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ORIGINAL RESEARCH

Synthesis of PbS–K₂La₂Ti₃O₁₀ composite and its photocatalytic activity for hydrogen production

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Abstract Photocatalyst, lead sulfide (PbS)-intercalated layer perovskite-type compound (K₂La₂Ti₃O₁₀), was synthesized via ion-exchange reaction, butylamine pillaring and sulfuration processes under the assistance of the microwave irradiation. The structure of the photocatalysts was determined by means of powder X-ray diffraction, scanning electron microscope, ultraviolet-visible diffuse reflection spectra and photoluminescence measurement. And the photocatalytic activity of the composite compound for hydrogen production was also investigated. The experimental results showed that the intercalation of PbS in the layered space of K₂La₂Ti₃O₁₀ greatly improved the absorption edge and the photocatalytic activity. Hydrogen production of the PbS–K₂La₂Ti₃O₁₀ was 127.19 mmol/(g cat) after 3 h irradiation of ultraviolet light.

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1. Introduction

Currently, it was urgently needed to find new and clean energy since the issues of fossil fuels and the pollution of environmental are becoming more serious. The decomposition of water into hydrogen and oxygen by photoinduced processes employing a semiconductor irradiated with light is a process which can be used for sustainable solar energy conversion, and has been investigated widely [1,2]. Layered semiconductors are a group of compounds which demonstrate high activities for photocatalytic water splitting, and some of these semiconductors have been reported to using photo-processes [3,4]. K₂La₂Ti₃O₁₀ is a layered perovskite-type compound with octahedral perovskite-layers (La₂Ti₃O₁₀²⁻), and K⁺ ions located between the perovskite-layers [5–7]. The intercalation of some narrow bandgap semiconductors such as ferric oxide (Fe₂O₃) [8]

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and cadmium sulfide (CdS) [9] is a popular method adopted by many scientists to improve the photo-activity for layered compound. However, to our knowledge, lead sulfide (PbS) intercalated K₂La₂Ti₃O₁₀ photocatalysts have not been reported. The process for intercalation is so complicated that it usually requires several steps such as ion-exchange, butylamine intercalated and sulfuration, which often takes more than one week via a traditional water-logging procedure due to mass transfer limitations. We have developed a facile synthesis for intercalated materials with the assistance of microwaves in our previous study [10,11], which had greatly shortened the preparation time. Therefore, in the present work, we synthesized the PbS intercalated K₂La₂Ti₃O₁₀ photocatalysts with the assistance of microwave irradiation. The structure of the samples was characterized and the photocatalytic activities of the samples were tested on hydrogen evolution under ultraviolet (UV) light.

2. Experimental

2.1. Starting materials

All chemicals used in this work and their chemical abstract service (CAS) number are listed in Table 1. All materials were used without further purification.

2.2. Synthesis of catalysis

K₂La₂Ti₃O₁₀ powder was obtained by a stearic acid (octadecanoic acid, C₁₈H₃₆O₂) method as described in Ref. [12]. The detailed procedure was as follows: 10 g lanthanum nitrate [La(NO₃)₃] and then 2.5 g KOH were dissolved in 30 g C₁₈H₃₆O₂ solvent, respectively, and the solution was stirred magnetically at 130 °C for 2 h to remove the excess water. Then, 14.5 ml of titanium butoxide (tetrabutyl titanate, [CH₃(CH₂)₃O]₄Ti) was added to the solution, and the mixture was stirred magnetically for 0.5 h. The resulting mixture was burned in an electric furnace to remove the organic matter, and then calcined in a tube furnace at 1000 °C for 2 h. Finally, the powder was ground for further use.

The PbS intercalated K₂La₂Ti₃O₁₀ photocatalyst was synthesized under the assistance of microwave irradiation (Microwave oven, XH-100A, China). The detailed procedure is as follows [11]: First, the as-prepared K₂La₂Ti₃O₁₀ powder was added into 1 mol/L of HCl solution, and then stirred under microwave irradiation using power at 400 W and frequency at 2.45 GHz for 1 h in order to replace K⁺ with H⁺ in the layered space of K₂La₂Ti₃O₁₀. The microwave irradiation was used as an intermittent process, in which the microwave was suspended for 2 min after 2 min of irradiation

in order to avoid drastically boiling the solution. The temperature of the solution was maintained at about 90 °C during the course of the reaction. After the microwave treatment, the suspension was centrifuged and washed using distilled water and then dried at 60 °C in vacuum oven for 6 h. The sample prepared in this manner was designated as H₂La₂Ti₃O₁₀.

n-Butylamine intercalated K₂La₂Ti₃O₁₀ was synthesized via the reaction of *m*-H₂La₂Ti₃O₁₀ with 50 vol% *n*-butylamine in an aqueous solution under microwave irradiation at 65 °C for 3 h. After that irradiation period, the sample was centrifuged, washed and dried. This material was designated as C₄H₁₁N-H₂La₂Ti₃O₁₀.

To facilitate the ion-exchange, the C₄H₁₁N-H₂La₂Ti₃O₁₀ sample was reacted with Pb(CH₃COO)₂ in a 0.4 mol/L aqueous solution under microwave heating at 75 °C for 3 h. This suspension was centrifuged and washed carefully using distilled water until the pH value of the solution reached 7, indicating the removal of Pb²⁺ on the surface of K₂La₂Ti₃O₁₀. The dried Pb intercalated K₂La₂Ti₃O₁₀ product was then reacted with hydrogen sulfide (H₂S) in a U-tube, thereby intercalating PbS into the K₂La₂Ti₃O₁₀. H₂S was obtained by the reaction of sulfuric acid and Na₂S. The composite catalyst was designated as PbS-K₂La₂Ti₃O₁₀.

Pure PbS was synthesized by the reaction of the Pb(CH₃COOH)₂ (1 mol/L) and Na₂S (1 mol/L) in an aqueous solution. The sample named PbS/K₂La₂Ti₃O₁₀ was prepared by the direct mechanical mixing of PbS and K₂La₂Ti₃O₁₀ in an agate mortar.

2.3. Characterizations of catalysis

The crystal structure and the phase of the samples were determined by X-ray diffractometer (XRD) using a Rigaku D/MAX2500 PC diffractometer with Cu K α radiation, with an operating voltage of 40 kV and an operating current of 100 mA. The morphology of the samples was detected using a scanning electron microscope (SEM) (Hitachi, s-4800). UV-visible light (UV-vis) diffuse reflectance spectra were recorded on a UV-vis spectrometer (Puxi, UV1901). The luminescence of the powdered samples was measured using a spectrofluorometer (Hitachi, f7000).

2.4. Photocatalytic activity

The photocatalytic activities of hydrogen production for the photocatalyst samples were examined in an inner irradiation system (BL-GHX-TYPE, Shanghai). 0.50 g powder of photocatalyst was dispersed in 250 ml of aqueous solution of 0.10 mol/L Na₂S, 0.50 mol/L Na₂SO₃ and 1 mol/L KOH. The light source used was a 300 W mercury lamp. The

Table 1 The materials used in this study.

Material description	CAS number	Source
<i>n</i> -Butylamine (purity 99.5%)	109-73-9	Tianji Damao Chem. Comp. China
Lanthanum nitrate [La(NO ₃) ₃ · 6H ₂ O]	10277-43-7	Aldrich Chem. Comp. USA
Lead acetate [Pb(CH ₃ COO) ₂ · 3H ₂ O]	6080-56-4	Tianji Damao Chem. Comp. China
Titanium butoxide (purity 97%)	5593-70-4	Tianjin Guangfu Chem. Comp. China
Titanium oxide [TiO ₂]	13463-67-7	Panzhuhua Iron. Comp. China
Stearic acid [C ₁₈ H ₃₆ O ₂ , purity 95%]	57-11-4	Tianji Damao Chem. Comp. China

produced hydrogen was detected using an online gas chromatograph (GC, TCD, carbon molecular sieves 5 Å column, Ar carrier, FULI 9790, China) system.

3. Results and discussion

3.1. Characterization of catalysts

The powder X-ray diffraction (XRD) patterns of $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$, $\text{H}_2\text{La}_2\text{Ti}_3\text{O}_{10}$, $\text{C}_4\text{H}_{11}\text{N}-\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ and $\text{PbS}-\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ are shown in Fig. 1. The diffraction peaks were intense and sharp, indicating that the obtained $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ was well crystallized. The peak appeared at 5.94° , corresponding to the crystal plane of (002), indicating that the interplanar distance of (002) planes was measured to be 1.49 nm, according to the Bragg equation: $d = (\lambda/2 \sin \theta)$ (d —crystal, λ —wavelength, θ —diffraction angle), while $\text{H}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ samples displayed the main peak at 6.24° , indicating that the interplanar distance of (002) planes was 1.42 nm. This change could be attributed to the fact that K^+ ions were replaced by

H^+ , whose ion radius is slightly smaller than that of K^+ . The main peak corresponding to (002) crystal plane for $\text{C}_4\text{H}_{11}\text{N}-\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ sample shifted to the low angle, due to the larger radius of $\text{C}_4\text{H}_9\text{NH}_2^+$ compared with H^+ . This suggested that the expansion of the layered space was achieved through the intercalation of $\text{C}_4\text{H}_9\text{NH}_2$ into $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$, and the expansion of layered space is supposed to promote the intercalation of PbS semiconductors. As for the XRD patterns of $\text{PbS}-\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$, the peaks could be indexed to the $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$, indicating that the layered lattice structure of $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ was not changed too much during the procedures of ion-exchange reaction, *n*-butylamine pillaring and sulfuration processes. The diffraction peaks assigned to PbS were not observed due to a higher dispersion in the $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ samples.

The morphologies of $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ and $\text{PbS}-\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ samples were investigated by scanning electron microscope (SEM), as shown in Fig. 2. The SEM images showed the surface topography of these photocatalysts. The photocatalytic activities of photocatalysts depend on the surface topography and layers structure [13]. All the products exhibited aggregated sheet-like morphologies. Fig. 2a demonstrates that $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ particles exhibited relatively uniform size and smooth surface morphology. However, the layered structure and primary spacing changes could not be observed. The SEM image of $\text{PbS}-\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ in Fig. 2b displays a relatively clear layered structure, indicating that the material was stacked up layer by layer. Meanwhile, comparing with $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$, $\text{PbS}-\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ possessed a rough surface and a larger spacing distance, indicating that spacing distance increased obviously due to the intercalation.

Optical absorption of the as-prepared photocatalysts was investigated using a UV-vis spectrometer. Fig. 3 shows the UV-vis diffuse reflectance spectra of $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$, $\text{PbS}-\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ and $\text{PbS}/\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$. The pure $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ sample presented the absorption edge of 350 nm, corresponding to a band gap of approximately 3.5 eV, which cannot be responsive for visible light [12]. The absorption edge of $\text{PbS}/\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ was similar to $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ sample, and the absorption for visible light is slightly higher than that of $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$. The absorption edge of $\text{PbS}-\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ was determined to be 400 nm, and it is directly allowed optical absorption, which is longer than that of $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ sample. This factor can be attributed to the small particle size of PbS in $\text{PbS}-\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ composite. It is obvious that the absorption edge of $\text{PbS}-\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ appeared a red-shift into the

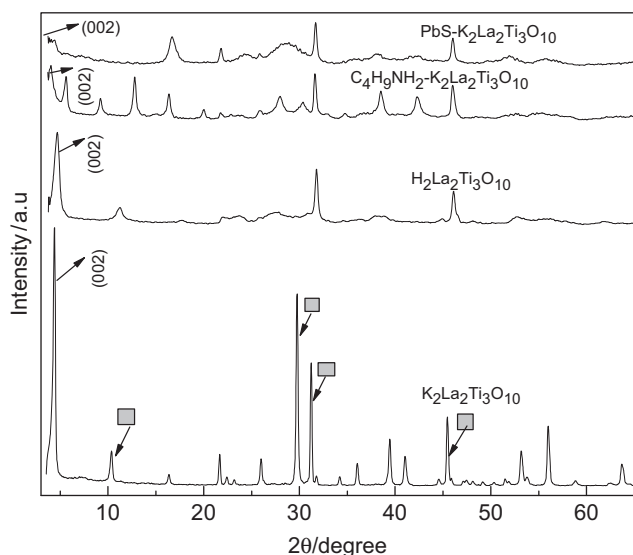


Fig. 1. The XRD spectrogram of the products each stage for synthesizing the $\text{PbS}-\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$.

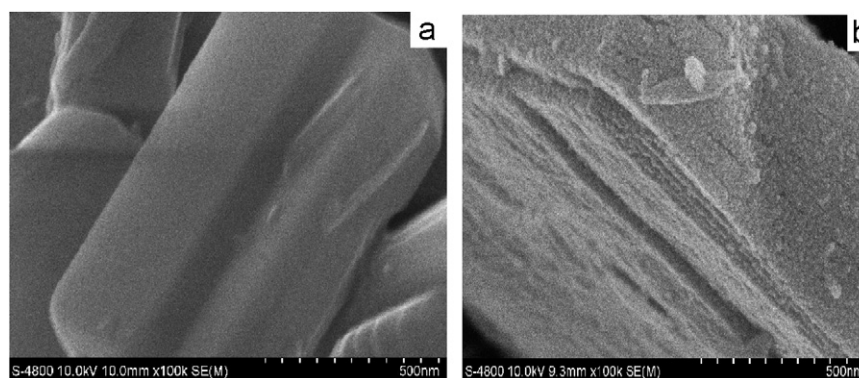


Fig. 2. SEM images of photocatalysts (a) $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$; (b) $\text{PbS}-\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$.

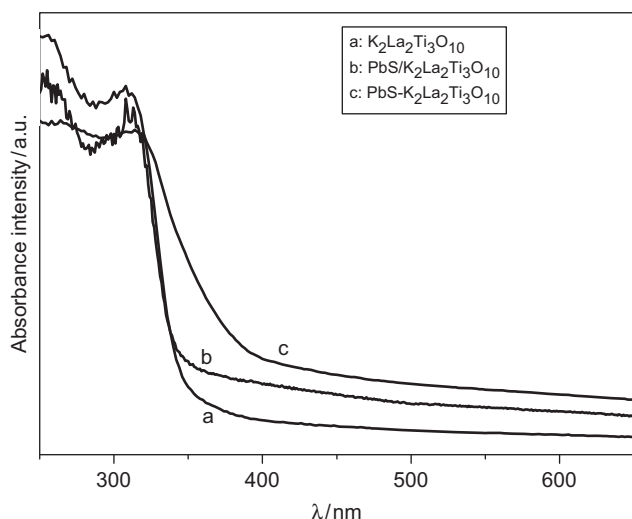


Fig. 3. The UV-vis diffuse absorption spectra of photocatalysts.

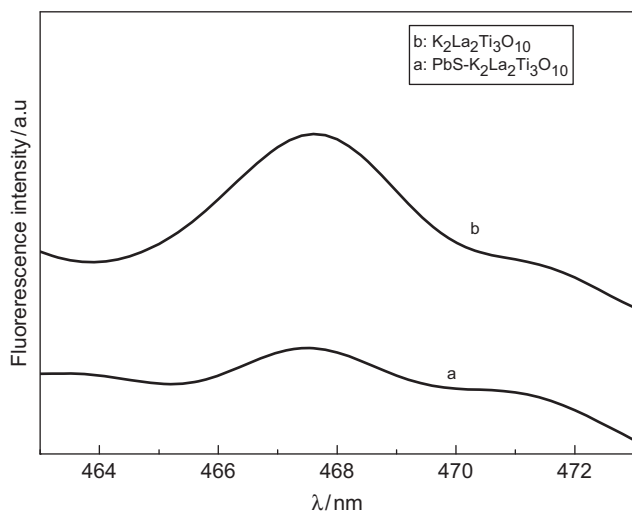


Fig. 4. The fluorescence spectra of K₂La₂Ti₃O₁₀ and PbS–K₂La₂Ti₃O₁₀.

visible light region, and this could be attributed to the interaction of PbS and K₂La₂Ti₃O₁₀ in the composite sample.

The photocatalytic activities can be analyzed from the aspect of the transition of the photogenerated electrons–holes [14]. The molecular fluorescence spectroscopy could reflect the migration and capture of photo-induced carriers [15]. Fig. 4 shows the molecular fluorescence spectroscopy of K₂La₂Ti₃O₁₀ and PbS–K₂La₂Ti₃O₁₀. Both PbS–K₂La₂Ti₃O₁₀ and K₂La₂Ti₃O₁₀ generated electrons and holes under UV irradiation. The molecular fluorescence spectroscopy was caused by the recombination of photo-induced electrons and holes. Therefore the higher photocatalytic activities may be due to the weak peak of molecular fluorescence spectroscopy. As shown in Fig. 4, the strong peak at around 470 nm was assigned to the emission of pure K₂La₂Ti₃O₁₀ [16]. Meanwhile, the emission intensity of PbS–K₂La₂Ti₃O₁₀ was drastically decreased, which may indicate that PbS was highly dispersed in the K₂La₂Ti₃O₁₀ samples, which could result in the migration of the photogenerated electrons from the conduction band of PbS to the conduction band of K₂La₂Ti₃O₁₀ and

the photogenerated holes from the valence band of K₂La₂Ti₃O₁₀ to the valence band of PbS. This facilitated the separation of the photogenerated electron–hole pairs, and caused the decreased intensity of the emission peak.

3.2. Photocatalytic performance

The photocatalytic hydrogen production activities of the PbS, K₂La₂Ti₃O₁₀, PbS–K₂La₂Ti₃O₁₀ and TiO₂ were examined under UV light irradiation for 3 h. The photocatalytic activities are displayed in Fig. 5. The results in Fig. 5 indicated that all photocatalysts exhibited photo-activities for hydrogen evolution. In all samples, PbS intercalated K₂La₂Ti₃O₁₀ photocatalyst showed the highest activity. The photocatalytic activity of the PbS–K₂La₂Ti₃O₁₀ photocatalyst for hydrogen production after 3 h irradiation was 127.19 mmol/(g cat), while the photocatalytic activity of PbS was 7.55 mmol/(g cat). The K₂La₂Ti₃O₁₀ and TiO₂ showed the photo-activities to be about 83.51 mmol/(g cat) and 57.9 mmol/(g cat) hydrogen produced after 3 h irradiation, respectively, under the same conditions. These factors may indicate that the narrow band gap semiconductor of PbS expanded the response for visible

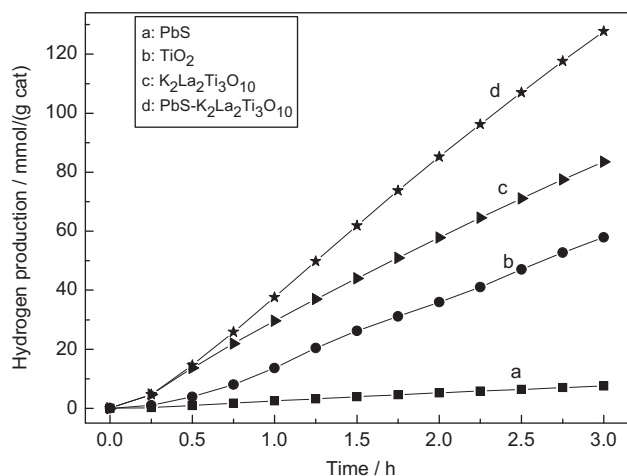


Fig. 5. The photocatalytic activities of the catalysts.

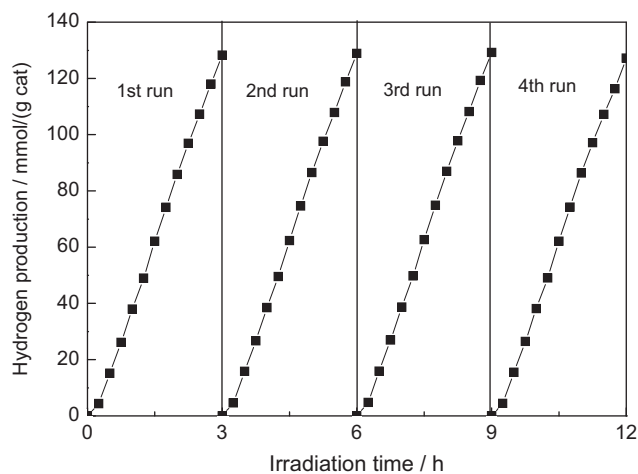


Fig. 6. Photocatalytic activities of repeated runs of photocatalysis over recycled sample under UV light.

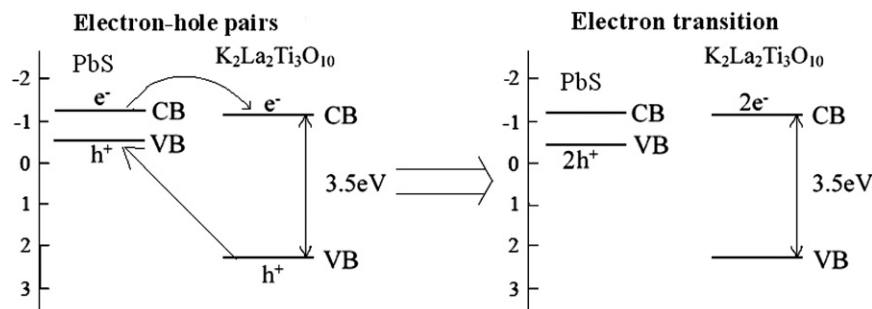


Fig. 7. Electron and positive hole transition under UV light.

light. This may also suggest that the synergetic effect of nano-sized PbS and the layered structure of $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ in the $\text{PbS-K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ photocatalysts was an important factor for the improvement of photocatalytic efficiency. The composite material inhibits the recombination of photogenerated electron-hole pairs and greatly enhances the photocatalytic activity. The low activity of PbS may be due to the relative large particle size, which could improve the recombination of photo-induced carriers.

Stability is an important parameter for photocatalysts. To evaluate the stability and reusability of the photocatalyst, we performed repeated runs for the photocatalytic hydrogen evolution over $\text{PbS-K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ under visible light, recycling the catalyst between runs. The photocatalytic activities of repeated runs of photocatalysis are shown in Fig. 6. As shown in Fig. 6, after four cycles of photocatalysis, the as-prepared catalyst did not exhibit any significant loss of activity, indicating that it possessed a good stability for repeated photocatalytic reaction.

3.3. Mechanism analysis

The photocatalytic mechanism was analyzed from the aspect of the transition of the photogenerated electrons-holes. Fig. 7 shows the electron and hole transition of $\text{PbS-K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ under UV light. For many titanates, valence band (VB) levels are known to be around +3 V vs. NHE (normal hydrogen electrode). The bandgap of $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ was estimated to be about 3.50 eV from the UV-vis diffuse reflectance spectrum. Therefore, the conduction band (CB) levels are around -0.50 V vs. NHE. It is possible for hydrogen generation through photo-catalysis of splitting water under $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$, due to the factor that the level of valence band is higher than electrode potential of H^+/H and the level of conduction band is lower than electrode potential of $\text{O}_2/\text{H}_2\text{O}$, according to the discussion above [17]. The bandgap of PbS was estimated to be about 0.40 eV [18]. The photocatalytic activity was improved after the narrow bandgap semiconductor of PbS was intercalated into the layered space of $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$. PbS appeared nano-size in the layered space, thus resulting in the enhanced photo-conversion efficiency of the composite photocatalyst. According to the relative position of the valence bands and conduction bands for PbS and $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$, the band structure of $\text{PbS-K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ was determined, and is depicted in Fig. 7. As shown in Fig. 7, both PbS and $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ generated electrons and holes under UV irradiation. The photogenerated electrons on the conduction band of PbS could migrate to the conduction band of $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$

with the higher potential, and the photogenerated holes on the valence band of $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ could migrate to the valence band of PbS with the lower potential. Thus, photogenerated electrons aggregated on the conduction band of $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ and holes aggregated on the valence band of PbS, which facilitated the separation of the photogenerated electron-hole pairs and acted to improve the photocatalytic activity.

4. Conclusions

The $\text{PbS-K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ photocatalyst was successfully synthesized under the assistance of microwave irradiation. The intercalation of PbS in the layered space of $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ greatly improved the absorption edge and the photocatalytic activity. The photocatalytic activity of the $\text{PbS-K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ photocatalyst for hydrogen production after 3 h irradiation was 127.19 mmol/(g cat) under UV light irradiation, which is much higher than that of $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ and TiO_2 .

Acknowledgments

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