Photocatalyst $Bi(OH)SO_4 \cdot H_2O$ with High Photocatalytic Performance

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Abstract

In this work, $Bi(OH)SO_4•H_2O$, a novel photocatalyst was prepared by a facile method. The sample was characterized by XRD, XPS, SEM, Mott-Schottky curve and ESR. The band gap of $Bi(OH)SO_4•H_2O$ is about 4.64 eV, and its CB and VB are estimated at –0.5 and 4.14 eV, respectively. Degradation of RhB and PhOH under UV light irradiation illustrates that the sample has good UV activity. The results of ESR spectra and tapping experiments indicate that the main active species in the photocatalytic reaction process are hydroxyl radicals, superoxide radicals and holes. A possible mechanism of catalytic degradation of organic pollutants was proposed. This semiconductor has a positive valence band and high oxidation capacity theoretically and it may have broad application in synthesizing highly efficient photocatalysts through doping other elements or creating heterojunctions.

Keywords: $Bi(OH)SO_4•H_2O$; photocatalyst; positive valence band.

1. Introduction

In recent years, photocatalytic technology has attracted the interest of researchers due to the advantages of low cost, high efficiency and non-pollution, which is thought to have broad application prospect to solve energy and environmental problems in the future.[1-4] Under light irradiation, semiconductors can be excited and produce electrons and holes, which can form strong oxidizing species. Thus photocatalysts are capable of effectively reducing H_2O to H_2 and completely mineralizing organic pollutants in water into CO_2 and H_2O.[5-10] However, the low utilization rate of solar energy and rapid recombination of photogenerated charge carriers limited the applications of photocatalytic technology for the industrial application.[11,12] Therefore, developing novel and highly efficient photocatalysts is significant for the application of photocatalytic technology.

The band structure of semiconductors is composed of a valence band filled with electrons and an empty conduction band [13,14]. The electrons on the conduction band have reducibility, and the holes in the valence band are oxidizing. Thus semiconductors have the corresponding redox potential [15]. In the process of photocatalytic reaction, the band structure is the most important factor affecting the catalytic activity [16-18]. Generally, raising the valence band of reducing the conduction band can both narrow the band gap and extend spectral response range [19-21]. Creating continuous stable valence band, which is more negative than the O2*p* level, can well narrow the band gap. One way is to introduce some nonmetal elements with lower electronegativity such as sulfur or nitrogen [22-25]. That is because their *p* orbital energy levels are higher than the 2*p* orbit of oxygen, mixing with the O2*p* orbit or forming a lower valence band independently, the band gap can be narrowed and the spectral response range can be extended. Another way is to introduce elements with a d10 electronic configuration such as silver zinc [26-29].

Recently, more works about reduced valence band and enhanced photocatalytic activity of semiconductors are reported. Zhang et al. prepared potassium doped g-C_3N_4 using potassium iodide and dicyandiamide as precursors. The introduction of potassium can reduce the valence band of g-C_3N_4 about 0.22 eV [30]. Zhang et al. synthesized Bi-doped Ag_3PO_4 by an ion exchange method and the valence band position was reduced [31]. Besides doping other elements, using conjugated molecules to reduce valence band positions is also an effective method. Bai et al. prepared C_{60}/C_3N_4 composite photocatalyst with reduced valence band and enhanced photocatalytic. Other conjugated carbon-based materials also have similar effects [32]. However, developing novel semiconductor photocatalysts with intrinsic low valence band and theoretical strong oxidation ability is rarely reported.

In this work, a novel photocatalyst $Bi(OH)SO_4{\bullet}H_2O$ with high oxidation ability theoretically is prepared by a facile method. Compared with the common Bi-based photocatalysts, it has a more positive valence band, suggesting it might possess the stronger oxidative ability and it may have broad application in synthesizing highly efficient photocatalysts through doping other elements or creating heterojunctions.

2. Experimental

All chemicals used were of reagent grade and used without further purification.

2.1. Synthesis of $Bi(OH)SO_4 \cdot H_2O$

2 g of $BiNO_3 \cdot 5H_2O$ was dried at 60 °C for 2 h and the obtained powder was transferred into a corundum crucible. After that, the sample was heated to 600 °C within 150 min and kept at that temperature for 4 h. The obtained yellow powder was Bi_2O_3. 1 g Bi_2O_3 was added into 20 ml (ω)98% H_2SO_4 and stirred for 12 h, during which process, the yellow suspension gradually changed to white. Then the white suspension was poured into 200 ml DI water with stirring. After 8 h, white acicular crystals were obtained and they were washed to neutral and dried at 60 °C for 12 h.

2.2. Characterization

X-ray diffraction (XRD) was obtained from a Rigaku D/max-2400 X-ray diffractometer with Cu *K*a. UV-vis diffuse reflectance spectra (DRS) were tested with a Hitachi U-3900 UV-vis spectrophotometer using $BaSO_4$ as reference. A Bruker electron paramagnetic resonance (ESR) 300E and radical scavenger dimethyl pyridine N-oxide (DMPO) was used to determine the ESR signal of hydroxyl radical and superoxide radical in methanol and water, respectively. Scanning electron microscope (SEM) images of the sample were obtained from a HITACHI SU-8010 field emission scanning electron microscope. The Energy Dispersive Spectrometer (EDS) images of the sample were obtained from an Oxford X-max 50 electron energy spectrometer mounted on the SEM. X-ray photoelectron spectroscopy (XPS) of the as-prepared samples was obtained from a PHI Quantera XPS microprobe.

2.3. Photocatalytic activity test

The photocatalytic activity of the sample was evaluated by the degradation of Rhodamine B (RhB) and Phenol (PhOH) under Ultraviolet (UV) light irradiation which was provided by a 500 W mercury lamp without using cutoffs and the average luminous intensity is 40 mW/cm^2.

Photocatalyst sample (50 mg) was uniformly dispersed in an aqueous solution of RhB (50 ml, 5 ppm) and PhOH (50 ml, 5 ppm), respectively. Before light irradiation, the suspensions were magnetically stirred in the dark for 30 min to ensure the absorption-desorption equilibrium. Then Hg lamp turned on and 3 mL aliquots were sampled at certain time intervals and filtered. The concentration of RhB was analyzed by measuring the maximum absorption wavelength (553 nm) using a Hitachi U-3900 UV-vis spectrophotometer. The concentration of PhOH was measured by high-performance liquid chromatography (HPLC) (Shimadzu LC-20AT).

3. Results and discussion

3.1. Morphology and structure

Fig. 1a and b are crystal structure model and XRD pattern of $Bi(OH)SO_4{\bullet}H_2O$ sample, respectively. The diffraction peaks of the sample in Fig. 1b can be indexed to $Bi(OH)SO_4{\bullet}H_2O$ (JCPDS = 057-0974). The apparent diffraction peaks of other substances are not found in Fig. 1b, indicating that the sample has a high purity. According to the Fig. 1a and the standard card, the $Bi(OH)SO_4{\bullet}H_2O$ crystallizes in the monoclinic space group $P2_1/n$ with the parameters a = 6.0118, b = 13.3355, c = 6.4854. The Fig. 1b and the standard card show that the diffraction peaks at 17.32°, 20.84° and 32.85° correspond to the crystal faces (110), (120) and (131), respectively.

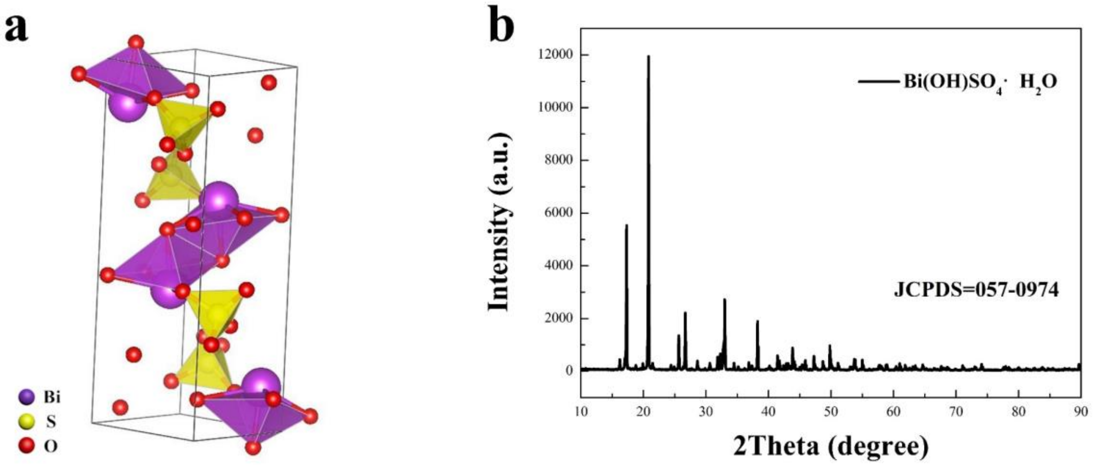


Fig. 1. (a) The crystal structure of $Bi(OH)SO_4{\bullet}H_2O$; (b) XRD pattern of $Bi(OH)SO_4{\bullet}H_2O$.

The chemical composition of the sample surface can be detected by XPS [33,34]. It can be seen from the XPS spectra of $Bi(OH)SO_4•H_2O$ sample (Fig. S1) that there are three elements of Bi, O, and S of the sample. The test result matches the elemental composition of the sample well.

From Fig. 2a, $Bi(OH)SO_4•H_2O$ appears as a rod-like structure under SEM. The X-ray energy dispersive spectrometer (EDS) images of the four elements of C, Bi, O, and S are shown in Fig. 2c-f, respectively. C is mainly from the conductive adhesive. It is easy to see that the prepared sample is uniformly distributed by three elements of Bi, O, and S.

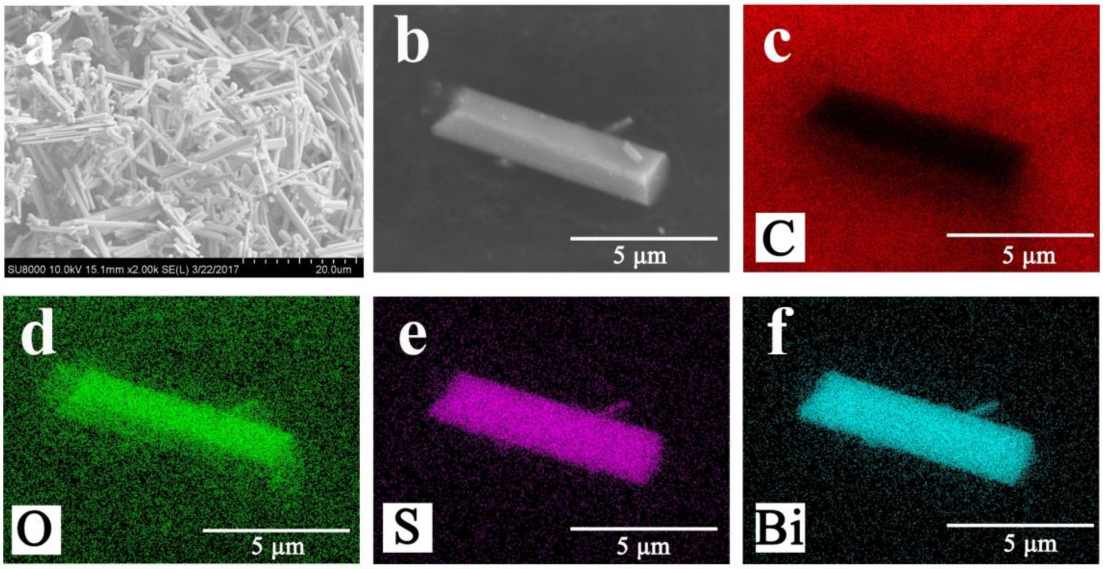


Fig. 2. Morphology and structure of the sample. SEM images of $Bi(OH)SO_4•H_2O$ (a-b) and EDS elemental distributions of C, O, S and Bi are shown in (c-f), respectively.

3.2. Photocatalytic activity

Fig. 3 shows the degradation effect of $Bi(OH)SO_4•H_2O$ on the RhB in aqueous solution under UV irradiation. The content of RhB decreased gradually with the increase of time. After 75 min, the concentration of RhB in solution was 33.9% of the initial solution. The result shows that $Bi(OH)SO_4•H_2O$ has good photocatalytic degradation activity for RhB.

To further study the UV activity of $Bi(OH)SO_4•H_2O$, $Bi(OH)SO_4•H_2O$ was used to degrade PhOH under UV irradiation. It can be concluded from the Fig. 3 that the content of PhOH in solution is gradually mineralized over time. After 65 min, the content of PhOH in the solution is reduced to 30.81% of the initial solution, which further shows that $Bi(OH)SO_4{\bullet}H_2O$ has good UV activity.

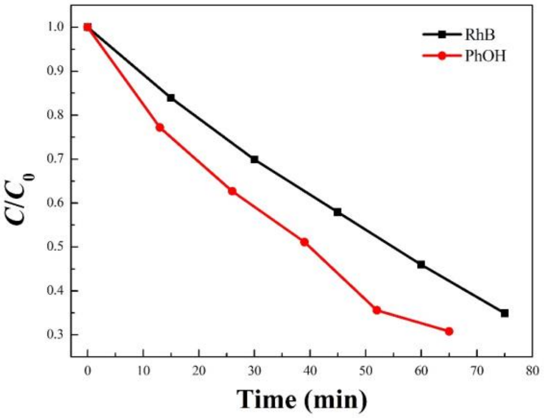


Fig. 3. Time dependence of RhB (a) and PhOH (b) in pure water under UV irradiation in the presence photocatalyst.

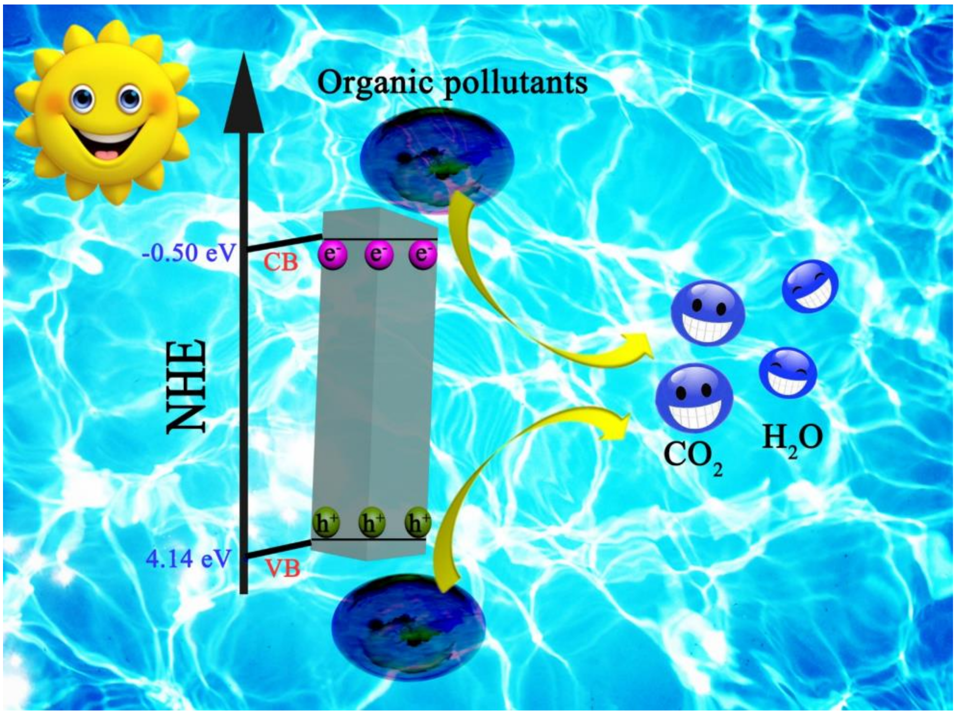
3.3. Mechanism for photocatalytic activity

Fig. S2a is the UV-vis diffuse reflectance spectra of $Bi(OH)SO_4{\bullet}H_2O$ sample. It can be informed that the absorption edge of $Bi(OH)SO_4{\bullet}H_2O$ is about 267.2 nm [35,36]. The band gap of $Bi(OH)SO_4{\bullet}H_2O$ is 4.64eV by extrapolating the straight line in Fig. S2b to the X axis indicating that $Bi(OH)SO_4{\bullet}H_2O$ can be excited by UV light [37].

In order to estimate the conduction band and valence band of $Bi(OH)SO_4{\bullet}H_2O$ sample, Mott-Schottky test was conducted [38,39]. The slope of the straight line is greater than zero, so the $Bi(OH)SO_4{\bullet}H_2O$ sample belongs to n-type semiconductor [40]. As can be seen from Fig. S3, the flat band potential of $Bi(OH)SO_4{\bullet}H_2O$ is –0.5 eV [41-43], indicating that the conduction band potential is approximate –0.5 eV. As can be seen from the above, the band gap is 4.64 eV, so the valence band potential is 4.14 eV.

The ESR spectra can help us to study the types and intensities of active radicals in the catalytic process and then to propose the mechanism of $Bi(OH)SO_4{\bullet}H_2O$ photocatalyst for the degradation of pollutants [44,45]. Fig. S4 indicates that the $Bi(OH)SO_4{\bullet}H_2O$ does not emit any signal in the dark environment, while under UV irradiation, the $Bi(OH)SO_4{\bullet}H_2O$ gives obvious signals of $O_2^{\bullet -}$ and $^{\bullet}OH$ [46,47]. The intensity of the two kinds of the signal increases with time going by. It can be confirmed that the main active species in the process of degradation is $O_2^{\bullet -}$ and $^{\bullet}OH$.

To further study the effect of various photoactive radicals on the degradation of organic pollutants by $Bi(OH)SO_4•H_2O$ catalyst, different free radical trapping agents were used to carry out the capture test. During the experiment, N_2 was used to remove O_2 to prevent the generation of superoxide radicals. IPA and $NaHCO_3$ could capture hydroxyl radicals and holes, respectively. It can be seen from Fig. S5 that the photocatalytic degradation activity of $Bi(OH)SO_4•H_2O$ obviously decreased after N_2, $NaHCO_3$ and IPA were introduced. This proved that the main active species in the process of degradation is $O_2^{•-}$, $^•OH$ and holes.



Scheme 1 A possible mechanism of $Bi(OH)SO_4•H_2O$ degradation of organic pollutants under UV irradiation.

The mechanism of $Bi(OH)SO_4•H_2O$ photocatalyst degradation of organic pollutants might be understood as follows (Scheme 1). Under sunlight irradiation, $Bi(OH)SO_4•H_2O$ is excited to produce electrons and holes (Equation 1). The electrons migrate to the surface of the catalyst and react with O_2 adsorbed on the surface of the catalyst to form a superoxide radical (Equation 2). Holes can react with H_2O to produce hydroxyl radicals with strong oxidation capacity (Equation 3). Holes, $O_2^{•-}$ and $^•OH$ are active species and exert strong oxidation ability in the photochemical reactions, which can react with organic pollutants adsorbed on the catalyst to achieve the purpose of degradation (Equation 4, 5 and 6).

$$Bi(OH)SO_4 \bullet H_2O + h\nu \rightarrow Bi(OH)SO_4 \bullet H_2O + e^- + h^+ \quad (1)$$

$$e^- + O_2 \rightarrow O_2^{\bullet -} \quad (2)$$

$$h^+ + H_2O \rightarrow {}^{\bullet}OH + H^+ \quad (3)$$

$$h^+ + \text{organic pollutants} \rightarrow H_2O + CO_2 \quad (4)$$

$$O_2^{\bullet -} + \text{organic pollutants} \rightarrow H_2O + CO_2 \quad (5)$$

$$^{\bullet}OH + \text{organic pollutants} \rightarrow H_2O + CO_2 \quad (6)$$

The position of VB is significant for the oxidation ability of semiconductors. Fig. 4 shows the CV and VB of some Bi-based photocatalysts. The valence bands of Bi_2MoO_6 [48], Bi_2WO_6 [49], $BiPO_4$ [48], $BiVO_4$ [50] and Bi_2SiO_5 [51] are 2.27, 2.94, 4.05, 2.78 and 2.41 eV, respectively. The VB of $Bi(OH)SO_4 \bullet H_2O$ is more positive than these photocatalysts, indicating that it might have stronger oxidation capacity than them. However, the band gap of 4.64 eV limits its light absorption efficiency. Creating heterojunctions with $Bi(OH)SO_4 \bullet H_2O$ or doping some elements to $Bi(OH)SO_4 \bullet H_2O$ is likely to enhance its photocatalytic activity.

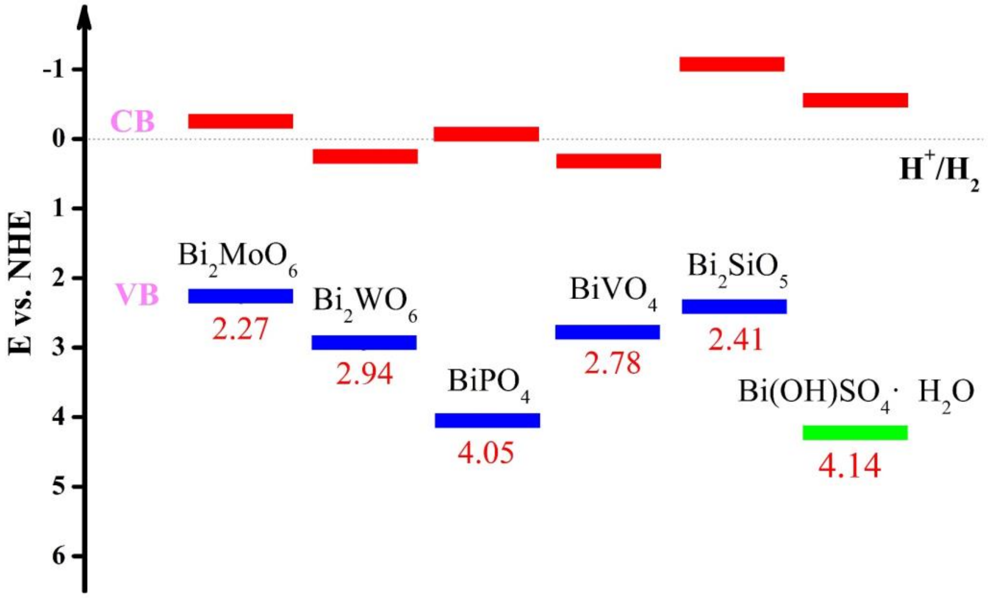


Fig. 4. Band positions of several kinds of Bismuth compounds and $Bi(OH)SO_4 \bullet H_2O$ sample.

4. Conclusions

In this work, a novel Bi-based photocatalyst, $Bi(OH)SO_4•H_2O$, with rod-like structure was prepared in a facile method. The band gap of $Bi(OH)SO_4•H_2O$ is 4.64 eV, and its CB and VB are estimated at –0.5 eV and 4.14 eV, respectively. Positive valence band makes it have high oxidation capacity theoretically. It has good photocatalytic activity under UV irradiation and the main active species are $O_2^{\bullet-}$, $^{\bullet}OH$ and holes. The study of this material probably provides a new resource for synthesizing highly efficient photocatalysts through doping other elements or creating heterojunctions.

Acknowledgement

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Supporting information

A novel Bi-based photocatalyst $Bi(OH)SO_4 \cdot H_2O$ with a positive valence band and highly photocatalytic performance

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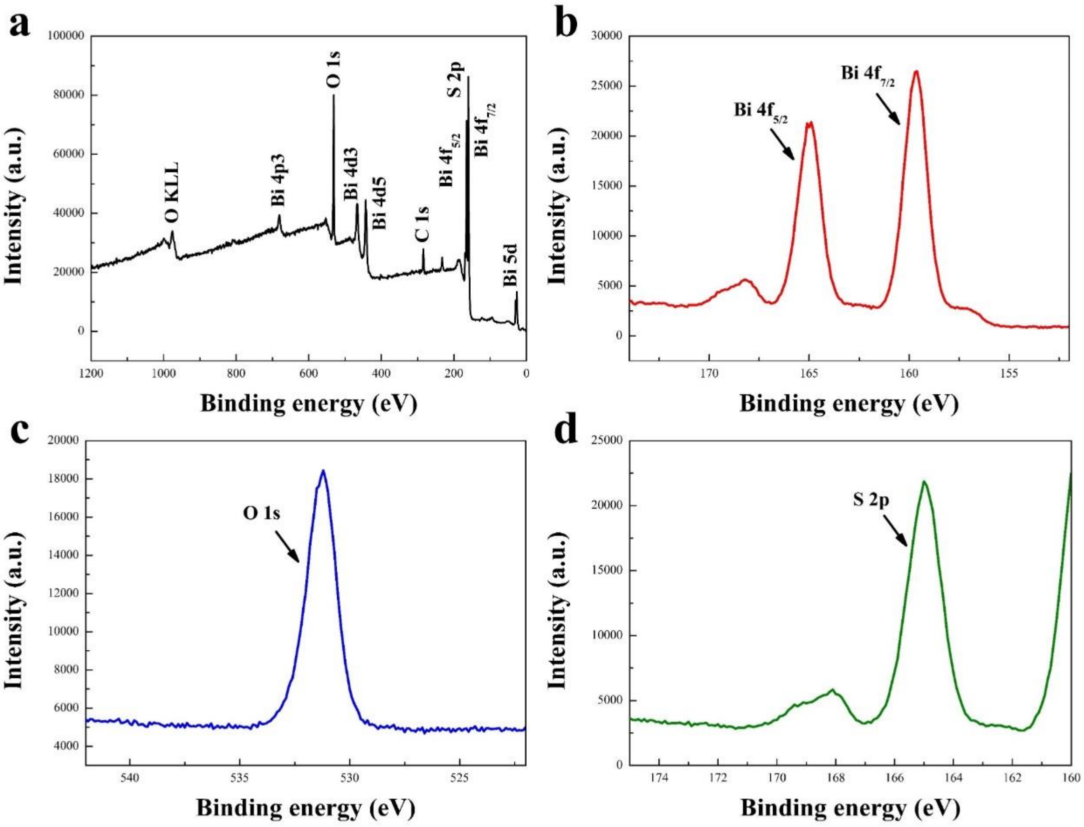

Fig. S1. Survey XPS spectrum of the $Bi(OH)SO_4•H_2O$ sample (a); narrow XPS spectrum of Bi 4*f* (b), O 1*s* (c) and S 2*p* (d) from the surface of the sample.

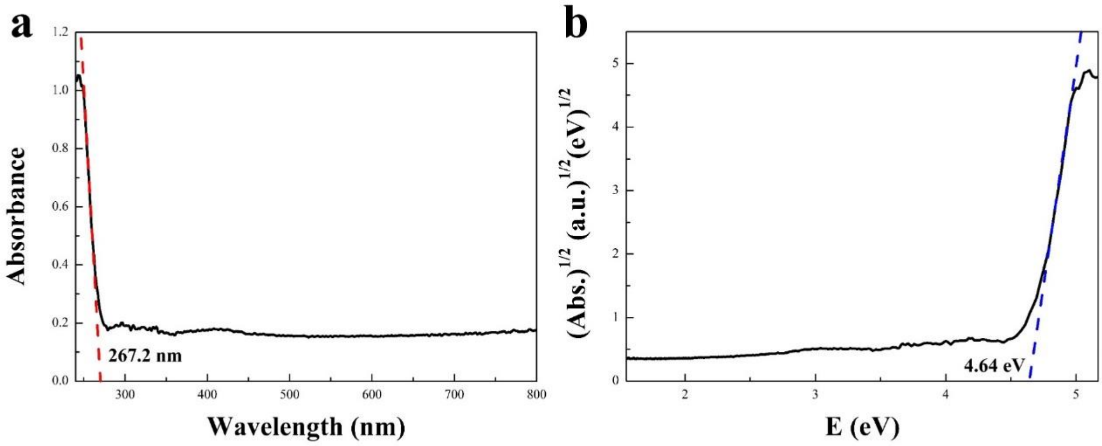

Fig. S2. (a) UV-vis diffuse reflectance spectra of $Bi(OH)SO_4•H_2O$; (b) The absorption$^{1/2}$ vs.

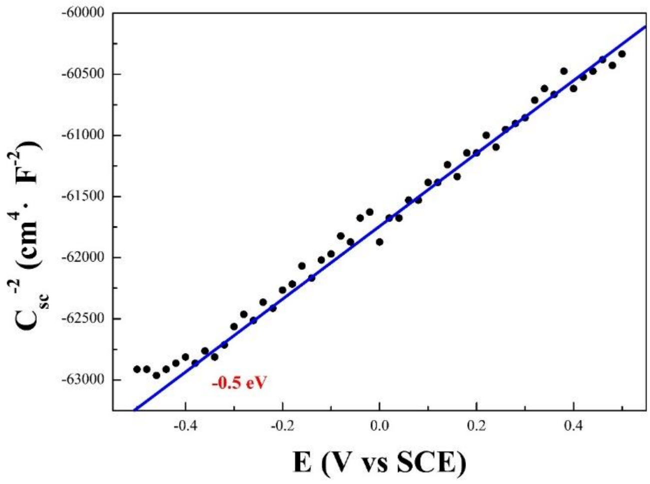

Fig. S3. Mott–Schottky plots of Bi(OH)SO$_4$•H$_2$O sample.

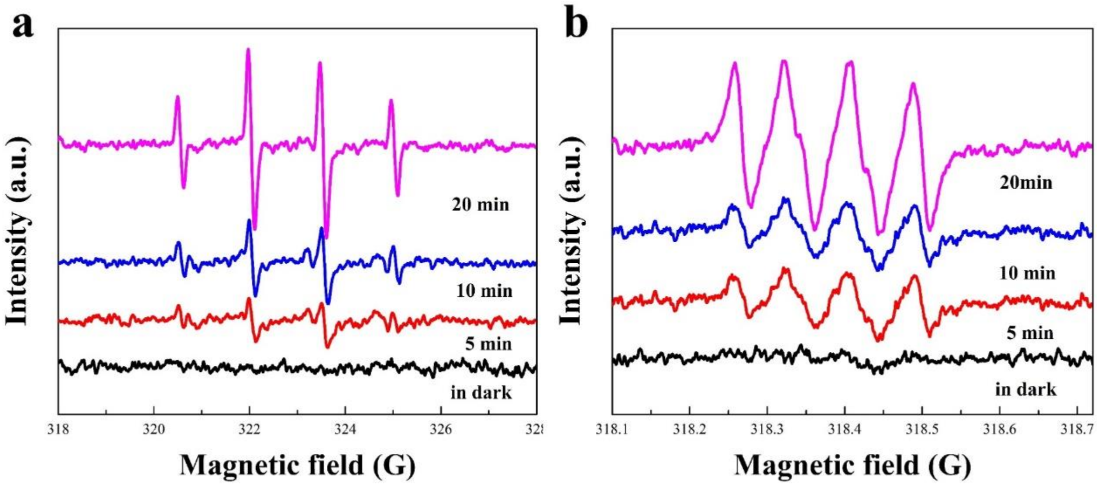

Fig. S4. ESR spectra of $^{\bullet}$OH (a) and $O_2^{\bullet-}$ (b).

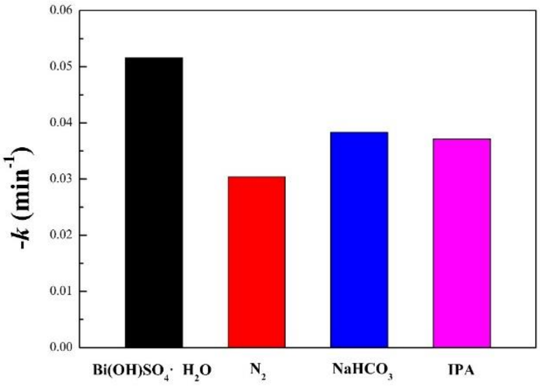

Fig. S5. Apparent rate constants for the photodegradation of RhB under UV irradiation in tapping experiment.