Photocatalytic Performance of BiPO₄ Nanorods adjusted via Defects

Yanyan Zhu^{a, b}, Qiang Ling^b, Yanfang Liu^c, Hua Wang^b and Yongfa Zhu^{a, *}

^a Department of Chemistry, Beijing Key Laboratory for Analytical Methods and Instrumentation, Tsinghua University, Beijing 100084, P.R. China;

^b Institute of Aeronautical Meteorology and Chemical Defence, Beijing 100085, P.R. China-;

^c Sinopec Research Institute of Petroleum Processing , Beijing 100083, P.R. China.

Abstract: The effect of defect on the photocatalytic and photoelectric performance of BiPO₄ has been revealed. The bulk defects of BiPO₄ such as bismuth vacancies(V_{Bi}), oxygen vacancies(V_O) and so on were formed during the ball-milling process. These bulk defects of BiPO₄ inhibited the separation of photo-generated charges greatly and thus reduced photocatalytic activity. Most of the bulk defects were repaired and the photocatalytic activity of BiPO₄ was also recovered mostly via calcination and reflux. Reflux could repair the bulk defects of BiPO₄ much better than calcination. The mechanism of the photocatalytic degradation of pollutants over BiPO₄ was not changed by defects, and the main oxidation active species of BiPO₄ is photo-generated hole.

Keywords: Defect; BiPO₄; Ball-milling; Photocatalytic degradation

1. Introduction

As an oxy-acid salt photocatalyst, BiPO_4 possesses many advantages such as high photocatalytic activity, stable chemical structure, exceptional optical and electronic properties, fast rate of settlement separation and strong mineralization ability[1, 2]. There are three kinds of crystal structure of BiPO_4 (HBIP, mMBIP and nMBIP). Among them, the photocatalytic activity of HBIP is the worst, with its band gap being 4.6 eV. mMBIP and nMBIP possess higher photocatalytic activity, and their band gaps are 4.2 eV and 3.8 eV respectively. Moreover, the photocatalytic activity of nMBIP BiPO_4 is much better than that of Degussa P25 TiO_2 [3, 4]. To expand the absorption range and improve the photocatalytic activity of BiPO_4 , many different kinds of methods such as doping[5], compositing[6-8], surface defects[2, 9, 10] and high-energy facet adjusting[11] have been employed, and they are proved to be efficient in enhancing its ultraviolet photocatalytic performance or expanding the range of absorption spectrum to visible light region.

The photocatalytic performances of semiconductor materials are mainly decided by particle size, crystal structure, band gap, lattice plane, surface area, morphology, defect and so on. Among them, defect has significant influence on the formation, separation and migration of photo-generated electrons and holes, as well as light-absorption range. There are two kinds of defects, surface defects and bulk defects[12-14]. Surface defects are shallow defects, which could quickly capture and then release photo-generated charges, and the temporary capture might accelerate the separation of photo-generated electrons and holes. In addition, surface defects are the adsorption site of O_2 , which reacts with surface photo-generated electrons to form $\cdot\text{O}_2^-$, and $\cdot\text{O}_2^-$ will degrade organic pollutants. Therefore, surface defects not only accelerate the separation of photo-generated charges but also increase the number of active sites, and further enhancing photocatalytic activity. TiO_2 [15-20], ZnO [21, 22], BiPO_4 [2, 9, 10], $\text{Bi}_6\text{S}_2\text{O}_{15}$ [23], CeO_2 [24], $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ [25] and Bi_2MO_6 [26] with surface defect synthesized via vacuum de-oxygen, high temperature calcination and hydrogen reduction possess not only superior UV photocatalytic performance but also wide light absorption range. As deep defects, bulk defects capture photo-generated charges but do not release them easily, which become the recombination center of photo-generated charges and further decrease the photocatalytic performance[13, 14, 27]. Defects widely exist in the semiconductor photocatalyst materials as an inherent structure.

Therefore, it is of great value to study the effect of defect on the photocatalytic performance of semiconductor materials.

In this work, the defects in BiPO₄ were controllably formed via adjusting ball-milling time and rate, and most of them could be repaired via calcination and reflux in water. The influence of defects on the photocatalytic and photoelectric performances of BiPO₄ was revealed. The mechanism for the effect of defects on the photocatalytic activity of BiPO₄ was also investigated.

2. Experimental Section

2.1 Formation and Repair of Defects in BiPO₄

Precursor BiPO₄ nanorod was obtained by reflux in 100 °C water for 48 h[4]. 1.0 g BiPO₄ and 2.0 ml ethanol were added into agate jar and mixed evenly, and different sizes of agate balls were added subsequently. Afterwards the mixtures were ball-milled at the rate of 300 rpm for different time and at different rate for 2.0 h on the XQM-4.0 planetary ball mill, and then the samples were dried in air to remove ethanol completely to obtain defect BiPO₄. At last, the defect BiPO₄ formed at 300 rpm for 2.0 h were calcined in the range of 200~600 °C for 4.0 h or refluxed at 100 °C in water for 12.0~48.0 h to repair its defects.

2.2 Evaluation of Photocatalytic Activity and Photoelectrochemical Performance

The photocatalytic activity of BiPO₄ were evaluated on the degradation of methylene blue (MB) in aqueous solution under 20 W 254 nm UV lamp and the average light intensity was 1.0 mW·cm⁻². 25 mg photocatalyst was added into 50 mL 3.0×10⁻⁵ mol·L⁻¹ MB aqueous solution. The suspension was ultrasonically dispersed for 0.5 h and magnetically stirred for 1.0 h in dark to obtain the establishment of adsorption-desorption equilibrium before UV irradiation. At 20 min intervals, 3.5 mL suspension was taken out and separated through centrifugation (12000 rpm, 10 min). The concentration of MB solution was analyzed at the maximal absorption band (663 nm) using a Hitachi U-3010 UV-Vis spectrophotometer.

The photocurrent and electrochemical impedance spectroscopy (EIS) of BiPO₄ were performed on CHI-660B electrochemical system (Shanghai, China) using a standard three-electrode cell with a working electrode (ITO/BiPO₄), using a standard calomel electrode (SCE) as reference electrode and a platinum wire as counter electrode. ITO/BiPO₄ was prepared by a dip-coating method. Photoelectrochemical

properties were measured with an 11 W UV germicidal lamp, and the intensity of light at the film electrode was $1.5 \text{ mW}\cdot\text{cm}^{-2}$ at the wavelength of 254 nm and $0.1 \text{ mol}\cdot\text{L}^{-1}$ Na_2SO_4 electrolyte was used. The photoelectric responses of the photocatalysts with light-on and light-off were measured at 0.0 V. EIS was carried out at the open circuit potential, and a sinusoidal ac perturbation of 5 mV was applied to the electrode over the frequency range of $10^{-2}\sim 10^5$ Hz.

2.3 Materials Characterization

The crystal-phase structure and crystallinity of BiPO_4 samples were characterized by X-ray diffraction (XRD) on a Bruker D8 Advance diffractometer using ($\text{Cu K}\alpha=1.5418 \text{ \AA}$, tube voltage=40 kV, tube current=20 mA) at a scan rate of $2^\circ\cdot\text{min}^{-1}$ in the 2θ range from 10° to 60° . The lattice planes and fringes of BiPO_4 were obtained from the high-resolution transmission electron microscope (HRTEM, JEM 2010F), and it was operated at an accelerating voltage of 200 kV. The photoluminescence (PL) emission spectra of BiPO_4 samples were measured on HR800 spectrometer with 325 nm exciting light of He-Cd laser under the condition of 77 K. The Raman spectrum of samples were measured at room temperature using HORIBAR 800 microscopic confocal Raman spectrometer in the range of 200 to 1200 cm^{-1} for three times, and the excitation light was 514.5 nm from an Ar^+ laser with 30 mW output power.

The UV–Vis diffuse reflectance absorption spectra of BiPO_4 samples were performed on Hitachi U-3010 spectroscopy equipped with an integrated sphere attachment in the range of 200 to 800 nm, and BaSO_4 was used as reference. The particle sizes of BiPO_4 samples were measured on the HITACHI HT7700 transmission electron microscopy (TEM) with an accelerating voltage 100 kV. The electron paramagnetic resonance (EPR) of photocatalyst was tested on an Endor spectrometer (JEOL ES-ED3X) at 77 K, and the splitting factor g was obtained by taking the signal of manganese (Mn) as standard.

3. Results and Discussion

3.1 Controllable Formation and Repair of Defects in BiPO_4

The presence and disappearance of defects, as well as the crystal lattice parameters of BiPO_4 were examined by HRTEM. As shown in Fig.1a, the precursor BiPO_4 was monazite monoclinic structure, with the distances between adjacent lattice fringes measured as 0.307 nm. This corresponds to inter planar distances of BiPO_4

(120) and is in excellent agreement with the literature value of the (120) lattice distance (JCPDS 80-0209). In addition, the lattice fringes of precursor BiPO_4 were very clear. The HRTEM image of ball-milled BiPO_4 revealed that its lattice spacing was 0.467 nm, corresponding to the (011) lattice plane (Fig. 1b). In addition, lattice mismatch, vacancy defects and lots of plane defects were shown in the (011) lattice plane. At the same time, the partial lattice fringes were very obscure. These phenomena were mainly ascribed to the formation of many defects generated by ball-milling[27]. Part of the structure disorder and vacancy defects still existed in BiPO_4 after the repair of calcination (Fig. 1c), which indicated that the defects of ball-milled BiPO_4 were not completely repaired via calcination. However, reflux could better repair the defects of BiPO_4 than calcination (Fig. 1c and 1d), and the lattice fringes after reflux were very clear.

Fig. 1. The HRTEM images of BiPO_4 (a), BiPO_4 ball-milled at 300 rpm for 2.0 h (b), defect BiPO_4 repaired by calcination at 400 °C for 4.0 h in air (c) and defect BiPO_4 repaired by reflux at 100 °C for 24 .0 h in water solution (d)

Fig. 2. The UV-Vis DRS of precursor BiPO_4 , BiPO_4 ball-milled at 300 rpm for 2.0 h, defect BiPO_4 repaired by calcination at 400 °C for 4.0 h and reflux at 100 °C for 24.0 h

The UV-Vis diffuse reflectance spectra (DRS) of the precursor BiPO_4 , BiPO_4 ball-milled at 300 rpm for 2.0 h, defect BiPO_4 repaired by calcination at 400 °C for 4.0 h in air and BiPO_4 repaired by reflux in water solution at 100 °C for 4.0 h were shown in Fig. 2. The absorption band edge of precursor BiPO_4 was at about 300 nm. Ball-milling induced a 100 nm red shift in the absorption band edge of BiPO_4 and the absorption intensity in the range of 300~500 nm was also obviously enhanced, which was ascribed to the defect induced by ball-milling[23, 27, 28]. The defect of BiPO_4 generated via ball-milling would induce the ascending of valence band maximum and the descending of conduction band minimum to some degree, so the band gap decreased corresponding with BiPO_4 with OH defect[29]. The absorption band edges of defect BiPO_4 repaired via calcination and reflux shifted to shorter wavelength, but they couldn't return to the position of absorption band edge of precursor BiPO_4 . The change rule of UV-Vis DRS further illustrated that the majority of defects in BiPO_4 could be repaired via calcination and reflux.

Fig.3. PL spectra of precursor BiPO_4 , BiPO_4 ball-milled at 300 rpm for 2.0 h, defect BiPO_4 repaired by calcination at 400 °C for 4.0 h and reflux at 100 °C for 4.0 h in water solution (excitation wavelength: 325 nm)

PL spectrum is an important method to study the defect of photocatalysts[10, 27]. BiPO_4 , as a wide band gap photocatalyst, its valence band is made up of O 2p, Bi 6s, P 3s and P 3p and its conduction band is made up of Bi 6p[30]. Under the excitation of 325 nm wavelength, the characteristic green luminescence at 502 nm and blue luminescence at 441 nm were observed in precursor BiPO_4 , and the stronger green luminescence was ascribed to the transition of Bi^{3+} from $^3\text{P}_j$ to $^1\text{S}_0$ (Fig. 3)[31, 32]. The PL intensity of ball-milled BiPO_4 is much higher than that of precursor BiPO_4 in the range of 400~600 nm, which is caused by many defects generated via ball-milling[9, 10, 27]. According to literature[27], these defects could be assigned to V_o , O_i , $\text{O}_\text{o}^\text{x}$ and Bi_Bi . The more the defects are, the stronger the PL signal is. In general, the strong PL signal means high recombination rate of photo-generated charges and indicate slow photocatalytic performance. Therefore, the ball-milled BiPO_4 possessed the lowest photocatalytic activity among the four samples. On the other hand, the PL signals of defect repaired BiPO_4 by calcination and reflux became significantly weaker, which indicated that the number of defects in BiPO_4 decreased, and thus recovering the quick separation of the photo-generated charges.

Fig. 4. The EPR spectra of precursor BiPO_4 , BiPO_4 ball-milled at 300 rpm for 2.0 h, defect BiPO_4 repaired by calcination at 400 °C for 4.0 h and reflux at 100 °C for 4.0 h

In order to further testify the defect structure and characteristics of BiPO_4 , the EPR was performed at 77 K in liquid N_2 surroundings (Fig. 4). Because the electrons of Bi^{3+} , P^{5+} and O^{2-} in precursor BiPO_4 were all paired electrons, no EPR signal was observed. In the crystal structure of BiPO_4 , one Bi and eight O atoms formed eight ligand structure; one P and four O atoms formed four ligand structure; Bi and P atoms are connected by O and they are in 1:1 proportion[33]. However, a strong EPR signal at about $g=2.001$ was observed in ball-milled BiPO_4 , defect repaired BiPO_4 by calcination and defect repaired BiPO_4 by reflux, which was attributed to neutral oxygen vacancies (V_o)[2, 9, 10]. The EPR intensity of ball-milled BiPO_4 at $g \sim 2.001$ was the highest and that of BiPO_4 repaired by calcination and reflux became lower.

The morphology of precursor BiPO_4 was nanorod (Fig. 5a)[4], but it would be severely destroyed by ball-milling (Fig. 5b and 5c). Under the compressive and shear stress of ball-milling, BiPO_4 nanorods underwent deformation, which meant that these nanorods became shorter and some of them transformed to a lot of powder particles. The nanorods of ball-milled BiPO_4 treated by calcination and reflux were similar to that of ball-milled BiPO_4 , but their length was shorter than that of precursor BiPO_4 (Fig. 5d~5c). At the same time, the powder particles of repaired BiPO_4 similar to the amorphous structure disappeared after calcination and reflux, and a lot of spherical

particles were formed around BiPO₄nanorods.

Fig. 5. TEM images of BiPO₄ (a), BiPO₄ ball-milled at 300 rpm for 2.0 h (b and c), defect BiPO₄ repaired by calcination at 400 °C for 4.0 h in air (d) and BiPO₄ repaired by reflux at 100 °C for 4.0 h in water (e and f)

Based on the XRD and Raman results, defect of BiPO₄ didn't affect its crystal structure. It can be seen in Fig. S1 and S2 that the crystal structures of ball-milled BiPO₄ and repaired BiPO₄ after calcination and reflux were the same as that of precursor BiPO₄. They were all mainly made up of monazite monoclinic phase and minor of them were hexagonal phase. However, the Raman intensity of ball-milled BiPO₄ after 600 cm⁻¹ was enhanced on the whole, which could be attributed to the strong fluorescence excited by 325 nm laser irradiation.

3.2 Photocatalytic Activity and Photocurrents of Defect BiPO₄

The photocatalytic activity of the precursor BiPO₄ and the BiPO₄ ball-milled at 300 rpm for different time and at different ball-milling rotating rate for 2.0 h were shown in Fig. 6. The photocatalytic activities of defect BiPO₄ were all lower than that of precursor BiPO₄, which was caused by the formation of many bulk defects generated from high energy of ball-milling. The results are accorded with the change of photocatalytic performance of TiO₂ and ZnO before and after ball-milling[27, 28]. When the rate of ball-milling was 300 rpm, with the ball-milling time prolonging, more bulk defects were generated in BiPO₄; at the same time, the photocatalytic activity also decreased gradually (Fig. 6a). When the ball-milling time was 1.0 h and 2.0 h at 300 rpm ball-milling rate, the photocatalytic activity of BiPO₄ decreased obviously. The

apparent rate constant of BiPO₄ ball-milled for 2.0 h on the photocatalytic degradation of MB was 0.0107 min⁻¹, which was about half of that of precursor BiPO₄ ($k=0.0229\text{min}^{-1}$). When the ball-milling time were prolonged to 2.0 ~ 5.0 h, the photocatalytic activity of BiPO₄ decreased very slowly, which illustrated that the bulk defects generated more and more weakly with the ball-milling time further prolonging. The apparent rate constant of BiPO₄ ball-milled for 5.0 h was 0.0069 min⁻¹, which was about 1/3 of precursor BiPO₄. When the ball-milling time was 2.0 h, with the ball-milling rate increasing, the photocatalytic activity of BiPO₄ gradually decreased (Fig. 6b). The increase of ball-milling rate would transmit more mechanical energy to BiPO₄, so more bulk defects would be generated and then the photocatalytic activity of BiPO₄ decreased.

Fig. 6. The apparent rate constants of photocatalytic oxidation degradation of MB over BiPO₄ ball-milled at 300 rpm for different time (a) and at different ball-milling rotating rate for 2.0 h (b)

During the process of photocatalytic reaction, the separation and transfer of photo-generated electrons and holes for photocatalysis are the key steps that determine photocatalytic efficiency. The photocurrent of photocatalyst under light irradiation could illustrate the separation and transfer of photo-generated charges[34]. The photocurrents of precursor BiPO₄ and ball-milled BiPO₄ on different conditions were shown in Fig. 7. The photocurrents were stable and reversible at light-on and light-off for all BiPO₄ samples under 254 nm UV light irradiation. The photocurrent of precursor BiPO₄ was the highest (about 55 μA), and that of the ball-milled ones were all weaker than it. When the ball-milling rate was 300 rpm, with increasing ball-milling

time, the photocurrents of BiPO_4 would decrease gradually, which indicated that the bulk defect would become the recombination center of photo-generated charges and inhibit its quick separation and transfer. Meanwhile, with the increase of ball-milling rate, more bulk defects would form, leading to the gradual decrease of the photocurrents of BiPO_4 .

Fig. 7. The photocurrents of precursor BiPO_4 and BiPO_4 ball-milled on different conditions under 254 nm UV light irradiation (a, precursor BiPO_4 ; b, BiPO_4 ball-milled at 100 rpm for 2.0 h; c, BiPO_4 ball-milled at 300 rpm for 1.0 h; d, BiPO_4 ball-milled at 300 rpm for 2.0 h; e, BiPO_4 ball-milled at 300 rpm for 5.0 h; f, BiPO_4 ball-milled at 500 rpm for 2.0 h)

3.3 Photocatalytic Activity and Photocurrents of Defect Repaired BiPO_4

Calcination and reflux were used to repair the defect of BiPO_4 generated by ball-milling at 300 rpm for 2.0 h. The photocatalytic activities of the defect and defect repaired BiPO_4 were shown in Fig. 8. As is known, calcination could make material recrystallize and eliminate part of defect structure. The photocatalytic activity of TiO_2 , Ga_2O_3 and CdS calcined at appropriate temperatures would be enhanced obviously [35-37]. Moreover, reflux could also change the morphology and structure of materials and eliminate defects. For instance, the photocatalytic activity of C_3N_4 refluxed in methanol and sulphuric acid solution were greatly enhanced[38, 39]. The photocatalytic performance of defect BiPO_4 repaired via calcination in the range of 200 ~600°C were all higher than that of defect BiPO_4 , but lower than that of precursor

BiPO₄(Fig. 8a). In the range of 200 ~ 400°C with increasing the calcination temperature, the photocatalytic activity of defect BiPO₄ repaired were enhanced gradually. Further increasing the calcination temperature above 400 °C the photocatalytic activity of the defect repaired BiPO₄ decreased gradually. Therefore, proper calcination temperature could improve the photocatalytic performance of BiPO₄, but too high calcination temperature would change the crystal structure of BiPO₄ or induce agglomeration and further decrease the photocatalytic performance[35, 36]. Hence, the best calcination temperature for defect BiPO₄ was 400°C and the apparent rate constant of defect BiPO₄ repaired at 400°C on the photocatalytic degradation of MB was 0.0162 min⁻¹, which was about 1.5 and 0.71 times as high as that of defect BiPO₄ ball-milled at 300 rpm for 2.0 h and precursor BiPO₄. The photocatalytic activity of defect BiPO₄ repaired via reflux in water was enhanced obviously, and the apparent rate constant for the photocatalytic degradation of MB over BiPO₄ refluxed for 24.0 h was 0.0209 min⁻¹, which was about 1.95 times than that of defect BiPO₄ but lower than that of precursor BiPO₄. Both calcination and reflux could repair the defect in BiPO₄ and thus improve the photocatalytic performance, but reflux could have better repair effect for defect BiPO₄ than calcination.

Fig. 8. The apparent rate constants of photocatalytic oxidation degradation of MB over defect BiPO₄ repaired via calcination at different temperatures for 4.0 h (a) and reflux in water for different time (b)

The photocurrents of defect BiPO₄ ball-milled at 300 rpm for 2.0 h, defect BiPO₄ repaired via calcination and reflux under 254 nm UV light irradiation were shown in

Fig. S.3. The photocurrents of defect BiPO₄ repaired by calcination and reflux were all higher than that of defect BiPO₄. The above results further testified that calcination and reflux could repair and decrease vast bulk defect of ball-milled BiPO₄, which promoted the quick separation of photo-generated charges and enhanced the photocatalytic performance of BiPO₄.

3.4 Mechanism of defect on the photocatalytic performance of BiPO₄

Fig. 9. The plots of photo-generated charges trapping on the photocatalytic degradation of MB over precursor BiPO₄ (a), defect BiPO₄ ball-milled at 300 rpm for 2 h (b), defect BiPO₄ repaired via calcination at 400 °C for 4.0 h (c), defect BiPO₄ repaired via reflux at 100 °C for 24.0 h (d)

The photocatalytic mechanism of semiconductor photocatalyst could be verified by trapping experiment of radicals and holes, usually using ethylenediamine tetraacetic acid disodium salt (EDTA-2Na) and tertiary butyl alcohol (t-BuOH) as hole and hydroxyl radical scavengers[27, 30]. The oxidation species in the photocatalytic degradation of MB by precursor BiPO₄, defect BiPO₄ ball-milled at 300 rpm for 2.0 h, defect BiPO₄ repaired via calcination at 400 °C for 4.0 h and defect BiPO₄ repaired via reflux at 100 °C for 24.0 h were shown in Fig. 9. In the BiPO₄ system, the photocatalytic performance decreased greatly by addition of EDTA-2Na but changed very slightly by addition of t-BuOH (Fig. 9a), suggesting that the photo-generated holes are the main

oxidative species of BiPO_4 and the hydroxyl radicals only played an assistant role[9, 10]. Moreover, the main oxidative species of defect BiPO_4 ball-milled at 300 rpm for 2.0 h (Fig. 9b), defect repaired BiPO_4 via calcination at 400 °C for 4.0 h (Fig. 9c) and via reflux at 100 °C for 24.0 h (Fig. 9d) were all photo-generated holes, which proved that defect couldn't change the active oxidative species of BiPO_4 [22].

Fig. 10. The EIS Nyquist plots of BiPO_4 thin film electrodes in dark (a) and under UV light irradiation (b)

As is well known, the separation efficiency of photo-generated charges is a key factor to influence the photocatalytic activity. The efficiency of photo-generated electron-hole pairs can be evaluated by the typical electrochemical impedance spectra (EIS). The arc radius on the EIS spectra reflects the solid state interface layered resistance and the surface charges transfer resistance. The smallest arc radius on the EIS Nyquist plot indicates an efficient separation of the photo-generated electron-hole, and vice versa[39]. The EIS plots of precursor BiPO_4 , defect BiPO_4 ball-milled at 300 rpm for 2.0 h, the defect BiPO_4 repaired via calcination at 400 °C for 4.0 h and via reflux at 100 °C for 24.0 h were shown in Fig. 10. The Nyquist arc radii of precursor BiPO_4 in dark and under UV light irradiation were the smallest among the four BiPO_4 samples, suggesting that the reaction rate on this electrode surface was the maximum and the electrode resistance was the smallest, so the separation of photo-generated electrons and holes in precursor BiPO_4 was the fastest. However, the Nyquist arc radii of the defect BiPO_4 ball-milled was the biggest, so the reaction rate on this electrode surface was the smallest and the electrode resistance was the maximum; at the same time, the separation efficiency of photo-generated electron-hole pairs in this sample

was very low. The Nyquist arc radii of defect BiPO₄ repaired via calcination and reflux both in dark and under UV light irradiation were between that of precursor BiPO₄ and defect BiPO₄.

Scheme 1. The mechanism of charge separation and photocatalytic process over BiPO₄ under UV light irradiation

From the above results, a probable mechanism of charge separation and photocatalytic process over BiPO₄ under UV light irradiation was inferred in scheme 1. Under the UV light irradiation, the electrons of BiPO₄ were transited into conduction band and holes remained in the valence band, and then they reacted with O₂ and OH⁻ respectively to form ·O₂ and ·OH to degrade organic pollutants. The bulk defect of BiPO₄ formed by ball-milling became the recombination center of photo-generated charges and restrained its efficient separation. The defect BiPO₄ repaired via calcination and reflux revised many bulk defects and enhanced the separation efficiency of photo-generated electron-hole pairs, which further improved the photocatalytic activity of BiPO₄.

4. Conclusions

The defects in BiPO₄ were controllably formed by ball-milling, and most of them were repaired via calcination and reflux. The influence of defects on the photocatalytic and photoelectric performance of BiPO₄ have been elucidated. This work shed deeper light on the effect rule of bulk defect on photocatalytic performance of BiPO₄, and provided a referenced method for repairing the defect of other semiconductor photocatalysts and further improving their photocatalytic activity.

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