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Enhancement of Visible Light Photocatalysis Performances of Bi$_2$MoS$_2$O$_4$ Nanoplates

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Abstract: A novel Bi$_2$MoS$_2$O$_4$ nanoplate photocatalysts with high-energy efficiency and high-activity have been successfully synthesized by a reflux method. The visible-light response of Bi$_2$MoS$_2$O$_4$ could extend from 480 to 630nm compared with Bi$_2$MoO$_6$. Comparing with Bi$_2$MoO$_6$, the photocatalytic activities of Bi$_2$MoS$_2$O$_4$ sample increased about 0.4 and 4.6 times for degradation of methylene blue (MB) under UV and visible-light ($\lambda$>510nm) irradiation, respectively. Density functional calculations revealed that Bi$_2$MoS$_2$O$_4$ had narrower band gap and wider valence bandwidth compared with Bi$_2$MoO$_6$ because S 3p orbitals contributed to the valence band formation. The high energy efficiency of Bi$_2$MoS$_2$O$_4$ photocatalysts came from narrow bandgap and the high activity came from wider and dislocated valence band of Bi$_2$MoS$_2$O$_4$. Furthermore, the synthesizing of Bi$_2$MoS$_2$O$_4$ could afford guidance for designing the other high-energy efficient and high-active photocatalysts.

Keyword: photocatalyst, high energy efficiency, high activity, Bi$_2$MoS$_2$O$_4$
Introduction

Over the last 30 years, the studies of semiconductor photocatalysts for clean hydrogen energy production and environment decontamination have attracted much interest. In general, the efficient photocatalysts are usually wide-gap semiconductors, such as TiO$_2$, ZnO and SrTiO$_3$. These wide band gap semiconductors can only show activity under UV light irradiation, which limits their practical applications. From the viewpoint of solar energy utilization, the development of a photocatalyst with high activity under visible-light is indispensable. One effective way to narrow the band gap is to elevate the valence band of photocatalysts into a more negative position by anion substitution. The doping of foreign elements into UV active metal oxides is a conventional method employed for the preparation of visible-light-responsive photocatalysts. However, dopants in the photocatalyst act not only as visible-light absorption centers, but also as recombination sites between photogenerated electrons and holes. In contrast, some non-oxides, for example (oxy)nitrides and oxysulfides, contain N or S as constituent elements that form the tops of the valence band. Note that this type of material differs from materials doped with nitrogen or sulfur. Thus, photogenerated holes can migrate smoothly in the valence band of the material. A range of non-oxide materials for photocatalytic overall water splitting have been developed by Domen’ group. They found that non-oxides could be function as stable photocatalysts for water reduction and oxidation under visible-light irradiation. The discovery of non-oxide photocatalysts is expected to reinvigorate research on photocatalysts for solar energy.

Recently, some works revealed that Bi$_2$MoO$_6$ could perform as an photocatalytic material and possess excellent photo-to-current conversion efficiency. Its unique combination of physical and chemical properties, in terms of molecular and electronic versatility, reactivity, and stability,
make us believe they are fine photocatalytic candidate material. However, an intrinsic band gap of \( \text{Bi}_2\text{MoO}_6 \) allowed only a small portion of visible-light region to be absorbed. Therefore, further improving their visible-light response for practical application is significant and meaningful.

Fortunately, sulfidation of \( \text{Bi}_2\text{MoO}_6 \) could be a feasible method to solve this problem. To the best of our knowledge, there have been a few reports regarding the application of oxysulfides employed as photocatalysts with broad visible-light response. For example, \( \text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5 \) with a narrow band gap (about 2 eV) is a high-energy-efficient photocatalyst for \( \text{H}_2 \) and \( \text{O}_2 \) evolution with sacrificial reagent\(^{11}\). In contrast to the case of the large energy gap of \( \text{Sm}_2\text{Ti}_2\text{O}_7 \) (\( \sim 3.6 \) eV), the small band gap energy of \( \text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5 \) is attributable to the doping of \( \text{S}^{2-} \).

In our work, novel \( \text{Bi}_2\text{MoS}_2\text{O}_4 \) photocatalyst was successfully synthesized by a reflux method. And its photocatalytic and photoelectrochemical performances were investigated systematically. Density functional calculations revealed that when S anion replaces O anion in \( \text{Bi}_2\text{MoO}_6 \), \( \text{Bi}_2\text{MoS}_2\text{O}_4 \) had narrower band gaps and wider valence bandwidth compared with \( \text{Bi}_2\text{MoO}_6 \). Experimental results proved that \( \text{Bi}_2\text{MoS}_2\text{O}_4 \) possess high-efficiency and high-activity photocatalytic behavior.

**Experimental Section**

**Synthesis of the sample.**

\( \text{Bi}_2\text{MoS}_2\text{O}_4 \) was synthesized by a reflux method. All chemicals used were analytic grade reagents without further purification. In a typical synthesis process of \( \text{Bi}_2\text{MoS}_2\text{O}_4 \), \( \text{Na}_2\text{S} \) (3.6 g) was added into the mixture of \( \text{(NH}_4\text{)}_6\text{Mo}_7\text{O}_{24} \cdot 12\text{H}_2\text{O} \) (0.6621 g) and water (60 mL), and a stable, yellow homogeneous solution was obtained. The color of solution became brown after the pH value adjusted to 7—8 by HCl. Then, 3.6375 g \( \text{Bi(NO}_3\text{)}_3 \) was added and brown precipitate solution was
under reflux at 70°C for 10h. The resulting samples were collected and washed with deionized water and dried at 80°C in air. Bi$_2$MoO$_6$ sample was synthesized by hydrothermal reaction according to reference.$^{16}$

**Characterization.**

Purity and crystallinity of the as-prepared sample was characterized by XRD on Bruker D8-advance diffract-meter using CuKα radiation. The XRD data for indexing and cell-parameter calculation were collected in a scanning mode with a step length of 0.02° and a preset time of 3 s/step. The ratio of Bi/Mo/S in the sample was determined with a sequential X-ray fluorescence spectrometer (XRF-1700, Shimazu). The morphologies and structures of the prepared samples were examined by TEM. Images at low magnification were obtained on a JEOL JEM-1010 instrument operated at an accelerating voltage of 120kV. High-resolution images were obtained on a JEOL JEM-2010 instrument (accelerating voltage: 200kV). Diffuse reflection spectra (DRS) were obtained on a Hitachi U-3010 UV-Vis spectrophotometer. Chemical characterization of the sample surface was recorded with X-ray photoelectron spectroscopy (XPS ULVAC-PHI, Quantera). The charge effect was calibrated using the binding energy of C1s.

**Photocatalytic Tests and Photoelectrochemical Performances.**

The photocatalytic activities of the Bi$_2$MoS$_2$O$_4$ and Bi$_2$MoO$_6$ were evaluated by degradation of MB under 11-W bactericidal lamp with 254nm and 500W Xe lamp with the 420, 450, 480, 510nm cutoff filter. The reaction cell was placed in a sealed black box of which the top was opened and the varied cutoff filters were placed to provide visible light irradiation. In each run, 50mg of the Bi$_2$MoS$_2$O$_4$ or Bi$_2$MoO$_6$ catalyst was added to 100mL of the MB solution. After the suspension
was stirred for 60 min, the light was turned on to initiate the reaction. The concentration of the MB solution was monitored using a Hitachi UV-vis spectrophotometer each 30 min.

The electrochemical and photoelectric studies were performed on a CHI 660B electrochemical system (Shanghai, China) using a standard three-electrode cell with a working electrode, a platinum wire counter electrode, and a standard calomel electrode (SCE) reference electrode. The working electrodes were prepared by dip-coating: Briefly, 5 mg of photocatalyst was suspended in 3 mL water to produce a slurry, which was then dip-coated on a 20 mm×40 mm indium-tin oxide (ITO) glass electrode. Electrodes were exposed to UV light for 3 days to eliminate water and subsequently dried at 353 K for 2 days. All investigated working electrodes were of similar thickness (0.1-0.12 mm). Photoelectrochemical properties were measured with a 500 W Xe lamp. Unless otherwise stated, the intensity of light was 41 mW cm\(^{-2}\) with 420 nm cutoff filter. The photocurrents were measured at the potential of 0.5 V. The electrochemical impedance spectroscopy (EIS) was carried out at the open circuit potential. A sinusoidal ac-perturbation of 5 mV was applied to electrode over the frequency range of 0.05-10\(^{5}\) Hz. During all the measurements, the electrolyte was 0.1 M Na\(_2\)SO\(_4\) solution.

**Band Structure Calculation.**

In order to obtain insight into the special properties of the Bi\(_2\)MoS\(_X\)O\(_{6-X}\), a series of first-principle calculations were performed to assess the influence of S anion on the electronic states and optical properties of Bi\(_2\)MoS\(_X\)O\(_{6-X}\). The lattice parameters and the atomic coordinates of Bi\(_2\)MoO\(_6\), which were optimized and used in the calculations, are listed in the Supporting Information (Table S1). The plane-wave pseudo-potential method\(^{17-18}\) was used to optimize crystal geometries, to obtain the corresponding electronic band structure. In these calculations, the energy cutoff was chosen at
340 eV. The Brillouin-zone sampling was performed by using a k-grid of 2×2×2 points for the calculations. Ultrasoft pseudopotentials were used for bismuth, molybdenum, oxygen, and sulfur atoms. The generalized gradient approximation (GGA) with Perdew, Burke and Ernzerhof (PBE) exchange correlation functional was adopted. The presence of S anions was modeled by removing O anions in Bi$_2$MoO$_6$ cells, thus, forming Bi$_2$MoS$_x$O$_{6-x}$ compound.

**Results and discussion.**

**Effect of S anion Substitution on Energy Efficiency.**

The electronic structure was investigated on the basis of plane-wave density function theory program package CASTEP. To understand the qualitative impact of S ion on the band structure of Bi$_2$MoO$_6$, the unit cells of Bi$_2$MoS$_x$O$_{6-x}$ were constructed by different quantitative substituting S ion at O ion lattice site. The variations of band structures of Bi$_2$MoO$_6$, Bi$_2$MoS$_2$O$_4$ and Bi$_2$MoS$_6$ were shown in Fig. 1. The zero energy corresponds to Fermi-level (E$_F$). For the Bi$_2$MoO$_6$ sample, the band gap was estimated to be 1.25 eV. When S anions replaced O anions in Bi$_2$MoO$_6$, the electronic band structures started to change. The band gap of Bi$_2$MoS$_2$O$_4$ was estimated to be 0.30 eV. For the Bi$_2$MoS$_6$ sample, the band gap was not distinct and property of semiconductor had gone as shown in the Fig. 1c. Generally, the band gap calculated by DFT was smaller than that obtained by experiment, which was frequently pointed out as a common feature of DFT calculations. However, the trend of energy gap variation from the calculations was expected to be reasonable and reliable. The calculated results revealed the band gap of Bi$_2$MoS$_x$O$_{6-x}$ became narrow monotonically as the value of x increased, which played a crucial role in determining photocatalytic energy efficiency. The narrow band gap was one of the desirable properties of...
photocatalyst because light absorption for this kind of material can occur more efficiently as compared to that for material with a wide band gap.

Fig. 2 shows the UV-visible diffuse reflectance spectra of Bi$_2$MoO$_6$ and Bi$_2$MoS$_2$O$_4$. It is clear that the absorption edge of Bi$_2$MoS$_2$O$_4$ red shifted obviously compared with that of Bi$_2$MoO$_6$. The experimental data confirmed theoretical calculation results above. Their band gaps were calculated by the equation $\alpha \nu = A(\nu - E_g)^{n/2}$, in which $\alpha$, $\nu$, $A$ and $E_g$ are absorption coefficient, light frequency, proportionality constant, and band gap, respectively (in the equation, $n$ is decided by the characteristics of the transition in a semiconductor). So the band gaps were about 2.72 and 2.08 eV for Bi$_2$MoO$_6$ and Bi$_2$MoS$_2$O$_4$, respectively.

Furthermore, in order to better understand the differences of photoelectric response of Bi$_2$MoO$_6$ and Bi$_2$MoS$_2$O$_4$, Mott-Schotty (MS) measurements were used to investigate this issue as shown in the Fig. 3. The anodic photocurrent was observed both on Bi$_2$MoO$_6$/ITO and Bi$_2$MoS$_2$O$_4$/ITO electrode that was consistent with that of typical n-type semiconductors. During each switch-on and switch-off event, a fast and uniform photocurrent response was observed in both electrodes (Bi$_2$MoS$_2$O$_4$/ITO electrode and Bi$_2$MoO$_6$/ITO electrode) under visible-light irradiation ($\lambda>$450nm). This photoresponsive phenomenon was entirely reversible, which confirmed Bi$_2$MoS$_2$O$_4$ was a potential photofunctional material. Moreover, the photocurrent of Bi$_2$MoS$_2$O$_4$/ITO was about 3.5 times as high as that of Bi$_2$MoO$_6$/ITO, which indicated that the number of photoinduced electrons and holes was improved through the wider visible-light absorption region.

The photoactivity of the sample was evaluated by degradation of MB, a hazardous pollutant as well as a common model compound to test the photodegradation capability of photocatalysts.
Fig. 4 showed reaction constant of MB degradation over Bi$_2$MoO$_6$ and Bi$_2$MoS$_2$O$_4$ powder as a function of wavelength. When a 420nm cutoff filter was used, these two reaction constant of decomposition were similar ($k_1$=0.00491, $k_2$=0.00462, respectively). It was notable that the rate of MB decomposition decreased with increasing cutoff wavelength, which was in good agreement with the UV-vis diffuse reflectance spectra of Bi$_2$MoS$_2$O$_4$ and Bi$_2$MoO$_6$, indicating the present reaction was driven by a visible-light absorption. However, the trend of the rate descend was different. The activity of Bi$_2$MoS$_2$O$_4$ powder with visible light of a wide range (420nm$<\lambda<$510nm) was clearly observed. When the cutoff filter of 510nm was used, the activity (degradation rate constant $k=0.00282$) was also detected. While the activity of Bi$_2$MoO$_6$ powder was almost similar to that of blank experiment ($k_1=0.00050$, $k_2=0.00038$, respectively) when a cutoff filter of 510nm was used. It concluded that Bi$_2$MoS$_2$O$_4$ photocatalyst kept excellent degradation activity with broad visible-light irradiation, verifying the high energy efficiency property in a broad visible-light region.

**Effect of S anion Substitution on Activity.**

Fig. 5 showed the partial the densities of states (DOS) for Bi$_2$MoO$_6$, Bi$_2$MoS$_2$O$_4$ and Bi$_2$MoS$_6$. In an effort to obtain more exact information on the atom-specific character of each band, the DOS was further decomposed into the atom-orbital-projected DOS (PDOS) in term of atomic and angular momentum contribution. As shown in the Fig. 5a, the top of the valence band (VB) of Bi$_2$MoO$_6$ was mainly formed by O2p orbitals. The bottom of the conduction band (CB) was formed by Mo4d and O2p orbitals. The valence bandwidth of Bi$_2$MoO$_6$ was ca. 6.8 eV. When S anions replace O anions, S anion will take part in the formation of electronic band structure. In Fig. 5b, the top of the valence band of Bi$_2$MoS$_2$O$_4$ was formed by hybrid orbitals O2p and S3p. The
valence bandwidth of Bi$_2$MoS$_2$O$_4$ was ca. 7.2 eV, which was wider than that of Bi$_2$MoO$_6$ because the S3p orbitals contributed to the valence band formation. In Fig. 5c, the top of the valence band of Bi$_2$MoO$_6$ was mainly formed by S3p orbitals and its valence bandwidth was the widest of all. Although DOS obtained by the PW-DFT calculations did not indicate the absolute values, we can compare the degree of dispersion of the valence bands which play a crucial role in determining photocatalytic activity. Consequently, the substitution of S anions for O anions increased valence bandwidth owing to the wider hybrid orbitals of S3p and O2p.

In our investigation, valence band XPS spectra was used for the observation of extra electronic states above the valence band of Bi$_2$MoO$_6$. Fig. 6 showed the valence band XPS spectra of Bi$_2$MoO$_6$ and Bi$_2$MoS$_2$O$_4$. A comparison in the range of binding energy = 0—10 eV (Fig. 6) showed the difference between valence band of Bi$_2$MoO$_6$ and Bi$_2$MoS$_2$O$_4$. In valence band of Bi$_2$MoS$_2$O$_4$, additional diffusive electronic states (about 1.1 eV) were observed above the valence band edge of Bi$_2$MoO$_6$. The additional electron density of states can explain the red-shift absorption of Bi$_2$MoS$_2$O$_4$. S states would contribute to the band-gap narrowing and valence bandwidth broadening by mixing with O states. This result was accord with theoretical calculation conclusion. It was clear that substitution of S anions can extend the spectral response to the broad visible region and increase migration efficiency of photoinduced electrons and holes theoretically owing to the wider and more dispersed valence band.$^{19}$

In order to better understand the differences in activities of Bi$_2$MoO$_6$ and Bi$_2$MoS$_2$O$_4$, their electrode were further examined under electrochemical conditions. Electrochemical impedance spectroscopy (EIS) measurements were performed to investigate the photogenerated electron-hole pairs separation process on ITO/ Bi$_2$MoS$_2$O$_4$ electrode and ITO/Bi$_2$MoO$_6$ electrode (Fig. 7).
According to conventional double-layer theories, the electrical double layer at solid electrode behaved as a frequency distribution impedance instead of a pure capacitance due to the surface heterogeneity. When the charge transfer reaction occurred, the Nyquist plot was a semicircle; when semi-infinite diffusion was rate-determining step, a linear with a slope of 45° appeared. In our case, only one semicircle on the EIS plane suggested charge transfer occurring. The diameter of the arc radius on the EIS Nyquist plot of ITO/ Bi$_2$MoS$_2$O$_4$ electrode was smaller than that of ITO/Bi$_2$MoO$_6$ electrode both under UV and visible-light (λ>450nm) irradiation. The smaller arc radius of the EIS Nyquist plot suggested a higher efficiency of charge separation. Thus, in the case of Bi$_2$MoS$_2$O$_4$ the photogenerated electron-hole pairs were easier separated and transferred to the sample surface.

The photocatalytic activity of the Bi$_2$MoO$_6$ and Bi$_2$MoS$_2$O$_4$ has also been studied in photodegradation of MB under UV irradiation. As shown in the Fig. 8, the reaction constant for Bi$_2$MoO$_6$ was 0.0072. The photocatalytic activity of Bi$_2$MoS$_2$O$_4$ was significantly increased and the reaction constant is 0.0103 which increased 40% compared with that of Bi$_2$MoO$_6$. The excellent photocatalytic performance of Bi$_2$MoS$_2$O$_4$ was attributed to better efficiency of photogenerated electron-hole pairs, which resulted in the increment of probability of the surface reaction of electrons and holes with water molecules.

**Effect of S anion Substitution on Crystal Structure.**

To explore the chemical environment surrounding Mo and Bi element in Bi$_2$MoS$_2$O$_4$, the sample of Bi$_2$MoO$_6$ was selected as standard for XPS measurement. Mo3d and Bi5f XPS results of the Bi$_2$MoO$_6$ and Bi$_2$MoS$_2$O$_4$ samples were shown in Fig. 9a and 9b, respectively. The binding energies of Mo3d3/2 and Mo3d5/2 are 235.9 eV and 232.6 eV in the oxide form of Bi$_2$MoO$_6$,
which could be characteristic of Mo species in MoO₆ octahedron. But in the case of Bi₂MoS₂O₄, the binding energy of the peak of Mo3d3/2 and Mo3d5/2 reduced about 1.5 eV, which was attributable to the change of chemical environment surrounding Mo. Some mixed stated such as S—Mo—O may be the case. The large change of binding energy of Mo in the XPS results displayed that the S anions replace O anions in MoO₆ octahedron rather than were interstitial doping which could not influence the oxidation state of Mo element. The XPS spectra of Bi4f in Bi₂MoO₆ can be fitted as two spin orbital splitting peaks Bi4f7/2 and Bi4f5/2 at 159.4 eV and 164.8 eV, indicating that Bi ions were in Bi—O environment. Note that the same result was obtained in Bi₂MoS₂O₄, which ruled out the present of Bi—S environment. At last, we can make a conclusion that S anions replaced O anions which were in MoO₆ octahedron. Quantitive results by XRF gave the atomic ratio of 1.89:1:2.05 for Bi/Mo/S. It was close to the ideal value of 2:1:2 considering the instrument error. So the formula of the sample was Bi₂MoS₂O₄.

Supporting Information Fig. S1 showed the XRD patterns of Bi₂MoO₆ and Bi₂MoS₂O₄. Comparing with Bi₂MoO₆, it can be seen that most of diffraction peaks of Bi₂MoS₂O₄ were shifted to a lower-angle side. The shift was reasonable because the ion radii of S²⁻ was larger than that of O²⁻.

There are many reports about doping of a foreign element into photocatalysts with wide band gaps in order to respond to visible light. Unfortunately these doping ions act as defect recombination centers for the photoexcited charge carriers. These studies indicated that control of defects formation in the crystal structure was important for the photocatalytic properties. In Bi₂MoS₂O₄, when S anions were partly substituted for O anions sites in the crystal lattice of Bi₂MoO₆, S states contributed to the formation of valence by mixing with O states. The
visible-light response of Bi$_2$MoS$_2$O$_4$ was due to the electron transition from the electron donor levels formed by hybrid orbitals of S3p and O2p to the conduction band. Thus, a donor level in the forbidden band did not appeared, which did not cause the increase in the recombination centers between photogenerated electrons and holes.

**Morphologies and Durability of Bi$_2$MoS$_2$O$_4$.**

Morphologies and lattice structure of the Bi$_2$MoS$_2$O$_4$ were characterized by TEM. When the reaction time reached 10 h, some flake-shaped crystals emerge as shown in the Fig. 10a. The flake-shaped crystals in this sample displayed an irregularly flakes with size ranging from 100nm to 200nm. As shown in the corner of Fig. 10a, selective area electron diffraction (SAED) pattern of individual flat-lying nanoplates showed regular square diffraction spot array, which showed a typical single-crystalline structure array of sharp spots. The evidence for the formation of single-crystalline Bi$_2$MoS$_2$O$_4$ nanoplates could also be found in the magnified image as shown in Fig. 10b. The thickness of the nanoplates was difficult to clearly determine because the nanoplates were usually ultrathin and flat-lying on the Cu grid. The thickness was about 5 nm estimated through the enlarge edge in the Fig. 10b. HRTEM image was shown in Fig. 10c, which was the rectangle section in Fig. 10b. Combining the SAED pattern and HRTEM images, it can be measured that the interplanar distance was 0.349nm and 0.277nm, which agreed well with the lattice spacings of (131) and (002). Thus, the results suggested that the nanoplates could grow preferentially along these two directions. The nanoplate with the high crystallinity was advantageous for the photocatalytic activity.$^{23, 24}$

In order to further understand the mineralization properties of Bi$_2$MoS$_2$O$_4$, the decrease of TOC in the photodegradation of MB by was shown in Supporting Information Fig. S2. Supporting
Information Fig. S3 showed the results of repeated experiment for the durability of MB bleaching on Bi$_2$MoS$_2$O$_4$ under visible-light irradiation ($\lambda$>420nm), suggesting that Bi$_2$MoS$_2$O$_4$ showed relatively stable performance for MB bleaching. We evaluated the XRD pattern of the sample after the fifth run. The XRD pattern was almost similar to that of the asprepared sample (see Supporting Information Fig. S4). The stability of a photocatalyst is important to its application, doped TiO$_2$ photocatalysts sometimes suffer from this problem.

**Mechanism of Highly Energy Efficient and Highly Active Decomposing MB over Bi$_2$MoS$_2$O$_4$ nanoplate.**

Fig. 11 showed the band structures of Bi$_2$MoO$_6$ and Bi$_2$MoS$_2$O$_4$ derived from diffuse reflectance spectra and valence band XPS spectra. The band gap of Bi$_2$MoS$_2$O$_4$ was 0.64eV narrower than that of Bi$_2$MoO$_6$ because the S3p and O2p orbitals formed new hybrid valence bands at a more negative level than the O2p orbitals. In view of the efficient utilization of visible light and artificial light sources, photocatalyst with narrow band gap is desirable. In the Bi$_2$MoS$_2$O$_4$ powder, the number of photogenerated electrons and holes was increased because of the narrow band gap. Thus, the probability of the surface reaction of electrons and holes with MB molecules was increased. The enhancement of photocurrent of Bi$_2$MoS$_2$O$_4$/ITO under visible-light irradiation ($\lambda$>450nm) and the activity of Bi$_2$MoS$_2$O$_4$ powder with visible light of a wide range (420nm$<\lambda<$510nm), as mentioned above, could prove Bi$_2$MoS$_2$O$_4$ had the highly energy efficient property in a wide visible-light region.

According to the theoretical calculation and valence band XPS result, S3p orbitals contributed to the valence band formation and broaden valence bandwidth by mixing with O states (as shown in Fig. 11). The increasing of degree of dispersion and bandwidth of valence bands will promote
migration efficiency of photoinduced electrons and holes, and subsequently their diffusion. In the Bi$_2$MoS$_2$O$_4$ powder, as the migration efficiency of photoinduced electrons and holes was promoted, the possibility of the recombination of electrons and holes pairs was decreased. Thus, the number of the electrons and holes which were coupled with MB molecules was increased. EIS measurements above proved well this argument. Moreover, the degradation rate constant of Bi$_2$MoS$_2$O$_4$ was 1.4 times as that of Bi$_2$MoO$_6$ under UV irradiation due to much more electrons and holes taking part in photocatalytic process. It was clear that wide and dispersed valence band was responsible for the high photocatalytic activity.

Generally, photoogenerated electrons and holes have to migrate in a long distance to the surface active sites in photocatalysts with a large size. However, Bi$_2$MoS$_2$O$_4$ possess nanoplate structure, the size effects would decrease recombination of electrons and holes pairs. After all, the nanoplate was only several nanometers thick. Plenty of holes generated inside the crystalline had opportunity to transfer to the surface and act with the MB molecules.

**Conclusion.**

In summary, we have successfully developed a novel photocatalyst nanoplates Bi$_2$MoS$_2$O$_4$. This material showed favorable photocatalytic activity in bleaching MB. The enhanced photocatalytic efficiency and activity were attributed to modulated electronic structure by the substitution of S anion. Furthermore, this work provided some insight into design of new green heterogeneous photocatalysts for degradation of organic contaminants.

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References.


Figure caption

Fig. 1. Electronic band structures of (a) Bi$_2$MoO$_6$, (b) Bi$_2$MoS$_2$O$_4$ and (c) Bi$_2$MoS$_6$ calculated by a density of functional method.

Fig. 2. UV-vis spectra of Bi$_2$MoS$_2$O$_4$ nanoplates and Bi$_2$MoO$_6$ sample.

Fig. 3. Photoelectrochemical responses of Bi$_2$MoS$_2$O$_4$ and Bi$_2$MoO$_6$ electrodes under visible-light ($\lambda>450$nm) irradiation.

Fig. 4. The reaction constant of Bi$_2$MoO$_6$ and Bi$_2$MoS$_2$O$_4$ under various cutoff filters

Fig. 5. Projected densities of states of (a) Bi$_2$MoO$_6$, (b) Bi$_2$MoS$_2$O$_4$ and (c) Bi$_2$MoS$_6$ calculated by a density of functional method.

Fig. 6. Valence bands XPS spectra (-4 - 12 eV) of Bi$_2$MoO$_6$ and Bi$_2$MoS$_2$O$_4$.

Fig. 7. Electrochemical impedance spectroscopy (EIS) Nyquist plots of Bi$_2$MoS$_2$O$_4$ and Bi$_2$MoO$_6$ electrodes under UV irradiation and visible-light ($\lambda>450$nm).

Fig. 8. The reaction constant of Bi$_2$MoO$_6$ and Bi$_2$MoS$_2$O$_4$ under UV irradiation.

Fig. 9. X-ray photoelectron spectra of Bi$_2$MoO$_6$ and Bi$_2$MoS$_2$O$_4$, (a) Mo3d, (b) Bi4f.

Fig. 10. TEM images of Bi$_2$MoS$_2$O$_4$ sample: (a) treat in 70°C for 10 h. (b) HRTEM images of Bi$_2$MoS$_2$O$_4$ nanoplates, (c) HRTEM images of rectangle in b.

Fig. 11. Band structure of Bi$_2$MoO$_6$ and Bi$_2$MoS$_2$O$_4.$
Fig. 2.
Fig. 3.
Fig. 4.

![Graph showing reaction constant vs. wavelength for Bi2MoS2O4 and Bi2MoO6](image-url)
Fig. 5.

(a) Bi$_2$MoO$_6$
(c) $\text{Bi}_2\text{MoS}_6$
Fig. 6.
Fig. 7.
Fig. 8.

![Bar chart showing reaction rates](chart.png)
Fig. 9.
Fig. 10.
Fig. 11.

\[
\text{Bi}_2\text{MoO}_6 \\
\text{Conduction band} \\
e^- \\
\text{BG} = 2.72\text{eV} \\
h^+ \\
\text{Valence band O2p}
\]

\[
\text{Bi}_2\text{MoS}_2\text{O}_4 \\
\text{Conduction band} \\
e^- e^- e^- \\
\text{BG} = 2.08\text{eV} \\
h^+ h^+ h^+ \\
\text{Valence band S3p + O2p}
\]