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Effect of Pt loading and calcination temperature on the photocatalytic hydrogen production activity of TiO_2 microspheres

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Abstract

TiO_2 microspheres were synthesized by hydrothermal reaction using $Ti(OBu)_4$ as the precursor. In order to enhance the efficiency of water splitting by the TiO_2 microspheres, Pt-modified TiO_2 microspheres were prepared by the impregnation-reduction method. The diameter of TiO_2 microspheres is around 5–10 μm. The photocatalytic performances of the catalysts were measured by hydrogen generation from a mixture of water and methanol under UV light irradiation. The photocatalytic activity of the TiO_2 microspheres was remarkably enhanced by loading Pt. The optimal Pt loading is 1.2 wt%. Pt/TiO_2 microspheres exhibit about 125 times greater H_2 production rate than the unmodified TiO_2 microspheres. The effect of calcination temperature on photocatalytic activity of the TiO_2 microspheres was also investigated.

Keywords: A. Calcination; Pt/TiO_2 microspheres; Photocatalysis; Hydrogen production

1. Introduction

At present, most of the world's energy supply comes from fossil fuels [1,2]. However, combustion of fossil fuel causes severe air pollution and greenhouse effect. H_2 has been identified as an alternative energy carrier due to its high energy capacity and environmental friendliness [3–8]. Therefore, it is necessary to find an efficient and economic method for hydrogen production.

Since Fujishima and Honda first reported water splitting into hydrogen by TiO_2 photoelectrode [9], many studies have been focused on photocatalytic hydrogen production by semiconductors such as TiO_2, ZnO, CdS etc. [10–16]. Compared with other semiconductor photocatalysts, TiO_2 has been regarded as a promising candidate to support the future hydrogen economy because of its stability, abundant availability, non-toxicity, low-cost and environmental friendly nature [17–19].

Although TiO_2 shows superior activity to other semiconductors, it possesses a high rate of photogenerated electron–hole recombination. This leads to the low efficiency of photocatalytic H_2 production [20]. In order to prohibit the rapid electron–hole recombination in water splitting, several attempts have been made to improve the photocatalytic efficiency of TiO_2, such as noble metal loading [21,22], metal ion doping [23,24] and anion doping [25,26]. Among them, immobilization of noble metals such as Pt, Pd, Au, and Ag on photocatalysts is a very promising approach to improve photocatalytic activity by changing properties of the semiconductor surface.

In this study, TiO_2 microspheres were fabricated by a simple hydrothermal treatment of a mixed solution of tetrabutyl titanate and hydrofluoric acid. The effects of Pt loading and calcination temperature on the photocatalytic activity of TiO_2

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microspheres for hydrogen production were also investigated and discussed.

2. Experimental

2.1. Preparation of photocatalysts

TiO_2 microspheres were synthesized by hydrothermal method. In a typical procedure, 7 mL $Ti(OBu)_4$ (98%) was mixed with 28 mL anhydrous alcohol under vigorous stirring [27]. Then a solution of hydrofluoric acid (40%, 0.7 mL) was added. The mixed solution was stirred for 0.5 h, and then hydrothermally treated in Teflon autoclave at 180 °C for 2 h. Finally, the resulting white precipitation was washed with ethanol for several times, and dried in vacuum at 40 °C.

Pt/TiO_2 microspheres were prepared by impregnating TiO_2 with an aqueous solution of H_2PtCl_6. After stirred for 0.5 h and ultra-sonicated for 0.5 h, the suspension was irradiated with UV light (a 350 W high-pressure mercury lamp) for 1 h under stirring. Finally, the precipitate was washed with ethanol and dried. Different amounts of platinum (0.2–1.6 wt%) were loaded on the TiO_2 microspheres.

In order to study the effect of calcination temperature on the photocatalytic activity of the TiO_2 microspheres, the prepared TiO_2 microspheres were calcined in a muffle furnace over the temperatures range of 400–700 °C for 2 h at a heating rate of 5 °C/min and then cooled to the room temperature.

2.2. Photocatalyst characterization

The scanning electron microscopy (SEM) photographs of the prepared samples were taken using a HITACHI S-4800. The crystalline phases were characterized by X-ray diffraction (XRD) using Bruker D8 Advance diffractometer with monochromatic CuKα radiation. UV–vis diffuse reflection spectra (DRS) were obtained using a HITACHI U-4100 spectrophotometer, and the reflection data were converted to absorbance through the standard Kubelka–Munk method.

2.3. Photocatalytic hydrogen production experiments

The photocatalytic reaction was performed in a quartz reactor. A 350 W high-pressure mercury lamp was used as a light source, which was located at a distance of 10 cm from the quartz reactor. Hydrogen was produced from a mixture of water and methanol. In a typical experiment, 0.1 g catalyst was suspended in a mixture of 54 mL water and 6 mL anhydrous methanol with a magnetic stir. The heating effect of the UV light source was prevented by circulating cooling water. The amount of generated hydrogen was measured by gas chromatograph (thermal conductivity detector, molecular sieve 5 Å column, Ar carrier).

3. Results and discussion

3.1. Effect of Pt loading on TiO_2 microspheres

3.1.1. SEM micrographs

Fig. 1(a) and (b) shows the representative SEM images with different magnifications for the as-prepared TiO_2 microspheres. The microspheres are 5–10 μm in diameter and the surface of the TiO_2 microspheres is very smooth. Compared with unloaded TiO_2 microspheres, the surface

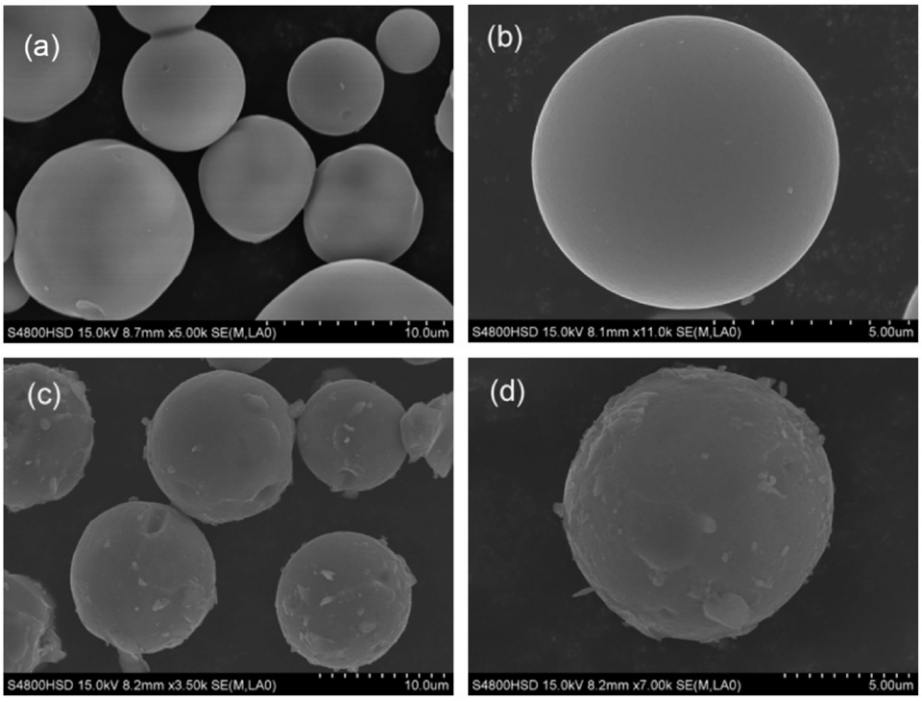

Fig. 1. SEM images of: (a and b) TiO_2 microspheres and (c and d) 1.2 wt% Pt/TiO_2 microspheres.

of Pt loaded TiO_2 microspheres becomes rough as shown in Fig. 1(c) and (d). It indicates that Pt particles were loaded on the surface of TiO_2 microspheres.

3.1.2. Optical-absorption properties

The optical properties of the TiO_2 microspheres and Pt loaded TiO_2 microspheres with different loading amounts of Pt were probed by UV–vis diffuse reflectance spectroscopy (DRS) and converted to the absorption spectra by the Kubelka–Munk method as shown in Fig. 2. The absorption edge of TiO_2 is located at 386.8 nm, corresponding to the band gap energy 3.21 eV. Compared with the bare TiO_2 microspheres, Pt loaded TiO_2 microspheres show an absorption in the visible region. The existence of the wide absorption band may be attributed to the surface plasmon resonance of Pt nanoparticles. The visible absorption band is strongly influenced by particle size, particle shape, particle size distribution etc. With an increase of Pt loading, Pt particle size increases, there is a slight red shift in the SPR due to the electromagnetic retardation in larger particles. Moreover, the surface plasmon absorption peak becomes broader due to a wide particle size distribution. [28,29].

3.1.3. Photocatalytic H_2 production activity of Pt/TiO_2 microspheres

The effect of Pt loading on the photocatalytic H_2 production activity of the TiO_2 microspheres was studied. The hydrogen production rate as a function of Pt loading is shown in Fig. 3. It can be seen that with the increase of Pt loading from 0.2 to 1.2 wt%, hydrogen production rate gradually increases. However, with further increase of Pt loading from 1.2 to 1.6 wt%, hydrogen production rate decreases. The optimal amount of Pt loading is 1.2 wt%. Hydrogen production rate of 1.2 wt% Pt/TiO_2 microspheres is about 125 times as much as the unmodified TiO_2 microspheres. The enhanced photocatalytic activity is

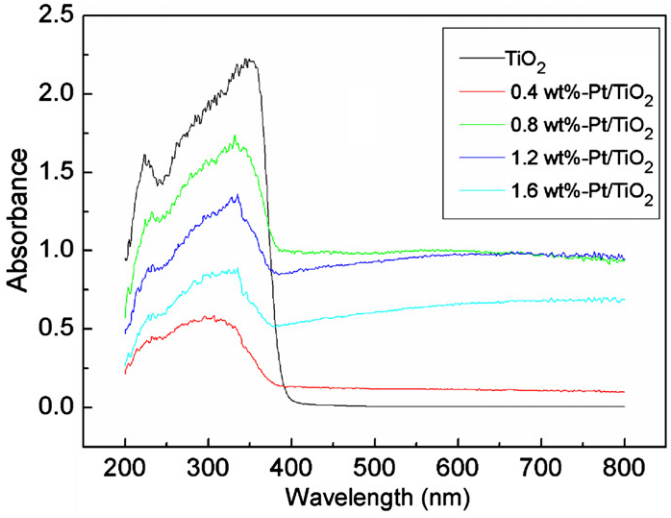

Fig. 2. UV–vis absorption spectra of TiO_2 microspheres and Pt loaded TiO_2 microspheres.

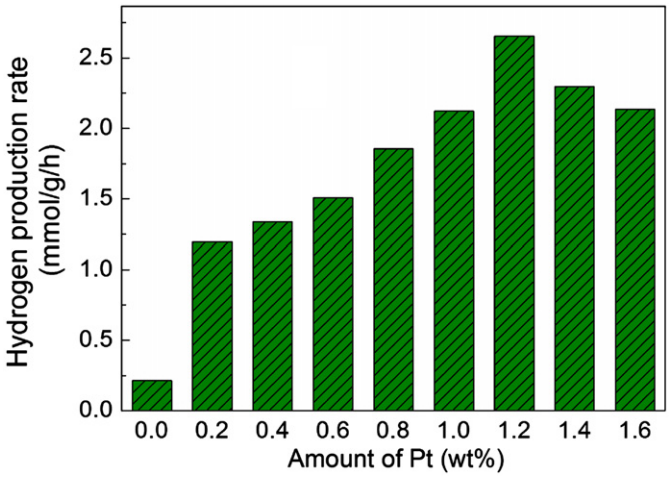

Fig. 3. Hydrogen generation rate of Pt loaded TiO_2 microspheres with different Pt loading amounts.

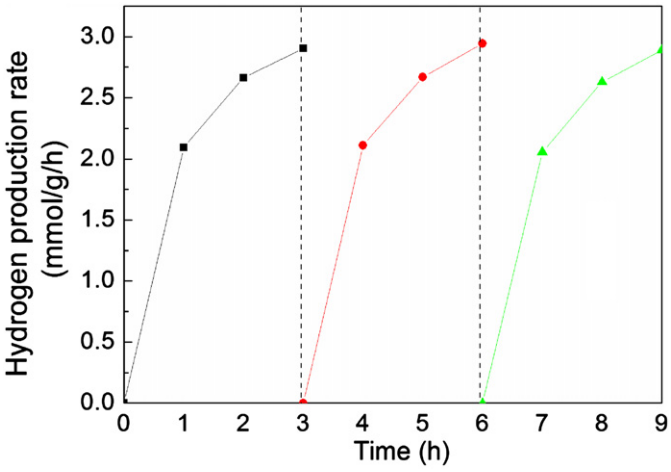

Fig. 4. Time courses of photocatalytic H_2 production over the 1.2 wt% Pt/TiO_2 microspheres.

attributed to the presence of Pt which can act as traps for photogenerated electrons and reduce the recombination of electrons and holes. With the increase of Pt loading, the electron traps increase, resulting in the enhancement of photocatalytic activity of Pt/TiO_2 microspheres. However, when the Pt loading content is more than 1.2 wt%, the active sites on TiO_2 surface are covered by excessive Pt particles [30,31]. Moreover, some of Pt particles may act as the recombination centers for electrons and holes, resulting in the decrease of photocatalytic activity [32].

3.1.4. The stability of Pt/TiO_2 microspheres photocatalyst

Stability is very important to realize the practical applications of photocatalysts for photocatalytic H_2 production from water splitting. To estimate the photocatalytic stability of the Pt/TiO_2 microspheres, the repeatability of the photocatalytic activity of 1.2 wt% Pt/TiO_2 microspheres was also tested for 3 cycles as shown in Fig. 4. It can be seen that hydrogen production rate gradually

increases with the increase of irradiation time in every cycle. Moreover, there is no significant decrease in the photocatalytic activity after 3 cycles. The experimental results demonstrate that the Pt/TiO_2 microspheres exhibit a stable photocatalytic activity.

3.2. Effect of calcination temperature on TiO_2 microspheres

3.2.1. X-ray diffraction

It is well known that calcination is a common treatment that can be used to improve the crystallinity and photocatalytic activity of TiO_2 [33]. Fig. 5 shows XRD patterns of the TiO_2 microspheres calcined at different temperatures varying from 400 to 700 °C under air for 2 h. As shown in Fig. 5, all of the samples have two kinds of crystalline phase: rutile and anatase. It is also found that the crystallinity of the uncalcined TiO_2 microspheres is very low. Moreover, the rutile and anatase characteristic peaks become stronger with the increase of calcination temperature.

3.2.2. Photocatalytic H_2 production activity of the calcined TiO_2 microspheres

In order to study the effect of calcination temperature on the photocatalytic activity of the TiO_2 microspheres, hydrogen production rate of the calcined TiO_2 microspheres was determined as shown in Fig. 6. It can be seen that with the increase of calcination temperature from 400 to 500 °C, hydrogen production rate gradually increases. However, with further increase of calcination temperature from 500 to 700 °C, hydrogen production rate decreases. This can be attributed to the synergetic effect between anatase and rutile phase. The coexistence of anatase and rutile phase in TiO_2 can reduce the recombination of electrons and holes, which results in the enhancement of the photocatalytic activity [34,35]. As can be seen from

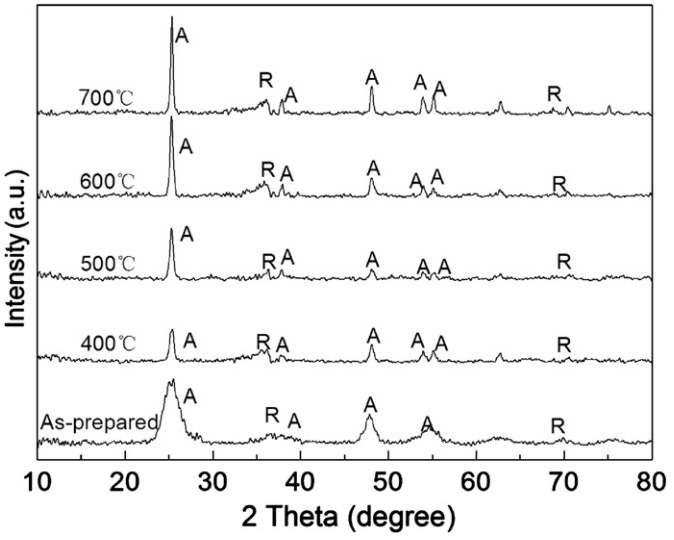

Fig. 5. XRD patterns of TiO_2 microspheres calcined at different temperatures.

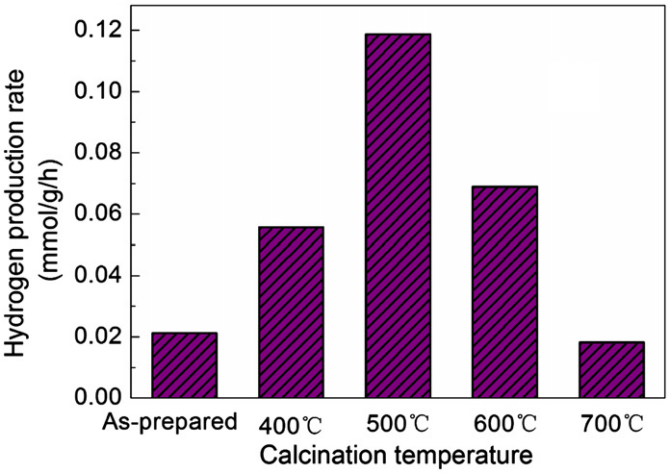

Fig. 6. Hydrogen generation rate of TiO_2 microspheres calcined at different temperatures.

Fig. 6, the TiO_2 microspheres calcined at 500 °C show the highest photocatalytic activity due to the optimal anatase/rutile ratio [36,37]. It can be deduced that the phase mixture of anatase and rutile can affect the photocatalytic activity of TiO_2 microspheres.

4. Conclusions

TiO_2 microspheres were prepared by hydrothermal method, and Pt was loaded on the surface of the as-prepared TiO_2 microspheres by the impregnation-reduction method. The experimental results show that Pt loading can enhance the photocatalytic hydrogen production activity of TiO_2 microspheres. The optimum amount of Pt loading is 1.2 wt%. The improvement of photocatalytic activity of Pt/TiO_2 microspheres is attributed to Pt loading which can reduce the electron–hole recombination rate. Calcination can also affect the photocatalytic activity of the TiO_2 microspheres. TiO_2 microspheres calcined at 500 °C exhibit much higher photocatalytic activity than the samples calcined at other temperatures.

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