

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science



journal homepage: www.elsevier.com/locate/jcis

Regular Article

Photocatalytic performances of heterojunction catalysts of silver phosphate modified by PANI and Cr-doped SrTiO₃ for organic pollutant removal from high salinity wastewater



Xiaochao Yu ^{a,b,1}, Yan Lin ^{a,b,1}, Haiyang Liu ^{c,1}, Chunping Yang ^{a,b,d,*}, Yanrong Peng ^{a,*}, Cheng Du ^b, Shaohua Wu ^{a,b}, Xiang Li ^{a,b}, Yuanyuan Zhong ^b

^a College of Environmental Science and Engineering, Hunan University and Key Laboratory of Environmental Biology and Pollution Control (Hunan University), Ministry of Education, Changsha, Hunan 410082, China

^b Guangdong Provincial Key Laboratory of Petrochemcial Pollution Processes and Control, School of Environmental Science and Engineering, Guangdong University of Petrochemical Technology, Maoming, Guangdong 525000, China

^c Datang Environment Industry Group Co., Ltd., Haidian, Beijing 100097, China

^d Hunan Province Environmental Protection Engineering Center for Organic Pollution Control of Urban Water and Wastewater, Changsha, Hunan 410001, China

G R A P H I C A L A B S T R A C T



ARTICLE INFO

Article history: Received 5 September 2019 Revised 30 October 2019 Accepted 31 October 2019 Available online 6 November 2019

Keywords: Photocatalysis PANI

ABSTRACT

In this work, $Ag_3PO_4/PANI/Cr:SrTiO_3$ photocatalysts were designed to effectively eliminate organic pollutants including Rhodamine B and phenol from high salinity wastewater under visible light. The phase composition, optical properties, and morphology of powders were studied, and the effects of inorganic salts on removal performance of the as-prepared particles were also tested. Results showed that the photocatalytic activities of $Ag_3PO_4/PANI/Cr:SrTiO_3$ composites for Rhodamine B and phenol reached 100% within 10 min and 18 min, respectively. The reaction rate of pure Ag_3PO_4 was 7 times less than that of the ternary composite with the adding of PANI and Cr:SrTiO_3. The activity of $Ag_3PO_4/PANI/Cr:SrTiO_3$ remained at 92.25% after five cycles, so the photocatalytic and recyclable performance of ternary composite was greatly improved. In addition, when there was SO_4^{2-} with a content of ranging from 1% to 21%, the

* Corresponding authors at: College of Environmental Science and Engineering, Hunan University and Key Laboratory of Environmental Biology and Pollution Control (Hunan University), Ministry of Education, Changsha, Hunan 410082, China.

E-mail addresses: yangc@hnu.edu.cn (C. Yang), pengyr@hnu.edu.cn (Y. Peng).

¹ These authors contribute equally to this paper.

https://doi.org/10.1016/j.jcis.2019.10.123 0021-9797/© 2019 Elsevier Inc. All rights reserved. Cr:SrTiO₃ Visible light Salinity Sulfate degradation activity of the ternary catalyst under visible light was not changed for Rhodamine B, which indicated that the ternary catalyst exhibited the excellent sulfate resistance ability. Results from ESR and radical trapping experiments showed that O_2^- and h^+ made an important contribution to visible-light photocatalytic activities.

© 2019 Elsevier Inc. All rights reserved.

1. Introduction

With the development of industrialization worldwide, different types of industrial wastewater were discharged to the environment, which has become the focus of sustainable development and protection for the environment [1,2]. Recently, high salinity wastewater with a total salt content of at least 1% were produced in many industries including electric power, oil refining, chemical industries, metallurgy, papermaking, and pesticide industries [3,4]. Salt substances, such as Cl⁻, SO₄²⁻, Na⁺, Ca²⁺, are essential nutrients for microbial growth, which play a key part in microbial growth [5,6], for example, accelerating enzyme catalysis, maintaining membrane equilibrium, and adjusting osmotic pressure. However, too high concentration of these ions would lead to inhibition and poisoning to microorganisms. Therefore, traditional biological methods (eg. activated sludge processes) for the treatment of high salinity wastewater are usually impracticable because high concentration of salt and high osmotic pressure would result in dehydration of microorganism cells and cell protoplast separation [7]. For instance, the high concentration of salt increases the density of wastewater, and it is easy to the activated sludge to float, which seriously affects the purification effect of biological treatment system [5,6]. In a word, it is important to develop other approaches to address this issue. Recently, semiconductor photocatalytic technique, a low-cost and environmentally friendly technology, has shown potentials for applications in electrochemistry, photochemistry, catalytic chemistry, biochemistry, and environmental protection [8–11]. TiO₂, as one of the most common photocatalysts, has utilization of ultraviolet radiation that is the proportion of 3%-5% of the solar energy. However, the quantum efficiency of TiO₂ is low (4%-10%) [12,13], so the improvement of effective visiblelight responses photocatalysts has drawn attention. Silver orthophosphate (Ag₃PO₄), a novel photocatalyst, has been widely used for water splitting and photodegradation of organic pollutants in water [14]. At a wavelength of about 420 nm, Ag_3PO_4 has a quantum efficiency of about 90% during water oxidation, and its performance is significantly higher than other semiconductor materials [15]. However, it remains a challenge for the practical application of Ag₃PO₄, due to some shortcomings such as low photocatalytic efficiency and severe photo-corrosion in photocatalytic processes [16].

In order to solve above problems, a large number of studies have been carried out, mainly focused on the improvement of the synthesis processes, such as changing the morphology and size of the materials, and doping other materials to synthesize heterostructured composite photocatalysts [15–17], for example, Ag₃PO₄/RuO₂ [18], Ag₃PO₄/BiPO₄ [19], AgBr/Ag₃PO₄ [20], and TiO₂/ Ag₃PO₄ [21].

Recently, since some materials with delocalized conjugated structures promote the rapid separation of photoinduced charges and inhibit charge recombination during electron transfer, they have been extensively studied. Generally, polyaniline (PANI) is regarded to be an important conductive polymer with a delocalized π - π conjugated structure. Because of its unique electrical, optical, and optoelectronic properties, easy preparation and excellent environmental stability, PANI has attracted wide attention [22,23]. In recent years, combining of PANI with another semicon-

ductor has been studied to enhance photocatalytic activity and photostability. For example, the photocatalytic activities of Bi₁₂-TiO₂₀ [24], FeUiO-66 [25], CdS [26] and ZnO [27] were significantly increased after hybridization with PANI. Hou et al [24] reported that the photogenerated holes in VB of Bi₁₂TiO₂₀ and the photoelectron could be transferred directly to the π -system of PANI and the CB of Bi₁₂TiO₂₀, respectively, so that the charge separation and stability could be achieved. Photoinduced holes in the valence band of CdS could be transported to the external area of photocatalyst using the Highest Occupied Molecular of PANI, and the photoinduced holes in the valence band of FeUiO-66 could also be migrated to the Highest Occupied Molecular Orbital (HOMO) of PANI. Finally, they reached to the external area of photocatalysts for direct oxidation of adsorbed pollutants. These examples show that PANI with a widely conjugated π -orbital is considered to be an excellent photo-hole transport material. It can improve hole mobility and promote carrier separation. Finally, the photocatalytic performance of photocatalysts is improved. As the report goes, PANI can improve the structural stability of Ag₃PO₄ by protecting Ag₃PO₄ from being be dissolved in other solutions [22]. Since PANI possesses the special structure and the intimate contact interfaces were strong interact on each other, and the conductivity rate is accelerated, which was favorable for the transport and separation of photoinduced carriers at the interface and the separation of photoelectron from holes. This synergistic effect inhibits photocorrosion of Ag₃PO₄. On consideration of these factors, this study focuses on the combination of Ag₃PO₄/PANI and other materials, which is helpful to the transfer of optical carriers between semiconductors, further enhancing their photocatalytic activities and anti-photocorrosion performance of Ag₃PO₄.

The Z-scheme system is derived from natural photosynthesis. Zscheme heterojunction means combining two different semiconductors using an appropriate shuttle redox mediator to form two photochemical systems and an electron-transfer system [28]. On one hand, the recombination efficiency of photogenerated carriers can be inhibited through carriers transfer at the interface. On the other hand, separated photogenerated carriers have superior redox ability, which is more favorable to involve in related reactions [29]. However, SrTiO₃ merely responds to ultraviolet light. It is beneficial to enhance the absorption of visible light by doping foreign elements into SrTiO₃ to create new donor or recipient energy levels in the bandgap. It is reported that the energy level of the occupied Cr^{3+} is ~2.2 eV lower than that of the conduction band (CB) formed by Ti 3d or ~1.0 eV and higher than that of the valence band (VB) formed by O 2p [30,31]. So chromium has aroused great concern. Compared with Ag₃PO₄, the conduction band and the valence band of SrTiO₃ are both in a negative position. Therefore, Ag₃PO₄ and Cr: SrTiO₃ heterojunction photocatalysts exhibited high stability and great photocatalytic performance [32].

In this paper, novel Ag₃PO₄/PANI/Cr:SrTiO₃ photocatalysts with good visible-light photocatalytic activity and environmental stability were synthesized. Ag₃PO₄/PANI/Cr:SrTiO₃ photocatalysts were characterized, and their photocatalytic activity of RhB and phenol were evaluated. The effects of various contents and different salt concentration on photocatalytic activity were concerned with systematic study, and the photocomposition mechanisms were studied by ESR and radical trapping assay.

2. Experimental

2.1. Chemicals

Disodium hydrogen phosphate dodecahydrate (Na_2HPO_4 ·12H₂O), ethanol (CH₃CH₂OH), phenol, N, *N*-dimethyl formamide (DMF), and silver nitrate (AgNO₃) were ordered from Shanghai Sinopharm Chemical Reagent Co., Ltd. Titanium isopropylate ([(CH₃)₂CHO]₄Ti) and strontium acetate (Sr (Ac)₂) were subpackaged by Mackin Biochemical Co. Ltd and Aladdin Biochemical Technology Co. Ltd (Shanghai, China), respectively. Polyaniline (PANI) was purchased by Shanghai Bide Pharmatech Ltd. All of reagents were of analytical purity, and deionized water was employed in the all experiment.

2.2. Preparation of silver phosphate (Ag₃PO₄)

The AgNO₃ (30 mL, 9 mmol) was put to the DMF of 30 mL via vigorous magnetic stirring in dark for 12 h. Na_2HPO_4 ·12H₂O (30 mL, 3 mmol) was introduced to the above solution drop by drop and kept 4-hour constant stirring without light. The golden precipitates were washed with ethanol and deionized water for several times, and then dried in vacuum (60 °C) overnight.

2.3. Preparation of Cr:SrTiO₃

Based on our previous reports, Cr:SrTiO₃ is synthesized by a facile method [30,33]. Briefly, stoichiometric $Cr(NO_3)_3 \cdot 9H_2O$, strontium acetate (Sr(Ac)₂), and titanium isopropylate ([(CH₃)₂CHO]₄Ti) were dissolved completely in ethylene glycol with a molar ratio of 0.05:0.95:1. The mixture evaporated completely after heating at 150 °C, and the as-prepared substances were introduced into 5 mol/L of NaOH solution. The solutions were added into the Teflon-lined stainless autoclave and this autoclave was kept at a

temperature of 180 °C for 36 h. Next, the obtained samples were processed by filtration, washed with ethanol and deionized water for several times, and dried in vacuum (60 °C) overnight.

2.4. Preparation of Ag₃PO₄/PANI

First of all, an amount of PANI was dissolved in the DMF by ultrasonic treatment for 1 h. Afterward, the $AgNO_3$ (30 mL, 9 mmol) was mixed to the above suspension. Then the reaction solution was in dark condition with 12-hour vigorous stir. Next, 30 mL of 3 mmol Na_2HPO_4 ·12H₂O solution was introduced to the mentioned above solution drop by drop and kept 4-hour constant stirring without light. The collected precipitates were washed with ethanol and deionized water for several times, and finally dried in vacuum (60 °C) overnight.

2.5. Preparation of Ag₃PO₄/PANI/Cr:SrTiO₃

 $0.30 \text{ g Ag}_3\text{PO}_4/\text{PANI}$ was introduced into distilled water via sonication for 3 min. While stirring, the appropriate concentration of polyvinylpyrrolidone (PVP) was joined to the above solution, followed by 0.5 h of stirring. Meanwhile, $0.009 \text{ g Cr:} \text{SrTiO}_3$ was introduced into deionized water via sonication for 0.5 h. Then the Cr: SrTiO_3 solution was introduced drop by drop into above suspension via sonication for 4 h. Finally, the obtained material was centrifuged and washed and dried in vacuum (60 °C) overnight.

2.6. Characterization

The crystal structures of materials were determined by X-ray diffractometer (Cu-Ka radiation Bruker AXS D-8 Advances) in the range of 10° - 80° . The morphologies and microstructures of materials were imaged with an F-20 transmission electron microscope (TEM, Tecnai-G2, FEI) and field-emission scanning electron



Fig. 1. SEM images of (a) Ag₃PO₄, (b) PANI, (c) Cr:SrTiO₃, (d) Ag₃PO₄/PANI composites.



Fig. 2. SEM-EDS elemental mapping images of $Ag_3PO_4/PANI/Cr:SrTiO_3$.



Fig. 3. TEM images analysis of Ag₃PO₄/PANI/Cr:SrTiO₃ composites.

microscopy (FE-SEM, Hitachi SU-8220). X-ray photoelectron spectroscopy (XPS) with a Thermo ESCALAB 250Xi spectrometer was used to analyze banding energies of all elements. Raman spectra were conducted at room temperature via a Horiba Jobin Yvon microscopic confocal Raman spectrometer (LABRAM HR-800) in the backscattering geometry with a 633 nm Ar⁺ laser as an excitation source. The ultraviolet-visible (UV-vis) diffused reflectance spectra (DRS) were done by a UV-4100 spectrophotometer (Hitachi) with an integrating sphere. A Hitachi F-7000 fluorescence spectrometer was used to test the photoluminescence (PL) spectra. The specific surface area was performed by applying the Barrett-Emmett-Teller (BET) method. The total organic carbon (TOC) data with a Shimadzu TOC-V_{CPH} analyzer was used to verify the mineralization capacity. 5, 5-dimethyl-l-pyrroline N-oxide (DMPO) as a probe, the electron spin resonance (ESR) were analyzed on a JES FA-200 (JEOL) spectrometer at room temperature. The photoelectrochemical responses and Electrochemical impedance spectroscopy (EIS) of samples were obtained by a CHI 660D electrochemical workstation in a classical three-electrode system. Ultraviolet photoelectron spectroscopy (UPS) were tested with a monochromatic He I light source (21.2 eV) and a VG Scienta R4000 analyzer.

2.7. Photocatalytic experiments

The enhancing photocatalytic ability of the materials was carried out by decomposition of phenol and Rhodamine B (RhB), using a 300 W xenon lamp with a 420-nm filter. The circulating water allowed the reaction system to cool and keep the temperature constant. In each experiment, 100 mL of phenol solution (25 mg/L) or RhB solution (20 mg/L) was introduced with 50 mg photocatalysts. At first, the suspensions were constantly stirred without light for 0.5 h. After the equilibrium of organic pollutant adsorptiondesorption, the light source was turned on. During visible-light irradiation, a specified volume of the suspensions was collected at given time interval and then separated the particles using a 0.22 µm membrane filter. The filtrates of RhB were monitored using a UV-vis spectrophotometer (wavelength = 554 nm). The high performance liquid chromatography (HPLC) was used to analyze the residual concentration of phenol with an Agilent ZORBAX SB-C18 column and adjusted by a UV detector. The mobile phase consisted of a 60%/40% of methanol/water. 20 μ L volume of sample was injected at a constant flow rate of 1 mL min⁻¹.

3. Results and discussion

3.1. Characterization of the as-prepared catalysts

The classical morphologies and nanostructure of the powders were characterized by SEM. As shown in Fig. 1a, the bulk Ag₃PO₄ exhibits particles of different sizes. Some irregular small spherical polyhedron nanoparticles were approximately a diameter of 0.4-1.2 um with the attachment of large nanoparticles, whose particle diameter was about 30 um. Fig. 1b exhibited chaotic and agglomerated shape for the PANI [22]. Fig. 1d was the SEM imaging of the Ag₃PO₄/PANI powders. As can be viewed, the Ag₃PO₄ were intimately adhering to the PANI. In Fig. 1c, the Cr:SrTiO₃ were the regular spherical particles, whose particle sizes were in the range of 100-300 nm. The SEM element confirmed that all mapping elements existed for Ag₃PO₄/PANI/Cr:SrTiO₃ (Fig. 2). For the sake of further demonstration, transmission electron microscopy (TEM) images were provided for Ag₃PO₄/PANI/Cr:SrTiO₃, and the corresponding results were presented in Fig. 3. It can be proved fairly that the Ag₃PO₄ and Cr:SrTiO₃ were well connected. The lattice stripes of Ag₃PO₄ can be distinctly performed and the interplanar spacing of the nanospheres is 0.245 nm, corresponding to the interplanar distance of the (2 1 1) plane of Ag₃PO₄ (JCPDS no. 06-0505. Fig. 4b). Besides, the interplanar spacing of 0.231 nm was in accordance with the interplanar distance of the (110) plane of SrTiO₃ (JCPDS card No. 35-0734. Fig. 4c).

The surface area of the as-synthesized Ag_3PO_4 , $Ag_3PO_4/PANI$, and $Ag_3PO_4/PANI/Cr:SrTiO_3$ photocatalysts were determined by the BET method and the data was provided in Table 1. The surface area of Ag_3PO_4 possessed a value of 10.37 m²/g and the BET specific surface area of $Ag_3PO_4/PANI$ and $Ag_3PO_4/PANI/Cr:SrTiO_3$ photocatalysts were 11.41 m²/g and 22.69 m²/g, respectively. After the addition of PANI and Cr:SrTiO_3, the surface area of $Ag_3PO_4/PANI/$ Cr:SrTiO_3 composites had been increased significantly. Therefore, due to their large specific surface area, more active substrates and reactants can be adsorbed on the outside of the complex materials, which are profitable to increase their photocatalytic performance [34].



Fig. 4. (a) XRD patterns of as-prepared samples; the standard XRD diffraction patterns of (b) Ag_3PO_4 ; (c) SrTiO₃.

 Table 1

 Surface area for pure Ag₃PO₄, Ag₃PO₄/PANI and Ag₃-PO₄/PANI/Cr:SrTiO₃ composites.

| Samples | Surface area (m ² /g) |
|---|----------------------------------|
| Ag ₃ PO ₄ | 10.3740 ± 2.7363 |
| Ag ₃ PO ₄ /PANI | 11.4126 ± 2.0054 |
| Ag ₃ PO ₄ /PANI/Cr:SrTiO ₃ | 22.6873 ± 2.8294 |



Fig. 5. Raman spectra of different samples.

The XRD analysis were performed to detect the crystal structure of Ag₃PO₄, PANI, Cr:SrTiO₃, Ag₃PO₄/PANI, and Ag₃PO₄/PANI/Cr: SrTiO₃ composites, as viewed in Fig. 4a. It was concluded that the diffraction peaks of Cr:SrTiO₃ was similar to the cubic perovskite structure of SrTiO₃, corresponding to the standard XRD patterns (JCPDS card No. 35-0734. Fig. 4c) [35]. Fig. 4a showed that the diffraction peaks of Ag₃PO₄ and Ag₃PO₄/PANI samples have no obvious distinction, which remarkably illustrated that the cubic phase of Ag₃PO₄ (JCPDS card No. 06-0505. Fig. 4b) has no changed. By comparison with pure Ag₃PO₄, the XRD pattern of binary composites has no change in peaks or shapes. The results showed that PANI has no influence on the crystal structure of Ag₃PO₄ [22]. Furthermore, there were no characteristic signals of PANI in binary composites and ternary composites, because the PANI in the composite existed in the form of amorphous. It was possible that the peaks of Cr:SrTiO₃ in Ag₃PO₄/PANI/Cr:SrTiO₃ composites could not be evidently noted because the amount of Cr:SrTiO₃ was so low [36]. The reason for the diffraction peaks appeared at 2*θ* = 20.9°, 29.7°, 33.3°, 36.6°, 42.5°, 47.8°, 52.7°, 55.0°, 57.3°, 61.6°, and 71.9° were (110), (200), (210), (211), (310), (222), (320), (321), (400), and (421) planes for Ag₃PO₄, respectively. Although the position of diffraction peaks was basically the same, the area of different peaks of Ag₃PO₄ had changed obviously in every material. Based on the results of previous literatures, the notable variation of the peak area ratio of crystal plane indicated the change of exposure of crystal surface [16,37]. The intensity ratio of the (110), (200), and (210) peaks were



Fig. 6. High resolution XPS spectra of (a) Ag 3d, (b) Cr 2p, (c) C 1s, (d) P 2p, (e) O 1s, (f) N 1s, (g) Sr 3d, (h) Ti 2d, and (i) XPS survey spectrum.

1:1.118:8.310, 1:1.251:9.693, and 1:1.377:10.511 for the Ag_3PO_4 , $Ag_3PO_4/PANI$ and $Ag_3PO_4/PANI/Cr:SrTiO_3$, respectively, which implied that the introduction of PANI and Cr:SrTiO_3 had effect on the crystal facet exposure of Ag_3PO_4 . This also indicated the changes in the microstructure and morphology of crystals.

Raman spectroscopy is considered a powerful technique for estimating the local structure of solids. Fig. 5 revealed the Raman spectra of Ag₃PO₄, PANI, Cr:SrTiO₃, binary Ag₃PO₄/PANI composites, and ternary Ag₃PO₄/PANI/Cr:SrTiO₃ composites. The apparent

peak at 910 cm^{-1} was involved in the terminal oxygen bond derived from the phosphate group, which was the effects of vibration. While the peak at 578 cm⁻¹ belongs to the P—O—P bonds that produced the symmetrical stretching [22,38]. From the view of Raman spectrum for PANI, the characteristic vibrational pattern of the C—H bending made a contribution to the peaks at 1180 cm⁻¹. The vibrational pattern of the quinonoid unit was contributed to a peak near 1356 cm⁻¹ and the bands around 1578 cm⁻¹ were related with the vibrational pattern rooted in



the benzenoid unit [39–41]. With the exception of the bands located at 1173 cm⁻¹, the two peak signals of 1347 cm⁻¹ and 1596 cm⁻¹ shifted to lower wavenumbers (Fig. 5). Judged on the red shift of these bands, the PANI conjugated bond were stretched by the way of weakening the bond strengths of C=N (C=C). Afterward, C-N and more conjugated structures involving PANI and Ag₃PO₄ were formed [22,38,42]. The result was similar to previous reports. For perovskite structural materials, Raman bands were usually observed around 800 cm⁻¹, which resulted in the ordered distribution of metal cations at the B sites. Because the bands only were shown in $AB_xB'_{1-x}O_3$ perovskites rather than in ordinary ABO_3 perovskites [43,44]. The appearance of a band at 812 cm⁻¹ for Cr: SrTiO₃ indicated that Cr³⁺ was replaced for Ti⁴⁺ sites in the crystal lattice of the SrTiO₃ host [45,46]. For Ag₃PO₄/PANI/Cr:SrTiO₃ composites, the Raman peak at 812 cm⁻¹ for Cr:SrTiO₃ can become conscious of the Raman spectra of the Ag₃PO₄/PANI/Cr:SrTiO₃. The above results suggested the existence of PANI and Cr:SrTiO₃. Moreover, it also was concluded that there was a close interact on each other at the interface.

The XPS was also put into effect to analyze the compositions and the chemical states of the ternary nanoparticles, and the results are shown in Fig. 6. The predominant elements could be noted in the full scanned XPS spectrum. The atomic percentage of Ag, P, O, C, and N were 31.76%, 10.80%, 43.00%, 22.22%, and 3.02%, respectively. Due to low content in ternary photocatalyst, the weight percentages of Cr, Sr, and Ti could not be found. For the sake of further proving the existence of these elements and investigating their chemical status, high-resolution XPS spectra were conducted. As discerned from the Ti 2p spectrum (Fig. 6h), classical peaks were at 458.1 eV and 463.2 eV due to the binding energies of Ti 2p1/2 and Ti 2p3/2, respectively. The main peak (Fig. 6g) emerging at the binding energies of 132.6 eV belonged to Sr 3d. The Cr 2p peak could be observed at 572.6 eV of binding energy. From the view of Fig. 6a, the binding energies of Ag were divided into two peaks at 367.5 (Ag $3d_{5/2}$) and 373.5 eV (Ag $3d_{3/2}$), attributed to representative values for Ag⁺ in Ag₃PO₄. The N 1s spectrum represented -N= (quinoid imine) at 395.1 eV, -NH-(benzoid amine) at 399.2 eV, and positively charged nitrogen (-HN⁺- and -HN⁺=) at 404.5 eV [40]. As discerned from the P 2p spectrum (Fig. 6d), the cross-section of the peak was situated at 132.8 eV, which is consistent with the phosphorus originated from PO₄³⁻. As presented in Fig. 6c, the C 1s spectrum of the ternary complexes could be made up of two individual peaks (284.4 eV and 287.2 eV). The peak centered at 284.4 eV was involved in the PANI frameworks (C–H or C=C), defect-containing sp²-hybridized carbon, while the peak at 287.2 eV can be chalked up to -C=O (carbonyl) functional group and C=N in PANI [22]. The O1s peaks could be made up of main obvious peaks at 530.5 eV and 532.7 eV [47]. Based on the XPS results, it can be concluded that there is a close combination among Ag_3PO_4 , PANI, and Cr:SrTiO₃ in ternary composites.

The absorption properties and optical bandgap of assynthesized powders were identified by UV/vis diffuse reflectance spectrum (DRS), and the results of characterization were illuminated in Fig. 7a. It is obvious that Ag₃PO₄, Ag₃PO₄/PANI, and Ag₃PO₄/PANI/Cr:SrTiO₃ revealed exceedingly good absorption when the wavelength was lower than 500 nm. In comparison with Ag₃PO₄, there was a remarkably intensive absorbance for binary complexes. In addition, Ag₃PO₄/PANI composites still possess good availability of light absorption coming from the wavelength of 500-800 nm, which revealed the distinctly intensive adsorption after the coupling of Ag₃PO₄ and PANI. Especially, Ag₃PO₄/PANI/ Cr:SrTiO₃ had the most stronger absorption in the range of 300-800 nm, revealing the expressly intensive adsorption with the combination of Cr:SrTiO₃. The connection between bandgap (Eg) of a material and absorption coefficient (α) were described by the Kubelka-Munke equation and the equation is as follows [36]:

$$(\alpha h v)^{n} = A(h v - Eg)$$
⁽¹⁾

where α represents Absorption coefficient of the semiconductor (cm⁻¹), υ stands for incident light frequency, h means Plank's constant (6.62607015 \times 10⁻³⁴ J·s), A is the proportionality constant and Eg is the bandgap, respectively. And n value belongs to 1/2 (direct gap semiconductor) or 2 (indirect gap semiconductor) [48]. Accord-

ing to the results in Fig. 7d, the transition bandgaps of Ag_3PO_4 was 2.34 eV. From previous studies, the bandgap energy of $Cr:SrTiO_3$ was approximately 2.50 eV [49]. Furthermore, photocatalytic activity depends not only on an appropriate bandgap but also on proper the matching of conduction band (CB) and valence band (VB) levels of a photocatalyst with the redox potentials of the photocatalytic reactions. Hence, ultraviolet photoelectron spectroscopy (UPS) was used to obtain the valence band energy (E_{VB}) of semiconductor by measuring VB spectra with a monochromatic He I light source (21.22 eV) [50]. As can be seen from Fig. 7b and Fig. 7c, the E_{VB} of Ag_3PO_4 and $Cr:SrTiO_3$ were +2.99 and +1.77 eV, respectively. The E_{CB} of Ag_3PO_4 and $Cr:SrTiO_3$ were acquired by following formula [51]:

$$E_{VB} = E_{CB} + Eg \tag{2}$$

The bandgap energy of Ag_3PO_4 was estimated to be 2.34 eV in the above UV/vis DRS discussion and the bandgap energy of Cr: SrTiO₃ was 2.50 eV. The VB positions of Ag_3PO_4 and Cr:SrTiO₃ were determined to be +2.99 and +1.77 eV, and the corresponding E_{CB} values were calculated to be +0.65 and -0.73 eV, respectively. Thus, the band energy potential difference and matching interactive energy band structure could drive the transfer of the photogenerated carriers easily between Ag_3PO_4 and Cr:SrTiO₃, which could facilitate the separation of electron-hole pairs.

For purpose of revealing the relationship between complexes and the recombination of photoproduced carriers in semiconductors, photoluminescence spectroscopy assays were performed



Fig. 7. (a) UV-vis diffuse reflectance spectra of different samples; ultraviolet photoelectron spectroscopy (UPS) spectra of (b) Ag₃PO₄; (c) Cr:SrTiO₃; (d) the band gap energy of different samples.



Fig. 8. (a) Photoluminescence (PL) spectra of the prepared samples; (b) photocurrent response density of as-prepared samples; (c) electrochemical impedance spectroscopy of as-prepared samples.

and the tests of transient photocurrent responses under detection wavelength of 320 nm in visible-light region were carried out. Fig. 8a illustrated the PL spectra of powders. It was obvious that Ag₃PO₄ presented the most dramatic PL peak intensity, which indicated that the electron-hole pair produced by light was easy to recombine [52]. By comparison with bare Ag₃PO₄, the intensity of the binary and ternary composites revealed a significant decrease



Fig. 9. TOC removal of phenol over various photocatalysts under visible light irradiation for 18 min.

in fluorescence. When the weaker the fluorescence intensity was, the lower the photoinduced electron-hole pairs recombination rates were. Ag₃PO₄/PANI/Cr:SrTiO₃ composites showed the most outstanding carrier separation ability. In addition, the transient photocurrent responses of pure Ag₃PO₄, binary complexes, ternary complexes were illustrated in Fig. 8b. A significant change in photoelectrochemical response could be observed while visible light was turned on and off. The enhanced photocurrent also showed that the separation efficiency of photogenerated electron-hole pairs was much higher by adding PANI and Cr:SrTiO₃. It was conducted that a helpful modified material was fabricated successfully, which facilitated the rapid transfer and separation of photoinduced carriers.

The electron transfer rate was evaluated by Electrochemical impedance spectroscopy (EIS) measurement. The smaller arc radius of the EIS Nyquist plot is, the smaller electron-transfer resistance is. As depicted in Fig. 8c, the ternary of Ag₃PO₄/PANI/Cr: SrTiO₃ composites performed the most excellent charge transfer efficiency compared to the pure Ag₃PO₄ and binary of Ag₃PO₄/PANI, which consistent with result of PL.

The TOC was employed to assess the mineralization degree of Ag_3PO_4 , $Ag_3PO_4/PANI$, $Ag_3PO_4/PANI/Cr:SrTiO_3$ for phenol. As shown in Fig. 9, the mineralization rate of phenol by pure Ag_3PO_4 was only 23.25%, while the mineralization efficiency phenol by $Ag_3PO_4/PANI$, $Ag_3PO_4/PANI/Cr:SrTiO_3$ composites are 71.44% and 89.60%, respectively. It was proved that $Ag_3PO_4/PANI/Cr:SrTiO_3$ composites had excellent mineralization capability for phenol decomposition.

3.2. Photostability and recyclability

Rhodamine B (RhB), as an organic pollutant, was chosen as the typical pollutant to express the photoactivity of materials. In each experiment, the 50 mg material was introduced in the RhB aqueous solution (20 mg/L, 100 mL), and then the mixed solution was stirred without the light source for 0.5 h to achieve the adsorption-desorption equilibrium. Finally, a 300 W xenon lamp ($\lambda > 420$ nm) was used as a light source for photodegradation experiment. As presented in Fig. 10a, it is poor for the photocatalytic activity of single Ag₃PO₄ with only 62.87% of RhB degradation after illuminating. All Ag₃PO₄/PANI composites showed higher photocatalytic activity than pure Ag₃PO₄. Especially after 18 min of visible light irradiation, about 100% of RhB had been degraded by Ag₃PO₄/PANI composites when the loading ratios of PANI was 3.0%, 5.0%, and 7.0%, respectively. Ag₃PO₄/5.0%PANI



Fig. 10. Photodegradation curves of RhB in the presence of as-prepared samples with different loading ratios of (a) PANI and (b) Cr:SrTiO₃; Photodegradation curves of phenol in the presence of as-prepared samples (c); Reaction kinetic curves (d–f) of as-prepared samples corresponding to the photodegradation curves (a–c), respectively.

showed the highest photocatalytic activity. Further, compared with Ag₃PO₄, PANI, Cr:SrTiO₃, and Ag₃PO₄/PANI composites, Ag₃PO₄/5%PANI/3%Cr:SrTiO₃ composites took on the most dramatic photocatalytic activity and the 100% of RhB was removed at a more outstanding rate within 10 min of irradiation. The kinetic linearised curves for degradation of dye pollutants with all powders can be viewed from Fig. 10d and Fig. 10e. Moreover, the removal of phenol as another representative typical pollutant was selected

to further prove the photocatalytic performance of the ternary composites. The phenol by $Ag_3PO_4/5$ %PANI/3%Cr:SrTiO₃ was almost completely removed within 18 min, which indicated that the $Ag_3PO_4/PANI/Cr$:SrTiO₃ composites had a much higher photocatalytic ability.

Furthermore, it is a pivotal factor to check the good stability for the excellent photocatalytic activity of the photocatalyst in RhB. A recycle experiment put into effect to verify the photocatalytic



Fig. 11. (a) Cycling test for the photocatalytic degradation of RhB (20 mg/L) in the presence of different as-prepared samples; (b) XRD patterns of the fresh and used Ag₃PO₄/PANI/Cr:SrTiO₃ composites after 5 cycles.

repeatability of the as-synthesized powders, and the results were revealed in Fig. 11a. It can be evidently noticed that the photocatalytic activity of Ag₃PO₄/PANI/Cr:SrTiO₃ composites had no obvious deactivation to decompose RhB after three times cycles under visible light illumination. In addition, the removal efficiency of RhB was still 93.98% in the fourth cycle, and 92.24% of RhB could be degraded for Ag₃PO₄/PANI/Cr:SrTiO₃ composites after the fifth cycle. Compared with the first cycle, removal efficiencies of the fifth cycle were reduced by 21.2%, 21.32%, and 7.76% for Ag₃PO₄, Ag₃PO₄/PANI, and Ag₃PO₄/PANI/Cr:SrTiO₃ composites, respectively. The results indicated that the Ag₃PO₄/PANI/Cr:SrTiO₃ composites had the highest stability with visible light exposure. Meanwhile, it is further proved that Ag₃PO₄/PANI/Cr:SrTiO₃ composites were effective and stable in the photocatalytic process. The comodification method obviously enhances photocatalytic performance and single-component photostability. The remarkable decline in the photocatalytic performance of Ag₃PO₄ may be due to part of Ag₃PO₄ in reduction state by photoelectron generation. In order to further verify the stability of ternary Ag₃PO₄/PANI/Cr: SrTiO₃ composites, XRD of original and recycled Ag₃PO₄/PANI/Cr: SrTiO₃ composites after 5 cycles were provided (Fig. 11b). The results indicated that crystal structure had no obvious difference. The (111) crystal plane of the metallic Ag could contribute to the weak peak signal at 2θ value of 38.12° , indicating that merely a small quantity of metallic Ag was formed during the photodecomposition process. It is reported that a great deal of Ag⁰ occupied main active sites on the surface of the catalyst, which not only caused damage to their crystal structure but also lost their light absorption efficiency, thus affecting their photocatalytic activity and stability [37].

3.3. Effects of inorganic salts coexistence and inorganic salt concentration

From the view of practical wastewater system, the concentration of inorganic salts and the coexistence of inorganic salts may be the main factors that aggravate the difficulty of dye wastewater treatment. Therefore, the effects of concentrations and different kinds of inorganic salts for the degradation of RhB were studied. Some familiar inorganic ions at the content of 0.1 mol/L [22,53-56] were introduced to the reaction system and the influence of multiple inorganic salts was reflected in Fig. 12a. There was no significant difference in the degradation curves when NaNO₃ or Na₂SO₄ were mixed with the reaction system. The result revealed that the photodegradation ability of Ag₃PO₄/PANI/Cr:SrTiO₃ composites remained unaffected in the existence of Na⁺, NO₃⁻, and SO_4^{2-} . Although Mack and Bolton et al [57,58] proposed that NO_3^{-} had a weak absorption when the wavelength was greater than 280 nm. Abdullah et al [59] reported that NO_3^- had little effect on the degradation of ethanol and 2-propanol by TiO₂ under ultraviolet light. The above results showed that the existence of NaNO₃ did not affect the photodegradation of RhB by Ag₃PO₄/PANI/Cr:SrTiO₃. The effects of SO_4^{2-} with the content of 1%, 3%, 5%, 8%, 12%, 15%, 18%, and 21% for the photocatalytic degradation of RhB and phenol by Ag₃PO₄/PANI/Cr:SrTiO₃ were showed in Fig. 12c and d. With the increase of SO_4^{2-} concentration, the photoreaction rate had remained more or less unchanged compared to the RhB solution or phenol without adding Na₂SO₄. According to Ksp (Ag₂SO₄) = 1.2×10^{-5} , Ksp (Ag₃PO₄) = 8.89×10^{-17} , there was no formation of Ag₂SO₄ after the addition of SO₄²⁻ [60]. The effect of SO₄²⁻ for photocatalytic activity may be realized mainly by trapping hole (h⁺) and hydroxyl radical (OH). During the reaction, they convert highly active h^+ and OH into other substances. Although SO₄ · also has certain oxidation ability and can oxidize organic matter, its volume is relatively large and the oxidation efficiency of OH is higher than that of SO_4^- , which has little effect on the reaction rate [61,62]. Moreover, SO_4^{2-} is a relatively stable anion. However, the removal efficiency of RhB was remarkably inhibited in the appearance of NaCl. It can be explained as follows: Firstly, it is possible that the AgCl layer produced was too thick, preventing migration of electron and hole. Secondly, the nanocrystal structure of Ag₃PO₄/ PANI/Cr:SrTiO₃ was completely destroyed and converted to AgCl. Thus, photocatalytic performance was sharply reduced because of the seriously damaged Ag₃PO₄ nanocrystal structure. Finally, the bandgap width of AgCl was 3.25 eV. The visible light could not be absorbed under the experimental condition ($\lambda \ge 420 \text{ nm}$), which resulted in a decrease of photocatalytic reaction rate. Moreover, the inhibitory effect has occurred with Na₂CO₃ addition, and one of the reasons is that CO_3^{2-} is a trapping agent for holes and hydroxyl radicals, which can convert highly active holes and hydroxyl radicals into other substances. Meanwhile, the activity of CO_3^{-} is relatively low, so the photocatalytic rate is decreased [53,63]. The above results indicated that when the catalyst is used to treat wastewater with CO_3^{2-} and Cl^- , appropriate pretreatment is needed. In spite of this defect, the relatively high performance can be obtained, which indicates that Ag₃PO₄/PANI/Cr:SrTiO₃ can be used as an effective photocatalyst for wastewater treatment.

3.4. Possible photocatalytic mechanisms of Ag₃PO₄/PANI/Cr:SrTiO₃

To propose the tentative reaction mechanisms for the photocatalytic decomposition of Rhodamine B over Ag₃PO₄/PANI/Cr:SrTiO₃



Fig. 12. Photodegradation curves of RhB with different inorganic salts (a) and corresponding reaction kinetic curves (b); Photodegradation curves of RhB (c) and phenol (d) at different concentrations of Na₂SO₄.

powders, a series of controlled experiments using several radical quenchers were put in practice and the results were revealed in Fig. 13a, the ethylenediaminetetraacetic acid disodium (EDTA-2Na), 1, 4-benzoquinone (BQ) were used as the quenchers of hole (h^+), superoxide radical species ($\cdot O_2^-$) and AgNO₃, Isopropanol (IPA) were introduced as the photogenerated electron (e⁻), hydroxyl radical ('OH), respectively. The degradation efficiency of RhB was significantly reduced by adding BQ or EDTA-2Na. In the existence of EDTA-2Na, Ag₃PO₄/PANI/Cr:SrTiO₃ photocatalysts were almost completely deactivated. The apparent kinetic constant of ternary complexes was 0.009 min⁻¹. By comparison to the kinetic constant (0.57 min⁻¹) without EDTA-2Na addition, the reaction rate was considerably reduced. The apparent kinetic of ternary complexes equal to 0.016 min⁻¹ with the introduction of BQ, which was much lower than apparent kinetic constant (0.57 min^{-1}) without BQ addition. The results clearly indicated that O_2^- along with h⁺ pushed forward an important influence on the removal of RhB. After adding AgNO₃, the photocatalytic efficiency was also relatively significantly reduced, showing that the part of photoinduced electrons is equally worthy of attention. IPA has almost little effect on degradation rate, indicating that only tiny amounts of 'OH participate in the photocatalytic process. It is clearly shown that $\cdot O_2^-$, e^- , h^+ , and $\cdot OH$ all exerted an enormous function on the degradation of proceeding, while the main active substances of the catalyst should be h^+ and $\cdot O_2^-$ from the trapping experiments. To make further efforts to identify free radical chain reaction in photocatalytic systems, the ESR spin-trap signals of O_2^-

and \cdot OH over the Ag₃PO₄/PANI/Cr:SrTiO₃ composites were performed. As presented in Fig. 13c and d, it was clear that there was no signal of the DMPO- \cdot O₂ and DMPO- \cdot OH could be observed without light, which signified the \cdot O₂ and \cdot OH species can be formed on the external area of the sample in visible-light region. As can be seen from Ag₃PO₄/PANI/Cr:SrTiO₃ complexes illuminated by visible light, we could see the four characteristic DMPO- \cdot O₂ singles and the four characteristic DMPO- \cdot OH singles. Most importantly, the peaks intensity enhanced remarkably when the irradiation time was from 5 min to 10 min. Hence, it is reasonable to presume that the generation of \cdot O₂ and \cdot OH radicals could explain charge transfer process. Therefore, it is reasonable for an explanation of the results of radical trapping experiments.

Take into consideration those theoretical analysis and experimental calculation results, a reasonable photocatalytic mechanism for decomposition of Ag₃PO₄/PANI/Cr:SrTiO₃ composites was proposed and briefly depicted in Fig. 14. As we all know, both PANI and Ag₃PO₄ can be photo-excited to produce holes and electrons via visible-light photons. When exposed to visible light, the HOMO and LUMO of PANI are capable of producing holes and electrons. Locating at +0.65 eV was the conduction band (CB) of Ag₃PO₄ and the valence band (VB) of Ag₃PO₄ was +2.99 eV. And Lowest Unoccupied Molecular Orbital and Highest Occupied Molecular of PANI were -2.1 eV and +1.3 eV, respectively [22,64]. The reason why PANI is widely used is that its specific π -conjugated structure facilitates the transmission of holes. It was easy to migrate to the surface and directly oxidize pollutants for holes [42,65,66]. In



Fig. 13. Degradation curves of RhB with additions of scavengers under visible light over $Ag_3PO_4/PANI/Cr:SrTiO_3$ composites (a, degradation curve;). ESR spectra of radical adducts trapped by DMPO in the $Ag_3PO_4/PANI/Cr:SrTiO_3$ in the dark and under visible light ($\lambda > 420$ nm) irradiation (irradiation time of 5 and 10 min): (b) in methanol dispersion for DMPO- O_2^- ; and (c) in aqueous dispersion for DMPO-OH.

comparison, the CB of Ag_3PO_4 possessed a more positive position than the Lowest Unoccupied Molecular Orbital potential of PANI. Therefore, taking advantage of a well-defined interface, the photogenerated electrons of PANI were able to pointedly move into the CB of Ag_3PO_4 and then photogenerated electrons were capable of

reacting with oxygen molecules to form O_2^- radicals. At the same time, the VB of Ag₃PO₄ was perfectly propitious to the Highest Occupied Molecular of PANI. The photo-induced holes in the valence band (VB) of Ag₃PO₄ can be rapidly transported to the external area of the photocatalyst by Highest Occupied Molecular of PANI, and the interaction of the heterojunction electric field at the interface of Ag₃PO₄ and PANI. Thus accordingly, the carrier transmission availably impeded the recombination of photoinduced electron-hole pairs. To further explain the enhanced photocatalytic response, it is necessary to investigate the band structure for Ag₃PO₄ and Cr:SrTiO₃. the conduction band (CB) of Cr:SrTiO₃ had value of -0.73 eV and the valence band (VB) was located at +1.77 eV [36]. The electrons on the VB of Ag₃PO₄ and Cr:SrTiO₃ are easily shifted to the CB, which induces the generation of holes in VB. It is reported to be a Z-scheme heterojunction system. The results showed that a handful of Ag⁰ species were produced under visible light irradiation. In this study, metallic silver isolated from the external area of Ag₃PO₄ acts as a photoinduced electron and hole trappers, which can promote the Z-scheme transfer mechanism. The electron at the conduction band (CB) of Ag₃PO₄ photocatalyst and the hole from the valence band (VB) of the Cr:SrTiO₃ photocatalyst are recombined on the silver particles conductor. The reason why Ag₃PO₄ possess a more negative conduction band than metallic Ag is that the Schottky barrier at the metal-semiconductor interface is higher [67]. In addition, Cr:SrTiO₃ has a higher VB potential than metallic Ag. As a result, their own recombination can be indirectly decreased in Ag₃PO₄ and Cr: SrTiO₃. Owing to more holes of Cr:SrTiO₃ are recombined with electrons of Ag₃PO₄, there will be more electrons of Cr:SrTiO₃ stay on the conduction band (CB) of Cr:SrTiO₃ and more holes of Ag₃PO₄ stay on the valence band (VB) of Ag₃PO₄. In this case, the electrons with higher reductivity on the conductive band (CB) of Cr:SrTiO₃ and the holes with higher oxidizability on the Ag₃PO₄ valence band (VB) can participate in this photoreaction process, thereby increasing the photocatalytic performance. As can be seen from the $O_2/O_2^$ potential (-0.33 eV), the Cr:SrTiO₃ possessed lower CB potential (-0.73 eV). The 'OH/OH⁻ potential is +2.40 eV, which is more negative than the VB potential of Ag₃PO₄ (+2.99 eV). More electrons in Cr:SrTiO₃ participate in the reduction of oxygen molecules adsorbed on the surface to form O_2^- , which promotes the degradation of organic pollutants. At the same time, more holes in Ag₃PO₄ can directly react with H₂O to form 'OH. Furthermore, photoinduced holes have a partiality for electrons from the adsorbed dye molecules, which are used to directly oxidize organic pollutants. The mechanism not only facilitates the separation of charge carriers but also preserves their own advantages [68]. In summary, the addition of PANI and Cr:SrTiO₃ on Ag₃PO₄ can facilitate charge separation and inhibit charge recombination more efficiently. Moreover, more active radicals are obtained and excellent photocatalytic performance is finally achieved. In summary, according to the above analysis, the possible ways to generate radicals in this Ag₃PO₄/PANI/Cr:SrTiO₃ photocatalytic system are as follows:

 $Ag_{3}PO_{4}/PANI/Cr:SrTiO_{3} + h\nu \rightarrow e^{-} + h^{+}$ (5)

$$e^- + O_2 \rightarrow \cdot O_2^- \tag{6}$$

 $h^{+} + H_{2}O \rightarrow \cdot OH \tag{7}$

$$h^+$$
 + RhB \rightarrow degraded products (8)

$$O_2^- + e^- + 2H^+ \to H_2O_2$$
 (9)

$$\cdot O_2^{-} + H_2 O_2 \rightarrow \cdot OH + OH^{-} + O_2 \tag{10}$$



Fig. 14. Schematic illustration of the separation and transfer of photoproduced electron-hole pairs by mechanism.

 $H_2O_2 \rightarrow 2 \cdot OH \tag{11}$

 $\cdot O_2^{-}/H_2O_2/OH + RhB \rightarrow degraded products$ (12)

4. Conclusions

In a few words, novel photocatalysts Ag₃PO₄/PANI/Cr:SrTiO₃ were synthesized facilely using an in-situ precipitation method. As can be seen from results, the doping of PANI and Cr:SrTiO₃ greatly improves the visible light response photocatalytic performance and photostability of Ag₃PO₄/PANI/Cr:SrTiO₃ photocatalysts. Under the optimized conditions, about 100% of RhB degradation could be achieved after 10 min visible light irradiation and the degradation efficiency of phenol reached 100% in 18 min. The test of recyclability revealed that Ag₃PO₄/PANI/Cr:SrTiO₃ still remained a good catalytic activity after five cycles. With the increase of SO_4^{2-} concentration, the activity of the Ag₃PO₄/PANI/ Cr:SrTiO₃ photocatalysts were not lost. Further analyses showed that O_2^- and h^+ produced in the photocatalytic process play an important role in photocatalytic degradation. In addition, the matching energy levels among Ag₃PO₄, PANI, and Cr:SrTiO₃ result in the effective separation and migration of photo-induced carriers among them, which were the main reasons for enhancement of photocatalytic activity. This work presents an eco-friendly and effective photocatalyst for environmental purification, which has a good prospect of practical application.

Declaration of Competing Interest

The authors declare no competing financial interest.

Acknowledgements

This work was supported by the project of the National Natural Science Foundation of China (Grant No.: 51978178, 51478172, 51521006), the Department of Science and Technology of Guangdong Province of China (Contract No.: 2019A1515012044, 2017A020108002, 2018S0011), the International S&T Cooperation Program of China (Contract No.: 2015DFG92750), and the Department of Science and Technology of Hunan Province of China (Contract No.: 2017JJ2029, 2017SK2362).

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcis.2019.10.123.

References

- [1] M. Ruokolainen, E. Ollikainen, T. Sikanen, T. Kotiaho, R. Kostiainen, Oxidation of tyrosine-phosphopeptides by titanium dioxide photocatalysis, J. Am. Chem. Soc. 138 (24) (2016) 7452–7455, https://doi.org/10.1021/jacs.6b02472.
- [2] K.X. Li, Z.X. Zeng, L.S. Yan, M.X. Huo, Y.H. Guo, S.L. Luo, X.B. Luo, Fabrication of C/X-TiO₂@C₃N₄ NTs (X=N, F, Cl) composites by using phenolic organic pollutants as raw materials and their visible-light photocatalytic performance in different photocatalytic systems, Appl. Catal. B 187 (2016) 269–280, https://doi.org/10.1016/j.apcatb.2016.01.046.
- [3] O. Lefebvre, R. Moletta, Treatment of organic pollution in industrial saline wastewater: a literature review, Water Res. 40 (20) (2006) 3671–3682, https:// doi.org/10.1016/j.watres.2006. 08.027.
- [4] T. Panswad, C. Anan, Impact of high chloride wastewater on an anaerobic/ anoxic/aerobic process with and without inoculation of chloride acclimated seeds, Water Res. 33 (5) (1999) 1165–1172, https://doi.org/10.1016/S0043-1354(98)00314-5.
- [5] Y.J. Chen, H.J. He, H.Y. Liu, H.R. Li, G.M. Zeng, X. Xia, C.P. Yang, Effect of salinity on removal performance and activated sludge characteristics in sequencing batch reactors, Bioresour. Technol. 249 (2018) 890–899, https://doi.org/ 10.1016/j.biortech.2017.10.092.
- [6] H.J. He, Y.J. Chen, X. Li, Y. Cheng, C.P. Yang, G.M. Zeng, Influence of salinity on microorganisms in activated sludge processes: a review, Int. Biodeterior. Biodegrad. 9 (2017), https://doi.org/10.1016/j.ibiod.2016.10.007.
- [7] Q. Zhou, Y. Lin, X. Li, C.P. Yang, Z.F. Han, G.M. Zeng, L. Lu, S.Y. He, Effect of zinc ions on nutrient removal and growth of Lemna aequinoctialis from anaerobically digested swine wastewater, Bioresour. Technol. 249 (2017) 457–463, https://doi.org/10.1016/j.biortech. 2017.10.044.
- [8] C.P. Yang, H. Chen, G.M. Zeng, G.L. Yu, S.L. Luo, Biomass accumulation and control strategies in gas biofiltration, Biotechnol. Adv. 28 (4) (2010) 531–540, https://doi.org/10.1016/j.biotechadv.2010.04.002.
- [9] J. Ângelo, P. Magalhães, L. Andrade, A. Mendes, Characterization of TiO₂-based semiconductors for photocatalysis by electrochemical impedance spectroscopy, Appl. Surf. Sci. 387 (2016) 183–189, https://doi.org/10.1016/j. apsusc.2016.06.101.
- [10] M. Shekofteh-Gohari, A. Habibi-Yangjeh, M. Abitorabi, A. Rouhi, Magnetically separable nanocomposites based on ZnO and their applications in photocatalytic processes: a review, Crit. Rev. Environ. Sci. Technol. 48 (10– 12) (2018) 806–857, https://doi.org/10.1080/10643389.2018.1487227.
- [11] M. Pirhashemi, A. Habibi-Yangjeh, S. Rahim Pouran, Review on the criteria anticipated for the fabrication of highly efficient ZnO-based visible-light-

driven photocatalysts, J. Ind. Eng. Chem. 62 (2018) 1–25, https://doi.org/ 10.1016/j.jiec.2018.01.012.

- [12] S.Q. Yu, J. Hu, J.L. Wang, Radiation-induced catalytic degradation of pnitrophenol (PNP) in the presence of TiO₂ nanoparticles, Radiat. Phys. Chem. 79 (10) (2010) 1039–1046, https://doi.org/10.1016/j. radphyschem.2010.05.008.
- [13] X. Li, P.Z. Duan, J.W. Lei, Z.R. Sun, X. Hu, Fabrication of Ti/TiO₂/SnO₂-Sb-Cu electrode for enhancing electrochemical degradation of ceftazidime in aqueous solution, J. Electroanal. Chem. 847 (2019), https://doi.org/10.1016/ j.jelechem.2019. 113231 113231.
- [14] J.F. Ma, Q. Liu, L.F. Zhu, J. Zou, K. Wang, M.R. Yang, S. Komarneni, Visible light photocatalytic activity enhancement of Ag₃PO₄ dispersed on exfoliated bentonite for degradation of rhodamine B, Appl. Catal. B 182 (2016) 26–32, https://doi.org/10.1016/j.apcatb.2015.09.004.
- [15] Y. Lin, X. Wu, Y. Han, C.P. Yang, Y. Ma, C. Du, Q. Teng, H.Y. Liu, Y.Y. Zhong, Spatial separation of photogenerated carriers and enhanced photocatalytic performance on Ag₃PO₄ catalysts via coupling with PPy and MWCNTs, Appl. Catal. B 258 (2019), https://doi.org/10.1016/j.apcatb.2019.117969 117969.
- [16] Y. Lin, S.H. Wu, C.P. Yang, M. Chen, X. Li, Preparation of size-controlled silver phosphate catalysts and their enhanced photocatalysis performance via synergetic effect with MWCNTs and PANI, Appl. Catal. B 245 (2019) 71–86, https://doi.org/10.1016/j.apcatb.2018.12.048.
- [17] Y.P. Liu, L. Fang, H.D. Lu, LJ. Liu, H. Wang, C.Z. Hu, Highly efficient and stable Ag/Ag₃PO₄ plasmonic photocatalyst in visible light, Catal. Commun. 17 (2012) 200–204, https://doi.org/10.1016/j.catcom.2011.11.001.
- [18] R. Dhanabal, S. Velmathi, A.C. Bose, Fabrication of RuO₂-Ag₃PO₄ heterostructure nanocomposites: Investigations of band alignment on the enhanced visible light photocatalytic activity, J. Hazard. Mater. 344 (2018) 865–874, https://doi.org/10.1016/j.jhazmat. 2017.11.034.
- [19] U. Sulaeman, H. Pratiwi, A. Riapanitra, P. Iswanto, S. Yin, T. Sato, Hydrothermal synthesis and photocatalytic properties of BiPO₄/Ag₃PO₄ heterostructure for phenol decomposition, Adv. Mater. Res. 911 (2014) 92–96, https://doi.org/ 10.4028/www.scientific.net/ AMR.911.92.
- [20] X.F. Wang, S.Z. Yuan, S.H. Chen, G.M. Chen, J. Zhang, L. Zhang, Synthesis of Ag₃PO₄-AgBr with a novel heterostructure, and its photocatalytic properties, Res. Chem. Intermed. 41 (8) (2015) 5137–5147, https://doi.org/10.1007/ s11164-014-1617-6.
- [21] C. Liu, X. Zhang, Y.Q. Zhang, G.H. Meng, H.F. Zhao, J.N. Wu, Z.Y. Liu, Preparation and characterization of spindle-shaped nanoporous anatase TiO₂-Ag₃PO₄ heterostructure with enhanced visible light driven photocatalytic performance, J. Porous Mater. 24 (1) (2016) 1–9, https://doi.org/10.1007/ s10934-016-0250-8.
- [22] L. Liu, L. Ding, Y.G. Liu, W.J. An, S.L. Lin, Y.H. Liang, W.Q. Cui, A stable Ag₃PO₄@PANI core@shell hybrid: enrichment photocatalytic degradation with π-π conjugation, Appl. Catal. B 201 (2017) 92–104, https://doi.org/10.1016/j. apcatb. 2016.08.005.
- [23] A. Habibi-Yangjeh, M. Shekofteh-Gohari, Synthesis of magnetically recoverable visible-light-induced photocatalysts by combination of Fe₃O₄/ZnO with BiOI and polyaniline, Progr. Nat. Sci.: Mater. Int. 29 (2) (2019) 145–155, https://doi. org/10.1016/j.pnsc.2019.03.003.
- [24] J.G. Hou, R. Cao, S.Q. Jiao, H.M. Zhu, R.V. Kumar, PANI/Bi₁₂TiO₂₀ complex architectures: controllable synthesis and enhanced visible-light photocatalytic activities, Appl. Catal. B 104 (3) (2011) 399–406, https://doi.org/10.1016/j. apcatb.2011. 02.032.
- [25] X.Q. Xu, R.X. Liu, Y.H. Cui, X.X. Liang, C. Lei, S.Y. Meng, Y.L. Ma, Z.Q. Lei, Z.W. Yang, PANI/FeUiO-66 nanohybrids with enhanced visible-light promoted photocatalytic activity for the selectively aerobic oxidation of aromatic alcohols, Appl. Catal. B 210 (2017) 484–494, https://doi.org/10.1016/j. apcatb.2017.04.021.
- [26] C. Wang, L. Wang, J. Jin, J. Liu, Y. Li, M. Wu, L.H. Chen, B.J. Wang, X.Y. Yang, B.L. Su, Probing effective photocorrosion inhibition and highly improved photocatalytic hydrogen production on monodisperse PANI@CdS core-shell nanospheres, Appl. Catal. B 188 (2016) 351–359, https://doi.org/10.1016/j. apcatb.2016.02.017.
- [27] H. Zhang, R.L. Zong, Y.F. Zhu, Photocorrosion inhibition and photoactivity enhancement for zinc oxide via hybridization with monolayer polyaniline, J. Phys. Chem. C 113 (11) (2014) 4605–4611, https://doi.org/10.1021/ jp810748u.
- [28] F. Deng, Q. Zhang, L.X. Yang, X.B. Luo, A.J. Wang, S.L. Luo, D.D. Dionysiou, Visible-light-responsive graphene-functionalized Bi-bridge Z-scheme black BiOCI /Bi₂O₃, heterojunction with oxygen vacancy and multiple charge transfer channels for efficient photocatalytic degradation of 2-nitrophenol and industrial wastewater treatment, Appl. Catal. B 238 (2018) 61–69, https:// doi.org/10.1016/j.apcatb.2018.05.004.
- [29] L.L. Zhang, W.H. Feng, B. Wang, K.Q. Wang, F. Gao, Y. Zhao, P. Liu, Construction of dual-channel for optimizing Z-scheme photocatalytic system, Appl. Catal. B 212 (2017) 80–88, https://doi.org/10.1016/j.apcatb.2017.04.049.
- [30] D.F. Wang, J.H. Ye, T. Kako, T. Kimura, Photophysical and photocatalytic properties of SrTiO₃ doped with Cr cations on different sites, J. Phys. Chem. B 110 (32) (2006) 15824–15830, https://doi.org/10.1021/jp062487p.
- [31] T. Umebayashi, T. Yamaki, H. Itoh, K. Asai, Analysis of electronic structures of 3d transition metal-doped TiO₂ based on band calculations, J. Phys. Chem. Solids 63 (10) (2002) 1909–1920, https://doi.org/10.1016/s0022-3697(02) 00177-4.
- [32] T. Cai, Y.T. Liu, L.L. Wang, S.Q. Zhang, Y.X. Zeng, J.L. Yuan, J.H. Ma, W.Y. Dong, C. B. Liu, S.L. Luo, Silver phosphate-based Z-Scheme photocatalytic system with

superior sunlight photocatalytic activities and anti-photocorrosion performance, Appl. Catal. B 208 (2017) 1–13, https://doi.org/10.1016/j. apcatb.2017.02.065.

- [33] R. Abe, K. Sayama, K. Domen, H. Arakawa, A new type of water splitting system composed of two different TiO₂ photocatalysts (anatase, rutile) and a IO₃/I⁻ shuttle redox mediator, Chem. Phys. Lett. 344 (2001) 339–344, https://doi.org/ 10.1016/s00092614(01) 00790-4.
- [34] Y.C. Deng, L. Tang, G.M. Zeng, Z.J. Zhu, M. Yan, Y.Y. Zhou, J.J. Wang, Y.N. Liu, J.J. Wang, Insight into highly efficient simultaneous photocatalytic removal of Cr (VI) and 2,4-diclorophenol under visible light irradiation by phosphorus doped porous ultrathin g-C₃N₄ nanosheets from aqueous media: performance and reaction mechanism, Appl. Catal. B 203 (2017) 343–354, https://doi.org/ 10.1016/j.apcatb.2016.10.046.
- [35] S. Tonda, S. Kumar, O. Anjaneyulu, V. Shanker, Synthesis of Cr and La-codoped SrTiO₃ nanoparticles for enhanced photocatalytic performance under sunlight irradiation, Phys. Chem. Chem. Phys. 16 (43) (2014) 23819–23828, https://doi. org/10.1039/c4cp02963a.
- [36] Y. Lin, S.H. Wu, X. Li, X. Wu, C.P. Yang, G.M. Zeng, Y.R. Peng, Q. Zhou, L. Lu, Microstructure and performance of Z-scheme photocatalyst of silver phosphate modified by MWCNTs and Cr-doped SrTiO₃ for malachite green degradation, Appl. Catal. B 227 (2018) 557–570, https://doi.org/10.1016/j. apcatb.2018.01.054.
- [37] X.J. Chen, Y.Z. Dai, X.Y. Wang, Methods and mechanism for improvement of photocatalytic activity and stability of Ag₃PO₄: a review, J. Alloy. Compd. 649 (2015) 910–932, https://doi.org/10.1016/j.jallcom.2015.07.174.
- [38] P.Y. Dong, Y.H. Wang, B.C. Cao, S.Y. Xin, L.N. Guo, J. Zhang, F.H. Li, Ag₃PO₄/ reduced graphite oxide sheets nanocomposites with highly enhanced visible light photocatalytic activity and stability, Appl. Catal. B 132 (2013) 45–53, https://doi.org/10.1016/j.apcatb.2012.11.022.
- [39] H. Zhang, Y.F. Zhu, Significant visible photoactivity and antiphotocorrosion performance of CdS photocatalysts after monolayer polyaniline hybridization, J. Phys. Chem. C 114 (13) (2010) 5822–5826, https://doi.org/10.1021/ jp910930t.
- [40] C.C. Zhao, Z.S. Yin, J.L. Wang, Efficient electrochemical conversion of CO₂ to HCOOH using in-situ-prepared Pd-polyaniline/CNT nanohybrids, ChemElectroChem 2 (12) (2015) 1974–1982, https://doi.org/10.1002/ celc.201500328.
- [41] S.H. Wu, H.R. Li, X. Li, H.J. He, C.P. Yang, Performances and mechanisms of efficient degradation of atrazine using peroxymonosulfate and ferrate as oxidants, Chem. Eng. J. 353 (2018) 533–541, https://doi.org/10.1016/j. cej.2018.06.133.
- [42] H. Zhang, R.L. Zong, J.C. Zhao, Y.F. Zhu, Dramatic visible photocatalytic degradation performances due to synergetic effect of TiO₂ with PANI, Environ. Sci. Technol. 42 (10) (2008) 3803–3807, https://doi.org/10.1021/ es703037x.
- [43] Q. Kuang, S.H. Yang, Template synthesis of single-crystal-like porous SrTiO₃ nanocube assemblies and their enhanced photocatalytic hydrogen evolution, ACS Appl. Mater. Interfaces 5 (9) (2013) 3683–3690, https://doi.org/10.1021/ am400254n.
- [44] R.B. Comes, P.V. Sushko, S.M. Heald, R.J. Colby, M.E. Bowden, S.A. Chambers, Band-gap reduction and dopant interaction in epitaxial La, Cr Co-doped SrTiO₃ thin films, Chem. Mater. 26 (24) (2014) 7073–7082, https://doi.org/10.1021/ cm503541u.
- [45] S. Shen, Y.S. Jia, F.T. Fan, Z.C. Feng, C. Li, Time-resolved infrared spectroscopic investigation of roles of valence states of Cr in (La, Cr)-doped SrTiO₃ photocatalysts, Chin. J. Catal. 34 (11) (2013) 2036–2040, https://doi.org/ 10.1016/S1872-2067(12)60702-5.
- [46] T.V.M. Rao, G. Deo, J.M. Jehng, I.E. Wachs, In situ UV-vis-NIR diffuse reflectance and Raman spectroscopy and catalytic activity studies of propane oxidative dehydrogenation over supported CrO₃/ZrO₂ catalysts, Langmuir ACS J. Surf. Colloids 20 (17) (2004) 7159–7165, https://doi.org/10.1021/la049590v.
- [47] T.Q. Wang, Z.F. Jiang, T.C. An, G.Y. Li, H.J. Zhao, P.K. Wong, Enhanced visible light-driven photocatalytic bacterial inactivation by ultrathin carbon-coated magnetic cobalt ferrite nanoparticles, Environ. Sci. Technol. 52 (8) (2018) 4774–4784, https://doi.org/10.1021/acs.est.7b06537.
- [48] W.P. Zhang, G.P. Li, W.J. Wang, Y.X. Qin, T.C. An, X.Y. Xiao, W.Y. Choi, Enhanced photocatalytic mechanism of Ag₃PO₄ nanosheets using MS₂ (M=Mo, W)/ rGO hybrids as co-catalysts for 4-nitrophenol degradation in water, Appl. Catal. B 232 (2018) 11–18, https://doi.org/10.1016/j.apcatb.2018.03.006.
- [49] J.J. Guo, S.X. Ouyang, P. Li, Y.J. Zhang, T. Kako, J.H. Ye, A new heterojunction Ag₃PO₄/Cr-SrTiO₃ photocatalyst towards efficient elimination of gaseous organic pollutants under visible light irradiation, Appl. Catal. B 134 (2013) 286–292, https://doi.org/10.1016/j.apcatb.2012.12.038.
- [50] J. Liu, Y. Liu, N.Y. Liu, Y.Z. Han, X. Zhang, H. Huang, Y. Lifshitz, S. Lee, J. Zhong, Z. H. Kang, Metal-free efficient photocatalyst for stable visible water splitting via a two-electron pathway, Science 347 (23) (2015) 970–974, https://doi.org/10.1126/science.aaa3145.
- [51] F. Chen, Q. Yang, J. Sun, F. Yao, S. Wang, Y. Wang, X. Wang, X. Li, C. Niu, D. Wang, G. Zeng, Enhanced photocatalytic degradation of tetracycline by Agl/ BiVO₄ heterojunction under visible-light irradiation: mineralization efficiency and mechanism, ACS Appl. Mater. Interfaces 8 (48) (2016) 32887–32900, https://doi.org/10.1021/acsami. 6b12278.
- [52] X. Jia, Q.F. Han, M.Y. Zheng, H.P. Bi, One pot milling route to fabricate stepscheme Agl/I-BiOAc photocatalyst: energy band structure optimized by the formation of solid solution, Appl. Surf. Sci. 489 (2019) 409–419, https://doi. org/10.1016/j.apsusc.2019.05.361.

- [53] Y.F. Wang, X.L. Wang, H. Li, K.F. Lin, P. Wang, J. Yang, Y.D. Liu, Z.Y. Sun, L.H. Fan, Z.M. Wu, Treatment of high salinity phenol-laden wastewater using a sequencing batch reactor containing halophilic bacterial community, Int. Biodeterior. Biodegrad. 93 (2014) 138–144, https://doi.org/10.1016/j. ibiod.2014.04.010.
- [54] Q. Zhou, X. Li, Y. Lin, C.P. Yang, W.C. Tang, S.H. Wu, D.H. Li, W. Luo, Effects of copper ions on removal of nutrients from swine wastewater and on release of dissolved organic matter in duckweed systems, Water Res. 158 (2019) 171– 181, https://doi.org/10.1016/j.watres.2019.04.036.
- [55] X. Li, W.L. Yang, H.J. He, S.H. Wu, Q. Zhou, C.P. Yang, G.M. Zeng, L. Luo, W. Lou, Responses of microalgae Coelastrella sp. to stress of cupric ions in treatment of anaerobically digested swine wastewater, Bioresour. Technol. 251 (2017) 274– 279, https://doi.org/10.1016/j.biortech. 2017.12.058.
- [56] H.N. Abubackar, Á. Fernández-Naveira, M.C. Veiga, C. Kennes, Impact of cyclic pH shifts on carbon monoxide fermentation to ethanol by Clostridium autoethanogenum, Fuel 178 (2016) 56–629, https://doi.org/10.1016/ j.fuel.2016.03.048.
- [57] J. Mack, J.R. Bolton, Photochemistry of nitrite and nitrate in aqueous solution: a review, J. Photochem. Photobiol., A 128 (1–3) (1999) 1–13, https://doi.org/ 10.1016/S1010-6030(99)00155-0.
- [58] A.G. Rincón, C. Pulgarin, Effect of pH, inorganic ions, organic matter and HO on : implications in solar water disinfection, Appl. Catal. B 51 (2004) 283–302, https://doi.org/10.1016/j.apcatb.2004.03.007.
- [59] M. Abdullah, G.K.C. Low, R.W. Matthews, Effects of common inorganic anions on rates of photocatalytic oxidation of organic carbon over illuminated titanium dioxide, J. Phys. Chem. 94 (17) (1990) 6820–6825, https://doi.org/ 10.1021/j100380a051.
- [60] K.H. Wang, Y.H. Hsieh, M.Y. Chou, C.Y Photocatalytic degradation of 2-chloro and 2-nitrophenol by titanium dioxide suspensions in aqueous solution, Appl. Catal. B 21 (1999) 1–8, https://doi.org/10.1016/S0926-3373(98)00116-7.
- [61] K.H. Wang, Y.H. Hsieh, C.H. Wu, C.Y. Chang, The pH and anion effects on the heterogeneous photocatalytic degradation of o-methylbenzoic acid in TiO₂

aqueous suspension, Chemosphere 40 (4) (2000) 389-394, https://doi.org/ 10.1016/s0045-6535(99)00252-0.

- [62] R.W. Matthews, H.A. Mahlman, T.J. Sworski, Elementary processes in the radiolysis of aqueous nitric acid solutions. Determination of both GOH and GNO₃, J. Phys. Chem. 76 (19) (1972) 2680–2684, https://doi.org/10.1021/ j100663a007.
- [63] H. Guillard, C. Lachheb, A. Houas, M. Ksibi, E. Elaloui, J.M. Herrmann, Influence of chemical structure of dyes, of pH and of inorganic salts on their photocatalytic degradation by TiO₂ comparison of the efficiency of powder and supported TiO₂, J. Photochem. Photobiol., A 158 (1) (2003) 27–36, https:// doi.org/10.1016/S1010-6030(03)00016-9.
- [64] Z.S. Yin, T.H. Hu, J.L. Wang, C. Wang, Z.X. Liu, J.W. Guo, Preparation of highly active and stable polyaniline-cobalt-carbon nanotube electrocatalyst for oxygen reduction reaction in polymer electrolyte membrane fuel cell, Electrochim. Acta 119 (2014) 144–154, https://doi.org/10.1016/ j.electacta.2013.12.072.
- [65] G.K.R. Senadeera, T. Kitamura, Y. Wada, S. Yanagida, Deposition of polyaniline via molecular self-assembly on TiO₂ and its uses as a sensitiser in solid-state solar cells, J. Photochem. Photobiol., A 164 (1–3) (2004) 61–66, https://doi.org/ 10.1016/j.jphotochem. 2003.12.026.
- [66] S.H. Wu, H.J. He, X. Li, C.P. Yang, G.M. Zeng, B. Wu, S.Y. He, L. Lu, Insights into atrazine degradation by persulfate activation using composite of nanoscale zero-valent iron and graphene: performances and mechanisms, Chem. Eng. J. 341 (2018) 126–136, https://doi.org/10.1016/j.cej.2018.01.136.
- [67] F. Chen, Q. Yang, Y.L. Wang, J.W. Zhao, D.B. Wang, X.M. Li, Z. Guo, H. Wang, Y.C. Deng, C.G. Niu, G.M. Zeng, Novel ternary heterojunction photococatalyst of Ag nanoparticles and g-C₃N₄ nanosheets co-modified BiVO₄ for wider spectrum visible-light photocatalytic degradation of refractory pollutant, Appl. Catal. B 205 (2017) 133–147, https://doi.org/10.1016/ji.apcatb.2016.12.017.
- [68] X.J. Guan, L.J. Guo, Cocatalytic effect of SrTiO₃ on Ag₃PO₄ toward enhanced photocatalytic water oxidation, ACS Catal. 4 (9) (2014) 3020–3026, https://doi. org/10.1021/cs5005079.