Synthesis and Photocatalytic Activity of Ag_3VO_4 NPs Decorated PAN Nanofibers

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***Abstract*—This report presents synthesis of well-dispersed Ag_3VO_4 nanoparticles@polyacrylonitrile (PAN) nanofibers by an easily controlled, template-free method as a photo-catalyst for the degradation of methylene blue. Their structural, optical, and photocatalytic properties have been studied by X-ray diffraction, transmission electron microscopy, field-emission scanning electron microscopy equipped with rapid energy dispersive analysis of X-ray, and photoluminescence. The characterization procedures revealed that the obtained material is PAN nanofibers decorated by Ag_3VO_4 nanoparticles. Photocatalytic degradation of methylene blue investigated in an aqueous solution under irradiation showed 99% degradation of the dye within 75 min. These results suggest that the developed inexpensive and functional nanomaterials can serve as a non-precious catalyst for environmental applications.**

Keywords-component; photocatalyst; ion exchange reaction; nanoparticles; PAN/Ag_3VO_4 composite nanofibers

I. INTRODUCTION

Water pollution has become one of the severe problems and attracted worldwide attention [1,2]. Contamination of various kinds of organic dyes in drinking water is increasing and threatening the safety of drinking water [3,4]. Therefore, removal of organic dyes from contaminated water has been an important topic for researchers. To address this challenge, in the past decade, various semiconductor photocatalysts such as $BiPO_4$, $BiPO_4/CeO_2$, TiO_2/CdS, etc. have been successfully prepared and reported in relation to the decomposition of organic compounds utilizing visible light [5,6]. Photocatalysts based on semiconductor materials involve the generation of electron and hole pairs, migrating to the surface of the semiconductor, which contributes to the conversion of organic pollutants and inorganic pollutants into harmless substances and destruction of bacteria by a series of redox processes [7].

Recently, photocatalytic activity of Ag_3VO_4 has been investigated for splitting of water into H_2 and O_2, as well as decomposing organic pollutants under visible light irradiation [8,9]. However, due to the poor adsorptive performance for pollutants and high electron-hole recombination rate, the activity of pure Ag_3VO_4 is limited. In efforts to improve the photocatalytic activity of Ag_3VO_4, heterojunction composites semiconductors have been investigated [10]. Blending of Ag_3VO_4 nanoparticles into nanofibers might extensively improve stability, provide sufficient area for interaction without agglomeration and ease of reusability. For this scenario, electrospinning, a simple and versatile technique, has been investigated for the fabrication of organic-inorganic nanofibers having prominent features such as high specific surface area and large aspect ratio. Numerous polymer nanofibers have been fabricated by the electrospinning technique, but polyacrylonitrile (PAN) has been frequently used as reusable catalyst due to its hydrophobicity, low density, and high environmental stability properties [11,12].

Herein, we report a low cost and high yield route to prepare a nano Ag_3VO_4 particles@PAN nanofibers composite and its use for photocatalytic degradation of methylene blue.

II. EXPERIMENTAL

A. Materials

N,N-dimethylformamide (DMF; 99.5 assay, Showa Chemical Ltd., Tokyo, Japan), PAN (molecular weight 150,000 g/mol, Sigma-Aldrich, USA), methylene blue (MB; Showa Chemical Ltd.), silver nitrate (Showa Chemical Ltd.), and sodium vanadate (Sigma-Aldrich) were used in this study without further purification.

B. Fabrication of PAN/Ag3VO4 Composite Nanofibers

First, 10 % PAN solution was prepared by dissolving in DMF. After stirring at room temperature for 12 h, a solution having 100 mg of silver nitrate (based on polymer solution) was prepared. The prepared sol-gel solution was subjected to electrospinning at 15 kV maintaining a tip-to-collector distance of 15 cm. The obtained PAN/$AgNO_3$ fiber mats were dried at 30 °C for 6 h in vacuum. For the fabrication of PAN/Ag_3VO_4 nanofibers, as-synthesized electrospun PAN/$AgNO_3$ mats were immersed into a Na_3VO_4 aqueous solution (0.2 M) containing 0.1 M polyvinylpyrrolidone (PVP) at room temperature for the ion exchange reaction. Within a few minutes, the color of the composite nanofibers was changed from white to yellow, indicating the formation of Ag_3VO_4 NPs on the surface of PAN nanofibers via the reaction of Ag^+ with VO_{4-3}. Finally, the as-prepared nanofiber mat was washed several times with distilled water to remove the PVP residue and immediately dried at 60°C for 6 h. The schematic illustration for the fabrication of PAN/Ag_3VO_4 composite nanofibers is shown in Figure I.

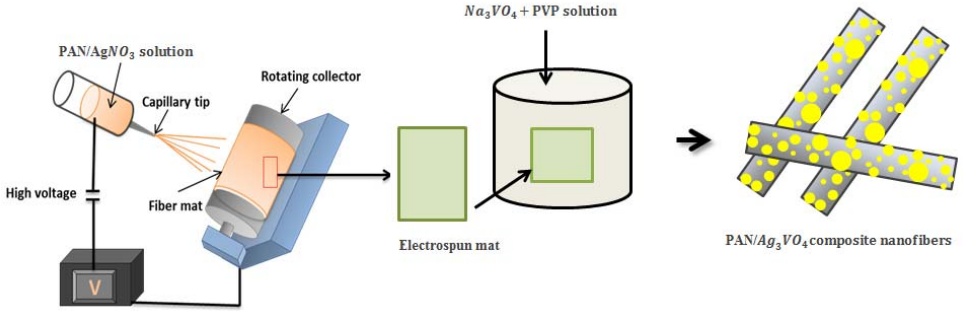

FIGURE I. SCHEMATIC ILLUSTRATION FOR THE FABRICATION OF PAN/AG_3VO_4 COMPOSITE NANOFIBERS.

C. *Characterization*

The morphology was investigated using field emission scanning electron microscope (FE-SEM; S-4700, Hitachi, Tokyo, Japan). The energy-dispersive X-ray spectroscopy (EDX) spectrum of the PAN/Ag_3VO_4 composite nanofibers was also recorded with the same FE-SEM instrument. High resolution images of different nanoparticles were obtained via transmission electron microscopy (TEM; JEM-2010, JEOL, Tokyo, Japan). Information about the phase and crystallinity was obtained with a Rigaku X-ray diffractometer (XRD; Rigaku, Tokyo, Japan) with Cu K(= 1.540A)˚ radiation over Bragg angles ranging from 100 to 600. The ultraviolet (UV)-visible spectra were obtained with a UV-visible spectrometer (LAMBDA 600, PerkinElmer, Waltham, MA, USA) over a range of 200–800 nm. Photoluminescence (PL) spectra were recorded by PerkinElmer Instruments (LS-55).

D. *Photocatalytic Activity Investigation*

Photocatalytic activity of the PAN/Ag_3VO_4 nanofiber was evaluated by monitoring the photodegradation of a MB aqueous solution under visible light irradiation. For the photodegradation experiments, 125 mg of PAN/Ag_3VO_4 nanofibers was put in 50 mL of a 10 ppm MB aqueous solution. Under magnetic stirring, the mixed solution was irradiated under visible light. At regular intervals of time, 2 mL of aliquots were taken out and the concentration of the dye was measured by UV–vis spectrophotometer. For the reusability test, the used mat was washed several times with distilled water and then photodegradation of MB dye was carried out under the same aforementioned conditions.

III. RESULT AND DISCUSSION

Figure II a shows the morphology of the pristine PAN and PAN/Ag_3VO_4 composite nanofibers. The pristine nanofibers show a continuous, bead free, and smooth morphology. Ag_3VO_4 NPs decorated PAN NFs can be seen in the case of PAN/Ag_3VO_4 composite nanofibers (Figure IIb). the distribution of Ag_3VO_4 NPs throughout the surface of PAN nanofiber was also confirmed by the TEM image (Figure IIc). Furthermore, EDX results obtained from FE-SEM images confirms the incorporation of Ag_3VO_4 nanoparticles in the PAN nanofibers (Figure IId).

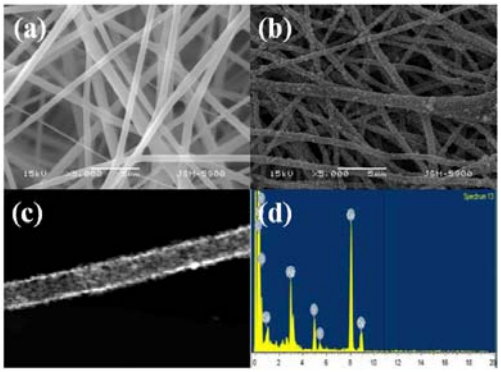

FIGURE II. FE-SEM IMAGES OF PRISTINE PAN NANOFIBERS (b), PAN/Ag_3VO_4 COMPOSITE NANOFIBER (b) TEM IMAGE OF PAN/Ag_3VO_4 COMPOSITE NANOFIBER (c), AND THE EDS SPECTRA OF PAN/Ag_3VO_4 COMPOSITE NANOFIBER (d).

Figure III exhibits the XRD pattern of PAN/Ag_3VO_4 composite nanofibers as compared to the pristine PAN nanofibers. In the pristine PAN nanofibers, a crystalline peak centered at about 17° is assigned to the PAN polymer phase. The existence of peaks 011, –121, 121, 301, 202, 022, 400, 132, and 331 in the PAN/Ag_3VO_4 composite nanofibers are attributed to the standard values of the monoclinic Ag_3VO_4 [13].

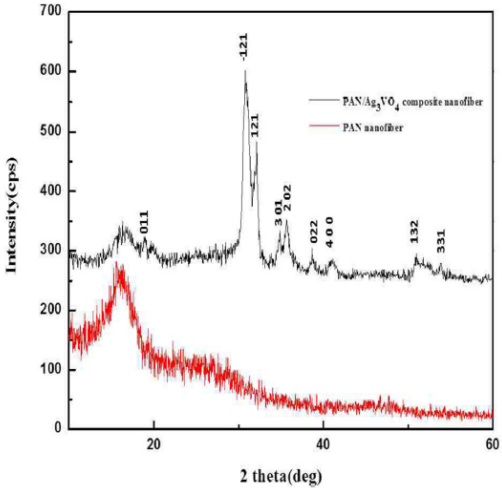

FIGURE III. XRD PATTERN OF PAN/Ag_3VO_4 COMPOSITE NANOFIBER AS COMPARED TO PRISTINE PAN NANOFIBER.

In order to investigate the recombination rate of electrons/holes of charge carrier trapping, migration, and transfer in of the synthesized materials, we carried out PL study. Figure IV shows the PL spectra of pristine PAN nanofiber and PAN/Ag_3VO_4 composite nanofibers. The PL intensity in the case of composite nanofibers is lower than that of the pristine PAN nanofibers. The lower intensity in the case of composite fiber indicates lower electron/hole recombination, which is preferable in the case of utilizing the material as a photocatalyst [14,15].

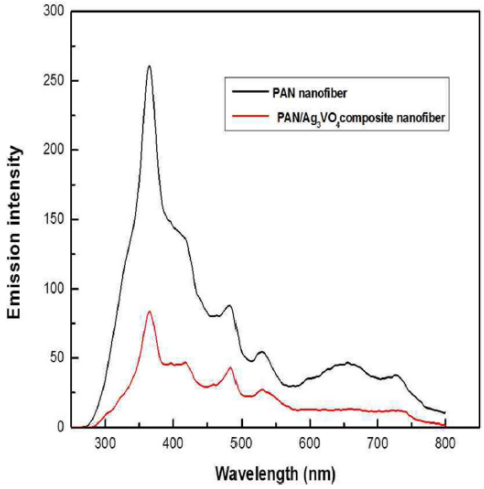

FIGURE IV. PL SPECTRA OF THE PAN/Ag_3VO_4 COMPOSITE NANOFIBER AS COMPARED TO PRISTINE PAN NANOFIBER.

The photocatalytic performance of the synthesized composite nanofibers was examined for the degradation of MB dye under visible light irradiation. From Figure Va, it is clear that the photocatalytic efficiency of PAN/Ag_3VO_4 composite nanofibers toward degradation of MB is significantly higher than that of PAN nanofibers. The enhanced decolorization of MB could be explained by the combined degradation properties of Ag_3VO_4 nanoparticles and adsorption properties of PAN nanofibers. Upon irradiation of visible light on the PAN/Ag_3VO_4 composite nanofibers, the electrons are excited from the VB to the conduction level of Ag_3VO_4, leaving holes behind. These electrons and holes migrate to the surface of Ag_3VO_4 and react with O_2 dissolved in the dye solution to produce $\bullet O^{2-}$ radicals. These $\bullet O^{2-}$ radicals can directly oxidize dyes and/or immediately react with H^+ ions to generate H_2O_2, followed by conversion into •OH radicals to oxidize dyes. Simultaneously, photogenetated holes can directly oxidize dyes, as well as react with H_2O and/or OH^- ions to produce •OH, and then oxidizes dyes. Furthermore, the reusability of the PAN/Ag_3VO_4 composite nanofibers was evaluated by performing four successive cyclic tests with the same composite nanofibers. As shown in Figure Vb, the efficacy of the initially used and reused composite photocatalyst up to four cycles is unchanged for the degradation of MB. This finding clearly indicated that the synthesized photocatalyst can be reused.

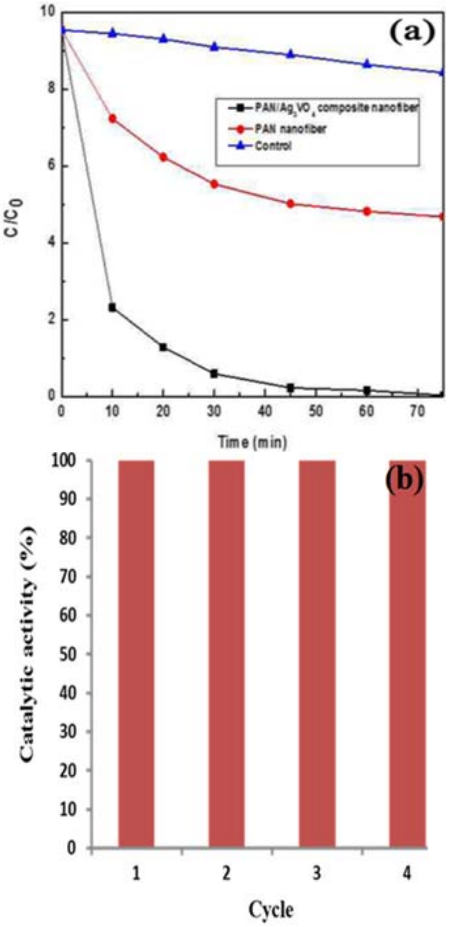

FIGURE V. COMPARISON OF METHYLENE BLUE PHOTODEGRADATION BY DIFFERENT SPECIMENS UNDER VISIBLE LIGHT IRRADIATION (a) AND THE CATALYTIC REUSABILITY OF PAN/Ag_3VO_4 COMPOSITE NANOFIBER MAT UP TO FOUR CYCLES (b)

IV. CONCLUSION

Highly active PAN/Ag_3VO_4 composite nanofibers photocatalyst was fabricated by a simple and versatile electrospinning technique followed by application of an ion exchange method. FE-SEM and TEM images revealed that Ag_3VO_4 nanoparticles were uniformly decorated on the PAN nanofibers. Photocatalytic experiments showed that the PAN/Ag_3VO_4 composite nanofibers enhanced efficiency towards the photo degradation of dye compared to the pristine PAN nanofibers. Thus, these composite nanofibers broadens their application as a promising candidate in water purification

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