

Enhancing photocatalytic CO₂ reduction with Z-scheme heterojunction Ag/Bi₂MoO₆/BiOBr composite films: Synthesis and mechanistic insights

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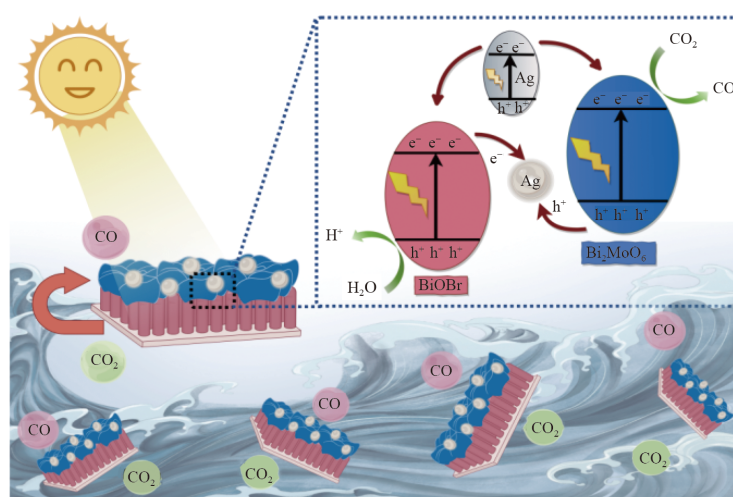
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Abstract: This study presents the successful synthesis of a novel Z-scheme heterojunction composite film consisting of Ag/Bi₂MoO₆/BiOBr through electrochemical processes and ion-exchange techniques, followed by the photodeposition of noble metal silver (Ag) onto the composite structure. The catalytic efficiency of semiconductor photocatalysts is greatly improved by utilizing the localized surface plasmon resonance (LSPR) effect observed in Ag nanoparticles (NPs). Furthermore, the noble metal Ag serves as an intermediary bridge facilitating charge transfer between Bi₂MoO₆ and BiOBr, while the formation

of a Schottky barrier effectively inhibits the recombination of photo-generated electron-hole pairs. As a result, the Ag-deposited Bi₂MoO₆/BiOBr film exhibits superior photocatalytic performance in the reduction of CO₂ compared to its unmodified counterpart. Our experimental results indicate a non-linear relationship between Ag deposition and the efficiency of photocatalytic CO₂ reduction to CO, characterized by an initial increase in efficiency followed by a decline. The optimized 1.5%-Ag/Bi₂MoO₆/BiOBr film demonstrates exceptional photocatalytic activity, attaining a CO production rate of 13.65 μmol/(g·h). This research explores the fundamental mechanisms that lead to improved photocatalytic CO₂ reduction capabilities of the Ag/Bi₂MoO₆/BiOBr film. Our research offers important perspectives for the thoughtful design and production of highly efficient photocatalysts, which are essential for advancing sustainable energy solutions.

Key words: photocatalytic CO₂ reduction; Ag NPs; Bi₂MoO₆/BiOBr composite film; Z-scheme heterojunction; *in situ* synthesis



The excessive combustion of fossil fuels results in the production of CO₂, contributing to the greenhouse effect and exacerbating energy scarcity. To address this issue, it is essential to reduce carbon dioxide emissions, advance the utilization of renewable energy sources, and decrease reliance on conventional fuels^[1-3]. Photocatalytic CO₂

reduction is a green technology that converts carbon dioxide into valuable chemicals and fuels^[4]. Through the photocatalytic process, CO₂ can be reduced to a variety of products, including monocarbon compounds (CO^[5], CH₄^[6], CH₃OH^[7], HCOOH^[8]) and polycarbon compounds (C₂H₄^[9], C₂H₆^[10], CH₃CHO^[11]). The core challenge in photocatalysis

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technology is the development of efficient photocatalytic systems. Most photocatalysts exhibit high surface charge recombination and low energies for CO₂ adsorption and activation, leading to inefficient CO₂ conversion and low selectivity for reduction products.

Over the past decade, bismuth-containing compounds have garnered significant attention as promising candidates for photocatalytic applications. A diverse array of bismuth-based materials has been extensively investigated, including, but not limited to, bismuth oxyhalides (BiOX, where X represents Cl, Br, or I)^[12–14], bismuth molybdate (Bi₂MoO₆)^[15–16], bismuth vanadate (BiVO₄)^[17], bismuth manganese oxide (Bi₁₂MnO₂₀)^[18], bismuth silicate (Bi₂SiO₅)^[19], bismuth tungstate (Bi₂WO₆)^[20] and bismuth oxycarbonate (Bi₂O₂CO₃)^[21]. These materials have demonstrated remarkable potential in various photocatalytic reactions, thereby paving the way for innovative solutions in environmental remediation and energy conversion. Among these photocatalysts, Bi₂MoO₆ (BMO) stands out because of its non-toxic properties, simple preparation process, and economical raw materials. Its layered structure and appropriate band gap further enhance its promise as a photocatalyst^[22–23]. As a member of the layered Aurivillius oxide family, Bi₂MoO₆ is made up of alternating [MoO₄]^{2–} and [Bi₂O₂]²⁺ layers. Additionally, given its adjustable band gap ranging from 2.5 to 2.8 eV, BMO is capable of more efficiently absorbing visible light and also offers sufficient reaction sites to enhance photocatalytic activity^[7]. Key factors affecting photocatalytic efficiency include the semiconductor's band gap, which influences solar light absorption, the speed of photogenerated carrier transfer affecting redox reactions, and the conduction band's position for thermodynamic feasibility. However, single BMO development is limited by weak visible light absorption, slow carrier migration, rapid recombination of electron-hole pairs and low quantum yield^[24].

There remains significant potential for the modification and exploration of BMO to improve its photocatalytic performance. Various strategies can be employed to enhance the photocatalytic activity of BMO. The formation of heterojunctions is particularly effective in facilitating light absorption and charge transfer^[25–26]. Introducing oxygen vacancies can alter the band gap of BMO, thereby creating additional active sites for photocatalysis^[27–29]. Elemental doping is another useful approach for introducing impurity energy levels and enhancing the intrinsic activity of BMO^[30–31]. Due to its unique variable band gap, BMO can be easily combined with other semiconductor materials to form heterojunctions. The integration of BMO-based semiconductor heterojunctions is advantageous for extending the range of visible light absorption. To overcome existing limitations, researchers often utilize heterojunction construction and noble metal modification to enhance photocatalytic performance. For instance, BiOBr (BOB), with its layered structure, facilitates electronic transfer and improves photocatalytic activity^[32–34]. The

integration of BMO/BOB heterojunctions significantly enhances catalytic efficacy, as demonstrated in previous studies^[35–37]. Additionally, precious metal-modified semiconductor catalysts have garnered significant attention in research and application due to their excellent electrical conductivity and unique optical properties. For example, the incorporation of precious metals such as platinum (Pt)^[38], palladium (Pd)^[39–40], silver (Ag)^[41–42], and others has been shown to enhance electron transfer and introduce Schottky barriers, thereby inhibiting the recombination of photogenerated electron-hole pairs and ultimately improving the photocatalytic efficiency. Among these, Ag has attracted significant interest because of its unique characteristics and cost-effectiveness. The localized surface plasmon resonance (LSPR) effect observed in Ag NPs can substantially enhance the visible light absorption and utilization of catalysts, facilitating the generation of active species, promoting carrier separation efficiency, and accelerating carrier regeneration, thereby boosting photocatalytic performance^[43–50]. Moreover, traditional powder-like photocatalysts suffer from drawbacks such as difficult solid-liquid separation, aggregation, and potential secondary pollution. Addressing these challenges, this study utilizes bismuth plates as substrates for the *in situ* preparation of bismuth-based films *via* electrochemical methods. Therefore, this approach, combined with the construction of Bi-based heterojunctions and the decoration of catalysts with Ag NPs, represent effective strategies for enhancing the performance of photocatalytic CO₂ reduction.

In this research, we utilized the photodeposition method to deposit the precious metal silver onto the prepared BMO/BOB film, leading to the creation of an Ag/BMO/BOB composite film that exhibited enhanced efficiency in the photocatalytic reduction of CO₂ into CO. In order to study the effect of different Ag deposition amounts on the photocatalytic CO₂ reduction performance, we deposited silver with different mass fractions onto the BMO/BOB composite film and subsequently evaluated its performance in the photocatalytic reduction of CO₂ to CO. The film was immobilized on a Bi plate, effectively addressing issues commonly associated with powder catalysts such as poor dispersion and separation difficulties in solid-liquid systems. This immobilization technique not only overcomes these challenges but also promotes environmentally friendly photocatalytic CO₂ reduction. We conducted comprehensive characterization and CO₂ reduction performance tests on both single and composite films. Based on the characterization data, we propose potential mechanisms for film formation and CO₂ photoreduction. The study further elucidates a plausible mechanism for the photocatalytic reduction of CO₂, occurring over the Z-scheme heterojunction of the Ag/BMO/BOB film. Our findings hold significant implications for catalyst fixation and the development of highly efficient Bi-based halide Z-scheme heterostructures to boost CO₂ photoreduction.

1 Experimental

1.1 Reagents

Sodium molybdate dihydrate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$) and potassium bromide (KBr) were obtained from Aladdin Biochemical Technology Co., Ltd. and were of analytical reagent grade. Nitric acid (HNO_3) was superior pure grade from Chengdu Kelong Chemicals Co., Ltd. Ethylenediaminetetraacetic acid disodium salt (EDTA-2Na) was an analytical reagent obtained from Tianjin Bodi Chemical Co., Ltd. Ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$) and ethanol ($\text{C}_2\text{H}_5\text{OH}$) were analytical reagent grade from Tianjin Kernel Chemical Reagent Co., Ltd. Analytical reagent grade sodium hydroxide (NaOH) was procured from Tianjin Guangfu Science and Technology Development Co., Ltd. Silver nitrate (AgNO_3) of the same grade was acquired from Sinopharm Group Chemical Reagent Co., Ltd. Bismuth plate (Bi) with dimensions $1.4 \text{ cm} \times 5 \text{ cm}$ and titanium sheet (Ti) with dimensions $1 \text{ cm} \times 5 \text{ cm}$ were produced by Wochang Metal Products Co., Ltd. These reagents are vital for the experiments and their details ensure the research's reliability and reproducibility.

1.2 Preparation of photocatalyst

1.2.1 Preparation of BiOBr and Bi_2MoO_6 thin films

Initially, precisely weigh 1.1 mmol of KBr and 1.478 mmol of EDTA-2Na into a beaker, and subsequently pour 120 mL of deionized water. The mixture was vigorously stirred to ensure the dissolution of KBr and EDTA-2Na. Once the substances were dissolved, the pH value of the solution was adjusted to 8 meticulously using a 2 mol/L NaOH solution. Thoroughly cleanse the previously polished Bi plate with deionized water and use it as the anode and substrate, while employing the equally polished Ti sheet as the cathode. A voltage of 5 V and a deposition time of 1.5 h are selected to fabricate the precursor BiOBr film. The deposited film was thoroughly rinsed with deionized water and absolute ethanol, followed by overnight drying at 60°C in an oven for storage. Next, the Bi_2MoO_6 film was prepared *via* the ion exchange method utilizing the precursor film. $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (2.48 mmol) was dissolved in 70 mL of deionized water under stirring. The resulting solution was transferred to a 100 mL high-pressure reactor after complete dissolution. Then, incline the previously prepared precursor film at an appropriate angle and position it within the reactor solution. In an oven, the Bi_2MoO_6 film was prepared by the optimal reaction time of 6 h at 160°C .

1.2.2 Preparation of $\text{Bi}_2\text{MoO}_6/\text{BiOBr}$ composite films

The $\text{Bi}_2\text{MoO}_6/\text{BiOBr}$ composite films were synthesized through a one-step electrochemical approach. 1.1 mmol KBr, 2.48 mmol $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ and 1.478 mmol EDTA-2Na were weighed accurately and dissolved in 120 mL of deionized water. The pH value was adjusted to 3 carefully with HNO_3 to prepare the electrolyte solution. A Bi plate (anode) and a Ti sheet (cathode) were used to electrodeposit the composite film at 5 V for 30 min in the prepared electrolyte. The resulting composite film was thoroughly rinsed with deionized water and absolute ethanol, and then dried in an oven for storage.

1.2.3 Preparation of $\text{Ag}/\text{Bi}_2\text{MoO}_6/\text{BiOBr}$ composite films

When depositing the precious metal Ag, the photoreduction method is employed for photodeposition under the irradiation of xenon lamp. Firstly, deionized water (70 mL) and ethylene glycol (10 mL) into a beaker and stirred the mixture to achieve a homogeneous blend. Secondly, place the prepared $\text{Bi}_2\text{MoO}_6/\text{BiOBr}$ film on a self-customized glass holder and position it in the reaction solution. Then, AgNO_3 solutions with varying mass fractions were added into the configured solution to explore the influence of the precious metal Ag content on the catalytic performance of the composite film. Subsequently, the solution was stirred in the dark for 0.5 h. Finally, the photodeposition process was conducted under a 300 W xenon lamp for 1.5 h, the Ag-loaded composite film was rinsed sequentially with deionized water and absolute ethanol, and then dried at 60°C in an oven for storage. Figure 1 illustrates schematic of the $\text{Ag}/\text{Bi}_2\text{MoO}_6/\text{BiOBr}$ composite film fabrication process. For comparison, a KBr film is synthesized without Na_2MoO_4 under identical conditions. Additionally, BiOBr is used as a sacrificial template to prepare a standalone Bi_2MoO_6 film.

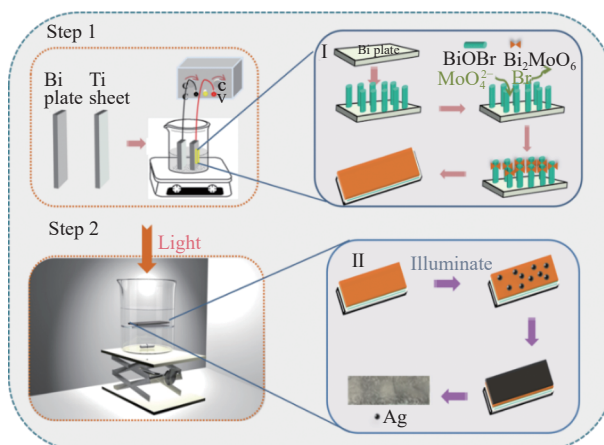


Fig. 1 Schematic of the fabrication process of $\text{Ag}/\text{Bi}_2\text{MoO}_6/\text{BiOBr}$ composite film

1.3 Characterization

The samples were characterized as follows: X-ray diffraction (XRD, DX-2700) and X-ray photoelectron spectroscopy (XPS, V.G. Scientific ESCALAB250) for structure and surface states, field emission scanning electron microscopy (FESEM, Nanosem 430) at 10 kV for morphology, UV-vis Diffuse Reflectance Spectroscopy (UV-vis DRS) for optical properties was conducted over UV-3600, transmission electron microscopy (TEM/HRTEM, JEOL JEM-2100(UHr)) at 200 kV for microstructure. UV-vis DRS arises from the transitions of valence electrons, utilizing the absorption of ultraviolet and visible light by molecules or ions. The obtained data can be used to analyze the light absorption range and absorption edge of the synthesized materials. The synthesized samples' band gap energy can be calculated from the Tauc plot analysis. In this study, the measurements are performed using a PE-Lambda 1050 spectrophotometer, with the wavelength range set from 200 to 800 nm. Photoelectrochemical properties, including electrochemical impedance and photocurrent response, are evaluated to assess the prepared materials. A standard three-electrode configuration is employed on a CHI760E electrochemical workstation. The setup utilizes a 0.5 mol/L Na₂SO₄ aqueous solution as the electrolyte, with a Pt plate counter electrode and an Ag/AgCl reference electrode. The working electrode is fabricated by coating the sample onto conductive glass to create a 1 cm × 1 cm active area. Photocatalytic CO₂ reduction is assessed in a CEL-SPH2N-D9 system (Beijing Chain Education Au-Light Co., Ltd.).

1.4 Photocatalytic activity measurement

Film samples were assessed for CO₂ photoreduction using a previously established method^[51] in a CEL-SPH2N-D9 system under a 300 W Xe lamp (320–780 nm). Specifically, the freshly fabricated film specimens were mounted horizontally in a quartz reactor filled with 50 mL of deionized water under magnetic stirring. The solution temperature was held at 3 °C by a cooling circulator. After evacuating and introducing high-purity CO₂, the system was irradiated for 10 h. Gaseous products were quantified *via* online gas chromatography (GC-7920, N₂ (25 mL/min), H₂ (30 mL/min) and air (400 mL/min)).

2 Results and discussion

The crystal structure of the synthesized films is analyzed by XRD, as shown in Figure 2. The positions of the principal diffraction peaks of the synthesized BiOBr aligned with those in the standard reference card PDF#78-348 for BiOBr. Similarly, for the Bi₂MoO₆ thin film, the figure clearly shows that each peak matched the standard reference card PDF#21-102 for Bi₂MoO₆. A series of diffraction peaks at 10.896°, 28.252°, 32.612°, 33.098°, 47.15°,

55.559° and 58.432° can be assigned to the (020), (131), (002), (060), (062), (133) and (262) planes of Bi₂MoO₆. For the XRD pattern of the BMO/BOB composite thin film, the peaks at 10.900°, 21.928°, 32.220° and 46.865° are indexed to the (001), (002), (110) and (113) planes of BiOBr. Correspondingly, the peaks at 10.927°, 27.334°, 56.251° and 55.585° could all be attributed to the (020), (140), (191) and (133) crystal planes of Bi₂MoO₆. In addition, XRD was carried out on the composite films prepared using various mass fractions of deposited Ag NPs. The resulting diffraction patterns, illustrated in Figure 2, demonstrate that the photodeposition of Ag at various mass loadings does not induce significant structural changes in the prepared composite film. This suggests that the crystal structure of the BMO/BOB film was not altered after the deposition of Ag NPs. No characteristic diffraction peaks of Ag NPs were detected in the Ag/BMO/BOB films, which is typically caused by the low Ag loading content^[41] and its high dispersion^[52].

XPS was used to verify the successful deposition of Ag on the 1.5% Ag/BMO/BOB composite film, and the results are compared with the unmodified BMO/BOB film (Figure 3). The presence of Mo, O, Br, Bi and Ag in the 1.5% Ag/BMO/BOB composite is verified by the survey spectrum (Figure 3(a)), which validates the successful photodeposition of Ag. High-resolution spectra further delineate characteristic peaks for Mo 3*d* (Figure 3(b)), O 1*s* (Figure 3(c)), Br 3*d* (Figure 3(d)), Bi 4*f* (Figure 3(e)) and Ag 3*d* (Figure 3(f)). The Mo 3*d* XPS spectrum (Figure 3(b)) showed a doublet with peaks at 231.44 (Mo 3*d*_{5/2}) and 234.57 eV (Mo 3*d*_{3/2}), characteristic of Mo⁶⁺^[7]. The O 1*s* spectrum ((Figure 3(c)) of BMO exhibited peaks at 529.17 and 530.61 eV, attributed to lattice oxygen and surface hydroxyl groups, respectively^[51]. In Figure 3(d), the Br 3*d* peaks located at 67.53 and 68.52 eV were associated with Br⁻ in Br 3*d*_{5/2} and Br 3*d*_{3/2}^[53]. The Bi 4*f* spectrum (Figure 3(e)) showed the characteristic doublet of Bi³⁺ at 158.96 (Bi 4*f*_{7/2}) and 164.35 eV (Bi 4*f*_{5/2})^[27]. Similarly, the Ag 3*d* region (Figure 3(f)) exhibited peaks at 368.18 (Ag 3*d*_{5/2}) and 374.18 eV (Ag 3*d*_{3/2}), with a characteristic 6 eV splitting, corresponding to the presence of metallic silver (Ag⁰)^[54].

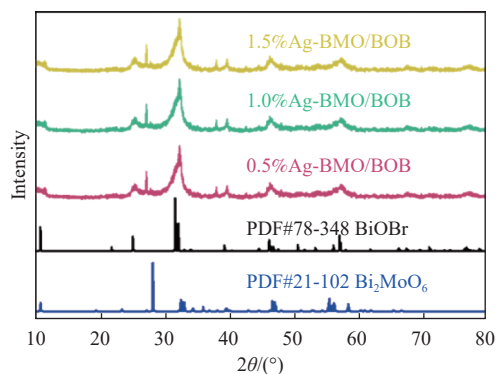


Fig. 2 XRD patterns for Ag/BMO/BOB composite films deposited with different amounts of Ag

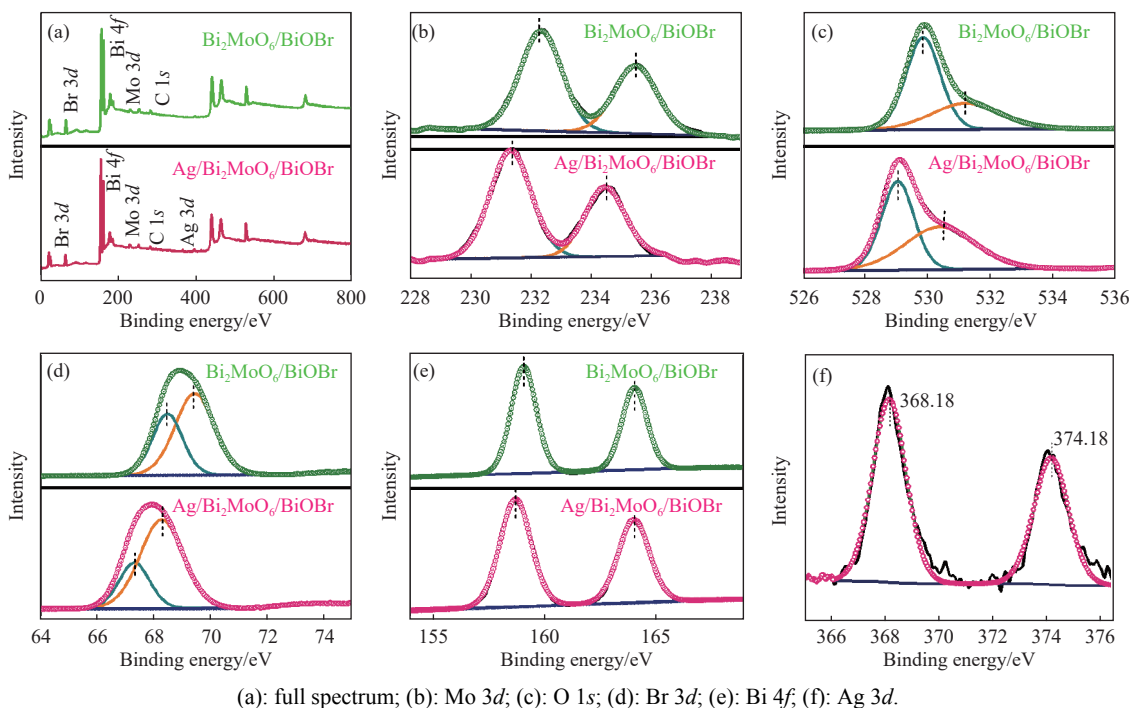
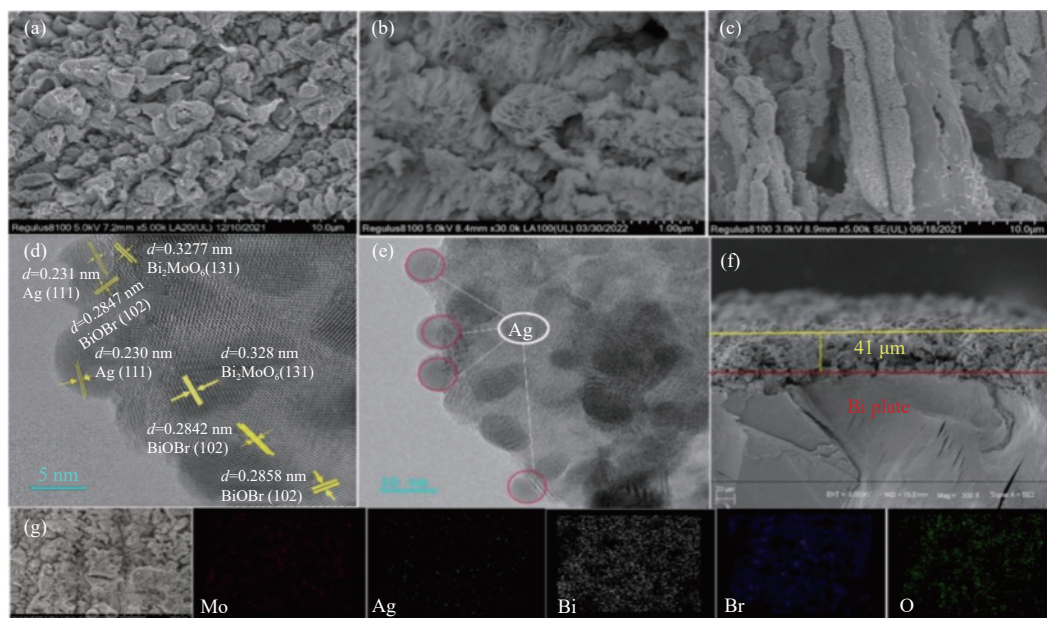


Fig. 3 XPS diagrams for the composite films of 1.5% Ag/BMO/BOB and BMO/BOB

Compared with the BMO/BOB composite film, the XPS peaks of all the elements in the Ag-deposited composite film catalyst show the slight shifts toward to the lower binding energies. This negative shift primarily stems from the increased electron density on the surface of the main heterojunction catalyst, revealing that the incorporation of Ag alters the chemical environment of the BMO/BOB heterojunction composite film. Here, Ag acts as an electron donor, transferring electrons to the host catalyst, which further confirms the successful incorporation of Ag^[29]. This

comprehensive XPS analysis provides compelling evidence for the formation of a well-integrated composite film with synergistic interactions among its components.

To verify the effective deposition of Ag and to detail the morphological traits of the composite films, SEM and TEM analyses are carried out. SEM micrographs (Figure 4 (a), (b)) reveal a distinctive fusiform morphology for the composite film with 1.5% Ag/BMO/BOB. The flake-like structures was clearly visible at higher magnification (Figure 4(b)) correspond to the morphological composition of the BMO/BOB composite films.



(a), (b): Surface SEM images of the 1.5% Ag/BMO/BOB composite; (c): SEM image of the pure BOB; (d), (e): TEM images of the 1.5% Ag/BMO/BOB composite; (f): Cross-sectional SEM image; (g): SEM-EDX elemental mapping of the 1.5% Ag/BMO/BOB composite.

Fig. 4 Microstructure characterizations of the composite films

In contrast, a pure BiOBr film prepared under identical conditions exhibited a sheet-like morphology (Figure 4(c)). Cross-sectional SEM images (Figure 4(f)) revealed that the composite film with 1.5% Ag/BMO/BOB possesses a thickness of approximately 41 μm . TEM analysis (Figure 4(d)) identifies lattice fringes with d -spacings of 0.230 nm (Ag (111))^[55] and 0.328 nm (Bi₂MoO₆ (131)). In addition, the (102) plane of BiOBr is linked to lattice fringes with d -spacings of 0.2842 and 0.2858 nm. Figure 4(e) directly shows the distribution of Ag nanoparticles on the composite film. EDX mapping (Figure 4(g)) confirms the homogeneous distribution of Bi, Mo, O, Br and Ag throughout the composite film, thereby verifying the successful synthesis for the composite film with 1.5% Ag/BMO/BOB.

The photocatalytic performance of composite films with different Ag contents (0.5%, 1.0%, 1.5% and 2.0%) is evaluated for CO₂ reduction under 300 W xenon lamp irradiation. Figure 5(a) presents a comparison of the CO yield from these composites with that of unmodified BMO, BOB and BMO/BOB films. The CO production rates for the single BMO, BOB and BMO/BOB composite films are determined to be 10.45, 8.64 and 11.71 $\mu\text{mol}/(\text{g}\cdot\text{h})$, respectively. The BMO/BOB composite outperforms single-component films, while Ag modification further enhances catalytic activity. The yields for Ag/BMO/BOB composite films with varying amounts of Ag mass fractions (0.5%, 1.0%, 1.5% and 2.0%) are recorded as 11.99, 12.31, 13.65 and 12.44 $\mu\text{mol}/(\text{g}\cdot\text{h})$, respectively. By optimizing the amount of deposited Ag, the Ag/BMO/BOB composite film exhibits a significantly higher activity for CO₂ reduction to CO than the pure BMO/BOB composite film. Detailed analysis shows that the composite film's photocatalytic performance initially rises with Ag deposition, hits a maximum, and then falls. A maximum CO yield of 13.65 $\mu\text{mol}/(\text{g}\cdot\text{h})$ is attained by the film with 1.5% Ag loading. This enhancement can be attributed to the optimal Ag loading, which functions as an electron-trapping cocatalyst, thereby increasing the surface electron concentration^[12]. Conversely, excessive Ag loading compromises photocatalytic efficiency, as the surplus Ag not only forms recombination centers for charge carriers^[56–57] but also agglomerates into larger particles, reducing the effective contact area and active sites^[58].

Figure 5(b) illustrates the transient photocurrent responses, revealing that the 1.5% Ag/BMO/BOB film demonstrates the highest current density and superior light responsiveness. This observation indirectly demonstrates that the composite film containing 1.5% Ag/BMO/BOB possesses the most efficient photogenerated electron-hole pair separation capability, resulting in a greater number of electrons participating in reduction processes^[59].

As shown in Figure 5(c), the electrochemical impedance spectroscopy (EIS) reveals that the arc radius is inversely proportional to the material's conductivity. The Nyquist circle diameter of the composite film with 1.5% Ag/BMO/BOB is significantly smaller than that of the BMO/BOB composite film, indicating lower interface charge transfer resistance in the former. This reduction in resistance facilitates the migration and separation of photogenerated carriers. The smaller arc radius observed for the Ag/BMO/BOB composite film indicates its enhanced ability to effectively separate photogenerated electron-hole pairs^[54,60].

Both the photocurrent and impedance analyses confirm that the Ag/BMO/BOB composite film further demonstrates superior carrier separation efficiency, thereby augmenting the photocatalytic efficiency of the composite material. This enhancement in carrier separation is a crucial factor contributing to the improved CO₂ to CO photocatalytic reduction performance observed in the composite film following noble metal Ag deposition.

The films' optical absorption characteristics were examined using UV-vis diffuse reflectance spectroscopy (Figure 6(a)). It can be observed that the intrinsic absorption edges of Ag/BMO/BOB, BMO/BOB and BOB films are largely consistent, with Ag/BMO/BOB exhibiting a minor red shift. Furthermore, the Ag/BMO/BOB composite film demonstrates enhanced light absorption intensity in the visible region (400–800 nm). This phenomenon can be attributed to the localized surface plasmon resonance (LSPR) effect of Ag NPs. The characteristic LSPR absorption peak of Ag is located around 400–430 nm, which overlaps with the intrinsic absorption edge of the semiconductor itself. As a result, no distinct characteristic peak was observed in Figure 6^[61–62]. Additionally, the existence of irradiation-induced hot electrons on Ag NPs promotes the transfer of photogenerated carriers, thus enhancing CO₂ photocatalysis^[63].

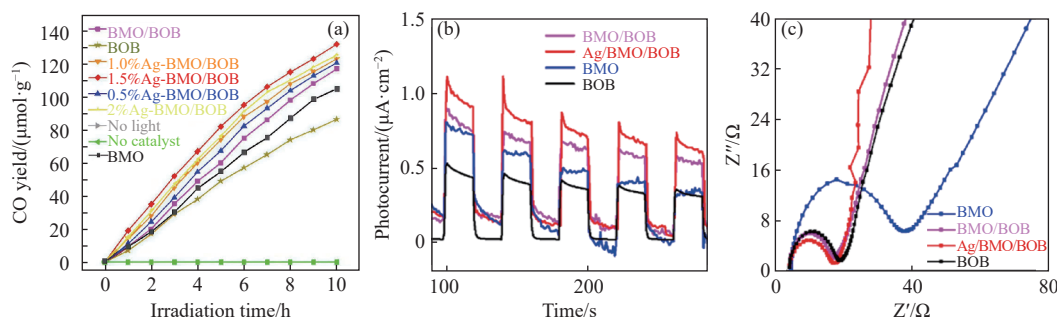


Fig. 5 (a) Photocatalytic reduction of CO₂ to CO yield diagram; (b) Photocurrent responses diagram; (c) Impedance diagram of single BMO, BOB film, BMO/BOB film and 1.5% Ag/BMO/BOB film

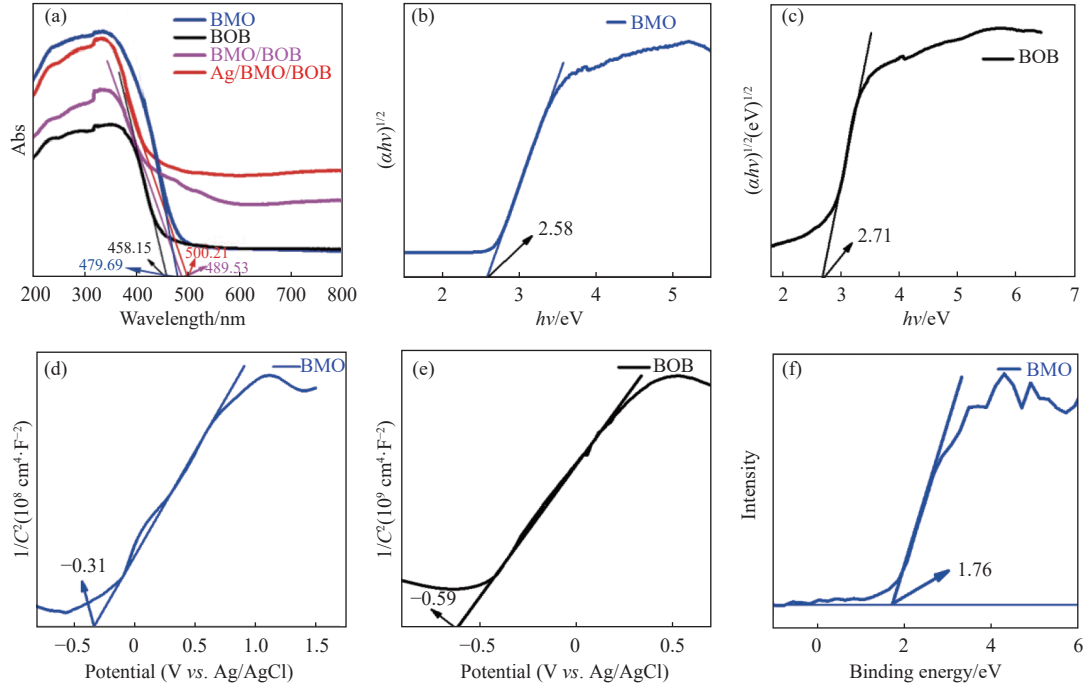


Fig. 6 (a): UV-vis DRS spectra of single and composite films; (b), (c): Tauc relation for BMO and BOB films; (d), (e): Mott-Schottky plots of BMO and BOB films; (f): VB-XPS spectrum of BMO film

The band gap energy is determined from the Tauc relation, $(\alpha h\nu)^{1/n} = A(h\nu - E_g)$, where the symbols α , h , ν , E_g and A denote the absorption coefficient, Planck constant, photon frequency, energy gap of photons, and a constant. The value of n is 1/2 for direct and 2 for indirect transitions^[64]. Both BOB and BMO are the typical indirect band gap semiconductors. Based on the Tauc plots in Figure 6(b), (c), the direct band gaps of the BMO and BOB films are determined to be 2.58 and 2.71 eV, respectively, obtained by extrapolating the linear portion of the $(\alpha h\nu)^{1/2}$ vs. $h\nu$ plots. The Mott-Schottky plots, presented in Figure 6 (d), (e), reveal a positive slope relationship between the potential values and $1/C^2$ for both BMO and BOB films, indicative of their n -type semiconductor characteristics^[40,65]. The BMO film demonstrates a flat band potential (E_{FB}) of -0.31 eV regarding the Ag/AgCl standard electrode. When referenced to the normal hydrogen electrode (NHE), the corresponding potential is -0.09 eV (equivalent to + 0.22 V vs. NHE)^[66]. As depicted in the VB-XPS spectrum of the BMO film (Figure 6(f)), the energy gap between the valence band and Fermi level is 1.76 eV. Given the fact that the flat band potential (E_{FB}) corresponds to the Fermi energy level (E_F), the E_{VBM} of the BMO film has been definitively ascertained to be 1.67 eV^[67]. Utilizing the formula $E_g = E_{VB} - E_{CB}$ ^[18], the conduction band value for BMO is calculated to be -0.91 eV. For the BOB film, we employ the equations $E_{VBM} = X - E_C + 0.5E_g$ and $E_g = E_{VB} - E_{CB}$ to determine its valence and conduction band energies. The calculations yielded $E_{VB} = 3.025$ and $E_{CB} = 0.315$ eV, where X represents the absolute electronegativity of the element ($X = 6.17$), and E_C denotes the electrode potential of a standard hydrogen electrode for free electrons ($E_C = 4.5$)^[68].

Drawing from the aforementioned data analysis, we

propose a Z-scheme heterojunction photocatalytic reduction mechanism for CO₂, as depicted in Figure 7. Electrons in the valence bands of BMO and BOB were excited under conditions of simulated solar irradiation and subsequently migrated to their respective conduction bands, leaving corresponding holes in the valence bands. The noble metal Ag, through its localized surface plasmon resonance (LSPR) effect, broadens the material's light absorption spectrum. Additionally, the high work function of Ag acts as an electron trap, successfully promoting the electron transfer from the semiconductor to the noble metal^[69]. The Ag NPs serves as a charge-transfer bridge, accepting electrons from the BOB valence band and facilitating their recombination with holes in the BMO valence band. This critical step preserves the valuable electrons and holes with higher redox potential, which in turn enhances photocatalytic performance.

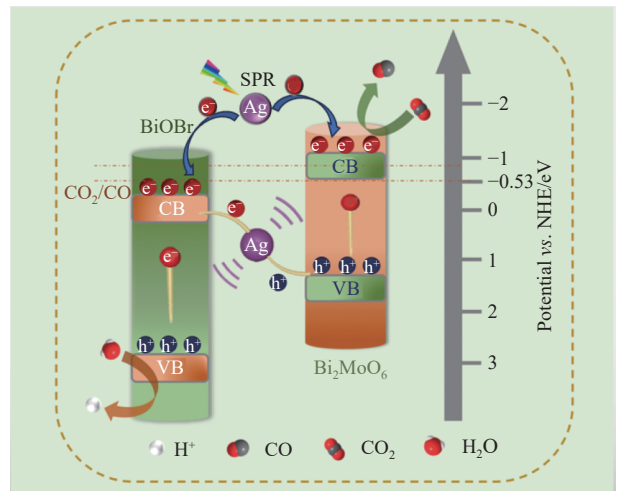


Fig. 7 Mechanism diagram of photocatalytic reduction of CO₂

The computational analysis reveals that the electron valence band (E_{VB}) of the BOB film exhibits a more positive potential compared to the oxidation potential for H₂O/O₂ ($E^{\circ} = +0.82$ V vs. NHE)^[40]. Concurrently, the electron conduction band (E_{CB}) of the BMO film displays a potential that is more negative than the reduction potential of CO₂/CO ($E^{\circ} = -0.53$ V vs. NHE)^[70]. These energetic configurations are sufficiently favorable to facilitate the occurrence of redox reactions, thereby enabling the reduction of CO₂ to CO. Therefore, in the BMO conduction band, electrons facilitate the reduction of CO₂ ($\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{CO} + \text{H}_2\text{O}$), and in the BOB valence band, holes are involved in the oxidation of H₂O ($2\text{H}_2\text{O} + 4\text{h}^+ \rightarrow 4\text{H}^+ + \text{O}_2$)^[23,71]. Based on the results, the deposited Ag plays a dual function. Firstly, it forms a Z-scheme heterojunction for efficient charge separation. Secondly, the LSPR effect induced by Ag NPs broadens the light absorption range. These combined effects lead to a significant improvement in photocatalytic performance. In the Ag/BMO/BOB composite films, the Schottky barrier function of the Ag NPs inhibits reverse charge transfer, thereby enhancing the stability of the photocatalytic system^[72]. This study provides critical insights into the rational design of multicomponent semiconductor-based photocatalytic systems for CO₂ reduction, facilitating future advancements in sustainable energy technologies.

3 Conclusions

In summary, an efficient Ag/BMO/BOB composite film for photocatalytic CO₂ reduction was successfully synthesized using an electrochemical method with a Bi plate substrate. The composite films, modified with 1.5% Ag, exhibited significantly enhanced photocatalytic performance, yielding an optimal CO production rate of 13.65 $\mu\text{mol}/(\text{g}\cdot\text{h})$. Photocurrent and impedance measurements corroborate the superior charge separation in the Ag-modified composites. The proposed Z-scheme mechanism elucidates the synergistic interactions among the components, thereby providing a scientific basis for the rational design of advanced photocatalysts and the development of immobilized systems for CO₂ reduction.

Declaration of Competing Interest

The authors declare no conflict of interest.

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Z 型异质结 Ag/Bi₂MoO₆/BiOBr 复合薄膜光催化 CO₂ 还原性能与增强机制研究

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摘 要: 本研究采用电化学-离子交换法结合光沉积技术在复合材料表面负载贵金属银纳米粒子, 构建了新型 Z 型异质结 Ag/Bi₂MoO₆/BiOBr 复合薄膜。借助 Ag 纳米粒子的局域表面等离子体共振(LSPR)效应显著提升了半导体材料的光催化性能。同时, 贵金属 Ag 作为电子传输媒介, 有效促进了 Bi₂MoO₆ 与 BiOBr 之间的界面电荷转移, 同时形成肖特基势垒, 显著抑制了光生电子-空穴对的复合。实验结果表明, Ag 修饰的 Bi₂MoO₆/BiOBr 薄膜在 CO₂ 光催化还原反应性能明显优于 Bi₂MoO₆/BiOBr 薄膜。实验发现, Ag 负载量与 CO₂ 还原制 CO 效率呈现先升高后降低的非线性关系。当 Ag 负载量为 1.5% 时, 复合材料表现出最优的光催化活性, CO 生成量达到 13.65 μmol/(g·h)。本研究系统阐明了 Ag/Bi₂MoO₆/BiOBr 薄膜增强光催化 CO₂ 还原性能的内在机制, 为设计高效光催化剂提供了重要参考, 对可持续能源技术发展具有重要意义。

关键词: 光催化 CO₂ 还原; 银纳米粒子; Bi₂MoO₆/BiOBr 复合薄膜; Z 型异质结; 原位合成

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