Photocatalytic degradation and antibacterial investigation of Nano synthesized Ag$_3$VO$_4$ particles @PAN nanofibers.

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Abstract

Well-dispersed Ag$_3$VO$_4$ nanoparticles @ PAN nanofibers as photo-catalyst for the degradation of methylene blue were synthesized by an easy-controlled template-free method. Their structural, optical, and photocatalytic properties have been studied by X-ray diffraction (XRD), transmission electron microscopy (TEM), field-emission scanning electron microscopy (FESEM) equipped with rapid EDX (energy dispersive analysis of X-ray), Photoluminescence (PL) and UV–visible spectroscopy. The fascinated characterization procedures acknowledged that the obtained material is PAN nanofibers decorated by Ag$_3$VO$_4$ nanoparticles. Photocatalytic degradation of Methylene blue was investigated in aqueous solution under irradiation showed 99 % degradation of the dye within 75 mins. Finally, the antibacterial performance of Ag$_3$VO$_4$ nanoparticles @ PAN composite nanofiber was experimentally verified by destruction of E. coli. These consequences suggested inexpensive and operative nanomaterials as non-precious catalyst for environmental applications.

Keywords: Photo-catalyst, Antibacterial, Ion exchange reaction, Nanoparticles, PAN/Ag$_3$VO$_4$ Composite nanofibers.
1. Introduction

Waste water comes from textiles industry during wet processing and dyeing brings serious problem both from health hazard and environmental points of view. Contaminations of various kinds of organic dyes in drinking water are increasing which will threaten safety of drinking water [1-3]. Therefore, removal of organic dyes from the contaminated water has been a hot topic for researchers. To address this challenge, in past decade, various semiconductor photocatalysts like BiPO4, BiPO4/ CeO2, TiO2/CdS and etc., have been successfully prepared and reported either in decomposition of organic compounds or antibacterial activities utilizing visible light [4–6]. Photocatalysts based on semiconductor materials involves the generation of electrons and holes pair, migrating to the surface of semiconductor which contribute to the conversion of organic pollutants and inorganic pollutants into harmless substance and destruction of bacteria by series of redox processes [7, 8]. From the past decades, TiO2 has focused because of its outstanding photocatalytic activity, easy availability, long-term stability and nontoxicity [9]. However, the photocatalytic activity of TiO2 is limited by the fast recombination of photogenerated carriers and its poor solar efficiency. Therefore, TiO2 has been modified either doping or coupling with other semiconductor to make visible light sensitive catalyst [10-13].
In recent years, silver containing compounds have much interest in the field of semiconductor photocatalysis due to their promising high-efficient photocatalytic and antibacterial effects [14-17]. Moreover, for these Ag-containing photocatalysts, the top of the valence band (VB) of them 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 valence band 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 (CB) that consists of relatively delocalized s and/or p orbitals which are largely dispersed and can accommodate high photogenetated electrons and holes mobility resulting to the enhancement of photocatalytic activity [18].

In the literature, photocatalytic activity of Ag\(_3\)VO\(_4\) has been investigated for splitting of water into H\(_2\) and O\(_2\), as well as decomposing of organic pollutants under visible light illumination [19-21]. However, due to the poor adsorptive performance for pollutants and high electron-hole recombination rate, the activity of pure Ag\(_3\)VO\(_4\) is limited. In order to improve the photocatalytic activity of Ag\(_3\)VO\(_4\), heterojunction composites semiconductors have been investigated [22-24]. Further, Ag\(_3\)VO\(_4\) nanoparticles have been well dispersed into sheet like structure materials like graphene and g-C\(_3\)N\(_4\) owing to its high surface area and electro mobility [25, 26]. However, irregular structure, uncontrolled combination and existence in granular or powder form may bring difficulties in their use for water purification and reusability as well.
Therefore, blending of nanoparticles into nanofibers might extensively improve stability, provide a sufficient area for interaction without agglomeration and ease in reusability. For this scenario, simple and versatile technique, electrospinning technique, has been investigated for the fabrication of organic-inorganic nanofiber having prominent features like high specific surface area and large aspect ratio. Numerous polymer nanofibers have been fabricated by the electrospinning technique, but PAN has been frequently used as reusable catalyst due to its hydrophobicity, low density, and high environmental stability properties [27, 28].

Herein, we report low cost and high yield route to prepare nano Ag$_3$VO$_4$ particles @ PAN nanofibers composite and their uses for photocatalytic degradation of dye and antibacterial performance.

2. Experimental procedure

2.1. Materials

$N,N$-dimethylformamide (DMF, 99.5 assay, Showa Chemical Ltd., Japan), polyacrylonitrile (PAN, MW 150,000 g/mol, Sigma–Aldrich), methylene blue (Showa Chemical Ltd., Japan), silver nitrate (Showa Chemical Ltd., Japan), sodium vanadate (Sigma-Aldrich) were used in this study without further treatment.

2.2. Fabrication of PAN/Ag$_3$VO$_4$ composite nanofibers

10 % PAN solution was prepared by dissolving the polymer granules in $N$, $N$-
dimethylformamide (DMF) with vigorous stirring at room temperature to form homogenous solution. After stirring at room temperature for 12 h, solution having 100 mg of silver nitrate (based on polymer solution) was prepared. Thus 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$_3$VO$_4$ composite nanofibers is shown in figure 1. The obtained PAN/AgNO$_3$ fiber mats were dried for 2 h in the air in order to remove the residual solvent. For the fabrication of PAN/Ag$_3$VO$_4$ nanofiber, as-synthesized electrospun PAN/AgNO$_3$ mats were immersed into a Na$_3$VO$_4$ aqueous solution (0.2 M) containing 0.1 M PVP at room temperature for ion exchange reaction. Within a few min, the color of the composite nanofibers was changed from white to yellow indicating the formation of Ag$_3$VO$_4$ nanoparticles on the surface of polymer nanofibers via the reaction of Ag$^+$ with VO$_4^{3-}$. At last, as-prepared nanofibers 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 FE-SEM (S-4700, Hitachi, Japan). The EDX spectrum of PAN/Ag$_3$VO$_4$ composite nanofibers were also recorded with the same FE-SEM instrument. High resolution images of different NPs were obtained via transmission electron microscopy (TEM, JEM- 2010, JEOL, Japan). Information about the phase and crystallinity was obtained with a Rigaku X-ray diffractometer (XRD,
Rigaku, Japan) with Cu K(= 1.540Å) radiation over Bragg angles ranging from 100 to 600. The UV-visible spectra were obtained with a UV-visible spectrometer (Lambda 600, PerkinElmer, USA) over the range of 200-800 nm. Photoluminescence (PL) spectrum was recorded by Perkin Elmer Instruments (LS-55).

2.4. Photocatalytic activity investigation

Photocatalytic activities of PAN/Ag₃VO₄ nanofiber photocatalyst were evaluated by monitoring the photodegradation of methylene blue aqueous solution under solar light irradiation according to our previous work [6]. The experiment was conducted in natural environment on sunny day (May 12, 2015) between 11:0 a.m. to 3:0 p.m. For the photodegradation experiments, 125 mg of PAN/Ag₃VO₄ nanofiber 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 photocatalytic activity of PAN mat and self-degradation of 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 the range of 200–900 nm, using a UV–vis spectrophotometer. In this experiment, the ability test of reused PAN/Ag₃VO₄ 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 condition.
2.5. Antibacterial property

Antibacterial activity of pristine PAN, and as-synthesized mats were investigated by the zone inhibition method using Escherichia coli (E. coli) as the model organism at room condition. Using a spread plate method, one colony of E. coli was taken out from the original stock in an agar plate, centrifuged at 200 rpm/min and was cultured lysogeny broth (LB) medium and were grown overnight in LB medium at 37°C for 24 h. Different nanofibers mats with same dimension 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/Ag₃VO₄ composite nanofibers were examined by FESEM measurement which can be seen in Fig. 2. Pristine nanofiber shows continuous, bead free, smooth and variable diameter size morphology. Fig.2B exhibited PAN/Ag₃VO₄ composites nanofibers obtained by treating PAN/AgNO₃ mat with sodium orthovanadate. Fig.2B reveals that Ag₃VO₄ nanoparticles are uniformly decorated onto the surface of PAN nanofibers. TEM image was taken to study the assembly of Ag₃VO₄ nanoparticles onto the surface of pristine nanofibers. Fig.3A reveals that the small crystalline nanoparticles were uniformly dispersed on the support nanofibers would be the Ag₃VO₄ nanoparticles which support the FESEM image Fig.2A. Furthermore, elemental analysis in 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 element are detected in the EDX spectrum of prepared composite nanofibers which confirms the incorporation of Ag$_3$VO$_4$ NPs in PAN nanofibers. Fig.4 exhibits the XRD pattern of pristine PAN nanofiber and PAN/Ag$_3$VO$_4$ composite nanofibers. In pristine PAN nanofiber, a crystalline peak centers at about 17° can be assigned to the PAN polymer phase. The existence of peaks 011, -121, 121, 301, 202, 022, 400, 132, and 331 in the PAN/Ag$_3$VO$_4$ composite nanofibers can be perfectly attributed to the standard values of the monoclinic Ag$_3$VO$_4$ [25]. XRD analysis is also simultaneously supported by EDX results obtained from FE-SEM images (Fig. 2B).

Photoluminescence (PL) spectroscopy is 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 electron/hole of charge carrier trapping, migration and transfer in the semiconductor materials. Fig.5 shows the photoluminescence (PL) spectra of pristine PAN nanofiber and PAN/Ag$_3$VO$_4$ composite nanofibers. As shown in Fig.5 the intensity of PL spectra of PAN/Ag$_3$VO$_4$ composite nanofibers is lower than that of pristine PAN nanofiber. This lower intensity of PL spectra indicates less chance for the electrons/hole recombination rate which is preferable in case of utilizing the materials as catalysts in the photoreactions [29]. To study the optical properties of as-synthesized sample, we measured the UV-vis absorption spectra and have shown in Fig.6. As shown in figure, PAN/Ag$_3$VO$_4$ composite nanofibers exhibited stronger absorption of visible light in the range between
400-800 nm, which confirms the successfully decoration of Ag$_3$VO$_4$ nanoparticles on the surface of PAN nanofibers. Remarkable absorption enhancement in visible-light region shows that as-synthesized nanocomposite fibers might utilize visible light more efficiently in photocatalytic reaction.

It is well known, photodegradation efficiency can be affected by the size and structure of Ag$_3$VO$_4$ 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 methylene blue (MB) dye under solar light irradiation. From Fig.7A, it clear that photocatalytic efficiency of PAN/Ag$_3$VO$_4$ composite nanofibers toward degradation of MB is significantly higher than that of PAN nanofiber. The enhanced decolorization of MB could be explained by combined degradation properties of Ag$_3$VO$_4$ nanoparticles and absorption properties of PAN nanofibers [14, 20]. On irradiation of solar light in the PAN/Ag$_3$VO$_4$ composite nanofiber, the electrons are excited from the valence band of to the conduction level of Ag$_3$VO$_4$ leaving holes behind. These electrons and holes migrate to the surface of Ag$_3$VO$_4$ and reacts O$_2$ dissolved in dyes solution to produce •O$_2^-$ radicals. These •O$_2^-$ radicals can directly oxidize dyes or/and immediately react with H$^+$ ions to generate H$_2$O$_2$, following on converting Into •OH radicals to oxidize dyes. Simultaneously, photogenetated holes can directly oxidize dyes, as well as react with H$_2$O and/or OH$^-$ ions to produce •OH, then oxidizes dyes. Our photoluminescence 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$_3$VO$_4$ composite nanofibers was carried by performing three successive cyclic tests with the same composite nanofibers which can be seen shown in Fig.7B. It is found that the efficacy of initially used and reused composite photocatalyst up to three cycles is nearly same 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 PAN nanofibers.

The objective of this contribution was not only removable of dyes but also destruction of bacteria from the waste water. Therefore, we performed antibacterial test of as-prepared composites nanofibers by the zone inhibition test method using E. coli as the model organism. Fig.8A shows no zone of inhibition, indicating no antibacterial activities. But PAN/Ag$_3$VO$_4$ composite nanofiber (Fig.8B) shows the clear zone of inhibition ring around it, suggesting antibacterial efficiency. The higher antibacterial efficiency of PAN/Ag$_3$VO$_4$ composite nanofibers is due to the contact between the hybrid nanomaterial and bacteria. Ag$_3$VO$_4$ nanoparticles when come in contact with bacteria, they bind to DNA, will affect the bacterial metabolism process, especially cell division which ultimately can cause cell damage or death. Moreover, Ag$_3$VO$_4$ is a semiconductor which generates electron- pair hole and react 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 [30].

4. Conclusion

Highly photocatalytic and antibacterial PAN/Ag$_3$VO$_4$ composites nanofibers were fabricated by simple and versatile electrospinning technique followed by ion exchange method. FESEM and TEM images revealed that Ag$_3$VO$_4$ nanoparticles have been uniformly decorated on PAN nanofiber. Photocatalytic experiments showed that the PAN/Ag$_3$VO$_4$ composite nanofibers enhanced efficiency towards the photodegradation of dye than the pristine PAN nanofiber. Moreover, these composites nanofibers also exhibited higher antibacterial activity, showing their potential application in water purification.

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References


Figure caption:

Fig.1. Schematic illustration for the fabrication of PAN/Ag₃VO₄ composite nanofibers.

Fig.2. FE-SEM images of pristine PAN nanofibers mat (A), PAN/Ag₃VO₄ composite nanofiber (B).

Fig.3. TEM image of PAN/Ag₃VO₄ composite nanofiber (A) and FE-SEM EDX of
PAN/Ag$_3$VO$_4$ composite nanofiber.

Fig.4. XRD pattern of PAN/Ag$_3$VO$_4$ composite nanofiber

Fig.5. PL measurements for the pristine PAN nanofibers compared to PAN/Ag$_3$VO$_4$ composite nanofiber.

Fig.6. UV-visible absorption spectra of pristine PAN nanofibers and PAN/Ag$_3$VO$_4$ nanocomposite fibers.

Fig.7. Comparison of the MB photodegradation by different specimens under solar radiation (A) and the catalytic reusability of PAN/Ag$_3$VO$_4$ composite nanofiber mat up to three cycles (B).

Fig.8. Bactericidal activity of E. coli, exposed to PAN nanofiber(A), and PAN/Ag$_3$VO$_4$ composite nanofiber (B).

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Fig. 8. Bactericidal activity of E. coli, exposed to PAN nanofiber (A), and PAN/Ag$_3$VO$_4$ composite nanofiber (B).