Synthesis of MoSe₂/SrTiO₃ Heterostructures with Enhanced Ultraviolet-Light-Driven and Visible-Light-Driven Photocatalytic Properties

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In this research, a series of novel MoSe₂/SrTiO₃ heterostructures were successfully prepared by a two-step hydrothermal method. The samples were characterized by XRD, UV-Vis, SEM, TEM, EDS and XPS. Results showed that the degradation of MO under UV is better than that under the visible light. And, MoSe₂ loaded on SrTiO₃ under UV irradiation demonstrated a higher catalytic activity. The degradation rate of methyl orange was 99.46% for MoSe₂/SrTiO₃ under the optimum loading weight (0.1 wt.%). This is mainly because the combination of MoSe₂ and SrTiO₃ prevents electrons and holes recombination in SrTiO₃ and ·O₂⁻ appears in the system. In general, MoSe₂/SrTiO₃ heterostructures have good environmental friendliness for photocatalytic degradation.

Keywords: Two-step hydrothermal method; MoSe₂/SrTiO₃; photocatalytic degradation; methyl orange.

1. Introduction

New renewable energies have been explored to replace traditional fossil fuels. And, development of semiconductors has become a hot spot.¹ Among those semiconductors, perovskite oxide is widely used as a photocatalyst in photodegradation and light hydrogen production because of its stable chemical structure and nontoxicity.²

Perovskite oxide generally refers to the oxide with ABO₃ or A₂BO₄ structure.³ In the ABO₃ structure, A is a rare earth metal with a large ionic radius, B is a transition metal with a small ionic

radius. A₂BO₄ structure consists of ABO₃ and AO layers alternately.⁴ In this frame, A is a larger cation at the edge of the structure, and B is a smaller cation located in the center octahedron.⁵ Among the perovskite oxides, strontium titanate (SrTiO₃) and strontium zirconate (SrZrO₃) are representative.⁶ The decomposition of water into hydrogen and oxygen is a nonspontaneous reaction. Thermodynamics requires that the conduction band and valence band position of the semiconductor photocatalyst must be matched with the reduction of water and the oxidation potential. That is to say, the

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conduction band of the semiconductor is lower than the H^+/H_2 (0 V versus NHE) level, the valence band is higher than the $\text{O}_2/\text{H}_2\text{O}$ (1.23 V). Thus, SrTiO_3 and SrZrO_3 are usually used to degrade dyes and decompose H_2O into H_2 and O_2 .^{7,8} Liu *et al.* proved that the $\text{MoS}_2/\text{SrTiO}_3$ composite material with 0.05 wt.% of MoS_2 showed the best photocatalytic activity, with a MO degradation rate as high as 99.81% after 60 min UV irradiation time.⁹ Tian *et al.* observed that the $\text{MoS}_2/\text{SrZrO}_3$ heterostructure with an optimal content of 0.05 wt.% MoS_2 exhibited the highest H_2 evolution rate of 5.31 mmol h^{-1} .¹⁰ Recently, studies have been carried out on SrTiO_3 based materials, including pure SrTiO_3 , SrTiO_3 supported heterostructures, metal ions doped SrTiO_3 and carbon nitride SrTiO_3 heterostructures.^{11–13}

Each Mo atom of MoSe_2 is surrounded by six Se atoms to form a triangular prism.¹⁴ Mo-Se also has many edges, resulting in a large specific surface area and excellent catalytic activity.^{15,16} At the same time, MoSe_2 belongs to the transition metal chalcogenides.¹⁷ Also, the band of MoSe_2 is narrow with great stability, which helps to improve the photocatalytic efficiency of SrTiO_3 support.¹⁸ This is important for solving energy shortages and environmental pollution.

In this study, a series of $\text{MoSe}_2/\text{SrTiO}_3$ heterostructures were synthesized by a simple two-step hydrothermal method. The photocatalytic performances in the degradation of methyl orange (MO) were investigated under both UV and visible light conditions. Research results indicated that MoSe_2 can transfer the metal properties of electrons and improve the photocatalytic activity of SrTiO_3 under UV irradiation. To the best of our knowledge, this is the first attempt to prepare the $\text{MoSe}_2/\text{SrTiO}_3$ heterostructures and apply them to the MO degradation system under UV light and visible light irradiation.

2. Materials and Methods

2.1. Chemicals and materials

Citric acid monohydrate ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$, 99.5%), tetraisopropyl orthotitanate ($\text{C}_{12}\text{H}_{28}\text{O}_4\text{Ti}$, 99.9%), strontium nitrate ($\text{Sr}(\text{NO}_3)_2$, 99.5%), sodium hydroxide (NaOH , 97.0%), sodium molybdate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, 99.0%), selenium powder (Se, 99.0%), sodium borohydride (NaBH_4 , 96.0%), MO

(96.0%), acetic acid (CH_3COOH , 99.8%) and anhydrous ethanol ($\text{C}_2\text{H}_5\text{OH}$, 99.7%) were all purchased from the Sinopharm Group Chemical Reagent Co., Ltd. in analytical grade, and were used as received without further purification. Deionized water was used throughout the whole experiment.

2.2. Synthesis of SrTiO_3

$\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ (1.26 g) was dissolved in ethanol (15 mL), followed by adding $\text{C}_{12}\text{H}_{28}\text{O}_4\text{Ti}$ (1.5 mL) to form solution 1. Solution 2 was prepared by dissolving $\text{Sr}(\text{NO}_3)_2$ (1.06 g) in deionized water (15 mL). NaOH (2 g) was dissolved in deionized water (15 mL) to form solution 3. The solution 2 and 3 were separately added to solution 1 with mechanical stirring for 30 min. Then, the mixed solution was sealed in a Teflon-lined stainless-steel autoclave. The autoclave was cooled down to room temperature, followed by centrifugation. The product obtained was washed three times with deionized water, acetic acid and ethanol. The product was vacuum-dried at 80°C for 24 h to obtain SrTiO_3 .

2.3. Synthesis of $\text{MoSe}_2/\text{SrTiO}_3$ heterocatalyst

1 g as-prepared SrTiO_3 was dissolved in the mixture containing 30 mL distilled water and 30 mL ethanol, a certain quality $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, Se, NaBH_4 were then added into the solution. The obtained suspension was stirred for 30 min for uniform dispersion. The mixed solution was then sealed in a PPL-lined stainless-steel autoclave. The autoclave was heated to 240°C for 48 h. After cooling to the room temperature, the product was separated by centrifugation, washed with distilled water and ethanol three times. Finally, the catalysts were dried in vacuum at 80°C for 24 h. The prepared samples with 0.01, 0.05, 0.1, 0.5, 1, 3, 5 wt.% MoSe_2 , defined as the weight ratios of MoSe_2 to SrTiO_3 , were named as S1, S2, S3, S4, S5, S6, S7.

2.4. Photocatalytic activity test

10 mg MO was dissolved in 500 mL deionized water to obtain MO dye solution with a concentration of 20 mg L^{-1} . 0.2 g photocatalyst was added into MO dye solution and stirred for 30 min in the absence of light to reach the adsorption equilibrium. The initial concentration of the mixed solution was designated as C_0 . Experiments were carried out to evaluate the

photocatalytic activity. Under UV-light and visible light irradiation, 4 mL of the liquid sample was periodically extracted every 15 min. Then the photocatalyst and the solution were separated by centrifugation. Finally, the absorbance of the filtrates was measured by a spectrophotometric technique. The photocatalytic performance was measured by the dye removal rate, which is calculated by the following formula:

$$D = \frac{C_0 - C}{C_0} \times 100\%,$$

where D (%) is the degradation rate, C_0 (mg L⁻¹) denotes the initial MO dye concentration, and C (mg L⁻¹) represents the MO dye concentration in the filtrates after irradiation.

2.5. Characterization of photocatalyst

D/max 2500PC X-ray diffractometer was used to analyze photocatalysts (CuK α as the radiation source, $\lambda = 1.54056$ Å). Scanning electron microscopy (SEM, JEOL/JSM-6360LA) and transmission electron microscopy (TEM, JEM-2010) were used to observe the morphology and other internal microstructure of photocatalysts. The elements and its valence were analyzed by X-ray photoelectron spectroscopy (XPS, Thermo-250XI) and energy dispersive spectrometer (EDS, Ametek Genesis-XM260S). UV-Vis absorption spectra were measured on a Hitachi U-4100 spectrometer.

3. Results and Discussion

The XRD patterns of the catalysts are shown in Fig. 1. All the peaks were assigned as cubic perovskite structure (JCPDS card 35-0734) at 2θ with angles of 32.4°, 39.9°, 46.5°, 57.7°, 67.6° and 77.1° corresponding to the indices of the (110), (111), (200), (211), (220) and (310) planes. However, no obvious peaks of heterojunctions attributed to MoSe₂ phase were observed in S1–S7 samples. This is mainly due to the low load, uniform distribution and poor crystallization of MoSe₂. The diffraction peaks of S1–S7 were similar to pure SrTiO₃ indicating that no new phase of SrTiO₃ was presented in MoSe₂/SrTiO₃.

The morphology of SrTiO₃ is a nanosphere [in Figs. 2(a), 2(b) and Figs. 3(a), 3(b)]. From Figs. 2(c) and 2(d), the flower-like MoSe₂ is loaded on the spherical SrTiO₃ surface. Therefore, it can be

Fig. 1. XRD patterns of SrTiO₃ S1, S2, S3, S4, S5, S6, S7.

proved indirectly that MoSe₂/SrTiO₃ heterostructure is successfully synthesized. The mechanism of MoSe₂ loading on SrTiO₃ surface was illustrated in Fig. 2(e). Figure 3(e) shows the presence of Sr, Ti, O, Mo and Se elements for the EDS of S3 samples. Based on the HRTEM of S3 in Figs. 3(c) and 3(d), the lattice spacing was calculated to be 0.65 nm, corresponding to the (002) plane of MoSe₂, indicating that MoSe₂ was successfully loaded on SrTiO₃ surface. As a result, MoSe₂/SrTiO₃ heterostructures were successfully prepared.

Based on the Kubelka–Munk theory, the UV-Vis of SrTiO₃ shows a significant steep absorption edge located at about 392 nm which can be assigned to its intrinsic bandgap absorption (in Fig. 4). The energy band of SrTiO₃ is calculated to be 3.2 eV according to the formula E (eV) = 1240/ λ (nm).¹⁹ The UV-Vis of S1, S2, S3, S4, S5, S6, S7 are similar to SrTiO₃ and are in the range of ultraviolet light. The UV absorption edge of MoSe₂ is at 710 nm, so the energy band of MoSe₂ is 1.75 eV.^{20,21}

No obvious spectrum difference was caused by MoSe₂ loading. Thus, the elements of sample S7 was investigated by XPS as shown in Fig. 5. Figure 5(a) shows a comparison of XPS for SrTiO₃ and S7 samples. The compositions of Sr, Ti and O elements for SrTiO₃ and S7 are shown in Figs. 5(b)–5(d). After the MoSe₂ was supported to SrTiO₃, a higher binding energy of Sr 3d, Ti 2p and O 1s of MoSe₂/SrTiO₃ shifted by about 0.25 eV can be observed, indicating that the electrons can transfer from SrTiO₃ to MoSe₂. Two peaks of Sr 3d in Fig. 5(b) at 133.7 eV and 135.3 eV are assigned to

Fig. 2. (a) and (b) SEM images of SrTiO_3 , (c) and (d) SEM images of S3 and (e) formation mechanism of S1–S7.

$\text{Sr } 3d_{5/2}$ and $\text{Sr } 3d_{3/2}$,²² and the binding energies corresponding to $\text{Ti } 2p_{3/2}$ and $\text{Ti } 2p_{1/2}$ are 458.1 eV and 463.9 eV in Fig. 5(c).²³ The binding energy of O 1s is 531.8 eV in Fig. 5(d).²⁴ In Fig. 5(e), the binding

Fig. 3. (a) and (b) TEM images of SrTiO_3 , (c) and (d) HRTEM images of S3 and (e) EDS of S3.

Fig. 4. UV-Vis absorption spectra of SrTiO_3 , S1, S2, S3, S4, S5, S6, S7 and MoSe_2 samples.

energies of $\text{Mo } 3d_{5/2}$ and $\text{Mo } 3d_{3/2}$ peaks are located at 229.1 eV and 232.3 eV,²⁵ respectively, suggesting that Mo^{4+} exists in the sample. Figure 5(f) shows a high-resolution XPS spectrum of Se 3d. The peak is split into two well-defined peaks at 54.5 eV and 55.4 eV, corresponding to the Se $3d_{5/2}$ and Se $3d_{3/2}$ peaks,²⁶ indicating that Se^{2-} exists in the sample. The ratio of atomic percentage of Mo and Se analyzed by XPS was 11.32:21.70, which is close to 1:2. In summary, the presence of MoSe_2 and SrTiO_3 in the S7 sample was further confirmed by the high resolution of the XPS spectrum, which is consistent with XRD and TEM analysis.

As indicated in Fig. 6, the degradation performance under UV light is better than that under visible light. Judging from Fig. 6(a), the MO has not been completely degraded after 75 min reaction,

Fig. 5. (a) XPS survey spectra of sample SrTiO_3 and S7, (b-f) high resolution XPS spectra of Sr, Ti, O, Mo and Se.

Fig. 5. (Continued)

Fig. 6. The degradation performance of pure SrTiO₃ and S1, S2, S3, S4, S5, S6, S7 in 75 min. (a) under UV light (b) under visible light.

indicating the relative poor activities of all SrTiO₃ based catalysts. Comparing samples S1–S5 with pure SrTiO₃, the degradation rate is higher for S1–S5. Therefore, loading MoSe₂ can improve the photocatalytic activity of SrTiO₃. Moreover, S3 sample with 0.1 wt.% loading demonstrated highest activity, with the degradation rate of 99.46%. This is because small amount of MoSe₂ caused an efficient charge separation of SrTiO₃, which suppressed the electron–hole recombination. However, when the MoSe₂ loading increased from 0.1 wt.% to 5 wt.% (S3–S7), the MO degradation rate decreased gradually. The major reason is that a large amount of MoSe₂ grew on the surface of SrTiO₃, covering a part of the catalytic activity center, and blocking the UV light needed in the reaction process with the increase of MoSe₂ content.

The intensity of the characteristic peaks in the UV-Vis absorption spectra of the MO concentrations is different, so the photocatalytic activity of the corresponding different catalysts can be evaluated. The higher the concentration of MO is, the stronger the peak is. In Fig. 7, the maximum absorption peak at 460 nm in the UV-Vis absorption spectra is the weakest after the degradation of MO solution for 45 min when S3 acted as the catalyst under UV irradiation. The peak intensity (Fig. 7) corresponds to the change of the degradation rate [Fig. 6(a)].

The stability and reusability of photocatalysts are important factors for its application. Herein, the stability of the 0.1 wt.% MoSe₂/SrTiO₃ (S3) is investigated. After six cycles of the photodegradation

Fig. 7. UV-Vis absorption of MO with the variation of MoSe₂ loading at 45 min irradiation time under UV irradiation.

Fig. 8. Recyclability of photodegradation of MO over S3 under UV irradiation for 75 min.

of MO, no significant loss in photocatalytic activity is observed, as shown in Fig. 8, indicating the excellent stability of MoSe₂/SrTiO₃ catalyst.

As shown in Fig. 9, the degradation rate of MO was not significantly reduced after addition of IPA,²⁷ indicating that $\cdot\text{OH}$ was not an important contributor to the degradation process. In contrast, the degradation rate of MO decreased significantly after adding TEOA and BQ into MO solution,^{28,29} indicating that h^+ was trapped by TEOA and $\cdot\text{O}_2^-$ was captured by BQ. Thus, h^+ and $\cdot\text{O}_2^-$ were the main active substances of the S3 catalyst under UV irradiation.

The valence band and conduction band of MoSe₂ and SrTiO₃ can be calculated according to the

Fig. 9. Photodegradation of MO using different radical scavenger over S3. (a) no scavenger under O₂-saturated condition, (b) IPA for $\cdot\text{OH}$ under O₂-saturated condition, (c) TEOA for h^+ under O₂-saturated condition, (d) BQ for $\cdot\text{O}_2^-$ under O₂-saturated condition.

formula of valence band energy E_{VB} and conduction band energy E_{CB} ³⁰⁻³²:

$$E_{\text{VB}} = X - E^c + 0.5E_g,$$

$$E_{\text{CB}} = X - E^c - 0.5E_g,$$

where X represents the geometrical mean of the absolute electronegativity of each atom in the semiconductor, E^c represents the electron free energy (in general 4.5 eV), E_g represents the semiconductor bandgap energy. $E_g(\text{SrTiO}_3) = 3.2 \text{ eV}$, $E_g(\text{MoSe}_2) = 1.75 \text{ eV}$ have been calculated from Fig. 4. From the table, $X(\text{SrTiO}_3) = 4.95$, $X(\text{MoSe}_2) = 5.13$ are obtained according to calculation. So final results are $E_{\text{VB}}(\text{SrTiO}_3) = 2.05 \text{ V}$, $E_{\text{CB}}(\text{SrTiO}_3) = -1.15 \text{ V}$, $E_{\text{VB}}(\text{MoSe}_2) = 1.51 \text{ V}$, $E_{\text{CB}}(\text{MoSe}_2) = -0.24 \text{ V}$. To this end we can propose the following mechanism (Fig. 10):

Fig. 10. The proposed mechanism of the charge transfer and separation process for the MoSe₂/SrTiO₃ heterostructures under UV irradiation.

The conduction band position of SrTiO₃ is higher than that of MoSe₂, the electrons can easily transfer from SrTiO₃ to MoSe₂. Under UV light irradiation, the photo-excited electrons VB of SrTiO₃ are directly transferred to CB of SrTiO₃, creating holes in the VB.³³ The photo-generated electrons and holes are inclined to recombine quickly without MoSe₂ loading, causing the low photocatalytic activity. However, after introducing MoSe₂, electrons in the CB of SrTiO₃ will migrate to the MoSe₂, which makes the electrons more mobile and provides highly active sites for the photocatalysis process. In addition, the holes left in the SrTiO₃ can be consumed by the MO dyes. Besides, O₂ receives excess electrons from MoSe₂ and combines it into ·O₂⁻. As we all know, ·O₂⁻ has a strong oxidizing property. Thus, the above-described mechanism can effectively suppress the recombination between electrons and holes, enhance interfacial charge transfer, lengthen the lifetime of charge carriers and enlarge the active sites.

4. Conclusions

In summary, the MoSe₂/SrTiO₃ heterostructures were prepared by the two-step hydrothermal method for the first time in the degradation of MO under UV light and visible light irradiation. It was found that the degradation rate of MO under UV irradiation was much higher than that under visible light. Under UV irradiation, the optimum loading of MoSe₂ is 0.1 wt.%. At 75 min, the degradation rate of MO reaches 99.46%, which is much higher than pure SrTiO₃. However, excessive loading can hinder the active center, affecting the process of photodegradation. The proposed mechanism shows that the proper amount of MoSe₂ can effectively suppress the recombination of electrons and holes in SrTiO₃, enhance the movement of interfacial electrons, prolong the time of electrons and increase the photocatalytic activity center. At the same time, ·O₂⁻ generation also plays a significant role. Therefore, the development of cheap nonprecious metal composites for photodegradation has great potential because of its high economic and catalytic activity.

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