



Photocatalytic reduction of bromate at C₆₀ modified Bi₂MoO₆ under visible light irradiation

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ABSTRACT

In the current work, Bi₂MoO₆ nanoparticles were prepared via hydrothermal method and obtained Bi₂MoO₆ nanoparticles were modified by C₆₀. The photocatalytic activity of the prepared Bi₂MoO₆ nanoparticles and C₆₀ modified Bi₂MoO₆ in the reduction of bromate ions were evaluated under visible light irradiation. It is observed that bromate ions can be reduced by Bi₂MoO₆ nanoparticles and the reduction rate of bromate ions was increased by the C₆₀ modification. Based on the analysis of photoluminescence spectra and electrochemical impedance spectroscopy of the Bi₂MoO₆ and C₆₀ modified Bi₂MoO₆, it is concluded that separation of photogenerated electron–hole pairs is enhanced via the modification of C₆₀ molecules onto Bi₂MoO₆. Thus, the photocatalytic activity of the Bi₂MoO₆ nanoparticles towards the reduction of bromate ions was enhanced. The effect of loading amount of C₆₀ on Bi₂MoO₆ nanoparticles on the bromate reduction was investigated. And, the reduction rate of bromate decreased with the solution pH value, which was discussed based on the electrostatic interaction. Effect of cations and anions on the reduction of bromate was investigated. The photogenerated electrons can be consumed by NO₃[−], which resulted in the decrease of BrO₃[−] reduction. The photocatalytic reduction of bromate decreased with the addition of K₂S₂O₈, which indicated that electrons played a dominant role in the reduction of bromate.

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1. Introduction

Bromide (Br[−]) is naturally present in surface water bodies, with concentrations varying from a few micrograms per liter to several milligrams per liter. It can be oxidized to form bromate (BrO₃[−]) in drinking water through disinfection processes such as ozonation, hypochlorination, chloramination, or a combination of ozonation and hypochlorination [1]. The World Health Organization recommends a provisional guideline value of 0.01 mg/L for drinking water. Various technologies for BrO₃[−] removal have been discussed, such as filtration, UV irradiation, arc discharge, coagulation, reducing agents such as ferrous iron, activated carbon techniques, and biological remediation [2–5]. However, an all-round removal technology of BrO₃[−] has not been established. Therefore, it is meaningful to develop a new option to remove BrO₃[−] from the water.

Recently, TiO₂ photocatalysis has been implemented to remove bromate ions. Mills et al. [6] reported that bromate was totally reduced to bromide in the presence of Pt/TiO₂ photocatalysts under UV irradiation of 254 nm. Noguchi et al. further investigated bromate decomposition using a TiO₂ photocatalyst that was modified

by pseudo-boehmite [7]. They found that the modified TiO₂ exhibited better performance in bromate reduction due to its higher isoelectric point as compared to unmodified TiO₂. Under UV irradiation, TiO₂ is excited to generate hole (h⁺) and electron (e[−]) pairs, and the holes subsequently react with adsorbed hydroxyl ions to generate hydroxyl radicals (•OH):



•OH is a strong oxidant while e[−] is a strong reducer. It has been widely agreed that e[−] takes part in reaction (3) to reduce bromate to bromide.

In recent years, the development of visible light photocatalysts has become one of the most important topics in photocatalysis research. Some novel complex photocatalysts responsible to visible light have been developed [8]. Kudo et al. found that Bi₂MoO₆ was able to carry out the photocatalytic O₂-evolution under visible light irradiation [9]. Bismuth molybdates have the general chemical formula of Bi₂O₃•nMoO₃ where n = 3, 2, and 1, corresponding to α, β, and γ phase, respectively. Such compounds and their mixtures are well-known owing to their good catalytic activities in selective oxidation of light hydrocarbons to produce many useful organic

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compounds [10]. Under visible light irradiation, the Bi_2MoO_6 with nanosize can be used as photocatalyst in degrading organic contaminants [11,12]. The above studies focus on the oxidation of organic contaminants via photogenerated hole and $\cdot\text{OH}$. On the other hand, application of photogenerated electrons of Bi_2MoO_6 in the removal of contaminants, especially reduction of bromate ions was not reported.

The fullerene C_{60} has been utilized in fuel cells, drug delivery devices, imaging agents in medicine, and because of its radical scavenging capability, even in cosmetics [13]. The electron-accepting characteristics of C_{60} have also led to its use as an n-type semiconductor in the fabrication of organic photovoltaic systems [14]. Fullerenes with the delocalized conjugated structures have gained extensive attentions for the interesting properties. One of the most remarkable properties in electron-transfer processes is that it can arouse a rapid photoinduced charge separation and a relatively slow charge recombination [15]. Many works have focused on the photochemical solar cells by the combination of C_{60} and nanoparticles, which can greatly increase the photoconversion of solar energy [16]. Generally, the photocatalytic activity of the photocatalyst can be promoted by increasing the separation efficiency of photoinduced electron–holes pairs. Thus, the combination of photocatalysts and C_{60} may be an ideal system to achieve an enhanced charge separation by photoinduced electron transfer.

Concerning the high photocatalytic activity of nanosized Bi_2MoO_6 , it is expected that the photoactivity of Bi_2MoO_6 photocatalyst is increased by adsorbing C_{60} on the surface of Bi_2MoO_6 . Herein, the photocatalytic removal of bromate ions has been largely enhanced by C_{60} coating onto Bi_2MoO_6 particles. It is postulated that the enhanced photoactivity of C_{60} modified Bi_2MoO_6 catalyst results from high migration efficiency of photoinduced electron–hole pairs.

2. Experimental

2.1. Preparation of photocatalysts

Bi_2MoO_6 was synthesized by the hydrothermal method. Briefly, the starting materials of Na_2MoO_4 and $\text{Bi}(\text{NO}_3)_3$ in 1:2 molar ration. Deionized water (100 mL) was added, then white precipitates appeared immediately, and the mixed solution was ultrasonicated for 10 min to promote the precipitate reaction. The collected precipitate after washing several times was added into a 50 mL Teflon-lined autoclave and filled with deionized water up to 80% of the total volume. The autoclave was maintained at 180°C for 12 hr. C_{60} modified Bi_2MoO_6 sample was prepared according to the literature [17]. Briefly, an appropriate amount of C_{60} was added into toluene and sonicated for 30 min to make C_{60} totally disperse. The as-prepared Bi_2MoO_6 powder (1 g) was added into the above solution and stirred for 24 h. The solvent was evaporated at 80°C for 10 h and stirred for 24 h. The solvent was evaporated and opaque powder was obtained after being dried. The amounts of C_{60} on the Bi_2MoO_6 particles were estimated to be 1%, 2%, and 3%.

The Brunauer–Emmett–Teller (BET) surface area measurements were performed by a Micromeritics (2010V 5.02H) surface area analyzer. High-resolution transmission electron microscopy (HRTEM) images were obtained by JEM 2010F field emission transmission electron microscope with an accelerating voltage of 200 kV. Raman spectra of Bi_2MoO_6 and C_{60} modified Bi_2MoO_6 were performed on a Renishaw RM1000 spectrometer, the wavelength of the laser light are 514 nm. The photoluminescence (PL) spectra of the samples were recorded with a PE LS 55 spectrofluorophotometer.

2.2. Photocatalytic experiment

Photocatalytic removal of bromate ions was performed under visible light irradiation of a 500 W Xe lamp with the 420 nm cut filter. The reaction cell was placed in a sealed black box which the top opened and placed the cut filter to provide visible light irradiation. In each experiment, 0.05 g photocatalysts was added into 60 mL bromate solution (1×10^{-5} mol/L). After being dispersed in ultrasonic bath for 5 min, the dispersion were kept under constant air-equilibrated condition before and during the irradiation and exposed to visible light irradiation. Bromate ions were analyzed using an ion chromatography system equipped with an AS-19 column with an AS 40 Automated Sampler (ICS-2000, Dionex, Sunnyvale, CA).

The electrochemical measurement employed a basic electrochemical system (Princeton Applied Research) connected with a counter-electrode (Pt wire, 70 mm in length with a 0.4-mm diameter), a working electrode (prepared film electrode, active area of 10 cm^2), and a reference electrode (SCE). 0.1 M Na_2SO_4 solution was used as electrolyte solution.

3. Results and discussion

3.1. Characterization of Bi_2MoO_6 and C_{60} modified Bi_2MoO_6

The Raman analysis was used to characterize the crystal structure of obtained Bi_2MoO_6 particles. As shown in Fig. 1(A), the crystalline phase of Bi_2MoO_6 with the specific band at 793.1 cm^{-1} appears. In Fig. 1(B), the specific band at 1476 cm^{-1} confirms the presence of C_{60} . Due to the low loading amount of C_{60} on the Bi_2MoO_6 surface, there is a slight signal of C_{60} for the C_{60} modified Bi_2MoO_6 particles (Fig. 1(C)). The bending vibration of C_{60} is observed at around 1476 cm^{-1} , which suggests that the C_{60} molecule maintains its original structure ideally after being bound to the surface of Bi_2MoO_6 [18]. These results indicate that the C_{60} is bound to the surface of Bi_2MoO_6 . As shown in Fig. 2, with the modification of C_{60} , the absorption value increases at the wavelength higher than 460 nm. The band gap of the Bi_2MoO_6 was estimated to be 2.59 eV, which has been reported in our previous work [12]. These results indicate that there exist some electron interactions between C_{60} and Bi_2MoO_6 , which may be favorable to the improvement of the photocatalytic activity of Bi_2MoO_6 , which will be discussed subsequently. In addition, high-resolution transmission electron microscopy (HRTEM) images were used to observe the Bi_2MoO_6 and C_{60} modified Bi_2MoO_6 . As shown in Fig. 3, the lattice structure of Bi_2MoO_6 was clear and there was no change of lattice structure of Bi_2MoO_6 after C_{60} adsorbed on the surface.

3.2. Photocatalytic reduction of BrO_3^- by Bi_2MoO_6 and C_{60} modified Bi_2MoO_6

As shown in Fig. 4, the removal of BrO_3^- was observed in photocatalysis in the presence of Bi_2MoO_6 under visible light irradiation. Furthermore, it can be observed that all the modified Bi_2MoO_6 samples exhibited higher photocatalytic activities than pure Bi_2MoO_6 . The blank experiment exhibited that BrO_3^- was not removed in the dark and under visible light irradiation without the addition of C_{60} modified Bi_2MoO_6 . Meantime, when Br^- was used as a starting compound, its concentration remained constant during the reaction and no BrO_3^- was detected in the system. This result indicates that Br^- is unable to be oxidized into BrO_3^- under such a condition. It has been discovered that BrO_3^- could be formed in the bromide solution, where OH is the only oxidant present (1). The OH was detected in the visible irradiation of Bi_2MoO_6 samples in our previous work [12]. However, the presence of electrons within

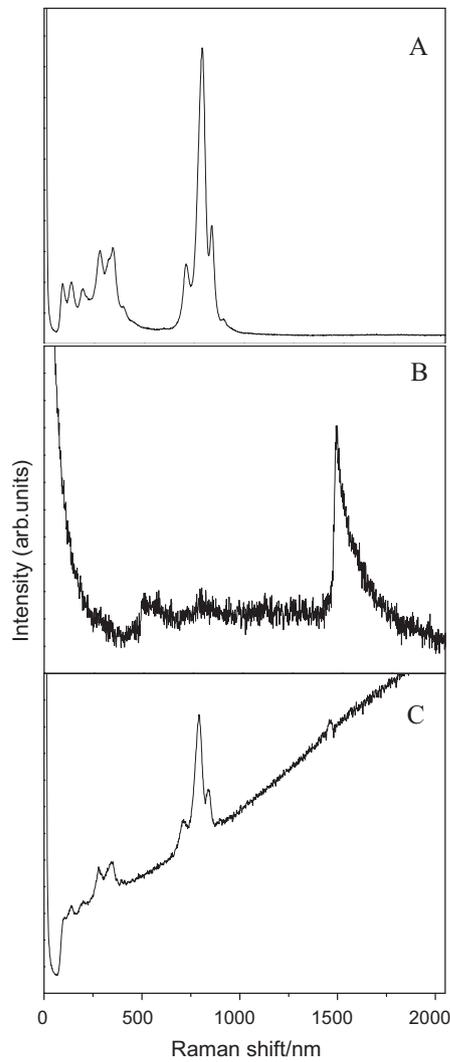


Fig. 1. Raman spectra of C₆₀ (A), Bi₂MoO₆ (B), and C₆₀ modified Bi₂MoO₆ particles (C).

the reaction process may be responsible for the no formation of BrO₃⁻.

The first-order linear relationship was observed by the plots of $\ln(C/C_0)$ vs. irradiation time. Generally, the loading amount of C₆₀ had a great influence on the photocatalytic activity of the prepared

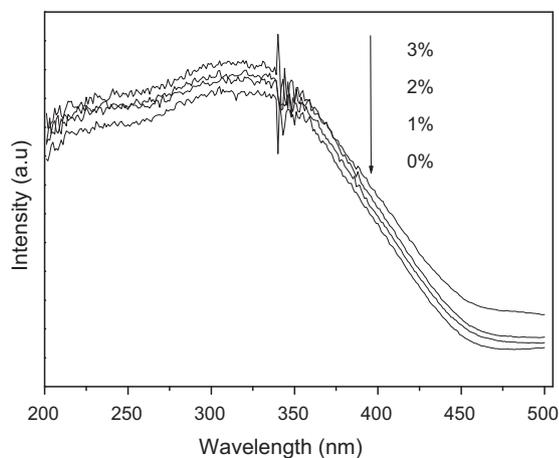


Fig. 2. UV-vis DR spectra of Bi₂MoO₆ particles loaded with various amount of C₆₀.

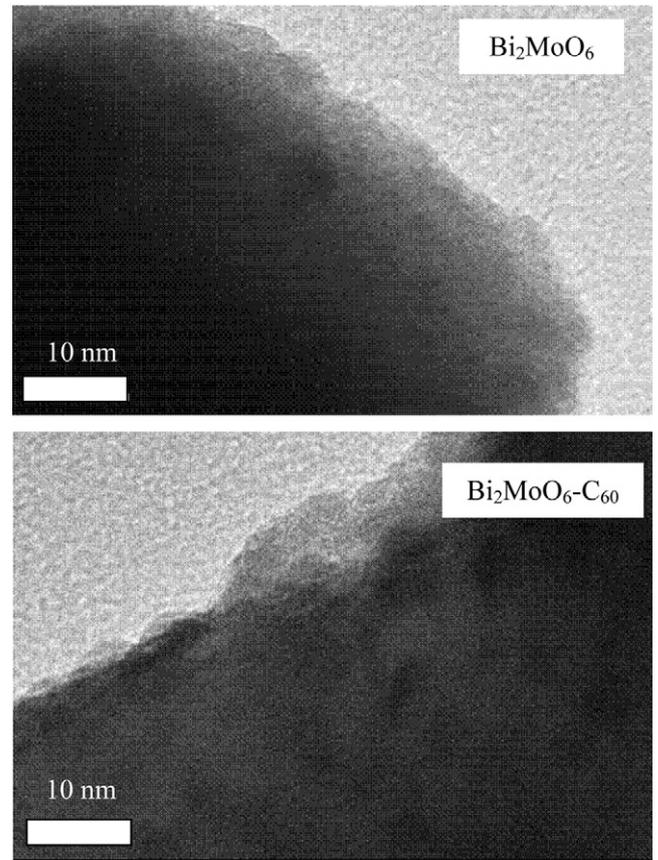


Fig. 3. HRTEM images of Bi₂MoO₆ and C₆₀-Bi₂MoO₆.

Bi₂MoO₆ samples. The influence of C₆₀ loading amounts upon the removal rate of BrO₃⁻ is shown in Fig. 5, the apparent reaction rate constants of k increase with the C₆₀ loading amounts and decrease with the furthermore increase of C₆₀ loading amounts. When the amount was higher than 3%, the C₆₀ tended to aggregate on the surface of Bi₂MoO₆, which can result in a relatively slower transmission of the photoinduced electrons.

3.3. Effect of pH on bromate removal

Fig. 6 shows the concentration variation of BrO₃⁻ ions during visible light irradiation in the C₆₀ modified Bi₂MoO₆ suspension at

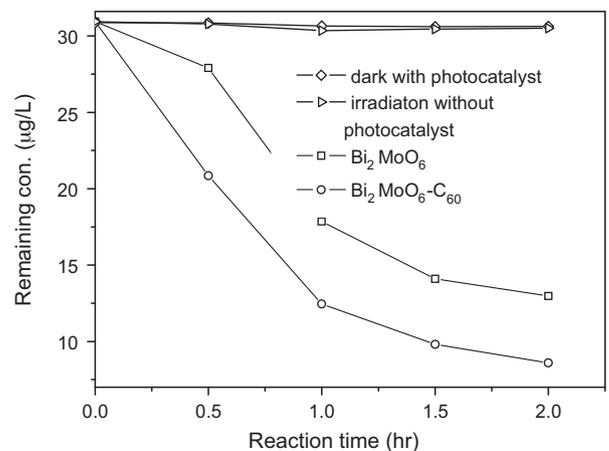


Fig. 4. Removal of bromate ions by photocatalysis process using Bi₂MoO₆ and C₆₀ modified Bi₂MoO₆ photocatalyst under visible light irradiation ($\lambda > 400$ nm).

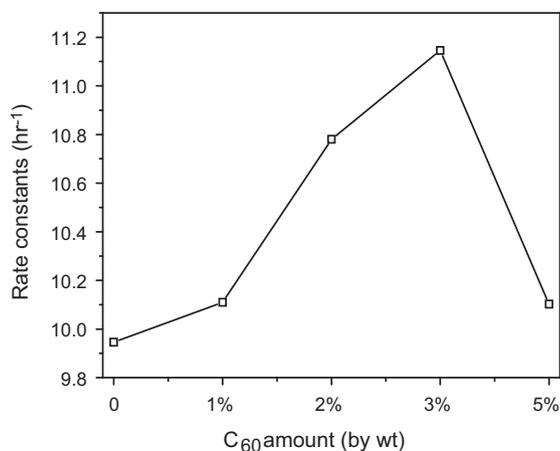


Fig. 5. Effect of C₆₀ amount on the removal rate of bromate ions by C₆₀ modified Bi₂MoO₆ photocatalyst under visible light irradiation.

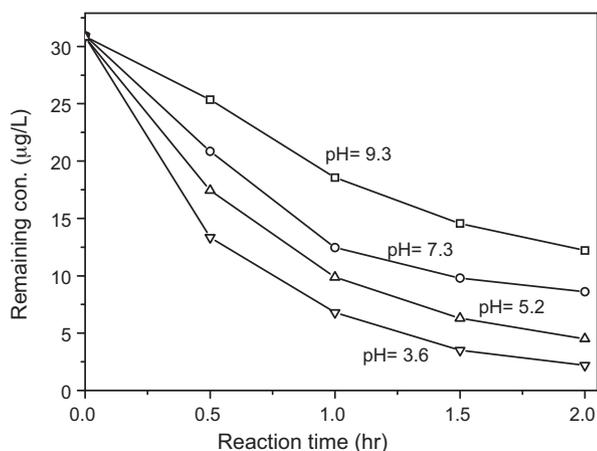


Fig. 6. Effect of pH on the removal rate of bromate ions by C₆₀ modified Bi₂MoO₆ photocatalyst under visible light irradiation.

different pH conditions. The reduction of BrO₃⁻ was highly dependent on the pH value, and the rate increased with a decrease of the pH from 7 to 5. The effect of pH on the amount of reduced BrO₃⁻ can be explained by the interaction between BrO₃⁻ and C₆₀ modified Bi₂MoO₆ particles. The charged surface of the C₆₀ modified Bi₂MoO₆ photocatalyst used in these experiments was 6.1 (Fig. 7). The surface of the C₆₀ modified Bi₂MoO₆ particles is predominantly negatively charged when the pH is higher than the isoelectric point.

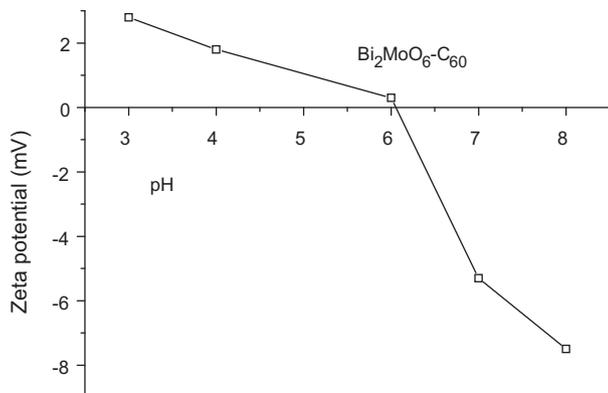


Fig. 7. Zero potential of C₆₀-modified Bi₂MoO₆ as a function of solution pH.

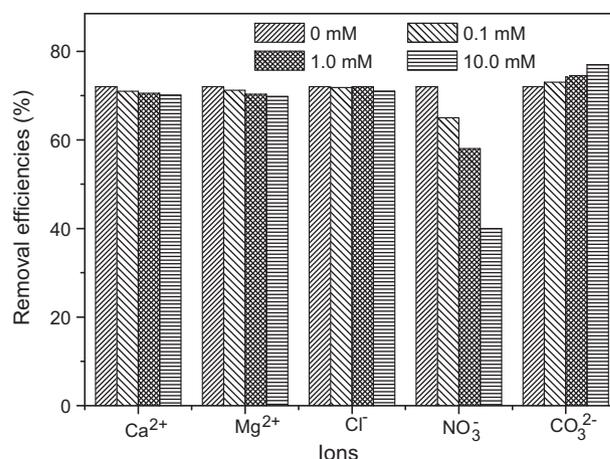


Fig. 8. Effects of co-existing ions on the removal of bromate ions by C₆₀ modified Bi₂MoO₆ photocatalyst under visible light irradiation.

As the pH is lowered, the functional groups are protonated and the proportion of the surface that is positively charged increased.

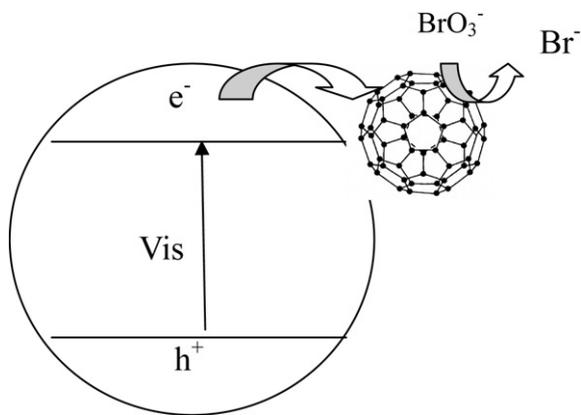
The surface becomes positively charged, and the number of adsorption sites may increase below the isoelectric point of the C₆₀ modified Bi₂MoO₆. This surface charge switching enhances the electrostatic interaction between BrO₃⁻ and C₆₀ modified Bi₂MoO₆ particles, which lead to the increase in the amount of adsorbed BrO₃⁻. In addition to the effect of the surface charge of the C₆₀ modified Bi₂MoO₆ photocatalyst, the promoting effect of lowering pH may also be attributed to the high reactivity of BrO₃⁻ at an acidic pH. BrO₃⁻ is a strong oxidant, and the reactivity of the BrO₃⁻ is observed to be proportional to the square of the proton concentration [19].

3.4. Effect of other ions on bromate removal

Generally, a number of cations and anions were present in the water. The effect of Ca²⁺ and Mg²⁺ on the removal of BrO₃⁻ was firstly investigated. The presence of Ca²⁺ and Mg²⁺ did not decrease the rate of BrO₃⁻ removal (Fig. 8). These concentrations of Ca²⁺ and Mg²⁺ cations are representative of levels found in municipal drinking water. Next, NO₃⁻ and Cl⁻ were investigated for their individual effects on BrO₃⁻ removal. It can be seen from Fig. 8 that the addition of chloride ions did not have an effect on BrO₃⁻ removal. However, in an electrolyte of 0.1 mmol NaNO₃, removal rate of BrO₃⁻ were decreased. And, the decrease in the removal efficiency becomes apparent with the increase of NaNO₃ concentration. It is suggested that NO₃⁻ will be reduced by the photogenerated electrons. Thus, the photogenerated electrons will be consumed by NO₃⁻. Thus, the reduction of BrO₃⁻ was inhibited.

3.5. Proposed mechanism in bromate removal

As discussed above, the C₆₀ modified Bi₂MoO₆ photocatalyst showed a high photocatalytic activity under visible light irradiation. The reason should be closely attributed to the interaction between Bi₂MoO₆ and C₆₀ which increased the photogenerated electron mobility in Bi₂MoO₆. The BET of bare Bi₂MoO₆ and C₆₀ modified Bi₂MoO₆ is determined to be 3.65 and 3.50 m² g⁻¹. Considering the diameter of C₆₀ (0.71 nm) and the BET surface area of Bi₂MoO₆ (3.65 m² g⁻¹), it can be estimated that the weight ratio about 3.5% with a nearly compact C₆₀ monolayer coverage on Bi₂MoO₆. There was no appreciable change in the surface area. The above results also implied that the modification of C₆₀ did not obviously change the surface characterization of Bi₂MoO₆. In this work, C₆₀ molecule



Scheme 1. Proposed pathway of the photoelectron transfer excited by visible light irradiation and photocatalytic reduction process.

was mainly covered on the surface of Bi_2MoO_6 . C_{60} could effectively transfer the photoelectrons from conduction band of Bi_2MoO_6 after being illuminated under visible light irradiation. The delocalized conjugated π structure of C_{60} made it easier to transfer the photoinduced electrons [16]. Accordingly, the photogenerated electrons in the modified Bi_2MoO_6 photocatalyst could easily migrate from the inner region to the surface to take part in the reduction reaction of bromate ions. Based on the above discussion, the schematic of photocatalytic mechanism was shown in Scheme 1.

The effect of C_{60} modification on the recombination of e^-/h^+ produced by Bi_2MoO_6 was also investigated. Electrochemical impedance spectroscopy (EIS) was used to investigate the photogenerated charge separation process on ITO/ Bi_2MoO_6 film and ITO/ $\text{Bi}_2\text{MoO}_6/\text{C}_{60}$ film, the film was prepared according to our previous work [20]. C_{60} was coated onto the Bi_2MoO_6 film via drying of given concentration of C_{60} toluene solution onto the Bi_2MoO_6 film. Fig. 9 shows EIS response of ITO/ Bi_2MoO_6 film and ITO/ $\text{Bi}_2\text{MoO}_6/\text{C}_{60}$ film sample under visible light irradiation. The radius of the arc on the EIS Nyquist plot reflects the reaction rate occurring at the surface of electrode. The arc radius on EIS Nyquist plot of ITO/ $\text{Bi}_2\text{MoO}_6/\text{C}_{60}$ film was smaller than that of ITO/ Bi_2MoO_6 film sample, which meant that an effective separation of photogenerated electron-hole pairs and fast interfacial charge transfer to the electron donor/electron acceptor occurred [21]. The effect of C_{60} on the recombination of electron-hole pairs of Bi_2MoO_6 was investigated with photoluminescence spectra. As shown in Fig. 10,

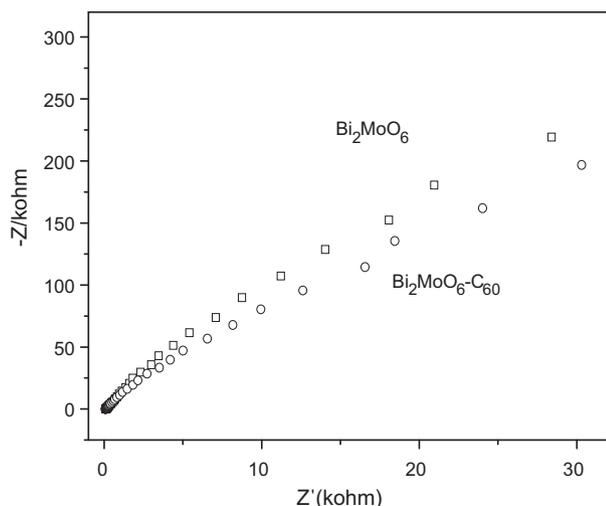


Fig. 9. EIS variation of Bi_2MoO_6 and C_{60} modified Bi_2MoO_6 film electrode under visible light irradiation.

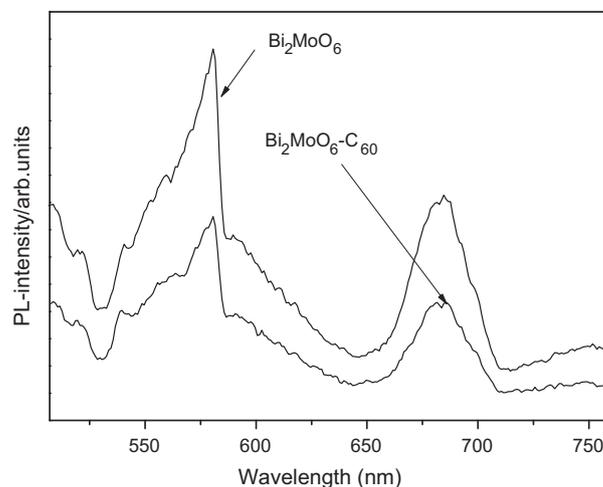


Fig. 10. Photoluminescence spectra of Bi_2MoO_6 and C_{60} modified Bi_2MoO_6 excited by monochromatic light (278 nm) at room temperature.

the photoluminescence intensity of the modified Bi_2MoO_6 is lower than that of individual Bi_2MoO_6 , which implied that the recombination of electron-hole pairs is restrained effectively due to the modification of C_{60} on Bi_2MoO_6 . To identify the role of electrons in the photocatalytic reduction of bromate, $\text{K}_2\text{S}_2\text{O}_8$, a quencher of electrons, was added into the solution. Electrons would react with $\text{S}_2\text{O}_8^{2-}$ rather than BrO_3^- ions due to a faster reaction rate with the former [22]. As shown in Fig. 11, the photocatalytic reduction of BrO_3^- ions decreased with the addition of 1 mmol/L $\text{K}_2\text{S}_2\text{O}_8$ and was completely inhibited in the presence of 5 mmol/L $\text{K}_2\text{S}_2\text{O}_8$. These results indicate that electrons played a dominant role in the reduction of BrO_3^- ions.

To test the photostability of the prepared C_{60} modified Bi_2MoO_6 particles, C_{60} modified Bi_2MoO_6 powders after photocatalytic reactions were collected and dried for the subsequent photocatalytic reaction cycles. Three runs of the BrO_3^- ions removal experiments were performed in the presence of sample particles under the same experimental conditions and the result was shown in Fig. 12. It can be easily seen from the picture that the photocatalytic ability of the catalyst used did not exhibit any significant loss. In each run, over 70% of BrO_3^- removal was achieved. These results demonstrate that the C_{60} modified Bi_2MoO_6 is stable.

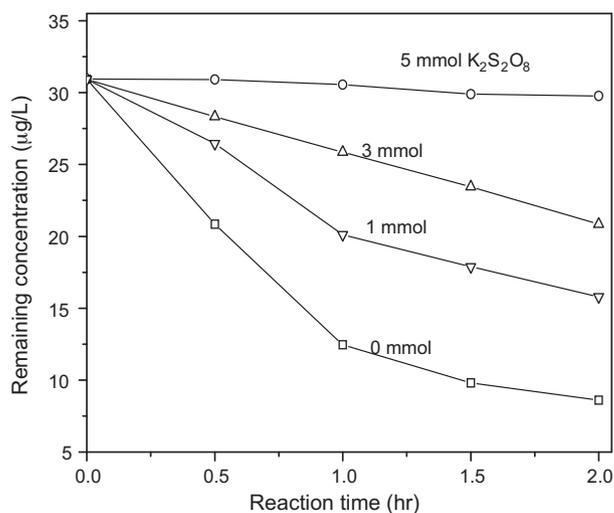


Fig. 11. Removal of bromate ions by photocatalysis process using Bi_2MoO_6 and C_{60} modified Bi_2MoO_6 photocatalyst under visible light irradiation with addition of $\text{K}_2\text{S}_2\text{O}_8$ ($\lambda > 400$ nm).

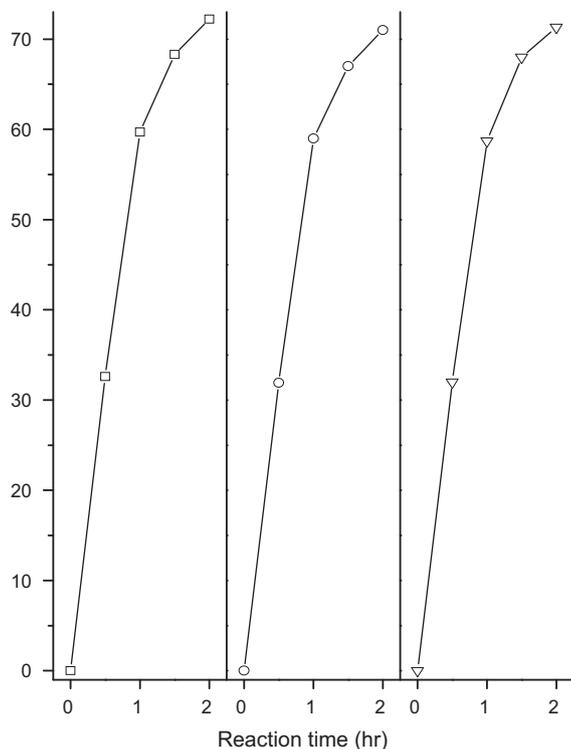


Fig. 12. Removal of bromate by photocatalysis process using C_{60} modified Bi_2MoO_6 photocatalyst under visible light irradiation for cycle experiments.

4. Conclusions

The obtained results indicated that bromate ions can be reduced by Bi_2MoO_6 nanoparticles and the reduction rate of bromate ions was increased by the C_{60} modification. The deposited C_{60} molecules facilitated the separation of photogenerated electron–hole pairs, and enhance the photocatalytic activity of the Bi_2MoO_6 nanopar-

ticles towards the reduction of bromate ions. The reduction rate of bromate decreased with the solution pH value. Due to the consumption of photogenerated electrons by NO_3^- , the reduction of BrO_3^- was inhibited. Combined with the analysis of bromate reduction in the presence of $K_2S_2O_8$, it is concluded that electrons played a dominant role in the reduction of bromate.

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