Short Communication

Preparation of WO_3-TiO_2 Photo-anode and Its Performance of Photocatalytic Hydrogen Production by Water Splitting

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WO_3-TiO_2 composite photo-anodes were prepared by sol–gel method with butyltitanate and sodium tungstate as main raw materials. WO_3 mass fraction was 0.5%, 1%, 2% and 3%. Structure of WO_3-TiO_2 photo-anode was investigated by XRD and SEM. The effects of WO_3 doping amount and heat treatment temperature on the Structure and photocatalytic properties were discussed. The results indicate that WO_3 doping improve the hydrogen production rate of WO_3-TiO_2 photo-anode. When the doped amount of WO_3 is at 2%, heat treatment temperature is at 400℃, number of coating layer is 3, and WO_3-TiO_2 photo-anode is anatase with high crystallinity, the WO_3-TiO_2 photo-anode has the best photocatalytic properties. The hydrogen production rate is 5.8μmol/h.

1. INTRODUCTION

In recent years, in the field of photo-chemical catalysis using solar power, TiO_2 semiconductor photocatalyst becomes the constant hotspot due to its advantages-- stable in chemical property, soluble, non-toxic and low in cost, etc. The anatase TiO_2 is one kind of n-type semiconductor with band gap at 3.2ev and it is larger than voltage used for water photodecomposition at 1.23ev, which makes it the ideal material of photocatalytic hydrogen production by water splitting. Besides, TiO_2 is also a good electronic conduction type semiconductor, which is widely applied to photo-chemical solar power battery, fuel batter and storage battery[1-2].

Currently most researchers are using TiO_2 nanometer particles suspended in water to conduct the study on hydrogen production by water splitting [3-5], in which anode and cathode stay on the same semiconductor particle and it might easily generate photo induced electron-hole pair

recombination. Although people have conducted a large amount of modification researches on TiO_2 photocatalyst including loaded noble metal[6], structural optimization[7], compound semiconductor[8] and hole trapping agent[9], etc, It is hard to effectively control the recombination of photo induced electron-hole pair. In comparison with suspended particles, nanometer TiO_2 film has highly ordered array structure and remarkable quantum size effect and it is able to fully capture sunlight, generate photo induced electron and hole quantum reaction and produce hydrogen by water splitting, which makes hydrogen production with low cost become possible. Besides, the studies on compound semiconductors including TiO_2/WO_3, TiO_2/CdS, TiO_2/SnO_2 and $TiO_2/CdSe$, etc indicate that compound semiconductors have better catalytic activity in comparison with single semiconductors. Semiconductors with narrow band gap such as WO_3, etc are able to absorb visible light and effectively overcome disadvantages of single-semiconductor photo catalysts in the aspect of low use rate of solar power.

In this paper, WO_3-TiO_2 compound photo-anode is prepared by sol-gel method, which is able to absorb sunlight to the maximum extent, effectively inhibit the recombination of photo induced electron and hole, and study the influence of film preparation techniques and structures on hydrogen production performance.

2. EXPERIMENTAL

2.1 WO₃-TiO₂ Photo-anode Preparation

Firstly, we shall prepare TiO_2 precursory sol. a certain amount of $Ti(OC_4H_9)_4$）with vigorously stir slowly drops into absolute ethyl alcohol and stir it for two hours to obtain the homogeneous and transparent jasmine precursor A. The solution mixed by H_2O, glacial acetic acid and absolute ethyl alcohol drop into the precursory A in vigorously stir. And keep stirring it for 1 hour to obtain jasmine TiO_2 precursory sol. Then prepare tungstic acid sol by using ion exchange method. Pour aqueous solution of sodium tungstate at 0.1mol/L into ion exchange column, control exchange rate at 3-4mL/min and obtain transparent yellow tungstic acid sol. Add tungstic acid sol into TiO_2 sol according to the certain quality ratio, mixing for 1 hour and aging for 24 hours, and obtain WO_3-TiO_2 mixed sol. WO_3 mass fraction is 0.5%, 1%, 2% and 3%.Finally, use dip-coating method to prepare WO_3-TiO_2 compound film with different layers on the surface of titanium substrate. Deal with heat treatment with coated titanium substrate at at 100℃, 200℃, 300℃, 400℃ and 500℃ for 2 hours respectively and obtain WO_3-TiO_2 film with uniform surface and make it into 5mm*5mm working electrode for later use.

2.2 Instrumental

Use X'Pert PRO X-ray diffractometer (Cu Kα radiographic source, voltage at 40KV, current at 40mA and wave length at 0.15405nm) manufactured by PANALYTICAL B.V. from Netherland to test the phase structure of sol powder; use SSX-550 scanning electron microscope by Shimadzu to test the microstructure of film.

2.3 Photo-catalytic Experiment

Photo-catalytic experiment is conducted in the self-made reactor. It uses the prepared WO_3-TiO_2 photo-anode as work electrode and platinum black electrode as counter electrode. The light source is 250W high-pressure mercury lamp. Add 0.5mol/LNaCl solution at 100mL into the reactor, inflow high-purity nitrogen before photocatalytic reaction to remove air in both reactor and air dissolved in water. Sampling every two hours after photocatalytic reaction and using gas chromatograph to analyze gaseous product. Detector is TCD, carrier gas is nitrogen and separation column is 13X molecular sieve column.

3. RESULT AND DISCUSSION

3.1 XRD Analysis

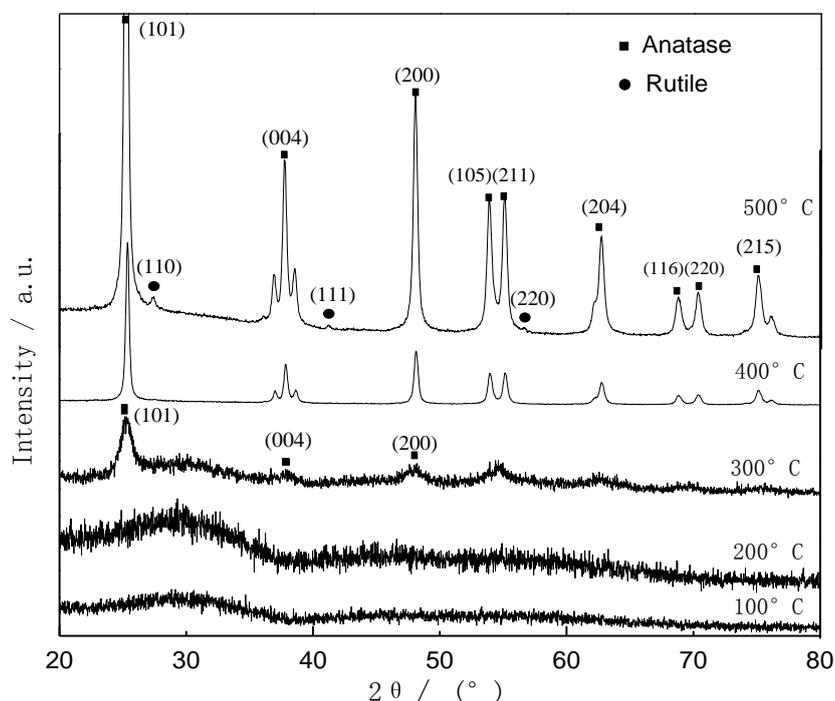Fig 1 is the XRD pattern of WO_3-TiO_2 gel powder with x(W)=2% under different heat treatment temperatures.

Figure 1. XRD spectra of WO_3-TiO_2 powder

We can see from Fig 1 that when the heat treatment temperature is 100℃ and 200℃, there is only one peak package in the diffraction pattern without the appearance of obvious crystallization peak, which indicates that WO_3-TiO_2 photo-anode under these temperatures has amorphous structure.

When the heat treatment temperature is 300℃, the widened dispersion peaks appear near 2θ＝25.4°, 37.9° and 48.0°, which respectively correspond to (101), (004) and (200) crystal plane of anatase phase. In this occasion, the diffraction peak is weak with incomplete crystal growth. When the heat-treatment temperature is 400℃, TiO_2 diffraction peak is gradually sharpened, which indicates the TiO_2 grains gradual grow up and crystallization degree strengthen，the WO_3-TiO_2 photo-anode has complete anatase structure. When the heat-treatment temperature is 500℃, diffraction peak of rutile phase appear near 2θ＝27.4°, 41.2° and 56.6°, which respectively correspond to (110), (111) and (220) crystal plane of rutile phases. TiO_2 convert from antase phase to rutile phase. No WO_3 characteristic diffraction peak appears in all WO_3-TiO_2 samples because the amount of WO_3 is small and it exceeds the detection limit of XRD. However, sputtering TiO_2 film is amorphous when the heat treatment temperature is less than 350℃, the anatase crystal is formed at 450℃[10]. The anatase crystal is formed at 350℃ when TiO_2 film is prepared by sol–gel methods with titanic chloride as main raw materials[11]. Therefore the crystallization temperature of TiO_2 film varies slightly when preparation process and raw materials are different.

3.2 SEM Analysis

Figure 2 is SEM scanning images of WO_3-TiO_2 photo-anode under different heat treatment temperatures and different coating layers. We can see that WO_3-TiO_2 photo-anode has smooth and flat surface without obvious particles when heat treatment temperature is 300℃.
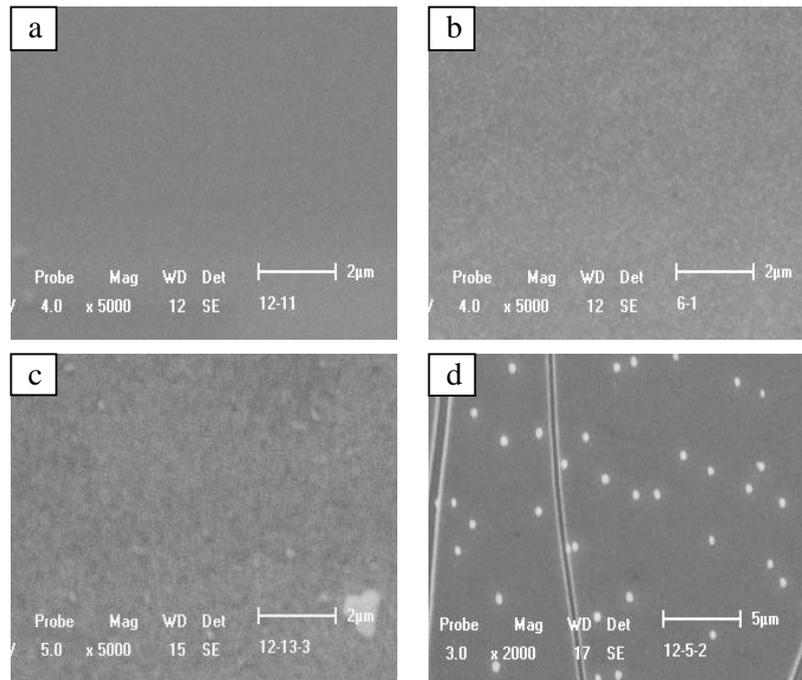

Figure 2. The SEM photographs of WO_3-TiO_2 photo-anode under different temperatures (a)300℃、3 layers；((b)400℃、3 layers；(c)500℃、3 layers (d) 400℃、4 layers

When the temperature is 400℃, TiO_2 starts crystallizing.WO_3-TiO_2 photo-anode is rough and uneven, which is composed of particles and particle aggregates. When the temperature is 500℃, TiO_2

particles grow up. WO$_3$-TiO$_2$ photo-anode is obvious granular film. Therefore with the rise of heat treatment temperature, the grain size of WO$_3$-TiO$_2$ photo-anode is larger and roughness increases.

In document[12], TiO$_2$ particle is smaller with average grain size of about 7nm when heat treatment temperature is at 120℃. When heat treatment temperature is at 350℃, TiO$_2$ particles grow up and the distribution is more uniform and compact. Some interlinked cracks are observed in the films surface. Therefore with the rise of heat treatment temperature, the grain size is larger and roughness increases.

Besides, WO$_3$-TiO$_2$ photo-anode surface is smooth when the number of coating layers is three. When the layer number is 4 or above (Figure 2 (d)), obvious crackles have appeared on the surface of WO$_3$-TiO$_2$ photo-anode because film is too thick. Therefore, the number of coating layers shall not be larger than 3.

3.3 Photocatalytic Performance Analysis

3.3.1 Influence of WO$_3$ doping amount on hydrogen production performance

Figure 3 is hydrogen production rate curves of WO$_3$-TiO$_2$ photo-anode by water splitting when heat treatment temperature is 400℃ and number of coating layers is 3. We can see that WO$_3$ doping largely improves the photocatalytic activity of WO$_3$-TiO$_2$ photo-anode. Hydrogen production rate in 10 hours for TiO$_2$ photo-anode without WO$_3$ doping is 3.2μmol/h and the rate is 3.9-5.8μmol/h with the doping of WO$_3$. When WO$_3$ doping amount is 2%, the hydrogen production rate of WO$_3$-TiO$_2$ photo-anode reaches the maximum amount. When WO$_3$ doping amount is over 2%, the hydrogen production rate starts dropping obvious.
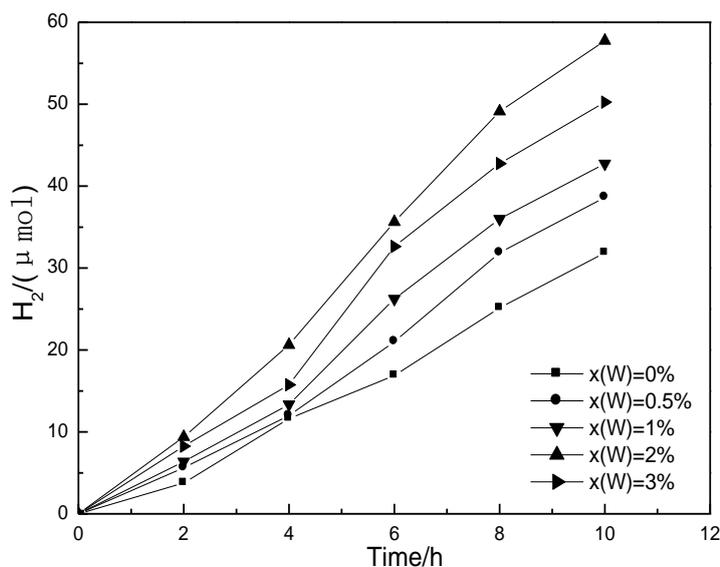

Figure 3. The hydrogen production rate curves of WO$_3$-TiO$_2$ photo-anode under different doping amount（400℃ and 3 layers）

According to the previous reports, similar phenomena also appear in photocatalytic activity research on rare-earth elements doped TiO_2 and ZnO[13-14].Therefore, we believe that the suitable amount of WO_3 doping is able to increase photocatalytic activity of WO_3-TiO_2 photo-anode because the existence of WO_3 reduces the recombination rate between photo induced electro and hole on semiconductor surface. On the other hand, no WO_3 characteristic diffraction peak appears in XRD analysis, which indicates that WO_3 is uniformly dispersed in TiO_2 nanometer particles in the form of small clusters and it might inhibit the Nucleation and growth of TiO_2 in thermal processing, improves TiO_2 particle superficial area and enhance photocatalytic activity of WO_3-TiO_2 photo-anode.

The increase of WO_3 doping amount leads to the increase of TiO_2 deficiency, damages the TiO2 crystal surface integrity, reduces the amount of TiO_2 active phase points and reduces its photocatalitic activity. Therefore, when WO_3 doping amount is 2%, WO_3-TiO_2 photo-anode has the largest hydrogen production rate at 5.8μmol/h.

3.3.2 Influence of heat treatment temperature on hydrogen production performance

Figure 4 is hydrogen production rate curves of WO_3-TiO_2 photo-anode by water splitting under different heat treatment temperature when WO_3 doping amount is 2% and number of coating layers is 3.

We can see that when heat treatment temperature is between 100℃ and 400℃, the higher the thermal processing temperature is, the larger the WO_3-TiO_2 photo-anode hydrogen production rate is. The rise of heat treatment temperature will make TiO_2 particles gradually grow and crystallinity enhance, which reduces recombination center of photo induced electro and hole and enhances photocatalytic activity of WO_3-TiO_2 photo-anode.
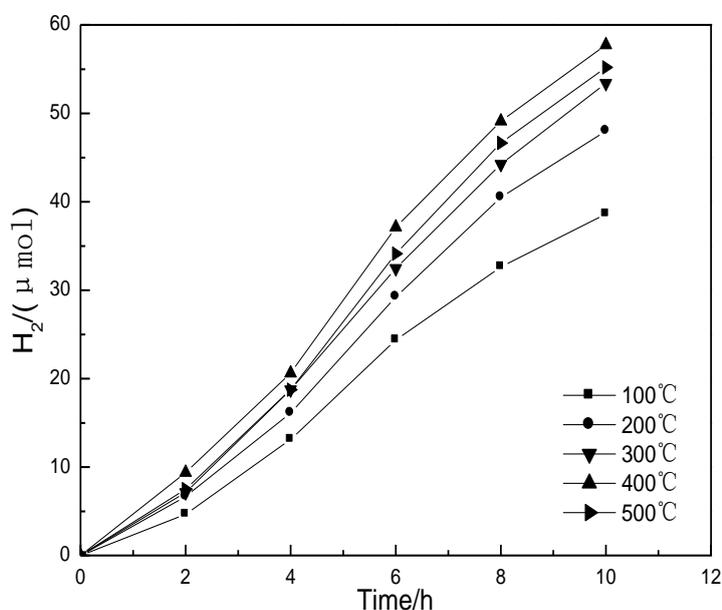

Figure 4. The hydrogen production rate curves of WO_3- TiO_2 photo-anode under different temperature （*x*(*w*)=2% and 3 layers）

When the temeprature reaches 500℃, WO_3-TiO_2 photo-anode hydrogen production rate drops to 5.5μmol/h because changes happen to crystal form of WO_3-TiO_2 photo-anode, namely, they start conversion from antase phase to rutile phase. Generally, the photocatalytic activity of anatase TiO_2 is better than that of rutile TiO_2[15]. This is because the anatase lattice contains more defects and dislocations, which can generate more oxygen vacancies to capture electrons and lead to the separation of electron and hole[16]. In addition, TiO_2 grain size is larger and the surface area decreases when heat treatment is at 500, which is not conducive to the absorption of light and adsorption of reactant molecules[17]. Therefore, when heat treatment temperature is 400℃, WO_3-TiO_2 photo-anode is anatase type with high crystallinity, it has the largest hydrogen production rate.

3.3.3 Influence of layer number on hydrogen production performance

Figure 5 is hydrogen production rate curves of WO_3-TiO_2 photo-anode by water splitting under different number of coating layers when WO_3 doping amount is 2% and heat treatment is 400℃. Numbers of coating layers are 2, 3 and 4.

We can see that when the number of coating layers of WO_3-TiO_2 photo-anode is smaller than 4, the increase of the number of coating layers of WO_3-TiO_2 photo-anode and the increase of film thickness, which will gradually enhance photocatalytic performance of WO_3-TiO_2 photo-anode. When the number is 3, it has the largest hydrogen production rate. Nevertheless, when the number is 4, the hydrogen production rate drops to 3.4μmol/h because severe cracks appear on the surface of WO_3-TiO_2 photo-anode (Figure 2 (d)) and they influence the photocatalytic performance of WO_3-TiO_2 photo-anode.
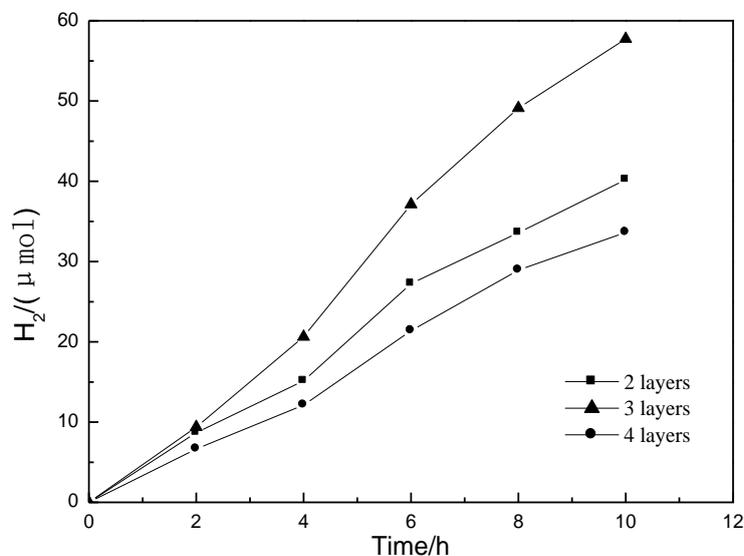

Figure 5. The hydrogen production rate curves of WO_3-TiO_2 photoanode under different layers （$x(w)$=2% and 400℃）

According to the literature, the thickness of TiO_2 film has a significant effect on the photocatalytic activity[18]. H. Dong prepared anatase TiO_2 films by DC magnetron sputtering and studied the photocatalytic activity of films. They found the thickness of film must reach a certain threshold (150-300nm), the film has significant catalytic activity[19]. According to previous reports[20], the best film thickness exists in TiO_2 photo-anode preparation process. The increase of film thickness will lead to the fall of porosity factor. Besides, it will cause agglomeration in thermal processing, reduce specific surface area of film and reduce photocatalytic activity. Therefore, the number of layers of WO_3-TiO_2 photo-anode is suitable for the 3 layer.

4. CONCLUSION

Using sol-gel method to prepare WO_3-TiO_2 compound photo-anode, which goes through heat treatment at 100℃, 200℃, 300℃, 400℃ and 500℃ respectively and the effects of film preparation techniques and structures on performance of photocatalytic hydrogen production by water splitting are studied. The results indicate that:

(1) When heat treatment temperature is 400℃, WO_3-TiO_2 photo-anode forms the complete antase structure; when heat treatment temperature is 500℃, WO_3-TiO_2 photo-anode simultaneously contain antase and rutile phase.

(2) WO_3 doping improves WO_3-TiO_2 photo-anode photocatalytic activity and the hydrogen production rate of water splitting rises from 3.2μmol/h to 3.9-5.8μmol/h.

(3) When the doped amount of WO_3 is at 2%, heat treatment temperature is at 400℃, number of coating layer is 3, and WO_3-TiO_2 photo-anode is anatase structure with high crystallinity, the WO_3-TiO_2 photo-anode has the best photocatalytic properties. The hydrogen production rate is 5.8μmol/h.

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