

Cite this: *RSC Adv.*, 2015, 5, 99712

Controllable synthesis of phosphate-modified BiPO₄ nanorods with high photocatalytic activity: surface hydroxyl groups concentrations effects

Yan Li,^{ab} Yawen Wang,^{*a} Yu Huang,^{*bc} Junji Cao,^{bc} Wingkei Ho,^d Shuncheng Lee^e and Caimei Fan^a

Surface properties of photocatalysts are crucial to improve their efficiency in the removal of wastewater pollutants. In this study, phosphate-modified BiPO₄ photocatalysts with different PO₄³⁻/Bi molar ratios were controllably synthesized through a one-pot hydrothermal method. The concentrations of surface hydroxyl groups on BiPO₄ samples can be tuned by adjusting the PO₄³⁻/Bi³⁺ molar ratios. XRD results showed that surface modification by phosphate could boost the crystallinity of BiPO₄, which was beneficial to photocatalytic performance. XPS and IR spectra revealed that PO₄³⁻ modified only the surface of BiPO₄. The optical absorption of phosphate-modified BiPO₄ samples showed an obvious blue shift compared with that of bare BiPO₄. Photocatalytic activities of the as-prepared samples were evaluated by the decomposition of methylene orange (MO) under ultraviolet light and simulated solar-light irradiation. Experimental results demonstrated that the photocatalytic performance of the modified samples significantly improved after the BiPO₄ surface was modified by different amounts of PO₄³⁻. Both an indirect scavenger method and an electron spin resonance method were adopted to determine the production and intensity of free radicals during photocatalytic degradation. Results suggested that MO was removed predominantly through oxidation by OH radicals, as confirmed by theoretical calculations. Moreover, the mechanism of photocatalytic degradation of MO over the as-prepared phosphate-modified BiPO₄ was proposed.

Received 3rd October 2015
Accepted 30th October 2015

DOI: 10.1039/c5ra20189f

www.rsc.org/advances

1. Introduction

Water pollution by organic pollutants such as dyes is a serious environmental problem for human society; the pollutants must be removed or reduced to an acceptable level before water is discharged into the natural environment.¹ Among various dye wastewater treatment techniques, photocatalysis has attracted more and more attention because of its ability to mineralize organic pollutants by absorbing solar light.² TiO₂ has good stability and low cost; thus, this material is considered an attractive photocatalyst of dye degradation. Nevertheless, the photocatalytic activity of TiO₂ is not high enough for industrial purposes because of the limitations of the absorption edge and

the recombination of photogenerated charges.^{3,4} Therefore, several efforts have been made to develop novel semiconductor photocatalysts or to modify traditional photocatalysts to overcome the drawbacks of TiO₂ to achieve maximum activity.^{5–7}

The photocatalyst BiPO₄ was first reported by Zhu's group⁴ in a study on the degradation of methylene blue (MB). This photocatalyst showed superior activity compared with commercial P25. Henceforth, BiPO₄ and its derivatives have been intensively investigated for the degradation of abundant pollutants such as methyl orange (MO),^{8–10} rhodamine B (RhB),^{2,11,12} methyl blue (MB),^{13–15} phenol,^{16,17} benzene,¹⁸ and carbamazepine.¹⁹ Moreover, BiPO₄ has been applied in catalysis, ion sensing, radio-active element separation and humidity sensing.^{20–23} Given its larger dipole moments, monoclinic BiPO₄ (space group: *P21/n*) exhibited superior activity over the two other crystal phases of BiPO₄: hexagon (space group: *P3₁23*) and monoclinic (space group: *P21/m*).¹⁴ However, the significant combination of photogenerated charge carriers produces low quantum efficiency of BiPO₄ photocatalysts. Therefore, various studies have been conducted to improve the electron–hole separation efficiency of BiPO₄. For example, the construction of heterojunction interfaces between BiPO₄ and other semiconductors can facilitate the separation and transfer of photogenerated electron–hole pairs.^{23,24} Precious metal deposits can accelerate the migration

^aCollege of Chemistry and Chemical Engineering, Taiyuan University of Technology, Taiyuan 030024, China. E-mail: wangyawen@tyut.edu.cn

^bKey Lab of Aerosol Chemistry & Physics, Institute of Earth Environment, Chinese Academy of Sciences, Xi'an 710075, China. E-mail: huangyu@ieecas.cn; Tel: +86-29-6233 6261

^cState Key Lab of Loess and Quaternary Geology (SKLLQG), Institute of Earth Environment, Chinese Academy of Sciences, Xi'an 710075, China

^dDepartment of Science and Environmental Studies, The Hong Kong Institute of Education, Tai Po, New Territories, Hong Kong

^eDepartment of Civil and Environmental Engineering, The Hong Kong Polytechnic University, Hung Hom, Hong Kong

of generated electrons from BiPO_4 to metal particles, which prolongs the lifetime of a hole to enhance BiPO_4 activity.²⁵ Nonmetal doping such as F-doping can increase polarizability, whereas N-doping can decrease electrical resistance;^{26,27} all these methods will eventually result in a high photocatalytic activity. Moreover, Ag-doped BiPO_4 is a product of metal doping that can enhance the electron–hole separation due to a change in the morphology and size of BiPO_4 , thereby promoting its anisotropic carrier transport.¹¹ In addition to the traditional methods, a study of surface modification carried out by Pan *et al.*² showed that the OH groups on the BiPO_4 surface can efficiently restrain the combination rate of photogenerated electron–hole pairs by forming $\cdot\text{OH}$ radicals. In addition, Lv *et al.*^{28,29} found that the broadening of the valence band (VB) induced by surface oxygen-vacancy states can enhance the high separation efficiency of photoinduced electron–hole pairs.

Moreover, surface modification is an alternative method for enhancing the photocatalytic performance of semiconductor photocatalysts. Inorganic oxyanions such as phosphate (PO_4^{3-}) are known to be strongly adsorbed on the surface of semiconductors; these ions greatly influence interfacial and surface chemistry.^{30–32} A previous study showed that phosphate surface modification over TiO_2 can largely accelerate the hydroxyl radical attack and hinder the direct hole oxidation pathways³³. Modifications with PO_4^{3-} can also promote O_2 adsorption, which prolongs the lifetime and enhances the separation of the photogenerated charge carriers of the resulting products.^{30,34,35} These results demonstrated that PO_4^{3-} definitely has an influence on the catalytic properties of photocatalysts, which is attributed to its sufficient efficiency for electron–hole separation. To the best of our knowledge, the surface modification of BiPO_4 by phosphate has been mentioned and predicted,^{4,36} but its related influence on photocatalytic performance has not been previously reported. Therefore, the potential effects of phosphate surface modification on the physical and chemical properties of BiPO_4 should be explored.

In this study, surface-modified BiPO_4 by phosphate was synthesized by a one-pot hydrothermal method. The effect of the surface medication by phosphate on the photocatalytic performance of BiPO_4 was elucidated in detail.

2. Experimental

2.1. Synthesis of bare BiPO_4 and phosphate-modified BiPO_4 samples

All solvents and reagents are of analytical grade and used directly without further purification. BiPO_4 and phosphate-modified BiPO_4 were synthesized by the hydrothermal method, with $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ as precursors. In a typical procedure, 1 mmol of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and different amounts of $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ were dissolved in 15 mL of deionized water under vigorous stirring for 1 h. The mixture was transferred to a Teflon-lined stainless steel autoclave (20 mL capacity) and maintained at 160 °C for 24 h. The as-prepared samples were collected by centrifugation, washed several times with deionized water, and dried at 60 °C in an oven. For the synthesis of bare BiPO_4 (denoted as $\text{BP}_{1.0}$), the molar ratios of $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ to $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ were controlled at 1.0. For

the synthesis of phosphate-modified BiPO_4 samples, the molar ratios of $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ to $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ were controlled at 1.1, 1.3, and 1.5, and the corresponding products were denoted as $\text{BP}_{1.1}$, $\text{BP}_{1.3}$, and $\text{BP}_{1.5}$, respectively.

2.2. Characterization

Various methods were used to characterize the physical and chemical properties of the as-prepared bare BiPO_4 and phosphate-modified BiPO_4 samples. The X-ray powder diffraction (XRD) patterns were recorded on a PANalytical XPert PRO X-ray diffractometer system with $\text{Cu K}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$) at a scan rate of $0.05^\circ 2\theta/\text{s}$. The accelerating voltage and the applied current were 40 kV and 30 mA, respectively. Scanning electron microscopy (SEM; JEOL JSM-6490) was used to characterize the morphology of the obtained products. Transmission electron microscopy (TEM) was performed with a JEOL JEM-2100HR CM-120 transmission electron microscope. The samples for TEM were prepared by dispersing the final powders in ethanol. The dispersion was then dropped on carbon copper grids. After the sample was vacuum-dried overnight at 573 K, the nitrogen adsorption and desorption isotherm at 77 K was measured by a Micromeritics ASAP 2010 system. A Varian Cary 100 UV-Visible scanning system equipped with a Labsphere diffuse reflectance accessory was used to obtain the reflectance spectra of the catalysts over a range of 200–800 nm. Labsphere USRS-99-010 was employed as a reflectance standard. The spectra were converted from reflection to absorbance by the Kubelka–Munk method. X-ray photoelectron spectroscopy (XPS) measurements were performed with an X-ray photoelectron spectrometer (Thermo ESCALAB 250). All the binding energies were calibrated to the C 1s peak at 284.8 eV of the surface adventitious carbon. Fourier transform infrared (FTIR) spectra were obtained on a FTIR absorption spectrometer (Magna-IR 750, Nicolet, USA), with KBr as the diluent. Photoluminescence (PL; F-7000, Hitachi, Japan) was used to investigate the optical properties of the as-prepared samples. The samples for electron spin-resonance spectroscopy (ESR; ER200-SRC, Bruker, Germany) were prepared by mixing 0.05 g of the as-prepared photocatalyst in a 25 mM 5,5'-dimethyl-1-pyrroline-N-oxide (DMPO) solution with a 50 mL aqueous dispersion for $\text{DMPO} \cdot \cdot\text{OH}$ or a 50 mL alcohol dispersion for $\text{DMPO} \cdot \cdot\text{O}_2^-$ under irradiation with 254 nm ultraviolet (UV) light.

2.3. Photoelectrochemical measurements

The photoelectrochemical properties of $\text{BP}_{1.0}$ and $\text{BP}_{1.3}$ were evaluated using a Parstat 4000 electrochemical workstation (USA) in a conventional three-electrode cell, in which a platinum plate and Ag/AgCl electrode were used as counter electrode and reference electrode, respectively. To fabricate the working electrode, ethyl cellulose and terpineol were added into BiPO_4 , which were then dispersed into ethanol to obtain a homogeneous suspension through bath sonication. Then, BiPO_4 films were modified onto the fluorine doped tin oxide (FTO) conducting glass by dip coating and dried at room temperature. The final films on FTO were composed of 0.18 wt% BiPO_4 , 0.09 wt% ethyl cellulose, and 0.73 wt% terpineol. Subsequently, the electrodes were

heat-treated in a furnace at 500 °C for 30 min to remove the additives. The current–time curves were measured at 0.0 V vs. Ag/AgCl in 0.1 mol L^{−1} Na₂SO₃ at ambient temperature under the irradiation of a 300 W Xenon lamp.

2.4. Photocatalytic activity test

The photocatalytic activities of bare BiPO₄ and phosphate-modified BiPO₄ samples were evaluated by the degradation of methyl orange (MO) under ultraviolet light and simulated solar-light irradiation, respectively. Briefly, 0.05 g of the as-prepared photocatalyst was added to 50 mL of 5 mg L^{−1} MO aqueous solution in a container with a cooling water jacket. The temperature of the solution during the photodegradation was maintained at approximately 25 °C. The MO solution with the photocatalyst was continuously stirred for 1 h to ensure the establishment of an adsorption–desorption equilibrium among the photocatalyst, MO, and water before the lamp was turned on. During the degradation, the MO solution with the photocatalyst was continuously stirred by a dynamoelectric stirrer. The concentration of MO was monitored by colorimetry with a U-3310 UV-Vis spectrometer (Hitachi) at fixed time intervals. The degradation rate of the MO solution after irradiation was calculated according to the following equation:

$$R = (A_0 - A_t)/A_0 \times 100\%$$

where R is the degradation rate, A_0 is the absorbance of the solution before irradiation, and A_t is the absorbance of the solution during different periods after irradiation.

3. Results and discussion

3.1. XRD patterns of the as-prepared photocatalysts

Fig. 1 shows the XRD patterns of the as-prepared bare BiPO₄ and phosphate-modified BiPO₄ samples. As shown in Fig. 1, the

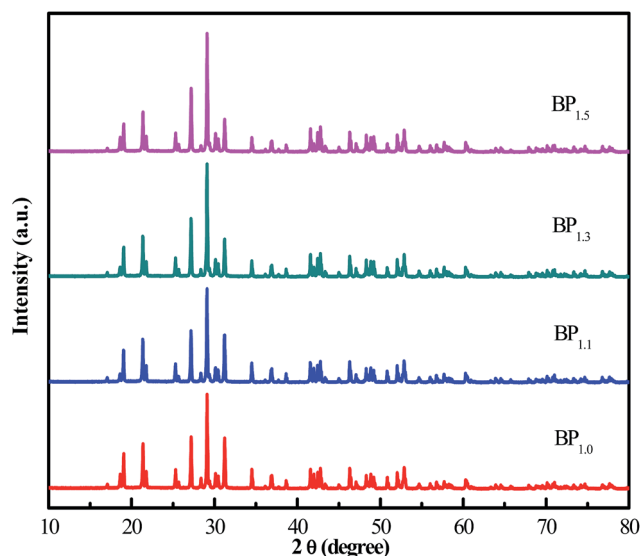


Fig. 1 XRD patterns of the as-prepared bare BiPO₄ (BP_{1.0}) and phosphate-modified BiPO₄ (BP_{1.1}, BP_{1.3}, and BP_{1.5}) samples.

XRD patterns of all the as-prepared BiPO₄ samples can be readily indexed as monoclinic BiPO₄ (JCPDS no. 80-209) with a space group of $P2_1/n$ (no. 14) and lattice constants of $a = 6.762$ Å, $b = 6.951$ Å, and $c = 6.482$ Å. No impurity peaks are observed in these patterns, thereby indicating the high purity of the products. The intense and sharp diffraction peaks suggest that the as-synthesized products are well crystallized. The intensity of the diffraction peaks clearly becomes stronger with increased PO₄^{3−} concentration until the molar ratio of PO₄^{3−} to Bi reached 1.5, thereby demonstrating that the surface modification by phosphate could boost the crystallinity of BiPO₄. This change is beneficial to photocatalytic performance because high crystallinity generally means fewer traps and stronger photocatalytic activity.³⁷

3.2. SEM

Fig. 2 depicts typical SEM images of the as-prepared bare BiPO₄ and phosphate-modified BiPO₄ photocatalysts. With increased PO₄^{3−}/Bi³⁺ molar ratio during material synthesis, the morphology and particle size of the products varied significantly. When the PO₄^{3−}/Bi³⁺ molar ratio was equal to 1.0, the bare BiPO₄ (BP_{1.0}, Fig. 2a) sample was composed of irregular octahedral crystals with sizes of approximately 1–2 μm. When the PO₄^{3−}/Bi³⁺ molar ratio varied from 1.1 to 1.5, the morphology of the products became much more uniform. These products predominantly consisted of nanorods with diameters of approximately 200 nm and lengths of 1 μm, as shown in Fig. 2b–d. This trend revealed that the surface modification by PO₄^{3−} could hinder the growth of BiPO₄ crystals. The crystal structure had a tendency to be closer to perfect and have fewer defects, which is consistent with the XRD results. These uniform nanorods are beneficial to the improvement of photocatalytic performance.

3.3. TEM

Fig. 3 presents the TEM characterization results of the as-prepared BP_{1.0} and BP_{1.3} samples. The TEM results are

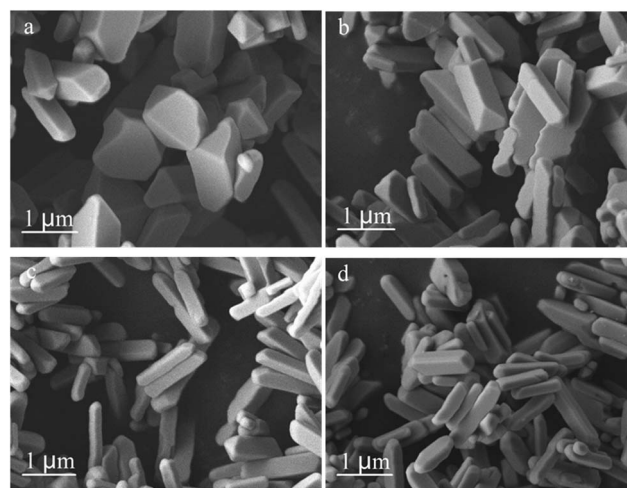


Fig. 2 SEM micrographs of the as-prepared products: (a) BP_{1.0}, (b) BP_{1.1}, (c) BP_{1.3} and (d) BP_{1.5}.

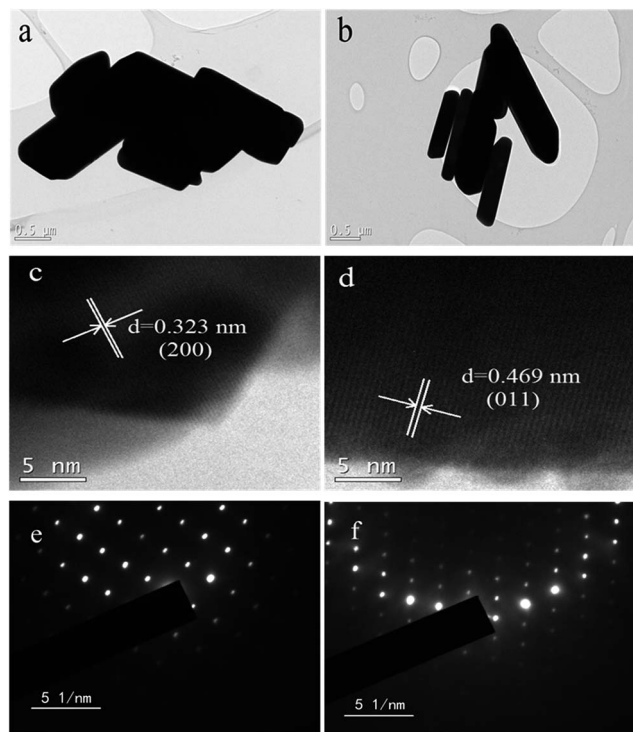


Fig. 3 TEM images: (a and b) low-magnification TEM images, (c and d) HR-TEM images and (e and f) SAED patterns of BP_{1.0} and BP_{1.3}, respectively.

consistent with those of SEM (Fig. 3a and b). As displayed in Fig. 3a and b, the BP_{1.0} sample was composed of irregular crystals with sizes of approximately 1–2 μm , whereas BP_{1.3} was composed of uniform nanorods and microrods (with diameters of 200 nm and lengths of 1 μm), thereby confirming the SEM characterization results. From Fig. 3c and d, the clear lattice fringes with d -spacing of 0.323 and 0.469 nm were corresponding to the (200) plane of BP_{1.0} and the (011) plane of BP_{1.3}, respectively. The corresponding SAED patterns (Fig. 3e and f) showed clear diffraction spots, thereby indicating that the as-prepared samples have a single crystalline phase.

Given the SEM and TEM results, when the $\text{PO}_4^{3-}/\text{Bi}^{3+}$ molar ratio varied from 1.0 to 1.5, the morphologies of the final products became more and more uniform, while the particle size decreased accordingly. This trend can be ascribed to the electrostatic repulsion of excess PO_4^{3-} on the surface of BiPO_4 during the crystal growth processes. The combination rate of the photo-excited electrons and holes is well known to have an important role in improving the photocatalytic activity of the final products. Therefore, the phosphate-modified BiPO_4 nanorods with high crystallinity tend to have superior photocatalytic activity because of the high separation efficiencies of electrons and holes, which eventually facilitates the generation of active species.

3.4. FTIR spectra

The surface properties of bare BiPO_4 and phosphate-modified BiPO_4 samples were characterized by FTIR. As shown in Fig. 4, the

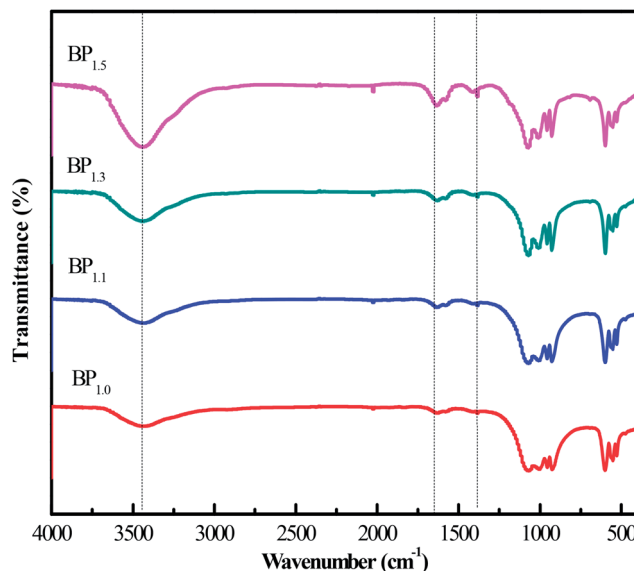


Fig. 4 FTIR spectra of the as-prepared bare BiPO_4 and phosphate-modified BiPO_4 samples.

peaks at 550, 850, 1000, and 1100 cm^{-1} are the characteristic ν_1 , ν_2 , ν_3 , and ν_4 vibrations of PO_4^{3-} from BiPO_4 ,² respectively. The peaks at 1300–1400 cm^{-1} can be assigned to the characteristic frequencies of phosphoryl bonds ($\text{P}=\text{O}$); their gradually enhanced intensity suggested the presence of PO_4^{3-} . The concentration of surface PO_4^{3-} increased as the $\text{PO}_4^{3-}/\text{Bi}^{3+}$ molar ratio varied from 1.0 to 1.5.^{38–40} The broad peaks at 3480 and 1630 cm^{-1} are related to the hydroxyl stretching vibration of surface-adsorbed water and hydroxyl groups, respectively.⁴¹ Clearly, the surface modification of BiPO_4 by PO_4^{3-} increased the concentrations of surface hydroxyl groups significantly, as shown in Fig. 4. Previous studies also showed that PO_4^{3-} interacts strongly with H_2O through hydrogen bonds and exhibits strong binding affinity to the surface of metal oxides,^{30,33} which is consistent with our experimental results in the present study.

3.5. XPS

XPS was performed to identify the chemical states of various elements in the as-prepared bare BiPO_4 and phosphate-modified BiPO_4 samples. Fig. 5a shows the survey spectra of the products, where Bi, O, P, and C were detected in all the samples. The C 1s region with the binding energy at 284.8 eV in Fig. 5b can be ascribed to the adventitious hydrocarbon; this spectrum was used as the reference standard. The high-resolution XPS spectra of Bi 4f, P 2p and O 1s on the surface of the samples are shown in Fig. 3c–e, respectively.

In Fig. 5c, the Bi 4f spectra of all the samples were characterized by a Bi 4f_{5/2} peak at approximately 165.1 eV and a Bi 4f_{7/2} peak at 159.7 eV, both of which belong to Bi^{3+} in BiPO_4 .^{42,43} The XPS spectra in the P 2p region (Fig. 5d) exhibited a broad signal peak at approximately 133.3 eV, which corresponded to P (+5) in PO_4^{3-} .¹¹ The O 1s spectra in Fig. 5e can be fitted by three peaks at 529.8, 530.5, and 531.5 eV, which correspond to the Bi–O, P–O, and OH groups, respectively.^{39,44} Interestingly, the binding energy of Bi 4f, P 2p, and O 1s shifted to a lower

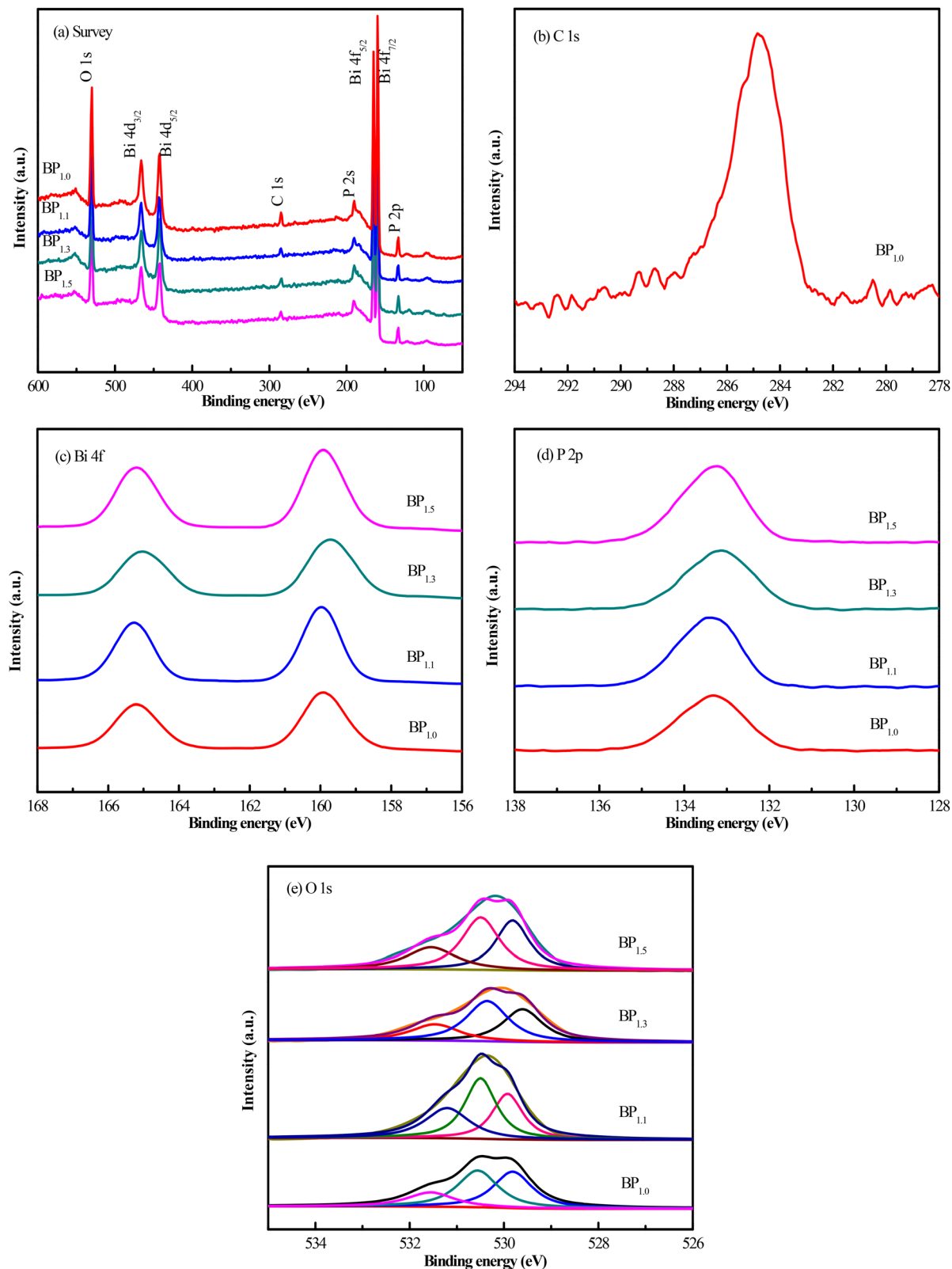


Fig. 5 High-resolution XPS spectra of the as-prepared BiPO_4 : (a) survey, (b) C 1s, (c) Bi 4f, (d) P 2p and (e) O 1s.

energy as the P/Bi ratio increased from 1.0 to 1.3, thereby indicating that the electron density increased after the phosphate modification reached a P/Bi ratio of 1.3. As we all know,

PO_4^{3-} groups possess a large electron cloud overlapping with high negative charges. Thus, the increased electron density is inferred to be caused by aggrandized PO_4^{3-} on the surface of

BiPO₄. Furthermore, PO₄^{3−} has the induced effect from the fact that the dipole moment induces the formation of local fields that prefer to attract holes and repel electrons, which helps the e[−]/h⁺ separation and benefits photocatalytic performance. The surface phosphate concentration becomes saturated when the P/Bi ratio exceeds 1.3, which is consistent with the FTIR results. The combined XPS spectra and IR results imply that the excess PO₄^{3−} was modified on the surface of BiPO₄.

3.6. UV-vis diffuse reflectance spectra (DRS)

Fig. 6 shows the typical UV-vis DRS of the as-prepared surface-modified and unmodified BiPO₄ samples. UV-vis DRS is normally used to characterize the electronic states of a semiconductor photocatalyst, wherein the electronic structure has a crucial role in photocatalytic activity. As displayed in Fig. 6, all the BiPO₄ products showed significant photo-absorption at wavelengths shorter than 300 nm, which is consistent with previously published results.¹³ Moreover, an obvious blue shift by several nanometers in the band gap transition appeared for the phosphate-modified BiPO₄ samples compared with the BP_{1.0} sample. This change indicates that the band gap of the phosphate-modified BiPO₄ is larger than that of the BP_{1.0} sample. The steep shape of the spectrum indicated that the UV light absorption was caused by the band gap transition rather than the transition from the impurity to the conduction band (CB). By assuming that BiPO₄ is an indirect semiconductor,⁴ the band gap energies of surface-modified BiPO₄ samples estimated from the $(\alpha h\nu)^{1/2}$ versus photon energy ($h\nu$) plots were 3.92, 3.95, 4.09, and 4.18 eV for BP_{1.0}, BP_{1.1}, BP_{1.3}, and BP_{1.5}, respectively (inset of Fig. 6). This trend indicates that the surface-modification by PO₄^{3−} can enlarge the band gap of BiPO₄. This effect was probably caused by the morphological

Table 1 Summary of surface area, total pore volume and pore diameter of the as-prepared BiPO₄

Sample	S_{BET} (m ² g ^{−1})	Total pore volume (cm ³ g ^{−1})	Pore diameter (nm)
BP _{1.0}	1.3008	0.00477	14.665
BP _{1.1}	1.1243	0.00635	22.596
BP _{1.3}	2.9507	0.00565	7.664
BP _{1.5}	4.1968	0.00664	6.330

and particle size changes of the products after the introduction of PO₄^{3−} during the synthesis processes.

3.7. BET

Furthermore, the BET surface area of the as-prepared samples grew larger, but the pore diameters became smaller with increased PO₄^{3−}/Bi³⁺ molar ratio (Table 1). These changes may be caused by the altered morphologies and sizes of BiPO₄. Notably, the changes in the total pore volume were not caused by the stable structures of the as-prepared BiPO₄. Therefore, the excess PO₄^{3−} can slightly increase the surface area of BiPO₄.

3.8. PL

PL emission is a useful technique for investigating the generation, transfer, and recombination of charge carriers. A low PL intensity has been proven to be generally indicative of a high separation efficiency of electron–hole pairs.⁴⁵ The PL spectra of BP_{1.0} and BP_{1.3} from Fig. 7 exhibited a broad emission peak centered at approximately 275–475 nm.¹⁷ BP_{1.3} showed significantly diminished PL intensity compared with BP_{1.0}, which suggests that the modification of PO₄^{3−} on the surface of BiPO₄ results in a remarkable decrease in the recombination rate of electron–hole pairs. This result is supported by the fact that

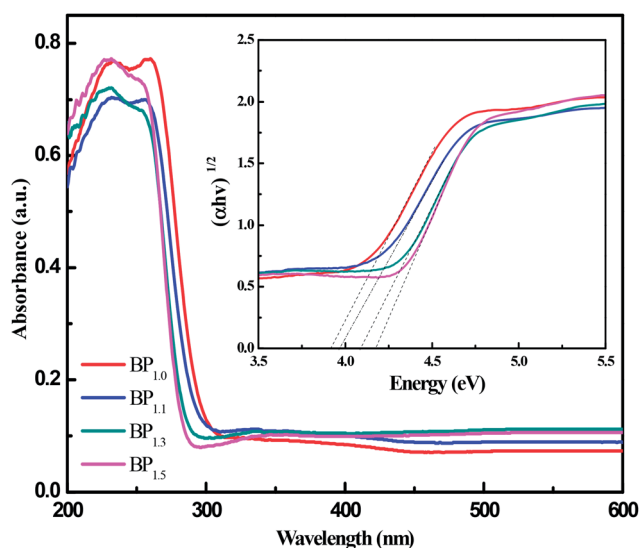


Fig. 6 UV-vis absorption spectra of the as-prepared phosphate-modified BiPO₄ samples (with P/Bi ratios varying from 1.0 to 1.5). The inset shows plots of $(\alpha h\nu)^{1/2}$ versus photon energy ($h\nu$), where α is the absorption coefficient.

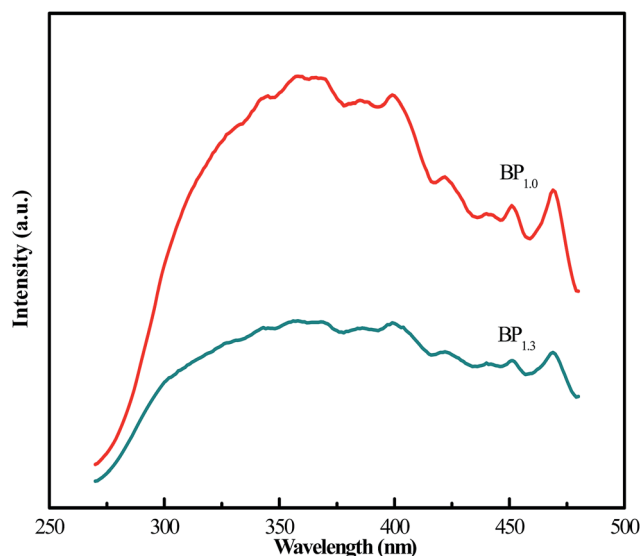


Fig. 7 PL spectra of BP_{1.0} and BP_{1.3}.

hydroxyl on the surface can function as a hole trap and contribute to electron-hole separation.

3.9. Photoelectrochemical property

From Fig. 8, it can be observed that the photocurrent was drastically increased when the irradiation was turned on, whereas the photocurrent value rapidly decreased to zero as soon as the irradiation was turned off. The measured photocurrent density of BP_{1.3} (about 4.2 $\mu\text{A cm}^{-2}$) was significantly larger than that of BP_{1.0} (1.3 $\mu\text{A cm}^{-2}$). This enhanced photocurrent indicated that the PO₄³⁻ modification for BiPO₄ could efficiently improve the separation of photogenerated electron-hole pairs.

3.10. Photocatalytic activity

The photocatalytic activity of the as-prepared samples was evaluated by the decomposition of MO under UV light and simulated solar-light irradiation, respectively. As shown in Fig. 9, the degradation efficiency of MO without photocatalysts was less than 10%. After the BiPO₄ surface was modified by different amounts of PO₄³⁻, the photocatalytic performance of the modified samples was significantly improved. For example, under UV light irradiation, the MO was degraded by approximately 80% of the original unmodified BiPO₄ sample after an hour of the reaction. In contrast, the same amount was completely destroyed by phosphate-modified BiPO₄ photocatalysts under identical conditions. Moreover, the BP_{1.3} and BP_{1.5} samples show activity much superior to BP_{1.1}, which is much more significant for the photocatalytic performance under simulated solar-light irradiation (Fig. 9b). These results indicated that the photocatalytic activities of the as-prepared products were significantly enhanced with the surface modification by PO₄³⁻. Interestingly, further increase in the PO₄³⁻ concentration (when the P/Bi ratio was over 1.3) in the synthetic system had an insignificant influence on the photocatalytic activity improvement of BiPO₄. This trend may be attributed

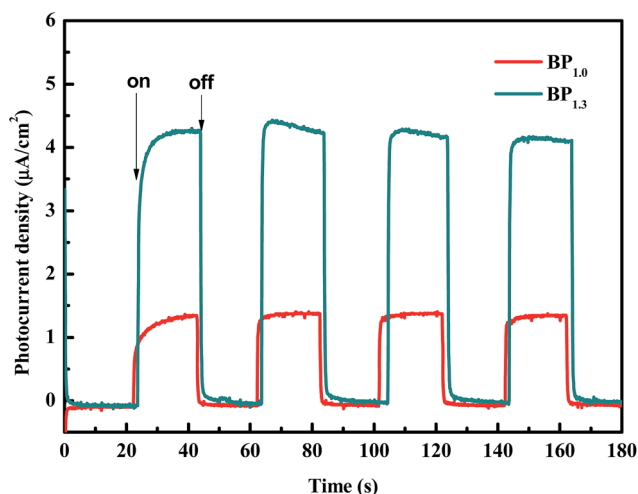


Fig. 8 Photocurrent transient with light on/off every 20 s for duration of 180 s for BP_{1.0} and BP_{1.3}.

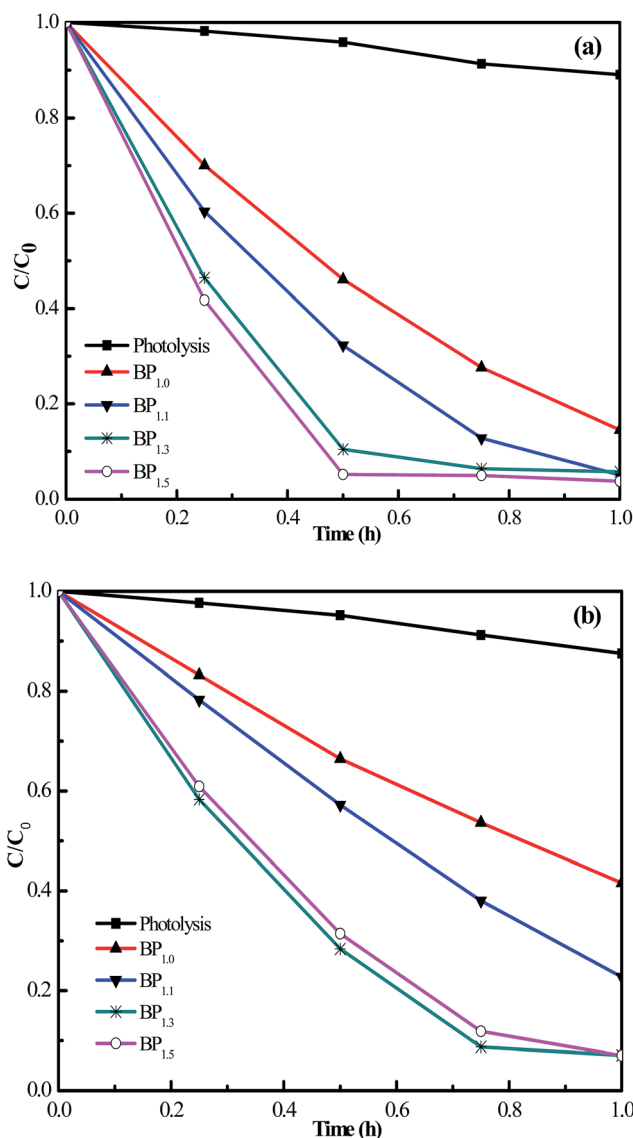


Fig. 9 Photocatalytic activity of the as-prepared phosphate-modified BiPO₄ samples for the degradation of MO under UV light (a) and simulated solar light (b) irradiation.

to the surface of bare BiPO₄, which was completely occupied by PO₄³⁻ at a P/Bi ratio of 1.3.

3.11. Reaction pathways for the photocatalytic degradation of MO with phosphate-modified BiPO₄ samples

During the photocatalytic degradation reactions in aqueous solutions, oxidative species, including hydroxyl free radicals ($\cdot\text{OH}$), holes (h^+), and free oxygen radicals ($\cdot\text{O}_2^-$), played an important role in the mineralization of pollutants. Different scavengers were added to the reaction systems to determine which species had a major role in the degradation of MO under simulated solar-light irradiation. As shown in Fig. 10, the MO degradation rate and efficiency of BP_{1.3} were significantly reduced after adding isopropyl alcohol (scavenger of $\cdot\text{OH}$) to the degradation system; thus, the removal efficiency was reduced

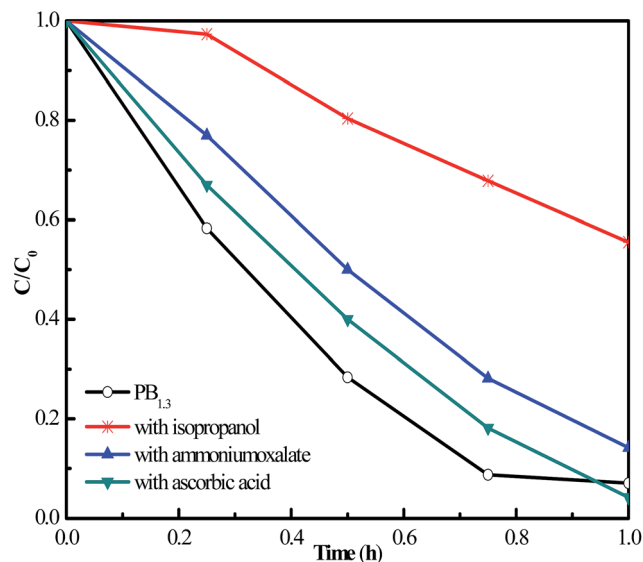


Fig. 10 Variations of MO photocatalytic removal efficiencies over a BP_{1.3} sample with and without the addition of radical scavengers under simulated solar-light irradiation.

from 90% to 40%. However, by adding ammonium oxalate (scavenger of h^+) and ascorbic acid (scavenger of $\cdot O_2^-$) to the degradation system, the MO removal rates and efficiencies were slightly suppressed. These experimental results indicated that oxidation by $\cdot OH$ is the dominant reaction pathway for MO removal with phosphate-modified BiPO₄ samples, whereas holes and free oxygen radicals do not have significant roles in MO mineralization.

Aside from the abovementioned indirect scavenger method, the ESR method was also adopted for the direct determination of the production and intensity of free radicals, with DMPO as the spin-trap reagent during the photocatalytic degradation processes under ultraviolet light irradiation with wavelength of 245 nm. As presented in Fig. 11a, no signals of $\cdot OH$ radicals were detected for the surface-modified and bare BiPO₄ photocatalysts (*i.e.* samples BP_{1.0} and BP_{1.3}) before simulated UV light irradiation. Moreover, the four characteristic peaks of DMPO- $\cdot OH$ with an intensity ratio of 1 : 2 : 2 : 1 were observed after 30 min of irradiation, which suggested generation of OH radicals during the photocatalytic degradation processes.⁴⁶ Moreover, the intensity of DMPO- $\cdot OH$ signals with BP_{1.3} was much higher than those with BP_{1.0}, thereby demonstrating that the phosphate modification can facilitate the generation of OH radicals during degradation. This result can probably be ascribed to the presence of a large amount of hydroxyl groups adsorbed on the surface of BP_{1.3} as compared with the bare BiPO₄. These groups can facilitate the separation of photogenerated charge carriers and eventually enhance the photocatalytic activity. Moreover, no free oxygen radicals ($\cdot O_2^-$) were detected by ESR methods, as shown in Fig. 11b, thereby indicating that MO was predominantly removed *via* oxidation by $\cdot OH$ radicals.

Theoretically, the band positions of BiPO₄ can be calculated by the following empirical equations:

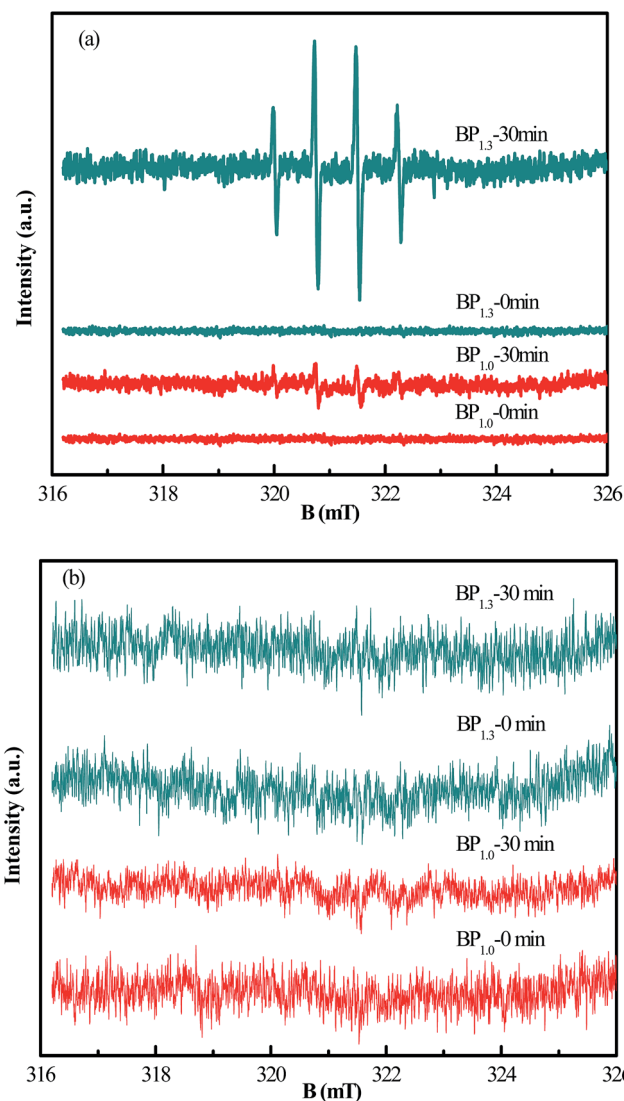


Fig. 11 DMPO spin-trapping ESR spectra under simulated solar-light irradiation for 0 and 30 min at room temperature of water (a) and ethanol (b) in the presence of BP_{1.0} and BP_{1.3}.

$$E_{VB} = X - E^c + 0.5E_g \quad (1)$$

$$E_{CB} = E_{VB} - E_g \quad (2)$$

where E_{VB} is the VB edge potential and E_{CB} is the CB edge potential. X is the electronegativity of the semiconductor, which is the geometric mean of the electronegativity of the constituent atoms, and the value of X for BiPO₄ is 6.49 eV. E^c is the energy of free electrons on the hydrogen scale (approximately 4.5 eV), whereas E_g is the band gap energy of the semiconductor photocatalyst.⁴⁷ Based on the band gap energies calculated from the UV-vis DRS characterization results, the VB edge potentials of the as-prepared bare BiPO₄, BP_{1.1}, BP_{1.3}, and BP_{1.5} samples are 3.89, 4.00, 4.05, and 4.09 eV, respectively. Moreover, the CB edge potentials of the corresponding bare BiPO₄, BP_{1.1}, BP_{1.3}, and BP_{1.5} samples are 0.09, -0.02, -0.05, and -0.11 eV, respectively. Given that the redox potential of $O_2/\cdot O_2^-$ is -0.33 eV,

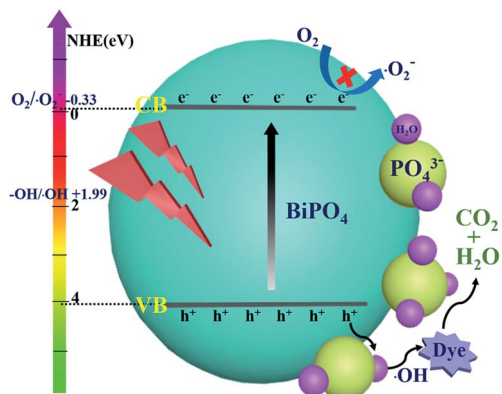


Fig. 12 Schematic of the photocatalytic degradation mechanism of MO with the as-prepared phosphate-modified BiPO_4 samples under simulated solar-light irradiation.

which is more negative than the CB edge potentials of all the as-prepared BiPO_4 samples, the CB electrons could not reduce O_2 to $\cdot\text{O}_2^-$. Furthermore, the potentials of the holes at the VB of all the as-prepared BiPO_4 are more positive than that of $\text{OH}^-/\cdot\text{OH}$ (1.99 eV); thus, the holes can oxidize OH^- into $\cdot\text{OH}$ radicals.¹⁶ These theoretical calculation results confirm the active species identification results from the scavenger and direct ESR methods.

Therefore, based on the characterization results, we proposed a photocatalytic degradation mechanism of MO over the as-prepared phosphate-modified BiPO_4 , as shown in Fig. 12. From the FTIR and XPS characterization results, the surface modification of BiPO_4 by PO_4^{3-} can enhance the surface hydroxyl group concentration and improve its hydrophilic property. The concentration of PO_4^{3-} adsorbed on the surfaces of the as-prepared samples would be saturated when the molar ratio of $\text{PO}_4^{3-}/\text{Bi}^{3+}$ exceeds 1.3, thereby preventing further photocatalytic activity improvement. Compared with bare BiPO_4 , the phosphate-modified BiPO_4 samples facilitated the separation of photogenerated electrons and holes under simulated solar-light irradiation because of the improved hydrophilic properties, which eventually enhanced MO degradation efficiency. Moreover, as depicted in Fig. 12, when the catalyst was irradiated with simulated solar light, excited electrons transferred from the VB to the CB. The holes left in VB could act with hydroxyl to form hydroxyl free radicals because of its suitable electrode potential position, thereby leading to the effective separation of photo-generated carriers. However, the electrons in CB were unable to reduce oxygen to $\cdot\text{O}_2^-$ because of its much more positive reduction potential. Therefore, the experimental and theoretical results evidenced that $\cdot\text{OH}$ is the predominant active species for MO degradation in the reaction system.

4. Conclusion

Surface modification by phosphate can efficiently improve the photocatalytic performance of BiPO_4 for the degradation of MO, which can be ascribed to the high crystallinity, uniform

morphology, and increased surface OH concentrations of the phosphate-modified BiPO_4 samples. According to the characterization results, PO_4^{3-} modification can facilitate the separation of photo-excited electrons and holes. The produced OH radicals were identified as the dominant active species for MO oxidation in the photocatalytic degradation system, rather than via the reaction with $\cdot\text{O}_2^-$ radicals. Therefore, PO_4^{3-} modification is an effective method for improving the activity of BiPO_4 .

Acknowledgements

This study was financially supported by the National Science Foundation of China (21303116, 41401567, 41573138), the Shanxi Province Science Foundation (2013021011-2) and partially supported by the Research Grants Council of Hong Kong (PolyU 152083/14E), a research grant of the Early Career Scheme (ECS 809813) from the Research Grant Council, the Hong Kong SAR Government, the Dean's Research Fund-Early Career Researchers (04022), the Research Equipment Grant (REG-2), and the Internal Research Grant (R3429) from The Hong Kong Institute of Education.

References

- 1 C. C. Chen, W. H. Ma and J. C. Zhao, *Chem. Soc. Rev.*, 2010, **39**, 4206.
- 2 C. S. Pan, J. Xu, Y. Chen and Y. F. Zhu, *Appl. Catal., B*, 2012, **115–116**, 314.
- 3 L. Körösi, S. Papp, I. Bertóti and I. Dékány, *Chem. Mater.*, 2007, **19**, 4811.
- 4 C. S. Pan and Y. F. Zhu, *Environ. Sci. Technol.*, 2010, **44**, 5570.
- 5 N. Zhang, M. Q. Yang, S. Q. Sun and Y. J. Xu, *Chem. Rev.*, 2015, **115**, 10307.
- 6 M. Q. Yang, N. Zhang, M. Pagliaro and Y. J. Xu, *Chem. Soc. Rev.*, 2014, **43**, 8240.
- 7 S. Q. Liu, Z. R. Tang, Y. G. Sun, J. C. Colmenares and Y. J. Xu, *Chem. Soc. Rev.*, 2015, **44**, 5053.
- 8 T. Lv, L. K. Pan, X. J. Liu and Z. Sun, *RSC Adv.*, 2012, **2**, 12706.
- 9 J. Cao, B. Y. Xu, H. L. Lin and S. F. Chen, *Chem. Eng. J.*, 2013, **228**, 482.
- 10 H. L. Lin, H. F. Ye, B. Y. Xu, J. Cao and S. F. Chen, *Catal. Commun.*, 2013, **37**, 55.
- 11 M. H. Fulekar, A. Singh, D. P. Dutta, M. Roy, A. Ballal and A. K. Tyagi, *RSC Adv.*, 2014, **4**, 10097.
- 12 Y. H. Lv, K. Huang, W. Zhang, B. Yang, F. L. Chi, S. L. Ran and X. G. Liu, *Ceram. Int.*, 2014, **40**, 8087.
- 13 C. S. Pan and Y. F. Zhu, *J. Mater. Chem.*, 2011, **21**, 4235.
- 14 C. S. Pan, D. Li, X. G. Ma, Y. Chen and Y. F. Zhu, *Catal. Sci. Technol.*, 2011, **1**, 1399.
- 15 B. Lu, X. G. Ma, C. S. Pan and Y. F. Zhu, *Appl. Catal., A*, 2012, **435–436**, 93.
- 16 Y. F. Liu, Y. Y. Zhu, J. Xu, X. J. Bai, R. L. Zong and Y. F. Zhu, *Appl. Catal., B*, 2013, **142–143**, 561.
- 17 Y. Y. Zhu, Y. F. Liu, Y. H. Lv, Q. Ling, D. Liu and Y. F. Zhu, *J. Mater. Chem. A*, 2014, **2**, 13041.
- 18 B. H. Long, J. H. Huang and X. C. Wang, *Prog. Nat. Sci.*, 2012, **22**, 644.

- 19 J. Xu, L. Li, C. S. Guo, Y. Zhang and W. Meng, *Appl. Catal., B*, 2013, **130–131**, 285.
- 20 M. Ruwet, S. Ceckiewicz and B. Delmon, *Ind. Eng. Chem. Res.*, 1987, **26**, 1981.
- 21 Z. Holgye, *J. Radioanal. Nucl. Chem.*, 1998, **227**, 127.
- 22 M. Sheng, L. L. Gu, R. Kontic, Y. Zhou, K. B. Zheng, G. R. Chen, X. L. Mo and G. R. Patzke, *Sens. Actuators, B*, 2012, **166**, 642.
- 23 C. S. Pan, J. Xu, Y. J. Wang, D. Li and Y. F. Zhu, *Adv. Funct. Mater.*, 2012, **22**, 1518.
- 24 F. F. Duo, Y. W. Wang, X. M. Mao, X. C. Zhang, Y. F. Wang and C. M. Fan, *Appl. Surf. Sci.*, 2015, **340**, 35.
- 25 Y. N. Zhang, H. Q. Fan, M. M. Li and H. L. Tian, *Dalton Trans.*, 2013, **42**, 13172.
- 26 Y. F. Liu, Y. H. Lv, Y. Y. Zhu, D. Liu, R. L. Zong and Y. F. Zhu, *Appl. Catal., B*, 2014, **147**, 851.
- 27 L. N. She, G. Q. Tan, H. J. Ren, J. Huang, C. Xu and A. Xia, *RSC Adv.*, 2015, **5**, 36642.
- 28 Y. H. Lv, Y. Y. Zhu and Y. F. Zhu, *J. Phys. Chem. C*, 2013, **117**, 18520.
- 29 Y. H. Lv, Y. F. Liu, Y. Y. Zhu and Y. F. Zhu, *J. Mater. Chem. A*, 2014, **2**, 1174.
- 30 J. Huang, W. Liu, D. S. Dolzhnikov, L. Protesescu, M. V. Kovalenko, B. Koo, S. Chattopadhyay, E. V. Shchenchenko and D. V. Talapin, *ACS Nano*, 2014, **8**, 9388.
- 31 H. Q. Cui, Y. Cao, L. Q. Jing, Y. B. Luan and N. Li, *ChemPlusChem*, 2014, **79**, 318.
- 32 P. Mohapatra and K. M. Parida, *J. Mol. Catal. A: Chem.*, 2006, **258**, 118.
- 33 D. Zhao, C. C. Chen, Y. F. Wang, H. W. Ji, W. H. Ma, L. Zang and J. C. Zhao, *J. Phys. Chem. C*, 2008, **112**, 5993.
- 34 L. M. He, L. Q. Jing, Z. J. Li, W. T. Sun and C. Liu, *RSC Adv.*, 2013, **3**, 7438.
- 35 L. Q. Jing, J. Zhou, J. R. Durrant, J. W. Tang, D. N. Liu and H. Q. Fu, *Energy Environ. Sci.*, 2012, **5**, 6552.
- 36 C. S. Pan and Y. F. Zhu, *Catal. Sci. Technol.*, 2015, **5**, 3071.
- 37 G. H. Tian, H. G. Fu, L. Q. Jing and C. G. Tian, *J. Hazard. Mater.*, 2009, **161**, 1122.
- 38 A. Bhaumik and S. Inagaki, *J. Am. Chem. Soc.*, 2001, **123**, 691.
- 39 J. Jiménez-Jiménez, P. Maireles-Torres, P. Olivera-Pastor, E. Rodríguez-Castellón, A. Jiménez-López, D. J. Jones and J. Rozière, *Adv. Mater.*, 1998, **10**, 812.
- 40 J. C. Yu, L. Z. Zhang, Z. Zheng and J. C. Zhao, *Chem. Mater.*, 2003, **15**, 2280.
- 41 X. Qin, L. Q. Jing, G. H. Tian, Y. C. Qu and Y. J. Feng, *J. Hazard. Mater.*, 2009, **172**, 1168.
- 42 H. Xu, Y. G. Xu, H. M. Li, J. Xia, J. X. Xiong, S. Yin, C. J. Huang and H. L. Wan, *Dalton Trans.*, 2012, **41**, 3387.
- 43 S. Y. Wu, H. Zheng, Y. W. Lian and Y. Y. Wu, *Mater. Res. Bull.*, 2013, **48**, 2901.
- 44 H. L. Lin, H. F. Ye, X. Li, J. Cao and S. F. Chen, *Ceram. Int.*, 2014, **40**, 9743.
- 45 F. Dong, Q. Y. Li, Y. J. Sun and W. K. Ho, *ACS Catal.*, 2014, **4**, 4341.
- 46 C. M. Arroyo, J. H. Kramer, B. F. Dickens and W. B. Weglicki, *FEBS Lett.*, 1987, **221**, 101.
- 47 X. Lin, D. Liu, X. Y. Guo, N. Sun, S. Zhao, L. M. Chang, H. J. Zhai and Q. W. Wang, *J. Phys. Chem. Solids*, 2015, **76**, 170.