

ENHANCEMENT OF PHOTOCATALYTIC ACTIVITY OF PAN-BASED NANOFIBERS CONTAINING SOL-GEL-DERIVED TiO₂ NANOPARTICLES BY E-BEAM IRRADIATION

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Abstract. In this study, a composite of polyacrylonitrile (PAN) mat containing sol-gel-derived TiO₂ of nanometer size was prepared using an electrospinning method. Subsequent PAN/TiO₂ composite nanofibers were treated with an e-beam (10,000 kGy) under an argon atmosphere. SEM and XRD measurements show that the fibers contain anatase crystallized TiO₂ particles on the fiber walls. EDS and TGA results suggest that the PAN/TiO₂ nanocomposite contains over 30% TiO₂ by mass. The photocatalytic activity of the PAN/TiO₂ nanofibrous mat against methylene blue in an aqueous solution improved by 24% for 3 h after each e-beam irradiation.

1. INTRODUCTION

Nanocomposite materials composed of TiO₂ nanoparticles contained in polymers have attracted much attention due to their catalytic, optical and electric properties that have potential applications in the fields of catalysis, photonics and electronics, respectively. Moreover, one-dimensional, fine-structured composites exhibit novel physical and chemical properties. A number of methods to fabricate one-dimensional composites have been reported, such as freeze-drying, thermal evaporation, physical vapor deposition and chemical vapor deposition [1-4]. These methods, however, involve multiple steps, some of which introduce impurities. Recently, the fabrication of one-dimensional polymeric nanocomposites by the electrospinning method has received much attention. Electrospinning is a simple

and cost-effective technique for producing polymeric fibers with diameters ranging from the nanoscale to submicron size [5].

However, use of TiO₂ catalyst is limited because UV excitation is required and the efficiency is low [6]. For these reasons, much effort has been made to enhance its photodegradation efficiency by using doping with dyes or metal ions. The addition of metal ions contributes to the rapid transfer of photogenerated electrons from the semiconductor to the noble metal particles, resulting in effective separation of the electrons and holes. Electron beam irradiation is also efficient in enhancing the optical properties, such as the band gap of metal oxides.

The aim of this study was to investigate the effects of electron beam irradiation on the photocatalytic properties of PAN-based, nanofibrous, non-

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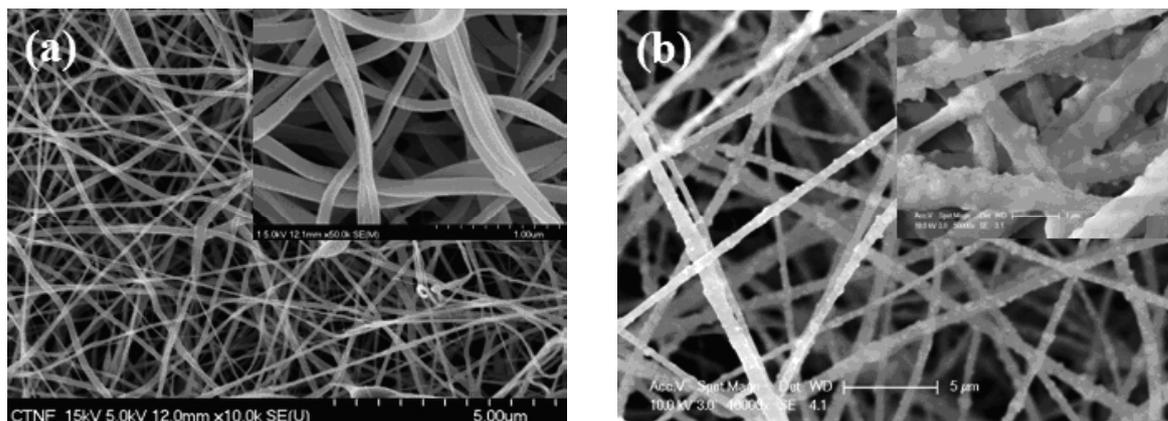


Fig. 1. SEM micrographs of the (a) PAN mat and the (b) PAN/TiO₂ mat.

woven mats containing sol-gel TiO₂ nanoparticles. The PAN/TiO₂ nanocomposite was prepared using an electrospinning method and was irradiated with an e-beam to enhance its photocatalytic activity. The resulting composite structure was characterized using scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDS), X-ray diffraction (XRD), and thermogravimetric analysis (TGA). The photoefficiency of the composite was tested using methylene blue degradation.

2. EXPERIMENTAL

2.1. Materials

Titanium(IV) isopropoxide (97%, Aldrich, USA), ethanol (95%, Aldrich, USA), hydrochloric acid standard solution (0.1 N in water, Aldrich, USA) and ammonium hydroxide solution (0.1 N in water, Aldrich, USA) were used as precursors. Polyacrylonitrile (PAN, average molecular weight = 1.5×10^5 g/mol, density = 1.18 g/cm^3 , Aldrich, USA) and *N,N*-dimethylformamide (DMF, 99%, Showa, Japan) were used for the electrospinning. Methylene blue (Aldrich, USA) was selected as a model pollutant for photodegradation.

2.2. Preparation of TiO₂ particles using sol-gel method

Titanium isopropoxide (20 mL) was added dropwise into 200 mL of ethanol in a round-bottom flask under vigorous stirring at 50 °C. After the hydrolysis, 200 mL of 0.05 M HCl and 0.05 M NH₄OH solutions were added dropwise, and the solution was stirred for 24 h. The TiO₂ sol was ultrasonicated for 1 h and collected by centrifugation at 8,000 rpm for 20 min

at -4 °C. The resultant precipitates were washed several times with distilled water and then dried at room temperature for 24 h. Finally, the TiO₂ particles were prepared after calcinations at 450 and 500 °C for 30 min and 2 h, respectively.

2.3. Preparation of PAN/TiO₂ nanofibers using the electrospinning method

The polymer solution was prepared using a weight ratio of PAN:TiO₂:DMF = 1:1:9. A PAN/TiO₂ solution was obtained by heating at 80 °C for 4 h with stirring. The apparatus for the electrospinning process included a glass syringe, stainless steel needle, syringe pump, high voltage power supply and collector. The polymer solution was drawn horizontally from the needle tip (inner diameter (ID) = 0.831 mm) and was driven by the electrostatic force generated from a high voltage maintained between the needle tip and the collector. The electrospun PAN/TiO₂ nanofibrous mat was collected on a collector drum placed 6 cm from the needle tip. A voltage of 15 kV was applied to the collector using a high voltage power supply. The flow rate of the polymer solution was 0.02 mL/min. After the solvent evaporated, the PAN/TiO₂ nanofibrous mat deposited on the collector formed a non-woven mat, which was dried at 60 °C under a vacuum for 12 h.

2.4. E-beam irradiation

The PAN/TiO₂ nanofibrous mat was placed in a stainless steel chamber, which was sealed after the introduction of argon gas. The sample was irradiated with e-beam at a dose rate of 7,200 kGy/h using an

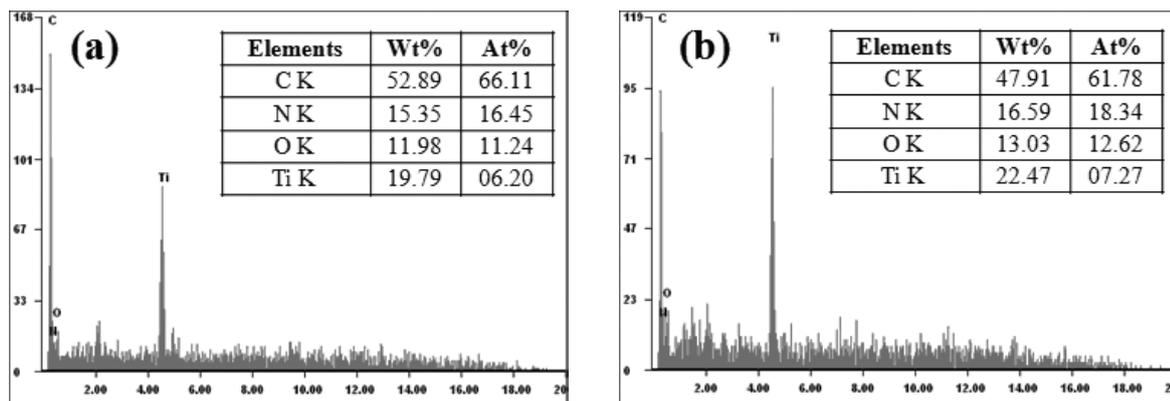


Fig. 2. EDS spectra of the (a) PAN/TiO₂ mat and the (b) e-beam-irradiated PAN/TiO₂ mat.

ELV-4 accelerator. The e-beam was generated with a 1 MeV acceleration voltage, 2 mA beam current and 10,000 kGy absorbed dose.

2.5. Photocatalytic activity test

The photocatalytic activities of the PAN/TiO₂ nanofibrous mats were determined from the decomposition rate of methylene blue in a dark, aqueous chamber. A 50 W lamp was used as a UV light source to irradiate the sample in a cylindrical glass vessel. The reaction was prepared by adding 10 mg of the PAN/TiO₂ mat into a beaker containing 300 mL of an aqueous solution of methylene blue (10 ppm). The mixture was maintained under constant air-equilibrated conditions both before and during the irradiation. Approximately 3 mL of the mixture was collected at 10, 20, 30, 60, 120, and 180 min after UV irradiation. Changes in the maximum absorption at 360 nm in the UV-vis spectrum versus irradiation time were recorded, reflecting the change in methylene blue concentration during photocatalysis.

2.6. Characterization

The compositions and the morphology of the PAN/TiO₂ nanofibrous mats were analyzed using a scanning electron microscope (SEM, Sirion, FEI, Netherlands) equipped with energy-dispersive spectroscopy (ISIS, OXFORD, UK). Power X-ray diffraction patterns were obtained to investigate the phases and crystal structure of the mat using an XRD apparatus (X'Pert PRO Multi-Purpose XRD, PANalytical, Netherlands). A UV-vis spectrophotometer (Optizen 2120 UV, Mecasys, Korea) was used to measure the dye concentration.

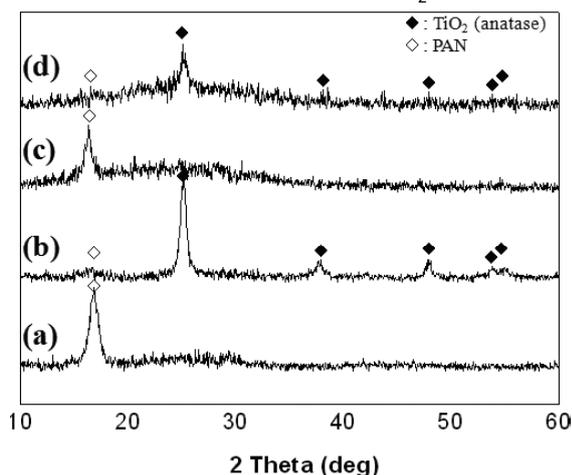


Fig. 3. XRD patterns of the (a) PAN mat, (b) PAN/TiO₂ mat, (c) e-beam-irradiated PAN mat and (d) e-beam-irradiated PAN/TiO₂ mat.

3. RESULTS AND DISCUSSION

The SEM images of the electrospun PAN fibrous mat and the electrospun PAN-based mat containing TiO₂ particles are shown in Fig. 1. In Fig. 1b, many TiO₂ nanoparticles are shown to be dispersed on the nanofibers. The morphologies of these particles are quasicircular, and their sizes primarily lie in the range between 80-300 nm. The TiO₂ particles with positive charges were repelled by the positive charges on the surface of fibers, and they aggregated in the middle of the fibers due to electrostatic repulsion [7]. Although the surface morphology of the PAN fibrous mat (Fig. 1a) is smooth, the diameter distribution of the fibers is broader than for the PAN/TiO₂ mat.

To observe detailed structures that could not be observed clearly by SEM analysis, an EDS technique was applied to evaluate the elemental content by analyzing the corresponding SEM images.

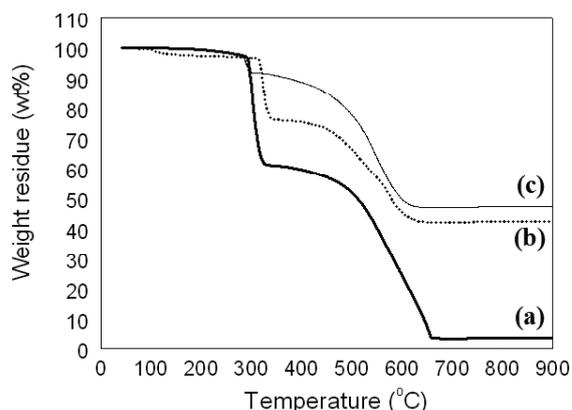


Fig. 4. TGA curves of the (a) electrospun PAN fibrous mat and the PAN/TiO₂ fibrous mats (b) before and (c) after e-beam treatment.

As shown in Fig. 2, the elemental compositions of C, N, O and Ti were 52.89, 15.35, 11.98, and 19.79 wt.%, respectively, in the electrospun PAN/TiO₂ fibrous mat. However, after e-beam irradiation, the elemental compositions of C, N, O, and Ti changed to 47.91, 16.59, 13.03, and 22.47 wt.%, respectively.

The XRD patterns of the electrospun PAN and PAN/TiO₂ fibrous mats before and after e-beam treatment are shown in Fig. 3. The XRD pattern exhibits diffraction peaks at 25.2° and 47.9°, suggesting that the electrospun PAN/TiO₂ fibrous mat has an anatase phase with a tetragonal structure, that has photocatalytic activity [8]. In addition, the electrospun mats treated by the e-beam are rougher than the non-irradiated mats.

Typical thermogram curves of electrospun PAN fibrous mats and PAN/TiO₂ fibrous mats before and after e-beam irradiation are shown in Fig. 4. TGA thermograms of PAN/TiO₂ mats can evaluate its thermal and decomposition at certain temperature. E-beam irradiated sample displays a significant change in thermal properties compared to the original one. The weight residue of electrospun PAN mat is 3% at 655 °C and those of the PAN/TiO₂ fibrous mat before and after e-beam irradiation are 42.5% and 47.2%, respectively, at 635 °C.

The photocatalytic activity of the PAN/TiO₂ fiber mat was evaluated based on the degradation of methylene blue under UV irradiation. Fig. 5 shows the photocatalytic degradation of the methylene blue dye as a function of UV irradiation time. The non-irradiated PAN/TiO₂ fibrous mat (Fig. 5b) degraded methylene blue at the low rate of 58.6% for 3 h.

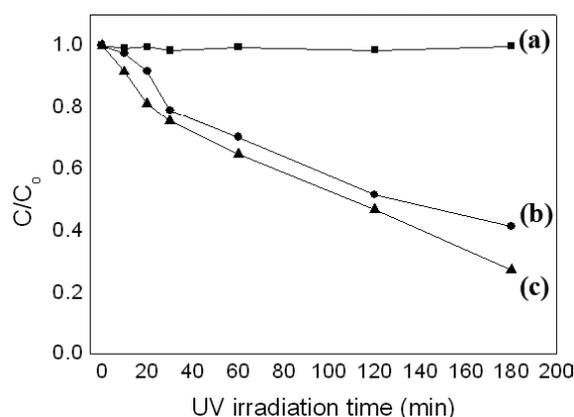


Fig. 5. Photodegradation of a methylene blue dye solution as a function of UV irradiation time: (a) no catalyst, (b) non-irradiated PAN/TiO₂ mat, (c) e-beam irradiated PAN/TiO₂ mat.

However, after treatment with the e-beam, a significant increase in the photodegradation of methylene blue was observed. In total, 72.5% of the methylene blue was degraded during 3 h by the PAN/TiO₂ fibrous mat that had irradiated by an e-beam. In this study, the methylene blue was barely degraded under UV illumination without a photocatalyst.

4. CONCLUSIONS

A PAN-based nanofibrous mat containing TiO₂ nanoparticles was prepared using an electrospinning method with a solution that contained PAN and sol-gel-derived TiO₂. The size of the prepared PAN/TiO₂ mat fibers were of the order of several nanometers in diameter and contained over 30 wt.% of crystallized anatase TiO₂ particles on their surface. Non-irradiated PAN/TiO₂ mat exhibits a very sharp decomposition behavior at about 280 °C, caused by the oligomerization of nitrile groups. Compared to non-irradiated PAN/TiO₂ mat, e-beam irradiated PAN/TiO₂ mat shows a more mild decomposition behavior and a higher char yields. The photocatalytic efficiency of the PAN/TiO₂ nanofibrous mats is also enhanced by treating e-beam irradiation.

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REFERENCES

- [1] D.L. Ma, L.S. Schadier, R.W. Siegel and J. Hong // *Appl. Phys. Lett.* **83** (2003) 1839.
- [2] Y.J. Chen, J.B. Li and J.H. Dai // *Chem. Phys. Lett.* **344** (2001) 450.
- [3] B. Xiang, Y. Zhang, Z. Wang, X.H. Luo, Y.W. Zhu, H.Z. Zhang and D.P. Yu, // *J. Phys. D: Appl. Phys.* **38** (2005) 1152.
- [4] N. Ozaki, Y. Ohno and S. Takeda // *Appl. Phys. Lett.* **73** (1998) 3700.
- [5] P. Heikkila and A. Harlin // *Eur. Polym. J.* **44** (2008) 3067.
- [6] D.S. Kim and Y.S. Park // *Chem. Eng. J.* **116** (2006) 133.
- [7] S. Madhugiri, B. Sun, P.G. Smirniotis, JP. Ferraris and J.K. Balkus // *Micro Meso Mater.* **69** (2004) 77.
- [8] J. Zhao, C. Jia, H. Duan, H. Li and E. Xie // *J. Alloy. Compd.* **461** (2008) 447.