

Influence of calcination atmosphere on photocatalytic reactivity of $K_2La_2Ti_3O_{10}$ for water splitting

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Abstract: The layered perovskite type oxide $K_2La_2Ti_3O_{10}$ powders were prepared under air, Ar and H_2 calcination atmospheres by sol-gel method and characterized by X-ray diffractometry, UV-Vis diffuse reflectance and X-ray photoelectron spectroscopy. The influence of the calcination atmosphere on the photocatalytic reactivity of $K_2La_2Ti_3O_{10}$ for hydrogen production was investigated. The photocatalytic reactivity of $K_2La_2Ti_3O_{10}$ prepared under air, Ar and H_2 atmospheres was compared with that prepared under ultraviolet and visible light radiation using I^- as electronic donor. The results show that $K_2La_2Ti_3O_{10}$ prepared under Ar and H_2 atmospheres has higher photocatalytic activity for hydrogen production than that prepared under air atmosphere. The hydrogen production rates under ultraviolet irradiation are 127.5, 81.3 and 57.0 $\mu\text{mol}/(\text{L}\cdot\text{h})$ and those under visible light irradiation are 40.2, 30.2 and 16.5 $\mu\text{mol}/(\text{L}\cdot\text{h})$ respectively when $K_2La_2Ti_3O_{10}$ is prepared under Ar, H_2 and air atmospheres.

Key words: $K_2La_2Ti_3O_{10}$; calcination atmosphere; photocatalytic activity; hydrogen

1 Introduction

Because of its high chemical stability and favorable energy band structure, the layered perovskite photocatalyst $K_2La_2Ti_3O_{10}$ has drawn much attention for its applications in water photocatalytic splitting for H_2 and O_2 production from potassium hydroxide aqueous solution[1–3]. The photocatalyst $K_2La_2Ti_3O_{10}$ has one interlayer and this structure is favorable for the improvement of its photocatalytic reactivity for water splitting. Under light irradiation, the light-generated electrons move from the interlayer of $K_2La_2Ti_3O_{10}$ to external surface and light-generated holes oxidize the water to produce O_2 in the interlayer. The photocatalytic reactivity of semiconductors is well known to depend not only on their bulk energy band structure, but also to a great extent, on the point deficiency[4–5]. The metallic vacancy and oxygen vacancy are the common point defects and are affected by the preparation process. $K_2La_2Ti_3O_{10}$ is usually calcined and/or crystallized in oxidizing atmospheres, such as air and oxygen. The effect of inert atmosphere, such as Ar, and reductive atmosphere, such as H_2 , has been overlooked. In this

study, the effect of calcination atmospheres, including Ar, H_2 and air on the photocatalytic reactivity of $K_2La_2Ti_3O_{10}$ for H_2 production from potassium hydroxide aqueous solution under ultraviolet light and visible light irradiation was studied, respectively. The relations between the photocatalytic reactivity and calcination atmospheres were also investigated by X-ray photoelectron spectroscopy(XPS) and ultraviolet-visible (UV-Vis) spectroscopy.

2 Experimental

2.1 Main apparatus and reagents

D/max2250 power X-ray diffraction analyzer was employed to measure the crystal structure of $K_2La_2Ti_3O_{10}$. Lambda900 UV-Vis spectrometer (Labsphere integrating sphere) was used to measure the UV-Vis diffuse reflectance spectrum of $K_2La_2Ti_3O_{10}$. X-ray photoelectron spectrometer (Mg K_{α} X-ray source, 1253.6 eV, 16 mA $\times$ 12 kV) was used to analyze XPS of $K_2La_2Ti_3O_{10}$. SP-2305 gas phase chromatography instrument (thermal conductivity detector, Ar carrier, molecular sieve 5 A column) was adopted to determine the evolved hydrogen.

Analytical reagents of titanium tetrabutyl ($\text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti}$), KNO_3 , $\text{La}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$, KI, KOH, $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ were used in the experiments.

2.2 Preparation of photocatalyst $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$

The photocatalyst $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ powders were prepared by sol-gel method[6–7]. Solution A was obtained by dissolving the starting materials of 0.02 mol $\text{La}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ and 0.04 mol KNO_3 in 22 mL water, and solution B was obtained by dissolving the starting material of 0.03 mol $\text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti}$ in 80 mL isopropanol. Solution A was dropwise added to solution B with severe agitation for 5–10 min to get the gelatinous solution. The resulted gelatinous solution was dried and aged under infrared lamp irradiation for 3–4 h when water and isopropanol were separated from the gel. The gel was then crushed and calcined under Ar, H_2 and air atmospheres at 950 °C for 4 h respectively, and $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ powders were gained.

In order to get high photocatalytic reactivity, RuO_2 was loaded on the photocatalyst $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ powders using impregnation method[8–9]. The $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ powders were dispersed in RuCl_3 aqueous solution by a magnetic stirrer and were heated until water was completely volatilized. The $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ powders were ground and oxidized at 500 °C for 5 h in air to make RuO_2 loaded $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$.

2.3 Photocatalytic water splitting reaction

Photocatalytic water splitting reaction was carried out in a home-made gas-closed inner irradiation cell made of quartz (see Fig.1). The photocatalyst powder was dispersed in 650 mL potassium iodide aqueous solution (a given amount of KI was added to pure water after boiling for 30 min to remove the dissolved oxygen). KOH was added to control the pH value of solution. The light source was a 250 W high-pressure Hg lamp, of which the radiative wavelength was about 300–400 nm, the intensity of illumination was $15 \times 10^3 \mu\text{W}/\text{cm}^2$ and

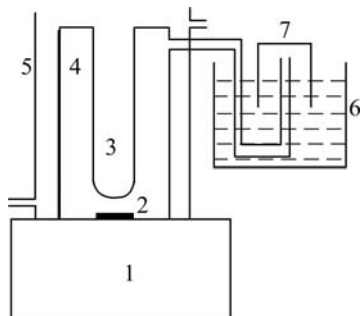


Fig.1 Device for photocatalytic water splitting: 1 Magnetic stirrer; 2 Magnetic bar; 3 250 W high-pressure Hg lamp or xenon lamp; 4 Gas-closed inner irradiation cell; 5 Cooling jacket; 6 Water channel; 7 Gas collector

the average luminous flux was $75 \times 10^4 \text{ lx}$. During the photocatalytic reaction, the infrared wave was removed by cooling water in the jacket of inner irradiation quartz cell. The evolved gases were determined with TCD gas chromatograph and its volume was collected and confirmed by drainage method.

The 250 W high-pressure Hg lamp was substituted by a 250 W xenon lamp whose average luminous flux was $15 \times 10^4 \text{ lx}$. The xenon lamp had about the same characteristic spectrum with sunlight. The same experimental procedure described above was carried out to measure photocatalytic reactivity of $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ under visible light irradiation.

3 Results and discussion

3.1 XRD patterns of $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ powders

Fig.2 shows the XRD patterns of $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ powders prepared under Ar, H_2 and air atmospheres respectively, which shows that all the powders have perfect crystal structure and remain almost the same under different atmospheres.

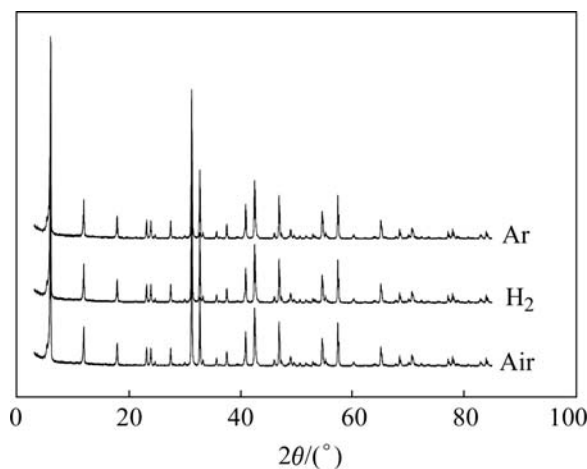


Fig.2 XRD patterns of $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ photocatalyst calcined under different atmospheres

3.2 Influence of calcination atmosphere on photocatalytic reactivity of $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$

The photocatalytic reactivity of $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ prepared in air, Ar and H_2 atmospheres was compared under ultraviolet and visible light radiation using Γ^- as electron donor. Fig.3, Fig.4 and Table 1 illustrate that $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ prepared under Ar and H_2 atmosphere has higher photocatalytic activity for hydrogen production than that prepared under air atmospheres. The photocatalyst calcined under Ar atmosphere exhibits the highest hydrogen production rate. The hydrogen production rates under ultraviolet irradiation are 127.5, 81.3 and $57.0 \mu\text{mol}/(\text{L} \cdot \text{h})$ and those under visible light

irradiation are 40.2, 30.2 and 16.5 $\mu\text{mol}/(\text{L}\cdot\text{h})$ respectively when $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ is prepared under Ar, H_2 and air atmospheres.

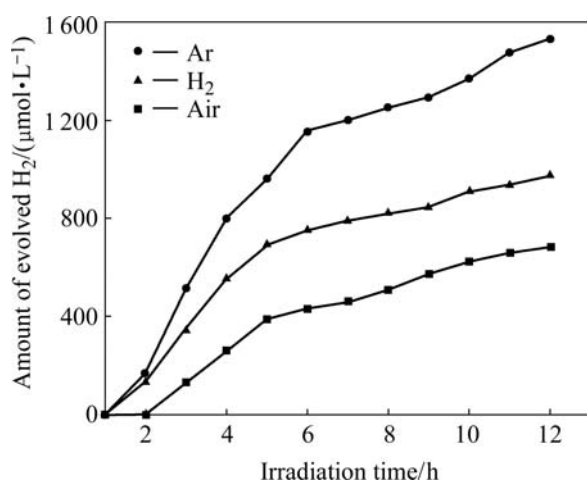


Fig.3 Dependence of photocatalytic reactivity of $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ on calcination atmosphere for hydrogen production under ultraviolet radiation

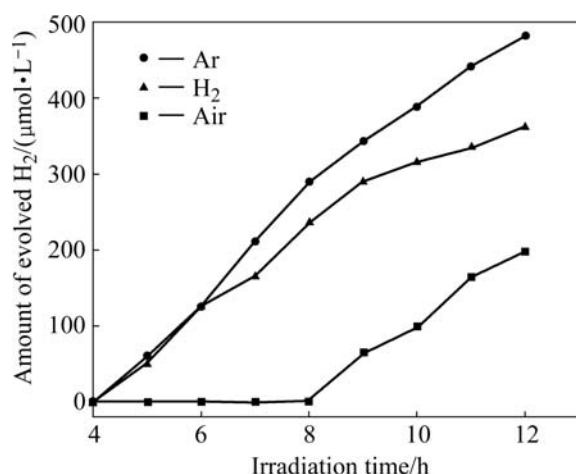


Fig.4 Dependence of photocatalytic reactivity of $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ on calcination atmosphere for hydrogen production under visible radiation

Table 1 Rates of hydrogen evolution of $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ calcined under different atmospheres ($\mu\text{mol}\cdot\text{L}^{-1}\cdot\text{h}^{-1}$)

Light source	Calcination atmosphere		
	Air	Ar	H_2
Ultraviolet	57.0	127.5	81.3
Visible	16.5	40.2	30.2

Fig.5 shows the diffuse reflectance spectra of $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ photocatalysts calcined under different atmospheres. All the photocatalysts show sharp UV absorptions near 300 nm, which are consistent with the theoretical band gap energy. Their visible light absorption behavior at 400–500 nm is different. The

$\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ powders calcined under Ar and H_2 show large visible-light adsorption correlated consistently with their activities.

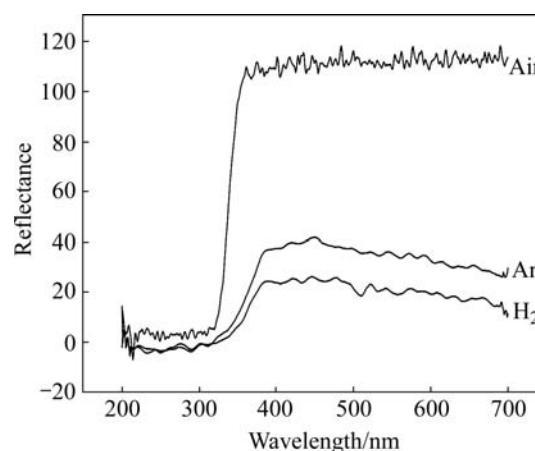


Fig.5 Dependence of diffuse reflectance spectrum of $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ photocatalyst on calcination atmosphere

Of the transition metal (composite) oxide, the presence of oxygen defects must be considered in the $[\text{TiO}_6]$ octahedron. The divalent oxygen ion cannot illustrate the existing state of oxygen in the transition metal (composite) oxide. The oxygen defects will affect the photocatalytic reactivity of $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ for water splitting. O(1s) XPS studies (see Fig.6 and Table 2) indicate that there exist mainly two types of surface oxygen, i.e. lattice oxygen(α) whose binding energy is 529.3 eV and adsorption oxygen(β) whose binding energy is 530.9 eV. The binding energies of Ti 2p (457.8 eV for Ti 2p_{1/2} and 463.6 eV for Ti 2p_{3/2}) for the three samples are typical of Ti^{4+} (see Fig.7 and Table 3).

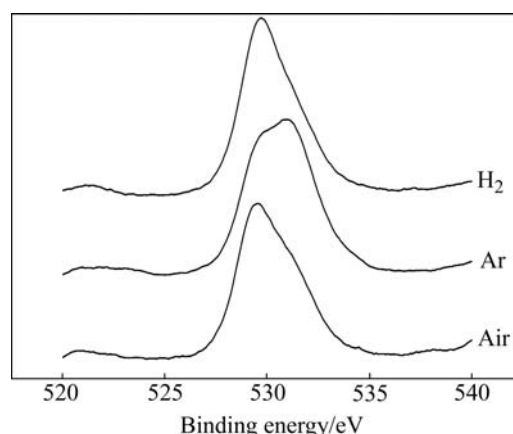


Fig.6 O1s-XPS spectra of $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ prepared under different calcination atmospheres

The ratio of adsorption oxygen(β) of $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ calcined under Ar is 66.9%, which is higher than that of $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ calcined under H_2 and air. This indicates that $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ calcined under Ar has higher oxygen

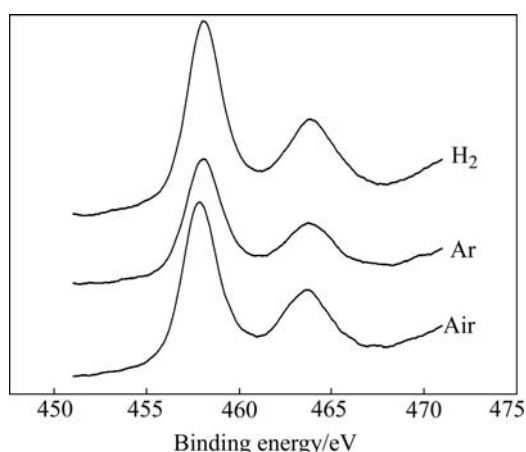


Fig.7 Ti2p-XPS spectra of $K_2La_2Ti_3O_{10}$ prepared under different calcination atmospheres

Table 2 Molar ratios of lattice and adsorption oxygen of $K_2La_2Ti_3O_{10}$ under different calcination atmospheres (%)

Oxygen species	Calcination atmosphere		
	Air	Ar	H ₂
Lattice oxygen(α)	55.0	33.1	75.4
Adsorption oxygen(β)	45.0	66.9	24.6

Table 3 Molar ratios of Ti 2p_{1/2} and Ti 2p_{3/2} of $K_2La_2Ti_3O_{10}$ under different calcination atmospheres (%)

Titanium species	Calcination atmosphere		
	Air	Ar	H ₂
Ti 2p _{1/2}	66.7	66.7	66.7
Ti 2p _{3/2}	33.3	33.3	33.3

vacancy ratio and less metal vacancy ratio[10]. The non-stoichiometry oxygen due to thermal treatment in reductive H₂ atmosphere leads to lower valence of Ti ions, most likely Ti³⁺. The typical XPS peak of Ti³⁺ is not obvious because of its low content. The migration of oxygen in $K_2La_2Ti_3O_{10}$ semiconductor will produce oxygen vacancy when being calcined under Ar atmosphere. The oxygen vacancy can not only trap the photo-generated electrons but also increase the ratio of adsorption oxygen(β) on the surface of $K_2La_2Ti_3O_{10}$ semiconductor[11].

When $K_2La_2Ti_3O_{10}$ powders are calcined under H₂ atmosphere, the possible reactions may be described as follows[12]:



In the above equations, O_o^* is the lattice oxygen (O^{2-}), V_M' is the metal vacancy and V_o' and V_o'' are the oxygen vacancies. Both oxygen vacancies belong to positive centers and are easily excited to the conduction band of $K_2La_2Ti_3O_{10}$ semiconductor and act as donor. The donor band level(E_D) is at the bottom of conduction band(E_C). But the metal vacancy belongs to negative center and is easily excited to the valence band of $K_2La_2Ti_3O_{10}$ semiconductor as acceptor. The acceptor band level(E_A) is at the top of valence band(E_V) (see Fig.8).



Fig.8 Band structure of $K_2La_2Ti_3O_{10}$ with oxygen vacancy and metal vacancy

Because of the formation of acceptor band level and donor band level of $K_2La_2Ti_3O_{10}$ calcined under Ar and H₂ atmospheres, the photo-generated electrons can jump step by step and reduce the energy gap compared with $K_2La_2Ti_3O_{10}$ calcined under air. Though the ratio of adsorption oxygen(β) of $K_2La_2Ti_3O_{10}$ calcined under H₂ is low(24.6%) compared with that of $K_2La_2Ti_3O_{10}$ calcined Ar and air (see Table 2), the metal vacancy plays the same part in the reduction of energy gap as the oxygen vacancy[13]. This may explain the observation that there is an optimum visible-light absorption for higher hydrogen rate.

4 Conclusions

1) $K_2La_2Ti_3O_{10}$ has higher photocatalytic activity for hydrogen production when being calcined under Ar and H₂ atmospheres than under air atmosphere.

2) The hydrogen production rates under ultraviolet irradiation are 127.5, 81.3 and 57.0 $\mu\text{mol}/(\text{L}\cdot\text{h})$ respectively when $K_2La_2Ti_3O_{10}$ is prepared under Ar, H₂ and air atmospheres.

3) The hydrogen production rates under visible light irradiation are 40.2, 30.2 and 16.5 $\mu\text{mol}/(\text{L}\cdot\text{h})$ respectively when $K_2La_2Ti_3O_{10}$ is prepared under Ar, H₂ and air atmospheres.

References

- [1] TAKATA T, SHINOHARA K, TANAKA A, HARA M, KONDO J N, DOMEN K. A highly active photocatalyst for overall water splitting with a hydrated layered perovskite structure[J]. Journal of Photochemistry and Photobiology A: Chemistry, 1997, 106(1/3): 45-49.
- [2] THAMINIMULLA C T K, TAKATA T, HARA M, KONDO J N,

- DOMEN K. Effect of chromium addition for photocatalytic overall water splitting on Ni-K₂La₂Ti₃O₁₀ [J]. Journal of Catalysis, 2000, 196(2): 362–365.
- [3] IKEDA S, HARA M, KONDO J N, DOMEN K, TAKAHASHI H, OKUBO T, KAKIHANA M. Preparation of K₂La₂Ti₃O₁₀ by polymerized complex method and photocatalytic decomposition of water [J]. Chemistry of Materials, 1998, 10(1): 72–77.
- [4] GAO You-liang, CHEN Qi-yuan, YIN Zhou-lan, HU Hui-ping, LI Jie. Influence of oxygen vacancies of WO₃ on photocatalytic activity for O₂ evolution [J]. Chinese Journal of Inorganic Chemistry, 2005, 21(10): 1510–1514. (in Chinese)
- [5] WU N L, LEE M S, PON Z J, HSU J Z. Effect of calcination atmosphere on TiO₂ photocatalysis in hydrogen production from methanol/water solution [J]. Journal of Photochemistry and Photobiology A: Chemistry, 2004, 163(1/2): 277–280.
- [6] CHEN Zhen-liang, WANG Zheng-cun, SHEN Cheng-min, JIA Yong-zhong, YANG Jin-xian. Preparation of nanocrystalline strontium titanate by the sol-gel process [J]. Journal of Functional Materials, 1999, 30(6): 633–635. (in Chinese)
- [7] LI Kun, CHEN-WANG Li-hua, CAI Zhong-long, LI Jin-hua. Preparation and properties of (Sr_{0.12}Ba_{0.18})TiO₃ solution [J]. Journal of Jiangsu Institute of Petrochemical Technology, 2000, 12(1): 1–4. (in Chinese)
- [8] WANG Chuan-yi, LIU Chun-yan, SHEN Tao. Surface modification of semiconductor photocatalyst [J]. Chemical Journal of Chinese University, 1998, 19(12): 2013–2019. (in Chinese)
- [9] AMY L L, LU G Q, JOHN T Y. Photocatalysis on TiO₂ surfaces: Principles, mechanisms, and selected results [J]. Chemical Reviews, 1995, 95(3): 735–758.
- [10] PENA M A, FIERRO J L G. Chemical structures and performance of perovskite oxides [J]. Chemical Reviews, 2001, 101(7): 1981–2017.
- [11] SANG Li-xia, ZHONG Shun-he, FU Xi-xian. Oxygen migration and photocatalytic activity of perovskite-type oxides [J]. Chemical Journal of Chinese University, 2003, 24(2): 320–323. (in Chinese)
- [12] XU Yu-long. Semiconductor basis on oxides and compounds [M]. Xi'an: Xi'an University of Electronic Science and Technology Press, 1991: 49–55. (in Chinese)
- [13] FU Xi-xian, YANG Qiu-hua, SANG Li-xia. Studies on photocatalytic activity of perovskite type LaFe_{1-x}Cu_xO₃ [J]. Chemical Journal of Chinese University, 2002, 23(2): 283–286. (in Chinese)

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