

Effect of doping TiO₂ with alkaline-earth metal ions on its photocatalytic activity

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Abstract: TiO₂ photocatalysts doped with alkaline-earth metal ions were prepared by the impregnation and coprecipitation methods. The samples were characterized by XRD, XPS and IR spectroscopy. Their activities were evaluated by the photocatalytic production of hydrogen. The activities of the doped photocatalysts depended on the size of the dopant ions and the doping method. The optimum molar contents of dopant ions Be²⁺, Mg²⁺, Ca²⁺, Sr²⁺, Ba²⁺ were 1.25, 1.25, 2.25, 2.25 and 2.25 at. %, respectively. The optimum calcination temperature and time were 400 °C and 1 h.

Keywords: photocatalysis, titanium dioxide, doping, alkaline-earth metal, activity.

INTRODUCTION

Since the first photocatalyst for splitting water into hydrogen and oxygen was developed in 1972,¹ semiconductor-based photocatalysis has received a great deal of attention.^{2–4} Photocatalytic production of hydrogen by water-splitting has been considered a promising approach, because the attempt was aimed not only at producing hydrogen from water by utilizing clean solar energy, but also at finding methods of use the photosynthetic process for green plants. Although many semiconducting oxides have been investigated as potential photocatalysts,^{5–7} TiO₂ has been the focus of photocatalysis under UV irradiation because of its physical and chemical stability, low cost, ease of availability, non-toxicity, and electronic and optical properties. The photocatalytic efficiency of TiO₂ depends partially on interfacial charge-transfer reactions.⁸ In order to slow down the recombination rate of electron-hole pairs and to utilize visible light, researches have modified TiO₂ particles by selective surface treatments, such as doping metal ions at TiO₂,^{9,10} dye photosensitization on the TiO₂ surface,¹¹ deposition of noble metals,¹² etc. There have been many reports on transition metal, rare earth and noble metal ion doping of TiO₂, but studies on alkaline-earth metal ion doping of TiO₂ and

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their photocatalytic properties have seldom been reported. In this study, alkaline-earth metal ion doped TiO₂ photocatalysts were prepared by the impregnation and coprecipitation method and a comparative study of the photocatalytic efficiency of pure TiO₂ and doped TiO₂ was performed. The effect of doping TiO₂ with alkaline-earth metal ions on its photocatalytic activity was characterized by the photocatalytic generation of hydrogen in suspension. It was found that the activities of the doped photocatalysts depended on the size of the dopant ion and the doping method.

EXPERIMENTAL

Preparation of the photocatalysts

All reagents were of analytic grade. Undoped TiO₂ was prepared by the sol-gel method using Ti(OBu)₄ as the precursor. Ti(OBu)₄ (5 mL) was dissolved in 20 mL ethanol under stirring and then 0.5 mL HNO₃ solution ($V_{\text{HNO}_3} : V_{\text{H}_2\text{O}} = 1:1$) and 1 mL H₂O were added dropwise to the above solution. The mixture was vigorously stirred at room temperature for 30 min to obtain a transparent sol. The gel was obtained after aging the sol for 24 h at room temperature. Pure TiO₂ was prepared by drying the gel at 100 °C for 24 h and calcinating in air at 400 °C for 1 h.

The alkaline-earth metal ion doped TiO₂ photocatalysts were prepared by two methods. For the coprecipitation synthesis of M²⁺-TiO₂ photocatalysts (denoted as M²⁺-CP-TiO₂; M=Be, Mg, Ca, Sr, Ba) the same procedure was adopted as for the pure TiO₂ except an aqueous MCl₂ (M= Be, Mg, Ca, Sr, Ba) solution was used instead of H₂O. For the impregnation synthesis of M²⁺-TiO₂ photocatalyst (denoted as M²⁺-IP-TiO₂, M=Be, Mg, Ca, Sr, Ba) the required amount of pure TiO₂ powder was added into a given concentration of MCl₂ (M=Be, Mg, Cr, Sr, Ba) solution. The mixture was dispersed in an ultrasonic bath for 10 min. After impregnation for 1 h, the mixture was kept at 110 °C to remove water by evaporation. Except when studying the photocatalytic activity vs. calcination temperature and time, the samples were treated at 400 °C in air for 1 h.

Characterization of photocatalysts

The X-ray diffraction (XRD) patterns of the prepared photocatalysts were determined on a D/Max-III A diffractometer. The particle lattice parameters were obtained by the Bragg law ($2d \sin \theta = \lambda$) and the formula for a tetragonal system: $1/d^2 = (h^2+k^2)/a^2+1^2/c^2$. The contents of Ti and dopants alkaline-earth metal ions on the photocatalyst surface were measured by X-ray photoelectron spectroscopy (XPS) using a UG-ESCALAB 210 instrument. The IR analysis was carried out using KBr discs in the region of 4000–400 cm⁻¹ on a FTIR-NICOLET-740 spectrophotometer.

Photocatalytic activities

The photocatalytic reaction was carried out in a Pyrex flask of $\approx 216 \text{ cm}^3$ with a flat window. In the cell, 100 mL of an aqueous mixture containing 1 mL C₂H₅OH (electron donor) and 0.33 mL $1.93 \times 10^{-3} \text{ M H}_2\text{PtCl}_6$ (platinum source). In all experiments, 50 mg of the photocatalyst was dispersed in 100 mL solution using an ultrasonic bath and nitrogen was bubbled through the reaction mixture for 30 min to remove oxygen. Then top of the cell was sealed with a silicone rubber septum. The catalysts was maintained in suspension by means of magnetic stirring. A 250 W high pressure Hg lamp was used as the light source. The irradiation time was 1 h. Hydrogen was analyzed by gas chromatography (using a GC102 with a TCD detector, N₂ as gas carrier, and a 13 X molecular sieve column).

RESULTS AND DISCUSSION

Catalyst characterization

The X-ray diffraction patterns of pure TiO₂ and the alkaline-earth metal ion doped TiO₂ prepared by impregnation method showed that only the anatase phase

was found in the pure TiO₂ and in all the samples of M²⁺-IP-TiO₂ (M=1.25 at. % Be, 1.25 at. % Mg, 2.25 at.% Ca, 2.25 at.% Sr, 2.25 at. % Ba), indicating that doping with alkaline-earth metal ions did not influence the crystal patterns of the TiO₂ particle. No M-O peaks could be observed in the XRD and IR spectra of the M²⁺-IP-TiO₂ samples calcinated at 400 °C and 600 °C. The reason was that the contents of the alkaline-earth metal ion dopants were very low and possibly the alkaline-earth metal ion deposits were well dispersed on the TiO₂ particles.

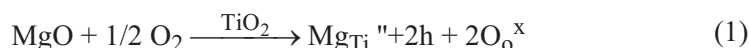
TABLE I. Effect of calcination temperature on TiO₂ lattice parameters

Sample	Calcination temperature/°C	Lattice parameters	
		<i>a</i> /nm	<i>c</i> /nm
1.25 at % Be ²⁺ -IP-TiO ₂	300	0.3785	0.9485
	400	0.3788	0.9534
	500	0.3789	0.9579
1.25 at % Mg ²⁺ -IP-TiO ₂	300	0.3785	0.9405
	400	0.3789	0.9396
	500	0.3787	0.9389
2.25 at % Ca ²⁺ -IP-TiO ₂	300	0.3786	0.9470
	400	0.3789	0.9521
	500	0.3791	0.9548
2.25 at % Sr ²⁺ -IP-TiO ₂	300	0.3788	0.9431
	400	0.3791	0.9435
	500	0.3792	0.9441
2.25 at % Ba ²⁺ -IP-TiO ₂	300	0.3788	0.9420
	400	0.3791	0.9432
	500	0.3789	0.9438
Pure TiO ₂	400	0.3788	0.9412

The lattice parameters of the M²⁺-IP-TiO₂ samples calcined at various temperatures and of pure TiO₂ are presented in Table I. Clearly, there is almost no change in the lattice parameter *a* of all samples, but for Be²⁺ and Ca²⁺ doped TiO₂, there are obvious increases in the lattice parameters *c*; whereas for Mg²⁺ doped TiO₂, there is a very small decrease in the lattice parameter *c*. These results indicate that Be²⁺, Ca²⁺ and Mg²⁺ doping distorts the *c* axis of the TiO₂, which causes an expanding or contraction of the unit cell. The ionic radii of Ti⁴⁺, Be²⁺, Mg²⁺, Ca²⁺, Sr²⁺ and Ba²⁺ are 68.31, 65.99, 113 and 135 pm, respectively.¹³ As the radius of Be²⁺ is much smaller than that of Ti⁴⁺, it would be difficult for Be²⁺ to replace a Ti⁴⁺ site; instead, it is very likely that Be²⁺ enters into the interstitial site of the TiO₂ crystal. The XRD results indicate that with increasing calcination temperature, the expansion of the unit cell of Be²⁺ doped TiO₂ is much larger than for the other alkaline-earth metal doped TiO₂, which proves that Be²⁺ enters into the inter-

stitial site. As the radius of Mg^{2+} is only slightly smaller than that of Ti^{4+} , the Mg^{2+} ion could easily enter into the lattice of TiO_2 to replace the Ti^{4+} site, which makes the cell contract. The radius of Ca^{2+} is rather larger than that of Ti^{4+} , hence the dopant could also be intercalated into the TiO_2 lattice to some extent and produced a lattice deformation. The radii of Sr^{2+} and Ba^{2+} are much larger than that of Ti^{4+} . It is clearly shown from Table I that with increasing calcination temperature there is not much change in the lattice parameters of Sr^{2+} and Ba^{2+} doped TiO_2 , which obviously indicates that Sr^{2+} and Ba^{2+} hardly enter into the lattice of TiO_2 .

The radius of Mg^{2+} is close to that of Ti^{4+} , it can be introduced substitutionally in the TiO_2 lattice. When Mg^{2+} replaces a Ti^{4+} site, the defective reaction can be expressed as follows:¹⁴



Where Mg_{Ti}'' represents Mg^{2+} in a Ti^{4+} lattice site; $\text{O}_\text{o}^{\times}$ represents O^{2-} in a normal lattice site. Thus, when Mg^{2+} replaces Ti^{4+} site, the hole density of Mg^{2+} doped TiO_2 increases and the electron density decreases. When Ca^{2+} replaces a Ti^{4+} site, the defective reaction is similar to (1).

When Be^{2+} enters into an interstitial site of TiO_2 the defective reaction as follows occurs:



The formed V_{Ti}'' can dissociate to produce two electrons:



where Be_i'' represents Be^{2+} in an interstitial site of the TiO_2 lattice; $\text{O}_\text{o}^{\times}$ represents O^{2-} in a normal lattice site; V_{Ti}'' and $\text{V}_{\text{Ti}}^{\times}$ represent a titanium vacancy. With the production of a titanium vacancy, the electron density of Be^{2+} doped TiO_2 increases.

TABLE II. The oxidation state and amount of metal element on the surface of the catalyst determined by XPS

Catalyst	E_B/eV	Oxidation state	[M]:[Ti]	
			400 °C	600 °C
1.25 at.% Be^{2+} -IP- TiO_2	113.68	+2	4.3 at. %	1.67 at. %
1.25 at.% Mg^{2+} -IP- TiO_2	49.26	+2	4.41 at. %	1.75 at. %
1.25 at.% Ca^{2+} -IP- TiO_2	346.14	+2	4.62 at. %	3.06 at. %

The amount of surface and the state of beryllium, magnesium, calcium and titanium of M^{2+} -IP- TiO_2 (M=1.25 at. % Be, 1.25 at. % Mg and 1.25 at. % Ca) photocatalysts were analyzed by XPS. The results given in Table II show the Be/Ti, Mg/Ti and Ca/Ti ratios of the samples calcinated at 400 °C were 4.34, 4.41 and 4.62 at %, respectively, while the ratios at 600 °C were 1.67, 1.75 and 3.06 at. %, respectively. The surface Be/Ti and Mg/Ti ratios were much lower at 600 °C than at 400 °C, which indicates that with increasing temperature, the contents of Be^{2+}

and Mg²⁺ ions permeating into TiO₂ lattice should be larger. The results also indicate that Be²⁺ and Mg²⁺ reside mainly on the surface and near the surface of TiO₂ at the lower calcination temperature, while they enter into the deep bulk phase at the higher temperature. The change of the Ca/Ti ratio was smaller between 400 °C and 600 °C, indicating that the dopant Ca²⁺ ion enters into the lattice of TiO₂ with more difficulty than the Be²⁺ and Mg²⁺ ion. The result of the XPS analysis basically agreed with those from XRD.

Comparison of the photocatalytic activities

The change in the photocatalytic activity of TiO₂ prepared by the impregnation method with various contents of alkaline-earth metal ions is shown in Fig. 1. At lower concentrations, the hydrogen production activity increase with increasing

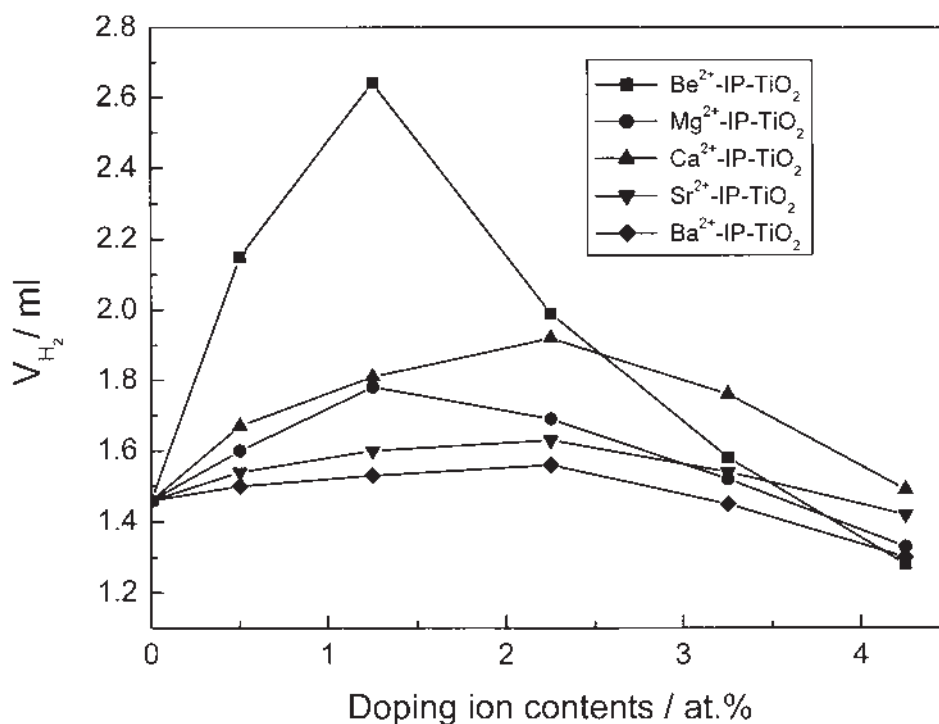


Fig. 1. Effect of different content of doping ions on the photocatalytic production of hydrogen.

concentration of dopant, but decreases at higher concentrations. The optimum molar contents of the dopants Be²⁺, Mg²⁺, Ca²⁺, Sr²⁺ and Ba²⁺ ions are 1.25, 1.25, 2.25, 2.25 and 2.25 at. %, respectively. Several factors can have a positive impact on the photocatalytic activity doped TiO₂. Firstly, the MO deposited on the TiO₂ particles can form a space charge layer, which can separate the photoinduced electron-hole pairs. As the concentration of dopant ions increases, the surface barrier becomes higher and the electron-hole pairs within the region are efficiently sepa-

rated by the large electric field.¹⁵ Secondly, due to the difference of the electron negativity between Ti and M, the Ti–O–M formed *via* M^{2+} entering into the shallow surface of TiO_2 could promote the charges to transfer, resulting in an increase of the photocatalytic activity. Thirdly, alkaline-earth metal ion doping can cause a lattice deformation and produce defects in the crystal.¹⁶ The defects can inhibit the recombination of the electron-hole pairs and, eventually, enhance the activity. However, an excess amount of alkaline-earth metal oxides at the surface of TiO_2 could notably screen the TiO_2 from the UV light and inhibit the interfacial electron and hole to transfer, which would result in a low photoactivity. Consequently, there are optimum concentrations for the dopants.

It can be seen from Fig. 1 that among all the doping samples, Be^{2+} doped TiO_2 has the highest photocatalytic activity. TiO_2 is an n type semiconductor. As shown in Eq. (1), Eq. (2) and Eq. (3), when a Be^{2+} ion is located in an interstitial site of TiO_2 , the electron density of the doped TiO_2 increases, which would increase the photocatalytic activity; while when a Mg^{2+} or Ca^{2+} ion is located in a substitutional site of TiO_2 , the electron density of the doped TiO_2 decreases and even the TiO_2 could change into a p type semiconductor, which would decrease the photocatalytic activity. Thus, the activity of TiO_2 doped with Be^{2+} is the highest. As the radius of Ca^{2+} is larger than that of Ti^{4+} , the number of doping Ca^{2+} ions entering into the lattice of TiO_2 is smaller than that of doping Mg^{2+} , and the above detrimental effect is smaller. Therefore, the photocatalytic activity of Mg^{2+} doped TiO_2 is lower than that of Ca^{2+} doped TiO_2 and the amount of doping Ca^{2+} is larger. The radii of Sr^{2+} and Ba^{2+} are too large for the ions to enter into the lattice of TiO_2 . Therefore, Sr^{2+} and Ba^{2+} are mainly on the surface of TiO_2 , which might favor separation of the charge carriers to some extent, and eventually cause a slight enhancement of the reactivity. Hence, photocatalytic activities of the doped TiO_2 are in the order: $Be^{2+} \gg Ca^{2+} > Mg^{2+} > Sr^{2+} \approx Ba^{2+}$.

TABLE III. Comparison of the metal element on the surface of the catalyst, determined by XPS

Catalyst	[M]:[Ti]
1.25 at. % Be^{2+} -IP- TiO_2	4.34 at. %
1.25 at. % Be^{2+} -CP- TiO_2	1.67 at. %
1.25 at. % Ca^{2+} -IP- TiO_2	4.62 at. %
1.25 at. % Ca^{2+} -CP- TiO_2	3.33 at. %

The influence of the doping method on the photoactivity for hydrogen production is shown in Fig. 2. The activities of 1.25 at. % Be^{2+} -IP, 1.25 at. % Mg^{2+} -IP, 2.25 at. % Ca^{2+} -IP, 2.25 at. % Sr^{2+} -IP and 2.25 at. % Ba^{2+} -IP- TiO_2 samples increase 80.8, 21.9, 31.5, 11.0 and 7.1 % compared to pure TiO_2 , respectively. However, the activities of the 1.25 at. % Be^{2+} -CP, 1.25 at. % Mg^{2+} -CP, 2.25 at. % Ca^{2+} -CP, 2.25 at. % Sr^{2+} -CP and 2.25 at. % Ba^{2+} -CP- TiO_2 samples decrease 39.7, 17.8, 10.1, 6.8 and 3.3 %, compared to pure TiO_2 , respectively.

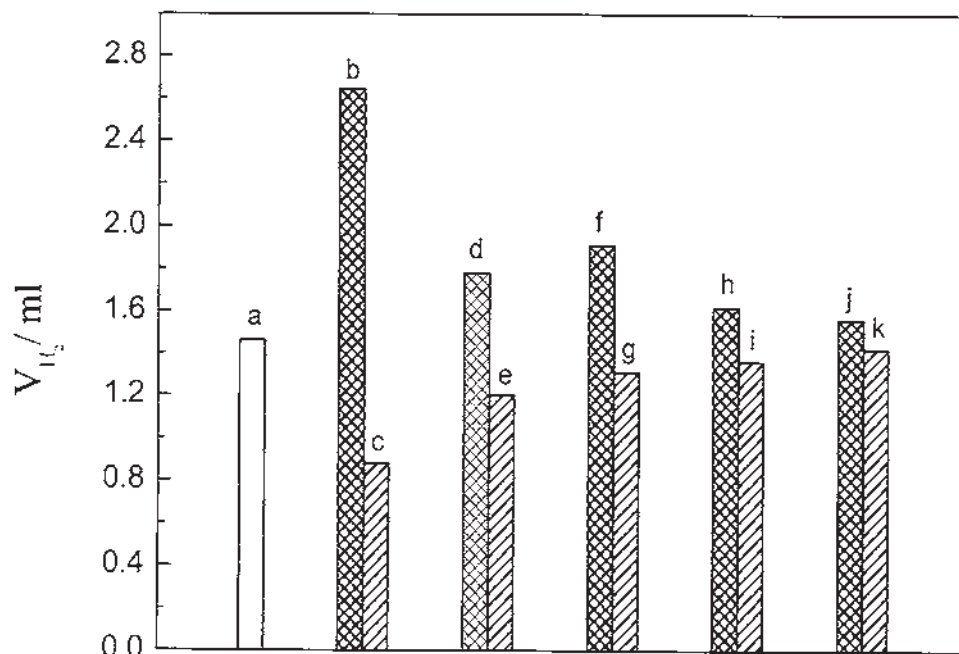


Fig. 2. Effect of doping method on photocatalytic production of hydrogen: a—pure TiO₂; b—1.25 at. % Be²⁺-IP-TiO₂; c—1.25 at. % Be²⁺-CP-TiO₂; d—1.25 at. % Mg²⁺-IP-TiO₂; e—1.25 at. % Mg²⁺-CP-TiO₂; f—2.25 at. % Ca²⁺-IP-TiO₂; g—2.25 at. % Ca²⁺-CP-TiO₂; h—2.25 at. % Sr²⁺-IP-TiO₂; i—2.25 at. % Sr²⁺-CP-TiO₂; j—2.25 at. % Ba²⁺-IP-TiO₂; k—2.25 at. % Ba²⁺-CP-TiO₂.

As shown in Table III the samples prepared by the coprecipitation method had fewer alkaline-earth metal ions on the TiO₂ surface than by impregnation method. This indicates that the ions can exist more easily in the bulk of the TiO₂ in form of doping ions or in form of very small oxide particles.

A prerequisite for an effective dopant involves the possibility of charge detrapping and migration to the surface of catalysts. For the sample prepared by impregnation, the doping metal ions are located mainly on the shallow surface of TiO₂ and can induce defects. The defects could become the centers of shallow electrons or holes traps, which would improve efficiently of the separate of the electrons and holes. Hence the photocatalyst has a high photocatalytic activity. For the sample prepared by coprecipitation, because the doping metal ions reside in the deep bulk phase by entering the TiO₂ lattice (by doping Be²⁺, Mg²⁺ and Ca²⁺) or the formation of a few small Ca²⁺, Sr²⁺ and Ba²⁺ oxide particles inside TiO₂, defects can be induced in the bulk TiO₂, which become trapping centers of the photoexcited electrons or holes. The trapped electrons or holes can then not easily migrate to the TiO₂ surface, so that the photocatalytic reaction hardly occurred, or the trapped electrons or holes became centers of electron-hole recombination. Thus, the photocatalyst has a low photocatalytic activity.

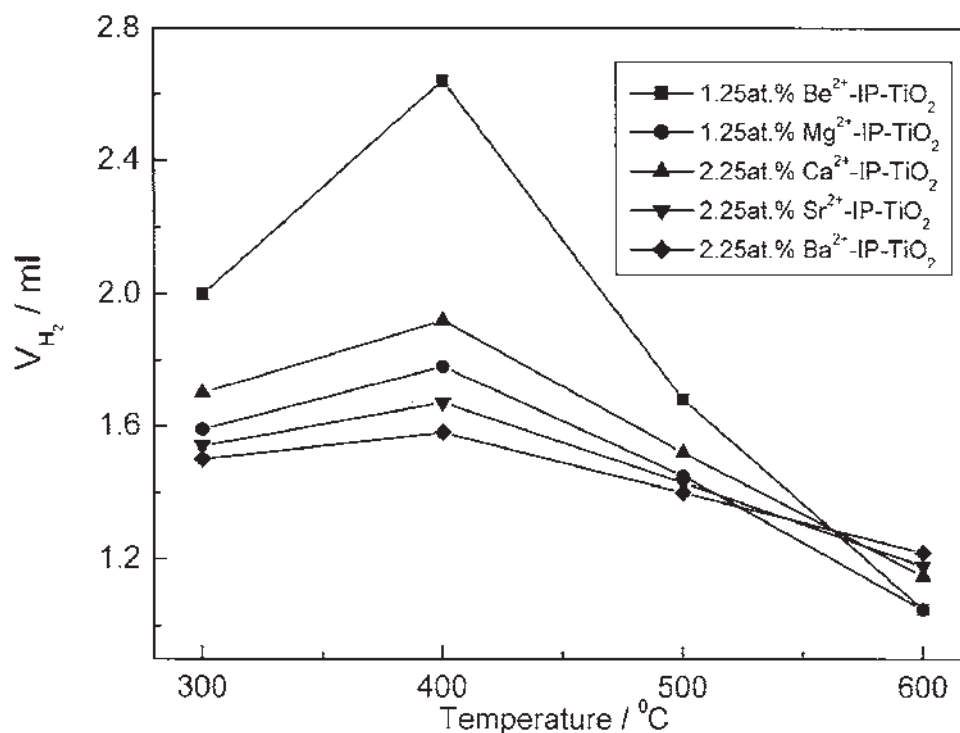


Fig. 3. Photocatalytic production of hydrogen as a function of the calcination temperature with calcination time 1 h.

The change of the photocatalytic activity of the M^{2+} -IP-TiO₂ with calcination temperature and time are shown in Fig. 3 and Fig. 4, respectively. It can be seen that the photocatalytic activity increases at first and then decrease. The optimum calcination temperature and time are 400 °C and 1 h, respectively. At the lower temperature and shorter time, the doping ions were mainly on the surface and in the near surface of the sample; with increasing temperature and time, more doping ions could enter into the bulk. As discussed above, doping alkaline-earth metal ions on or in the shallow surface are beneficial, while in the bulk phase they are determined. When calcination temperature and time are below 400 °C and 1 h, respectively, the former factor is dominant, but above 400 °C and 1 h, respectively, the latter is important. The radius of Be²⁺ is the smallest among all the alkaline-earth metal ions, hence the Be²⁺ enters most easily into the lattice of TiO₂; thus the influence of calcination temperature and time on the activity of Be²⁺ doped TiO₂ is the largest. As Mg²⁺ and Ca²⁺ ions can also enter the lattice of TiO₂ easily, the influence of calcination temperature and time was large. Sr²⁺ and Ba²⁺ ions only enter with difficulty into the lattice of TiO₂. Thus, the consequence of increasing the calcination temperature and time had the smallest effect on the activity of Sr²⁺ and Ba²⁺ doped TiO₂. In addition, with increasing calcination temperature,

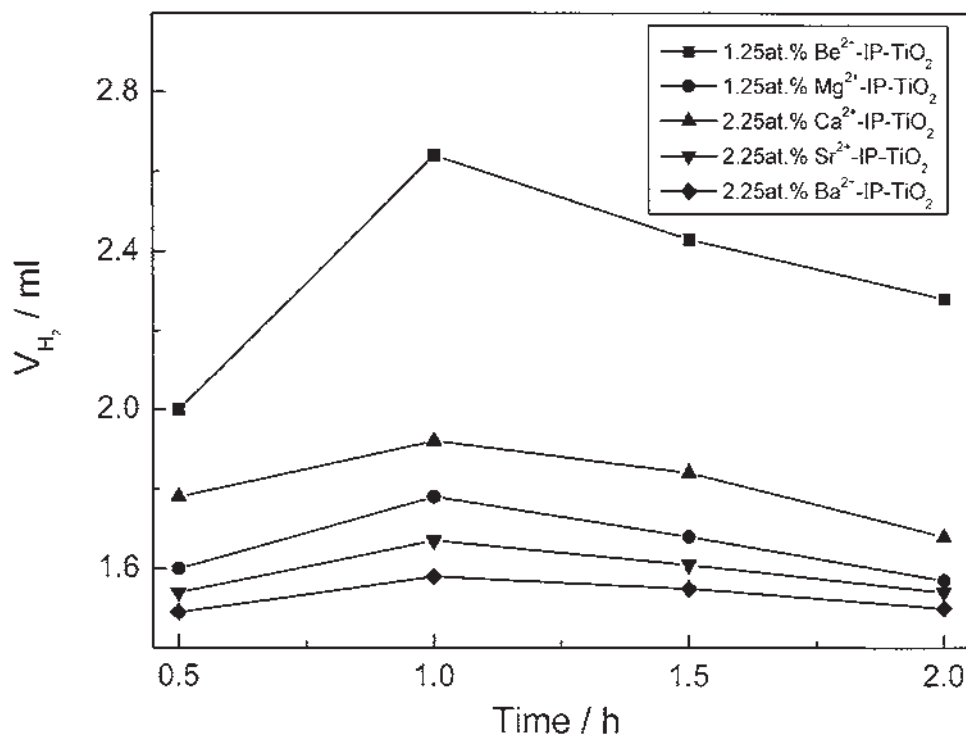


Fig. 4. Photocatalytic production of hydrogen as a function of the calcination time with calcination temperature 400 °C.

the particle size of the samples should increase, which would also result in a decrease of the photocatalytic activities. Thus an optimum calcination temperature and time exist.

CONCLUSION

Doping TiO₂ with alkaline-earth metal ions can increase the photocatalytic activity. The optimum doping molar contents of Be²⁺, Mg²⁺, Ca²⁺, Sr²⁺ and Ba²⁺ were 1.25, 1.25, 2.25, 2.25 and 2.25 at. %, respectively. The optimum calcination temperature and time of doping TiO₂ were 400 °C and 1 h. The photocatalytic activities of doped TiO₂ photocatalysts depended on the size of the dopant ions and the doping method. When the radius of the doping ion was smaller than or similar to that of Ti⁴⁺, the doping effect was obvious; while when the radius of the doping ion was much larger than that of Ti⁴⁺, the effect of doping was smaller. In particular, when the doping ion was in the shallow surface, doping was beneficial; while when it was in the deep bulk, the doping was detrimental.

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ИЗВОД

ЕФЕКАТ ДОПОВАЊА TiO₂ ЈОНИМА ЗЕМНОАЛКАЛНИХ МЕТАЛА НА
ЊЕГОВУ ФОТОКАТАЛИТИЧКУ АКТИВНОСТYEXIANG LI^{*1}, SHAOQIN PENG,¹ FENGYI JIANG,² GONGXUAN LU³ и SHUBEN LI³

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Фотокатализатор TiO₂ допован јонима земноалкалних метала припремљен је методама импрегнације и копреципитације. Узорци су окарактерисани XRD, XPS и IR спектроскопијом. Испитивана је њихова активност у фотокаталитичком добијању водоника. Активност допованих фотокатализатора зависила је од величине јона допанта и методе доповања. Оптимални молски садржаји јона допанта Be²⁺, Mg²⁺, Ca²⁺, Sr²⁺, и Ba²⁺ били су 1,25, 1,25, 2,25, 2,25 и 2,25 at.%, респективно. Оптимална температура и време калцинације износили су 400 °C, односно 1 h.

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REFERENCES

1. A. Fujishima, K. Honda, *J. Nature* **238** (1972) 37
2. A. Kudo, H. Kato, *J. Chem. Lett.* **26** (1997) 867
3. A. Kudo, K. Omori, H. Kato, *J. Am. Chem. Soc.* **12** (1999) 11459
4. A. Kudo, H. Kato, S. Nakagawa, *J. Phys. Chem. B.* **104** (2000) 571
5. J. Kiwii, M. Graetzel, *J. Phys. Chem.* **88** (1984) 1302
6. K. Sayama, H. Arakawa, *J. Phys. Chem.* **97** (1993) 531
7. S. Chatterjee, S. Sarkar, S. N. Bhattacharyya, *J. Photochem. Photobiol. A: Chem.* **72** (1993) 183
8. M. R. Hoffman, S. T. Martin, W. Choi, *Chem. Rev.* **95** (1995) 69
9. W. Choi, A. Termin, M. R. Hoffmann, *J. Phys. Chem.* **98** (1994) 13669
10. Y. Li, T. Wang, S. Peng, *Acta Phys-Chim. Sin.* **20** (2004) 1434
11. J. Zhao, T. Wu, K. Wu, *Environ. Sci. Technol.* **32** (1998) 2394
12. V. Subramanian, E. Wolf, P. V. Kamat, *J. Phys. Chem. B* **105** (2001) 11439
13. R. C. Evans, *An Introduction to Crystal Chemistry*, 2nd Ed, Cambridge Univ. Press, Cambridge, 1964, p. 38
14. Y. Wang, L. Zhang, H. Cheng, *Chem. J. Chinese Universities* **20** (2000) 958
15. A. Xu, Y. Gao, H. Liu, *J. Catal.* **207** (2002) 151
16. R. Rodriguez-Talavera, S. Vargas, R. Arroyo-Murillo, *J. Mater. Res.* **12** (1997) 439.