ISSN(Print) 1229-0033
ISSN(Online) 2234-036X
http://dx.doi.org/10.5764/TCF.2013.25.2.94
Textile Coloration and Finishing Vol.25,No.2

〈Research Paper〉

Photocatalytic Activity of Electrospun PAN/TiO_2 Nanofibers in Dye Photodecomposition

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(Received: January 24, 2013 / Revised: February 27, 2013 / Accepted: June 17, 2013)

Abstract: Poly(acrylonitrile) (PAN) nanofibers containing different amounts of titanium dioxide (TiO_2) have been prepared by electrospinning technique. Photocatalytic activity of these electrospun PAN/TiO_2 nanofibers and the effect of TiO_2 content on the photocatalytic efficiency of PAN/TiO_2 nanofibers have been evaluated by monitoring the photodecomposition of fluorescein dye, rhodamine B and methylene blue under UV irradiation with respect to irradiation time. Moreover, the effect of hydrogen peroxide (H_2O_2) on the photocatalytic behavior of PAN/TiO_2 nanofibers has also been investigated. The results showed that PAN/TiO_2 nanofibers are effective photocatalyst and their photocatalytic efficiency increases with the increase of TiO_2 content in the PAN/TiO_2 nanofibers. It is also observed that the presence of H_2O_2 significantly enhances the photocatalytic ability of PAN/TiO_2 nanofibers. The morphology and the photocatalytic behavior of the PAN/TiO_2 nanofibers containing different amounts of TiO_2 nanoparticles have been investigated by field-emission scanning electron microscopy (FE-SEM) and UV/Visible spectroscopy, respectively.

Keywords: *electrospinning, poly(acrylonitrile), titanium dioxide, nanofibers, photocatalysis*

1. Introduction

Among the various metal oxides, extensive efforts are given to the research on titanium dioxide (TiO_2) for its wide range of applications such as sunscreen, photocatalyst, sensor, solar cell, hydrogen storage, organic waste management etc.[1-5]. Recently, titanium dioxide (TiO_2) based photocatalysts have attracted much interest to the environmental scientist for their potential application in environmental remediation by degrading many organic pollutants[4-7]. Electrospinning of TiO_2 nanoparticles with polymer solution, such as polyacrylonitrile (PAN) solution, is preferred to immobilize it on nanofibers in order to facilitate the photocatalyst recovery process, prevent particles agglomeration and increase the photocatalytic activity by increasing surface area which overcome the difficulties of applying pure TiO_2 nanoparticles as a photocatalyst[4,8]. Deposition of TiO_2 nanoparticles on the surfaces of nanofibers by electrospinning allow them better exposure to radiation and consequently, increased their photocatalytic activity[8].

Good stability, superior fiber-forming and mechanical properties have made PAN a potential candidate for fabricating nanofibers in its pristine, blend or composite forms by electrospinning technique[4,8-10].

Electrospinning is a widely used efficient technique to fabricate polymer nanofibers with excellent architectures and advanced properties. These nanofibers have wide range of applications such as separation filters, sensors, protective clothing, catalysis reaction, wound dressing materials, tissue scaffold, drag delivery, etc.[11-16]. Though the principle of this process is simple but solution properties and process parameters have a great influence on the structures and properties of the electrospun nanofibers[17-21].

In this work we have prepared PAN/TiO_2 nanofibers containing different amount of TiO_2 and investigated their photocatalytic behaviors in degrading three organic dyes such as fluorescein, rhodamine B, and methylene blue. Effect of TiO_2 content on the degradation process has been evaluated by using variable amount of TiO_2 in PAN/TiO_2 nanofibers. In addition, influence of hydrogen peroxide (H_2O_2) upon the catalytic performance of PAN/TiO_2 has also been studied. The morphologies and morphological changes of the

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prepared PAN/TiO_2 nanofibers varying TiO_2 content were observed by field-emission scanning electron microscopy (FE-SEM). The photocatalytic performance of electrospun PAN/TiO_2 nanofibers on the photodecomposition of above mentioned dyes under UV light were evaluated by UV-visible spectroscopy.

2. Experimental

2.1 Materials

Poly(acrylonitrile) (PAN), rhodamine B, fluorescein and methylene blue were purchased from Aldrich, N, N′-dimethyl formamide (DMF), hydrogen peroxide (H_2O_2) and methyl alcohol were obtained from Duksan Pure Chemicals Co. Ltd. and TiO_2 nanoparticles (P-25, average particle diameter = 30 nm) was collected from Degussa. All of the chemicals were used as received without further purifications.

2.2 Preparation of PAN/TiO_2 blend solution for electrospinning

10 weight % of PAN was dissolved in DMF under magnetic stirring for 2 hours at room temperature. Variable amounts of TiO_2 were dispersed separately into the PAN solution and stirring was continued for another 1 hour for complete dispersion of TiO_2.

Different PAN/TiO_2 mixing ratios were maintained during different experiments.

2.3 Electrospinning

During electrospinning, a high voltage power was applied to the PAN solution contained in a syringe via an alligator clip attached to the syringe needle. The applied voltage was 15 kV. The solution was delivered to the blunt needle tip via syringe pump to control the solution flow rate. The electrospun nanofibers were collected on an electrically grounded aluminum foil placed at 15 cm vertical distance to the needle tip[22,23].

2.4 Characterization

The morphologies of the electrospun PAN/TiO_2 nanofibers containing different amount of TiO_2 nanoparticles were observed with a field-emission scanning electron microscope (FE-SEM) (JEOL, model JSM-6380LV, Japan) after gold coating. Photocatalytic efficiency of the electrospun PAN/TiO_2 nanofibers and TiO_2 only nanoparticles were investigated by irradiating UV light (365 nm) from a 300 W lamp of a UV-visible Spectrophotometer (UV-1700, Simadzu Co., Japan). Three organic dyes were used to perform photocatalytic experiment under UV-irradiation. 0.2 g of PAN/TiO_2 nanofibers were placed into 200 ml of fluorescein dye solution (10^{-3} mol/L) in methanol, rhodamine B dye solution (10^{-5} mol/L) in water, and methylene blue solution (5 x 10^{-5} mol/L) in methanol, separately. 0.1 g of TiO_2 only nanoparticles were used to compare with the photocatalytic efficiency of the electrospun PAN/TiO_2 nanofibers (1:1 w/w) in degrading fluorescein dye solution (10^{-3} mol/L) in methanol.

3. Results and Discussion

Figure 1 shows the FE-SEM images of electrospun PAN/TiO_2 nanofibers containing variable amount of TiO_2. The insets on each image represent their corresponding high magnification image and the frequency distribution in terms of average fiber diameters (nm). The PAN concentration was 10 wt. % throughout the experiment. These images reveal the effect of TiO_2 contents on the fiber's morphology. Uniform PAN only nanofibers with smooth surface are observed in Figure 1 (a). Figure 1 (b) demonstrates that the fiber surfaces become rough when an equivalent amount (w/w) of TiO_2 nanoparticles (PAN/TiO_2 mixing ratio = 1:1) is added and TiO_2 nanoparticles remain clung to the surfaces of PAN nanofibers. The fiber surface become rougher and the average diameters increase with the increasing amount of TiO_2 nanoparticles added. The huge amount of TiO_2 nanoparticles causes an aggregation and hence they stack on the surfaces of nanofibers. Consequently, some parts of a fiber become thick and some remains narrow like PAN only nanofibers. These results indicate that mixing a comparable amount (w/w) of PAN and TiO_2 nanoparticles leads to the formation of PAN/TiO_2 nanofibers with a regular size and shape.

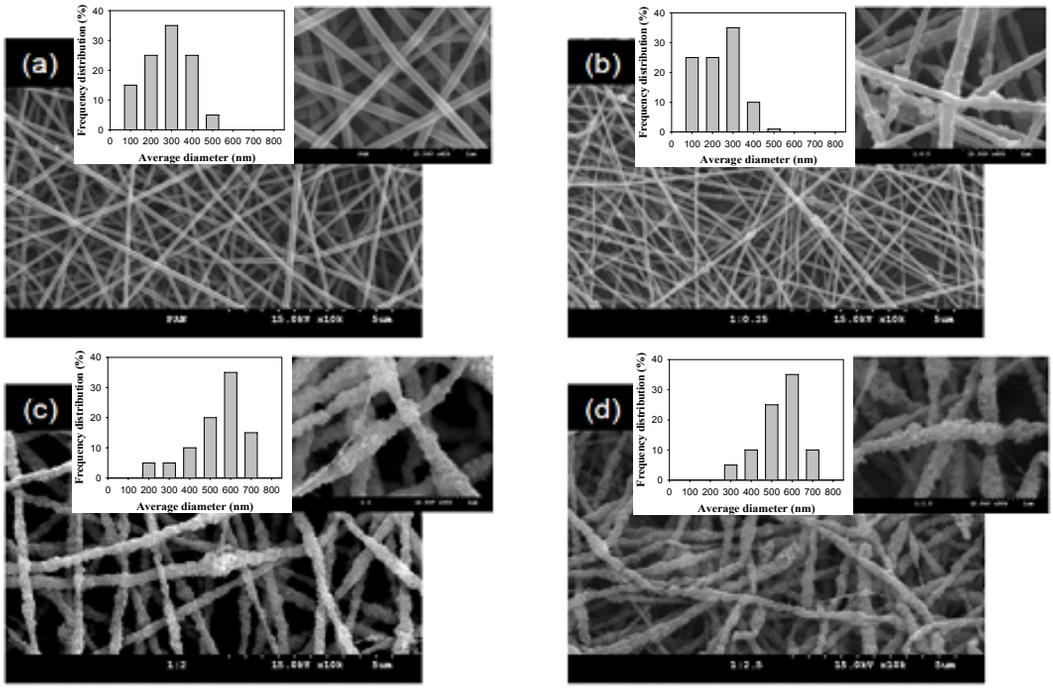

Figure 1. FE-SEM images of PAN/TiO_2 nanofibers which were electrospun with various PAN/TiO_2 mixture ratios of (a) PAN/TiO_2 = 1:0, (b) PAN/TiO_2 = 1:1, (c) PAN/TiO_2 = 1:2 and (d) PAN/TiO_2 = 1:2.5 (PAN solution concentration = 10 wt. %, TCD = 15 cm and applied voltage = 15 kV).

A large excess of TiO_2 nanoparticles causes an irregular morphology with a very uneven surface which is clearly seen in Figure 1 (c) and (d).

The photocatalytic performance of PAN/TiO_2 composite nanofibers and TiO_2 only nanoparticles were compared with fluorescein dye photocatalyzed by PAN/TiO_2 nanofibers and TiO_2 only nanoparticles separately. The results are compared by plotting the conversion rate of fluorescein dye with respect to exposure time in Figure 2 (upper part). In addition, the images of fluorescein dye with PAN/TiO_2 nanofibers and TiO_2 nanoparticles are compared in the bottom part of Figure 2. The amount of TiO_2 in the PAN/TiO_2 nanofibers (1:1 w/w) is a fraction of total mass (0.2 g) so the amount of TiO_2 in PAN/TiO_2 nanofibers is assumed same (0.1 g) of pure TiO_2 nanoparticles. It is observed from the Figure 2 that the PAN/TiO_2 nanofibers show higher dye conversion efficiency than pure TiO_2 nanoparticles. The conversion rate implies to the degradation of dye due to photocatalysis. It can be seen from Figure 2 that about 90% of dye was degraded by PAN/TiO_2 nanofibers in 3.5 h of

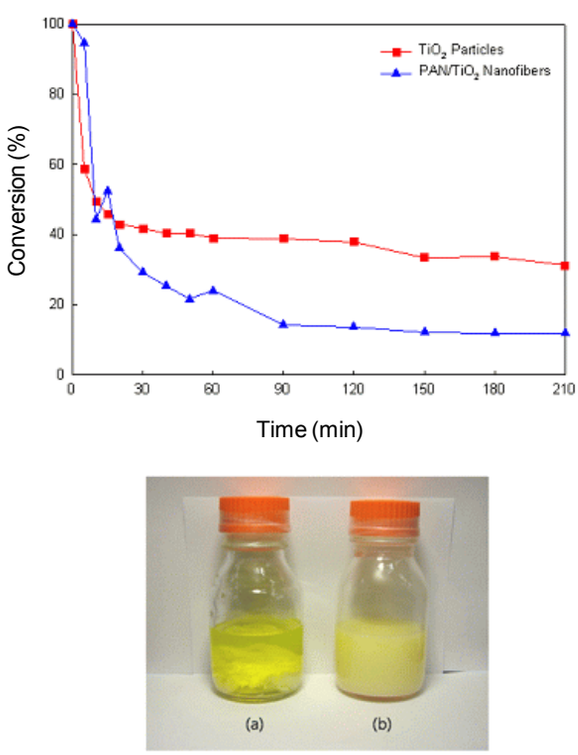

Figure 2. Photocatalytic degradation of fluorescein by TiO_2 nanoparticles and PAN/TiO_2 nanofibers (top), and image of fluorescein dye solution containing (a) PAN/TiO_2 nanofibers and (b) TiO_2 nanoparticles (bottom).

irradiation. The conversion caused by TiO_2 nanoparticles is only 65% at the same time. The less photocatalytic performance of TiO_2 nanoparticles was because of high agglomeration tendency of TiO_2 nanoparticles. In PAN/TiO_2 nanofibers TiO_2 nanoparticles are remaining distributed within polymer matrix and consequently, show better photocatalytic performance due to the maximum exposure at expanded surface area. These results indicate that PAN/TiO_2 composite nanofibers are more effective photocatalyst than TiO_2 nanoparticles.

In order to understand the effect of TiO_2 content on the photodecomposition rate, fluorescein dye was photocatalyzed by PAN/TiO_2 nanofibers containing variable amounts of TiO_2 nanoparticle (PAN/TiO_2 mixing ratios = 1:0.5, 1:0.75 and 1:1 w/w) and the conversion rate of fluorescein dye with respect to exposure time is plotted in Figure 3. It can be seen that the conversion rate after 2.5 hours of photocatalysis is 65% while PAN/TiO_2 (1:0.5) nanofibers were applied and it reaches up to 90% in case of PAN/TiO_2 (1:1) nanofibers. The corresponding PAN/TiO_2 mixing ratios are shown within the bracket. These results indicate that higher TiO_2 content in PAN/TiO_2 nanofibers accelerates the photocatalytic degradation process. It should be noted that higher amount of TiO_2 only nanoparticles does not show better photocatalytic performance due to their agglomeration but as they remain distributed in PAN/TiO_2 nanofibers so the amount of TiO_2 could give an effect on the photocatalytic degradation process.

The photocatalytic degradation of fluorescein dye by using PAN/TiO_2 nanofibers under UV light has been investigated at different irradiation times and the corresponding time effluence of the absorption spectra of the degraded dye solution is shown in Figure 4 (a). The characteristic absorption peak intensities of fluorescein dye at 453 nm and 485 nm decreased gradually with the irradiation time elapsed. Also, a slight red shift is observed with the increasing irradiation time. On the other hand, the color change of dye solution due to photocatalytic degradation has been shown by digital images taken at different irradiation

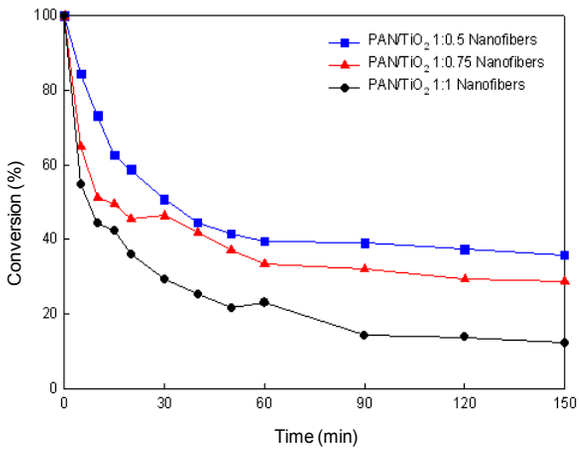

Figure 3. Photocatalytic degradation of fluorescein by PAN/TiO_2 nanofibers containing different amount of TiO_2 nanoparticles.

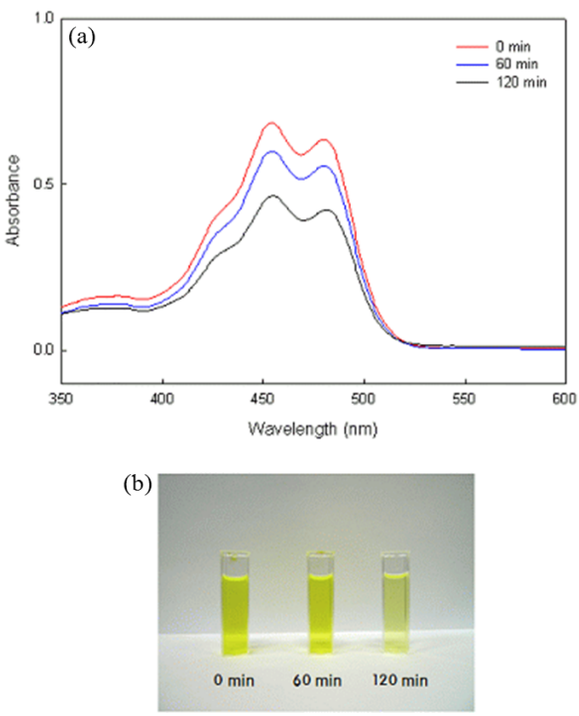

Figure 4. (a) Time effluence on photocatalytic degradation of fluorescein dye using PAN/TiO_2 nanofibers under UV irradiation. (b) The digital photographs of dye solution at different irradiation times to show color change due to photocatalytic degradation of fluorescein.

time. The decoloration of dye solution with irradiation time is clearly seen in Figure 4 (b). These results indicate that as a photocatalyst, PAN/TiO_2 nanofibers are effective enough to degrade fluorescein dye rapidly.

Rhodamine B dye was also photocatalyzed by PAN /TiO_2 nanofibers containing variable amounts of TiO_2 nanoparticle (PAN/TiO_2 mixing ratios = 1:0.5, 1:0.75 and 1:1 w/w) to investigate the effect of TiO_2 content on the photocatalytic degradation of rhodamine B. Figure 5 demonstrates the conversion rate of rhodamine B dye with respect to exposure time. In case of rhodamine B, PAN/TiO_2 (1:0.5) nanofibers containing lowest amount of TiO_2 nanoparticles shows only 47% conversion after 2.5 hours of photocatalysis.

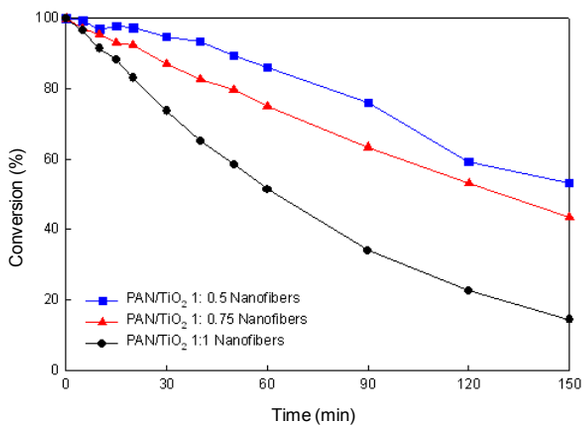

Figure 5. Photocatalytic degradation of rhodamine B by PAN/TiO_2 nanofibers containing different amount of TiO_2 nanoparticles.

On the other hand, the conversion rate reaches to 87 % at the same time by PAN/TiO_2 (1:1) nanofibers containing the highest amount of TiO_2 nanoparticles in this work. These results indicate that like fluorescein dye, higher TiO_2 content in PAN/TiO_2 (1:1) nanofibers enhances the photodecomposition process. Time influence of the absorption spectra of the degraded rhodamine B dye is presented in Figure 6 (a). The characteristic absorption peak intensity at 552 nm significantly decreased within 2 hours of UV irradiation. Also, a slight blue-shift is observed with the increasing irradiation time. On the other hand, the color change of dye solution at different irradiation time due to photocatalytic degradation has been shown in Figure 6 (b) by digital images. The degradation of rhodamine B dye is clearly understood from the color change of dye solution with irradiation time and it has been almost colorless within 2 hours of irradiation.

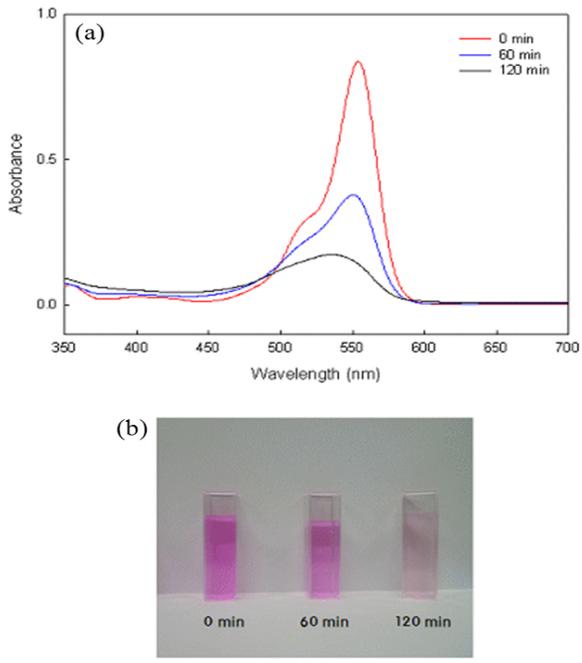

Figure 6. (a) Time effluence on photocatalytic degradation of rhodamine B using PAN/TiO_2 nanofibers under UV irradiation. (b) The digital photographs of dye solution at different irradiation times to show color change due to photocatalytic degradation of rhodamine B.

These results indicate that PAN/TiO_2 nanofibers degrade rhodamine B dye efficiently due to their excellent photocatalytic properties.

Photocatalytic degradation of methylene blue by PAN/TiO_2 nanofibers has been conducted following the way mentioned above and the decrease of dye concentration with exposure time is plotted as conversion rate vs. irradiation time in Figure 7.

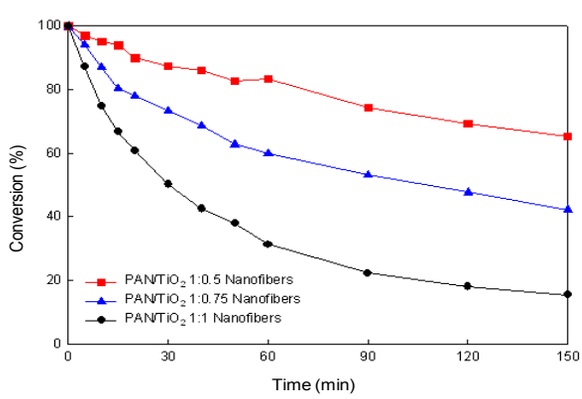

Figure 7. Photocatalytic degradation of methylene blue by PAN/TiO_2 nanofibers containing different amount of TiO_2 nanoparticles.

The effect of TiO_2 content on the degradation process is the same as found in case of fluorescein and rhodamine B. The highest TiO_2 content in PAN/TiO_2 nanofibers converts 85% of methylene blue within 2.5 hours of UV irradiation. The influence of irradiation time on the degradation process has been evaluated by the decrease in characteristic absorption peak intensity at 662 nm with the increasing irradiation time which is shown in Figure 8 (a). The color change of the degraded dye solution after 2 hours of UV irradiation shown in Figure 8 (b) indicates a slow degradation process which implies that PAN/TiO_2 nanofibers work as a mild photocatalyst. From the above discussion, it is observed that PAN/TiO_2 nanofibers with 1:1 (w/w) mixing ratios show highest photocatalytic efficiency with rhodamine B.

Hydrogen peroxide (H_2O_2) is a powerful oxidizer and used in some photocatalytic degradation processes as a co-oxidant with TiO_2. Aqueous H_2O_2 produces powerful hydroxyl radicals under UV irradiation[24].

Rhodamine B dye was photocatalyzed by PAN /TiO_2 (1:0.75) in presence of H_2O_2 and the conversion rate is plotted against irradiation time in Figure 9. The effects of H_2O_2 and UV irradiation on the photocatalytic process have been evaluated by comparing the results obtained by using PAN/TiO_2 (1:0.75) nanofibers in presence or absence of H_2O_2 and UV irradiation.

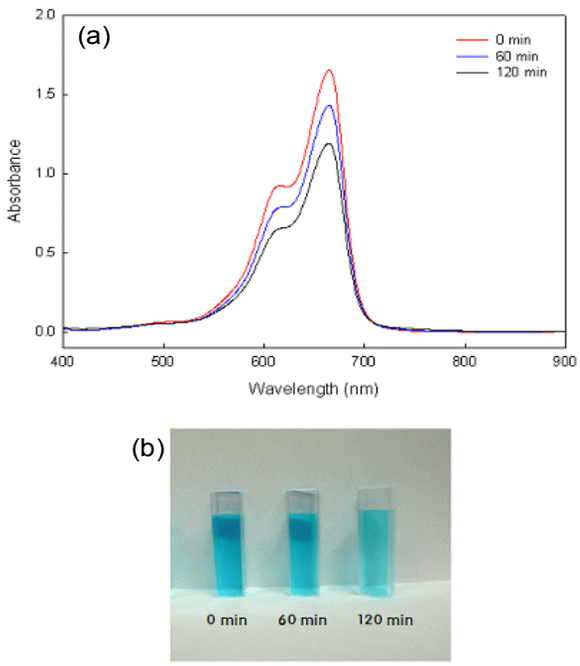

Figure 8. (a) Time effluence on photocatalytic degradation of methylene blue using PAN/TiO_2 nanofibers under UV irradiation. (b) The digital photographs of dye solution at different irradiation times to show color change due to photocatalytic degradation of methylene blue.

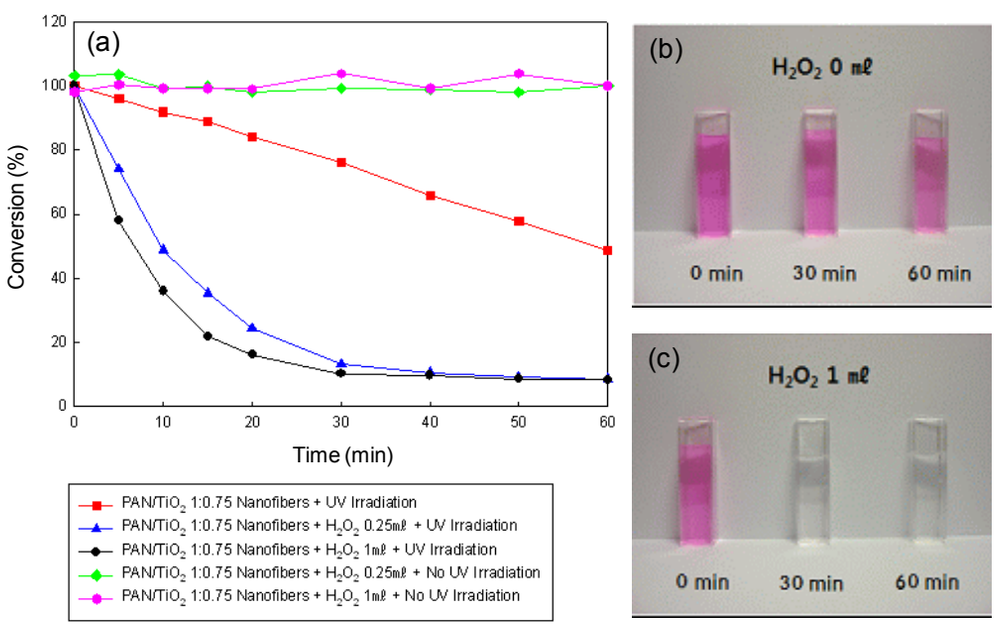

Figure 9. Photocatalytic degradation of rhodamine B by PAN/TiO_2 (1:0.75) nanofibers in presence of different amount of H_2O_2.

It can be seen from the Figure 9 (a) that ~52 % conversion is obtained by PAN/TiO_2 (1:0.75) nanofibers within 1 hour of UV irradiation but it increases up to 90% in presence of H_2O_2. Though much amount of H_2O_2 enhances the conversion rate but after 1 hour of UV irradiation the same result is obtained. On the other hand, there is no ultimate conversion observed in absence of UV irradiation. This result indicates that H_2O_2 enhances the photocatalytic process and hence conversion rate increased under UV irradiation. The color change of the degraded dye solution after 1 hour is presented in Figure 9 (b) and (c). Within 30 minutes of UV irradiation rhodamine dye solution become colorless due to complete degradation which is resemble to the decrease of dye concentration shown in Figure 9 (a). These results indicate that regardless of the amount, H_2O_2 accelerates the photocatalytic efficiency of PAN /TiO_2 nanofibers under UV irradiation.

4. Conclusion

Photocatalytic efficiency of electrospun PAN/TiO_2 nanofibers containing different TiO_2 content have been investigated on degrading three organic dyes such as fluorescein, rhodamine B and methylene blue under UV irradiation. Their morphologies have also been studied and it is observed that the more TiO_2 nanoparticles in the PAN/TiO_2 nanofibers the large fiber diameter with irregular sizes, shapes and rougher surfaces. Mixing a comparable amount of PAN and TiO_2 nanoparticles leads to a uniform PAN/TiO_2 nanofibers. PAN/TiO_2 nanofibers are found more effective photocatalyst than TiO_2 only nanoparticles. Increased amount of TiO_2 nanoparticles in PAN/TiO_2 nanofibers increase their photocatalytic performance. Addition of H_2O_2 with PAN/TiO_2 nanofibers accelerates photocatalytic efficiency regardless of H_2O_2 amount. It can be concluded that PAN/TiO_2 nanofibers could be used as an effective photocatalyst to degrade pollutant from the environment.

Acknowledgement

This research was supported by Kyungpook National University Research Fund, 2010.

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