chen, X. B. Jing and Y. Wei, *Materials Letters*, Vol. 59, 2005, pp. 3046-3049.
- [5] P. Rujitanaroj, N. Pimpha and P. Supaphol, Wiley Inter-Science, 2010. <http://dx.doi.org/10.1002/app.31498>
- [6] L. Francis, F. Giunco, A. Balakrishnan, E. Marsano, Syn-

- thesis, *Current Applied Physics*, Vol. 10, 2010, pp. 1005-1008. <http://dx.doi.org/10.1016/j.cap.2009.12.025>
- [7] J. Bai, Q. B. Yang, S. Wang and Y. X. Li, *Korean Journal of Chemical Engineering*, Vol. 28, No. 8, 2011, pp. 1761-1763. <http://dx.doi.org/10.1007/s11814-011-0006-8>
- [8] H. H. Chae, B.-H. Kim, K. S. Yang and J. I. Rhee, *Synthetic Metals*, Vol. 161, 2011, pp. 2124-2128.
- [9] P. Jain and T. Pradeep, Wiley InterScience, 2011. <http://dx.doi.org/10.1002/bit.20368>
- [10] D. Lee, K. Lee, B. Kim and N. Cho, *Journal of Sol-Gel Science and Technology*, Vol. 54, 2010, pp. 63-68. <http://dx.doi.org/10.1007/s10971-010-2158-0>
- [11] K. Juengsuwattananon, P. Rujitanaroj, P. Supaphol, N. Pimpha and S. Matsuzawa, *Materials Science*, Vol. 569, 2008, pp. 25-28.
- [12] J. Bai, Q. Yang, S. Wang and Y. Li, *Korean Journal of Chemical Engineering*, Vol. 28, No. 8, 2011, pp. 1761-1763.
- [13] T. Amna, M. Hassan, N. Barakat, D. Pandeya, S. Hong, M. Khil and H. Kim, *Applied Microbiology and Biotechnology*, Vol. 93, 2012, pp. 743-751. <http://dx.doi.org/10.1007/s00253-011-3459-0>
- [14] M. Kanjwal, N. Barakat, F. Sheikh, W. Baek, M. Khil, and H. Kim, *Fibers and Polymers*, Vol. 11, No. 5, 2010, pp. 700-709. <http://dx.doi.org/10.1007/s12221-010-0700-x>
- [15] D. Tiwari, J. Behari and P. Sen, *World Applied Sciences Journal*, Vol. 3, No. 3, 2008, pp. 417-433.
- [16] H. Bai, Z. Liu and D. Sun, *Applied Catalysis B: Environmental*, 2012, pp. 571-577. <http://dx.doi.org/10.1016/j.apcatb.2011.11.009>
- [17] T. Matsunaga, R. Tomoda, T. Nakajima, N. Nakamura and T. Komine, *Applied and Environmental Microbiology*, Vol. 54, 1988, p. 1330.
- [18] M. R. Hoffmann, S. T. Martin, W. Choi and D. W. Bahnemann, *Chemical Reviews*, Vol. 95, 1995, p. 69. <http://dx.doi.org/10.1021/cr00033a004>
- [19] K. Jian, P. N. Pintauro and R. Ponangi, *Journal of Membrane Science*, Vol. 117, 1996, p. 117. [http://dx.doi.org/10.1016/0376-7388\(96\)00065-8](http://dx.doi.org/10.1016/0376-7388(96)00065-8)
- [20] A. Bottino, G. Capannelli and S. Munari, *Journal of Applied Polymer Science*, Vol. 30, 1985, p. 3009. <http://dx.doi.org/10.1002/app.1985.070300723>
- [21] Z. Xu, L. Li, F. Wu, S. Tan and Z. Zhang, *Journal of Membrane Science*, Vol. 255, 2005, p. 125. <http://dx.doi.org/10.1016/j.memsci.2005.02.001>
- [22] A. Bottino, G. Capannelli, V. D'Asti and P. Piaggio, *Separation and Purification Technology*, Vol. 22-23, 2001, p. 269. [http://dx.doi.org/10.1016/S1383-5866\(00\)00127-1](http://dx.doi.org/10.1016/S1383-5866(00)00127-1)
- [23] A. Bottino, G. Capannelli, O. Monticelli and P. Piaggio, *Journal of Membrane Science*, Vol. 166, 2000, p. 23. [http://dx.doi.org/10.1016/S0376-7388\(99\)00253-7](http://dx.doi.org/10.1016/S0376-7388(99)00253-7)
- [24] J. F. Hester, S. C. Olugebefola and A. M. Mayes, *Journal of Membrane Science*, Vol. 208, 2002, p. 375. [http://dx.doi.org/10.1016/S0376-7388\(02\)00317-4](http://dx.doi.org/10.1016/S0376-7388(02)00317-4)
- [25] T. H. Bae and T. M. Tak, *Journal of Membrane Science*, Vol. 249, 2005, p. 1. <http://dx.doi.org/10.1016/j.memsci.2004.09.008>
- [26] S. H. Kim, S. Y. Kwak, B. H. Sohn and T. H. Park, *Journal of Membrane Science*, Vol. 211, 2003, p. 157. [http://dx.doi.org/10.1016/S0376-7388\(02\)00418-0](http://dx.doi.org/10.1016/S0376-7388(02)00418-0)
- [27] J. Li, Y. Liang, H. Wang, X. Sun and L. Wang, *Acta Polymerica Sinica*, 2004, p. 709.
- [28] S. Megelski, J. S. Stephens, D. B. Chase and J. F. Rabolt, *Macromolecules*, Vol. 35, 2002, pp. 8456-8466. <http://dx.doi.org/10.1021/ma020444a>