International Journal of Applied Engineering Research ISSN 0973-4562 Volume 13, Number 14 (2018) pp. 11680-11685

Optimization of Nylon Nanowires/Graphene Composite Process by Surface Response Methodology Approach

Coba-Daza. Sebastian[a], Hernández-Bautista Katherine[a], Pataquiva-Mateus Alis[a*], Pazos. Jhon[b], Hurtado-Morales, Mikel[b,c,d*]

[a] *Nanotechnology Laboratory, Universidad de Bogotá Jorge Tadeo Lozano,*
[b] *Research Cluster NBIC, Universidad Central,*
[c] *Electronic Engineering Department, Universidad Central, Bogotá, Colombia.*
[d] *Civil Engineering Department, Universidad Minuto de Dios, Bogotá, Colombia.*

Abstract

This work shows electrospinning and electrochemical exfoliation techniques to produce nylon nanowires/graphene composite seeking an optimization process. SEM, AFM, XRD, and UV blocking analyses and techniques were performed for raw and composite materials. Experimental design optimization parameters were carried out to obtain graphene and nylon nanowires: some of those parameters were polarization potential around 11.45 V using $(NH_4)_2SO_4$ 0.68 M, electric field of 2.39 kV/cm and pumping rate of 2.30 mL/h to produce nylon-based nanofibers by electrospinning process. The final composite exhibit significantly UV radiation blocking properties to be consider in the use of smart textile and IoT applications.

Keywords: Graphene, Electrospinning, Nanowires, Electrochemical Exfoliation.

INTRODUCTION

Graphene is a material that consists of a two-dimensional (2D) sheet of three covalently bonded carbon atoms in a sp^2 hybridization resulting in a hexagonal lattice [1]. Graphene properties are highly attractive because of their performance in different fields [2-5].

There are different ways to synthesized graphene [5-10]. Electrochemical exfoliation is advisable for the mass production of graphene and has advantages like less energy consumption and open atmosphere processing [11]. The electrochemical exfoliation based on $(NH_4)_2SO_4$, an environmental friendly reagents, is low cost and easily-made synthesis to produce graphene [9-12]. In this work was used an optimization model like Central Composite Design (CCD) to find optimal variables values. When graphene is added to a polymeric matrix, a lot of properties might be increased, and the possible applications are even more than pristine graphene [13-14].

There are different ways to fabricate polymer/graphene composite material as solvent processing; melt mixing, in situ polymerization, and spraying [13]. The solvent processing method includes electrospinning technique, which is possible to produce nanometric materials using the electrical forces between polymer surface and the collector, causing an electrically charged cone to be ejected in wire form [15-21]. Nanocomposite materials fabrication via electrospinning process is fast and applied to wide range of applications [21-22]. In this work, nylon nanowires/graphene composite was investigated and optimized showing interesting properties to be used in smart textile sector.

MATERIALS AND METHODOLOGY

Graphene synthesis

Graphene was synthetized from electrochemical exfoliation method using pencil-graphite mines in $(NH_4)_2SO_4$ solution based on [23-24]; this method use graphite electrodes in an electrochemical cell and voltage provided by experimental design (ED) in terms of yield percent. Were used voltages between 8-12 V and $(NH_4)_2SO_4$ concentrations between 0.1-1.0 M as coded factors. Reaction products were centrifuged at 4000 rpm during 45 min, and the precipitated was dried at 200 °C.

Electrospinning process

Commercial nylon number 6 was dissolved into formic acid (10 % w/v) at 18.0°C. Polymeric solution of nylon was placed into a syringe of 20 mL with a diameter needle of 2 mm, with positive electrode (needle) while negative electrode (collector aluminium foil). Voltage conditions, flow and collector-needle distance were used to carry out an optimization process by surface response methodology, which had average diameter as a response. Table 1 shows coded and current values used in ED.

Table 1. Values of the central composite experimental design for nanowires production.

Factor	Coded Factor		
	-1	0	1
Voltage (kV)	27	28	29
Flow (mL/h)	1	2	3
Collector needle distance (cm)	9	11	13

The graphene produced using optimal conditions was added to a nylon solution in formic acid (1% w/v). The mixture was placed in a 20 mL syringe which is attached to electrospinning equipment and optimal conditions given by the response surface were adjusted to produce nylon nanowires/graphene composite.

Response surface methodology

Response surface methodology was used to analyse both experimental designs which are the fabrication of graphene and nylon nanowires production; then, central composite design of experiments (CCD) was used by the aid of Design Expert software (version 6.0.8, StatEase Inc., Minneapolis, MN, USA). Second order model was adjusted for the experimental data for both process, and the reliability of the models were verified by determination coefficient (R^2) and ANOVA analysis. Finally, graphene production model was maximized to find optimal value that gives a higher percent of yield in the range of evaluated conditions.

Nylon nanowires and nylon nanowires/graphene composite were studied using a scanning electron microscope (JEOL JSM-6490LV) images. An AFM equipment (Asylum Research, MFP-3D) in tapping mode was used to imaging and analysing the composites. X-Ray diffraction were obtained using PANalytical X'Pert PRO MPD with Cu Kα (λ=1.54056 Å) for the different studied materials.

To perform the antibiogram, 10 g of TSA agar was dissolved in 250 mL of distillate water. Liquid culture of *Micrococcus luteus* was used in the study. 100 µL of culture was inoculated in a petri dish with TSA. Three samples of 1 cm^2 were put in the petri plate whit the culture and finally, all were inoculated at 30°C for 24 h. UV–visible spectrometer (Thermo Scientific, Evolution 300) was used to investigate the blocking ability of UV rays in the composites.

RESULTS AND DISCUSSION

Optimization of graphene production and parameters effect

Surface response methodology and central composed design (Figure 1 (a)) were used to investigate the effect of variables voltage and concentration of $(NH_4)_2SO_4$ solution in graphene production by electrochemical exfoliation process.

$$Y(\%) = -566.89 + 111.31\, x_1 + 52.74\, x_2 - 4.98\, x^2_1 - 36.23\, x^2_2 - 0.82\, x_1 x_2 \quad (1)$$

Equation 1 represents a second order polynomial model that correlates voltage x_1 (V) and concentration x_2 [M] with yield Y(%).

Analysis of variance confirms the significance of the model. Statistically the ANOVA ***p***-value = 0.0047 indicates that the model is statistically significant because $p<0.05$. The lack of fit value (0.1051) and R^2 0.9809 make evident that model is well adjusted to experimental data and it can be used in order to know the yield at certain conditions.

With this model was maximized the yield percent (Y) to bring the optimal values; Figure 1(a) shows the surface response.

Parvez et. al., [12] investigated the $(NH_4)_2SO_4$ concentration effect in electrochemical exfoliation synthesis (EES) for graphene production. Results demonstrated that the concentration of salt and voltage produce low yield (~ 5%), which suggests that limited number of ions are available to exfoliate. In contrast when concentration increases to 1.0 M, the yield is ~ 75%, also when concentration is high (3 to 5 M) the yield was <50%, and it is due to the formation of OH^- moieties were suppressed because of the low water content, and SO_4^{2-} ion intercalation processes are expected to be relatively slow. In this work, the optimal values obtained were 11.45V and 0.68 M $(NH_4)_2SO_4$ to obtain a yield of 67.21±10.01%.

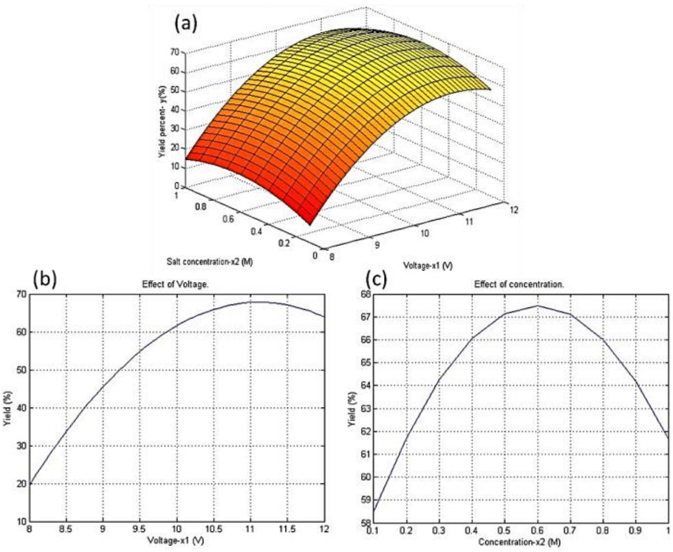

Figure 1 (a) Surface response for graphene production by EES. **(b)** Voltage effect in EES at $(NH_4)_2SO_4$ constant concentration (0.68 M), and **(c)** $(NH_4)_2SO_4$ Concentration effect in EES at constant voltage (11.45 V).

Effect of variable voltage is shown in Figure 1(b), as the voltage increases at concentration constant (0.68 M), yield also increases until the value of 11.45 V, and it is because that with higher voltage applied the pencil-graphite mine breaks and the exfoliation process finished. Using maximum voltage (12 V) resulted in a decrease of 3.33% respect to maximum value in terms of yield.

The $(NH_4)_2SO_4$ concentration showed similar effect than voltage. Figure 1(c) shows that higher salt concentration than 0.60 M induces electrode (pencil-graphite mine) to break, finishing faster the exfoliation process. Using maximum concentration (1 M) yield was decreases in 5.60% respect to maximum value.

Optimization of nylon nanowires production and effect of parameters

The effect of variables: voltage, flow and collector-needle distance for nylon nanowires was studied using the central composite design (CCD) showed in Figure 2.

$$D = -24896.68 + 1861.61\, z_1 + 17.80\, z_2 - 205.01\, z_3 - 33.82\, z^2{}_1 - 4.32\, z^2{}_2 + 4.79\, z^2{}_3 - 0.62\, z_1 z_2 + 3.43\, z_1 z_3 + 1.43\, z_2 z_3 \quad (2)$$

Equation 2 represents a second order polynomial model that correlates mean diameter D (nm) with Voltage z_1 (kV), Flow z_2 (mL/h) and collector-needle distance z_3 (cm)

To confirm the reliability of model, ANOVA analysis was used. The ANOVA for quadratic model of nylon nanowires production, ***p***-value=0.0047 probes that the model is statistically significant (the lack of fit value equal to 0.52 and coefficient of determination (R^2) equal to 0.96).

This model was minimized to find values of variables that makes average diameter minimum. Figure 2 (a)(b)(c) shows the surface response of the model which optimal values were 27 kV, 2.30 mL/h, and 11.40 cm of collector-needle distance, in order to obtain 65.83 ±12.09 nm of diameter.

Figure 2(a)(b),(c) shows effect of voltage in average nanowires diameter, there is a parabolic behaviour with inflection point in 28.1 kV on the ***x*** axis, while the extremes of the range evaluated predict a smaller fiber diameter as showing by Zhang et. al., [25] and showed that high voltage favours the narrowing of wire diameter [26]. The optimal value is which one that makes the fiber had minimum diameter using the smallest possible applied voltage, bringing to the process the best alternative in terms of input energy.

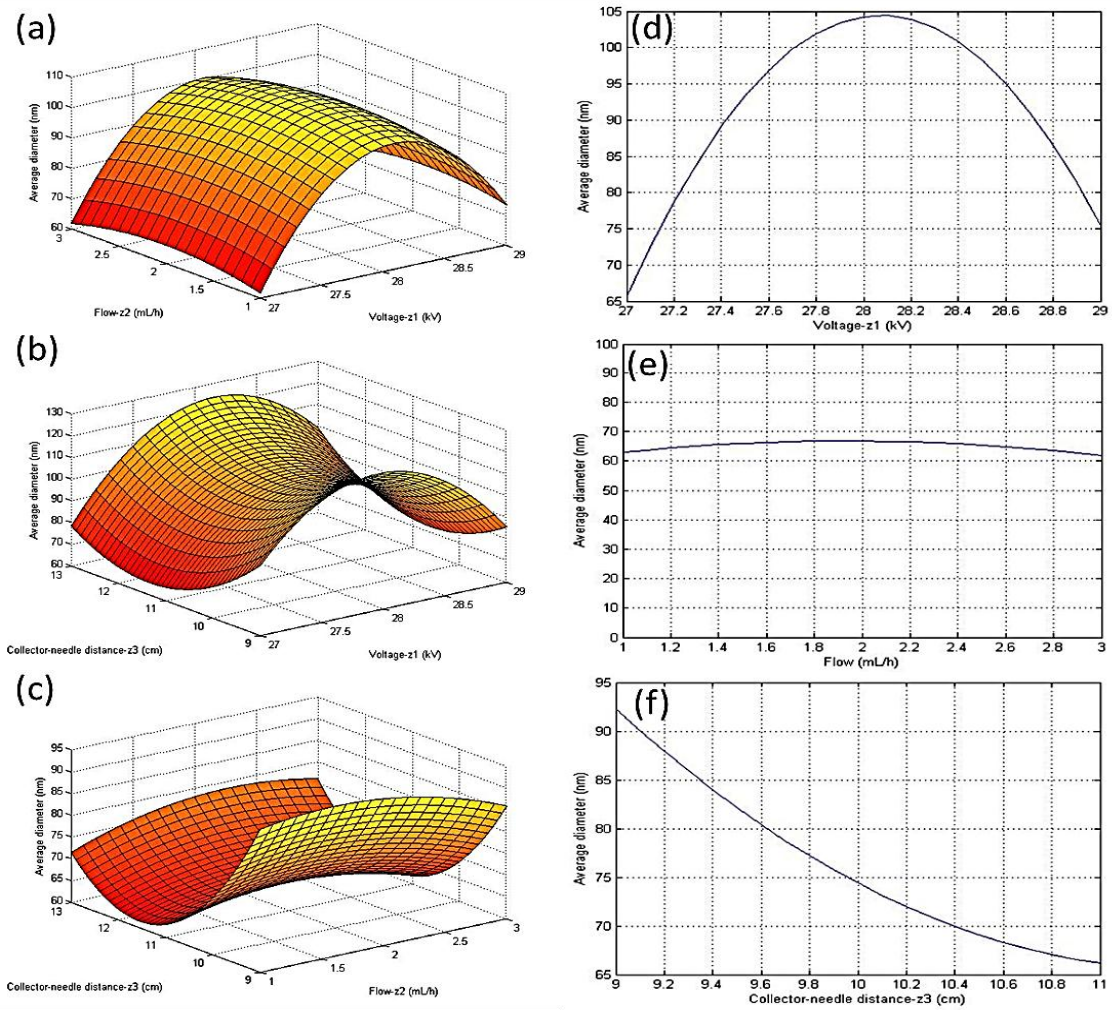

Figure 2. Surface response representation for nylon nanowires production showing effects between interactions of (a) Flow and voltage with constant distance equal to 11.40 cm, (b) Collector-needle distance and voltage with constant flow equal to 2.30 mL/h and (c) collector needle distance and flow with constant voltage equal to 27 kV, (d) Effect of Voltage with flow and collector-needle distance constant equal to 2.3 mL/h and 11 cm respectively in average diameter, (e) Effect of flow with voltage and collector-needle distance constant equal to 27 kV and 11 cm respectively in average diameter, and (f) Effect of Collector-needle distance with voltage and flow constant equal to 27 kV and 2.3 mL/h respectively in average diameter.

Effect of flow in electrospinning process is shown in Figure 2(e), as the flow increases, average diameter presents a quasi-constant pattern, it means that in comparison with the other effects, flow is not considered a crucial parameter. Figure 2(f) shows effect of collector-needle distance in fiber diameter. Here, when the distance diameter of nanowires, consistent with literature [27] where it is demonstrated that if the distance is too long, bead-wires can be obtained, and diameter are increased, while the distance is too short, there is no enough time for fiber solidification before reaching the collector [25-26].

Characterization of obtained materials

Figure 3(a) shows micrographs of single layer (red line) and figure 3(b) few layers of graphene obtained by electrochemical exfoliation (thickness of graphene sheets are in a range of 33-70 nm).

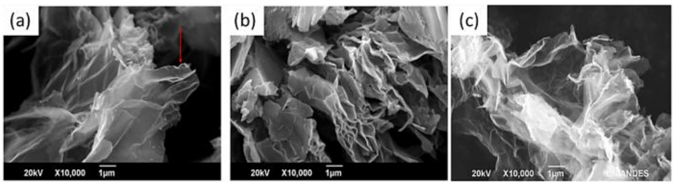

Figure. 3(a) SEM images of single layer, **(b)** few-layer graphene sheets after electrochemical exfoliation process, and **(c)** SEM image obtained using optimal conditions via electrochemical exfoliation.

Figure 3(c) shows the product of the exfoliation process of pencil-graphite mines under optimal conditions presented in section 3.1 (Optimization of graphene production and parameters effects).

XRD patterns of graphite and graphene after electrochemical process can be seen in the Figure 4; a weak peak appeared at 2θ = 54.6° for graphite (a) that corresponds to (1 0 1) plane and is absent in the graphene diffractogram (b) [28]. Main diffraction peak of both spectrums are located at 2θ = 26.5° which relates to (0 0 2) crystal plane of carbon with different intensities and interlayer distance of 0.94 Å using.

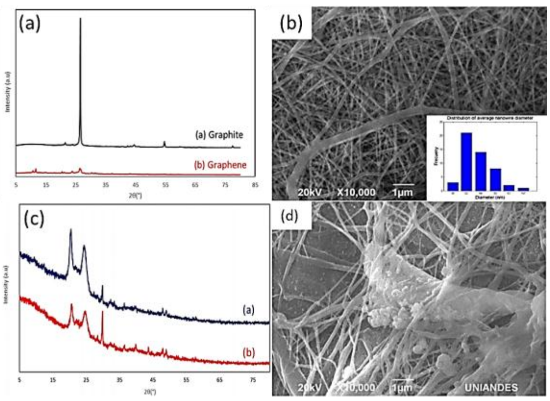

Figure. 4 (a) XRD Patterns of graphite and electrochemical exfoliated graphene, **(b)** SEM image of the optimal nylon nanowire material. Insert: Diameter distribution in the sample, (c) X-Ray diffraction patterns of (red-line) nylon nanowires and (blue-line) nylon nanowires/graphene composite and **(d)** SEM image of optimal nylon nanowires/graphene composite material

Figure 4(b) shows a SEM image proving the nylon nanowire distribution. Average diameter of nanowires is 69±15 nm while the model for these conditions predicts is 65.83±12 nm clearly demonstrating the consistency of proposed model.

Optimal nylon nanowires/graphene composite

Figure 4(c) shows comparison between XRD patterns of nylon nanowires and nylon nanowires/graphene composite. The addition of 1% of graphene in to the mixture, decreases the intensity of 20.45° and 24.53° 2θ peaks and increase 28.89° 2θ peak, it is because addition of graphene gives a greater proportion of the plane (0 0 2) and decrease the intensity of the characteristic nylon plane in the sample.

In Figure 4(d) nylon nanowires/graphene composite can be observed. Here, graphene is not crossed but is bonded and surrounding the nylon nanowires. This suggests that graphene has hydrophilic groups that can interact with amide groups of nylon; being according to [29].

Nylon nanowires/graphene composite was analysed using atomic force microscope. This material presented two zones, the first one is observed in Figure 5 (a), that shows typical nanowires obtained from electrospinning process with roughness of 68.1 nm in diameter; Figure 5(c) also shows the roughness profile in the sample (black line in Figure 5(a)). Figure 5(b) shows sections where graphene can be found, agglomerations are present in the same sample, because there are clusters of graphene layers between nylon, roughness profile of this section is presented in Figure 5(d) where principal roughness parameter R_a was 113.5 nm. The difference in roughness between both sections of the sample was 45.4 nm.

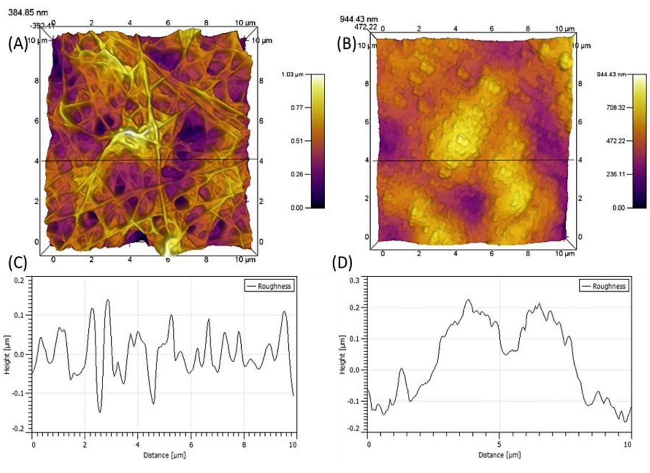

Figure 5 . Topography of nylon nanowires/graphene composite employing AFM. (a) Isolated nanowires and (b) nylon nanowires/graphene composite, and (c) – (d) show line scan data corresponding to the black lines in (a) and (b), respectively.

Antimicrobial test and UV-Blocking test

Antimicrobial activity of nylon nanowires/graphene composite for Micrococcus luteus, section revelled inhibition halo with 0.92 cm of diameter. Composite material film does not have any antibiotic and for this reason this material inhibits activity for this microorganism, this property is attributed to graphene in the polymeric matrix [30]. Ultraviolet light is harmful to living organisms.

To investigate UV blocking properties of nylon nanowires/graphene composites measure process was carried out at room 18°C. The absorbance spectra of nylon nanowires and nylon nanowires/graphene composites where performed. When, the addition is 1% of graphene the light absorption of different wavelengths increases by an average of 70% because of the absorbance of UV light for transferring the electron from the valance band to the conduction band (semiconducting behaviour). There are similar reports in literature with other composites [31]. Above results demonstrate the possibility about to use nylon nanowires/graphene composite material in textile industries taking advantage of the UV blocking property.

CONCLUSIONS

In the present study, the optimal conditions to produce graphene and nylon nanowires were assessed, for which it was obtained that applied voltage equal to 11.45 V and 0.68 M concentration of $(NH_4)_2SO_4$ gives a 67.21% of yield in graphene production and applied voltage equal to 27 kV, flow equal to 2.3 mL/h and collector-needle distance of 11.40 cm for nylon nanowires production gives average diameter fiber of 65.83 ±12.09. The properties of nanometric materials were confirmed via different characterizations as SEM, AFM, FTIR and XRD. Optimal materials were used to fabricate composite via electrospinning process. Composite material was analysed by SEM, AFM, FTIR, XRD, UV-visible spectroscopy and antimicrobial. This material has the ability of blocking UV rays 70% times more than pristine nylon nanowires, and, present antimicrobial activity for *Micrococcus luteus*. Further studies about conductivity assessment can support that this material can be used in e-textile industry. Finally, the techniques presented in this work can be potential ways to recycle nylon to avoid polymer contamination.

ACKNOWLEDGEMENTS

Thanks to Universidad Nacional de Colombia and Universidad Central for supporting XRD and AFM characterizations, respectively.

REFERENCES

[1] C. Lee, X. Wei, J. W. Kysar, and J. Hone, “Measurement of the Elastic Properties and Intrinsic Strength of Monolayer Graphene,” Science (80-.)., vol. 321, no. 5887, 2008.

[2] S. C. Ray, “Chapter 1 - Application and Uses of Graphene,” S. C. Ray, Ed. Oxford: William Andrew Publishing, 2015, pp. 1–38.

[3] M. Stoller, S. Park, Y. Zhu, J. An, and R. Ruoff, “Graphene-Based Ultracapacitors,” - Nano Letters, no. 10. p. 3498, 2008.

[4] S. Stankovich et al., “Graphene-based composite materials,” Nature, vol. 442, no. 7100, pp. 282–286, 2006.

[5] X. Lu, M. Yu, H. Huang, and R. S. Ruoff, “Tailoring graphite with the goal of achieving single sheets,” Nanotechnology, vol. 10, no. 3, p. 269, 1999.

[6] Y. L. Zhong and T. M. Swager, “Enhanced electrochemical expansion of graphite for in situ electrochemical functionalization,” J. Am. Chem. Soc., vol. 134, no. 43, pp. 17896–17899, 2012.

[7] X. Li et al., “Large-area graphene single crystals grown by low-pressure chemical vapor deposition of methane on copper,” J. Am. Chem. Soc., vol. 133, no. 9, pp. 2816–2819, 2011.

[8] W. S. H. Jr and R. E. Offeman, “Preparation of graphitic oxide,” J. Am. Chem. Soc., vol. 80, no. 6, p. 1339, 1958.

[9] K. Chen, D. Xue, and S. Komarneni, “Nanoclay assisted electrochemical exfoliation of pencil core to high conductive graphene thin-film electrode,” J. Colloid Interface Sci., vol. 487, pp. 156–161, 2017.

[10] R. I. Jibrael and M. K. A. Mohammed, “Production of graphene powder by electrochemical exfoliation of graphite electrodes immersed in aqueous solution,” Opt. - Int. J. Light Electron Opt., vol. 127, no. 16, pp. 6384–6389, Aug. 2016.

[11] Y. L. Zhong, Z. Tian, G. P. Simon, and D. Li, “Scalable production of graphene via wet chemistry: progress and challenges,” Mater. Today, vol. 18, no. 2, pp. 73–78, Mar. 2015.

[12] K. Parvez et al., “Exfoliation of Graphite into Graphene in Aqueous Solutions of Inorganic Salts.”

[13] X. Ji, Y. Xu, W. Zhang, L. Cui, and J. Liu, “Review of functionalization, structure and properties of graphene/polymer composite fibers,” Compos. Part A Appl. Sci. Manuf., vol. 87, pp. 29–45, 2016.

[14] G. Ren et al., “Influence of functional graphene as filler on the tribological behaviors of Nomex fabric/phenolic composite,” Compos. Part A Appl. Sci. Manuf., vol. 49, pp. 157–164, 2013.

[15] D. Reneker and I. Chun, “Nanometre diameter fibres of polymer, produced by electrospinning,” - Nanotechnology, vol. 3, no. 3. p. 216, 1996.

[16] M. H. El-Newehy, S. S. Al-Deyab, E.-R. Kenawy, and A. Abdel-Megeed, “Nanospider Technology for the Production of Nylon-6 Nanofibers for Biomedical Applications,” J. Nanomater., vol. 2011, pp. 1–8, 2011.

[17] S. Zhang, W. S. Shim, and J. Kim, "Design of ultra-fine nonwovens via electrospinning of Nylon 6: Spinning parameters and filtration efficiency," Mater. Des., vol. 30, no. 9, pp. 3659–3666, Oct. 2009.

[18] A. Pedicini and R. J. Farris, "Thermally induced color change in electrospun fiber mats," J. Polym. Sci. Part B Polym. Phys., vol. 42, no. 5, pp. 752–757, Mar. 2004.

[19] J. Deitzel, "Electrospinning of polymer nanofibers with specific surface chemistry," Polymer (Guildf)., vol. 43, no. 3, pp. 1025–1029, Feb. 2002.

[20] R. Nirmala, R. Navamathavan, M. H. El-Newehy, and H. Y. Kim, "Preparation and electrical characterization of polyamide-6/chitosan composite nanofibers via electrospinning," Mater. Lett., vol. 65, no. 3, pp. 493–496, Feb. 2011.

[21] Z.-M. Huang, Y.-Z. Zhang, M. Kotaki, and S. Ramakrishna, "A review on polymer nanofibers by electrospinning and their applications in nanocomposites," Compos. Sci. Technol., vol. 63, no. 15, pp. 2223–2253, Nov. 2003.

[22] C. T. Laurencin, A. M. A. Ambrosio, M. D. Borden, and J. A. Cooper Jr, "Tissue engineering: orthopedic applications," Annu. Rev. Biomed. Eng., vol. 1, no. 1, pp. 19–46, 1999.

[23] R. I. Jibrael and M. K. A. Mohammed, "Production of graphene powder by electrochemical exfoliation of graphite electrodes immersed in aqueous solution," Opt. - Int. J. Light Electron Opt., vol. 127, no. 16, pp. 6384–6389, 2016.

[24] C. A. Schneider, W. S. Rasband, and K. W. Eliceiri, "NIH Image to ImageJ: 25 years of image analysis.," Nat. Methods, vol. 9, no. 7, pp. 671–5, Jul. 2012.

[25] C. Zhang, X. Yuan, L. Wu, Y. Han, and J. Sheng, "Study on morphology of electrospun poly(vinyl alcohol) mats," Eur. Polym. J., vol. 41, no. 3, pp. 423–432, Mar. 2005.

[26] C. S. Ki, D. H. Baek, K. D. Gang, K. H. Lee, I. C. Um, and Y. H. Park, "Characterization of gelatin nanofiber prepared from gelatin–formic acid solution," Polymer (Guildf)., vol. 46, no. 14, pp. 5094–5102, Jun. 2005.

[27] Z. Li and C. Wang, "Effects of Working Parameters on Electrospinning," Springer Berlin Heidelberg, 2013, pp. 15–28.

[28] A. Hadi, J. Karimi-Sabet, S. M. A. Moosavian, and S. Ghorbanian, "Optimization of graphene production by exfoliation of graphite in supercritical ethanol: A response surface methodology approach," J. Supercrit. Fluids, vol. 107, pp. 92–105, Jan. 2016.

[29] C. Menchaca-Campos, C. García-Pérez, I. Castañeda, M. A. García-Sánchez, R. Guardián, and J. Uruchurtu, "Nylon/graphene oxide electrospun composite coating," Int. J. Polym. Sci., vol. 2013, 2013.

[30] C. M. Santos et al., "Antimicrobial graphene polymer (PVK-GO) nanocomposite films," Chem. Commun., vol. 47, no. 31, p. 8892, Jul. 2011.

[31] H. R. Pant et al., "Electrospun nylon-6 spider-net like nanofiber mat containing TiO2 nanoparticles: A multifunctional nanocomposite textile material," J. Hazard. Mater., vol. 185, no. 1, pp. 124–130, Jan. 2011.