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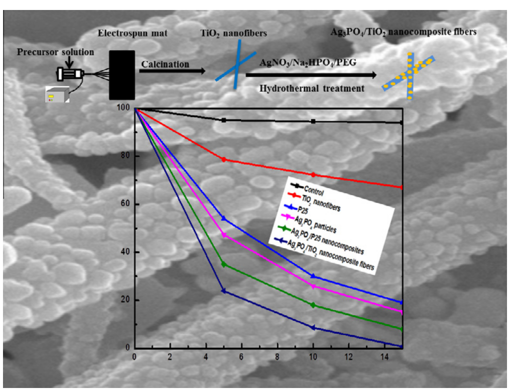
Effective photocatalytic efficacy of hydrothermally synthesized silver phosphate decorated titanium dioxide nanocomposite fibers

Prem Singh Saud [a,b], Bishweshwar Pant [a], Arjun Prasad Twari [d], Zafar Khan Ghouri [a], Mira Park [c,*], Hak-Yong Kim [a,c,*]

[a] Department of BIN Convergence Technology, Chonbuk National University, 561-756, Republic of Korea
[b] Department of Chemistry (Affiliated to Tribhuvan University), Kailali Multiple Campus, Dhangadhi, Kailali, Nepal
[c] Department of Organic Materials and Fiber Engineering, Chonbuk National University, Jeonju, Republic of Korea
[d] Department of Bionanosystem, Chonbuk National University, 561-756, Republic of Korea

GRAPHICAL ABSTRACT



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ABSTRACT

Hierarchical Ag_3PO_4/TiO_2 nanocomposite fibers were prepared by combining electrospinning technique and hydro-thermal growth method. As-synthesized samples were characterized by using field-emission scanning electron microscopy (FE-SEM), Transmission electron microscopy (TEM), X-ray diffraction (XRD), Photoluminescence (PL), and Fourier transform infra-red (FT-IR) spectroscopy. The FE-SEM image revealed a uniform decoration of Ag_3PO_4 nanoparticles without aggregation on primary TiO_2 nanofibers. The photocatalytic and antibacterial studies were performed and results were shown that the Ag_3PO_4/TiO_2 nanocomposite fibers show an enhanced photocatalytic and antibacterial activity toward the degradation of dye methylene blue and bacteria (*Escherichia coli, Staphylococcus aureus*) respectively. Our results can provide new insights of Ag_3PO_4/TiO_2 nanocomposite fibers for the potential applications in antibacterial and waste water treatment.

1. Introduction

Water resources are being polluted by different organic substances produced from textile industries during dye process.

* Corresponding authors at: Department of Organic Materials and Fiber Engineering, Chonbuk National University, Jeonju, Republic of Korea (H.-Y. Kim).
E-mail addresses: wonderfulmira@jbnu.ac.kr (M. Park), khy@jbnu.ac.kr (H.-Y. Kim).

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Contamination of such organic dye and various type of bacteria such as Pseudomonas, Staphylococcus, and Escherichia species in drinking water resources bring serious problem both aquatic living and human beings [1–3]. Many techniques like adsorption, photocatalysis, anaerobic treatment, membrane filtration, chemical oxidation, and coagulation have been investigated for the purification of waste water [4–7]. Among them, semiconductor based photocatalysts have been investigated as effective technique for simultaneous reduction of both microbial contamination and organic pollutant in waste water. Irradiation of light of suitable wavelength on semiconductor photocatalysts, electron hole–pairs are generated, which are responsible for degradation of organic pollutant by redox reaction at photocatalyst surface and also react with cell wall, DNA of cell as well leading to destruction of bacteria [8–10]

TiO_2 photocatalyst has been studied from the past decades because of its promising properties like photosensitivity, easy availability, long-term stability and non-toxicity [11–13]. However, TiO_2 is only active in ultraviolet light due to its high bandgap energy and the photocatalytic activity of TiO_2 is limited by recombination of photo-generated carriers within nanoseconds. Therefore, solar energy cannot be utilized efficiently in real applications. To overcome such limitation, TiO_2 has been coupled or doped with lower bandgap semiconductors which result visible light sensitive catalyst [14–18]. Recently, silver based compounds like AgI, AgBr, Ag_2CO_3, Ag_3VO_4, and Ag_3PO_4 have been used in the field of semiconductor photocatalysis for photodegradation and bactericidal activity owing their sufficient charge separation ability under visible light [19–23]. Moreover, Ag_3PO_4 has been reported in the literature as highly efficient visible light active photocatalyst toward the photodegradation of dye. Therefore, it has inspired with great enthusiasm [24]. However, bare Ag_3PO_4 nanoparticles undergo photocorrosion in the absence of electron acceptors and also slightly soluble in aqueous solution which hinders its structural stability [25]. Several research have been carried out to address the problem by combining Ag_3PO_4 nanoparticles with different materials like $SrTiO_3$ [26], CNT [27], C_3N_4 [28], GO [29], carbon quantum dots [30]. However, as-synthesized heterostructure composites have been reported in irregular, uncontrolled and powder form, which might bring difficulties in separation during re-usability. To overcome such problem, nanoparticles have been incorporated into polymer nanofibers [21,31]. But, incorporating of Ag_3PO_4 nanoparticles into semiconductor nanofibers having appropriate bandgap energy structure might enhance the photocatalytic activity, chemical stability and reusability as well. Notably, recent fabrication of Ag_3PO_4 nanoparticles onto TiO_2 nanobelts and nanotube has been carried out to study the photodegradation of dye [32,33]. However their synthesized samples have no uniform decoration of Ag_3PO_4 nanoparticles onto the nanobelts and nanotube. Such not well rooted Ag_3PO_4 nanoparticles might detach from their template and bring difficulties during dye degradation and reuse. By considering these points in mind, we decorated the secondary Ag_3PO_4 nanoparticles uniformly onto the primary TiO_2 nanofibers by facile electrospinning and hydrothermal method.

To the best of our knowledge, this is the first time study to report decoration of Ag_3PO_4 nanoparticles onto the TiO_2 nanofibers surface by hydrothermal method. The main target of this contribution is to synthesize efficient and easily separable uniformly well rooted Ag_3PO_4/TiO_2 nanocomposite fibers for the simultaneous removal of dye and destruction of bacteria. Thus prepared hierarchical Ag_3PO_4/TiO_2 nanocomposite fibers displayed an excellent photocatalytic activity toward the photodegradation of organic dye and destruction of bacteria.

2. Experimental procedure

2.1. Materials

Poly-vinyl pyrrolidone (PVP, MW 130,000 g/mol, Sigma–Aldrich), titanium tetra-isopropoxide (Ti(Iso), 97%, Sigma–Aldrich), acetic acid (Showa Chemicals Co. Ltd., Japan), Disodium hydrogen phosphate dihydrate ($Na_2HPO_4.2H_2O$, Sigma–Aldrich, USA), Silver nitrate ($AgNO_3$, Sigma–Aldrich, USA), Polyethylene glycol (Showa Chemicals Co. Ltd., Japan),and methylene blue (MB) (Showa Chemical Ltd., Japan) were used directly in this experiment without further treatment.

2.2. Preparation of TiO_2 nanofibers

TiO_2 nanofibers were prepared according to our previous work [16]. Briefly, 1.5 g of titanium tetra-isopropoxide was mixed with 3 g of acetic acid. After stirring for 10 min, 0.45 g of PVP, and 4 g of ethyl alcohol were added and stirred for 6 h at room temperature. The obtained solution was electrospun at 15 kV maintaining tip to collector distance of 15 cm. As-spun nanofibers were collected in polyethylene sheet and, vacuum dried at 60 °C for 12 h. After calcination in air at 600 °C for 3 h (heating rate 2.5 °C/min), the TiO_2 nanofibers were obtained.

2.3. Preparation of Ag_3PO_4/TiO_2 nanocomposite fibers

Ag_3PO_4/TiO_2 nanocomposite fibers were prepared by using hydrothermal method. 100 mg of TiO_2 nanofiber was dispersed 25 ml of deionized water and sonicated for 10 min. 80 mg of $AgNO_3$ and 3–4 drops of poly-ethylene glycol were also added to above mixture after sonication and kept stirring for 30 min. After stirring, 80 mg of $Na_2HPO_4.2H_2O$ was added and again kept stirring for 1 h. Then, whole mixture was poured into 50 ml Teflon autoclave and maintained temperature 160 °C for 3 h. Thus, synthesized composite nanofibers after cooling at room temperature, was filtered off, and then washed repeatedly with distilled water and ethanol. Finally, Ag_3PO_4/TiO_2 nanocomposite fibers were dried in vacuum at 100 °C for 24 h. The schematic illustration for the preparation of Ag_3PO_4/TiO_2 nanocomposite fibers is shown in Fig. 1. For the comparison, Ag_3PO_4 particles were also prepared by stirring in absence of TiO_2 nanofibers.

2.4. Characterization methods

The surface morphology of the as-synthesized nanocomposite fibers was investigated using FE-SEM (S-4700, Hitachi, Japan) and transmission electron microscopy (TEM, JEM- 2010, JEOL, Japan). The EDX spectrum of nanocomposite fibers was also recorded with the same FE-SEM instrument. The crystallographic structure of the resulting compositions were visualized by using XRD instrument Rigaku with Cu Kα (λ = 1.540 Å) with radiation over Bragg angles ranging from 20° to 80°. The bonding configuration was characterized by using Fourier transform infrared (FTIR, FT/IR-4200, Jasco international Co., Ltd.). 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).

2.5. Investigation of photocatalytic effect

Photocatalytic activity of Ag_3PO_4/TiO_2 nanocomposite fibers was evaluated by monitoring the photodegradation of methylene blue aqueous solution under solar light irradiation according to