Towards the Enhancement in Photocatalytic Performance of Ag₃PO₄ Nanoparticles through Sulfate Doping and Anchoring on Electrospun Nanofibers

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Abstract: Present work reports the enhancement in photocatalytic performance of Ag₃PO₄ nanoparticles through sulfate doping and anchoring on Polyacrylonitrile (PAN)-electrospun nanofibers (SO₄²⁻-Ag₃PO₄-PAN-electrospun nanofibers) via electrosprinning followed by ion-exchange reaction. Morphology, structure, chemical composition, and optical properties of the prepared sample were characterized using XRD, FESEM, FTIR, XPS, and DRS. The anchoring of SO₄²⁻-Ag₃PO₄ nanoparticles on the surface of PAN-electrospun nanofibers was evidenced by the change in color of the PAN nanofibers mat from white to yellow after ion-exchange reaction. FESEM analysis revealed the existence of numerous SO₄²⁻-Ag₃PO₄ nanoparticles on the surface of PAN nanofibers. Photocatalytic activity and stability of the prepared sample was tested for the degradation of Methylene blue (MB) and Rhodamine B (RhB) dyes under visible light irradiation for three continuous cycles. Experimental results showed enhanced photodegradation activity of SO₄²⁻-Ag₃PO₄-PAN-electrospun nanofibers compared to that of sulfate undoped sample (Ag₃PO₄/PAN-electrospun nanofibers). Doping of SO₄²⁻ into Ag₃PO₄ crystal lattice could increase the photogenerated electron–hole separation capability, and PAN nanofibers served as support for nanoparticles to prevent from agglomeration.

Keywords: electrospinning; SO₄²⁻-Ag₃PO₄ nanoparticles; organic dyes; photocatalyst; visible light

1. Introduction

The breakthrough work carried out by Yi et al. [1] opened a new door to engineer and synthesize silver phosphate (Ag₃PO₄)-based photocatalysts with enhanced performance that can find potential applications in dye photodegradation, hydrogen evolution, and killing microbes [2–5]. Ag₃PO₄ is a narrow band gap (2.36 eV) semiconductor material, which can generate reactive oxygen species (ROS) like OH⁻ or O₂⁻ from electron–hole pairs under visible light irradiation. Thus, generated ROS are responsible for its photocatalytic activities [6,7]. Application of Ag₃PO₄ as a visible light-driven photocatalyst is limited due to poor chemical stability, when applied in absence of sacrificial agent [1,8]. Therefore, successive investigations have been carried out for designing and fabricating Ag₃PO₄-based photocatalysts to overcome this limitation and improve their performance. In this regard, various studies have been reported, such as fabricating composites [9–13], coupling with other semiconductor materials [14,15] and doping suitable ions [16–18]. Out of these, doping of suitable ions into the crystal lattice of semiconductor materials could be an alternate strategy to enhance their photocatalytic property. It is reported that semiconductor material doped with suitable
ions could prevent the recombination of photogenerated electron–hole pairs and consequently increases its stability and photocatalytic performance [19].

On that note, various results regarding the enhanced photocatalytic performance of Ag$_3$PO$_4$ via cations doping into its crystal lattice have been reported [20,21]. On the contrary, photocatalytic activities of Ag$_3$PO$_4$ doped with suitable anions have not been reported frequently. Meanwhile, a recent report has demonstrated the enhanced photocatalytic activity of sulfur-doped Ag$_3$PO$_4$ on the basis of hybrid density-functional calculation [22]; however, due to the strong P-O bond, doping of sulfur into Ag$_3$PO$_4$ crystal lattice seems more difficult. Therefore, instead of sulfur, SO$_4^{2-}$ might be a suitable anion as a dopant to replace PO$_4^{3-}$ from Ag$_3$PO$_4$ crystal lattice due to smaller radius of SO$_4^{2-}$ (0.218 nm) compared to that of PO$_4^{3-}$ (0.230 nm) [23,24]. On the other hand, use of photocatalyst nanoparticles in powder form creates a serious problem of agglomeration during photocatalysis, which leads to a reduction of surface area and ultimately, a decrease in photocatalytic performance [25]. In addition, the separation process of photocatalyst from solution becomes more difficult after use. To deal with these difficulties and avoid the loss of photocatalyst, polymer-electrospun nanofibers are being widely used as supports for nanoparticles [26–28]. Due to its excellent characteristics, like environmental stability, easy processability, and low density, PAN polymer is being extensively used for the fabrication of nanofibers as flexible support for photocatalyst nanoparticles using simple and versatile electrospinning technique [29,30].

Hence to realize the synergistic effect of sulfate-doped Ag$_3$PO$_4$ nanoparticles and PAN-electrospun nanofibers as support, our work is focused on the fabrication of SO$_4^{2-}$-Ag$_3$PO$_4$/PAN-electrospun nanofibers by combining electrospinning and ion-exchange reaction. Visible light photocatalytic activity of as fabricated sample was evaluated by observing photodegradation of MB and RhB dye solutions. Finally, we hope this visible-light-driven photocatalyst would be a promising candidate for the degradation of organic dyes from waste water to avoid negative effects to the dependent living ecology. To the best of our knowledge this type of work has not been reported so far.

2. Materials and Methods

2.1. Chemicals

The chemicals used in this work are Polyacrylonitrile (PAN, MW-150000, Sigma-Aldrich, St. Louis, MO, USA), Disodium hydrogen phosphate dihydrate (Na$_2$HPO$_4$.2H$_2$O, Sigma-Aldrich, St. Louis, MO, USA), Silver nitrate (AgNO$_3$, Sigma-Aldrich, St. Louis, MO, USA), Sodium sulfate (Na$_2$SO$_4$, Sigma-Aldrich, St. Louis, MO, USA), Silver nitrate (AgNO$_3$, Sigma-Aldrich, St. Louis, MO, USA), Methylene blue (MB, Sigma-Aldrich, St. Louis, MO, USA), Rhodamine B (RhB, Sigma-Aldrich, St. Louis, MO, USA) and N,N-dimethylformamide (DMF, SAMCHUN PURE CHEMICAL, Mogok-dong 117, Gyeonggi-d, Korea). All the chemicals were of AR grade and used without further purification. Distilled water was used to prepared aqueous solutions.

2.2. Fabrication of Na$_2$HPO$_4$/PAN Nanofiber

First, fine powder of Na$_2$HPO$_4$ (0.46 g) was dispersed in DMF (14 mL) and ultrasonicated for 1 h. Then 1.5 g powder of PAN polymer was added to the above dispersion and magnetically stirred for 12 h to prepare electrospinning solution. Electrospinning of the prepared solution was carried out by loading into a plastic syringe fitted with plastic micro-tip. The applied voltage and distance between needle tip to collector were set as 18 kV and 12 cm, respectively. The developing nanofibers were collected on rotating drum collector connected to DC motor. Thus obtained Na$_2$HPO$_4$/PAN-electrospun nanofibers were vacuum dried for 12 h at 70 °C.

2.3. Fabrication of SO$_4^{2-}$-Ag$_3$PO$_4$/PAN-Electrospun Nanofibers

SO$_4^{2-}$-Ag$_3$PO$_4$/PAN-electrospun nanofibers were prepared following ion-exchange reaction. Briefly, Na$_2$HPO$_4$/PAN nanofiber mat (0.1 g) was immersed in 500 mL of AgNO$_3$ solution containing SO$_4^{2-}$ ions for 30 min. Concentration of AgNO$_3$ and Na$_2$SO$_4$ was maintained at 0.02 M and 0.01 M, respectively. Change in color of nanofibers mat from white to yellow during ion-exchange reaction
indicated the anchoring of $\text{SO}_4^{2-}$-$\text{Ag}_3\text{PO}_4$ nanoparticles on the surface of PAN nanofibers. For comparison, $\text{Ag}_3\text{PO}_4$/PAN-electrospun nanofibers were also fabricated without adding $\text{SO}_4^{2-}$ ions into the AgNO$_3$ solution under similar conditions. The resulting nanofibers mats were washed with deionized water and dried at 60 °C for 6 h before characterization. The schematic for the fabrication of $\text{SO}_4^{2-}$-$\text{Ag}_3\text{PO}_4$/PAN-electrospun nanofibers is illustrated in Scheme 1. For the convenience of description, different samples are named as pristine PAN, AP/PAN, and SAP/PAN corresponding to pristine PAN-electrospun nanofibers, $\text{Ag}_3\text{PO}_4$/PAN-electrospun nanofibers, and $\text{SO}_4^{2-}$-$\text{Ag}_3\text{PO}_4$/PAN-electrospun nanofibers, respectively.

Scheme 1. Schematic illustration for the fabrication of (SAP/PAN) $\text{SO}_4^{2-}$-$\text{Ag}_3\text{PO}_4$/PAN-electrospun nanofibers.

2.4. Characterization

Crystalline nature of the samples was investigated using X-ray diffractometer (XRD, Empyrean, PANalytical, Eindhoven 5651 GH, Netherlands) with Cu Kα (λ = 1.540 Å) radiation over Bragg angles ranging from 10° to 80°. Field emission scanning electron microscope (FESEM, GeminiSEM 500, Carl Zeiss Microscopy GmbH, 73447, Oberkochen, Germany) equipped with energy dispersive X-ray spectroscopy (EDS) was used to study the morphology and elemental composition of the samples. Bonding configuration of the samples was characterized applying Fourier-transform infrared (FT-IR, FT/IR-4200, Jasco international Co., Ltd., 4-21, Sennin-cho 2-chome, Hachioji, Tokyo 193-0835, Japan) through attenuated total reflectance mode (ATR). Furthermore, the surface element composition analysis of $\text{SO}_4^{2-}$-doped/undoped samples was studied using X-ray photoelectron spectroscopy (XPS, AXIS-NOVA, Kratos Analytical Ltd., Manchester, M17 1GP, UK), and the light absorption properties of the prepared samples was evaluated from UV-vis diffusive reflectance spectra (DRS) obtained from UV-vis spectrophotometer (UV-2600 240 EN, SHIMADZU CORPORATION, Kyoto, Japan).

2.5. Investigation of Photocatalytic Activity

To investigate the photocatalytic performance, as fabricated samples (pristine PAN, AP/PAN, and SAP/PAN) were utilized as visible-light-driven photocatalysts for the degradation of MB and RhB solutions at 10 ppm using a solar simulator having an internal xenon lamp (DYX300P, DYE TECH Co., Seoul, Korea) equipped with a UV cutoff filter. The experiments were carried out in a
glass vial containing dye solution (50 mL) and photocatalyst (100 mg). Prior to irradiation, the suspension was magnetically stirred under dark conditions for 30 min to establish adsorption/desorption equilibrium. Afterward, visible light obtained from the 200-W xenon lamp was irradiated under continuous magnetic stirring. Aliquots were taken at regular time intervals (10 min) and the concentration of the dye solution was measured spectrophotometrically by recording the absorbance using a UV-vis spectrophotometer (HP 8453 UV–vis spectroscopy system, Hudson, MA, USA). The total organic carbon (TOC) content in residual solution was determined with a TOC analyzer (multi N/C 3100, Analytik Jena, Konrad-Zuse-Strasses 1 07745 Jena, Germany).

3. Results and Discussion

XRD analysis was applied to investigate the crystallinity and effect of sulfate doping into Ag₃PO₄ crystal lattice. Figure 1a displays XRD patterns of pristine PAN, AP/PAN, and SAP/PAN. A broad and noncrystalline peak at 2θ of 20–30° in all formulations was assigned to the (110) crystal plane of PAN polymer [29]. Besides, the diffraction peaks at 2θ of 20.89°, 29.69°, 33.31°, 36.51°, 42.42°, 47.74°, 52.66°, 55.10°, 57.29°, 61.63°, 65.71°, 70.06°, 71.89°, and 73.78° in AP/PAN and SAP/PAN were attributed to the crystal planes of (110), (200), (210), (211), (220), (310), (222), (320), (321), (400), (411), (420), (421), and (332) of Ag₃PO₄, respectively (JCPDS card No: 06-0505). Effect of sulfate doping into Ag₃PO₄ crystal lattice was examined by observing the magnified XRD patterns of AP/PAN and SAP/PAN (Figure 1b). The gradual shift of peaks corresponding to (210) and (211) crystal planes of SAP/PAN towards higher 2θ angle was observed. Such shifting might be attributed to the decrease in crystal lattice constant due to SO₄²⁻ ions entering into Ag₃PO₄ crystal lattice by replacing PO₄³⁻ ions since SO₄²⁻ has a smaller ionic radius than that of PO₄³⁻ [24,31].

Figure 2a–c show the typical FESEM images of Na₂HPO₄/PAN electrospun nanofibers, AP/PAN, and SAP/PAN fabricated by electrospinning. All samples exhibited bead-free, continuous, and randomly oriented nanofibers having an average diameter of 430 nm. Na₂HPO₄/PAN nanofibers could serve as both support and source to subsequent ion-exchange reaction to fabricate sulfate undoped/doped Ag₃PO₄/PAN nanofibers. After the growth of nanoparticles by ion-exchange reaction, the surface of nanofibers (AP/PAN) (Figure 2b) and (SAP/PAN) (Figure 2c) was no longer smooth compared to Na₂HPO₄/PAN nanofibers. The nanoparticles with some agglomerations were uniformly anchored on PAN nanofiber surface, which was evidenced through the color change of Na₂HPO₄/PAN nanofibers mate from white to yellow after ion-exchange reaction (insets Figure 2a–c). In order to elucidate the stability of photocatalyst, FESEM characterization of used SAP/PAN was
performed. As depicted in the Figure (inset of Figure 2d), the used sample could keep its integrity even after three cycle tests without distinct loss of nanoparticles. Furthermore, elemental composition of SAP/PAN was investigated by FESEM-EDS (Figure 2d). The EDS spectra indicated the presence of considerable amount of C, O, P, S, and Ag in SAP/PAN without other impurities, justifying the sample being composed of sulfate-doped Ag₃PO₄ and PAN. Similarly, existence of sulfate-doped Ag₃PO₄ nanoparticles on PAN nanofibers was further confirmed, observing spatial distribution of O, P, S, and Ag elements by elemental mapping of SAP/PAN (Figure 3). As shown in the mapping images, all the elements are almost homogeneously distributed on PAN nanofiber surface, specifying the presence of sulfate-doped Ag₃PO₄ nanoparticles.

**Figure 2.** FESEM images; (a) Na₂HPO₄/PAN nanofibers, (b) AP/PAN, (c) SAP/PAN. Panel (d) represents the corresponding EDS of (c). Insets in Figure (a, b, and c) are digital photograph of corresponding nanofibers and inset in Figure (d) is FESEM image of used SAP/PAN.

Figure 4 represents the FTIR spectra of pristine PAN, AP/PAN, and SAP/PAN. The absorption band centered at about 2243 cm⁻¹ in all samples is assigned to the nitrile group (C≡N) of PAN. Similarly, all samples possessing characteristics bands attributed to aliphatic CH group vibrations of different modes in the methylene group of PAN were located in the regions 1220–1270 cm⁻¹, 1350–1380 cm⁻¹, 1450–1460 cm⁻¹, and 2870–2931 cm⁻¹ [32]. Moreover, the absorption bands located at about 1600 cm⁻¹ and 3400–3500 cm⁻¹ were assigned to stretching vibration of H-O-H and bending O-H to denote the presence of physically absorbed water molecules [33]. Furthermore, absorption bands located at about 550 cm⁻¹ and 981 cm⁻¹ in AP/PAN and SAP/PAN were due to the molecular vibration of PO₄³⁻ [30,34]. However, the absorption band that locates at about 983 cm⁻¹ [35,36] corresponding to SO₄²⁻ in SAP/PAN was not apparent, which could be due to overlapping with the absorption band of PO₄³⁻ or small amount of SO₄²⁻. Hence, all these FTIR results suggested SO₄²⁻-doped/undoped Ag₃PO₄ nanoparticles were immobilized on PAN nanofibers.
The coexistence of SO$_{4}^{2-}$ in Ag$_3$PO$_4$ and PAN in SAP/PAN was confirmed by performing XPS analysis. As shown in survey spectrum (Figure 5a), P, S, Ag, and O elements coming from SO$_{4}^{2-}$ - Ag$_3$PO$_4$ and C and N elements corresponding to PAN were clearly observed. Moreover, specific nature of S in SAP/PAN and Ag, P, and O in both samples was obtained from high-resolution XPS spectra. As depicted in Figure 5b, a peak located at around 168.38 eV in high-resolution spectra of S 2p in SAP/PAN was attributed to S$^{6+}$ [37]. This result also indicated the incorporation of SO$_{4}^{2-}$ into Ag$_3$PO$_4$ crystal lattice during synthesis process. In case of Ag 3d and P 2p peaks of SAP/PAN, slight shifting of these peaks to higher values of binding energies was observed compared to that of AP/PAN (Figure 5c,d). This shifting might happen due to doping of SO$_{4}^{2-}$, which could decrease electron density around Ag and P due to higher electronegativity of S [38]. Similar behavior was observed for O 1s peak of SAP/PAN compared to AP/PAN (Figure 5e). Hence, all these XPS results further confirmed the existence of S in the form of SO$_{4}^{2-}$ in Ag$_3$PO$_4$ crystal lattice due to its strong electronic interactions with Ag, P, and O [19].
Figure 5. XPS spectra; survey spectrum of SAP/PAN (a). Panels (b–e) represent the high-resolution spectra of AP/PAN and SAP/PAN.

UV-vis diffusive reflectance spectra (DRS) of pristine PAN, AP/PAN, and SAP/PAN were measured to determine their light absorption behavior and the results are plotted in Figure 6. As seen, two absorption bands presented in the range of 200–350 nm were assigned to the pristine PAN, which is in agreement with the result of a previously reported study [39]. After loading sulfate undoped/doped nanoparticles on PAN nanofibers, visible light absorption behavior could be observed. Both the samples (AP/PAN and SAP/PAN) displayed continuous absorption in visible range (520–700 nm), however the absorption intensity of SAP/PAN was found to be slightly increased. Therefore, these results signified the visible light harvesting capability of AP/PAN and SAP/PAN.
Figure 6. UV-vis diffusive reflectance spectra of prepared photocatalysts.

Photodegradation performances of different samples under visible light irradiation were investigated using MB and RhB dye solutions and results are presented in Figure 7a,b. The photodegradation is represented as the variation of \( (C_t/C_0) \) with irradiation time, where \( C_0 \) is the initial concentration and \( C_t \) is remaining concentration of dyes solution at time \( t \). As presented in figure, pristine PAN could show negligible capability of photodegradation of MB and RhB dye solutions. In contrary, more than 95% of MB was degraded by SAP/PAN within 40 min, while only 88% of MB was degraded within this time period utilizing AP/PAN. Likewise, SAP/PAN could exhibit superior performance over AP/PAN towards the photodegradation of RhB. In this case, SAP/PAN could degrade 95% of RhB within 50 min, but within this time period, AP/PAN could degrade about 87% of RhB. On the basis of these results, SAP/PAN was found to be a more advantageous visible-light-driven photocatalyst over AP/PAN. Figure 7c,d show the time-dependent absorbance variations of MB and RhB dye solutions utilizing SAP/PAN under visible light irradiation. Corresponding absorbance peaks of MB at 665 nm and RhB at 554 nm are gradually diminished with the increase in irradiation time. Importantly, the maximum wavelength of MB and RhB were not found to be shifted, which indicated that benzene/heterocyclic rings were decomposed rather than decolorized due to adsorption of dye molecules on the surface of photocatalyst [40,41]. Insets (Figure 7c,d) show gradual decline in color of corresponding dye solution utilizing SAP/PAN.

The changes of TOC during photodegradation of MB and RhB utilizing SAP/PAN under visible light irradiation are displayed in Figure 8. As displayed in the figure, TOC of MB with SAP/PAN after 10, 20, 30, and 40 min of irradiation were 2.75, 2.3, 1.6, and 1.4 mg/L, respectively. Similarly, TOC of RhB with SAP/PAN after 10, 20, 30, 40, and 50 min of irradiation were 3.97, 3.39, 3.19, 2.75, and 2.5 mg/L, respectively. These results showed that TOCs were lower than that of original dye solutions (MB = 3.9 mg/L and RhB = 4.56 mg/L). Furthermore, the rate of TOC change for both MB and RhB dyes was lower compared to their photodegradation rate, which is assigned to the partial decomposition of dye molecules into intermediate products resulting in the disappearance of color and partial mineralization [42,43].
Figure 7. Photocatalytic performances of pristine PAN, AP/PAN, and SAP/PAN towards photodegradation of MB (a) and RhB (b) solutions. Absorbance variation of MB (c) and RhB (d) solutions utilizing SAP/PAN. Insets; digital photographs showing the color change of corresponding dye solution with irradiation time.

Figure 8. Changes in total organic carbon (TOC) during photodegradation of (a) MB and (b) RhB with SAP/PAN.

Photodegradation stability of SAP/PAN was examined by performing cycling experiments for MB and RhB degradation under visible light irradiation (Figure 9a,b). For cycling experiments, the used sample was separated, washed, and dried at room temperature then reapplied for photodegradation under similar conditions. Experimental results showed good stability of SAP/PAN up to third cycle, however slight decrease was observed in the performance during cycling experiments, which could happen due to loss of photocatalyst during separation process. Furthermore, Langmuir–Hinshelwood model was applied to evaluate the photodegradation kinetics of MB and RhB solutions utilizing AP/PAN and SAP/PAN.
\[ r = \frac{-dc}{dt} = \frac{k_rKC}{1 + KC} \]  

(1)

Since the initial concentration of MB and RhB was very low \((C_o = 10 \text{ mg/L})\), equation (1) can be considered a pseudo first-order kinetics equation \([44]\) as

\[ \ln \frac{C_o}{C_t} = k_{app}t, \]  

(2)

where \(C_o\) and \(C_t\) represent the initial concentration and concentration at time \((t)\), respectively. \(k_{app}\) is the apparent rate constant \((\text{min}^{-1})\), which can be obtained by plotting \(\ln \frac{C_o}{C_t}\) vs. reaction time. Hence, degradation kinetics of MB and RhB solutions were calculated by applying equation (2) and the results are shown in Figure 9c,d. The linear relationship between \(\ln \frac{C_o}{C_t}\) vs. reaction time suggested the pseudo first-order kinetics of photodegradation. From the results, apparent rate constants of MB degradation utilizing AP/PAN and SAP/PAN were determined to be 0.057 \(\text{min}^{-1}\) and 0.075 \(\text{min}^{-1}\), respectively. Similarly, the apparent rate constants 0.043 \(\text{min}^{-1}\) and 0.064 \(\text{min}^{-1}\) were determined for RhB degradation utilizing AP/PAN and SAP/PAN, respectively. All these results indicated that sulfate doping could provide significant capability to \(\text{Ag}_3\text{PO}_4\) to enhance its photodegradation performance.

![Figure 9](image)

**Figure 9.** Cycling experiments of photodegradation of MB (a) and RhB (b) solutions utilizing SAP/PAN. Photodegradation Kinetics of MB (c) and RhB (d) solutions over different photocatalysts under visible light irradiation.

On the basis of above results, an overall mechanism is proposed for photodegradation of organic dyes. \(\text{Ag}_3\text{PO}_4\), being a semiconductor material, generates electron–hole pairs under visible light irradiation. The photo-excited electrons travel to conduction band (CB) from valence band (VB) and react with dissolved oxygen molecules to produce ROS, i.e., oxygen peroxide radicals \((\text{O}_2^{•-})\), which are strong oxidizing agents and degrade dye molecules effectively. On the other hand, holes at VB directly react with dye molecules \([45]\). In this way, these ROS and holes can photocatalytically degrade organic dyes as
Organic dyes + O$_2$•$^-$ → CO$_2$ + H$_2$O + mineralization products. \hspace{1cm} (3)

It is well known that semiconductor photocatalysts having improved separation capability and low recombination rate of photoinduced electron–hole pairs can exhibit enhanced performances. Hence, in this work the enhanced photocatalytic performances of SAP/PAN compared to that of AP/PAN can be explained with the role of SO$_\text{4}^2$− as dopant, which could play an important role to trap and transfer photoinduced electrons to CB, thereby providing improved separation capability of electron–hole pairs to SO$_\text{4}^2$−-Ag$_3$PO$_4$ (Figure 10). Moreover, SO$_\text{4}^2$−-Ag$_3$PO$_4$ could receive additional electrons due to higher electronegativity of S than that of P. As a result, the Fermi level of SO$_\text{4}^2$−-Ag$_3$PO$_4$ gets shifted towards CB and possesses n-type conductivity. In this way, doping of SO$_\text{4}^2$− into the Ag$_3$PO$_4$ crystal lattice can improve its separation capability and lower recombination rate of photoinduced electron–hole pairs, which ultimately increases the production of ROS and enhances the photocatalytic performance of SO$_\text{4}^2$−-Ag$_3$PO$_4$ [22,46,47].

Figure 10. Schematic illustration for the degradation of dye by sulfate-doped Ag$_3$PO$_4$/PAN under visible light irradiation.

4. Conclusions

In summary, SO$_\text{4}^2$−-Ag$_3$PO$_4$/PAN-electrospun nanofibers were fabricated successfully by combining electrospinning and ion-exchange reaction. Different characterization techniques were used to study the morphology, structure, chemical composition, and optical properties of the samples. Photocatalytic activity of the fabricated samples was investigated by photodegradation of MB and RhB dye solutions under visible light irradiation. In both investigations, SO$_\text{4}^2$−-Ag$_3$PO$_4$/PAN-electrospun nanofibers could show enhanced performance compared to Ag$_3$PO$_4$/PAN-electrospun nanofibers. We believe that the enhanced performances of SO$_\text{4}^2$−-Ag$_3$PO$_4$/PAN-electrospun nanofibers were attributed to the sufficient electron–hole separation capability of SO$_\text{4}^2$−-Ag$_3$PO$_4$ nanoparticles to produce ROS due to doping effect of SO$_\text{4}^2$− ions into the Ag$_3$PO$_4$ crystal lattice. Therefore, thus fabricated SO$_\text{4}^2$−-Ag$_3$PO$_4$/PAN-electrospun nanofibers can find potential application as visible-light-driven photocatalyst with good flexibility and reusability for wastewater treatment.

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References

1. Yi, Z.; Ye, J.; Kikugawa, N.; Kako, T.; Ouyang, S.; Williams, H.S.; Yang, H.; Cao, J.; Luo, W.; Li, Z. An orthophosphate semiconductor with photooxidation properties under visible-light irradiation. Nat. Mater. 2010, 9, 559–564.

2. Yan, Y.; Guan, H.; Liu, S.; Jiang, R. AgPO/FeO composite photocatalysts with an n–n heterojunction semiconductor structure under visible-light irradiation. Ceram. Int. 2014, 40, 9095–9100.

3. Chava, R.M.; Do, J.Y.; Kang, M. Fabrication of CdS–AgPO heteronanostructures for improved visible photocatalytic hydrogen evolution. J. Alloys Compd. 2017, 727, 86–93.

4. Buckley, J.J.; Lee, A.F.; Olivi, L.; Wilson, K. Hydroxyapatite supported antibacterial AgPO nanoparticles. J. Mater. Chem. 2010, 20, 8056–8063.

5. Liu, B.; Xue, Y.; Zhang, J.; Han, B.; Zhang, J.; Suo, X.; Mu, L.; Shi, H. Visible-light driven TiO2/AgPO heterostructures with enhanced antifungal activity against agricultural pathogenic fungi Fusarium graminearum and mechanism insight. Environ. Sci. Nano 2017, 4, 255–264.

6. Wang, J.; Tafven, D.N.; Lewis, J.P.; Hong, Z.; Manivannan, A.; Zhi, M.; Wu, N. Origin of Photocatalytic Activity of Nitrogen-Doped TiO2 Nanobelts. J. Am. Chem. Soc. 2009, 131, 12290–12297.

7. Li, Y.; Zang, W.; Niu, J.; Chen, Y. Mechanism of Photogenerated Reactive Oxygen Species and Correlation with Metal-Oxide Nanoparticles. ACS Nano 2012, 6, 5164–5173.

8. Liu, W.; Shen, J.; Yang, X.; Liu, Q.; Tang, H. Dual Z-Scheme gC3N4/AgPO4/Ag2MoO4 Ternary Composite Photocatalyst for Solar Oxygen Evolution from Water Splitting. Appl. Surf. Sci. 2018, 456, 369–378.

9. Yang, X.; Qin, J.; Jiang, Y.; Li, R.; Li, Y.; Tang, H. Bifunctional TiO2/AgPO/graphene composites with superior visible light photocatalytic performance and synergistic inactivation of bacteria. RSC Adv. 2014, 4, 18627–18636.

10. Liang, Q.; Shi, Y.; Ma, W.; Li, Z.; Yang, X. Enhanced photocatalytic activity and structural stability by hybridizing AgPO nanostructures with graphene oxide sheets. Phys. Chem. Chem. Phys. 2012, 14, 15657–15665.

11. Tian, J.; Li, H.; Xing, Z.; Wang, L.; Asiri, A.M.; Youbi, A.O.A.; Sun, X. Facile synthesis of MWCNTs/AgPO–PO nanocomposites with enhanced photocatalytic activity under visible light. J. Nanoparticle Res. 2013, 15, 1453–1460.

12. Wang, Z.; Yin, L.; Zhang, M.; Zhou, G.; Fei, H.; Shi, H.; Dai, H. Synthesis and characterization of AgPO/multivalved carbon nanotube composite photocatalyst with enhanced photocatalytic activity and stability under visible light. J. Mater. Sci. 2014, 49, 1585–1593.

13. Ma, J.; Zou, J.; Li, L.; Yao, C.; Kong, Y.; Cui, B.; Zhu, R.; Li, D. Nanocomposite of attapulgite-AgPO4 for Orange II photodegradation. Appl. Catal. B-Environ. 2014, 144, 36–40.

14. Xu, J.W.; Gao, Z.D.; Han, K.; Liu, Y.; Song, Y.Y. Synthesis of Magnetically Separable AgPO/TiO2/Fe2O3 Heterostructure with Enhanced Photocatalytic Performance under Visible Light for Photoinactivation of Bacteria. ACS Appl. Mater. Interfaces 2014, 6, 15122–15131.

15. Lin, W.; Zhang, S.; Wang, D.; Zhang, C.; Sun, D. Ultrasound-assisted synthesis of high-efficiency AgPO/CoO: heterojunction photocatalyst. Ceram. Int. 2015, 41, 8956–8963.

16. Kim, D.S.; Cho, Y.I.; Park, J.; Yoon, J.; Jo, Y.; Jung, M.H. (Mn, Zn) Co-doped CdS nanowires. J. Phys. Chem. C 2007, 111, 10861–10868.

17. Chandramohan, S.; Kanjilal, A.; Sarangi, S.N.; Majumder, S.; Sathyamooorthy, R.; Hong, C.H.; Som, T. Effect of substrate temperature on implantation doping of Co in CdS nanocrystalline thin films. Nanoscale 2010, 2, 1155–1159.

18. Li, J.X.; Xu, J.H.; Dai, W.L.; Li, H.X.; Fan, K.N. Direct hydro-alcohol thermal synthesis of special core-shell structured Fe-doped titania microspheres with extended visible light response and enhanced photoactivity. Appl. Catal. B 2009, 85, 162–170.

19. Zhang, S.N.; Zhang, S.J.; Song, L.M. Super-high activity of Bi+ doped AgPO and enhanced photocatalytic mechanism. Appl. Catal. B Environ. 2014, 152–153, 129–139.

20. Xie, Y.P.; Wang, G.S. Visible light responsive porous Lanthanum-doped AgPO photocatalyst with high photocatalytic water oxidation activity. J. Colloid Interface Sci. 2014, 430, 1–5.
21. Yu, H.C.; Kang, H.X.; Jiao, Z.B.; Lü, G.X.; Bi, Y.P. Tunable photocatalytic selectivity and stability of Ba-doped Ag/POs hollow nanosheets. *Chin. J. Catal.* 2015, 36, 1587–1595.

22. Reunchan, P.; Umezawa, N. Sulfur and Silicon Doping in Ag/POs. *J. Phys. Chem. C* 2015, 119, 2284–2289.

23. Cao, W.; Gui, Z.; Chen, L.; Zhu, X.; Qi, Z. Facile synthesis of sulfate-doped Ag/POs with enhanced visible light photocatalytic activity. *Appl. Catal. B Environ.* 2017, 200, 681–689.

24. Roodbottom, H.K.; Jenkins, H.D.B.; Passmore, J.; Glasser, L. Thermochemical Radii of Complex Ions. *J. Chem. Educ.* 1999, 76, 1570–1573.

25. Zhu, M.; Qin, C.; Wang, J-J.; Sun, J.; Dai, L. Cone-like titanate immobilized on polyacrylonitrile nanofibers: Hierarchical architecture for effective photocatalytic activity. *Dalton Trans.* 2020, 49, 4067–4077.

26. Tao, R.; Yang, S.; Shao, C.; Li, X.; Li, X.; Liu, S.; Zhang, J.; Liu, Y. Reusable and Flexible g-C3N4/Ag/POs/Polyacrylonitrile Heterojunction Nanofibers for Photocatalytic Dye Degradation and Oxygen Evolution. *ACS Appl. Nano Mater.* 2019, 2, 3081–3090.

27. Gangemi, C.M.A.; Iudici, M.; Spitaleri, L.; Randazzo, R.; Gaeta, M.; D’Urso, A.; Gulino, A.; Purrello, R.; Fragalà, M.E. Polyethersulfone Mats Functionalized with Porphyrin for Removal of Para-nitroaniline from Aqueous Solution. *Molecules* 2019, 24, 3344.

28. Panthi, G.; Park, S.-J.; Kim, T.-W.; Chung, H.-J.; Hong, S.-T.; Park, M.; Kim, H.-Y. Electrospray composite nanofibers of polyacrylonitrile and AgCO3 nanoparticles for visible light photocatalysis and antibacterial applications. *J. Mater. Sci.* 2015, 50, 4477–4485.

29. Panthi, G.; Park, S.-J.; Chae, S.-H.; Kim, T.-W.; Chung, H.-J.; Hong, S.-T.; Park, M.; Kim, H.-Y. Immobilization of Ag/POs nanoparticles on electrospray PAN nanofibers via surface oximation: Bifunctional composite membrane with enhanced photocatalytic and antimicrobial activities. *J. Ind. Eng. Chem.* 2017, 25, 277–286.

30. Wang, Q.; Cui, J.; Li, G.; Zhang, J.; Li, D.; Huang, F.; Wei, Q. Laccase Immobilized on a PAN/Adsorbents Composite Nanofibrous Membrane for Catechol Treatment by a Biocatalysis/Adsorption Process. *Molecules* 2014, 19, 3376–3388.

31. Anisimov, V.I.; Zaanan, J.; Andersen, O.K. Band theory and Mott insulators: Hubbard U instead of Stoner. *I. Phys. Rev. B* 1991, 44, 943–954.

32. Zhang, W.; Liu, J.; Wu, G. Evolution of structure and properties of PAN precursors during their conversion to carbon fibers. *Carbon* 2003, 41, 2805–2812.

33. Huang, G.L.; Zhu, Y.F. Enhanced Photocatalytic Activity of ZnWO4 Catalyst via Fluorine Doping. *J. Phys. Chem. C* 2007, 111, 11952–11958.

34. Miller, L.M.; Vairavamurthi, V.; Chance, M.R.; Mendelsohn, R.; Paschalis, E.P.; Betts, F.; Boskey, A.L. In situ analysis of mineral content and crystallinity in bone using infrared micro-spectroscopy of the ν3 PO4−vibration. *Biochim. Biophys. Acta* 2001, 1527, 11–19.

35. Sifontes, A.B.; Cañizales, E.; Toro-Mendoza, J.; Ávila, E.; Hernández, P.; Delgado, B.A.; Gutiérrez, G.B.; Díaz, Y.; Cruz-Barrios, E. Obtaining Highly Crystalline Barium Sulphate Nanoparticles via Chemical Precipitation and Quenching in Absence of Polymer Stabilizers. *J. Nanomater.* 2015, 2015, 1–8.

36. Gomez, M.A.; Han, B.; Yao, S.; Chen, Y.; Li, S.; Zhang, D.; Wang, S.; Jia, Y. A new and improved synthesis method for the formation of ZnFe-CO3 and ZnFe-SO4 Hydrotalcites free from impurities. *Appl. Clay Sci.* 2019, 181, 105215–105224.

37. Yang, T.; Yang, H.; Zhen, S.J.; Huang, C.Z. Hydrogen-Bond-Mediated in Situ Fabrication of AgNPs/Agar/PAN Electrospray Nanofibers as Reproducible SERS Substrates. *ACS Appl. Mater. Interfaces* 2015, 7, 1586–1594.

38. Cao, W.R.; Chen, L.F.; Qi, Z.W. Microwave-assisted synthesis of Ag/Ag2SO4/ZnO nanostructures for efficient visible-light driven photocatalysis. *J. Mol. Catal. A Chem.* 2015, 401, 81–89.

39. Yu, D.; Liang, H.; Wang, J.; Li, C. A new fabrication of AgX (X = Br, I)-TiO2 nanoparticles immobilized on polycrlyonitrile (PAN) nanofibers with high photocatalytic activity and renewable property. *RSC Adv.* 2015, 5, 91457–91465.

40. Panthi, G.; Park, M.; Park, S.J.; Kim, H.K. PAN Electrospray Nanofibers Reinforced with AgCO3 Nanoparticles: Highly Efficient Visible Light Photocatalyst for Photodegradation of Organic Contaminants in Waste Water. *Macromol. Res.* 2015, 23, 149–155.

41. Zhuang, J.; Dai, W.; Tian, Q.; Li, Z.; Xie, L.; Wang, J.; Lü, P.; Shi, X.; Wang, D. Photocatalytic Degradation of RhB over TiO2 Bilayer Films: Effect of Defects and Their Location. *Langmuir* 2010, 26, 9686–9694.
42. Song, L.; Li, T.; Zhang, S. Synthesis and characterization of Ag/AgBrO₃ photocatalyst with high photocatalytic activity. *Mater. Chem. Phys.* **2016**, *182*, 1–6.

43. Anku, W.W.; Oppong, S.O.-B.; Shukla, S.K.; Govender, P.P. Comparative Photocatalytic Degradation of Monoazo and Diazo Dyes Under Simulated Visible Light Using Fe³⁺/C/S doped-TiO₂ Nanoparticles. *Acta Chim. Slov.* **2016**, *63*, 380–391.

44. Zhang, Z.; Shao, C.; Li, X.; Wang, C.; Zhang, M.; Liu, Y. Electrospun Nanofibers of p-Type NiO/n-Type ZnO Heterojunctions with Enhanced Photocatalytic Activity. *ACS Appl. Mater. Interfaces* **2010**, *2*, 2915–2923.

45. Zhao, J.; Ji, Z.; Chen, X.; Shen, X.; Ma, L.; Liu, X. Hydrothermal syntheses of silver phosphate nanostructures and their photocatalytic performance for organic pollutant degradation. *Cryst. Res. Technol.* **2014**, *49*, 975–981.

46. Jo, W.J.; Jang, J.W.; Kong, K.; Kang, H.J.; Kim, J.Y.; Jun, H.; Parmar, K.P.S.; Lee, J.S. Phosphate doping into monoclinic BiVO₄ for enhanced photoelectrochemical water oxidation activity. *Angew. Chem. Int. Ed.* **2012**, *51*, 3147–3151.

47. Kung, M.-L.; Tai, M.-H.; Lin, P.-Y.; Wu, D.-C.; Wu, W.-J.; Yeh, B.-W.; Hung, H.-S.; Kuo, C.-H.; Chen, Y.-W.; Hsieh, S.-L. Silver decorated copper oxide (Ag@CuO) nanocomposite enhances ROS-mediated bacterial architecture collapse. *Colloids Surf. B* **2017**, *155*, 399–407.