Enhanced Photocatalytic Performance for the BiPO$_{4-x}$ Nanorod Induced by Surface Oxygen Vacancy

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ABSTRACT: The BiPO$_{4-x}$ nanorod with surface oxygen vacancy was fabricated via vacuum deoxidation. The concentration and kind of oxygen vacancy could be controlled by tuning the deoxidation temperature and time in vacuum. The photocatalytic activity depended on the concentration and kind of surface oxygen vacancy, and the optimum photocatalytic activity and photocurrent of the BiPO$_{4-x}$ nanorod was about 1.5 and 2.5 times as high as that of pure BiPO$_4$, respectively. Besides, the photocatalytic response wave range of the BiPO$_{4-x}$ nanorod has been expanded to more than 365 nm. The enhancement of photocatalytic activity is attributed to the high separation efficiency of photoinduced electron–hole pairs due to the broadening of the valence band (VB) induced by surface oxygen-vacancy states, and the extending of photoresponse is considered to be the narrowing of energy band gap resulting from the rise of the valence band maximum (VBM).

1. INTRODUCTION

Photocatalysis technology has attracted enormous interest in organic wastewater treatment for environmental remediation because it is an inexpensive and convenient method that can totally decompose dye molecules into inorganic small molecules. Heterogeneous photocatalysts afford great potential for converting photon energy into chemical energy and for decomposing organic pollutants. Especially, surface oxygen defects can serve as photoinduced charge traps as well as adsorption sites where the charge transfer to adsorbed species can prevent the electron–hole recombination, which is conductive to the improvement of photocatalytic activity and the photoresponse range can be expanded by introducing surface oxygen vacancies, due to the narrowing of band gap induced by surface oxygen-vacancy states. Oxygen vacancy properties have been deeply surveyed in simple semiconductors, such as TiO$_2$, ZnO, and Fe$_2$O$_3$, however, complicated oxyacid salt with a wide band gap has seldom been reported. In this work, we attempt to enhance the photocatalytic activity and expand the photoresponse of BiPO$_4$ by introducing surface oxygen vacancies.

Here, BiPO$_{4-x}$ with surface oxygen vacancy is first fabricated by a facile soft-chemical approach, vacuum deoxidation. After surface oxygen vacancies were introduced on vacancy BiPO$_{4-x}$, its photocatalytic activity and photocurrent were improved about 1.5 and 2.5 times, respectively ($\lambda = 254$ nm). Although no visible photoactivity was observed for vacancy BiPO$_{4-x}$, its photoactivity was generated under 365 nm light irradiation. As is well-known, the bandgap of monoclinic BiPO$_4$ is about 4.1 eV (about 300 nm), which cannot be excited by $\lambda = 365$ nm UV light. So the photoresponse of vacancy BiPO$_{4-x}$ was expanded, induced by surface oxygen vacancies. The reduced total organic carbon (TOC) of methylene blue (MB) solution by vacancy BiPO$_{4-x}$ after 25 min degradation is 85%, indicating that vacancy BiPO$_{4-x}$ has a good capability of mineralization. In addition, the degradations of the other three kinds of organic pollutants were also investigated. Vacancy BiPO$_{4-x}$ shows higher activity on all of them than that of BiPO$_4$, indicating that the high activity of BiPO$_{4-x}$ may be general and essential for environmental application.

2. EXPERIMENTAL SECTION

2.1. Materials Preparation. The BiPO$_4$ nanorod (7.63 m$^2$g$^{-1}$) was synthesized through the reported method by our groups previously. All chemicals used were analytic grade reagents without further purification. Vacuum deoxidation...
treated BiPO₄ samples were prepared as follows: (1) the temperature-programmed deoxidizing (TPD) measurement using helium (He) gas was performed in a specially designed quartz tube with 0.023 g of the BiPO₄ nanorod sample. The tube was put in a cylindrical electric furnace. The temperature of the furnace was controlled by a programmable regulator with the thermocouple. A thermal conductivity detector (TCD) was used to detect He consumption during the vacuum treatment process. The BiPO₄ sample was pretreated by nitrogen (N₂) gas from room temperature to 100 °C at a temperature ramping rate of 5 °C·min⁻¹ for 1.5 h. Then, it cooled naturally to room temperature. Afterward, He gas was introduced into the homemade quartz tube equipped with the BiPO₄ sample, and the gas flow rate was 25 mL·min⁻¹ accompanied by the temperature gradually increasing to 600 °C for 5 min. (2) According to the TPD graph, the deoxidation temperature range was 110−160 °C at 10 °C intervals, and 260 °C was also chosen; the time was 1, 2, 3, 4, and 5 h. The vacuum deoxidation process was performed to prepare BiPO₄ samples for the photocatalytic degradation reaction. The as-prepared BiPO₄ nanorod was put into a self-made quartz tube and then placed into a furnace connected with a vacuum pump and a program heating device. Pressure in the vacuum deoxidation process was about 1×10⁻³~10⁻⁴ Torr. The temperature was increased from room temperature to the designed temperature at an increasing rate of 10 °C·min⁻¹, and the time was kept for 1, 2, 3, 4, and 5 h, respectively. Finally, the samples were cooled naturally to room temperature.

BiPO₄ and BiPO₄ₓ⁻electrodes were prepared as follows: 7 mg of as-prepared photocatalyst was suspended in 1 mL of ethanol to produce a slurry, which was then dip-coated onto a 2 cm × 4 cm indium–tin oxide (ITO) glass electrode. Electrodes were exposed to UV light for 12 h to remove ethanol and subsequently calcined at 120 °C for 10 h. All investigated electrodes were of similar thickness (0.8−1.0 μm).

2.2. Characterizations. A high-resolution transmission electron microscope (HR-TEM, JEM 2010F) was operated at an accelerating voltage of 200 kV. The electron paramagnetic resonance (EPR) measurement of photocatalyst powder was carried out using an Endor spectrometer (JEOL ES-ED3X) at 77 K. The g factor was obtained by taking the signal of manganese. The electron spin resonance (ESR) signals of radicals spin-trapped by spin-trap reagent DMPO (5,5′-dimethyl-1-pyrroline-N-oxide) (Sigma Chemical Co.) in water were examined on a Bruker model ESR JES-FA200 spectrometer equipped with a quanta-Ray Nd:YAG laser system as the irradiation source (λ = 270−410 nm, 10 Hz). To minimize experimental errors, the same type of quartz capillary tube was used for all ESR measurements. The EPR (or ESR) spectrometer was coupled to a computer for data acquisition and instrument control. Magnetic parameters of the radicals detected were obtained from direct measurements of magnetic field and microwave frequency. The room-temperature photoluminescence (PL) spectra of BiPO₄ and vacancy BiPO₄ₓ samples were investigated utilizing the Perkin-Elmer LS55 spectrophotometer equipped with a xenon (Xe) lamp with an excitation wavelength of 270 nm. The photocurrent and electrochemical impedance spectroscopy (EIS) were measured on an electrochemical system (CHI-660B, China). UV light 254 nm was obtained from an 11 W germicidal lamp.

Figure 1. UV photocatalytic activity of BiPO₄, untreated and vacuum treated with (A) various temperatures for 3 h and (B) various times at 140 °C on the degradation of MB. Insets: degradation rate constant k of BiPO₄ and vacancy BiPO₄ₓ photocatalysts (λ = 254 nm). (C) Photocurrents of BiPO₄ and vacancy BiPO₄ₓ (treated for 3 h at 130, 140, 160, and 260 °C, respectively) electrodes, under UV light (λ = 254 nm). (D) TOC removal plots of MB over BiPO₄ and vacancy BiPO₄ₓ (treated at 140 °C for 3 h), under UV light (λ = 254 nm).
(Institute for Electric Light Sources, Beijing). A standard three-electrode cell with ITO/BiPO₄ as a working electrode, a platinum wire as a counter electrode, and a standard calomel electrode (SCE) as reference electrode were used in photoelectric studies. 0.1 M Na₂SO₄ was used as the electrolyte solution. Potentials were given with reference to the SCE. The photoelectric responses of the photocatalysts as light on and off were measured at 0.0 V. Total organic carbon analyzer (TOC-Vwp, Shimadzu, Japan) was employed for mineralization degree analysis of MB solutions. Ultraviolet–visible diffuse reflectance spectroscopy (UV-DRS) was performed in Hitachi U-3010, and BaSO₄ was used as reference.

2.3. Photocatalytic Evaluations. The photocatalytic activities of the as-prepared samples were evaluated by the decomposition of methylene blue (MB) in solution under UV light. The UV light source was obtained by a 15 W UV germicidal lamp (λ = 254 nm), and the average light intensity was 0.82 mW·cm⁻². An amount of 25 mg of photocatalyst was added into prepared 50 mL of 1×10⁻⁵ M MB aqueous solution. Before the light irradiation, the suspensions were first ultrasonic dispersed in dark for 15 min and then magnetically stirred for 15 min to reach the absorption–desorption equilibrium. At given time intervals, 3 mL aliquots were sampled and centrifuged to remove the photocatalyst particles. Synchronously, the filtrates of MB solutions at different times were analyzed by recording variations of the concentration and kind of oxygen vacancy. This result is in agreement with the photocatalytic activity of the as-prepared photocatalysts.

3. RESULTS AND DISCUSSION

3.1. Enhancement of Photocatalytic Activity and Photocurrent. Figure 1A and B shows the UV photocatalytic activities of pure BiPO₄ and vacuum deoxidation BiPO₄₋ₓ treated with various temperatures for 3 h and various times at 140 °C on the degradation of MB (λ = 254 nm). The degradation process is fitted to pseudo-first-order kinetics, and the value of the rate constant k is equal to the corresponding slope of the fitting line. After vacuum treatment, the photocatalytic activities of BiPO₄₋ₓ samples gradually enhanced with the increase of vacuum temperature and time; when the temperature reaches 140 °C, time is 3 h, and vacuum BiPO₄₋ₓ displays the highest photocatalytic activity. The apparent rate constant k = 0.300 min⁻¹, and it is about 1.5 times as high as that of pure BiPO₄. Further increasing the temperature or prolonging the time, however, the degradation rate decreases. Even after 260 °C 3 h vacuum deoxidation, the photocatalytic activity of BiPO₄₋ₓ is slightly lower than that of pure BiPO₄. From the inset graph of Figure 1A and B, it can be seen that the temperature and time in the process of vacuum deoxidation both greatly influence the photocatalytic activity of BiPO₄₋ₓ photocatalysts. To further understand the mineralization property of the as-prepared photocatalyst, the removal of TOC in the UV photodegradation of MB over BiPO₄ and vacuum BiPO₄₋ₓ (treated at 140 °C for 3 h, following is the same, except special directions) photocatalysts was investigated (see Figure 1C). It can be found that the TOC removal percentage is about 63% and 85% for BiPO₄ and vacuum BiPO₄₋ₓ after 25 min photocatalytic reaction, respectively. This indicates that the mineralization property of vacuum BiPO₄₋ₓ is evidently enhanced.

The photocurrent responses of BiPO₄ and BiPO₄₋ₓ after deposition on ITO electrodes, under UV light (λ = 254 nm), are provided in Figure 1D. It can be seen that BiPO₄₋ₓ electrodes after vacuum deoxidation at 130, 140, 160, and 260 °C for 3 h show different photocurrent density. The photocurrent of BiPO₄₋ₓ samples gradually enhanced with the increase of vacuum temperature: when the temperature reaches 140 °C, vacuum BiPO₄₋ₓ displays the highest photocurrent, which is about 2.5 times as high as that of pure BiPO₄; however, the photocurrent of BiPO₄₋ₓ (vacuum treated at 260 °C for 3 h) is lower than that of pure BiPO₄ (only about 2/3 of pure BiPO₄). The enhancement/decrease of photocurrent demonstrates that the increase/decrease of photoinduced carriers transport rate and the boost/inhibition of photogenerated electron–hole pair separation leads to the enhancement/decrease of photocatalytic activity, which is controlled by the concentration and kind of oxygen vacancy. This result is in accord with the photocatalytic activity of the as-prepared samples.

To check the extending of photoresponse range, under UV (λ = 365 nm) light, the photocatalytic activity of BiPO₄ and vacuum BiPO₄₋ₓ on degradation of MB was investigated, as shown in Figure 2A. As reported previously, the bandgap of monoclinic BiPO₄ is about 4.1 eV, and its absorption edge is no more than 300 nm.26 So, under λ = 365 nm light, pure BiPO₄₄
shows almost no photocatalytic activity. However, vacancy BiPO$_4$ reveals a significant photoactivity, and its reaction rate constant $k$ reaches to 0.012 min$^{-1}$, which is about 10 times that of pure BiPO$_4$ (the inset of Figure 2A). Incident photon-to-current conversion efficiency (IPCE) is a better parameter to characterize the photoconversion efficiency of different photoanodes because it is independent from the light sources and filters used in the measurement.\textsuperscript{17,27,28} IPCE measurements were performed on an as-prepared electrode in a two-electrode cell, as shown in Figure 2B. ITO/BiPO$_4$ samples or standard electrode served as a working electrode and a platinum wire as the counter electrode, and 0.1 M Na$_2$SO$_4$ was used as the electrolyte solution. The irradiation source was a 75 W xenon lamp powered by a high precision constant current source coupled to a f4 matched monochromator with 1200 lines/in. gratings. IPCEs at each incident wavelength (at intervals of 5 nm) were calculated from the equation

$$\text{IPCE}(\lambda) = \frac{(1240I_{ph})}{\lambda P_0}$$

In this equation, $I_{ph}$ is the incident photocurrent density in mA$\cdot$cm$^{-2}$; $\lambda$ is the wavelength of incident radiation in nm; and $P_0$ is the photon flux in mW$\cdot$cm$^{-2}$. In comparison to pure BiPO$_4$, vacancy BiPO$_{4-x}$ exhibits significantly enhanced photoactivity from 300 to 380 nm. Although the IPCE max of vacancy BiPO$_{4-x}$ is only about 5.5% at 340 nm, it is direct evidence for illustrating the expanding of phoresopse range of vacancy BiPO$_{4-x}$ with surface oxygen vacancy.

### 3.2. Stability, Selectivity, and Intermediates.

To survey the stability of photodegradation, reaction and storage of reduced vacancy BiPO$_{4-x}$, UV photocatalytic degradation on MB with five recycles by vacancy BiPO$_{4-x}$, and UV photocatalytic activities of fresh and after storage for 10 months vacancy BiPO$_{4-x}$ on the degradation of MB, compared with pure BiPO$_4$, were examined. From Figure 3A, the photocatalyst vacancy BiPO$_{4-x}$ exhibits almost no significant loss of activity, confirming that vacancy BiPO$_{4-x}$ is stable during the photocatalytic oxidation of pollutant molecules. As seen from Figure 3B, the UV photocatalytic activity of vacancy BiPO$_{4-x}$ after storage for 10 months only decreases slightly ($k = 0.286$ min$^{-1}$), compared with that of fresh reduced ZnO$_{2-x}$ ($k = 0.300$ min$^{-1}$), but it is still much higher than that of pure BiPO$_4$ photocatalyst ($k = 0.154$ min$^{-1}$). These indicate that vacancy BiPO$_{4-x}$ has a good stability on both photocatalytic degradation and storage.

It is well-known that photoinduced holes are almost nonselective, and they will directly react with various organic pollutants owing to their strong oxidation ability. In fact, the photodegradation of organic dyes and transparent organic pollutant phenol by BiPO$_4$ and vacancy BiPO$_{4-x}$ samples (Figure 3C) confirm this conclusion. It can be seen that the degradation activity of vacancy BiPO$_{4-x}$ on anionic dye (rhodamine B (RhB)), cationic dye (methyl orange (MO)), and benzene ring compounds (phenol) is obviously higher than that of pure BiPO$_4$, which suggests that the high activity of vacancy BiPO$_{4-x}$ is not due to the special combination of the
catalysts to some specific substrates but due to the strong oxidation reactions of photoinduced holes. Therefore, the high photocatalytic activity of vacancy BiPO$_4$ may be general and essential for environmental application.

To demonstrate the change and reveal some details of the reaction process of pure BiPO$_4$ and vacancy BiPO$_{4-x}$, photodegradation intermediates distribution of phenol at intervals during the photocatalytic process were monitored by HPLC, and the results are displayed in Figure 3D. The intermediates at different retention time as references were shown in Table S1 (Supporting Information). At 5.3 min the product is phenol, and based on steric effect, those at about 2.7 min are 4,4′-dihydroxybiphenyl and 4-phenoxyphenol. The peak of phenol disappears more quickly in vacancy BiPO$_4$ than that in pure BiPO$_4$. Furthermore, peaks attributed to degradation intermediates increase and then decrease in the vacancy BiPO$_{4-x}$ system, while in pure BiPO$_4$ there was hardly any reduction. This indicates that the mineralization property on phenol of vacancy BiPO$_{4-x}$ is also evidently enhanced, compared with pure BiPO$_4$.

3.3. Formation of Surface Oxygen Vacancy. To investigate the deoxidation process, temperature-programmed deoxidation (TPD) was performed on the BiPO$_4$ nanorod, as shown in Figure 4A. Others are intermediates, HQ (2.5 min), P-BQ (3.1 min), and catechol (3.8 min), respectively. The peak of phenol disappears more quickly in vacancy BiPO$_{4-x}$ than that in pure BiPO$_4$. Furthermore, peaks attributed to degradation intermediates increase and then decrease in the vacancy BiPO$_{4-x}$ system, while in pure BiPO$_4$ there was hardly any reduction. This indicates that the mineralization property on phenol of vacancy BiPO$_{4-x}$ is also evidently enhanced, compared with pure BiPO$_4$. The Journal of Physical Chemistry C

Figure 4. (A) O$_2$-TPD profile of the BiPO$_4$ nanorod. Inset: the ball-and-stick model of BiPO$_4$ coordination. (B) UV–vis diffuse reflectance spectra and the color of BiPO$_4$ and vacancy BiPO$_{4-x}$. (C), (D) HR-TEM images of BiPO$_4$ and vacancy BiPO$_{4-x}$. (E) The PL spectra of BiPO$_4$ and vacancy BiPO$_{4-x}$ at wavelength 270 nm excitation. (F) Situ EPR spectra of BiPO$_4$ and vacancy BiPO$_{4-x}$ at 77 K.
several little broad peaks, which gradually enhanced with the rise of temperature in the 120−580 °C range. As seen from the inset of Figure 4A, the bond length between the oxygen (O) atom and phosphorus (P) atom or bismuth (Bi) atom is not equivalent in the BiPO_4 sample. On the basis of the difference of the bond length (representing bond energy) between each O atom and P or Bi, O atoms may be removed first from surface to bulk, and the order is from O1, O2, O4, to O3.35 Finally, the PO_4^{3−} is totally detached from BiPO_4, generating oxygen vacancies with different number and kind. These can be confirmed from the X-ray diffraction (XRD) patterns of pure BiPO_4 and BiPO_4−x samples (Figure S1, Supporting Information). No phase transformation or any impurity is observed for BiPO_4 after vacuum deoxidation at 140 °C for 3 h, so here most oxygen atoms are removed from the BiPO_4 surface, generating surface oxygen vacancies. However, after vacuum treatment at 260 °C for 3 h, the XRD peak of BiPO_4−x at 2θ = 27.1° (200) moves to a big angle slightly, indicating that the lattice spacing d decreases, which may be a result of the loss of lattice oxygen and the formation of bulk oxygen vacancy, and after 524.5 °C 3 h vacuum treatment, BiPO_4 loses PO_4^{3−} and totally becomes metal Bi (Figure S1A and B, Supporting Information).

UV−vis diffuse reflectance spectra (UV-DRS) of BiPO_4 and vacancy BiPO_4−x photocatalysts are shown in Figure 4B. BiPO_4 shows the characteristic spectrum with its fundamental absorption sharp edge at about 300 nm. The absorbance edge of vacancy BiPO_4−x photocatalysts exhibits only a little redshift from 300 to 305 nm. However, the absorbance of vacancy BiPO_4−x was enhanced in the range of 300−800 nm, which may be induced by oxygen vacancies. The color of BiPO_4 samples changes from white to light gray by vacuum deoxidation as shown in the inset of Figure 4B. Further study by HR-TEM (Figure 4C and D) showed that the BiPO_4 samples both are structurally uniform with a lattice spacing of about 0.328 nm corresponding to the (200) plane. Differently, pure BiPO_4 displays perfect lattice features, but the edge of vacancy BiPO_4−x particles becomes disordered (thickness about 1.5 nm), which indicates the surface structure is damaged and maybe surface oxygen vacancies are formed.

To further confirm the existence of oxygen vacancies, in situ electron paramagnetic resonance (EPR) of BiPO_4 samples was performed at 77 K. It can provide a sensitive and direct method to monitor various behaviors of the presence of oxygen defects.36 The intensity of the EPR signal at g ~ 2.001 of vacancy BiPO_4−x is much higher than that of pure BiPO_4 under the same conditions, as seen from Figure 4E. As reported previously, the peak at g ~ 2.001−2.004 can be attributed to neutral oxygen vacancies about the surface.37−39 Otherwise, two other peaks at g ~ 2.038 correspond to chemisorbed oxygen O_2−40,41 and g ~ 1.967 is controversial and is assigned to shallow donors or singly ionized oxygen vacancy (Vo+).41,42 However, these indicate that other defects may be produced on BiPO_4, besides those that surface oxygen vacancy mainly generates. In addition, it was reported previously that surface oxygen vacancy is positively related with the photoluminescence spectra (PL) signal in ZnO and TiO_2.18,22 From the photoluminescence (PL) spectra of BiPO_4 and vacancy BiPO_4−x at wavelength 270 nm excitation in Figure 4F, it can be seen that the PL peak of vacancy BiPO_4−x is obviously enhanced in the range of 300−520 nm, which might be induced
by surface oxygen vacancy.\textsuperscript{43,44} The larger the surface oxygen-vacancy concentration, the stronger the PL signal.\textsuperscript{18,21,22} Therefore, under the same conditions, the strengthening of the PL spectrum of vacancy BiPO\textsubscript{4-x} may be attributed to the formation of surface oxygen vacancies.

3.4. Mechanism of Enhancement of Photocatalytic Activity. The photocatalytic mechanism can be studied by an electron spin resonance (ESR) spin-trap technique and trapping experiments of radicals and holes.\textsuperscript{45,46} DMPO (2,2-dimethyl-1-pyrroline N-oxide) is a nitrene spin trap generally used for trapping radicals due to the generation of some stable radicals, DMPO-hydroxyl radical (•OH) and DMPO-superoxide radical (•O\textsubscript{2}•\textsuperscript{-}). The ESR spin-trap technique was employed to monitor the reactive oxygen species generated during the irradiation of the pure BiPO\textsubscript{4} and vacancy BiPO\textsubscript{4-x} system with DMPO in water, and the results were shown in Figure 5A and B. Both the signals of the DMPO-hydroxyl radical (•OH) and the DMPO-superoxide radical (•O\textsubscript{2}•\textsuperscript{-}) could be observed when pure BiPO\textsubscript{4} and vacancy BiPO\textsubscript{4-x} suspension were irradiated for 3 min by a Quanta-Ray Nd:YAG pulsed laser system (λ = 270–410 nm, 10 Hz). However, the intensity of •OH radicals is higher than that of •O\textsubscript{2}•\textsuperscript{-} radicals. Therefore, •OH radicals play a more important role than •O\textsubscript{2}•\textsuperscript{-} radicals in the photocatalysis process (•OH > •O\textsubscript{2}•\textsuperscript{-}). Furthermore, the holes and hydroxyl radicals during the photodegradation of MB over pure BiPO\textsubscript{4} and vacancy BiPO\textsubscript{4-x} were also investigated with the addition of EDTA-2Na (holes scavenger)\textsuperscript{47} and t-BuOH (hydroxyl radicals scavenger),\textsuperscript{48} as shown in Figure 5C and D. In the BiPO\textsubscript{4} system, the addition of 0.5 mM t-BuOH as a hydroxyl radicals scavenger only caused a small decrease of the photocatalytic degradation of MB, while the photodegradation of MB could be greatly prevented with the addition of a scavenger for holes (EDTA-2Na), suggesting that the photoinduced holes are the main oxidative species of the BiPO\textsubscript{4} system and that hydroxyl radicals play an assistant role. From Figure 5D, in the vacancy BiPO\textsubscript{4-x} system, the photocatalytic degradation of MB is also greatly suppressed by the addition of EDTA-2Na, and the main oxidative species is the same as that as in the BiPO\textsubscript{4} system. These results indicate that the photocatalytic degradation mechanism of vacancy BiPO\textsubscript{4-x} on MB is not changed (holes > •OH > •O\textsubscript{2}•\textsuperscript{-}), compared with that of the pure BiPO\textsubscript{4} photocatalyst.

As discussed above, the degradation mechanism of vacancy BiPO\textsubscript{4-x} is not changed, and particle size and the crystal phase structure (Figure S1, Supporting Information) are not evidently changed. Also, the limited adsorptivity enhancement (Figure S2, Supporting Information) is not the major factor of the enhancement of the photocatalytic activity of the vacancy BiPO\textsubscript{4-x} photocatalyst. As is well-known, the influence of separation efficiency of photoinduced electron–hole pairs is a crucial factor for the enhancement of photocatalytic activity. The charge separation efficiency can be investigated by the typical electrochemical impedance spectroscopy (EIS) (presented as Nyquist plots). From Figure 6, the EIS Nyquist plots of BiPO\textsubscript{4} and vacancy BiPO\textsubscript{4-x} electrodes show that the arc radius of the vacancy BiPO\textsubscript{4-x} electrode is smaller than that of the BiPO\textsubscript{4} electrode, with and without UV-light irradiation. The smaller the arc radius of an EIS Nyquist plot, the smaller the electric resistance of the electrode and the higher the efficiency of charge separation, so the photocatalytic activity of vacancy BiPO\textsubscript{4-x} improves. Therefore, the significant enhancement of UV photocatalytic activity is mainly attributed to the increase of the separation efficiency of photoinduced electron–hole pairs due to the broadening of the valence band (VB) width induced by surface oxygen-vacancy states.

On the basis of the results above, a proposed schematic diagram for the separation of electron–hole pairs and the photocatalytic reaction process of the vacancy BiPO\textsubscript{4-x} photocatalyst is shown in Figure 7. Surface oxygen vacancy is a shallow defect, which may be near the conduction band minimum (CBM) or above the valence band maximum (VBM). It was reported previously by Zhao and coauthors that the band gap of the PO\textsubscript{4} salt LiTi\textsubscript{2}(PO\textsubscript{4})\textsubscript{3} significantly reduced due to the formation of oxygen-vacancy states above the VB, under poor oxygen conditions.\textsuperscript{53} Our experiments also showed that for vacancy BiPO\textsubscript{4-x}, not only its UV photocatalytic performance distinctly increased but also the photosresponse range was expanded, compared with pure BiPO\textsubscript{4}. The enhancement of the UV photoactivity is attributed to the broadening of the VB width due to the rising of the VBM induced by surface oxygen-vacancy states, which is above and partly overlapping with the VB of BiPO\textsubscript{4}. This is conducive to increase the transport rate of photoinduced carriers, resulting in more efficient charge separation and reducing the probability of photoinduced electron–hole recombination, then leading to an enhanced photocatalytic activity.
obviously enhanced photoactivity. Owing to the rising of the VBM, the energy band gap of vacancy BiPO$_4$ is reduced, and the photoresponse range of vacancy BiPO$_{4-x}$ can be expanded (from less than 300 nm for pure BiPO$_4$ to more than 365 nm for vacancy BiPO$_{4-x}$), although not to the visible light region. This is because the band gap of pure BiPO$_4$ is wide (about 4.1 eV), and the rising of the VBM caused by a shallow DOS of surface oxygen vacancies is not high enough to be in the visible light region (about 2.9 eV). Nevertheless, the photoresponse range of vacancy BiPO$_{4-x}$ is still expanded by surface oxygen vacancies. In addition, the introduction of surface oxygen vacancy only caused the small rising of the VBM and the small narrowing of band gap for BiPO$_4$ and hardly any other change of the energy band structure, so the degradation mechanism was the same as that of pure BiPO$_4$, excepting the enhancement of photoactivity and the expanding of photoresponse range.

Furthermore, the concentration and kind of oxygen vacancy, controlled by tuning the temperature and time in vacuum, greatly influence the photocatalytic activity/photocurrent of BiPO$_{4-x}$ samples. When the concentration of oxygen vacancies is low (low temperature or time), the photocatalytic activity/photocurrent only improves slightly and enhances gradually with the increase of the concentration of surface oxygen vacancy; when the concentration is too high (high temperature or time), bulk oxygen vacancy can easily generate in the deep of the forbidden band, which is the recombination center of electron–hole pairs and will result in the decrease of photocatalytic activity/photocurrent, as shown in Figure 1A and C. Therefore, only high oxygen-vacancy concentration controlled on the surface of BiPO$_{4-x}$, and almost no bulk oxygen vacancy generated can obtain the highest photocatalytic activity of vacancy BiPO$_{4-x}$. So the concentration and kind of oxygen vacancy controlled by tuning vacuum deoxidation temperature and time play an important role in improving the photocatalytic activity.

4. CONCLUSIONS

BiPO$_{4-x}$ photocatalysts with surface oxygen vacancies were prepared via a facile economic vacuum deoxidation method. After vacuum treatment, the BiPO$_{4-x}$ photocatalyst possessed significant enhancement of photocatalytic activity, and its photoresponse range can be extended visibly; however, the photocatalytic process is not changed, and the main active species are still photoinduced holes. The distinct enhancement of UV activity is attributed to high separation efficiency of photoinduced electron–hole pairs caused by the broadening of the VB width induced by surface oxygen-vacancy states, and the expanding of photoresponse range originates from the narrow energy band gap due to the rise of valence band maximum (VBM). This facile and effective approach is proposed to develop a new type of optical materials and to be extended for other wide bandgap materials.

## ASSOCIATED CONTENT

*Supporting Information*

XRD, adsorption curves in dark of pure BiPO$_4$ and BiPO$_{4-x}$-MB HPLC on MB, and intermediate distribution of phenol by pure BiPO$_4$ and BiPO$_{4-x}$. This material is available free of charge via the Internet at [http://pubs.acs.org](http://pubs.acs.org).

## REFERENCES


