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Hydrothermal growth of mop-brush-shaped ZnO rods on the surface of electrospun nylon-6 nanofibers

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Abstract

This study is focused on forming a spider-wave-like nano-nets of nylon-6 decorated with unique mop-brush-shaped ZnO rods. The nanocomposite is prepared in two steps. First, ZnO nano-seeds containing electrospun nylon-6 nano-nets were fabricated by blending ZnO nanoparticles with nylon-6 solution. Second, the electrospun ZnO/nylon-6 composite was hydrothermalized with ZnO precursor solution to grow long ZnO mop-brush-shaped rods on the surface of fibers. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), and FT-IR revealed that simultaneous formation of spider-wave-like nano-nets and effective uploading of ZnO nano-seeds were carried out by electrospinning from the blend solution. Field-scanning electron microscopy (FE-SEM) showed that unique mop-brush-shaped ZnO rods were effectively grown on the surface of nylon-6 fibers. As-synthesized spider-wave-like nano-nets of nylon-6 decorated with large number of mop-brush-shaped ZnO rods showed good hydrophilicity, photocatalytic property, and UV-shielding property. Furthermore, uploading technique of nano-seeds with small amounts during electrospinning and successive grown of sufficient amount of mop-brush-shaped ZnO rods nucleated by these nano-seeds during hydrothermal treatment provide a good stability of ZnO rods on the surface of fibers. Therefore, as-synthesized inorganic/organic nanocomposite (IONC) fibers may be used as potential textile for water treatment and protective clothing.

Keywords: B. Nanocomposite; D. ZnO; Electrospinning; Nylon-6

1. Introduction

Recent scientific and technological interest has focused on inorganic/organic nanocomposites (IONCs) over the last few years. The incorporation of inorganic nanoparticles (NPs) on/into polymer matrix can provide high-performance novel materials that find important applications in different fields, ranging from photocatalysis and photovoltaic to biomedical engineering [1–6]. The integration of inorganic NPs into a polymer matrix allows both properties from NPs and polymer to be enhanced and thus new material with unique properties can be generated to IONCs [7–10]. As a result of the development in nanotechnology, metal and metal oxide NPs have been incorporated into the polymer matrix using different fabrication techniques [11,12]. In recent years, electrospinning has been widely investigated as a facile and robust technique for the fabrication of nano IONCs [13,14]. However, loading of sufficient amounts of inorganic NPs on polymer fibers during electrospinning is still challenging. Therefore, post-electrospinning treatment of electrospun nanofibers is carried out to load sufficient amount of NPs on polymer fibers [8,15]. For proper loading of NPs, surface-fictionalization of nanofibers is required. It is important to select the suitable materials and appropriate methods to introduce the desired functionality onto the nanofibers surface to meet specific needs.

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ZnO nano/micro-structures are among some of the most important inorganic NPs that exhibit semiconducting, pyroelectric and piezoelectric properties [16,17]. There are many reports to control its size and shape which leads to the novel and enhanced chemical, electrical, and optical properties of ZnO particles [18,19]. By tuning the material/process parameters, ZnO particles can be engineered in different shape and size [20]. Furthermore, deposition of unique structured ZnO particles as well as their proper attachment on the surface of polymer fibers is an interesting field for IONCs engineering. Recently, ZnO particles were grown on the surface of polymer fibers using seeding method by Chang et al. [21]. He has reported that firecracker-shaped ZnO particles could be deposited on electrospun PI fibers by immobilization of ZnO seeds onto electrospun PI nanofibers followed by deposition of ZnO nanorods using hydrothermal process [21]. However, post-electrospinning immobilization of ZnO NPs seeds on electrospun fibers is weaker than that of incorporation of NPs prior to electrospinning. The functionalities of polymer molecules and ZnO NPs can interact with each other in solution during electrospinning and provide good attachment of ZnO NPs on/into polymer matrix compared to the post electrospinning immobilization of NPs. Weak attachment of photocatalytic ZnO nanorods due to post-electrospinning immobilization of ZnO NPs seeds could not prevent from the wash of photocatalyst during its use in aqueous medium. To avoid the weak attachment of ZnO particles on the surface of polymer fibers, we reported a facile and effective strategy of immobilization of ZnO nanoseeds on fiber by blending ZnO NPs and polymer solution prior to electrospinning. These well incorporated ZnO nanoseeds on/into polymer fibers could easily provide the nucleation sites to grow ZnO rods during hydrothermal treatment. The formation process of mop-brush-shaped ZnO rods decorated nylon-6 fibers is shown in Fig. 1. As-synthesized ZnO/nylon-6 hybrid mats with large amount of spider-wave-like nano-nets can sufficiently increase the hydrophilicity of nylon-6 mat and should become a potential media for water filtration. The composite mat not only showed good photocatalytic activity towards dyes but also showed the effective reusability. Hence, this novel IONCs could become an environmentally and economically friendly photocatalyst.

2. Materials and methods

2.1. Preparation of ZnO nano-seeds incorporated nylon-6 fibers

Commercial nylon-6 (Mw ≈ 35,000, Kolon, Korea) was used as the polymer in the present study. ZnO NPs (Aldrich, particle size of ≈ 30 nm), formic acid, and acetic acid were used as-received. Different nylon-6 mats were electrospun from 20 wt% nylon-6 solution dissolved in 4:1 formic acid/acetic acid solvents that containing 0, 5, 10, and 20 wt% ZnO NPs with respect to nylon-6. Polymer solution was fed through the metal capillary (nozzle) having di = 0.21 mm (21 G) attached to a 1-D robot-system that moves laterally controlled by LabVIEW 9.0 program (National Instrument). The feeding rate via a controllable syringe pump was maintained at 0.3 ml/h. Electrospinning process was carried out at 18 kV electric voltage and 18 cm working distance at room temperature where electrified polymeric nylon-6 solution with ZnO NPs was extruded through a spinneret and collected as a mat on the polyethylene sheet coated on rotating drum. After vacuum dried for 24 h, the fiber mats were used for further analysis.

2.2. Hydrothermal growth of mop-brush-shaped ZnO rods on nylon-6 fibers

Mop-brush like ZnO rods were grown on nylon-6 nanofibers using hydrothermal treatment of as-prepared electrospun hybrid nylon-6 mat with ZnO precursor solution. Prepared aqueous solutions of zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) (0.025 M) and hexamethylenetetramine ($C_6H_{12}N_4$) (0.1 M) were mixed and stirring for 0.5 h. As-prepared hybrid electrospun mats (6 cm × 6 cm) with this mixture was then taken into a Teflon crucible and kept inside the autoclave. This autoclave was kept at 110 °C for 4 h. The obtained mat after cooling was washed several times with distilled water and alcohol. After vacuum drying for 12 h at 30 °C, the mat was further dried in an oven at 100 °C for 6 h before characterization and measurements.

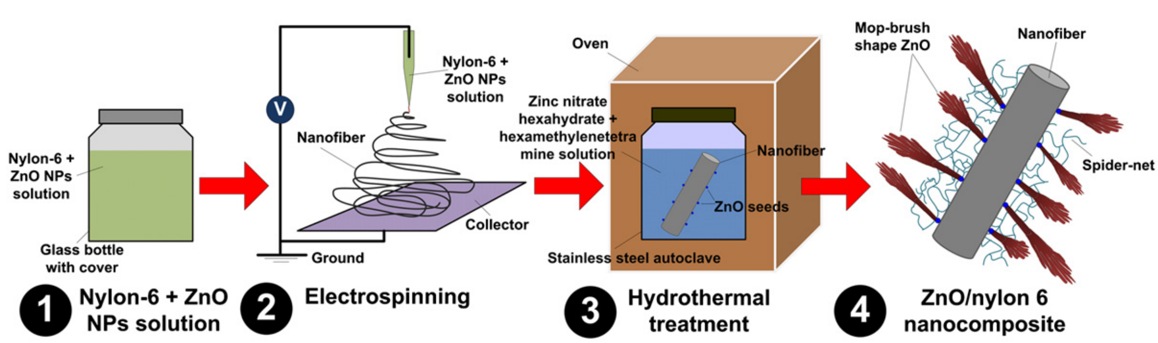

Fig. 1. Schematic illustration of fabrication of mop-brush-shaped ZnO rods on the surface of electrospun nylon-6 fiber.

2.3. Characterization and measurements

The surface morphology of different electrospun mats was analyzed by using scanning electron microscopy (SEM, JSM-5900, JEOL, Japan) and field-emission scanning electron microscopy (FE-SEM, S-7400, Hitachi, Japan). TEM images of nanofibers containing ZnO nano-seeds were obtained via transmission electron microscopy (TEM, H-7650, Hitachi). Incorporation of ZnO particles into/on nylon-6 fibers was also evaluated by using a UV–visible spectrometer (Lambda 900, Perkin-Elmer, USA) in the 200–800 nm range. The nanofibers mats of $3\times3\ cm^2$ in size (about 0.02 mm thick) were directly used for testing. The wettability of the electrospun mats was measured with deionized water contact angle measurements using a contact angle meter (GBX, Digidrop, France). Deionized water was automatically dropped (drop diameter 6 μm) onto the mat.

The photocatalytic activity of different mats was evaluated by observing the degradation of aqueous solution of methylene blue (MB) in a simple photochemical reactor. In the present investigation, the reactions were carried out in glass bottles of 4.5 cm in height and 5 cm in diameter under UV light. The bottles containing mat ($4\times4\ cm^2$) with 20 ml MB solution (10 ppm) was equipped with the tip of a light-guide (5 mm in diameter) of mercury-vapor lamp (OmniCure, EXFO). The UV light of very low intensity (30%) is used in this experiment. The distance between solution and tip of light-guide was 5 cm. At specific time intervals, 1 ml of the sample was withdrawn from the system and then the absorbance intensity was measured at the corresponding wavelength with a UV–visible spectrophotometer (HP 8453 UV–vis spectroscopy system, Germany). For cycling use experiments, mats were removed from the solution and washed with water and ethanol repeatedly. The washed mat was dried at 100 °C for 1 h and used for further measurement.

3. Results and discussion

The morphologies of pristine nylon-6 and ZnO nano-seeds containing nylon-6 hybrid mats are shown in Fig. 2 (SEM images). In pristine nylon-6 electrospun mat (Fig. 2a), the fibers appear ultrafine without any spider-wave-like nano-nets. The mats obtained from the nylon-6 solutions containing different amounts of ZnO NPs showed some changes in fiber morphology (Fig. 2b–d). As ZnO NPs was added into polymer solution, a double-layered spider-wave-like morphology (thick and thin fibers) was noticeable, and became even more apparent at an amount of 10 wt% of ZnO in nylon-6 solution (Fig. 2c). Further increase of ZnO NPs in nylon-6 solution

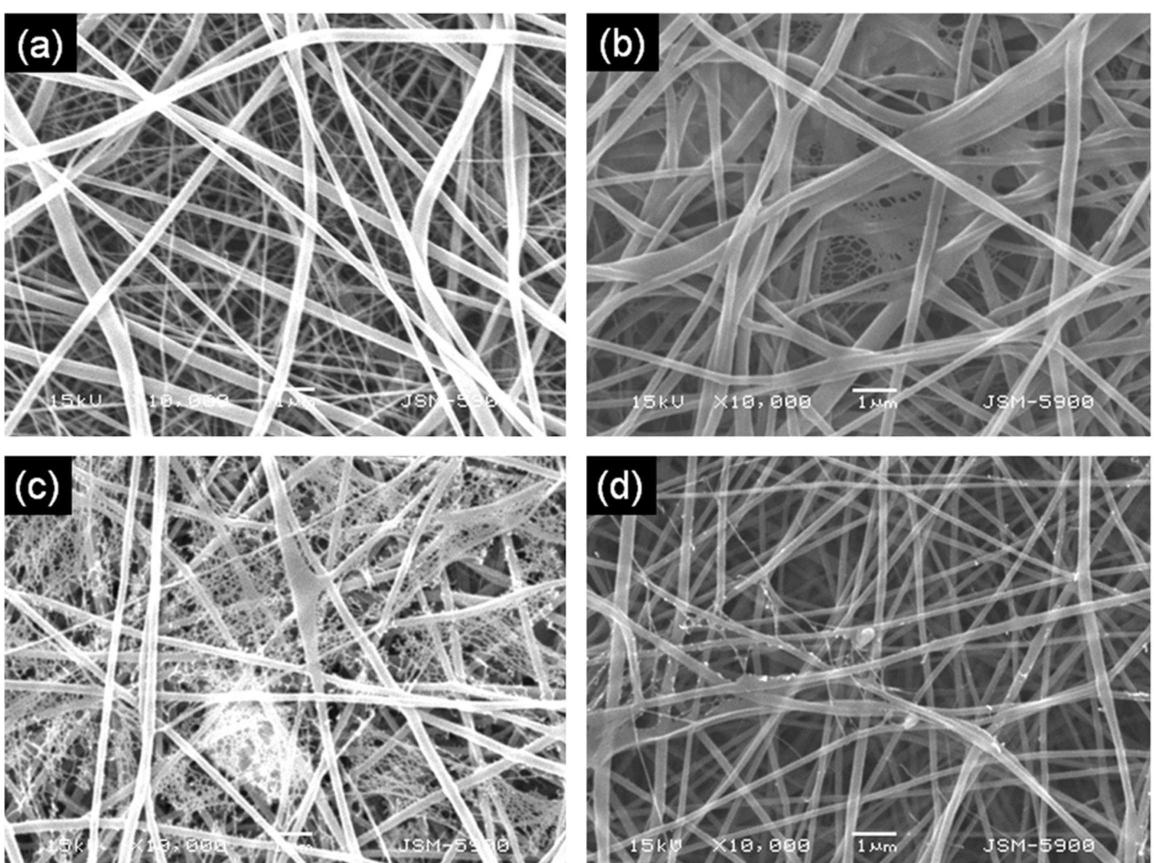

Fig. 2. SEM images of electrospun nylon-6 mats obtained from (a) 0, (b) 5, (c) 10 and (d) 20 wt% ZnO nano-seeds containing nylon-6 solutions.

not only decreased the spider-wave-like structure but also hindered the spinnability of the solution and formed non-smooth fibers (Fig. 2d). This trend in morphology showed that NPs were well dispersed with polymer solution up to 10 wt% ZnO concentrations and therefore they are properly loaded on/into polymer fibers. The well dispersion of NPs can accelerate the solvent degradation of nylon-6 (caused by formic acid) and increased portion of degraded nylon-6 should be responsible for the formation of spider-wave-like structure during phase separation, which is explained in author's previous reports [22,23]. The spider-wave-like structure mats are useful to decrease the pore size for NPs filtration from contaminated water.

Fig. 3 shows the recorded TEM images of pristine nylon-6 and ZnO nano-seeds containing nylon-6 nanofibers. The TEM samples were prepared by direct collecting of fiber onto Cu-grids during electrospinning. Hybrid nylon-6 fiber containing 10 wt% ZnO particles showed well dispersed ZnO nano-seeds throughout the cylindrical and smooth fiber (Fig. 3b), while the hybrid fiber containing 20 wt% ZnO particles showed the agglomeration of NPs and destroyed the smoothness morphology of composite fiber (Fig. 3c). It could be explained by the fact that, according to the increasing amount of ZnO, the ZnO/nylon-6 electrospinning solution became more viscous, which could increase the energy needed to overcome surface tension for electrospinning [24], resulting in more beads-on-string and thicker fibers with rough surfaces, as shown in Figs. 2d and 3c. The similar trend was also observed in author's previous report when TiO_2 NPs were blended with nylon-6 solution [10].

The loading of ZnO nano-seeds and their proper interaction with polymer molecules on nylon-6 fibers was demonstrated by FT-IR. The functionalities (C=O and N–H groups) of nylon-6 can easily interact with ZnO NPs through the formation of donor–acceptor complexes or hydrogen bonding which was clearly observed from the shifting of different IR bands (Fig. 4) of nylon-6 in composite mats. Fig. 4a and b show the FT-IR spectra of different electrospun mats. The characteristic peaks of pristine electrospun nylon-6 mat are explained in author's previous work [25]. Compared with the pristine nylon-6 mat, ZnO nano-seeds containing mats showed the shifting of different peaks towards higher values (Fig. 4a and b) and signifying an interaction between ZnO NPs and nylon-6 molecules. This shifting was pronounced in 10 wt% ZnO NPs containing mat compared to the pristine and other ZnO wt% containing mats. Therefore, the result indicated that at 10 wt% ZnO concentration there was proper interaction of ZnO with nylon-6 molecules which was also supported by SEM images (Fig. 2) because 10 wt% containing nylon-6 solution could produce the large amount of spider-wave-like nano-nets.

From SEM, TEM, and FT-IR spectra, it is clear that the 10 wt% ZnO containing nylon-6 mat with large amount of spider-wave-like structure has good affinity for the proper loading of ZnO nano-seeds for providing the nucleation sites for the crystal growth of ZnO rods during hydrothermal treatment. Therefore, the mat obtained from the 10 wt% ZnO containing nylon-6 solution was taken for the hydrothermal treatment. SEM as well as FE-SEM was used to investigate the morphology of hydrothermally grown ZnO rods on the surface of ZnO nano-seeds containing nylon-6 fibers. These images with different magnifications (Fig. 5) indicate that sufficient amounts of ZnO rods with mop-brush-shaped are decorated on the surface of fibers. From Fig. 5c and d, it is clearly seen that some mop-brush ZnO rods are grown on surface of outer fibers of mat and some are on the surface of interior fibers of the mat. Fig. 5d reveals that rods are grown from the inner fiber of the mat and developed rods are well trapped by surface fibers. Therefore, we believe that these rods could not be washed out during aqueous solution treatment for long time and the properties of IONCs offered by ZnO should be maintained for repeated use of the composites. The long rods up to 5 μm with open morphology in mop-brush-shaped can provide the sufficient surface area for the photocatalytic reaction caused by ZnO NPs on the surface of spider-wave-like nano-nets of nylon-6 mat. Furthermore, presence of spider-wave-like nano-nets as well as long ZnO rods attached to the nylon-6 fibers could increase the hydrophilicity of the mat which is essential for effective water filtration [10]. It is well known that electrospun nylon fibers are commercially used for filter media. However, hydrophobicity of nylon-6 mat hinders its application in water filtration [8]. Therefore, proper

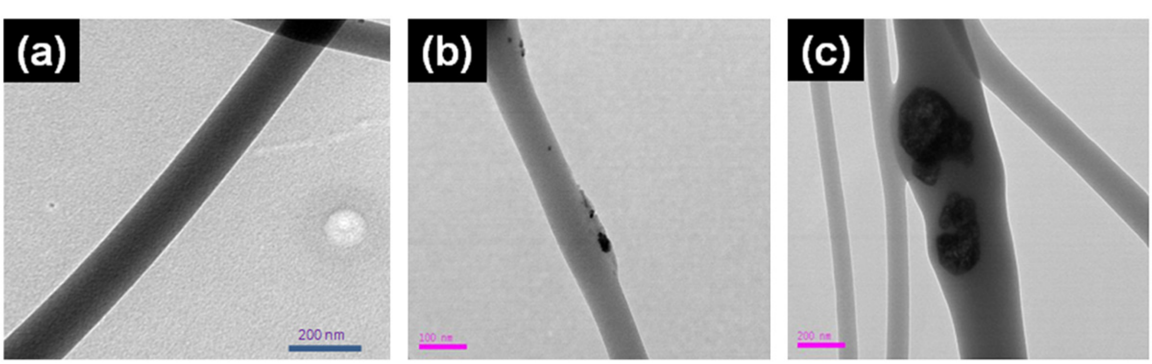

Fig. 3. TEM images of electrospun nylon-6 fibers obtained from (a) 0, (b) 10 0 and (c) 20 wt% ZnO nano-seeds containing nylon-6 solutions.

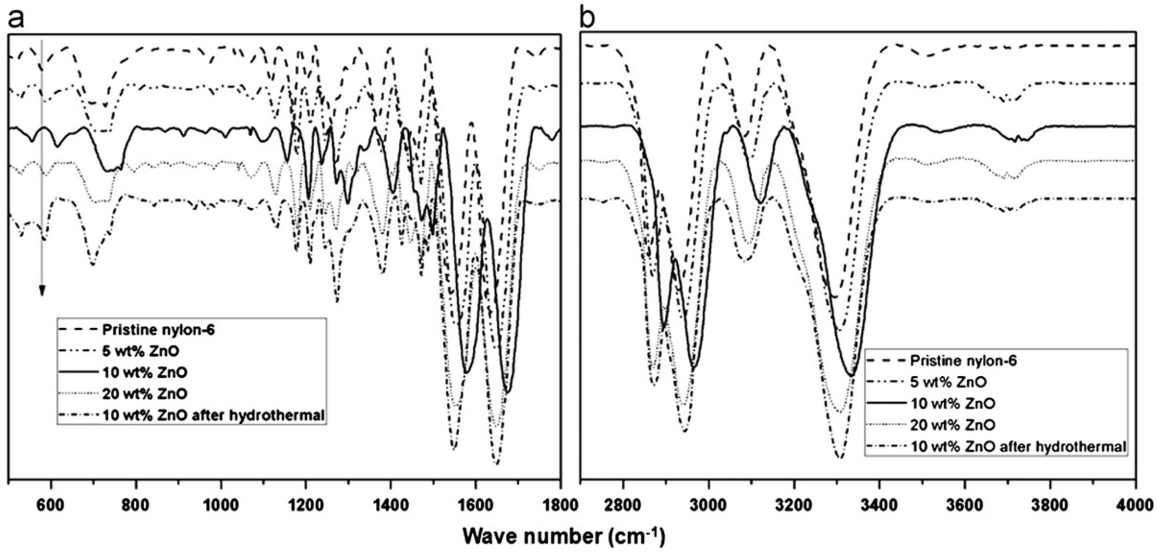

Fig. 4. FT-IR spectra of different electrospun nylon-6 mats: (a) low and (b) high wave number region.

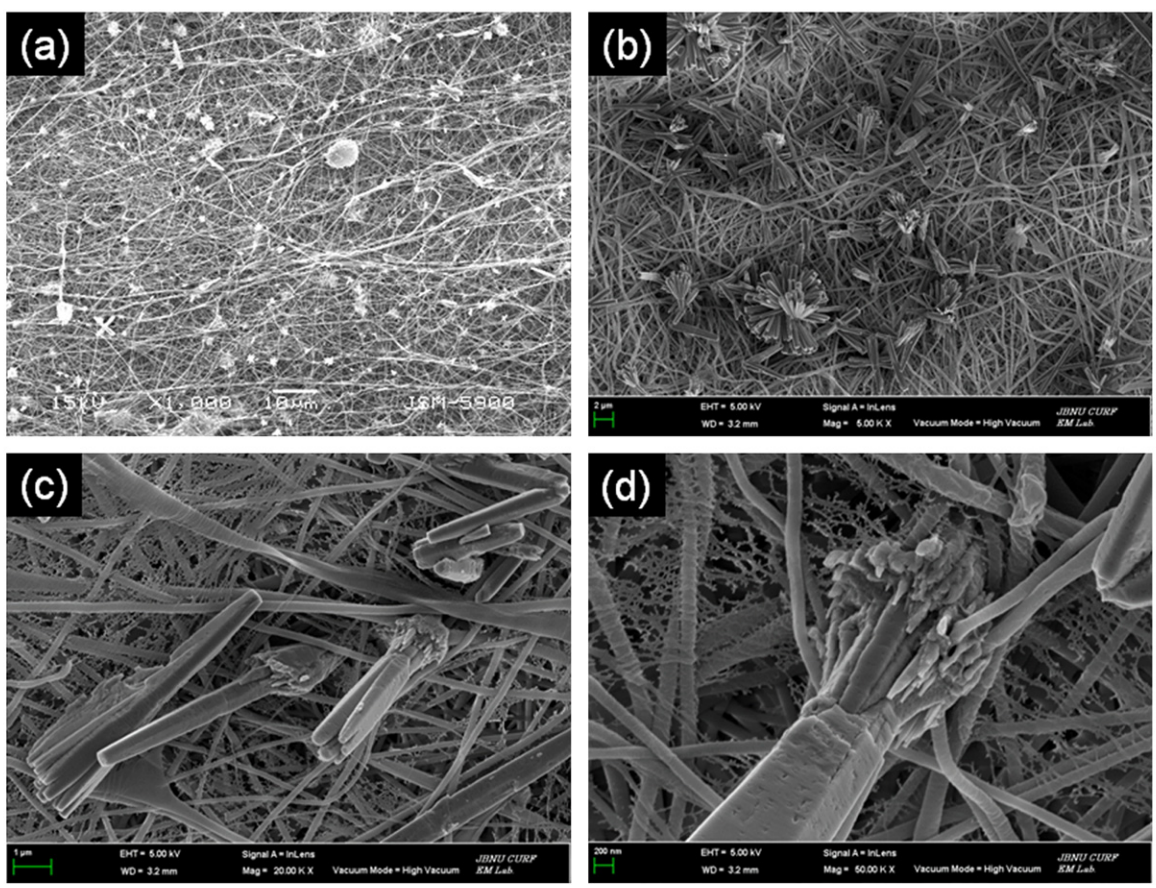

Fig. 5. SEM and FE-SEM images: (a) SEM images of mop-brush shaped ZnO rods containing nylon-6 mat at low magnification whereas (b), (c), and (d) are FE-SEM images of the same mat at different magnification.

modification of nylon-6 fibers using different material/process parameter is the important aspect in different fields [26,27].

The contact angle (CA) measurement of the pristine nylon-6 mat and 10 wt% ZnO nano-seeds containing nylon-6 mats before and after hydrothermal treatment is shown in Fig. 6. Contact angle is a quantitative measure of the wettability of a surface which varies according to the surface energy and roughness of the surface [28]. For water filtration, hydrophobic surfaces tend to have higher

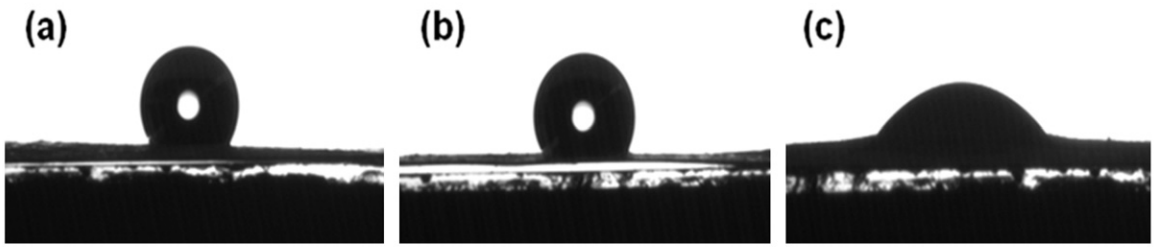

Fig. 6. Water contact angle of pristine nylon-6 mat (a), and 10 wt% ZnO nano-seeds containing nylon-6 mats before (b) and after (c) hydrothermal treatment.

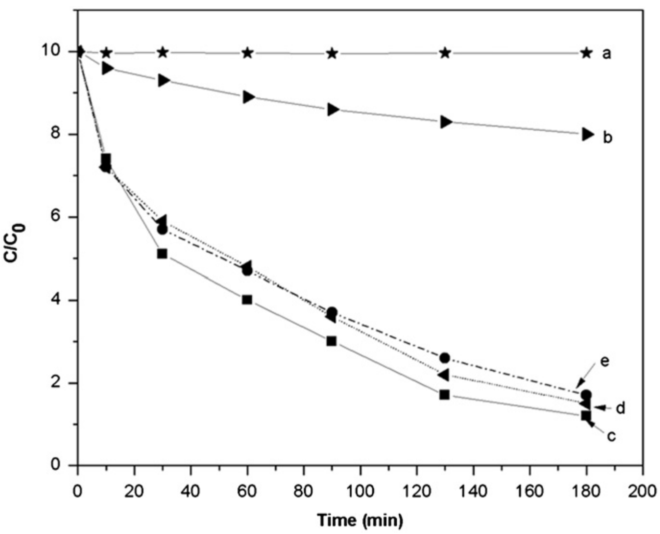

Fig. 7. Comparison of MB photodegradation in different specimens under UV radiation; (a) pristine nylon-6 and (b) 10 wt% ZnO nano-seeds containing mat before hydrothermal treatment (c) cycle I (d) cycle II, and (e) cycle III photodegradation of 10 wt% ZnO nano-seeds containing mat after hydrothermal treatment.

tendency of fouling than hydrophilic surfaces [29]. Therefore, different researchers have focused on the modification of fibrous materials to enhance their hydrophilicity. The pristine nylon-6 nanofibrous mat showed a hydrophobic surface at CA = 128°. Upon the incorporation of 10 wt% ZnO nano-seeds, the composite mat showed slightly increase in hydrophilicity (CA = 116°). However, deposition of mop-brushed rods on the surface of nanofibers showed highly hydrophilic surface of 54°. The hydrophilic behavior of the ZnO/nylon-6 composite obtained from hydrothermal treatment is attributed to the presence of well dispersed large number of mop-brushed ZnO rods with open morphology.

The photocatalytic performance of the pristine nylon-6, and composite ZnO/nylon-6 mats before and after hydrothermal treatment was evaluated by degrading methylene blue (MB) under UV-light irradiation. It is clear from Fig. 7 that the hydrothermalized ZnO/nylon-6 composite mat shows significant progress in the photodegradation of MB compared to pristine nylon-6 and ZnO/nylon-6 mat before hydrothermal treatment. This outcome may occur because of the large number of long mop-brush-shaped ZnO rods with open morphology on composite mat. The effect of morphology of ZnO NPs on photodegradation is explained everywhere in literatures [30,31]. Furthermore, the lower photocatalytic activity of composite mat before hydrothermal treatment comparing to the mat after hydrothermal treatment is due to the decrease in exposed surface area of ZnO nano-seeds in on polymer matrix. The incorporation of ZnO NPs prior to electrospinning can decrease the exposed surface area of photocatalytic NPs because they are effectively embedded on the polymer matrix. Because our aim is to make relatively cost-effective photocatalyst, we performed the durability test of used hydrothermalized ZnO/nylon-6 mat for further photocatalytic reaction. The photodegradation of MB was monitored for three consecutive cycles, each for 3 h. After each cycle, the composite mat was washed thoroughly with distilled water/alcohol and further used for fresh MB solution. Fig. 7 shows that there was no significant decrease in photodegradation rate during the three consecutive cycles, indicating the excellent stability of composite photocatalyst. Recycling process showed slightly decrease in photocatalytic efficiency of composite mat which might be either due to the deposition of byproduct particles on the surfaces of the NPs or slightly washing off of ZnO mop-brush rods from the surface of the fibers [20].

The stability of nanofibers and long lasting attachment of ZnO mop-brush on the surface of fibers is essential for water purification. The UV resistance capacity of the fibrous mat (substrate) is also important aspect to the durability of ZnO/polymer composite photocatalyst because the photocatalytic process is carried out under UV irradiation. SEM images (Fig. 8a) shows that hydrothermalized composite mat has no any measurable effect (such as degradation of fibers) upon UV irradiation when it is applied for photodegradation up to three cycles (i.e., 9 h continuous exposing to UV light). Moreover, it is clear from SEM images (Fig. 8a) that sufficient ZnO mop-brushes were still remaining on the surface of fiber even though the mat was washed many times with water/alcohol followed by UV irradiation. The stability of ZnO mop-brushes on the fiber is attributed to the effective interaction of ZnO nano-seeds with polymer molecules [29] which were incorporated to the fiber prior to electrospinning. Further grow of ZnO crystal in the form of mop-brush on the effectively embedded ZnO nano-seeds in composite

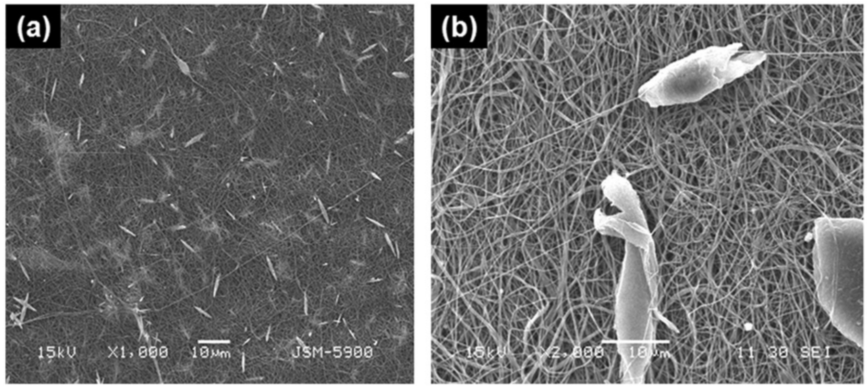

Fig. 8. SEM images of mop-brush ZnO rods containing mat (a) after 9 h UV irradiation during dye degradation and (b) continuous vagarious shaking of the mat for one week.

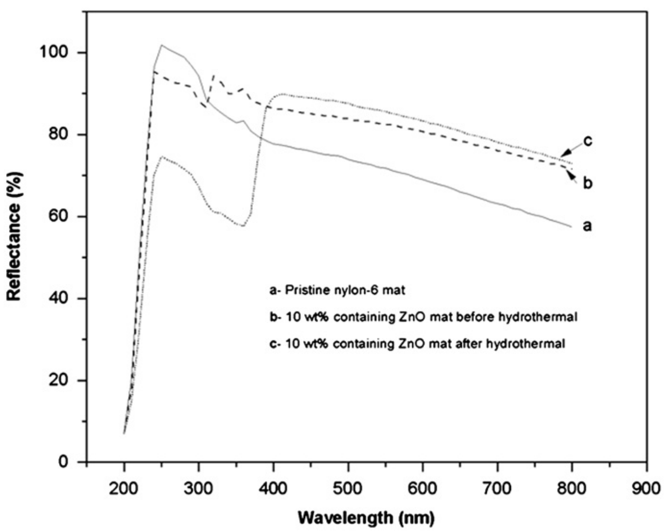

Fig. 9. UV–visible spectra of different nylon-6 mats.

mat can prevent from the wash out of ZnO mop-brushes during water treatment. Furthermore, to evaluate the effect of ZnO nano-seeds for providing proper attachment of ZnO mop-brushes on the surface of fibers, the hydrothermalized mat was kept into water for one week with continuous shaking at 200 rpm using a shaking incubator. The SEM images (Fig. 8b) clearly show that few mop-brushes are still remaining on the mat. The mop-brushes which are grown from the surface of inner fibers could exist on the mat as they are trapped by outer fibers (Figs. 5d and 8b) but the mop-brushes which are grown on surface fiber are almost washed way due to this vigorous shaking.

Another possible application of this as-synthesized composite fibrous mat may be UV-protective clothing. Therefore, UV–vis spectra of different mats were measured and result is shown in Fig. 9. It can be seen from Fig. 9 that growth of ZnO mop-brushes causes a reflection decrease in wavelength from 250 to 400 nm. The lowest reflection percentage of mat at 358 nm indicates a better UV-shielding property of the ZnO mop-brush containing nylon-6 composite mat compared to the pristine nylon-6 and ZnO nano-seeds containing nylon-6 composite mat. Moreover, UV–vis spectra indicated the successful loading of ZnO nano-seeds on/into nylon-6 fibers during electrospinning as well as increased the ZnO content on fiber due to the growth of mop-brush ZnO rods during hydrothermal treatment.

4. Conclusion

In this study, the synthesis of ZnO/nylon-6 hybrid nanofibers could be obviously characterized as a novel mop-brush-shaped ZnO nanorods on the surface of electrospun nylon-6 nanofibers. The suitable amount of ZnO nano-seeds not only produce large amount of spider-wave-like nano-nets but also provide nucleation site for the growth of rod-like long ZnO mop-brushes on the electrospun nylon-6 fibers. The incorporation of ZnO nano-seeds through the fiber prior to electrospinning could easily enhance the stability of hydrothermally grown ZnO mop-brushes on the surface of nylon-6 fibers. The presence of mop-brush-shaped ZnO rods on nylon-6 fibers was found to improve the hydrophilicity (antifouling effect), photocatalytic activity and UV protecting ability of electrospun mats. The resultant ZnO/nylon-6 spider-wave-like composite mat with antifouling effect may be a potential candidate for industrial filter application in future and its combined enhanced UV-shielding and photocatalytic property makes it as a pioneer in protective clothing.

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