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Efficient Photocatalytic Hydrogen Evolution over Platinum and Boron Co-doped TiO_2 Photocatalysts

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In this paper, the new photocatalyst, $Pt^{x-}/TiO_{2-y}B_y$ was prepared by impregnation method via coupling with a inorganic water splitting system, namely, a ternary system K^+,$Na^+/B_4O_7^{2-}$- H_2O for hydrogen evolution. The integration process of the preparation for B doping Pt/TiO_2 with the significant photocatalytic hydrogen evolution in the ternary system K^+,$Mg^{2+}/B_4O_7^{2-}$- H_2O and K^+,$Na^+/B_4O_7^{2-}$- H_2O were accomplished by impregnation in situ. The photocatalyst $Pt^{x-}/TiO_{2-y}B_y$ synthesis and the photocatalytic hydrogen production of the isothermal solubility of the ternary system K^+,$Mg^{2+}/B_4O_7^{2-}$- H_2O and K^+,$Na^+/B_4O_7^{2-}$- H_2O at 25 °C have been studied. Thus, the present challenge is not only to demonstrate a suitable photocatalytical system that can efficiently produce hydrogen under the borate excited, but also research that the addition of borate to the suspensions greatly enhanced the stability of the photocatalysts over semiconductor catalysts. The results show that borate solution is a suitable for B doped TiO_2 photocatalysts preparation and a novel photocatalyst $Pt^{x-}/TiO_{2-y}B_y$ was successfully prepared by this way. XRD and XPS characterization showed that both anatase and rutile coexist and the B is incorporated into the crystal of the TiO_2.So the TiO_2 can be denoted as $TiO_{2-x}B_x$. The effect of borate on the photocatalytic properties were investigated. The results showed that the amount of hydrogen evolved is enhanced by factors of 4 with the addition of H_3BO_3 to the ethanol/water reaction solutions. The role of boron anion does not act as a sacrificial electron donors.

Keywords: boron, platinum, photocatalysts, hydrogen evolution.

1. INTRODUCTION

Based on the fact that hydrogen is an ideal energy carrier, the production of hydrogen from photocatalytic water splitting becomes an important subject since it can provide an efficient rout to storage and conversion of solar energy [1]. A growing interest in photocatalytic water splitting to produce hydrogen follows the pioneering works of A. Fujishima, K. Honda [2, 3] and A. J. Bard [4]. Although there has been a remarkable progress over the last few decades for photocatalysts working under Uv-light and for construction of efficient photocatalytic water splitting system in the absence of an electron donor as well, this progress has been rarely extended to the visible light region and their activity is still relatively low [5 – 9]. To prepare visible light photocatalysts with higher activity, to construct effectively photocatalytic water splitting system under no sacrificial electron donor existed, therefore, have become the most important two topics in the photocatalysis research today [10 – 12].

China is one of the most important countries in the world that has abundant salt lakes in number, distribution, type and resource [13]. Moreover, the sub-type magnesium sulphate salt lakes rich in boron are rarely found in the world with rather complicated composition and crystallization route. With a view to prepare more active photocatalyst, to construct new efficient water photocatalytic splitting system, to comprehensive utilize salt lake resources such as boron etc, to understand the bittern behavior in the process of photocatalytic reaction, in the present study, we have reported the preparation of B-doped Pt/TiO_2 photocatalysts by impregnation in situ coupled with the process of photocatalytic hydrogen evolution with an excellent reproducibility in the ternary system of K^+,$Mg^{2+}/B_4O_7^{2-}$- H_2O and K^+,$Na^+/B_4O_7^{2-}$- H_2O at 25 ºC, which is a subsystem of Zhabuye salt lake brines located in Qinghai-Tibet plateau, China [13].

2. EXPERIMENTAL DETAILS

In this studies, Degussa P25 TiO_2 semiconductors were purchased from Sachtleben and the Pt/TiO_2 photocatalyst was prepared as stated in reference [14]. $Na_2B_4O_7\cdot 10H_2O$ employed in this experiment was crystallized by double e-crystallization. Other chemicals, such as $K_2B_4O_7\cdot 4H_2O$ and alcohol, were of analytic reagent grade and used without further purification. All the solutions were prepared in triple distilled water. Photocatalytic experiments were conducted in a one-compartment Pyrex cell (120 cm^3) with a flat window (14 cm^2) for illumination at a constant temperature of 25 °C. Photocatalytic hydrogen evolution experiments were performed in a 120 ml quartz flask with a flat window. The light source was a 300 W high-pressure Hg lamp. 20 mg of catalyst was suspended in 75 ml of solution. The mixtures were stirred with a magnetic stirrer. The reactant mixtures were placed in the flask and purged with argon gas for 40 minutes in order to remove the dissolved oxygen and ensure an anaerobic condition. During the photocatalytic process, 0.5 mL gas sample in the top of reactor was collected intermittently through the septum and the amount of hydrogen evolution was measured with gas chromatography [15].

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X-ray diffraction (XRD) patterns of the samples were recorded on a Rigaku B/Max-RB diffractometer with a nickel filtrated Cu Kα radiation operated at 40 kV and 40 mA. X-ray photoelectron spectroscopy (XPS) analysis was performed using a VG Scientific ESCALAB210-XPS photoelectron spectrometer with an Mg Kα X-ray resource. [16].

3. RESULTS AND DISCUSSION

3.1. Preparation and Characterization of Photoatalysts

3.1.1. XRD characterization

XRD patterns of the 1 wt % $Pt^{x-}/TiO_{2-y}B_y$ are shown in Fig. 1. The 2θ values of 25.23, 47.98 and 37.78 degree are the anatase characteristic peaks. The 2θ values of 27.55, 54.20 and 36.00 degree are the rutile characteristic peaks. It means that both anatase and rutile coexist. Pt loading doesn't change the phase structure of P25 TiO_2. The weak B characteristic peak was observed in $2\theta = 4.94$ degree, signified that the B is incorporated into the crystal of the TiO_2 [15].

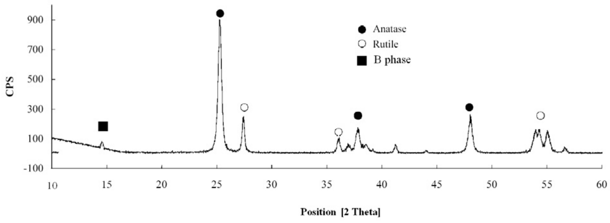

Fig. 1. The XRD patterns for 1wt % $Pt^x/TiO_{2-y}B_y$ catalyst

3.1.2. XPS characterization

The X-ray photoelectron spectra profile of Pt particles of the 1 wt % Pt/TiO_2 catalyst is provided in Fig. 2. The binding energy (BE) value of Pt $4f_{5/2}$ and $4f_{7/2}$ are 74.29 eV and 70.85 eV, respectively, which indicate that the Pt species are present on TiO_2 surface as Pt^0.

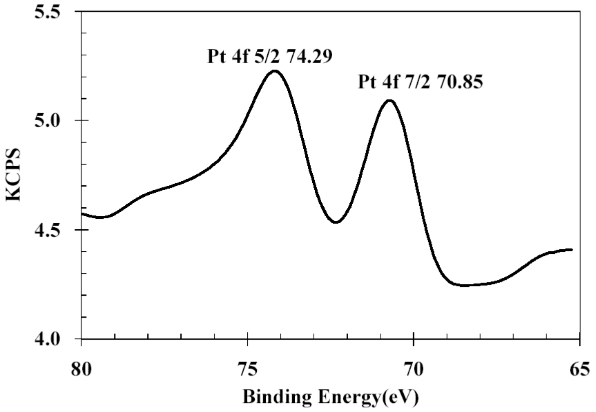

Fig. 2. The Pt 4f XPS of the 1.0 wt % Pt/TiO_2 photocatalyst

Fig. 3 shows the XPS survey spectrum of Pt-doped TiO_2 powders prepared in $Na_2B_4O_7\cdot10H_2O$ saturated solution under Uv-light for 12 hours and then by filtering, drying at 50 ºC. XPS peaks show that the B_{1s} bonding energy was 192.03 eV, which is some transformation from that of $Na_2B_4O_7\cdot10H_2O$ (BE 192.2 eV). With the consideration of the standard bond energy of B–O bonds for B_{1s} in $Na_3(BO_2)_3$ (191.80 eV) and the standard bond energy of B–Ti bonds for B_{1s} in TiB_2 (187.3 eV), the result showed that the B atom was weaved into TiO_2 or transformed into $Na_3(BO_2)_3$ etc. rather than existing in the formation of $Na_2B_4O_7\cdot10H_2O$. We propose that the mixed state such as B–Ti–O exist [17]. The TiO_2 can be denoted as $TiO_{2-x}B_x$ to some extent. Fig. 4 shows the quite difference of XPS character of $Pt_{4f7/2}$ in Pt/TiO_2 powders absorbed $Na_2B_4O_7\cdot10H_2O$ at 70.30 eV. The similar results were observed in reference [15].

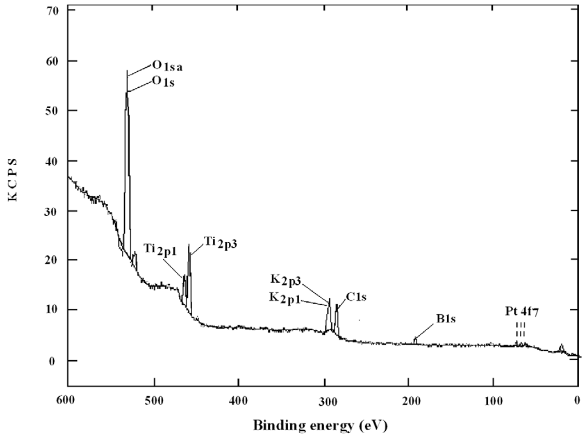

Fig. 3. The XPS survey spectrum of 1 wt % $Pt^{x-}/TiO_{2-y}B_y$ catalyst. Note: KCPS(kilocycles per second)

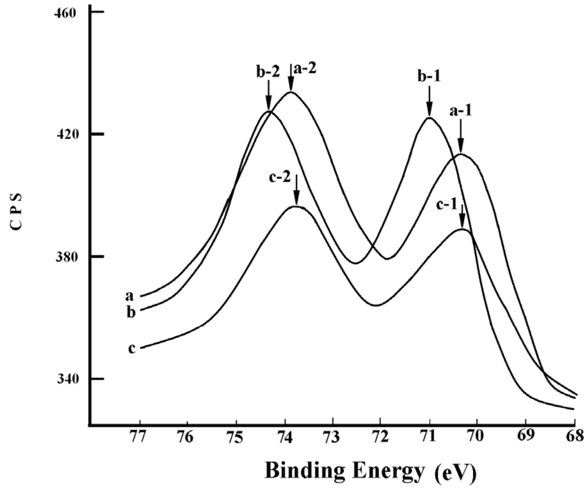

Fig. 4. XPS spectrum of Pt in 1 wt % $Pt^{x-}/TiO_{2-y}B_y$ catalyst: (a) – 1 wt % $Pt^{x-}/TiO_{2-y}B_y$ (prepared under Uv-light irradiation; a-1: $Pt4f_{7/2} = 70.30$ eV; a-2: $Pt4f_{5/2} = 73.76$ eV); (b) – 1 wt % Pt/TiO_2 (b-1: $Pt4f_{7/2} = 70.87$ eV; b-2: $Pt4f_{5/2} = 74.39$ eV,); (c) – 1 wt % $Pt^{x-}/TiO_{2-y}B_y$ (prepared in dark; c-1: $Pt4f_{7/2} = 70.33$ eV; c-2: $Pt4f_{5/2} = 73.79$ eV)

3.2 The effect of Pt loading (wt %) on the photocatalytic hydrogen generation rates

The effect of Pt loading (wt %) on the photocatalytic hydrogen generation rates from water splitting was discussed here with photocatalytic decomposition of organic waste using ethanolamine as an electron donors. The result showed that the photocatalytic hydrogen generation rate increases with the increase of Pt loading under 0.5 wt % as it is shown in Fig. 5. When the Pt loading exceeds 0.5 wt %, the photocatalytic hydrogen generation rate remains an approximate constant. The reason of which was that, for a photocatalyst with a higher Pt-loading content, Pt particles are not only the photocatalytic center of the reaction $2H^+$(or H) + $2e^- = H_2$, but also they are the photoelectron and photo-hole recombination centers. As for TiO_2 photocatalyst, the optimal Pt loading is 0.5 wt %.

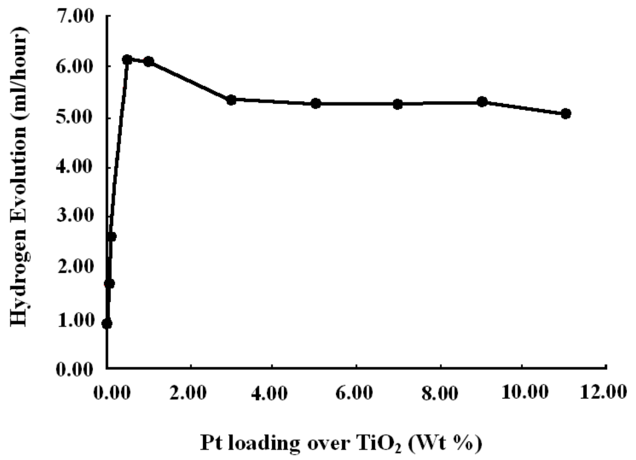

Fig. 5. The effects of Pt loading (wt %) on hydrogen generation rate

3.3. Effect of photocatalytic hydrogen evolution in the ternary system $K^+,Na^+/B_4O_7^{2-}$- H_2O

Fig. 6 shows the amount of photocatalytic hydrogen production over $Pt^{x-}/TiO_{2-y}B_y$. In the case of $Na_2B_4O_7\cdot 10H_2O$ addition, hydrogen production rate is not only increased, but also is constant. The moles of produced hydrogen is more than moles of the photocatalyst and no structural change takes place both the $Na_2B_4O_7\cdot 10H_2O$ re-crystallized and in the photocatalysts $Pt^{x-}/TiO_{2-y}B_y$ after reaction as it follows from XRD measurements.

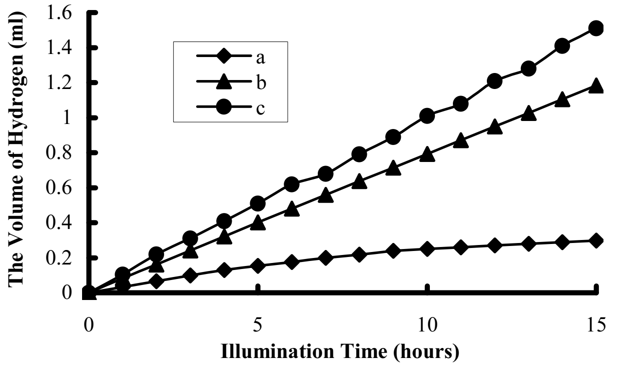

Fig. 6. Reaction time-course of photocatalytic hydrogen evolution over 1 wt % $Pt^{x-}/TiO_{2-y}B_y$: (a) – distilled water; (b) – the ternary system $K^+,Mg^{2+}/B_4O_7^{2-}$- H_2O solution; (c) – the ternary system $K^+,Na^+/B_4O_7^{2-}$- H_2O solution)

3.4 Effect of borate on the photocatalytic hydrogen evolution from 20 % volume of ethanol / volume of water solution (v/v)

In order to understand the enhancement mechanism in depth, the effect of borate on the photocatalytic properties from 20 % (v/v) ethanol/water solution containing P25 TiO_2 powders were investigated. Fig. 7 shows the effect of borate on the photocatalytic hydrogen production from 20 % (v/v) ethanol/water. The amount of hydrogen evolved is enhanced by factors of 4 with the addition of 0.1 mg H_3BO_3 to the 75 mL 20 % (v/v) ethanol/water reaction solutions.

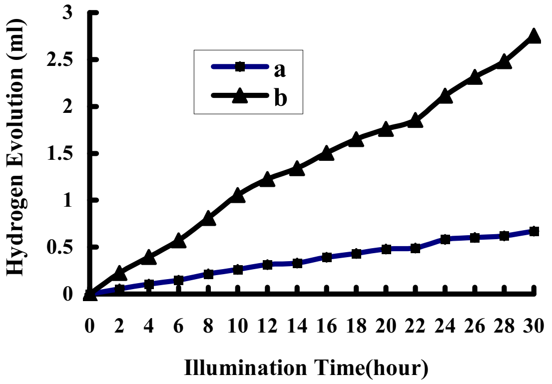

Fig. 7. Reaction time-course of photocatalytic hydrogen evolution over Degussa P25 in 70 ml 20 % (v/v) ethanol/water solutions: (a) – without addition of boric acid; (b) – with the addition of 0.1 mg H_3BO_3

3.5. Functions of Borate

As for boron, which valence electron is $2s^22p^1$, being an amphoteric atom, lacking of electrons and great electronegativity, the particular character is that boron is most likely capable to accept 1 – 5 electrons. Based on its amphoteric character, boron is capable of release electrons to some extent in specific condition to form covalent compounds too. In general, a photocatalytic reaction is initiated by the photoexcitation of TiO_2 and it leads to the formation of electron-hole pairs and the other redox reaction as well:

$TiO_2 + 2hv = 2e^- + 2h^+$ (excitation of TiO_2 by light); (1)
$H_2O + 2h^+ = (1/2)O_2 + 2H^+$ (at the TiO_2 electrode); (2)
$2H^+ + 2e^- = H_2$ (at Pt electrode). (3)

It is necessary to note that almost all of the borate is composed of the annular or chain structure of BO_3, BO_4. The structure of $Na_2B_4O_7\cdot 10H_2O$ may transforme into $[(BO_2)_3]^{3-}$ in some conditions. Based on the above mentioned facts, it can be infered that the $(BO_2)_3^{3-}$ monolayer (as show in Fig. 8 [18]) is formed on the Pt particles.

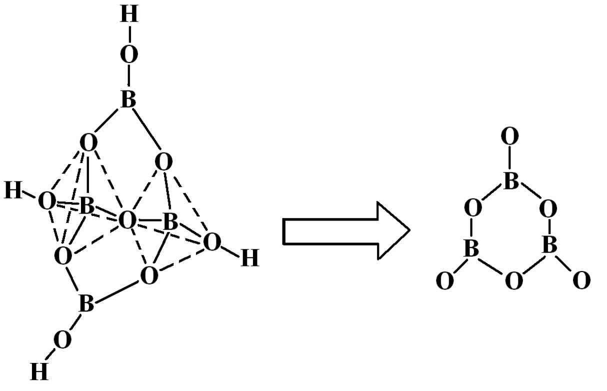

Fig. 8. The process of $[B_4O_5(OH)_4]^{2-}$ transformed into $[(BO_2)_3]^{3-}$

The $(BO_2)_3^{3-}$ monolayer possibly suppresses the backward reaction of $(1/2)O_2 + 2H^+ = H_2O$ occurred on the Pt particles. We speculate that the addition of borate to a suspension had changed the photocatalytic process by change the semiconductor surface properties. It is due to the particular property of boron, i. e. lacking of electrons and that the boron atom is combined with the semiconductor by coordination bond. This closely combination formed the best electron capture at the Schottky barrier of the boron in contact with a semiconductor surface. As result of that, the electron-hole recombination is efficiently suppressed [15].

4. CONCLUSIONS

This study demonstrates a new photocatalytic system, in which significant promotion effect of hydrogen evolution over TiO_2 semiconductor photocatalysts takes place. The significant promotion effect of hydrogen evolution using Pt-loaded TiO_2 photocatalysts was observed. A novel photocatalyst, $Pt^{x-}/TiO_{2-y}B_y$ was prepared by a very simple method coupled with the hydrogen evolution. The photocatalyst $Pt^{x-}/TiO_{2-y}B_y$ synthesis and the photocatalytic hydrogen evolution in the ternary system K^+, $Na^+/B_4O_7^{2-}$-H_2O at 25 ºC have been studied. All of these effects obtained are due to particular character of boron atom. The results show that borate solution is a suitable system, in which the B doped Pt/TiO_2 photocatalyst, namely, photocatalyst $Pt^{x-}/TiO_{2-y}B_y$ can be successfully prepared by this way.

Acknowledgments

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