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Photocatalytic activity of $ANbO_3$(A= Li, Na, K) ①

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Abstract: The perovskite-photocatalysts $ANbO_3$(A= Li, Na, K) were prepared by solid-state reaction and characterized by power X-ray diffraction and UV-vis diffuse reflectance. The photocatalytic activity of $ANbO_3$(A= Li, Na, K) were investigated with methanol as electron donor and Pt as promoter catalyst under 400 nm UV irradiation. The difference of photocatalytic activity among the three $ANbO_3$(A= Li, Na, K) was also discussed, the individual rate of hydrogen evolution for the $ANbO_3$(A= Li, Na, K) photocatalysts are 1.37, 1.9, 5.49 $mmol \cdot L^{-1} \cdot h^{-1}$, respectively.

Key words: perovskite-photocatalysts; photocatalytic; hydrogen
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1 INTRODUCTION

Because the amount of coal, petroleum and other fossil fuel used nowdays increases, their storage decreases and depletion is inevitable. It is urgent to find out renewal energy which is independent on petroleum, coal and other fossil fuel. Hydrogen is a secondary energy to overcome energy crisis. The photocatalytic splitting of water using oxide semiconductor materials under solar energy is an ideal route to generate hydrogen. In the past several decades, much progress[1-10] has been made in the water photocatalytic cleavage using TiO_2[11] and other oxide semiconductor materials to produce hydrogen. However, the number of photocatalyst materials known up to now is yet limited, and their activity is still low. Therefore, developing new types of photocatalysts with higher activity and making them respond to visible light attracts an increasing interest. Owing to their variations in the structure and compositions, more and more attention is focused on the perovskite-photocatalysts such as $K_2La_2Ti_3O_{10}$[12], $Sr_2M_2O_7$(M = Nb, Ta)[13], $ATaO_3$(A= Li, Ta, K)[14]. The perovskite-photocatalysts $ANbO_3$(A = Li, Na, K) were prepared by solid-state reaction and characterized by power X-ray diffraction and UV-vis diffuse reflectance in this paper. The photocatalytic activity of $ANbO_3$(A = Li, Na, K) was investigated from methanol aqueous solution.

2 EXPERIMENTAL

2.1 Main apparatus and reagents

Japanese D/max2250 power X-ray diffraction analyzer was employed to measure the crystal structure of $ANbO_3$(A = Li, Na, K); America Lambda900 UV-vis spectrometer (Labsphere integrating sphere) was used to measure the UV-vis diffuse reflectance spectrum of $ANbO_3$(A= Li, Na, K); SP-2305 gas phase chromatography instrument (thermal conductivity detector, Ar carrier, molecular sieve 5A column) was adopted to determine the evolved hydrogen.

Analytic reagents of A_2CO_3(A= Li, Na, K), Nb_2O_5, $H_2PtCl_6 \cdot 6H_2O$, CH_3OH, H_2SO_4 were used in the experiments.

2.2 Preparation of photocatalysts

Alkali niobates, $ANbO_3$(A= Li, Na, K) powders were prepared by conventional solid-state reactions. The starting materials of alkali carbonates A_2CO_3(A= Li, Na, K) and Nb_2O_5 were mixed by mechanical grinding in a motor in the presence of excess amounts(5%－10%) of alkali to compensate for the volatilization. The mixtures were calcined at 1 100 ℃ for 8 h in air. The excess alkali was washed out with water after the calcination. The washed powders were then calcined at 1 100 ℃ for 8 h in air again. In order to get high photocatalytic activity, the photocatalyst powders were dispersed in aqueous $H_2PtCl_6 \cdot 6H_2O$ solution by a magnetic stirrer and irradiated under 250 W high-pressure Hg Lamp for 10 h so that Pt was deposited homogeneously onto the surface of the photocatalyst powders. The suspensions were centrifugally filtrated, then the powders were dried in vacuum at 120 ℃ for 5 h to get the photocatalyst powders of Pt-$ANbO_3$(A = Li, Na, K).

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2.3 Photocatalytic reactions

Photocatalytic reactions were carried out in a home-made gas-closed inner irradiation cell made of quartz. The photocatalysts powder was dispersed in 650 mL methanol aqueous solution (a given amount of methanol was added to pure water). In some cases, H_2SO_4 was added to control the pH of solution. The light source was a 250 W high-pressure Hg lamp whose radiative wavelength was about 300 ~ 400 nm. In the course of 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. After photocatalytic reactions, the suspensions were centrifugally filtrated, then the powders were dried out to confirm their structure using power X-ray diffraction analyzer.

3 RESULTS AND DISCUSSIONS

3.1 XRD and DRS patterns of photocatalyst powders

Fig. 1 illustrates the XRD patterns of ANbO$_3$ before and after photocatalytic reactions. It shows that all thepowders have perfect crystal wherein LiNbO$_3$ crystallized in hexagonal and NaNbO$_3$, KNbO$_3$ in orthorhombic. There are no obvious structural changes between the catalysts before and after photocatalytic reactions. Therefore, there is not photooxidation or photodegradation for the photocatalysts[15, 16]. Fig. 2 illustrates the diffuse reflectance spectrums of ANbO$_3$ photocatalysts with the main absorption at 300 nm. The absorption edges of catalysts were in UV region up to 400nm. The band gap was estimated from the absorption edge[14] of the catalysts to be 2.95 eV in LiNbO$_3$, 2.90 eV in NaNbO$_3$ and 3.10 eV in KNbO$_3$, respectively.

3.2 Effect of CH$_3$OH on photocatalytic activity of ANbO$_3$ for H$_2$ evolution

Table 1 shows the effects of CH$_3$OH and Pt on the photocatalytic activity of ANbO$_3$ for H$_2$ evolution. During the photocatalytic reactions, the addition of CH$_3$OH to the solutions and the loading of Pt onto the photocatalyst powders were indispensable in order to obtain high photocatalytic activity for H$_2$ evolution. The fermi energy level of Pt was above that of ANbO$_3$(A= Li, Na, K)[17]. When Pt was loaded onto the surface of the catalyst powders, the fermi energy level will remain at the same level so that the photogenerated electrons in the conduction band of photocatalysts transfer spontaneously to Pt. Thus Pt was an active site for hydrogen evolution to enhance the photogenerated charges separation. At the same time, Pt can reduce the overpotential of hydrogen to favor the hydrogen evolution. The presence of CH$_3$OH as electron donor can consume the photogenerated hole and favor the photogenerated charges separation. Therefore Pt and CH$_3$OH can accelerate the hydrogen evolution.

Table 1 Effects of CH$_3$OH and Pt on photocatalytic activity of ANbO$_3$ for H$_2$ evolution

Photocatalytic reactions system	Rate of H$_2$ evolution/(mmol·L^{-1}·h^{-1})
Pt-KNbO$_3$(1.0 g)	0
KNbO$_3$(1.0 g) + CH$_3$OH(30 mL)	0.91
Pt-KNbO$_3$(1.0 g) + CH$_3$OH(30 mL)	5.49

3.3 Effect of counterions on photocatalytic activity of ANbO$_3$ for H$_2$ evolution

Fig. 3 illustrates the effect of counterions on the photocatalytic activity of ANbO$_3$ for H$_2$ evolution. The counterions of photocatalysts have a marked influence on photocatalytic hydrogen evolution. The rate of hydrogen evolution with Li-NbO$_3$, NaNbO$_3$ and KNbO$_3$ as photocatalysts was 1.37, 1.90 and 5.49 mmol·L^{-1}·h^{-1}, respectively. The band structure of perovskite-photocatalysts such as ANbO$_3$(A = Li, Na, K) is generally defined by d-level and O 2p level[15]. When the

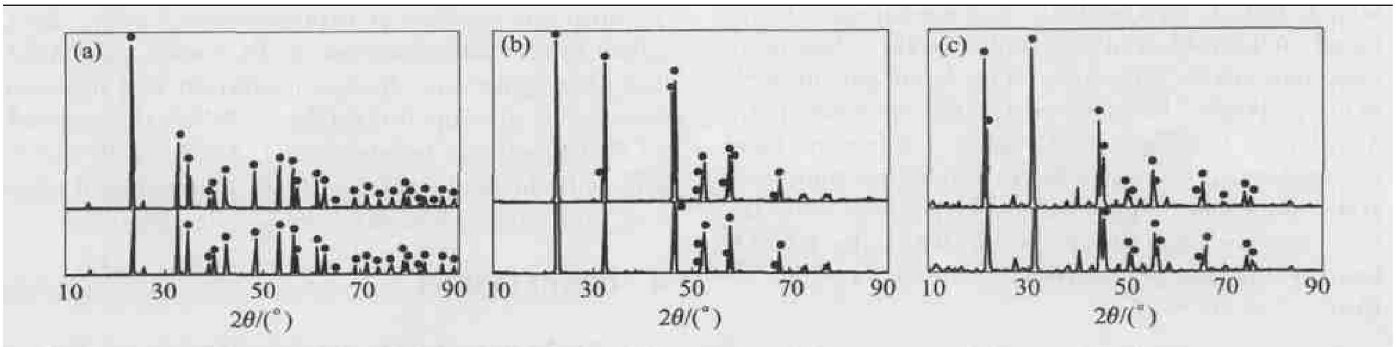

Fig. 1 XRD patterns of catalysts before and after photocatalytic reactions
(a) —LiNbO$_3$; (b) —NaNbO$_3$; (c) —KNbO$_3$

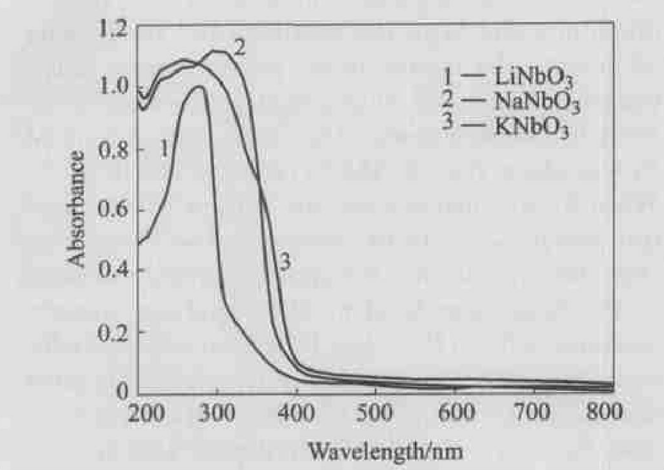

Fig. 2 Diffuse reflectance spectrums of $ANbO_3$

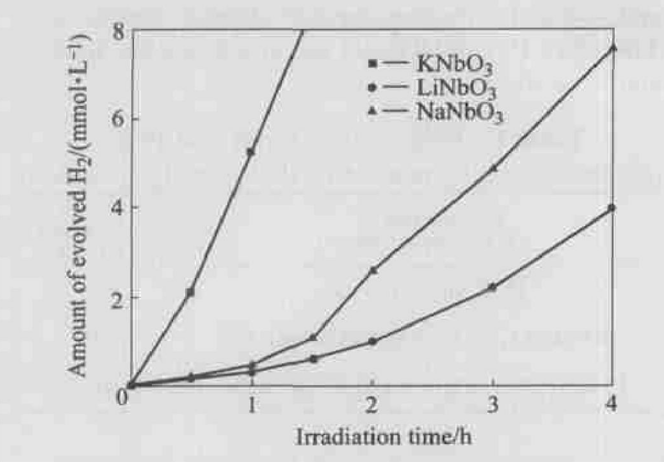

Fig. 3 Dependence of photocatalytic H_2 evolution on irradiation time

compound contains octahedral NbO_6, the valence band energy should be assumed by the O 2p levels of oxygen in NbO_6 and the conduction band assumed by 4d levels of Nb in NbO_6. The crystals of catalysts contain the same octahedral NbO_6, but they have different band gap and different photocatalytic activity with different counterions. The ionic radius of Li^+, Na^+, K^+ was 0.068, 0.095 and 0.133 nm respectively. The corresponding tolerance factor[3] of $LiNbO_3$, $NANbO_3$ and $KNbO_3$ was 0.469, 0.496 and 0.525 respectively. Compared to $LiNbO_3$ and $NaNbO_3$, $KNbO_3$ has more ideal perovskite structure. The band gap of $KNbO_3$ was larger than that of $LiNbO_3$ and $NaNbO_3$. The larger band gap and higher conduction band energy level the catalyst have, the higher photocatalytic activities of photocatalysts possess with the same valence band energy level. Thus the $KNbO_3$ has the highest photocatalytic activity among the three catalysts.

3.4 Effect of acidity on photocatalytic activity of $ANbO_3$ for H_2 evolution

Fig. 4 illustrates the effect of acidity on the photocatalytic activity of $ANbO_3$ for H_2 evolution. It shows that photocatalytic hydrogen evolution of $LiNbO_3$, $NaNbO_3$ and $KNbO_3$ increased from 1.37, 1.06, 3.12 $mmol \cdot L^{-1} \cdot h^{-1}$ ($pH = 7$) to 1.75, 1.41, 9.15 $mmol \cdot L^{-1} \cdot h^{-1}$ ($pH = 1.5$), respectively. Acidity increasement lead to photocatalytic activity enhancement, which may result from two reasons. One is that the increasement of H^+ concentration changes the energy level of catalysts[18] to the enhancement of the photocatalytic activity. The other is the increasement of absolute number of H^+ involving in photocatalytic reactions to the enhancement of the photocatalytic activity.

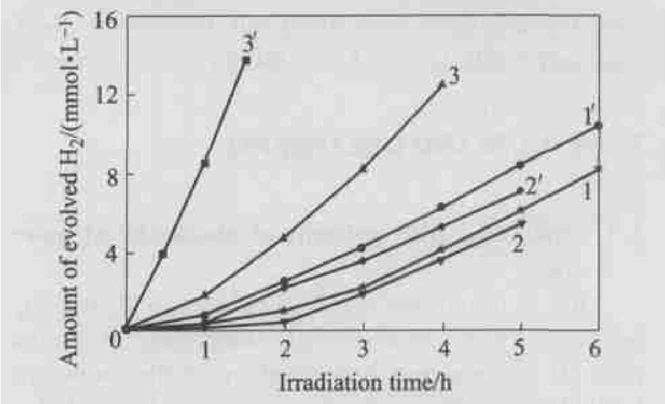

Fig. 4 Dependence of acidity on photocatalytic reactivity of $LiNbO_3$, $NANbO_3$, $KNbO_3$
1 — $LiNbO_3$($pH = 7.0$); 1′ — $LiNbO_3$($pH = 1.5$);
2 — $NaNbO_3$($pH = 7.0$); 2′ — $NaNbO_3$($pH = 1.5$);
3 — $KNbO_3$($pH = 7.0$); 3′ — $KNbO_3$($pH = 1.5$)

3.5 Effect of Pt loaded on photocatalytic activity of $KNbO_3$ for H_2 evolution

Table 1 illustrates that the addition of CH_3OH to the solutions and the loading of Pt onto the photocatalyst powders were indispensable in order to get high photocatalytic activity for H_2 evolution. With the viewpoint of application, it is necessary to determine the optimal amount of Pt onto the surface of catalysts. Fig. 5 shows the effect of Pt loaded on the the photocatalytic activity of $KNbO_3$ for H_2 evolution. The optimal loading of Pt onto the surface of catalysts was 1.2%. In a given range, increasement of Pt loaded will favor the photogenerated charge separation and increase the active sites on the catalyst. When the amount of Pt loaded was higher than 1.2%, the Pt particles will shield the catalyst from absorption of photon, and make photocatalytic activity decrease.

4 CONCLUSIONS

1) As a promoter catalyst, Pt can accelerate hydrogen evolution, the optimal amount of Pt loaded on $KNbO_3$ is 1.2%.

2) In CH_3OH aqueous solution, $ANbO_3$($A = $ Li,

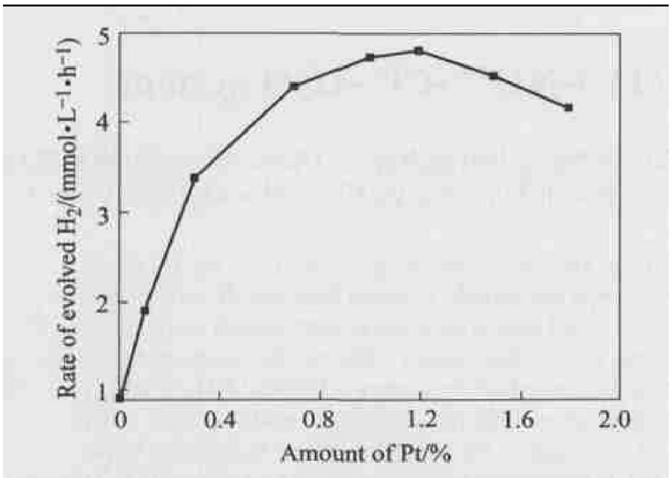

Fig. 5 Dependence of Pt loaded on photocatalytic activity of $KNbO_3$ for H_2 evolution

Na, K) possesses high photocatalytic hydrogen evolution. $KNbO_3$ has the best photocatalytic activity and its photocatalytic hydrogen evolution rate is 5. 49 mmol•L^{-1}•h^{-1} with Pt as promoter catalyst.

3) Acidity increasement leads to a high photocatalytic activity .

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