Fabrication of flexible titania/polyacrylonitrile co-axial nanofibers via electrospinning

Jerawut Kaewsaeenee, Farkfun Duriyasart and Varong Pavarajarn

1. Introduction

Titania is a common photocatalyst, capable of being used in the degradation of toxic contaminants in water [1–3]. Its catalytic activity increases with the decrease of titania particle size down to the nanometer scale. Although titania nanoparticles are mainly used for photo-degradation, nanoparticles are difficult to handle and difficult to remove from water after the reaction is complete. Enhancement of the process is being pursued in the form of titania nanofibers because they can be more easily handled and provide greater surface area. One of the techniques that has been used to produce these nanofibers is electrospinning; titania has been synthesized into nanofiber form by incorporating the sol-gel method into the electrospinning technique [4–6]. However, while titania nanofibers can be more easily handled than titania in nanoparticle form, these nanofibers are brittle and can crumble into powder after repeated use.

Recently, the co-axial electrospinning technique was introduced to the fabrication of nanofibers in form of co-axial nanofibers [7,8]. In the co-axial electrospinning process, two different materials are delivered independently through a co-axial capillary and drawn to generate nanofiber in a core-sheath configuration. The core material and sheath material are delivered independently through a co-axial capillary, forming compound droplets, and these compound droplets are charged when high voltage is supplied. Charges are induced predominantly on the surface of sheath fluid. Above the critical value of electrical potential supplied, the fluid droplet will be distorted via repulsive force of charges, resulting in a small jet forming from the compound cone of materials. The rapid stretching of the sheath material can create strong viscous stress inside the sheath fluid that is transferred to the core material. The core part is stretched and elongated by the shear stress at the interface between the core and sheath. The obtained product is a nanofiber in the formation of a co-axial nanofiber [9,10]. In this work, a polymer is introduced as core of the nanofiber, while titania is fabricated in the sheath. The polymer core allows the titania nanofibers to be more flexible, preventing the loss of nanosized titania grains during the reaction.

The main objective of the present work is to investigate the effects of using a polyacrylonitrile (PAN) as the core polymer, while a mixture solution of titanium tetraisopropoxide (TTIP) and polyvinylpyrrolidone (PVP) is used to form the titania sheath for the co-axial nanofibers. Upon calcination of the as-synthesized fibers, the titania/PAN co-axial nanofibers are obtained. The photocatalytic activities of these fibers were investigated, based on the photo-oxidation reaction of methylene blue (MB) as a model compound.

2. Materials and methods

The core solution for co-axial electrospinning was prepared by dissolving 8 wt% of polyacrylonitrile (PAN;
Sigma-Aldrich, average MW of 86,200, polydispersity index of 3.81) in n, n-dimethylformamide (DMF; Kanto Chemical) at 60°C for 1 h. The sheath solution was prepared by combining the PVP solution and the titania precursor solution. The PVP solution was prepared by dissolving 10 wt% polyvinylpyrrolidone (PVP; Sigma-Aldrich, average MW of 1,300,000, polydispersity index of 3.61) in DMF at room temperature for 1 h, and the titania precursor solution was prepared in another vial by stirring 3 ml of titanium (IV) isopropoxide (TTIP; Wako Pure Chemical Industries, Ltd.) with 6 ml DMF and 6 ml acetic acid at room temperature for 15 min. The titania precursor solution was slowly added into the PVP solution and stirred for 60 min to obtain the sheath solution. Finally, the core solution and the sheath solution were joined to obtain the titania(PVP)/PAN solution of the co-axial electrospinning process.

In the co-axial electrospinning process, each of the freshly prepared spinning solutions was loaded into two plastic syringes, each of which was connected to a co-axial nozzle with an inner core diameter of 0.7 mm. The process used an aluminum foil as a collector, and the flow rates were controlled by two syringe pumps. The emitting electrode from a Gamma High Voltage Research ES30P power supply capable of generating DC voltages up to 30 kV was attached to the nozzle. The grounding electrode from the same power supply was attached to the collector plate, a Shimadzu UV-2550 UV-visible (UV-vis) scanning spectrophotometer. The absorbance of the solution at 665 nm using a Hamamatsu R928 photomultiplier was periodically monitored by measuring the optical density of the reactor was measured by a radiometer (IL1700 Research Radiometer) and found to be 8 W/cm². The temperature of the solution was constantly monitored and controlled at 35 ± 1°C. The concentration of MB in the reactor was periodically monitored by measuring the absorbance of the solution at 665 nm using a Shimadzu UV-2550 UV-visible (UV-vis) scanning spectrophotometer.

3. Results and discussion
3.1. Properties of as-spun co-axial nanofibers

The co-axial electrospinning of the prepared solution resulted in the ejection of the jet of the solution and the deposition of ultrathin fibers as a non-woven mat on the collector plate. Exposure to the ambient moisture, hydrolysis, and subsequent condensation of TTIP within sheath fibers resulted in the formation of the titania(PVP)/PAN co-axial nanofibers.

The thermal behavior of titania(PVP)/PAN co-axial nanofibers was studied because the calcination temperature needs to be high enough to remove PVP within the sheath of co-axial fibers and to crystallize titania into anatase phase, yet the temperature should not be too high to burn out PAN in the core of the fibers. The decomposition temperature was studied by using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The mechanical property of the fibers was examined by Lloyd Universal Testing Machine, using the rate of 10 N/min. The co-axial fiber products were cut into 1 cm × 3 cm rectangles. The mechanical property of the fibers was examined by Lloyd Universal Testing Machine, using the rate of 10 N/min. The co-axial fiber products were cut into 1 cm × 3 cm rectangles.
steps, at temperatures of 260°C, 320°C, 320°C to 530°C and 530°C, respectively.

In the first step of this mass loss, the mass of co-axial fibers gradually decreased by approximately 10% at the temperature around 260°C, which should correspond to the loss of physically absorbed moisture and/or remaining solvent being present on or within the co-axial fibers [12,13]. The second step was identified when the mass of co-axial fibers had sharply decreased by approximately 30%, accompanied by a distinct exothermic DSC signal at the temperature of 320°C. This corresponds to the removal of PVP from the fibers via calcination. It should be noted that the crystallization of titania within the sheath of the fibers into anatase phase has been reported to take place at this range of temperature [13]. In the third step, the mass of the co-axial fibers decreased by around 45% at a temperature in the range of 320°C to 530°C, which should correspond to the degradation of PAN. The PAN degradation took place with partial evaporation of small compounds, such as NH₃ and HCN, from the fragmentation of polymers. The change in sample mass in this step was gradual and the exothermic DSC signal was quite broad, which indicates continuous fragmentation as the sample was heated up. It should also be noted that this behavior is different from thermal polymerization of nitrile groups of PAN in inert atmosphere [14] because the TGA and DSC analyzes in this work were conducted in oxygen. In the fourth step, at 530°C, complete degradation of PAN polymer in co-axial fibers is expected [15]. At temperature higher than 530°C, the sample mass remained at approximately 7% of the original mass corresponding to titania content in the fibers, since all carbonaceous materials, including PVP and PAN polymers, should be totally decomposed by reacting with oxygen gas.

The flow rates of the sheath and the core solution were varied, in the range of 0.9 to 1.2 mL/h, to determine their effects on the morphology of titania-(PVP)/PAN co-axial nanofibers. The applied electrostatic field strength and distance between the nozzle and the collector were fixed at 22 kV and 22 cm, respectively. Morphology of the obtained co-axial fibers was investigated by the STEM images.

The process was first tested using a fixed flow rate of core solution, while the flow rate of the sheath solution was being varied. The morphology of these co-axial fibers is shown in Figure 2(a-c). The increased flow rate of the sheath solution did not significantly affect the average diameters of obtained co-axial fibers; the average diameters of obtained co-axial fibers were changed from 370 to 390 nm when the flow rate of the sheath solution was increased from 0.9 to 1.5 mL/h. The change was within the standard deviations of the data (see Figure S1 in supplementary information).

After first testing with the flow rate of the core solution fixed at 1.2 mL/h, the process was next tested with an increased flow rate of the core solution, while the flow rate of the sheath solution was fixed at 1.2 mL/h. The morphology of the resulting co-axial fibers is shown in Figure 2(d,f). As expected, the rough surface of the obtained co-axial fibers increased with the increased flow rate of the core solution, and the average diameters of these obtained co-axial fibers increased as well. The average diameters of obtained co-axial fibers were 350, 380, and 580 nm when the flow rate of the core solution was 0.9, 1.2, and 1.5 mL/h, respectively. The increase in diameter of the obtained co-axial fibers was due to the fact that the amount of supplied core material was increased within the confined coverage of the sheath solution. With the fixed flow rate of the sheath solution and the fixed applied electrostatic potential, the stress at the interface between the core solution and the sheath solution was not effectively transferred to the center of a large droplet of the core solution; hence the increase in diameter of the fibers. This is different when the flow...
rate of the sheath solution was increased because the sheath solution was subjected to the applied potential directly; the more sheath solution was provided, the greater amount of the fibers was formed.

3.2. Properties of calcined co-axial fibers

The titania(PVP)/PAN co-axial nanofibers were synthesized by using the applied electrostatic field strength of 22 kV, distance of 22 cm, and the flow rates of the sheath and core solutions of 1.2/1.2 mL/h. As the obtained co-axial fibers were subjected to calcination, the residual solvent and PVP were removed from the sheath of the fibers, while titania crystallized in the sheath fibers, and PAN stabilized as core fibers.

The morphology of the obtained co-axial fibers, both before and after calcination, was investigated to confirm the fiber structure during calcination by SEM images, as shown in Figure 2. The results show that all obtained products remain in fiber form; further, it was found that these fibers are cross-sectionally round with a smooth surface. The diameters of the as-calcined fibers decreased with increasing calcination temperature, with the average diameters shown in Table 1. The obtained fibers, after calcination at 300°C, were similar to as-spun fibers in size and morphology because no polymer loss occurs below 320°C, which is supported with TGA/DSC. The fibers calcined at 450°C resulted in decreased diameters because of the loss of mass associated with the loss of PVP together with PAN stabilization as core fibers. When the calcination temperature was raised to 800°C, which is higher than the decomposition of both PVP and PAN, all carbonaceous materials were removed from the fibers, resulting in short fibers with a rough surface and a chain-like structure. This structure was formed by the agglomeration and sintering of titania particles. It should be noted that titania could not retain the structure as long fibers because of the low content of titania within the co-axial fibers.

The functional groups of obtained co-axial fibers, both before and after calcination, were investigated by FT-IR, as shown in Figure 3. The FT-IR shows spectra recorded in the wavenumber range of 400 to 4000 cm$^{-1}$ to confirm the removal of PVP, and the stabilization of PAN as core fibers. The obtained spectra of the as-spun co-axial nanofibers in Figure 3(a) showed a major absorption band at 2244 cm$^{-1}$, which is a signal that corresponds to C≡N of PAN [15], and an absorption band at 1630 cm$^{-1}$ which further corresponds to the carbonyl stretching vibration of the amide group of PVP [13]. Additionally, the minor bands at wavenumbers around 2850, 2939, 1444, 1353, and 1253 cm$^{-1}$ were assigned to the aliphatic CH group vibrations of different modes in CH, CH$_2$, and CH$_3$ vibrations of both polymers [15]. The absorption bands at 1630, 1715 and 930 cm$^{-1}$ correspond to the bending and stretching frequencies of the C = O bond of the DMF solvent, the carbonyl group of acetic acid, and the isoproxy groups of TTIP that were changed into ethoxy groups, respectively [13].

As the calcination temperature was raised to 300°C, the bands of aliphatic CH groups decreased due to the partial evaporation of small molecules from the polymer, and then disappeared with the increase in temperature to 450°C. This result is consistent with the previously explained TGA/DSC results. It is accompanied

![Figure 2. STEM images of as-spun titania(PVP)/PAN co-axial nanofibers obtained from co-axial electrospinning using flow rate ratio between core solution and sheath solution of (a) 0.9:1.2, (b) 1.2:1.2, (c) 1.5:1.2, (d) 1.2:0.9, and (f) 1.2:1.5 mL/h: mL/h.]
by a decrease in the diameter of the fibers. While PVP was removed by the calcination, PAN was stabilized by heat. One of the most important reactions in the stabilization process is cyclization, which is a formation of reaction-producing stable ladder polymer. Although the sample was heated in air; hence the fragmentation of PAN would be different than the thermal decomposition of PAN in an inert atmosphere, the cyclization was still confirmed by the fact that the intensity of C≡N stretching band decreased when the calcination temperature was increased to 300°C and 450°C. The new peak assigned to the stretching bond of C=N was identified at the wavenumber of 1590 cm\(^{-1}\) and heating up results in conjugation in the cyclic structure of PAN-forming aromatic rings, which was confirmed by the band of aromatic C=C at the wavenumber of 810 cm\(^{-1}\) [14]. Moreover, the band associated with the vibrational mode of Ti–O–Ti bonding of the anatase phase was clearly observed at a wavenumber of around 470 cm\(^{-1}\) [12,13]. When the calcination temperature was increased to 800°C, the bands of both PVP and PAN diminished after the calcination. Instead, the Ti–O–Ti band shifted to 700 cm\(^{-1}\), evidence of the formation of the rutile phase [12,13], which is also in agreement with the XRD analysis. Further, the results confirmed that the PVP was completely depleted, and the PAN polymer is stabilized as core fibers at the calcination temperature of 450°C.

The crystallographic structure of titania/PAN co-axial nanofibers was investigated by X-ray diffraction. According to the XRD results shown in Figure 5, the as-spun titania(PVP)/PAN co-axial nanofibers revealed no evidence of crystalline phase. When the obtained co-axial fibers were calcined at 300°C for 2 h, titania particles within the sheath of the co-axial fibers crystallized into anatase phase without contamination of the

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**Table 1.** Diameter and physical properties of titania/PAN co-axial fibers.

| Calcination temperature (°C) | Average fiber diameter (nm) | Fraction of phase (%) | Crystallite size (nm) |
|-----------------------------|-----------------------------|-----------------------|-----------------------|
|                             |                             | Anatase    | Rutile | Anatase | Rutile | Anatase | Rutile |
| As-spun                     | 380                         | -          | -      | -       | -      | -       | -       |
| 300                         | 360                         | 100        | -      | 6       | -      | -       | -       |
| 450                         | 160                         | 75         | 25     | 8       | 10     | -       | -       |
| 800                         | 80                          | -          | 100    | -       | 50     | -       | -       |

Figure 3. SEM micrographs of as-spun titania(PVP)/PAN co-axial nanofibers (a) comparing with the fibers calcined at 300°C (b), 450°C (c), and 800°C (d) for 2 h. The fibers were fabricated using the applied potential of 22 kV, tip-to-collector distance of 22 cm, a flow rate of core solution of 1.2 mL/h, and flow rate of sheath solution of 1.2 mL/h.

Figure 4. FT-IR spectra of as-spun titania(PVP)/PAN co-axial nanofibers (a) comparing with the fibers calcined at 300°C (b), 450°C (c), and 800°C (d) for 2 h.
other phases. The crystallite size of the anatase titania, calculated using XRD line broadening of the peak at 2$\theta$ of 25.5° via the Scherrer equation, was about 6 nm. As the calcination temperature was increased to 450°C, anatase crystals grew to 8 nm, while part of them transformed into rutile phase. The crystallite size of the rutile was about 10 nm. After the calcination at 800°C, only the rutile phase was detected. The crystal growth was significant because of the disappearance of PVP and PAN, which deterred crystalline agglomeration. All experiments suggested that the calcination at 450°C is expedient in the formation of flexible photocatalytic nanofibers because the anatase phase is formed with the complete removal of PVP in the sheath of the fibers, while PAN is stabilized as the core providing flexibility.

Further, the obtained co-axial fibers were investigated using transmission electron microscopy (TEM), as shown in Figure 6. The core/sheath structure is observed from the as-spun co-axial fiber, although the interface between PVP sheath and PAN core is not clearly defined; hence, the as-spun fibers are composite fibers having amorphous titania embedded within the sheath (see Figure 6(a)). When the co-axial fibers were calcined at 450°C, the crystallization of titania within the sheath of co-axial fibers could be clearly observed. The titania sheath thoroughly covers the PAN core (Figure 6(b)). In addition, the cross section of the calcined titania/PAN co-axial nanofibers (Figure 6(c)) shows that the sheath consists of aggregated titania nanoparticles without polymer. Although the interface between the sheath and the core of the fiber is not well defined, the thickness of the sheath is approximately 20–30 nm. The selected area electron diffraction (SAED) pattern confirms that titania in the sheath is polycrystalline.

Because of the pliability of the fibers, the conventional bending test could not be performed on the products. Instead, the flexibility of the obtained co-axial nanofibers, both before and after calcination, was investigated by Lloyd Universal Testing Machine under

![Figure 5. XRD patterns of as-spun titania(PVP)/PAN co-axial nanofibers (a) comparing with the fibers calcined at 300°C (b), 450°C (c), and 800°C (d) for 2 h.](image)

![Figure 6. TEM images of (a) as-spun titania(PVP)/PAN co-axial nanofibers, (b) the fibers calcined at 450°C for 2 h, (c) cross-section view of the calcined fiber, and (d) SAED pattern of the calcined fiber.](image)
tensile mode. According to the results in Figure 7, the titania/PAN co-axial nanofibers after being calcined at 450°C for 2 h show similar behavior as the as-spun fibers. The flexibility of the nanofibers was indirectly confirmed from the existence of the plastic region in the stress-strain diagram. It should be noted that the titania nanofibers fabricated without PAN core did not yield any result because they were crumbled before any load could be applied, while the calcined titania/PAN co-axial nanofibers retained their flexibility even after the tensile test. The calcination results in a slight decrease in strength of the fibers. Nevertheless, it is proved that the introduction of PAN core provides flexibility to the titania nanofibers.

3.3. Photocatalytic activity of titania/PAN co-axial nanofibers

The photocatalytic degradation of MB was used to investigate the photocatalytic activity of the titania/PAN co-axial nanofibers. The data were fitted to the Langmuir–Hinshelwood kinetic model to obtain the apparent rate constants ($k_{app}$). The experimental data fitted the model well, as shown in Figure 8. The apparent rate constants for the photocatalytic degradation of MB using titania/PAN co-axial nanofibers calcined at 300°C, 450°C, and 800°C were 0.12, 0.17, and 0.03 h$^{-1}$, respectively. When the fibers were calcined at 300°C, although all titania were in photo-active form, i.e. anatase phase, PVP still remained within the sheath of the fibers inhibiting exposure of MB to the titania. As the calcination was increased to 450°C, the apparent degradation rate was enhanced because all PVP were removed while majority of titania was still in anatase phase. At 800°C, however, titania was converted to rutile phase; hence the photocatalytic activity was drastically decreased [16,17].

To ensure that the flexibility of the titania/PAN co-axial nanofibers facilitated the catalyst recovery after the use, the repeated degradation was performed. After being test in MB degradation for 5 h, the catalyst calcined at 450°C was removed from the solution, washed with deionized water, dried at room temperature, and tested for MB degradation again. The degradation data still followed the kinetic model well (see Figure S2) and the apparent rate constant for the degradation using used catalyst was similar to that of the fresh catalyst, i.e. 0.15 h$^{-1}$ versus 0.17 h$^{-1}$. The result indicates no significant loss of titania sheath during the photocatalytic reaction. Moreover, to test whether the core PAN was suffered from photodegradation by titania sheath, the used catalyst was subjected to a tensile test. The results shown in Figure 7 reveal the same stress-strain behavior of the used catalyst, which suggests the retained integrity of the PAN core even after the photocatalytic reaction.

4. Conclusion

Flexible titania nanofibers could be fabricated by introducing polymer core via co-axial electrospinning. PAN is a suitable polymer for being the core because it can withstand high temperature required for the phase transformation of titania into anatase phase. The optimum calcination temperature is needed to ensure complete removal of a polymer required for electrospinning of titania (e.g. PVP in this work), yet it is not high enough to degrade the polymer core. In this work, the flexible titania/PAN co-axial nanofibers that are still photocatalytically active were achieved from the calcination of the titania(PVP)/PAN co-axial nanofibers at 450°C for 2 h. The fibers were 160 nm in average diameter with anatase crystallites formed as sheath of the fibers. The fibers were still flexible in a similar manner as the as-spun fibers.

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