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Fabrication and photocatalysis of nanostructured TiO_2 for solar hydrogen production

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Abstract

Photoelectrochemical cells (PEC) based on metal-doped (Be and Fe) and Pt-loaded nanostructured-TiO_2 films were fabricated to make working electrodes for solar hydrogen production. Anatase nanocrystalline titania (nano-TiO_2) thin films were deposited on glass slide and Ti metal sheet substrates by a sol–gel dip-coating method. Titanium tetraisopropoxide was used as a precursor. The synthesis process and annealing temperatures play an important role on the crystallite size and the phase transformation of nano-TiO_2. The diameter of the particles in the rage of 5–50 nm was obtained in different methods of making the sol-gels and annealing temperatures. Without an external applied potential, the photocurrent density of Be-doped PEC occurred of 0.32 mA/cm^2 under illumination of 75 mW/cm^2 and the device produced hydrogen by water photoelectrolysis at the rate of 0.1 ml/h cm^2, with a photoconversion efficiencies of 0.52%. The maximum photocurrent density of Fe-doped PEC occurred of 0.80 mA/cm^2 without an external applied potential and under the illumination of 100 mW/cm^2 corresponding with photoconversion efficiency of 0.98%. Impurity phase and undesired phases may be the cause of electron–hole recombination that results in decreasing photocatalytic activity.

Keywords: A. Sol–gel processes; D. Titanium dioxide (TiO_2); E. Electrodes; Solar hydrogen production

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1. Introduction

Solar hydrogen production has become a topic of international interest and challenge since the discovery of photoelectrolysis of water on titanium dioxide (TiO_2) by Fujishima and Honda [1]. TiO_2 has attracted a great deal of study due to its high catalytic activity, stability and environmentally sound property. The excitation of TiO_2 can only be stimulated by high energy ultraviolet (UV) irradiation region with energy at least 3.2 eV corresponding to a wavelength of 387.5 nm. This practically rules out the use of sunlight as energy source for the photoelectrolysis because the solar spectrum with energy at least 3.2 eV contains less than 4% of the entire energy [2]. To extend the light absorption of TiO_2 into the visible light region and prevent the recombination of excited electrons and holes for highly active photocatalysts, different preparation methods and various dopants have been carried out in many efforts. A wide range of metal ions, in particular transition metal ions such as beryllium, cobalt, aluminum, iron, and nickel [3] has been used as dopants for TiO_2 to enhance photocatalytic activity and extending absorption into the range of the visible light spectrum. In addition, noble metal loading such as Pt, Au and Pd has also been made to reduce electron–hole recombination [3]. Many research groups have developed methods to make better TiO_2 photoanodes. Several methods have been introduced to deposit TiO_2 films for photoanodes including anodization [4], chemical vapor deposition, CVD [5] and sol–gel [6]. Among different methods of film deposition, sol–gel dip-coating is the simplest, cheapest and the most convenient. In this work, we present the fabrication of Be and Fe-doped and Pt-loaded TiO_2 as well as photoelectrolysis efficiency of TiO_2 nanocrystalline working electrodes for solar hydrogen generation.

2. Experimental

TiO_2 films were prepared by sol–gel dip-coating on transparent conducting oxide (TCO) glass substrates. The

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chemicals used in this work were research grades. We prepared the sol–gel by using following steps. To dope TiO_2 with Fe, we mixed appropriate portions of titanium tetraisopropoxide (TTIP) and $Fe(NO_3)_3$ solution in mixture of ethanol in the presence of diethanolamine. To prepare Be-doped TiO_2, we mixed the appropriate portions of TTIP and $BeSO_4$ solutions. The mixtures solution was added slowly to 0.1 M NHO_3 drop-wise under vigorous stirring condition with magnetic stirrer in nitrogen atmosphere using a home-made nitrogen dry box. During the addition, a white precipitate was formed. The mixture of the solution was stirred and the temperature was increased and maintained about 80 °C for 10 h for peptization. In this way, white nanoparticles of TiO_2 colloids were obtained as indicated by the appearance of turbidity. To load Pt on the titanium dioxide sol–gel, an appropriate amount of 1.0×10^{-4} M of H_2PtCl_6 in methanol of 0.2 wt% of TiO_2 was incorporated. Finally, Carbowax M-20000, aqueous polyethylene glycol with molecular weight of 20,000 solution, with 40% by weight of TiO_2 was added to get the viscous dispersion of TiO_2 colloidal solution. TiO_2 thin films were deposited on the TCO and Ti sheet substrates by a dip-coating method. The films were dried in air and then calcined in ambient atmosphere at 450 °C for 2 h. The resultant films were examined by X-ray diffraction (XRD), UV–vis spectroscopy, and scanning electron microscopy (SEM) and served as photoanodes working electrodes for PEC cells.

A rectangular PEC cell was made and equipped with a quartz window for light illumination. The quartz window allowed light pass through and was used to minimize the light scattering and absorption and also facilitate the optimum incident light on the surface of the working anodes. The electrolyte was a mixture 1.0 M of KOH and 1.0×10^{-4} M of H_2PtCl_6 in methanol. Pt metal sheet served as the counter electrode. Nafion membrane, proton exchange membrane, was used to separate photoanode from counter electrode and to prevent a reverse reaction on the counter electrode, recombination of protons and oxygen to reform water. The photocurrent was carried out by illuminating light of 100 mW/cm^2 through the quartz window and the photocurrent can be measured by PAR173 PAR 173 Potentiostat/Galvanostat.

3. Results and discussion

The XRD patterns of TiO_2 films compared with Degussa P25 commercial titanium dioxide are shown in Fig. 1. Multiphase analysis using Rietveld refinement of XRD data revealed that our specimen was pure and single phase of anatase TiO_2 when calcined at 450 °C. The XRD patterns of different doping levels were not different when calcinations temperature was the same. When calcination temperature increased to 500 °C the films contained anatase and rutile phases with the ratio of 0.90 and 0.10, respectively. The crystallite sizes of the film calculated from XRD peaks according to the Scherrer's equation were found to be 6 nm when calcined at 450 °C. The crystallite sizes increased when the calcination temperature increased as shown by the narrow shapes of diffraction lines. The size of particles was confirmed by SEM images (not shown). The SEM image reveals a porous structure of the film. These results indicate that the sol–gel processing has an effect on the structure and stability of the films. The porosity may occur when aqueous polyethylene glycol which was used as a binder leaves the surface of the substrate at high calcination temperature.

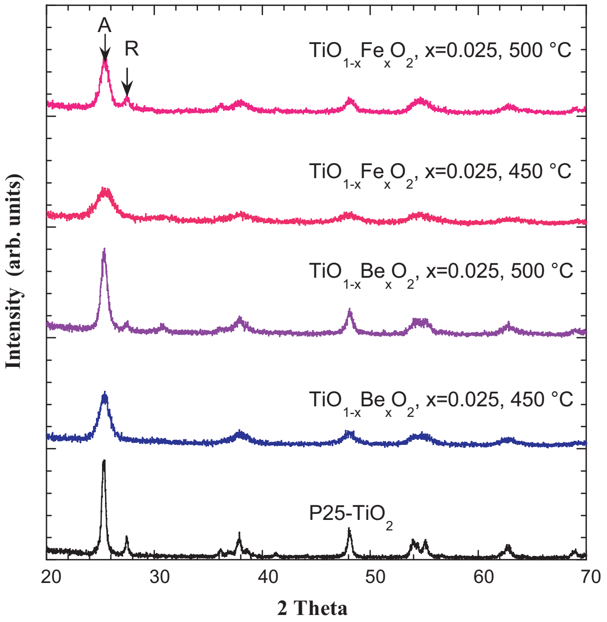

Fig. 1. XRD patterns of TiO_2 films of the specimen calcined at 450 and 500 °C. The symbols A and R represent anatase and rutile phases, respectively.

The photocurrent density–voltage curves (*J–V*) for Be and Fe-doped TiO_2 are shown in Figs. 2 and 3, respectively. The photocurrents increase with increment of Be and Fe dopants and reach the highest when the amounts of the dopants $x = 0.02$, and 0.025 for Be and Fe-doped TiO_2, respectively, yet photocurrents decrease when the amounts of the dopants are larger than 0.02 and 0.025 for Be and Fe dopants, respectively. The *J–V* curves also indicate that the films calcined at 450 °C

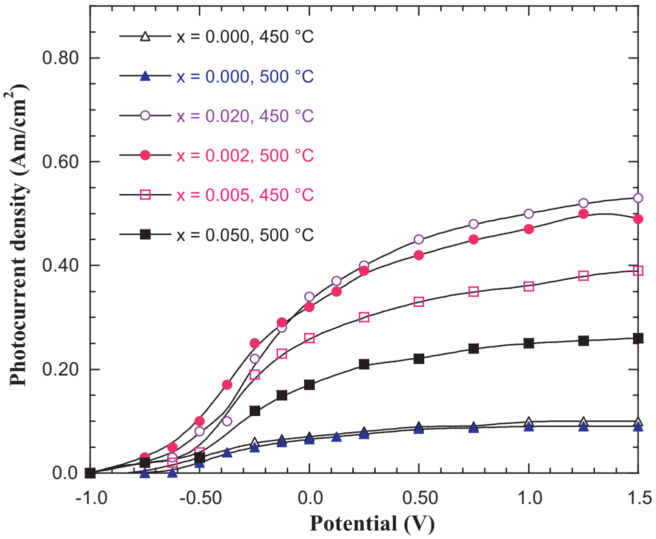

Fig. 2. Photocurrent density–applied potential characteristic curves of PEC for $Ti_{1-x}Be_xO_2$ working electrodes, where $x = 0.00$, 0.02, and 0.050 at 450 °C and 500 °C.

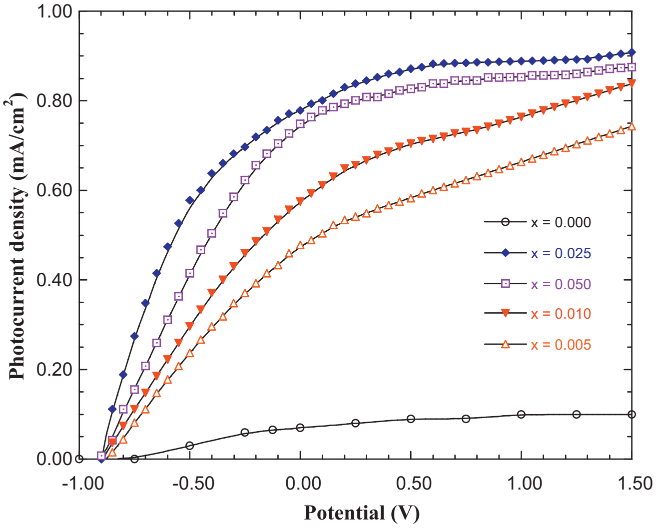

Fig. 3. Photocurrent density–applied potential characteristic curves of PEC for $Ti_{1-x}Fe_xO_2$ working electrodes, where $x = 0.000, 0.005, 0.010, 0.025$, and 0.050 at 450 °C.

yield higher efficiency than the films calcined at 500 °C. The films calcined at 500 °C make low photocurrent density because they contain impurities such as undesired rutile phased and their crystallite sizes are also large. These results imply that the anatase TiO_2 films are more favorable for photoelectrolysis. The gaseous bubbles of oxygen and hydrogen evolving from the photoanode and counter electrode, respectively, were observed. We calculated the experimental efficiency of hydrogen production based on the hydrogen volume with 285.6 kJ/mol and intensity of the incident light. The hydrogen gas obtained from the counter electrode was examined by gas chromatography (GC) to confirm the water splitting reaction. The theoretical photoconversion efficiency of the PEC can be obtained by the standard equation [2,7]:

$$\eta\,(\%) = \frac{(1.23 - |V_{\mathrm{App}}|)J}{I_0} \times 100 \tag{1}$$

where 1.23 V is threshold energy or threshold potential, V_{App} is externally applied potential, J is photocurrent density and I_0 is the intensity of the incident light. The maximum efficiency of Be-doped TiO_2 photoanode PEC was 0.52% under illumination of 75 mW/cm^2. The maximum efficiency of PEC with $Ti_{1-x}Fe_xO_2$ working electrode at $x = 0.025$ was 0.98% under illumination of 100 mW/cm^2. When dopant level increases the optical band gap decreases (the data is not shown), and the films can absorb more energy from the incident light. However, when amount of the dopant is large ($x = 0.050\%$) and the calcinations temperature is high (500 °C) the films may contain some impurities or undesired phases leading to decreasing photoactivity [2,8].

4. Conclusion

We have synthesized Pt-loaded, Be-doped and Fe-doped TiO_2 films on TCO glass substrates by sol–gel dip-coating method. The sol–gel preparation processing has an effect greatly on the film structure and stability. The films were purely anatase TiO_2 nanostructures. The films calcined at 450 °C were suitable to make photoanodes of PEC cells for solar hydrogen production. The efficiency of the working electrodes increases as the amounts of Be and Fe dopants increase and the amount of Be and Fe dopants are optimal at 2.0% and 2.5%, respectively. Further increment of the dopants yields low efficiency due to the impurities of the films that cause a high rate of electron–hole recombination. The maximum efficiency of the cells of 0.98% was achieved when TiO_2 was doped with Fe of 2.5%.

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