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Photocatalytic degradation and antibacterial investigation of nano synthesized Ag_3VO_4 particles @PAN nanofibers

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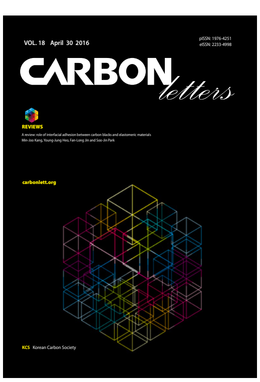

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Abstract

Well-dispersed Ag_3VO_4 nanoparticles @polyacrylonitrile (PAN) nanofibers were synthesized 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, photoluminescence, and ultraviolet–visible spectroscopy. 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. Finally, the antibacterial performance of Ag_3VO_4 nanoparticles @PAN composite nanofibers was experimentally verified by the destruction of *Escherichia coli*. These results suggest that the developed inexpensive and functional nanomaterials can serve as a non-precious catalyst for environmental applications.

Key words: photo-catalyst, antibacterial, ion exchange reaction, nanoparticles, PAN/Ag_3VO_4 composite nanofibers

1. Introduction

Water and energy have become severe problems and attracted worldwide attention and are basic components of life, economic growth, and human progress [1-9]. Waste water comes from many sources including the textiles industry during wet processing and dyeing, and presents a health hazard and is harmful to the environment. Contamination of various kinds of organic dyes in drinking water is increasing and threatening the safety of drinking water [10-12]. 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 BiPO4, $BiPO_4/CeO_2$, TiO_2/CdS, etc. have been successfully prepared and reported in relation to the decomposition of organic compounds or antibacterial activities utilizing visible light [13-15]. 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 [16,17]. In the past decades, TiO_2 has been focused upon because of its outstanding photocatalytic activity, ready availability, long-term stability, and nontoxicity [18]. However, the photocatalytic activity of TiO_2 is limited by the fast recombination of photogenerated carriers and its poor solar efficiency. Therefore, TiO_2 has been modified through either doping or coupling with another semiconductor to produce a visible light sensitive catalyst [19-22].

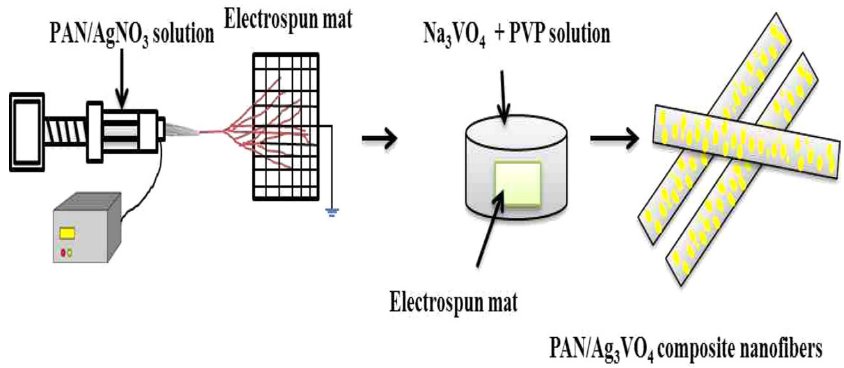

Fig. 1. Schematic illustration for the fabrication of polyacrylonitrile (PAN)/Ag_3VO_4 composite nanofibers. PVP, polyvinylpyrrolidone.

In recent years, silver containing compounds have garnered interest in the field of semiconductor photocatalysis due to their promising highly-efficient photocatalytic and antibacterial effects [23-26]. Moreover, for these Ag-containing photocatalysts, the top of their valence band (VB) consists of hybridized Ag 4d and O 2p orbitals. The hybridization of the O $2p^6$ orbitals with the completely filled $4d^{10}$ orbitals of silver ions could form a VB at a more positive energy level than that of O $2p^6$, resulting in a narrowed band gap. On the other hand, the bottom of the conduction band consists of relatively delocalized s and/or p orbitals, which are largely dispersed and can accommodate high photogenerated electrons and holes mobility, resulting in enhancement of photocatalytic activity [27].

In the literature, 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 illumination [28-30]. 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 [31-33]. Further, Ag_3VO_4 nanoparticles have been well dispersed into sheet-like structure materials such as graphene and g-C_3N_4 owing to their high surface area and electro-mobility [34,35]. However, irregular structure, uncontrolled combination, and existence in granular or powder form may bring difficulties in their use for water purification and reusability. Therefore, blending of 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 [36,37].

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 dye and antibacterial performance.

2. Experimental

2. 1. 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 treatment.

2.2. Fabrication of PAN/Ag_3VO_4 composite nanofibers

A 10 % PAN solution was prepared by dissolving the polymer granules in DMF with vigorous stirring at room temperature to form a homogenous solution. 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 schematic illustration for the fabrication of PAN/Ag_3VO_4 composite nanofibers is shown in Fig. 1. The obtained PAN/$AgNO_3$ fiber mats were dried for 2 h in air in order to remove the residual solvent. 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 nanoparticles on the surface of polymer 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 3 h.

2.3. 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).

2.4. Photocatalytic activity investigation

Photocatalytic activities of the PAN/Ag_3VO_4 nanofiber photocatalyst were evaluated by monitoring the photodegradation of a MB aqueous solution under solar light irradiation according to our previous work [6]. The experiment was conducted in a natural environment on a sunny day (May 12, 2015) between 11:00 a.m. and 3:00 p.m. 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 sunlight. In addition, a control experiment with 125 mg of pristine PAN mat and catalyst-free were also carried out to monitor the photocatalytic activity of the PAN mat and self-degradation of the dye, respectively. At regular intervals of time, 2 mL of aliquots were taken out and the concentration of the dye was measured by recording the UV absorbance in a range of 200–900 nm, using a UV–vis spectrophotometer. In this experiment, an ability test of the reused PAN/Ag_3VO_4 mat was also performed after full treatment. For this purpose, the used mat was washed several times with distilled water and then photodegradation of MB dye was carried out under the same aforementioned conditions.

2.5. Antibacterial property

Antibacterial activity of pristine PAN and as-synthesized mats was investigated by the zone inhibition method using *Escherichia coli (E. coli)* as the model organism at room conditions. Using a spread plate method, one colony of *E. coli* was taken out from the original stock in an agar plate and centrifuged at 200 rpm/min and then cultured in a lysogeny broth (LB) medium and grown overnight in the LB medium at 37°C for 24 h. Different nanofibers mats with the same dimensions were transferred on the inoculated plates, and were then incubated at 37°C for 24 h.

3. Results and Discussion

The morphology of pristine PAN and PAN/Ag_3VO_4 composite nanofibers was examined by FE-SEM measurement, as presented in Fig. 2a. Pristine nanofibers show a continuous, bead free, and smooth morphology with variable diameter. Fig. 2b exhibits PAN/Ag_3VO_4 composite nanofibers obtained by treating PAN/$AgNO_3$ mat with sodium orthovanadate. Fig. 2b reveals that Ag_3VO_4 nanoparticles are uniformly decorated onto the surface of the PAN nanofibers. TEM images were taken to study the assembly of Ag_3VO_4 nanoparticles onto the surface of pristine nanofibers. Fig. 3 reveals that the small crystalline nanoparticles

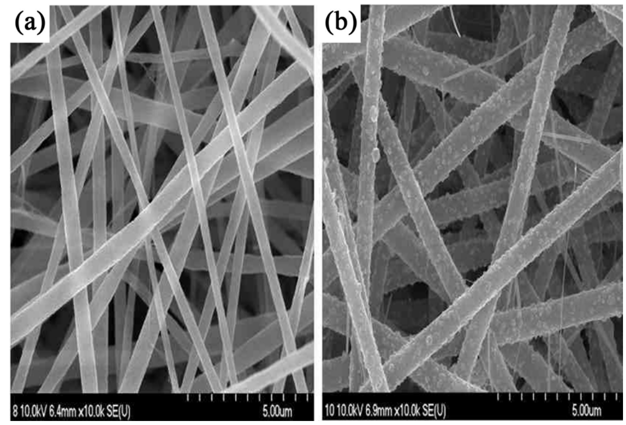

Fig. 2. Field-emission scanning electron microscopy images of pristine polyacrylonitrile (PAN) nanofibers mat (a) PAN/Ag_3VO_4 composite nanofiber (b).

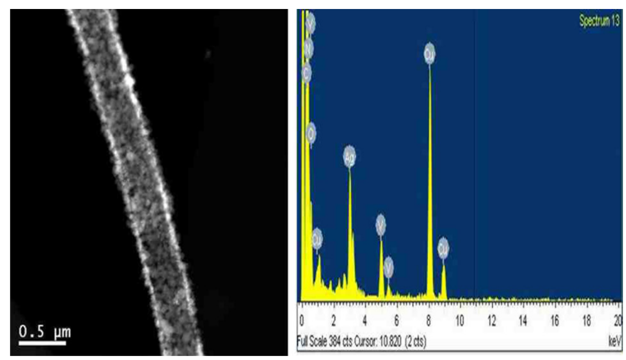

Fig. 3. Transmission electron microscopy image of polyacrylonitrile (PAN)/Ag_3VO_4 composite nanofiber and field-emission scanning electron microscopy energy-dispersive X-ray spectroscopy of PAN/Ag_3VO_4 composite nanofiber.

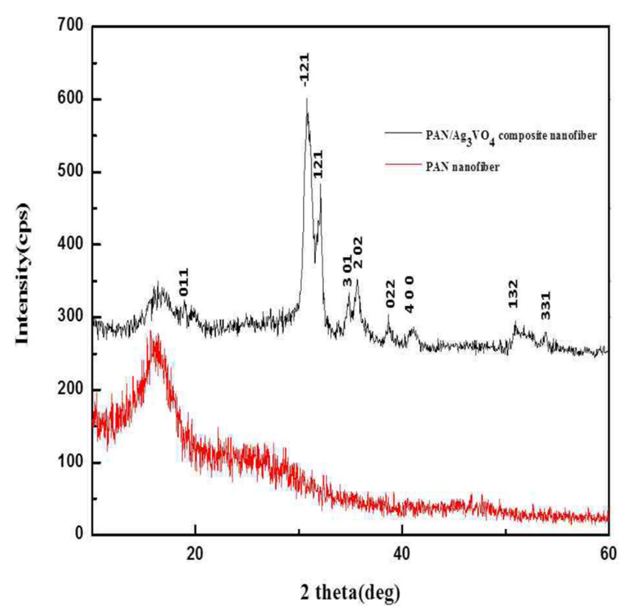

Fig. 4. X-ray diffraction pattern of polyacrylonitrile (PAN)/Ag_3VO_4 composite nanofiber.

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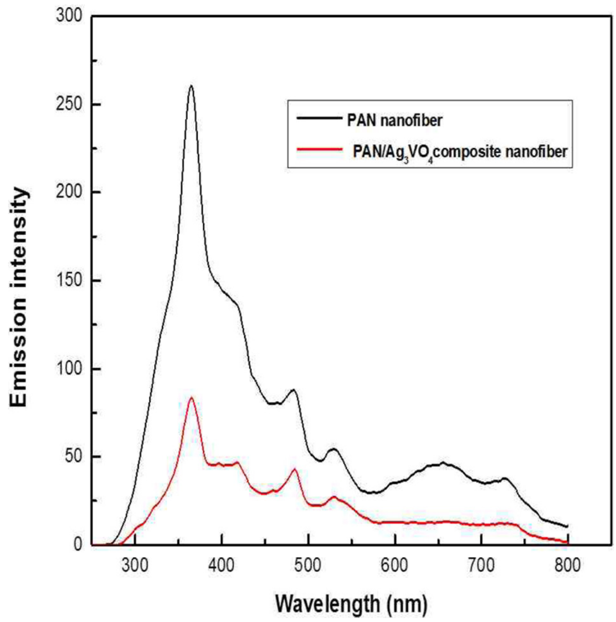

Fig. 5. Photoluminescence measurements for the pristine polyacrylonitrile (PAN) nanofibers compared to PAN/Ag_3VO_4 composite nanofiber.

were uniformly dispersed on the support nanofibers are Ag_3VO_4 nanoparticles, consistent with the FE-SEM image in Fig. 2a. Furthermore, an elemental analysis of the composite nanofibers was carried out by EDX results obtained from FE-SEM images (Fig. 2b). Except C, Ag, V, N, and O, no other peaks related with any impurity elements are detected in the EDX spectrum of the prepared composite nanofibers, confirming the incorporation of Ag_3VO_4 nanoparticles in the PAN nanofibers. Fig. 4 exhibits the XRD pattern of pristine PAN nanofibers and PAN/Ag_3VO_4 composite 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 [34]. XRD analysis result also supported EDX results obtained from FE-SEM images (Fig. 2b).

PL spectroscopy is based on the spontaneous emission of light from a material under optical excitation. It is used to investigate the optical properties of semiconductor materials as well as the recombination rate of electrons/holes of charge carrier trapping, migration, and transfer in the semiconductor materials. Fig. 5 shows the PL spectra of pristine PAN nanofiber and PAN/Ag_3VO_4 composite nanofibers. As shown in Fig. 5, the intensity of the PL spectra of the PAN/Ag_3VO_4 composite nanofibers is lower than that of the pristine PAN nanofibers. The lower intensity of the PL spectra indicates lower likelihood of electron/hole recombination, which is preferable in the case of utilizing the material as a catalyst in photoreactions [38].

To study the optical properties of the as-synthesized sample, we measured the UV-vis absorption spectra, as shown in Fig. 6. As shown in the Fig. 6, PAN/Ag_3VO_4 composite nanofibers exhibited stronger absorption of visible light in the range between 400–800 nm, which confirms the successfully decoration of Ag_3VO_4 nanoparticles on the surface of PAN nanofibers. Remarkable absorption enhancement in the visible-light region shows that the as-synthesized nanocomposite fibers might utilize visible light more efficiently in photocatalytic reactions.

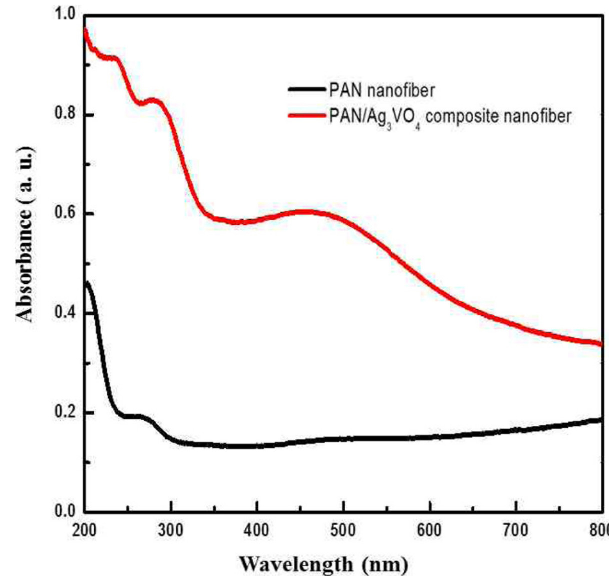

Fig. 6. Ultraviolet-visible absorption spectra of pristine polyacrylonitrile (PAN) nanofibers and PAN/Ag_3VO_4 nanocomposite fibers.

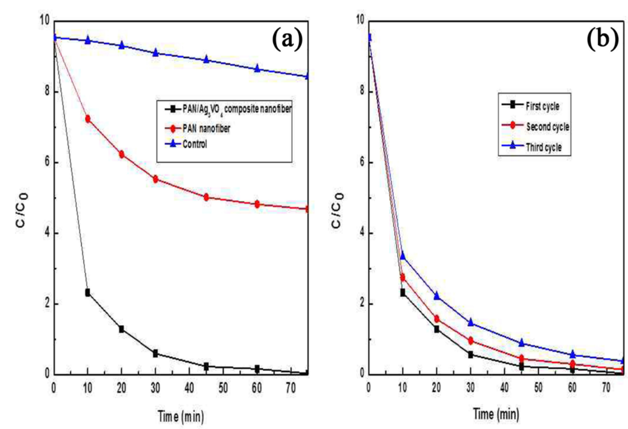

Fig. 7. Comparison of methylene blue photodegradation by different specimens under solar radiation (a) and the catalytic reusability of polyacrylonitrile (PAN)/Ag_3VO_4 composite nanofiber mat up to three cycles (b).

It is well known that photodegradation efficiency can be affected by the size and structure of Ag_3VO_4 particles as well as their manner of attachment onto the surface of PAN nanofibers. The photocatalytic performance of the synthesized composite nanofibers was examined for the degradation of MB dye under solar light irradiation. From Fig. 7a, 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 absorption properties of PAN nanofibers [23,29]. Upon irradiation of solar light on the PAN/Ag_3VO_4 composite nanofibers, the electrons are excited from the VB to the conduction level of

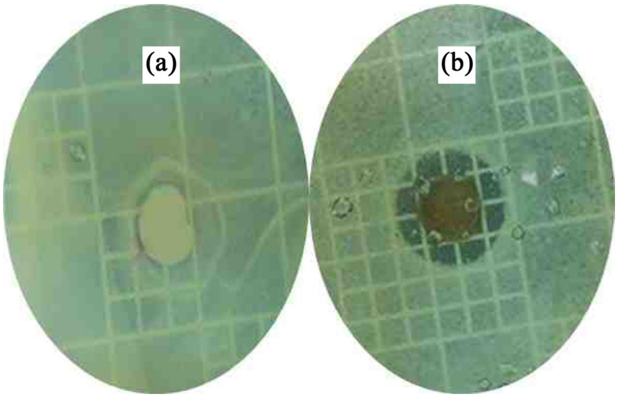

Fig. 8. Bactericidal activity of *Escherichia coli*, exposed to polyacrylonitrile (PAN) nanofiber (a) and PAN/Ag_3VO_4 composite nanofiber (b).

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. Our PL data (Fig. 5) also supported this mechanism. The catalyst's lifetime or reusability is an important parameter of the photocatalytic process in waste water treatment. The reusability of the PAN/Ag_3VO_4 composite nanofibers was evaluated by performing three successive cyclic tests with the same composite nanofibers as shown in Fig. 7b. It is found that the efficacy of the initially used and reused composite photocatalyst up to three cycles is nearly unchanged for the degradation of MB. The slightly decrease in photocatalytic activity during cyclic use might be due to the blockage of active absorption sites of the PAN nanofibers.

The objective of this study was not only to remove dyes but also to destroy bacteria from waste water. Therefore, we performed an antibacterial test of as-prepared composite nanofibers by the zone inhibition test method using *E. coli* as the model organism. Fig. 8a shows there is no zone of inhibition, indicating no antibacterial activities. But the PAN/Ag_3VO_4 composite nanofiber (Fig. 8b) clearly shows a zone of inhibition in a ring form around the fiber, suggesting antibacterial efficiency. The higher antibacterial efficiency of the PAN/Ag_3VO_4 composite nanofibers is due to the contact between the hybrid nanomaterial and bacteria. When Ag_3VO_4 nanoparticles come in contact with bacteria, they bind to DNA, and this will affect the bacterial metabolism process, especially cell division, which ultimately can cause cell damage or death. Moreover, Ag_3VO_4 is a semiconductor that generates electron-pair holes and reacts with O_2 or OH^- to give rise to active oxygen species, which react with cell membranes, DNA, and cellular proteins, leading to bacterial cell death [39].

4. Conclusions

Highly photocatalytic and antibacterial PAN/Ag_3VO_4 composite nanofibers were 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. Moreover, these composite nanofibers also exhibited higher antibacterial activity, showing their potential application in water purification.

Conflict of Interest

No potential conflict of interest relevant to this article was reported.

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