1. Introduction

Heterogeneous photocatalysts afford a great potential for converting photon energy into chemical energy and for decomposing organic pollutants.\(^1\)–\(^3\) BiPO\(_4\) as one of the oxyacid salt photocatalysts exhibits more attractive activity on the degradation of dyes than that of P25 (TiO\(_2\)) because of its exceptional optical and electronic properties, nontoxicity, low cost and higher photocatalytic efficiency.\(^4\)–\(^5\) Nevertheless, monoclinic phase BiPO\(_4\) photocatalyst also has its disadvantages: wide bandgap (about 4.1 eV), the photoresponse wavelength range is narrow (\(\lambda < 300\) nm)\(^6\) and the separation efficiency of photoinduced electron–hole pairs is not high enough. It will be very significant to find a new method which can reduce the recombination of photoinduced electron–hole pairs as well as expand the photoresponse wavelength range. It has been reported previously that the photoabsorption and photocatalytic performance of some simple photocatalysts can be expanded or enhanced by introducing oxygen vacancies.\(^7\)–\(^11\) As is well known, bulk oxygen defects can only act as charge carrier traps where photoinduced electron–hole pairs recombine, resulting in the decrease of photoactivity;\(^12\) whereas, if oxygen defects could be controlled on the photocatalyst surface, they can not only serve as photoinduced charge traps but also as adsorption sites where the charge transfers to adsorbed species, which can prevent photoinduced electron–hole pairs recombination, thus leading to enhancement of photocatalytic activity.\(^13\) The relationship of surface oxygen vacancies with photoluminescence (PL) of ZnO and TiO\(_2\) photocatalysts have been previously reported by Jing and coauthors.\(^10\)–\(^14\),\(^15\) In our previous work, simple semiconductor ZnO with surface oxygen vacancies have been successfully fabricated via vacuum deoxidation and hydrogen reduction, and it possesses visible photoactivity as well as high UV photoactivity;\(^16\),\(^17\) and high UV photoactivity BiPO\(_4\) was also fabricated via vacuum deoxidation.\(^18\) However, could an economically facile method, controllable hydrogen reduction, introduce surface oxygen vacancies on the BiPO\(_4\) surface, and how is the photocatalytic performance and photocurrent of BiPO\(_4\) changed with a different number and extent oxygen vacancies?

In this work, BiPO\(_4\) nanorods with surface oxygen vacancies were fabricated via an economically facile approach of controllable hydrogen reduction. After surface oxygen vacancies were introduced on the BiPO\(_4\) sample, the photocatalytic activity and photocurrent could be improved significantly and the photoresponse wavelength range could be extended. However, the photocatalytic performance and photocurrent of BiPO\(_4\) with bulk oxygen vacancies was decreased slightly.

2. Experimental

2.1. Materials preparation

A BiPO\(_4\) nanorod (7.63 m\(^2\) g\(^{-1}\)) was synthesized through the reported method by our group previously.\(^3\) All chemicals used were analytical grade reagents without further purification. BiPO\(_{4-x}\) samples were prepared as follows: (1) the temperature-programmed reduction (TPR) measurement (ChemiSorb 2720, Micromeritics, America) using H\(_2\) gas was performed in a specially designed quartz tube with 0.051 g of BiPO\(_4\) nanorod.
The tube was put in a cylindrical electric furnace. The temperature of the furnace was controlled by a programmable regulator with the thermocouple. The thermocouple was put into the quartz tube and attached to the BiPO₄ sample. A thermal conductivity detector (TCD) was used to detect H₂ consumption during the process of H₂ reduction. BiPO₄ sample was pretreated by helium (He) gas from room temperature (about 25 °C) to 130 °C at a rising rate of 10 °C min⁻¹ for 1.5 h, then naturally cooled to room temperature again in He atmosphere. Afterwards, H₂/Ar mixture gas (mole ratio = 1 : 9) was introduced into the homemade quartz tube equipped with BiPO₄ sample, and the gas flow rate was 25 mL min⁻¹ accompanied with the temperature increasing to 700 °C for 5 min. The off-gas was degassed by using liquid nitrogen mixed with glycol. (2) Based on the TPR graph, the H₂ reduction process (temperature from 240 to 400 °C, time in the range of 1–5 h at 1 h intervals) was performed to prepare BiPO₄₋ₓ samples for a photocatalytic degradation reaction. The synthesized BiPO₄ sample was put into a self-made quartz tube which was then placed into an oven connected with a program warming device. BiPO₄ samples were pretreated by He gas, and the conditions were the same as above (1). Then the H₂/Ar mixture gas (mole ratio = 1 : 9) was introduced into the tube at a flow rate of 25 mL min⁻¹. The temperature in the process was increased from 25 °C to the designed temperature at a rising rate of 10 °C min⁻¹, the time was kept for 1–5 h at 1 h intervals. Finally, the samples were cooled down to room temperature naturally, maintaining the flow of H₂/Ar mixture gas.

2.2. Materials characterization

Total organic carbon analyzer (TOC-Vwp, Shimadzu) was employed for mineralization degree analysis of MB solutions. Atmospheric gas analysis system (HIDEN QIC20-MS) was utilized to survey the vent gas formed in the process of H₂ reduction of BiPO₄ at 270 °C for 3 h. UV-vis diffuse reflectance spectroscopy (UV-DRS) was performed on Hitachi U-3010, BaSO₄ was used as reference. A high-resolution transmission electron microscope (HR-TEM, JEM 2010F) was operated at an accelerating voltage of 200 kV. *In situ* electron paramagnetic resonance (EPR) measurement was carried out using an Endor spectrometer (JEOL ES-ED3X) at 77 K in liquid nitrogen. The g factor was obtained by taking the signal of manganese as standard. The EPR spectrometer was coupled to a computer for data acquisition and instrument control. Magnetic parameters of the radicals detected were obtained from direct measurements of the magnetic field and microwave frequency. Raman scattering was conducted in the near-backscattering geometry using an Ar⁺ laser (514.5 nm) with a power of 20 mW. The photocurrents and electrochemical impedance spectroscopy (EIS) were measured on an electrochemical system (CHI-660B, China). UV light was obtained from a 15 W mercury lamp (λ = 254 nm) and the average light intensity was 0.82 mW cm⁻². Photocatalyst (25 mg) was added into the prepared 50 mL 1 × 10⁻⁴ M of MB aqueous solution. Before light irradiation, the suspensions were first ultrasonically dispersed in the dark for 15 min, then magnetically stirred for 15 min to reach the adsorption–desorption equilibrium. At given time intervals, 3 mL aliquots were sampled and centrifuged to remove the photocatalyst particles. Synchronously, the filtered MB solutions at different conditions were analyzed by recording variations of the maximum absorption peak in the UV-vis spectra using a Hitachi U-3010 UV-vis spectrophotometer. In addition, 365 nm UV source was obtained from a 300 W high pressure mercury lamp with a 365 nm cut-off filter. The method was similar to the above mentioned 254 nm UV degradation.

Photocatalytic measurements were carried out in a conventional three-electrode system, single-compartment glass cell, fitted with a synthesized quartz window, using a potentiostat. A standard three-electrode cell with a working electrode (ITO/BiPO₄ and ITO/BiPO₄₋ₓ electrodes), a platinum wire as counter electrode and a standard calomel electrode (SCE) as reference electrode were used in the photoelectric studies. 0.1 M Na₂SO₄ was used as the electrolyte solution. The 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. ITO/BiPO₄ and ITO/BiPO₄₋ₓ electrodes were prepared by a dip-coating method: 5 mg of photocatalyst was suspended in 1 mL ethanol to make a slurry, the slurry was then dip-coated onto a 2 × 4 cm indium-tin oxide (ITO) glass electrode. The as-prepared electrodes were dried under ambient conditions, and then calcined at 80 °C for 5 h in air.

3. Results and discussions

3.1. Enhancement of the photocatalytic activity and photocurrent

The UV photocatalytic activities of BiPO₄ and BiPO₄₋ₓ samples after H₂ treatment at various temperatures for 3 h and various times at 140 °C on the degradation of MB (λ = 254 nm) are shown in Fig. 1A and B, respectively. 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 H₂ reduction, the photocatalytic activities of BiPO₄₋ₓ samples gradually increased with the increase of temperature and time; when the temperature reached 270 °C, time was 3 h, the oxygen-vacancy BiPO₄₋ₓ displayed the highest photocatalytic activity. The apparent rate constant k was 0.247 min⁻¹ and was about 1.6 times as high as that of pure BiPO₄ (k = 0.155 min⁻¹). However, on further increasing the temperature or prolonging the time, the degradation rate began to decrease.
Even after H$_2$ reduction at 400 °C for 3 h, the photoactivity of BiPO$_4$ was slightly lower than that of pure BiPO$_4$. The photocatalytic performance of BiPO$_4$ photocatalysts are greatly influenced by the concentration and kind of oxygen vacancies, which are controlled by tuning the temperature and time in the process of H$_2$ reduction. As is well known, a high concentration of surface oxygen vacancies contributes to the separation efficiency of photoinduced electron–hole pairs, improving the photocatalytic activity, while a bulk oxygen vacancy as charge capture center will inhibit photoactivity.

In addition, temporal UV-vis absorption spectral changes of MB solution during a UV photodegradation process over BiPO$_4$ and oxygen-vacancy BiPO$_4$ (treated at 270 °C for 3 h, the following is the same, except special directions) were investigated, as shown in Fig. 1C and D, respectively. The absorbance of MB solution gradually decreases with the degradation time by a BiPO$_4$ photocatalyst and after 25 min of UV-light irradiation, the peak of MB absorbance disappears. However, in an oxygen-vacancy BiPO$_4$ system, after only 15 min of UV-light irradiation the MB could be decomposed totally. This displays the great enhancement of the photocatalytic activity of oxygen-vacancy BiPO$_4$ photocatalyst, compared with that of pure BiPO$_4$. In addition, the degradation of MB has two mechanisms: one is the direct oxidation of MB, the other is the double electrons reduced into the structure of colorless Leuco-MB (LMB), which can be confirmed through spectral absorption at 256 nm.$^{19}$ As can be seen from Fig. 1C and D, with the increase of UV-light irradiation time, the intensity of the MB absorption peak at 245, 290 and 664 nm gradually decreased. The characteristic LMB absorption peak at 256 nm did not occur, indicating that the degradation mechanism of MB is direct oxidative degradation, but not reduced to LMB. With prolonging the irradiation time, the maximum absorption peak (664 nm) of MB decreased rapidly, at the same time the absorption peak at 290 nm also reduced quickly, which illustrates that not only the chromophore of MB was reduced but also the benzene ring was cracked down during the discoloration process of MB by BiPO$_4$ and oxygen-vacancy BiPO$_4$ photocatalysts.

The photocurrents of as-prepared photocatalysts after deposition on ITO electrodes are shown in Fig. 2A, under UV light ($\lambda = 254$ nm). The photocurrents of BiPO$_4$ electrode (reduction treated at 250, 270, and 330 °C for 3 h, respectively) electrodes are all higher at different level than that of pure BiPO$_4$. Especially, the oxygen-vacancy BiPO$_4$ electrode shows the highest photocurrent, which is about 2.6 times as high as that of pure BiPO$_4$. However, the BiPO$_4$ electrode (reduction treated at 400 °C for 3 h) electrode photocurrent was slightly lower than that of pure BiPO$_4$ electrode. The enhanced/decreased photocurrents demonstrate that the increase/decrease of the photoinduced carriers transport rate and the improvement/decrease of
photoinduced electron–hole pairs separation, lead to boosting/dropping the photocurrent, which is associated with the number and extent of oxygen vacancies. These results are well in accord with the change (improve or reduce) of the photocatalytic activity for the as-prepared samples.

In addition, to further understand the mineralization property of the as-prepared photocatalysts, the removal rates of TOC in UV photodegradation of MB over BiPO₄ and oxygen-vacancy BiPO₄ₓ photocatalysts were investigated (see Fig. 2B). The TOC removal rate of MB can reach 83% for oxygen-vacancy BiPO₄ₓ after 25 min of UV photocatalytic reaction, while it is only about 63% for pure BiPO₄. This indicates that the mineralization property of oxygen-vacancy BiPO₄ₓ is evidently enhanced.

3.2. Formation and structure of the surface oxygen vacancy

The H₂-TPR profile of BiPO₄ sample exhibits several peaks, the main peak is at about 535 °C, and from the inset three other reduction peaks are generated at 263, 303 and 370 °C, respectively (Fig. 4A). The intensities of these reduction peaks gradually increased with the rise of the temperature. As seen from Fig. S1, the bond length between the oxygen (O) atom and the phosphorus (P) atom or the bismuth (Bi) atom are not equal in BiPO₄. Based on the bond length (representing the bond energy) between each two atoms, the O atom may be removed from the surface to the bulk, and the order is from O₁, O₂, O₃ to O₄, even when PO₄³⁻ is totally detached from BiPO₄, generating oxygen vacancies with a different number and extent. These can be confirmed from the X-ray diffraction (XRD) patterns of pure BiPO₄ and BiPO₄ₓ samples (Fig. S2†), no phase transformation or any impurity is observed for BiPO₄ after H₂ reduction at 270 °C for 3 h, so most O atoms are removed from BiPO₄ surface, generating surface oxygen vacancies. However, after H₂ reduction at 400 °C for 3 h, the XRD peak of BiPO₄ₓ at 2θ = 27.1° (200) moves to a big angle slightly and the lattice spacing d decreases, and the peak intensity at 2θ = 29.4° (021) reduces and crystallinity is decreased, which result from the loss of lattice oxygen and formation of a bulk oxygen vacancy. After 535 °C, 3 h, H₂ reduction treated, BiPO₄ loses PO₄³⁻ totally, becoming metal Bi (Fig. S2A†). This is well along with the result of H₂-TPR of BiPO₄ sample. In addition, the mass spectrum (MS) of H₂O in vent gas during H₂ reduction (at 270 °C for 3 h) of
BiPO$_4$ was investigated, as shown in Fig. 4B. It can be found that H$_2$O is generated during H$_2$ reduction on a BiPO$_4$ sample at 270°C for 3 h, and the O atom in H$_2$O can only come from BiPO$_4$, which shows generation of oxygen vacancies.

Fig. 5A shows UV-vis diffuse reflectance spectra (UV-DRS) of BiPO$_4$ and oxygen-vacancy BiPO$_{4-x}$ powders. Compared with BiPO$_4$, the absorption sharp edge of oxygen-vacancy BiPO$_4$ has hardly any change (still about 300 nm). However, the absorbance of oxygen-vacancy BiPO$_{4-x}$ is enhanced in the range of 300–800 nm, which is induced by oxygen-vacancy states. From the inset of Fig. 5A, the color of the as-prepared photocatalysts changed from white BiPO$_4$ to light-gray oxygen-vacancy BiPO$_{4-x}$.
by H$_2$ reduction, which is caused by the formation of oxygen vacancies. Further study by HR-TEM of BiPO$_4$ and oxygen-vacancy BiPO$_4$$_{4-x}$ samples reveal that both are structurally uniform with a lattice spacing of about 0.328 nm corresponding to the (200) plane, as shown in Fig. 5B and C. Pure BiPO$_4$ displays perfect lattice features, however the edge of oxygen-vacancy BiPO$_4$$_{4-x}$ particles becomes dim and disordered (thickness about 2.33 nm), which indicates that the surface structure of oxygen-vacancy BiPO$_4$$_{4-x}$ is damaged and surface oxygen vacancies are formed.

Electron paramagnetic resonance (EPR) of the as-prepared samples was performed at 77 K in liquid N$_2$, which is a sensitive and direct method to monitor various behaviors to the presence of oxygen defects.$^{29}$ From Fig. 5D, it can be found that the intensity of the EPR signal at g factor $\sim$2.001 for oxygen-vacancy BiPO$_4$$_{4-x}$ is much higher than that of pure BiPO$_4$. The peak at g $\sim$ 2.001–2.004 has been reported previously that it can be attributed to natural surface oxygen vacancies.$^{30,31}$ Otherwise, the other peak at $g \sim$ 2.038 corresponds to chemisorbed oxygen O$_2^\cdot$. In any case, these indicate that oxygen vacancies were formed.

The structure of BiPO$_4$ and oxygen-vacancy BiPO$_4$$_{4-x}$ samples were also further characterized by Raman spectroscopy in the range of 300–1200 cm$^{-1}$. The Raman spectra of BiPO$_4$ have rarely been investigated. The experimental frequency values of the PO$_4$ units. From Fig. 5E, it can be found that the peak intensities of oxygen-vacancy BiPO$_4$$_{4-x}$ are lower than those of pure BiPO$_4$, and most peaks of oxygen-vacancy BiPO$_4$$_{4-x}$ widen. Especially, a new peak appears at 989 cm$^{-1}$ near the v$_1$ PO$_4$ symmetric stretching mode (966 cm$^{-1}$), and v$_2$ bending modes (460 cm$^{-1}$) split into two peaks 445 and 476 cm$^{-1}$. Meanwhile, the relative intensity of a vibration mode around 597 cm$^{-1}$ obviously increases for an oxygen-vacancy BiPO$_4$$_{4-x}$ sample. This peak can be assigned to the contribution of oxygen vacancies.$^{11,29}$ These indicate that the crystallinity and symmetry of oxygen-vacancy BiPO$_4$$_{4-x}$ are decreased because some oxygen atoms have been removed from BiPO$_4$, causing the formation of an oxygen vacancy.

### 3.3. Mechanism of the enhancement photocatalytic activity

The photocatalytic mechanism can be elucidated by trapping experiments of radicals and holes, and the electron spin resonance (ESR) spin-trap technique.$^{30-32}$ The main oxidative species in the photocatalytic process could be detected through the trapping experiments of hydroxyl radicals (‘OH) and holes using t-BuOH (‘OH scavenger),$^{33}$ EDTA-2Na (hole scavenger),$^{34}$ respectively. From Fig. S3A, it can be found that the photoactivity of BiPO$_4$ could be greatly prevented by the addition of EDTA-2Na, however the addition of t-BuOH only causes a small change in the photodegradation of MB. The results suggest that the photogenerated holes are the main oxidative species of the BiPO$_4$ system. From Fig. S3B, it can be seen that in an oxygen-vacancy BiPO$_4$$_{4-x}$ system, photocatalytic activity is also greatly inhibited by addition of EDTA-2Na, so the main oxidative species is the same (holes) as that of in a pure BiPO$_4$ system, and ‘OH plays an assisting role. Furthermore, the ESR spin-trap technique (with DMPO) was also employed to monitor the reactive oxygen species (‘OH and ‘O$_2^\cdot$) of the as-prepared photocatalysts system during UV irradiation, as shown in Fig. S3C and D. The signal intensity of ‘OH (with DMPO) is much higher than that of ‘O$_2^\cdot$ (with DMPO) in both BiPO$_4$ and oxygen-vacancy BiPO$_4$$_{4-x}$ system. Therefore, the photocatalytic degradation mechanism of BiPO$_4$ with and without oxygen vacancies on MB is not changed and the main oxidative species are still holes.

It is well known that photocatalytic activity is mainly governed by the crystal phase structure, adsorption ability, and separation efficiency of photoinduced electron–hole pairs. As seen from the XRD spectra (Fig. S2†), the crystal phase structures are not changed for BiPO$_4$ with and without surface oxygen vacancies. The adsorptivity of oxygen-vacancy BiPO$_4$$_{4-x}$ is slightly improved from about 3% for pure BiPO$_4$ to about 11% after equilibration in the dark for 10 min, as shown in Fig. S4.† However, there are no significant changes in the BET surface area (BiPO$_4$: 7.63 m$^2$ g$^{-1}$; oxygen-vacancy BiPO$_4$$_{4-x}$: 7.95 m$^2$ g$^{-1}$), indicating the MB adsorption should not just originate from simply physical adsorption. The enhancement of adsorptivity on cationic dyes MB can be attributed to the changes of the zeta potential (28.0 mV, –55.2 mV for pure BiPO$_4$, oxygen-vacancy BiPO$_4$$_{4-x}$, respectively) due to loss of surface oxygen atoms. The enhanced adsorptivity is a good supplement for the high photocatalytic activity of oxygen-vacancy BiPO$_4$$_{4-x}$. The separation efficiency of photoinduced electron–hole pairs plays an important role in photocatalysis, and can be investigated using typical electrochemical impedance spectra (EIS). The EIS Nyquist plots of pure BiPO$_4$ and oxygen-vacancy BiPO$_4$$_{4-x}$ after deposition on ITO electrodes show that the arc radius of oxygen-vacancy BiPO$_4$$_{4-x}$ electrode is smaller than that of BiPO$_4$ electrode, with and without UV-light irradiation ($\lambda$ = 254 nm), as shown in Fig. 6. The smaller the arc radius of an EIS Nyquist plot, the smaller the electric resistance of the electrode, the higher the efficiency of charge separation and the higher the photocatalytic activity. Therefore, the improvement of the photocatalytic performance is mainly resulted from the enhancement of the charge separation efficiency due to broadening of the valence band (VB) width induced by surface oxygen-vacancy states, which will be discussed in the following.

Based on the results above, a proposed schematic diagram for the density of states (DOS) of pure BiPO$_4$ and oxygen-vacancy BiPO$_4$$_{4-x}$, the mechanism of charge separation and photocatalytic reaction of oxygen-vacancy BiPO$_4$$_{4-x}$ photocatalyst, under UV light, are shown in Fig. 7A and B, respectively. The forbidden gap of monoclinic BiPO$_4$ is wide (about 4.1 eV), which can only be excited by UV light wavelength less than 300 nm.
However, after surface oxygen vacancies were introduced on BiPO₄, many shallow surface oxygen-vacancy states (SOv. states) appear above and partly overlapping with the VB of BiPO₄ (Fig. 7A). This can result in rising of the valence band maximum (VBM) and narrowing the bandgap width, expanding the photoreponse wavelength range (more than 365 nm), as reported previously by Zhao and coauthors about the oxygen-vacancy states in other PO₄ salts such as LiTi₂(PO₄)₃. As shown in Fig. 7B, the rising of VBM also can expand the VB width, which contributes to increasing the transport rate of photoinduced carriers, leading to enhancement of the separation efficiency of photoinduced electron–hole pairs, thus the photocatalytic activity can be improved.

Furthermore, the concentration and extent of oxygen vacancies, controlled by tuning the temperature and time of H₂ reduction, influence the DOS and location of oxygen-vacancy states in the forbidden band of BiPO₄ sample, the photocatalytic activity and photocurrent will be affected correspondingly. When the oxygen-vacancy concentration is low, the DOS of surface oxygen vacancy located above and partly overlapping with the VB is small, the photocatalytic activity and photocurrent only increase slightly and will improve gradually with the increase of surface oxygen-vacancy concentration; while when the concentration of oxygen-vacancy is redundant, a bulk oxygen vacancy can be easily generated in the deep of the forbidden band, which is the recombination center of photoinduced electron–hole pairs, thus the photocatalytic activity and photocurrent will decrease. So only controlling the high concentration of oxygen vacancies on the surface layers and almost no bulk oxygen vacancies generated can obtain the highest photocatalytic activity and photocurrent of BiPO₄ₓ photocatalysts. Therefore the concentration and extent of oxygen vacancies play an important role in improving the photocatalytic activity and increasing the photocurrent.

3.4. Stability and selectivity

The stabilities of oxygen-vacancy BiPO₄ₓ on the photodegradation reaction and storage were investigated, as shown in Fig. 8A and B, respectively. Fig. 8A shows UV photocalytic degradation on MB four recycles by oxygen-vacancy BiPO₄ₓ. After four recycles, oxygen-vacancy BiPO₄ₓ shows hardly any obvious loss of photocatalytic activity, which confirms that it is a stable photocatalyst during the photocatalytic oxidation of pollutant molecules. In addition, the UV photoactivities of pure BiPO₄, fresh oxygen-vacancy BiPO₄ₓ and oxygen-vacancy BiPO₄ₓ after storage for 10 months on the degradation of MB were also surveyed (Fig. 8B). It can be seen that the UV photocatalytic activity of oxygen-vacancy BiPO₄ₓ after storage for 10 months is only decreased slightly (k = 0.209 min⁻¹), as compared with that of fresh oxygen-vacancy BiPO₄ₓ (k = 0.218 min⁻¹). Little reduced photoactivity may be caused by some small organic material or other substances in the air absorbed on the surface of oxygen-vacancy BiPO₄ₓ for a long time. In any case, it is still much higher than that of pure BiPO₄ photocatalyst (k = 0.154 min⁻¹). So the oxygen-vacancy BiPO₄ₓ has good stability not only on the photocatalytic degradation reaction but also on prolonged storage.

Fig. 7  Schematic diagram illustrating (A) the density of states (DOS) of pure BiPO₄ and oxygen-vacancy BiPO₄ₓ; (B) the mechanism of charge separation and photocatalytic reaction of oxygen-vacancy BiPO₄ₓ photocatalyst, under UV light.
It is well known that photoinduced holes (main active species) can directly react with various organic pollutants owing to their strong oxidation ability, and they are almost nonselective on reaction with pollutants. Actually, the effective photodegradation on organic dyes and transparent organic pollutant phenol by BiPO$_4$ and oxygen-vacancy BiPO$_{4-x}$ samples confirm this conclusion (Fig. 8C). The photodegradation activities of oxygen-vacancy BiPO$_{4-x}$ on the anionic dye (Methyl Orange (MO)), cationic dye (rhodamine B (RhB)) and benzene ring compounds (phenol) are all obviously higher than that of pure BiPO$_4$, which suggest that the high activity of oxygen-vacancy BiPO$_{4-x}$ is not due to the special combination of the catalysts to some specific substrates but to the strong oxidation reactions of photoinduced holes. Therefore, the high photocatalytic activity of oxygen-vacancy BiPO$_{4-x}$ is general and essential for environmental application.

4. Conclusions

The greyish BiPO$_{4-x}$ photocatalysts with a broadening valence band and a narrowing bandgap were fabricated by a facile controllable hydrogen reduction method. From HR-TEM, it can be visually observed that oxygen vacancies were introduced on the BiPO$_4$ particle surface layers. The high concentration of surface oxygen vacancies can create an impurity level (surface oxygen-vacancy states) above and partly overlapping with the valence band, thus inducing the broadening of the valence band and the narrowing of the bandgap. The enhancement of the photocurrent and photocatalytic performance and expanding of the photosresponse wavelength range can confirm these results. Furthermore, oxygen-vacancy BiPO$_{4-x}$ has a good stability and almost no selectivity on the decomposition of organic pollutants (dyes or transparent phenol).

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