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Enhancement of Visible Photocatalytic Performances of Bi_2MoO_6-BiOCl nanocomposite with plate-on-plate Heterojunction Structure

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Abstract

A visible-light-sensitive Bi_2MoO_6-BiOCl heterojunction photocatalyst was synthesized via a hydrothermal process. The as-prepared Bi_2MoO_6-BiOCl composite shows an irregular multi-plate structure with length ranging from 100 nm to 1μm, indicating a possibility of the plate-on-plate structure by covering Bi_2MoO_6 and BiOCl nanoplate to each other. The Bi_2MoO_6-BiOCl photocatalyst not only had a good visible-light photocatalytic performance, but exhibited higher photocatalytic activity than pure BiOCl and Bi_2MoO_6. The optimal Bi_2MoO_6 content for the photocatalytic activity of the Bi_2MoO_6-BiOCl composites is 30%. The photoactivity is almost 2.0 times as high as that of pure Bi_2MoO_6 for the RhB photodegradation, and 1.5 times for the phenol photodegradation under visilbe light irradation. The photocatalytic mechanism was elucidated via active species trapping experiments and ESR. The $\cdot OH$ and $\cdot O_2^-$ took the key roles in the degradation of RhB via Bi_2MoO_6-BiOCl composite. Finally, the possible charge transfer mechanism of enhanced visible light photocatalytic activity was proposed.

KEYWORDS: photocatalysis, BiOCl, Bi_2MoO_6, visible light photocatalyst, Rhodamine B, phenol, heterojunction.

1. Introduction

Semiconductor photocatalysis has been put forward as an effective strategy for organic pollutant remediation and water splitting. TiO_2, the key photocatalyst for convenient wastewater treatment and other essential cleaning processes, however, suffers from such problems as ineffective sunlight capture and conversion.[1-3] In recent years, the development of efficient visible-light-active photocatalysts has become a buzzword in photocatalysis. Bismuth-based photocatalytic materials such as Bi_2O_3, Bi_2WO_6, $BiVO_4$, BiOI etc.[4.5] have recently aroused great interest in the scientific community due to their intriguing electronic structures. Among these compounds, bismuth oxyhalides with layered structures show great promise owing to their mechanical robustness, outstanding photocatalytic activities and chemical stability.[6,7] In particular, BiOCl, which has a layered structure consisting of $[Bi_2O_2]^{2+}$ layers sandwiched between two sheets of Cl ions with an internal electric field along the [001] direction, has been demonstrated to show superior photocatalytic performance under ultraviolet light irradiation.[8] However, BiOCl is a wide-band-gap (Eg = 3.5 eV) semiconductor [9-11] and can only absorb ultraviolet light, leading to poor photocatalytic performance under visible-light irradiation .[12, 13]

Construction of heterostructure photocatlayst might be an effective way to enhance the visible light photocatalytic activity of BiOCl. Semiconductor heterostructure not only can broaden the light absorption but also can highly separate the photoinduced electron–hole pairs, which ultimately obtains excellent photocatalytic activity. Thus BiOCl based heterostructure photocatalysts such as BiOCl-Bi_2O_3, BiOCl-BiOBr and

BiOCl-Bi_2WO_4 et al were developed to enable the utilization of BiOCl in the visible-light region and improve the photocatalytic activity.[14-16] Bi_2MoO_6 is another layered Aurivillius related oxide, consisting of $[Bi_2O_2]^{2+}$ layers sandwiched between MoO_4^{2-} slabs.[17-19] It is a semiconductor with a smaller band gap (2.5-2.8 eV), capable of capturing visible light ($420 \leq \lambda \leq 500$ nm) and exhibiting photocatalytic activity for water splitting and degradation of organic pollutants.[17,18] However, enhancing the photocatalytic efficiency of Bi_2MoO_6 to meet the practical application requirements remains a challenge because of the poor quantum yield, which is due to the rapid recombination of photoinduced electrons and holes.[22,23] Actually, isolated component usually is no longer sufficient to cope with technological challenges involved in the development of an environmentally benign energy infrastructure. To date, a lot of Bi_2MoO_6-based heterostructure photocatalysts have also drawn great attention for its excellent visible light harvesting ability and the high visible light photocatalytic activity.[24-26] It have been reported that the band edge potentials of CB and VB for BiOCl are 0.26 and 3.56 eV,[27] while those for Bi_2MoO_6 are -0.32 and 2.20 eV,[28] respectively. Therefore, the well-matched overlapping band-structure of BiOCl and Bi_2MoO_6 is supposed to be quite suitable to construct heterostructures that would bring an effective separation and transfer of photogenerated charges. Additionally, both BiOCl and Bi_2MoO_6 belong to the layered Aurivillius related oxide family, consisting of $[Bi_2O_2]^{2+}$ layers sandwiched between two slabs of Cl or MoO_4^{2-} ions. They can easily grow together to form heterostructures with morphology and component being controlled by tuning the ratio of Cl and MoO_4^{2-} ions.

In our work, we report the fabrication of the Bi_2MoO_6-BiOCl heterojunction via a hydrothermal process for the first time. The structural features of the heterojunction were confirmed using XRD, TEM, SEM, ESR, PL etc. characterization techniques. The Bi_2MoO_6-BiOCl composites exhibit much higher photocatalytic activity than the single phase Bi_2MoO_6 or BiOCl towards the degradation of RhB and phenol under visible light illumination. The possible mechanisms of the enhancement of photocatalytic activity were systematically investigated. Finally, the role of the main reactive species for the photocatalytic process is elucidated through the radical trap experiments and ESR.

2. Experimental

2.1 Sample preparation

All the chemicals are of analytical reagent grade and were used without further purification. Distilled water was used in all our experiments. The Bi_2MoO_6-BiOCl composite was synthesized via a hydrothermal process, using deionized water as solution. In typical experiments, an appropriate amount of $Bi(NO_3)_3\cdot 5H_2O$ was added into deionized water then the $Na_2MoO_4\cdot 2H_2O$ powder was added into the above solution. The pH values of the mixtures were adjusted to 7 by addition of NaOH solution. The mixture was stirred for 60min at room temperature. Then the solution was transferred into 100ml Teflon-lined stainless steel autoclave. The autoclave was sealed and maintained at a constant temperature of 160°C for 12h. After cooling to room temperature, the resulting product was filtered, washed with ethanol and water for several times, and finally dried at 60°C. A series of Bi_2MoO_6-BiOCl photocatalysts with the different mass ratios were prepared by adjusting the concentrations of Cl or MoO_4^{2-} ions. The prepared samples were denoted as xBi_2MoO_6-BiOCl, where x refers to the mass ratio of Bi_2MoO_6 (x = 0%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, 100%). For comparison, pure Bi_2MoO_6 and BiOCl were also prepared using the same method as Bi_2MoO_6-BiOCl photocatalyst.

2.2 Characterization

X-ray diffraction (XRD) patterns of the powders were recorded at room temperature by a Bruker D8 Advance X-ray diffractometer. The Fourier transform infrared (FT-IR) spectrum of the sample was recorded on a FT-IR spectrometer using conventional KBr pellets. Morphologies and structures of the prepared samples were further examined with a high-resolution transmission electron microscopy (HRTEM) images were obtained by a JEOL JEM-2011F field emission transmission electron microscope with an accelerating voltage of 200 kV. The UV-vis diffuse reflectance spectra (DRS) of the samples were recorded in the range from 200 to 800 nm using a TU-1901 double beam UV-Vis spectrophotometer, and $BaSO_4$ was used as a reference. Photoluminescence spectra (PL) were conducted on a HITACHI F-4600 Fluorescence Spectrophotometer. Electrochemical and photoelectrochemical measurements were performed in three-electrode quartz cells with a 0.1M Na_2SO_4 electrolyte solution. Platinum wire was used as the counter electrode, and saturated calomel electrodes (SCE) were used as the reference electrodes, respectively. The as-prepared photocatalyst film electrodes on ITO served as the working electrode. The photoelectrochemical experiment results were recorded using an electrochemical system (CHI-660B, China). The intensity of light was 1 m·W/cm^2. The electron spin resonance (ESR) signals of radicals spin-trapped by spin-trap reagent 5,5'-dimethyl-1-pirroline-N-oxide (DMPO) (purchased from Sigma Chemical Co.) were examined on a Bruker model ESR JES-FA200 spectrometer equipped with a quanta-Ray Nd:YAG laser system as the irradiation source (λ = 365/420 nm). Magnetic parameters of the radicals detected were obtained from direct measurements of magnetic field and microwave frequency.

2.3 Photodegradation experiment

The photocatalytic activities were evaluated by the decomposition of Rhodamine B(RhB) under the visible light irradiation (λ > 420nm). In a typical photocatalytic experiment, the photocatalyst (1g/L) was dispersed in Rhodamine B(RhB) with an initial concentration of 10mgl/L. Prior to irradiation, the suspension(50mL) was magnetically stirred in the dark for 1h to achieve the adsorption-desorption equilibrium on the surface of the photocatalyst. Light irradiation was conducted using a 500W xenon lamp with a 420nm cutoff filter. During RhB photodecomposition process, samples were withdrawn at regular intervals and centrifuged to remove photocatalyst for analysis. The filtrate was then analyzed using a UV–vis spectrophotometer to measure the absorption of RhB in the range of 300-700nm.

For the purpose of investigating the effects of related reactive species, hydroxyl radicals (•OH), superoxide radical (O_2•$^-$) and holes (h^+) were investigated by adding 1.0 mM tert-butanol, 1 mM BQ (p-benzoquinone) or 1 mM ethylenediamine tetraacetic acid disodium salt (EDTA-2Na) into the RhB solution prior to addition of the photocatalyst, respectively.[29,30] The experiment process was similar to the photodegradation experiment.

3 Results and discussion

3.1 Plate-on-plate heterojunction structure

The crystalline structures of the as-prepared samples were examined by X-ray diffraction. Figure 1 shows the XRD patterns of the pure BiOCl, Bi_2MoO_6 and Bi_2MoO_6-BiOCl compostis with the different mass ration. Two series of XRD peaks can be observed in Figure 1. The diffraction peaks with $2\theta = 11.9°$, 25.9°, 32.5°, 41.0°, 46.8° and 54.1° could be indexed to the (001), (101), (110), (112), (200) and (211) crystal planes of BiOCl. While the diffraction peaks with $2\theta = 23.6°$, 28.4°, 32.7°, 46.9° and 55.6° correspond to (111), (131), (200), (202) and (331) crystal planes of Bi_2MoO_6. The XRD analysis indicates the co-existence of BiOCl and Bi_2MoO_6 phases in the as-prepared Bi_2MoO_6-BiOCl nanocomposite, and no other new phases are observed in the XRD patterns. With increasing the contents of Bi_2MoO_6 in the composites, the peak intensities of the unique Bi_2MoO_6 increased, meanwhile those of the BiOCl lowered gradually.

Figure 2 shows the FT-IR spectra of BiOCl, Bi_2MoO_6, and 30%Bi_2MoO_6-BiOCl, respectively. One region in the 950-700 cm^{-1} range can be obviously observed in Bi_2MoO_6 and 30%Bi_2MoO_6-BiOCl samlpe, which is due to the Mo-O stretching bands. The XRD and FT-IR results indicate that this heterojunction contain two fundamental components of BiOCl and Bi_2MoO_6 and that no appreciable chemical reaction occurred between BiOCl and Bi_2MoO_6.

The morphology of the products was characterized by SEM, TEM, and HRTEM. Figure 3 displays the SEM images of pure BiOCl （a, b), Bi_2MoO_6 (c, d) and the 30% Bi_2MoO_6-BiOCl composite photocatalyst (e, f). The morphology of as-prepared BiOCl (Figure 3 a and b) is sheet-shaped structure with the length ranging from 200 nm to 1μm. The average thickness of BiOCl nanoflakes is about 40-55 nm. Bi_2MoO_6 also demonstrates nanoplatelet feature having nearly the same thinkness with BiOCl (Figure 3 c and d). While, compared with BiOCl, the length of Bi_2MoO_6 is much smaller, ranging from 60 nm to 100 nm. Both Bi_2MoO_6 and BiOCl nanoplates have no obvious aggregation or stacking. For the Bi_2MoO_6-BiOCl composites, an irregular multi-plate structure with length ranging from 100 nm to 1μm can be observed, indicating a possibility of the plate-on-plate structure by covering Bi_2MoO_6 and BiOCl nanoplate to each other. The thickness of Bi_2MoO_6-BiOCl composite is about 20-30 nm, which is much thinner than that of the individual Bi_2MoO_6 or BiOCl nanoplatelet. It can be seen that all as-prepared sample show the typical lamellar nanoplatelets. Actually, the layered nature of the Bi based composite oxides favors the self-assembly of the units to form the characteristic platelet-like nanostructure of the materials. Furthuremore, the similarly layered structures of the BiOCl and Bi_2MoO_6 are favorable for the formation of the heterostructure.

More detailed structural information of the Bi_2MoO_6-BiOCl composite is provided by TEM analysis. Figure 4 shows the TEM of 30%Bi_2MoO_6-BiOCl composite. The irregular platelet-shaped nanostructure of Bi_2MoO_6-BiOCl composite with lengths of 200 nm to 1 μm can be observed in Figure 4a, which is consistent with the SEM observations in Figure 3. The typical HRTEM of BiOCl-Bi_2MoO_6 composite, as shown in Figure 4 b and c, further demonstrate the detailed nanojunction structure. In Figure 4 b, the lattice fringes at 0.26 and 0.39 nm coincide with the fringe spacing of the (110) lattice plane of the tetragonal BiOCl sheet and the (040) crystal plane of Bi_2MoO_6. The formation of the nanojunction structure can also be observed in Figure 4c. In order to show clearly the lattice fringes in Figure 4c, the fast Fourier transform (FFT) and its cosponding inverse fast flourier transformation (IFFT) image were given in Figure 4d, e, f and g. The FFT corresponding to red area in Figure 4c marked as d (Figure 4d) and its cosponding IFFT image (Figure 4e) were indexed as Bi_2MoO_6. The two diffraction sopts could be indexed as (131) plane of Bi_2MoO_6 with planar spacing of 0.31nm. Meawhile, the FFT corresponding to red area f in Figure 4c marked as f (Figure 4f) and its cosponding IFFT image (Figure 4g) were indexed as BiOCl. The fringe spacing of 0.26 nm agrees with the spacing of BiOCl (110) planes. These planes also manifest themselves in the XRD peaks at 32.7° and 28.4° of the Bi_2MoO_6-BiOCl catalyst. These observations indicate that the BiOCl and Bi_2MoO_6 nanoplates intertwine inside the Bi_2MoO_6-BiOCl composite matrix. Therefore, the as-prepared Bi_2MoO_6-BiOCl composite is considered to be a strongly interacting heterostructure between BiOCl and Bi_2MoO_6 formed in nanoscale. All of the above results clearly demonstrate that Bi_2MoO_6-BiOCl heterostructures were successfully fabricated.

To reveal the optical response of the obtained samples, the photocatalysts were characterized by a UV-vis spectrum. Figure 5 gives the UV–vis diffuse reflectance spectra of the pure BiOCl, Bi_2MoO_6 and Bi_2MoO_6-BiOCl composite. As shown in Figure 5, the pure BiOCl exhibits a fundamental absorption edge at 360 nm, corresponding to the band gap of 3.4 eV. The absorption edge of Bi_2MoO_6 is at 475 nm, which indicates that the band gap of Bi_2MoO_6 is about 2.6 eV. The spectra of Bi_2MoO_6-BiOCl heterostructures show the combinations of the individual spectrum of Bi_2MoO_6 and BiOCl. An increasing red shift of the absorption edge of Bi_2MoO_6-BiOCl composite can be clearly observed with the increasing the of Bi_2MoO_6 content. The increase of the visible light absorption allows for more efficient utilization of the solar spectrum to create more photogenerated electrons and holes.

3.2 Ehancement of photocatalytic activity and photocurrent

In our photodegradation system, the colourful dye Rhodamine B (RhB) and colorless organic contaminant phenol are chosen as representative organic substances to evaluate the photocatalytic activity of the synthesized Bi_2MoO_6-BiOCl composites. It is well known that the photocatalytic degradation process of organic contaminant followed the apparently pseudo-first-order model[31,32] expressed as

$$\ln C_0/C_t = k_{app}t$$

where k_{app} is the apparent pseudo-first-order rate constant(min^{-1}), C_t is organic substance concentration(mg/L) in aqueous solution at time, and C_0 is initial organic substance concentration(mg/L). Figure 6 gives the photocatalytic degradation rates of RhB under visible light ($\lambda > 420$ nm) on the pure Bi_2MoO_6, BiOCl and Bi_2MoO_6-BiOCl composites. In the control experiment, no degradation of RhB and phenol is observed in the absence of photocatalyst, which demonstrates that RhB and phenol are quite stable and excludes the possibility of a self photolysis process under visible light irradiation. It can be seen that all the Bi_2MoO_6-BiOCl photocatalysts exhibited higher visible light photocatalytic activity than the pure BiOCl and Bi_2MoO_6 sample, which suggests the existence of a synergistic effect between BiOCl and Bi_2MoO_6. The photocatalytic activity of Bi_2MoO_6-BiOCl increases gradually with the decrease of the weight precetange of Bi_2MoO_6 and reaches the optimum activity when the loading amount of Bi_2MoO_6 reaches to 30 wt%. The apparent rate constant of 30% Bi_2MoO_6-BiOCl is 0.022 min^{-1}, which is about 2.0 times as high as that of Bi_2MoO_6 ($k=0.011 min^{-1}$) and 20.0 times as that of BiOCl ($k=0.001 min^{-1}$). However, as the loading amount of Bi_2MoO_6 further decreases, the degradation rate gradually decreases. In fact, the optimum content of the Bi_2MoO_6 in the hybrid samples can be closely related to the recombination rate of photogenerated electrons and holes. It is reported that there is a suitable value of the space charge region potential for the efficient separation of electron–hole pairs (equal to the light penetration depth).[33] Accordingly, when the Bi_2MoO_6 content is above its optimal value, the space charge region might become very narrow and the penetration depth of light into BiOCl might exceed the space charge layer, so the recombination of the photogenerated electron–hole pairs in semiconductors becomes easier.

In order to prove the visible light photocatalytic activity of Bi_2MoO_6-BiOCl composite comes from the excitation of photocatalyst rather than the sensitization of the dye, the photocatalytic activity of uncolored organic pollution (phenol) degradation was examined under visible light as shown in Figure7. It is clear that the efficiency of phenol removal is consistent with the RhB. The Bi_2MoO_6 –BiOCl composite shows the significant improvement in the photodegradation of phenol compared with the pure BiOCl and Bi_2MoO_6. When the loading amount of Bi_2MoO_6 reaches to 30 wt%, the efficiency of phenol removal achieved the highest. The photocatalytic rate constant of 30%Bi_2MoO_6-BiOCl for phenol degradation is 0.23 h^{-1}, which is 12.7 and 2.3 times faster then individual BiOCl and Bi_2MoO_6, respectively.

The photodegradation of RhB and phenol with the composites under UV light and UV-vis light were carried out in order to be compared with the photoactivities under the visible light. The photodegradation of RhB and phenol under UV light over BiOCl, Bi_2MoO_6 and Bi_2MoO_6-BiOCl composites are compared and shown in Fig S1 and S2, respectively. BiOCl exhibits the highest photocatalytic activity for the degradation of both RhB and phenol under UV light. The reason is that BiOCl has the band-gap of 3.5 eV which can be excited by the ultraviolet light. The wide band gap is favorable for the oxidation reactions. The photodegradation of RhB and phenol under UV-vis light over BiOCl, Bi_2MoO_6 and Bi_2MoO_6-BiOCl composites are shown in Fig S3 and S4, respectively. The photocatalytic activity of BiOCl, Bi_2MoO_6 and Bi_2MoO_6-BiOCl composites for the degradation of RhB and phenol under UV-vis light are consistent with that of visible light. The Bi_2MoO_6-BiOCl composites have the higher photocatayltic activity than single Bi_2MoO_6 and BiOCl. The photocatalytic activity of Bi_2MoO_6-BiOCl increases gradually with the decrease of the weight precetange of Bi_2MoO_6 and reaches the optimum activity when the loading amount of Bi_2MoO_6 reaches to 30 wt%. The apparent rate constant of 30% Bi_2MoO_6-BiOCl for RhB is

0.0384 min-1, which is about 4.0 times as high as that of Bi_2MoO_6 (k=0.0086min^{-1}) and 3.0 times as that of BiOCl (k=0.0189min^{-1}). And the apparent rate constant of 30% Bi_2MoO_6-BiOCl for phenol is 0.012 min-1, which is about 4.0 times as high as that of Bi_2MoO_6 (k=0.0031min^{-1}) and 2.0 times as that of BiOCl (k=0.0089min^{-1}).

The transient photocurrent responses of a photocatalysis may directly correlate with the recombination efficiency of the photogenerated carriers. To investigate the photocurrent properties of the as-synthesized BiOCl, Bi_2MoO_6 and Bi_2MoO_6-BiOCl heterostructure, photoresponses were performed under several on/off sunlight irradiation cycles shown in Figure 8. At the beginning, the photocurrent does not reach equilibrium. After about 100 seconds, the photocurrent value becomes stable and decreases to zero as soon as the incident light on the photoanode is turned off and returns to the original value only when the light is turned on again. The Bi_2MoO_6-BiOCl heterojunction exhibited a higher transient photocurrent density (about 0.3-0.4uA·cm^{-2}) than those of the Bi_2MoO_6 sample and the BiOCl sample, which indicates that the separation efficiency of photogenerated electrons and holes is significantly improved at their interface.

3.3 Mechanism of photocatalytic activity enhancement

Photoluminescence (PL) spectra were further used to investigate the efficiency of charge carrier trapping, migration, and transfer of the prepared samples to understand the fate of electron-hole pairs in semiconductor particles. The peak intensities are strongly dependent on the recombination between photoinduced electrons and holes. As shown in Figure S5, the PL spectra of the samples obtained with an excitation wavelength of 325nm display an emission peak in the range of 300-700nm. The 30%Bi_2MoO_6-BiOCl sample shows the lower PL intensity than BiOCl. Figure 9 gives the room-temperature decay curves and lifetimes of BiOCl, Bi_2MoO_6 and Bi_2MoO_6-BiOCl heterostructure emission at 425 nm. As shown in Figure 9, the decay curves are well fitted by a first-order exponential function

$$I(t) = A \exp(-t/\tau) \qquad (1)$$

where I is the luminescence intensity at time t, A is constant, t is the time, and τ is the decay time for the exponential components. On the basis of equation (1) and decay curves, the decay times were determined to be 1.8, 7.2 and 13.6ns for the BiOCl and Bi_2MoO_6 and 30%- Bi_2MoO_6-BiOCl, respectively. Both the PL spectra and decay curves imply that the electron-hole recombination could be effectively prohibited due to the formation of Bi_2MoO_6-BiOCl heterostructure, so the quantum efficiency of the samples is improved.

To further investigate the photocatalytic mechanism of the samples on the photodegradation of RhB, the trapping experiment for detecting active species was conducted during the photocatalytic reaction. 1mmol/L EDTA-2Na, 1mmol/L tert-butanol (t-BuOH) and 1mmol/L benzoquinone were added as h^+ sinks, ·OH scavengers and $\cdot O_2^-$ scavengers, respectively. As showed in Figure 10a and b, EDTA-2Na has less effect on photocatalytic efficiency, while the photodegradation of RhB is obviously inhibited by the addition of the tert-butanol and benzoquinone**.** This fact demonstrates that the ·OH and $\cdot O_2^-$ are the two main active species and play key roles in the degradation of RhB rather than h^+ in the presence of Bi_2MoO_6 or

Bi_2MoO_6-BiOCl composite. Nevertheless, the reduction speed of the photocatalytic activity by adding the t-BuOH is faster than that by adding the benzoquinone, suggesting that the ·OH play a more important role in the RhB degradation than the $\cdot O_2^-$ do.

Electron spin resonance (ESR) spectroscopy with water and 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) spin-trapping adducts allows the detection of hydroxyl radicals (·OH) and superoxide radicals ($\cdot O_2^-$). Consequently, ESR spin-trapping analysis was employed to probe the nature of the reactive species generated during irradiation of the present system. As indicated in Figure 11a, four apparent signals were generated, which were attributed to ·OH in Bi_2MoO_6 or Bi_2MoO_6-BiOCl under visible light irradiation for 10 min, while no ·OH signal was detected in dark under identical conditions. Furthurmore, these •OH radical signals for Bi_2MoO_6-BiOCl are much stronger than those for Bi_2MoO_6, accounting for a higher photocatalytic performance of Bi_2MoO_6-BiOCl than BiOCl toward the degradation of pollutants. In Figure 11b, no signal of $\cdot O_2^-$ was detected in the system containing BiOCl or BiOCl-Bi_2MoO_6 under visible light irradiation, which suggests that $\cdot O_2^-$ is not the main reaction during photocatalytic process. This result is not consistent with the trapping experiment. The reason might be that the amount of $\cdot O_2^-$ produced from the reaction between e^- and O_2 is too little to detect. This fact further confirms that most of •OH radicals mainly come from the reaction between h^+ and H_2O.

Therefore, based on the above result, a possible photocatalytic mechanism of Bi_2MoO_6-BiOCl heterojunction composite was proposed, as is shown in Figure 12. It has been reported that the the band edge potentials of CB and VB for BiOCl are 0.26 and 3.56 eV,[25] while those for Bi_2MoO_6 are -0.32 and 2.20 eV,[26] respectively. According to the obtained band gap energies, only Bi_2MoO_6 can be activated under the visible light illumination, consequently the photogenerated electrons (e^-) in the VB of Bi_2MoO_6 were excited to the CB, with the same amount of holes (h^+) left in VB in Bi_2MoO_6. Since the CB of Bi_2MoO_6 is more negative than that of BiOCl, the photoinduced electrons would be easily injected from the CB of Bi_2MoO_6 to the CB of BiOCl. Then the eletrons stored in the CB of BiOCl are trapped by the O_2 near the surface of TiO_2 to form reactive $\bullet O_2^-$. At the same time, the h^+ left in VB in Bi_2MoO_6 can directly oxidize the organic compounds or reacte with H_2O to form ·OH radicals. Based on our ESR and trapping experiment result, it can be concluded that most of h^+ reacte with H_2O to form ·OH radicals because the ·OH is main active species in the photocatalytic process of RhB. Therefore, there is efficient separation of photoinduced electrons and holes on the heterojunction, which may greatly reduce the recombination of the photoinduced charge carriers.[34,35]

4 Conclusions

Bi_2MoO_6-BiOCl plate-on-plate heterojunction photocatalysts were successfully synthesized via a hydrothermal method. The visible light photocatalytic activity of Bi_2MoO_6-BiOCl was enhanced about 2.0 times for RhB degradation and 1.5 times for the phenol photodegradation compared to pure Bi_2MoO_6. The optimal Bi_2MoO_6 content for the photocatalytic activity of the Bi_2MoO_6-BiOCl composites is 30%. The formation of heterojunctions between BiOCl and Bi_2MoO_6 promoted the separation of the photogenerated electron–hole pairs and resulting in enhancement of photoactivity. The ·OH radical is the main active species during degradation for both Bi_2MoO_6 and Bi_2MoO_6-BiOCl composite.

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