

전자선 조사에 의한 PAN/TiO₂ 전기방사 나노섬유 제조 및 특성분석

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Preparation and Characterization of Electrospun PAN/TiO₂ Fiber Mat by Electron Beam Irradiation

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초록: 본 연구에서는 전자선 조사가 PAN/TiO₂ 나노섬유의 광촉매 활성에 미치는 영향을 평가하고자 하였다. PAN/TiO₂ 나노섬유는 polyacrylonitrile (PAN)과 titanium(IV) butoxide (Ti(OBu)₄)를 출발원료로 하여 다양한 고분자 용액 농도, 전기장 세기, 고분자 용액의 공급속도 등의 조건하에서 전기방사하여 얻을 수 있었다. Titanium(IV) butoxide 농도가 증가함에 따라 방사물은 비드 형태에서 섬유상으로 변화하였으며, 전기장의 세기가 증가함에 따라 섬유의 직경은 감소하였다. 제조된 나노섬유는 가교결합을 유도하고 광촉매 활성을 향상시키고자 전자선 가속기를 이용해 조사되었다. 전자선 조사 후 메틸렌 블루 용액과의 반응에서 시료의 광촉매 활성은 반응 3시간 후 조사하지 않은 시료에 비해 175%의 높은 광분해 특성을 보였으며, 휘발성 유기용매에 대한 높은 분해특성을 나타내었다.

Abstract: In this study, PAN/TiO₂ fiber mats were fabricated from polyacrylonitrile (PAN) and titanium(IV) butoxide (Ti(OBu)₄) by an electrospinning method with various solution concentrations, applied voltages and solution flow rates. The fiber mats were irradiated with an electron beam to induce structural crosslinking and enhance photocatalytic activity. As a result, uniform and bead-free fibers without pits or cracks on surface were obtained at 5 wt% of Ti(OBu)₄ solution with 15 kV and 0.02 mL/min flow rate. The PAN/TiO₂ fiber mats were irradiated with an electron beam of 1.14 MeV acceleration voltage, 4 mA of current and 1×10^4 kGy. Electron beam irradiation was enhanced the photocatalytic activity of PAN/TiO₂ nano fiber mat. The photocatalytic activity of the PAN/TiO₂ fiber mat was analyzed by degradation of methylene blue and volatile organic compounds.

Keywords: electron beam, electrospinning, polyacrylonitrile, TiO₂, photocatalytic activity.

Introduction

TiO₂ is known as one of the most stable and highly reactive photocatalyst. TiO₂ decompose toxic compounds to non-toxic inorganic compounds, such as carbon dioxide, water, ammonium or nitrates, and chloride ions.¹⁻⁴ However, its utilization was limited due to the need of UV light excitation and low efficiency in catalytic reaction limits its utilization. For this reason, a lot of efforts have been made to enhance its photodegradation efficiency such as doping of dyes or metal ions. The addition of metal ions may

attribute to the rapid transfer of photogenerated electron from semiconductor to the noble metal particles, resulting in the effective separation of the electrons and holes. Electron beam irradiation is an efficient method of reducing metal ions, which has been widely used for the synthesis of metal nanoparticles and enhancement of certain properties of oxides such as optical band gap. Also, TiO₂ is usually used as powder in solution. However, there are disadvantages to apply powder form such as low efficiency of light use, difficulty of stirring during reaction and separation after reaction. In order to achieve rapid and efficient decomposition of organic pollutants and easy manipulation in a total catalytic process, it may be effective to prepare photocatalyst with high surface areas to concentrate the pollutants around the photocatalyst. This problem could be potentially solved using woven struc-

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tures such as mats due to their high active surface areas.⁵⁻⁸

The electrospinning method provides an opportunities to obtain inorganic/organic hybrid nanocomposites and highly active surface area and electrospun fibers have received a great deal of attention for their wide application range in the field of tissue engineering, sensors, protective clothing, high-performance filters, electrochemical photovoltaic electrodes and carbon materials.^{9,10} Electrospinning is a simple and inexpensive technique for producing polymeric fibers with diameters ranging from nano-sized to submicron.¹¹ When the electrical force is higher than the surface tension of the solution, a charged jet are generally collected in the form of randomly oriented mats. The properties of the fibers depend on the properties of the polymer and the electrospinning process parameters, such as the average molecular weight of the polymers and solvents, the viscosity and conductivity of the solution, the strength of the applied electric field, and the deposition distance.^{12,13} PAN, a matrix of PAN/TiO₂ mat, has been intensively studied due to its high dielectric constant desirable for electrospinning.

In this study, we fabricated PAN/TiO₂ fiber mat with highly active surface area by electrospinning technique for photocatalytic filter. Filtering application is affected by the fiber size. Therefore, we investigate the systematic parameters such as a solution concentration, applied voltage and solution flow rate, and their individual and interactive effects on the diameter for high surface area. The photocatalytic activity of the PAN/TiO₂ fiber mat was analyzed by degradation of methylene blue and volatile organic compounds.

Experimental

Materials. PAN (average molecular weight = 1.5×10^5 g/mol, density = 1.18 g/cm³, Aldrich, USA) and (Ti(OBu)₄) (97%, Aldrich, USA) were used as precursors. *N,N*-dimethylformamide (DMF, 99%, Showa, Japan) was used as a solvent without any further purification. Acetic acid (97%, Showa, Japan) was used as a complex agent to control the rate of hydrolysis. Methylene blue (Aldrich, USA) was selected as a model pollutant for photodegradation.

Preparation of PAN/TiO₂ Fiber Mat by an Electrospinning Method. The polymer solutions were prepared by dissolving PAN in DMF with 1:9 ratio by weight with different Ti(OBu)₄ weight ratio, 5, 10 and 15 wt%. Acetic acid was added with a mole ratio of acetic acid to Ti(OBu)₄ was 2:1 and allowed to react. TiO₂ can be reproducibly obtained when the hydrolysis of Ti(OBu)₄ is performed in the presence of acetic acid. A homogenous PAN/TiO₂ solution was obtained by heating at 80 °C for 4 h with stirring.

The apparatus for the electrospinning process include a glass syringe, a stainless steel needle, a syringe pump, a high voltage power supply, and a collector. The polymer solution was drawn horizontally from the needle tip (inner diameter (ID) = 0.152 mm) and a distance from tip to collector was 10 cm. A high voltage power supply (12-18 kV) was employed to generate the electric field. A syringe pump was utilized to control the flow rate (0.02-0.08 mL/min) of the polymer solution droplet. After the solvent evaporated, the PAN/TiO₂ mat deposited on the collector form a non-woven mat, which was dried at 80 °C under a vacuum for 12 h.

Electron Beam Irradiation on PAN/TiO₂ Fiber Mat. The PAN/TiO₂ fiber mat was placed in a stainless still chamber and sealed after the introduction of N₂ gas. Electron beam irradiation was carried out at a dose rate of 1.4×10^4 kGy/h using accelerator at KAERI. The electron beam was generated with a 1.14 MeV acceleration voltage, 4 mA of current and 1×10^4 kGy absorbed dose.

Photocatalytic Activity Test. The photocatalytic activity of the PAN/TiO₂ fiber mat was determined from the decomposition rate of methylene blue in a dark, aqueous chamber. A 50 W lamp was used as a UV light source (365 nm) to irradiate the sample in a cylindrical glass vessel (diameter = 8 cm, height = 10 cm). The reaction was prepared by using known weight and size (100 mg, $5 \times 5 \times 0.01$ cm³) of PAN/TiO₂ mat into the beaker containing 300 mL of an aqueous solution of methylene blue (10 ppm). Approximately 3 mL of the mixture was collected at 10, 20, 30, 60, 120, 180, 240, 300, 360, 420 and 480 min after UV irradiation. Changes in the maximum absorption at 365 nm in the UV-Vis spectrum versus irradiation time were recorded, reflecting the change in methylene blue concentration during photocatalysis.

The photocatalytic degradation of the PAN/TiO₂ mat was evaluated by the degradation of a standard gas of volatile organic compounds (VOCs; toluene, benzene, ethylbenzene, xylene, styrene) in a photochemical reactor. The PAN/TiO₂ mat was irradiated by UV light through the quartz cover and the injected gas (1 mL) was continuously stirred during the photocatalytic reaction. A gas chromatograph equipped with a thermal conductivity quantitatively measured the concentration of residual VOCs in the reaction vessel. All experiments were carried out more than three times at room temperature (25±1 °C) and the standard deviations were within 5 % in each photodegradation test.

The solution viscosity measurements were performed using a Brookfield DV-II programmable viscometer. Electrical conductivity was measured with a HD 2156.2 conductivity meter at room temperature. The microstructure of the PAN/TiO₂ fiber mats was observed with a field emission scanning

electron microscope (Sirion, FEI, Netherlands). The average diameter of electrospun PAN/TiO₂ fiber mats were determined by measuring the diameters of the fibers at 100 different points. The compositions of the PAN/TiO₂ fiber mats were analyzed using an energy dispersive spectroscopy (ISIS, OXFORD, UK). Photoluminescence (PL) characterization of the obtained PAN/TiO₂ mats is performed at room temperature by exciting the sample with 325 nm He-Cd laser. The photocatalytic activity of PAN/TiO₂ fiber mats were analyzed UV vis spectrophotometer (Optizen 2120 UV, Mecasys, Korea) and gas chromatography.

Results and Discussion

Viscosities and conductivities of polymer solution with different Ti(OBu)₄ concentration of 0, 5, 10 and 15 wt% were shown in Figure 1. The viscosities of polymer solution was increased with increasing Ti(OBu)₄ concentration. Depending on the nature of the fluid and the polarity of applied potential, free electrons, ions or ion pairs may be generated as charge carriers in the fluid. The generation of charge carriers can be very sensitive to solution impurities. Therefore the solution conductivity is one of the main parameters in the electrospinning process since viscous polymer solution is being stretched due to the repulsion of the charges the present on its surface, and more charges can be carried at high solution conductivity. The increase in conductivity of solution results in production of bead-free uniform and thinner fibers since the polymer solution is subjected to more stretching under the high electric field. The conductivities of PAN/DMF solution with different Ti(OBu)₄ concentration 5, 10 and 15 wt% was 87.5, 74.6 and 58.3 μ S, respectively (Figure 1). Increasement of the solution conductivity was

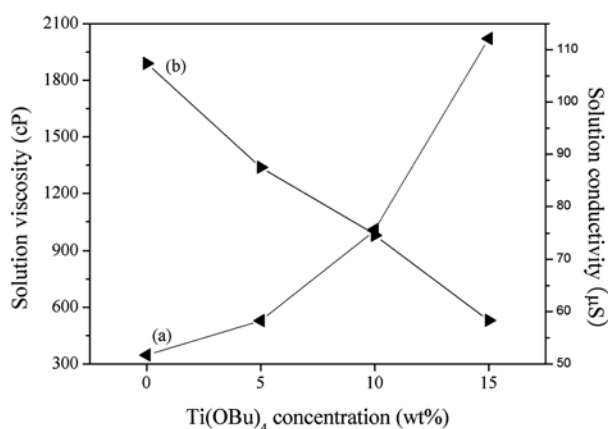


Figure 1. (a) Solution viscosity; (b) solution conductivity variation of PAN/DMF solutions with different Ti(OBu)₄ concentrations.

decreased with Ti(OBu)₄ concentration. The content of Ti(OBu)₄ concentration decreases the charge density of polymer solution, which causes a lower repulsion and a lower bending instability during electrospinning process.¹⁴

The three parameters that significantly affected the quality and dimensions of electrospun fibers were the composition of the polymer solution, applied voltage and the flow rate to the spinneret.

Figure 2 shows the SEM images of electrospun PAN/TiO₂ fiber mat from the PAN/DMF solutions with different Ti(OBu)₄ concentrations from 0 to 15 wt%. It was shown that 3D woven fiber mat was obtained. The other factors were fixed such as applied voltage (15 kV), flow rate (0.02 mL/min). The electrospun PAN/TiO₂ fiber mat from the PAN/DMF solutions with 5 wt% of Ti(OBu)₄ was uniform with an average diameter of 512 nm, which is about 60 nm bigger than PAN fiber mat. The uniform morphology was changed to beaded morphology, when the concentration of Ti(OBu)₄ was 10 wt%. In case of PAN/DMF solution with 15 wt% of Ti(OBu)₄, amounts of debris are observed. The morphology of fibers and their diameters were strongly influenced by the composition of the polymer solutions. The content of Ti(OBu)₄ in PAN/DMF solutions tended to increase the viscosity of polymer solution. The smaller diameters obtained with the lower viscosities are related to the higher mobility of the polymer chains and the stronger instabilities during electrospinning, which together enable and induce the higher stretching of the polymer solution jet. Highly viscous polymer solutions cannot be as easily stretched as a low viscosity dilute solution can be. The average diameters of PAN/TiO₂ fiber mat were 446, 512, 772, and

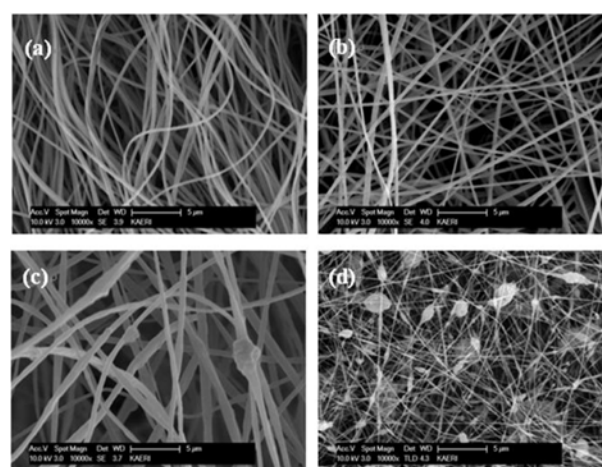


Figure 2. SEM images of electrospun PAN/TiO₂ fibers from PAN/DMF solutions with different Ti(OBu)₄ concentration: (a) 0; (b) 5; (c) 10; (d) 15 wt%.

174 nm as increasing the $\text{Ti}(\text{OBu})_4$ concentration from 0 to 15 wt%, respectively.

Applied voltage can be considered the most essential parameter in electrospinning, since it initiates the jetting and causes instabilities, which stretch the jet. The effects of the electric voltage from 12 to 18 kV were shown in Figure 2. Concentration of $\text{Ti}(\text{OBu})_4$ (5 wt%), flow rate (0.02 mL/min) and TCD (10 cm) were fixed. The applied voltage determines the average strength of the electric field together with the distance between the tip and the collector. Beaded morphology was observed at 12 kV. All the fibers showed exactly the same structural similarity of PAN fibers as shown in Figure 3, when applied voltage was 15 kV. When the voltage is further increased (18 kV) the diameter of PAN/ TiO_2 fiber mat was decreased. With a high electric field (18 kV), the solution is highly charged and high electric force overcomes the surface tension of solution, resulting in a decrease diameter. The solution will be removed from the capillary tip more quickly as the jet is ejected from the Taylor cone. This results in an increase of the fiber diameter. The average diameter of PAN/ TiO_2 fiber mat with different applied voltage of 12, 15 and 18 kV were 812, 512 and 208 nm, respectively. When increasing the electric field, the average diameter of PAN/ TiO_2 fibers decreased.

Effects of flow rate of electrospun PAN/ TiO_2 fiber mat from PAN/DMF solution with 5 wt% of $\text{Ti}(\text{OBu})_4$ polymer solution were shown in Figure 4. Applied voltage was 15 kV. At flow rate 0.02 mL/min, uniform circular shape and bead-free fibers were obtained. But, with a increasing the

flow rate, diameter of PAN/ TiO_2 fiber mats were increased and surface roughness of the fiber was increased. By increasing the flow rate at 15 kV, average diameter of PAN/ TiO_2 fiber increased due to the decrease of the charge in the unit volume of the solution. The average diameter of PAN/ TiO_2 fiber mat with flow rate 0.02, 0.04 and 0.08 mL/min were 512, 634 and 851 nm, respectively.

To observe detailed structures that could not be observed clearly by SEM analysis, an EDX technique was applied to evaluate elemental content by analyzing corresponding SEM images. As shown in Figure 5 the elemental composition of C, O and N was 69.5, 2.4 and 6.5 wt%, respectively in the

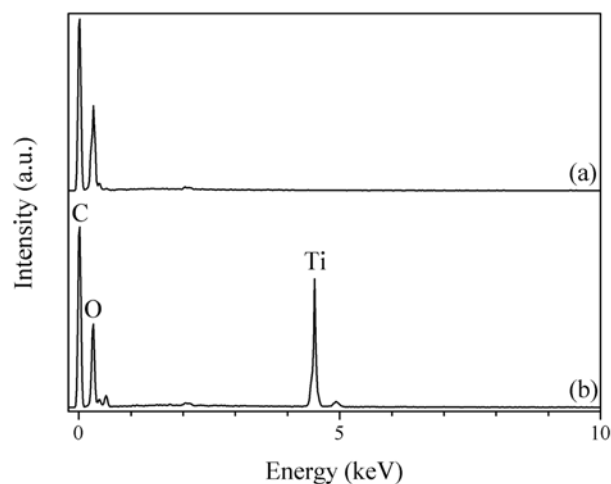


Figure 5. EDX spectra of electrospun (a) PAN; (b) PAN/ TiO_2 fibers.

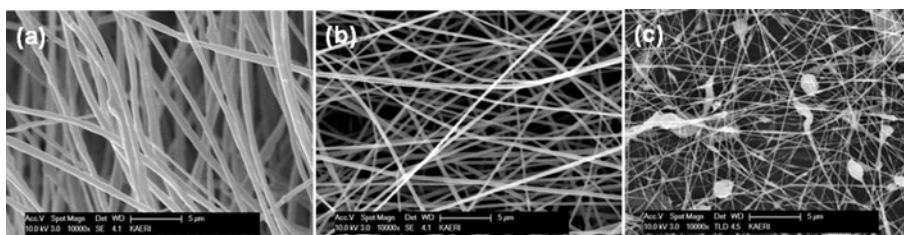


Figure 3. SEM images of the electrospun PAN/ TiO_2 fibers from PAN/DMF solutions with 5 wt% $\text{Ti}(\text{OBu})_4$ at different applied voltage: (a) 12; (b) 15; (c) 18 kV.

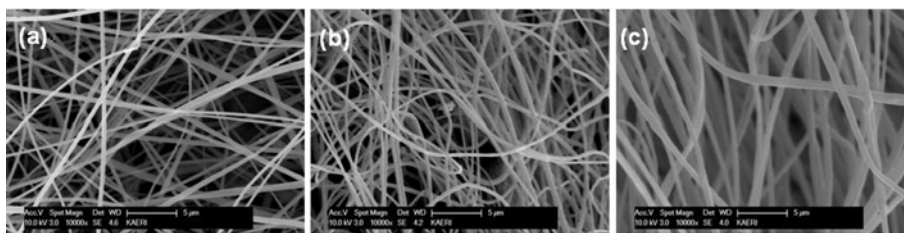


Figure 4. SEM images of the electrospun PAN/ TiO_2 fibers from PAN/DMF solutions with 5 wt% $\text{Ti}(\text{OBu})_4$ concentration at different flow rate: (a) 0.02; (b) 0.04; (c) 0.08 mL/min.

prepared PAN fiber mat. On the other hand, the elemental composition of C, O, N and Ti was 46.2, 21.43, 6.36 and 23.56 wt%, respectively in the prepared PAN/TiO₂ fiber mat.

It is well known and demonstrated that photoluminescence (PL) is high sensitive to the abundance of surface states in the band gap. Figure 6 shows the PL spectra of different electron beam irradiation dose. The luminescence band (550 nm) is assigned to recombination of self-trapped excitons (STEs). The STE in PAN/TiO₂ mat originates from band-to-band excitation where the excited electron and the remaining hole create a local deformation of TiO₆ octahedra and thus localize themselves into a state in the energy gap of TiO₂. The STE is supposed to be localized on a TiO₆ octahedron which is the unit structure of anatase. For single crystals the STE emission is strongly polarized in the direction perpendicular to the c-axis of the crystal and independent of the polarization of the excitation light. The rather small decay time

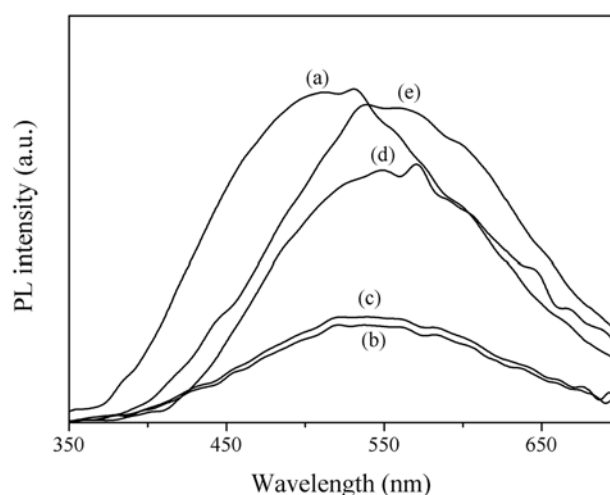
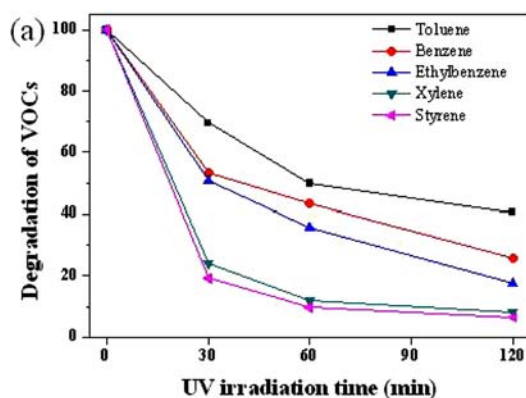


Figure 6. Photoluminescence spectra of PAN/TiO₂ mat by an electron beam irradiation: (a) 0; (b) 1×10^3 ; (c) 2×10^3 ; (d) 5×10^3 ; (e) 1×10^4 kGy.



(in nanosecond scale) and relatively high intensity of emission indicates a rapid formation of the STE state and high oscillator strength of the STE emission.

After electron beam irradiation PL spectra are very under interband excitation, anatase exhibits a broad luminescence band with a large Stokes shift.

The photocatalytic activity of the PAN/TiO₂ fiber mat was evaluated by the photocatalytic degradation of methylene blue under UV irradiation. Figure 7 shows the photocatalytic degradation of the dye with UV irradiation time. Non-irradiated PAN/TiO₂ fiber mat had low deprecating rate of methylene blue, which is 52.7% for 3 h. On the other hand, 92.3% of methylene blue was degraded by electron beam irradiated (1×10^4 kGy) PAN/TiO₂ fiber mat for 3 h. The methylene blue in this experiment was barely degraded under UV illumination without a photocatalyst.

The photocatalytic activity of the PAN/TiO₂ fiber mat was evaluated by the photocatalytic degradation of VOCs (toluene, benzene, ethylbenzene, xylene and styrene) under

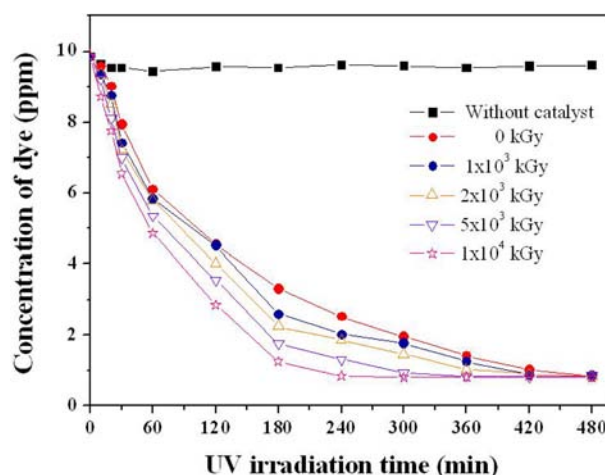


Figure 7. Removal of methylene blue by PAN/TiO₂ fibers.

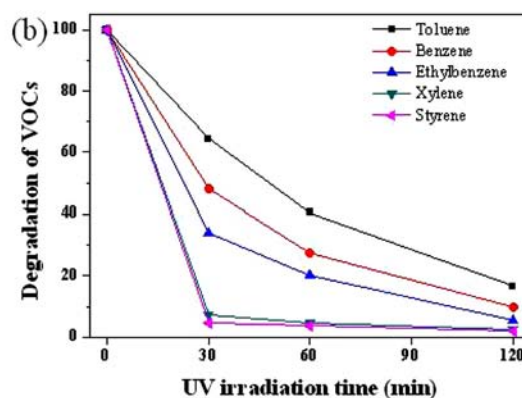


Figure 8. Removal of VOCs by PAN/TiO₂ fibers by electron beam irradiation: (a) 0; (b) 1×10^4 kGy.

UV irradiation. Figure 8 shows the photocatalytic degradation of the VOCs with UV irradiation. VOCs were degraded by PAN/TiO₂ fiber mat. After 30 min of UV illumination, 47.98% toluene was degraded by non-irradiated PAN/TiO₂ fiber mat. On the other hand, 58.87% toluene was degraded by electron beam irradiated (1×10^4 kGy) PAN/TiO₂ fiber mat. It is shown that electron beam irradiation was enhanced photocatalytic activity of PAN/TiO₂ fiber mat.

Conclusions

The PAN/TiO₂ mat was prepared using an electrospinning technique. The morphology of the fiber mat was controlled by several factors such as the polymer concentration, the applied voltage, and solution flow rate. With a decreasing the concentration of Ti(OBu)₄, the morphology of the PAN/TiO₂ mat was changed from beaded fiber to uniform fiber structure. When increasing the electric field, the average diameter of PAN/TiO₂ fibers decreased. Compared to non-irradiated fibers, electron beam irradiated fibers showed broad luminescence band. Photocatalytic efficiency of the PAN/TiO₂ mat was enhanced by treatment with electron beam.

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