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Significant Effect of Pressure on the H_2 Releasing from Photothermal-Catalytic Water Steam Splitting over $TiSi_2$ and Pt/TiO_2

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Abstract This study reports the significant pressure effect on the photocatalytic activity of hydrogen generation over two kinds of representative semiconductor catalysts ($TiSi_2$ and Pt/TiO_2). The photothermal-catalytic hydrogen generation from water steam splitting under visible light was achieved. And the physicochemical properties of the photocatalysts were characterized by XRD and XPS techniques. Compared to the conventional liquid-solid-phase photocatalytic method, this gas-solid-phase photothermal-catalytic method for hydrogen releasing from water steam exhibited a higher apparent quantum yield (22.01%) under the high pressure.

Keywords Pressure effect · Photocatalytic hydrogen generation · Water steam splitting

1 Introduction

Diminishing global energy and growing environmental deterioration indicate that sustainable sources of energy are needed in the near future. Hydrogen, one of energy carriers for renewable energy, has attracted extensive attention due to its environmentally clean character and recycling possibility. Hydrogen can be prepared *via* two approaches. One is from reforming of fossil fuels, and the other is from water splitting. Due to the environment pollution and the fast depletion of fossil fuels, the worldwide interest is strongly focused on hydrogen production from renewable energy. Solar energy and water source are abundant on the earth. One of the dreams of mankind is to capture the solar energy that is freely available from sunlight and split water to generate hydrogen. There have been many ways to convert sunlight into hydrogen by water, such as photoelectrochemical cells (PEC), homogeneous photo-assistant coordination catalysis, heterogeneous semiconductor photocatalysis, and so on. Among which, photocatalytic hydrogen production is comparatively simple, clean, cheap, and practical, so it is being widely and intensively investigated [1–3].

The rational for splitting water molecule to hydrogen on a semiconductor is to utilize the reduction properties of the excited electrons on the conduction band of a semiconductor. To achieve overall water splitting, the bottoms of the conduction bands must be located at a more negative potential than the reduction potential of H^+/H_2, while the tops of the valence bands must be positioned more positively than the oxidation potential of H_2O/O_2 [4]. Conventional photocatalytic water splitting reaction is always conducted in solid-liquid phase, and many semiconductor catalysts have been widely studied, such as oxides [5], nitrides [6], sulfides [7], oxynitrides [8], oxysulfides [9], and so on. The reaction activity is often influenced by the pH value of the aqueous solution, the crystallinity and composition of the photocatalysts, the loading kind and the amount of cocatalyst, electron donors, and reaction temperature [10–17]. However, the poor absorption of visible light, low solar conversion efficiency,

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and short stability of the existing photocatalysts are still the main obstacles for the development and application.

Gas-solid-phase photocatalytic hydrogen production from water splitting is also investigated, although the reports are less seldom. Thirty years ago, Damme and Hall reported the photoassisted decomposition of water at gas-solid interface on TiO_2, they thought the presence of Ti^{3+} ions on the surface was necessary for water decompositon [18]. Kawai and Sakata found that Hg-lamp irradiation of TiO_2 powders mixed with RuO_2 leaded to the continuous production of hydrogen and oxygen from gaseous water at room temperature. The activity of water splitting after the addition of RuO_2 to TiO_2 was due to the semiconductor-metal contact and the high activity of oxygen evolution from RuO_2. They also believed the key role of Ti^{3+} ions in water decomposition [19]. Wagner and Somorjai reported the sustained photogeneration of hydrogen from water vapor on metal-free and platinized $SrTiO_3$ single crystals illuminated in the presence of electrolyte films (NaOH, KOH, etc.). The basic deliquescent compound had an affinity for water steam adsorption, and turned into a pool of aqueous solution [20]. Recently, Yoshida et al. reported a new photocatalytic system producing hydrogen from methane and water steam, i.e., *photocatalytic steam reforming of methane* (PRSM). He found that the PRSM could produce H_2 more efficiently than the water-splitting steam [21]. Herein, we developed a novel photothermal-catalytic system to produce hydrogen from water steam. The photothermal-catalytic behaviour of hydrogen releasing from water over two kinds of representative photocatalysts (Pt/TiO_2, $TiSi_2$) was investigated, and the effect of the reaction pressure and temperature on the photocatalytic activity was discussed. To the best of our knowledge, this is the first time to study the pressure effect on the photocatalytic activity of hydrogen generation from gaseous water.

2 Experimental Methods

$TiSi_2$ (ca. 325 mesh) was purchased from Alfa. Pt/TiO_2 was prepared by the photo-reduction method, and the Pt loading content is 1% [11–15]. The photothermal-catalytic reaction of water splitting under different high pressure was carried out in a Pyrex flask of 118 mL with a flat window, and the efficient irradiation area was around 6 cm^2. Typically, 100 mg of photocatalysts and 1 mL of distilled water were added in the reaction system. While the reaction under normal pressure was conducted in an open system, the pressure remain unchanged as the temperature increases.

The light source was a 300 W tungsten halogen lamp. The intensity of the incident light was determined with a Ray virtual radiation actinometer (FU 100, silicon ray detector, light spectrum: 400–700 nm, sensitivity: 10–50 $\mu V\ \mu mol^{-1}\ m^{-2}\ s^{-1}$), which was 878.2 $\mu mol/s\ m^2$. The reaction pressure varied by changing the reaction temperature, which contained the pressure of water steam and air in the reaction flask. The apparent quantum yield was calculated by the following equation [11–13, 22]:

$$\Phi_{H_2} = \frac{2(\text{mole of hydrogen evolved})}{(\text{mole of incident photon})} \quad (1)$$

3 Results and Discussion

Figure 1 illustrates the ultraviolet-visible diffuse reflectance spectra (UV-vis DRS) of photocatalysts $TiSi_2$ and Pt/TiO_2. As can be seen, $TiSi_2$ has a strong absorption ability of ultraviolet-visible light, so it can participate in the visible-light-induced photocatalytic reaction. Pt/TiO_2 exhibits an absorption onset, which is at about 420 nm. The band gap of Pt/TiO_2 can be estimated to 2.95 eV according to the Kubelka-Munk functions [23].

The relationship between the hydrogen generation rate and the reaction pressure under visible light is outlined in Fig. 2. As can be seen obviously from the figure, the hydrogen generation rate increases as the increase of the reaction pressure for both $TiSi_2$ and Pt/TiO_2 photocatalysts, while there is almost no hydrogen production under normal pressure. This results indicate that the pressure has a significant effect on the photocatalytic activity of hydrogen generation. Under normal pressure, the photocatalytic activity does not improve apparently as the increase of the reaction temperature, which indicates that the temperature has little effect on the photocatalytic activity. Before the reaction of water steam splitting, the adsorption of water steam on the surface of the photocatalysts is necessary. The

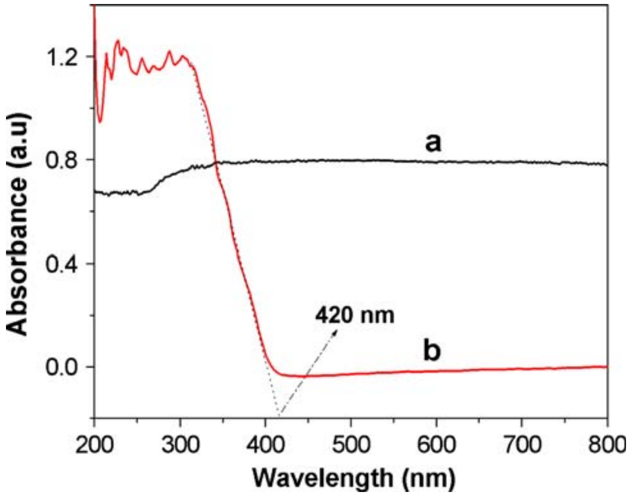

Fig. 1 UV-vis DRS spectra of $TiSi_2$ (a) and Pt/TiO_2 (b)

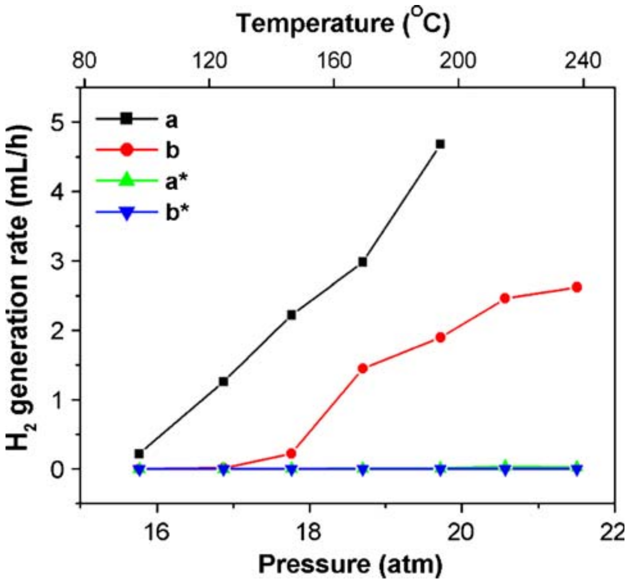

Fig. 2 Effect of reaction pressure on the photocatalytic H_2 generation rate a and b represent the photocatalytic hydrogen generation rate of $TiSi_2$ and Pt/TiO_2 under different high pressure; a* and b* represent the photocatalytic hydrogen generation rate of $TiSi_2$ and Pt/TiO_2 under normal pressure

high pressure may be advantageous for the dissociation of chemical adsorbed water molecules [24]. The hydrogen generation rate can reach 4.68 and 1.90 mL/h for $TiSi_2$ and Pt/TiO_2 photocatalysts under high pressure at 190°C. According to Eq. 1, we can calculate the apparent quantum yield of hydrogen generation of 22.01 and 12.32% over $TiSi_2$ and Pt/TiO_2 photocatalysts.

The XRD pattern of photocatalysts $TiSi_2$ and Pt/TiO_2 before and after the reaction are shown in Fig. 3. The main crystalline components of pattern a and a′ are $TiSi_2$, followed by a little TiSi, metallic Si and Ti. The crystalline phase after reaction is unchanged as compared to the starting $TiSi_2$. There are no reflections belonging to SiO_2 and TiO_2. The crystalline phase of Pt/TiO_2 contains anatase and rutile, which also remain unchanged after reaction.

Analyzing the XPS results, we find that the surface of catalysts $TiSi_2$ and Pt/TiO_2 were partly oxidized. The date is shown in Table 1. The surface oxygen content of $TiSi_2$ and Pt/TiO_2 after reaction increases from 57.891% to 58.864%, and 49.852% to 53.203%, respectively. Oxygen evolution from water splitting may be absorbed on the catalyst surface or enter into the lattice of the catalyst, which is probably the reason for the increase of oxygen content. We will study where is the oxygen with isotopically labelled water, H_2O [18], in our next work.

The stability of photocatalyst $TiSi_2$ was also studied and the results was shown in Fig. 4. As can been seen apparently, the photocatalytic activity of hydrogen production decreases sharply in the second run, which only maintains 60% of that of the first run. The deactivation of $TiSi_2$ are

Table 1 XPS data of TiSi2 and Pt/TiO2 before and after reaction

	Peak	[AT]% (before reaction)	[AT]% (after reaction)
$TiSi_2$	O1 s	57.891	58.864
	C1 s	48.357	47.399
	Ti2p3	8.354	8.788
	Si2p	20.377	20.248
Pt/TiO_2	O1 s	49.852	54.203
	C1 s	32.613	30.902
	Ti2p3	17.501	14.867
	Pt4f7	0.034	0.028

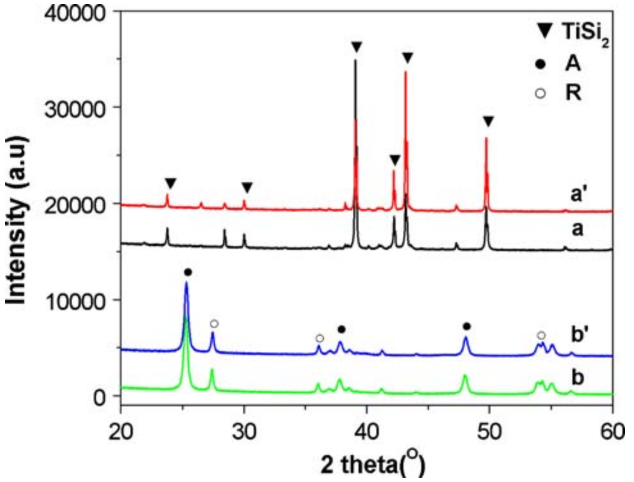

Fig. 3 XRD patterns of photocatalysts $TiSi_2$ and Pt/TiO_2 a and a′ represent $TiSi_2$ before and after reaction; b and b′ represent Pt/TiO_2 before and after reaction

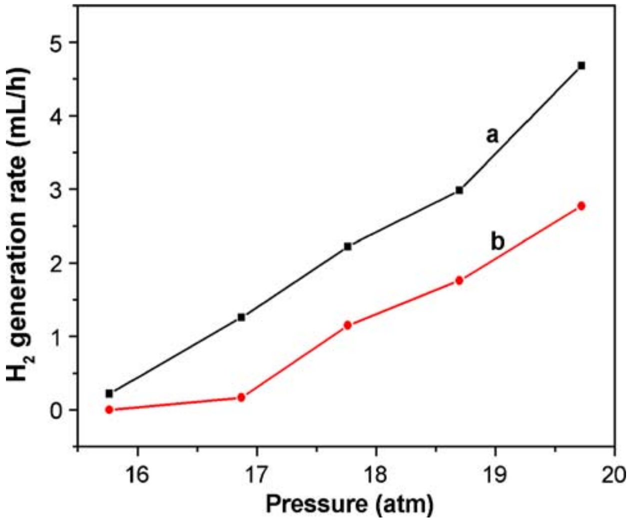

Fig. 4 Time courses of photothermal-catalytic hydrogen releasing from water splitting over $TiSi_2$. (a) The first run, (b) the second run

mainly due to the surface oxidation, which consists with the literature [17].

4 Conclusions

The photothermal-catalytic hydrogen releasing from water steam splitting is investigated, and the results indicate that the reaction pressure plays a significant effect on the photocatalytic hydrogen generation. There is almost no hydrogen production under the standard atmosphere pressure, while the highest apparent quantum yield of hydrogen production for $TiSi_2$ and Pt/TiO_2 can achieve 22.01 and 12.32% under the high pressure. The high pressure may be advantageous for the dissociation chemical adsorption of water molecules on the photocatalysts. The crystalline phase of photocatalysts do not change after reaction, while the catalysts surface are oxidized partly.

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