Photocatalytic Degradation of Methyl Orange over $BiOCl_xBr_{1-x}$ ($0 \le x \le 1$) Solid Solutions

Tan Qu
School of Materials Science and Technology
Harbin University of Science and Technology, HUST
Harbin, P. R. China
e-mail: 1019578924@qq.com

Xu Huanyan*
School of Materials Science and Technology
Harbin University of Science and Technology, HUST
Harbin, P. R. China
*Corresponding Author. e-mail: xhy7587@aliyun.com

Abstract—Objective: Due to possessing the layered structure and tunable band gap, Bismuth oxyhalide BiOX (X = Cl, Br, I) has been regarded as a novel photocatalyst with excellent photocatalytic activity for the degradation of organic pollutants. Methods: In this study, $BiOCl_xBr_{1-x}$ ($0 \le x \le 1$) solid solution photocatalytic materials were synthesized by a simple alcoholysis method at room temperature. The as-synthesized samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and diffuse reflectance spectroscopy (DRS). The photocatalytic activity of samples was evaluated by degrading Methyl Orange (MO) under the irradiation of UV light. Results: XRD results indicated that the as-prepared photocatalysts were tetragonal crystal structure. SEM observation showed that the particles of samples were regular with lamellar plate morphology. DRS calculation exhibited that their band gaps ranged between 3.23 and 2.83 eV with different Cl/Br ratios. The photocatalystic tests showed that $BiOCl_{0.5}Br_{0.5}$ exhibited the best photocatalystic activity with the MO discoloration ratio near 90% within 90 min irradiation at pH=7. Conclusion: $BiOCl_xBr_{1-x}$ ($0 \le x \le 1$) solid solution photocatalytic materials might have potential applications in the sewage treatment.

Keywords- Bismuth oxyhalide; alcoholysis method; Methyl Orange; Photocatalystic degradation; Band gap

I. INTRODUCTION

With the development of global industrialization process and the increasingly environmental pollution, environmental problem has become an important issue affecting human survival and development in the 21st century [1]. Because of photocatalytic technology can change solar energy into electrical energy and chemical energy, photocatalytic material has important applications in the respect of photodegradation of pollutants in air and water [2, 3]. In conventional photocatalytic material , TiO_2 is widely noted because of its non-toxic, good chemical stability, strong oxidation ability, etc. However, TiO_2 has a wide band gap (about 3.2eV), the absorption wavelength of it is less than 387nm, only can use the energy of ultraviolet light that is 4 % of sunlight, and response to a narrow range, which greatly limits its practical application [4-6].

Bismuth oxyhalide BiOX (X = Cl, Br, I) as a novel photocatalyst, exhibiting excellent photocatalytic performance because of its layered structure and suitable band gap, and the photocatalytic activity gradually increased with the atomic number of halogen increases [7, 8]. In Additional, Bismuth oxyhalide photocatalyst also has high stability and good development potential. Bismuth oxyhalide compounds have recently been found to possess remarkable photocatalytic activities under UV and visible-light illumination. The band gap of BiOX (Cl, Br, I) has been estimated to be between 3.19-3.44 eV, 2.64-2.91 eV and 1.77-1.92 eV, respectively. The structural feature of BiOX (Cl, Br, I) comprises a layer of $[Bi_2O_2]$ slabs interleaved by double slabs of halogen atoms. The internal static electric fields between the $[Bi_2O_2]^{2+}$ and halogen anionic layers are believed to induce the efficient separation of photogenerated electron–hole pairs [9].

Recently, BiOX (X=Cl, Br, I) has been attracted special attention because of its good photocatalytic activity and stability [10]. For Bismuth oxyhalide BiOX (X = Cl, Br, I), BiOCl can only absorb UV light because of its wide band gap , while the ultraviolet light in sun's was less than 4% , 60% of visible light can not be used , which limits its efficient use of solar energy [11-13]. Although BiOBr and BiOI are able to absorb a portion of visible light, they are not enough to apply to environmental pollution control in practical. In order to further improve the photocatalytic activity of BiOX, morphology modulation, noble metal loading and semiconductor combination have been widely applied [10]. Therefore, it is very important to improve its photocatalytic efficiency further to be suitable for practical applications; semiconductor composite is a good way [14-16]. Layered BiOX (X = Cl, Br, I) are a kind of newly exploited efficient photocatalysts, and their light response can be tuned from UV to visible light range. The properties of semiconductors are dependent on their morphologies and compositions as well as structures, and this also offers the guidelines for design of highly-efficient photocatalysts [17]. Until now, different BiOX micro/nanostructures have been successfully synthesized by utilizing hydro-/solvothermal, chemical vapor transport, reverse microemulsions, and sonochemical methods, which usually involved extremely high temperature, long reaction time, sharp thermal gradients, and hard-control process [18].

Herein, $BiOCl_xBr_{1-x}$ solid solution photocatalytic materials were synthesized by a simple alcoholysis

method, made a degradation of methyl orange (MO) under ultraviolet irradiation, $BiOCl_xBr_{1-x}$ composite photocatalytic materials exhibits higher photocatalytic activity than single-phase BiOCl or BiOBr , and $BiOCl_{0.5}Br_{0.5}$ have the best activity.

II. EXPERIMENTAL SECTION

A. Preparation

$BiOCl_xBr_{1-x}$ composite photocatalytic materials was synthesized by a simple alcohol solution at low temperature, All reagents were of analytical grade and used directly without further purification. First , 0.02mol Bi $(NO_3)_3 \cdot 5H_2O$ was added to a certain amount of absolute ethanol , ultrasound and magnetic stirring alternately until dissolved completely . The final sample with x is 1, 0.75, 0.5, 0.25 and 0 was labeled as BiOCl, $BiOCl_{0.75}Br_{0.25}$, $BiOCl_{0.5}Br_{0.5}$, $BiOCl_{0.25}Br_{0.75}$ and BiOBr. Then a stoichiometric ratio of KBr and KCl were dissolved in an appropriate amount of deionized water, and added into the mixed solution of Bi $(NO_3)_3 \cdot 5H_2O$ and absolute ethanol dropwise. After strong magnetic stirring for 6h, the resulting precipitates were filtered and washed several times with ethanol and distilled water until neutral. Finally, the precipitates were dried at 80 ℃.

B. Characterization

The phase analysis was characterized by D/MAX-3B type X-ray diffractometer(Japanese company), scanning speed is 4°/min, scanning range is 10~80℃, targe is Cu-K_α, wavelength is 1.5178Å, pipe pressure is 40KV, tube current is 30mA, and scanning way is continuous scanning. The morphology of the sample was carried by FEISirion200 scanning electron microscope(Dutch philips company), main technical indicators: when the resolution is more than 10 kv, 1.5 nm; Greater than 1 kv, 2.5 nm; More than 500 kv, 3.5 nm, accelerating voltage is 200V~30KV, interior diameter is 284nm, sample analysis working distance is 5mm. The Ultraviolet-visible diffuse reflection spectrum (DRS) was determinated by UV - vis DRS(shimadzu) with an integrating sphere attachment, $BaSO_4$ as the reference, scanning wavelength is 200 ~ 800 nm.

C. Photocatalytic activity measurements

The photocatalytic activity of sample was evaluated by degradeing methyl orange (MO) under the ultraviolet light, and its photocatalytic performance was testing on the ultraviolet-visible spectrophotometer. Generally, a certain gram of the photocatalyst was added to 100 mL of MO solution, and the suspensions were stirred in the dark for 60 min to ensure adsorption /desorption equilibrium prior to UV-light irradiation. At regular time intervals of irradiation, 5 ml of the samples was collected from the reactor for measurements of MO concentrations, using a 722- type UV–vis spectrophotometer at thewavelength of 482 nm. The discoloration ratio was calculated as follows: $D(\%)=(C_0-C_t)/C_0\times100$, where C_t and C_0 are the concentrations of MO at irradiation time t and 0 (the time to obtain absorption–desorption equilibrium) in the aqueous solution, respectively.

III. RESULTS AND DISCUSSION

A. Characterization results

The XRD patterns of $BiOCl_xBr_{1-x}$ composite material with different ratio are illustrated in Figure1, where it can be seen that the samples have intense diffraction and the catalysts are well crystallized. It is can been seen that BiOCl and BiOBr have no other impurity peak from the diffraction peak, explain the synthetic samples are pure phase(JCPDS6-249 and JCPDS 73- 2062). Moreover, It can be clearly observed that $BiOCl_{0.5}Br_{0.5}$ composite shows the coexitence features between BiOCl and BiOBr phase, and there are no other impurity phase. Interestingly, diffraction peaks at 2θ=24.12 ° , 32.57 ° and 54.3 ° shift to a smaller diffraction angle regularly, reveals that the as-prepared $BiOCl_xBr_{1-x}$ composites are a set of solid solutions. No other phase and impurity peak are detected, indicating that the as-prepared catalysts have extremely high purity and single phase.

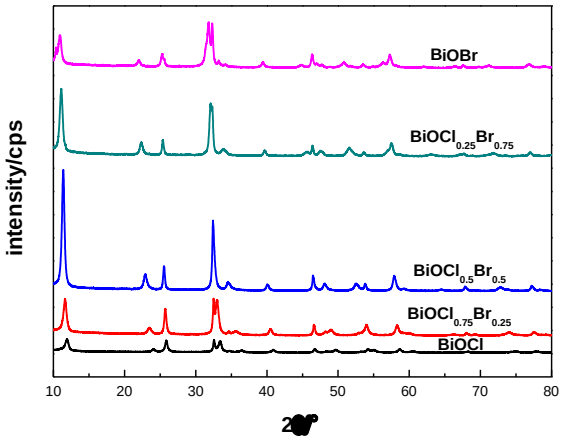

Figure1. XRD patterns of $BiOCl_xBr_{1-x}$ solid solutions

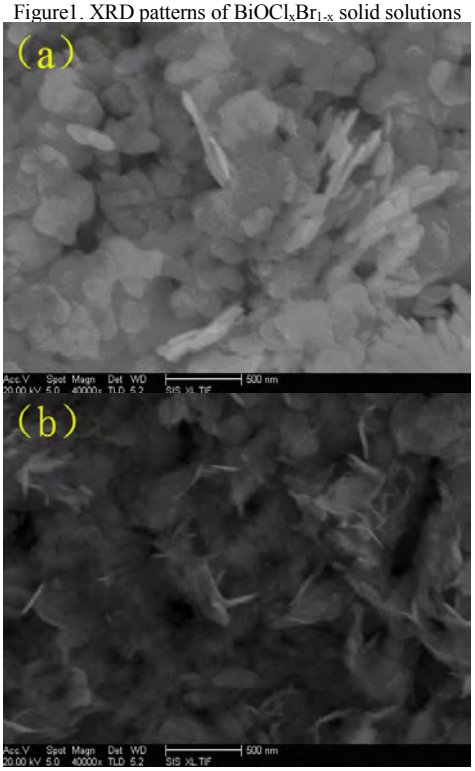

Figure 2. SEM images of $BiOCl_xBr_{1-x}$, (a)BiOCl; (b) $BiOCl_{0.5}Br_{0.5}$

The surface morphology of $BiOCl_xBr_{1-x}$ samples were observed by SEM as shown in Figure 2. Figure 2(a) showed that the as-prepared BiOCl catalyst is the lamellar structure of homogeneously, the crystallinity is high,the particle dispersion is good, and no obvious phenomenon of reunion between grain. Figure 2(b) illustrate that there are many more acicular structure on the basis of lamellar structure, making the advantages of BiOCl catalyst mainly include their bigger specific surface area, completely contact between with organic dye, and better photocatalytic effect.

Figure 3 shows the resulting of UV-vis diffuse reflection spectrum of the sample. As you can see from figure, the absorption of BiOCl in the visible area is negligible, and the absorption edge of $BiOCl_xBr_{1-x}$ gradually red shift with the increase of content of Br, the data listed in Table 1.

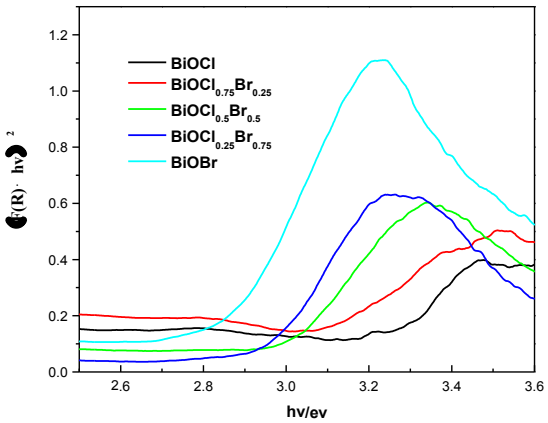

Figure 3. DRS patterns of $BiOCl_xBr_{1-x}$

TABLE 1. DRS calculation results of $BiOCl_xBr_{1-x}$

	BiOCl	$BiOCl_{0.75}Br_{0.25}$	$BiOCl_{0.5}Br_{0.5}$	$BiOCl_{0.25}Br_{0.75}$	BiOBr
Absorption wavelength / nm	252.22	267.41	343.05	361.84	381.65
Band gap / eV	3.23	3.05	3.03	2.96	2.83

The band gap energy of semiconductor can be calculated from the following formula: $Rhv=A(hv-Eg)^{1/2}$. Therefore, the band gap energy (E_g) of sample can be estimated by the figure of $(Rhv)^{1/2}$ to photon energy (hv). The intercept of tangent on the X axis is akin to the band gap energy of sample. The estimated band gap energy is also summarized in Table 1. The band gap of BiOBr was evaluated for 2.83 eV, and BiOCl was 3.23 eV, which showed a good agreement with related literature. It can be seen that the band gap energy of $BiOCl_xBr_{1-x}$ gradually decreases with the increase of content of Br.

B. Photocatalytic Evaluation

Figure 4 is the degradation curve of methyl orange with different concentration. What we can see from the figure is that the smaller the concentration of methyl orange is, the better the photocatalytic effect becomes, after 90min, the degradation rate of methyl orange solution with 5mg/L was about 90%, and 10mg/L reached about 53%, and the degradation rate has a tendency to continue to improve with the growth of time.

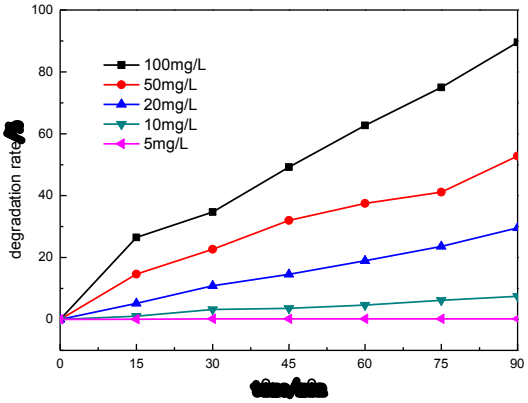

Figure 4. Effect of MO different concentrations on its decolorization rate

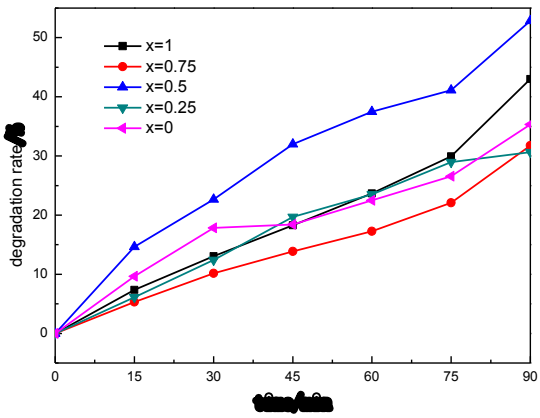

Figure 5. Effect of Cl/Br ratio on MO decolorization rate

Figure 5 shows degradation situation of $BiOCl_xBr_{1-x}$ composite materials with different composite ratio on methyl orange solution, as can be seen from the diagram, the photocatalytic effect of $BiOCl_{0.5}$ $Br_{0.5}$ is best, and the decoloring rate reach 53% after 90 min, the catalytic effect of BiOCl and BiOBr is not better than $BiOCl_{0.5}$ $Br_{0.5}$, but stronger a bit than $BiOCl_{0.75}$ $Br_{0.25}$ and $BiOCl_{0.25}$ $Br_{0.75}$.

The impact of the quality of $BiOCl_{0.5}$ $Br_{0.5}$ to light catalytic activity was evaluated by degradateing 10mg/L MO under ultraviolet light, as shown in Figure 6. It can be seen the photocatalytic effect is not obvious when m=0.1g, only about 10% after 90 min, the degradation rate has reached around 50% when m=0.2g, and the decolorization rate has a tendency to continue to improve with the time growth, the photocatalytic effect is also improved with the quality increases,but the effect is not obvious, so the best choice is 0.2g. The possible reason for this phenomenon might be attributed to the fact that, with catalyst dosage increasing below the optimum value, the active sites on the photocatalyst surface increased and accordingly reactive

species increased; when the catalyst dosage increased above the optimum value, photocatalytic activity decreased due to the interception of the light photon by the higher concentration suspending particles.

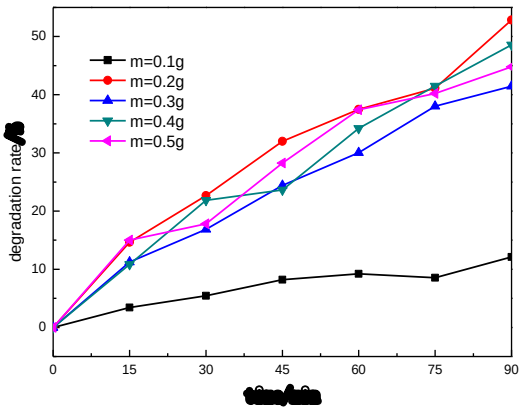

Figure 6. Effect of catalyst dosage on MO decolorization rate

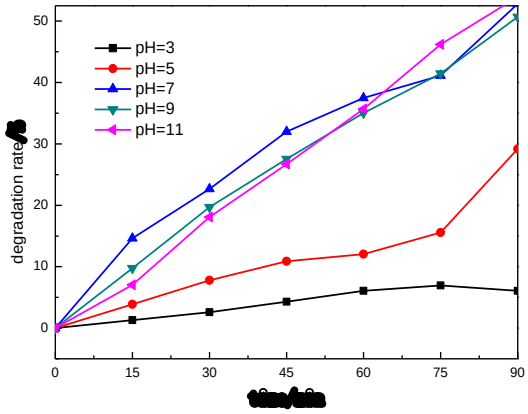

Figure 7. Effect of pH on MO decolorization rate

The pH is an important factor of the photocatalytic reation. You can see from figure 8 that catalytic effect is best when the methyl orange solution is neutral or alkaline, the decoloring rate is above 53% after 90 min, and the decolorization rate has a tendency to continue to improve. The effect is poorer under the condition of acidic, and the decoloring rate less than 10% after 90 min while pH = 3, So, by contrast, alkaline conditions ia more conducive to the light catalytic degradation of organic pollutants than acidic conditions.

IV. CONCLUSION

In this work, $BiOCl_xBr_{1-x}$ composite photocatalytic materials was synthesized by a simple alcohol solution at low temperature, and had high photocatalytic activity for MO photodegradation. XRD indicated that the as-prepared photocatalysts were tetragonal crystal structure, SEM showed that the particles of samples were lamellar plate morphology, and DRS told us that their band gaps were between 3.23 and 2.83 eV. $BiOCl_{0.5}Br_{0.5}$ photocatalyst had the best photocatalysis efficiency, and the degradation rate at 90min was about 90% when the concentration of MO was 5mg/L, the pH value was 7 and the the dosage of catalyst was 0.2g. therefore, $BiOCl_{0.5}Br_{0.5}$ composite photo catalyst might have potential applications in the sewage treatment.

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