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Photoelectrochemical characteristics of AB₅-type hydrogen storage alloy modified with SrTiO₃ photocatalyst^①

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Abstract: Perovskite-type SrTiO₃ powders were prepared by using strontium acetate, tetrabutyl titanate and sodium hydroxide via direct hydrolysis-precipitation process. AB₅-type hydrogen storage alloy (HSA) electrodes modified with SrTiO₃ powders were prepared and the photoelectrochemical characteristics of the as-prepared electrodes were investigated. The results of cyclic voltammogram show that the current of reduction peak increases remarkably under the light irradiation. The obvious photochargeable properties are obtained for the hydrogen storage alloys modified with Perovskite-type SrTiO₃ powders. During photocharging process, the potential of the electrode shifts quickly to negative direction and a potential plateau occurs. HSA electrode modified with SrTiO₃ powders prepared by direct hydrolysis-precipitation process gives the higher potential of about -0.90 V (vs Hg/HgO) under the light irradiation. SEM observation discloses that a large amount of microcracks occur on the surface of the electrode after photocharging process, which is caused by the formation of hydride in the bulk of electrode.

Key words: AB₅-type hydrogen storage alloys; SrTiO₃ photocatalysts; photoelectrochemical characteristics

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1 INTRODUCTION

Solar energy is a kind of clean and unexhaustable energy, the utilization and development of solar energy is becoming very imperative due to the serious energy problems today. Since Fujishima and Honda^[1] discovered the effect of photosensitization of TiO₂ electrode on the electrolysis of water into H₂ and O₂, the photocatalysis by TiO₂ and other semiconductors has received much attention and has been widely investigated. Many progresses have been made in the visible-light photocatalysis^[2-5] and a series of novel photocatalysts including layered titanate^[5-7], layered niobates^[8,9] and layered perovskite materials and their pillared-products^[10-13] were discovered.

Among these photocatalysts, perovskite-type SrTiO₃ oxide is one of the most widely used dielectric materials which have widespread applications in electronic devices^[14]. On the other hand, SrTiO₃ oxide is an efficient photocatalyst. Recently, Akuto and Sakurai^[15] performed an interesting photorechargeable metal hydride/air battery. In

this battery, SrTiO₃ powder was modified on hydrogen storage alloys to form a SrTiO₃-HSA photorechargeable electrode, and in combination with air electrode, a SrTiO₃-LaNi_{5-x}Al_xH_n|KOH|O₂ cell system was obtained. The experimental results showed that the above cell system can be recharged by light irradiation. This means that the light energy can be transferred into chemical energy and stored in the cells electrochemically.

In this paper, we prepared the perovskite-type SrTiO₃ photocatalysts by direct hydrolysis-precipitation process, and investigated the photoelectrochemical behaviors of the AB₅-type hydrogen storage alloy electrodes modified with SrTiO₃ powder.

2 EXPERIMENTAL

Perovskite-type SrTiO₃ oxide was prepared by a direct hydrolysis-precipitation process, in which the final heat treatment temperature was 700 °C. All chemicals are of commercially analytical purity. The procedures of direct hydrolysis-precipitation process are shown in Fig. 1.

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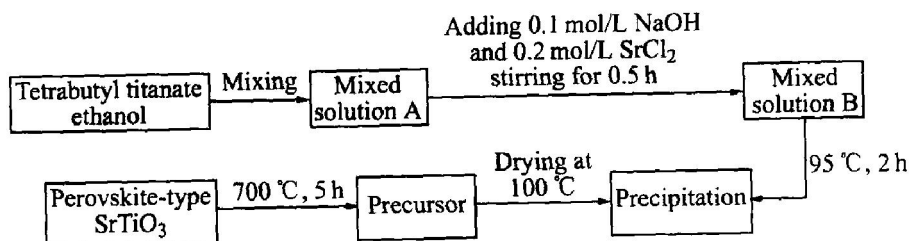


Fig. 1 Flow chart of preparing SrTiO_3 by direct hydrolysis-precipitation method

A commercial AB_5 -type hydrogen storage alloy (HSA) with the standard composition of $\text{MmMn}_{0.4}\text{Co}_{0.7}\text{Al}_{0.3}\text{Ni}_{3.6}$ was used to prepare hydrogen storage alloy electrode by a dry powder compression technique without additives. The as-prepared SrTiO_3 oxide was dissolved in 10% PTFE suspension and then the HSA electrode was put into the suspension for several seconds. Then the electrode was dried at about 60°C for about 3 min. The above procedures were repeated for 5 times until a thin layer of SrTiO_3 oxide was formed on the surface of HSA electrode. Finally the electrode was cool pressed at 10 MPa for 1 min. The size of the electrode was $1.0\text{ cm} \times 1.0\text{ cm} \times 0.03\text{ cm}$.

The photoelectrochemical behaviors were measured in a conventional three-electrode electrolysis cells, in which NiOOH was used as the counter electrode, Hg/HgO as the reference electrode, and the electrolyte was 6 mol/L KOH solution. All electrochemical measurements were performed by using a EG&G 273A potentiostat/galvanostat. A 500W xenon lamp was used as the light source when measuring the photocharge characteristics. The light intensity can be adjusted by changing the working power of the xenon lamp, and the corresponding light intensity was about $100\text{ mW}/\text{cm}^2$. To eliminate the influence of corrosion of HSA electrode in KOH solution upon the potential, the as-prepared electrodes were immersed into 6 mol/L KOH for 5 h before photocharging process. The discharge current was about 6 mA/g, and the cut-off potential was set at -0.5 V (vs Hg/HgO). All experiments were performed at 25°C .

3 RESULTS AND DISCUSSION

3.1 Crystal structure and morphology

Fig. 2 shows the XRD pattern of the as-prepared perovskite-type SrTiO_3 oxide. As shown in Fig. 2, the sample is composed of a single phase without other impurities. The lattice parameters calculated according to the diffraction data is $a = 0.3916\text{ nm}$, which is in accordance with the standard value, indicating that the heat treatment condition is suitable.

Fig. 3 shows the SEM image of as-prepared

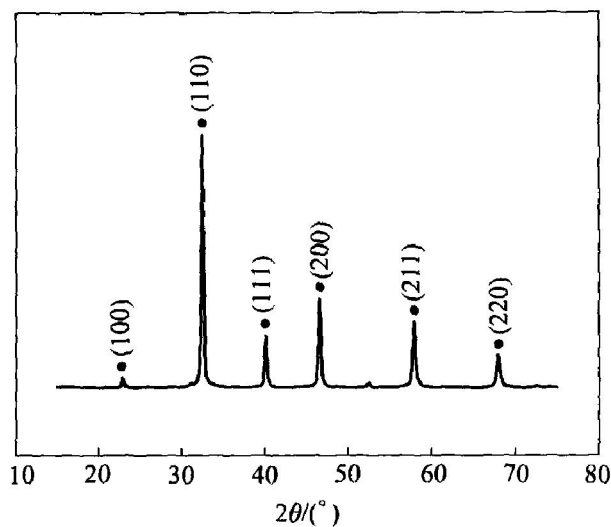


Fig. 2 XRD pattern of as-prepared perovskite-type SrTiO_3 oxide

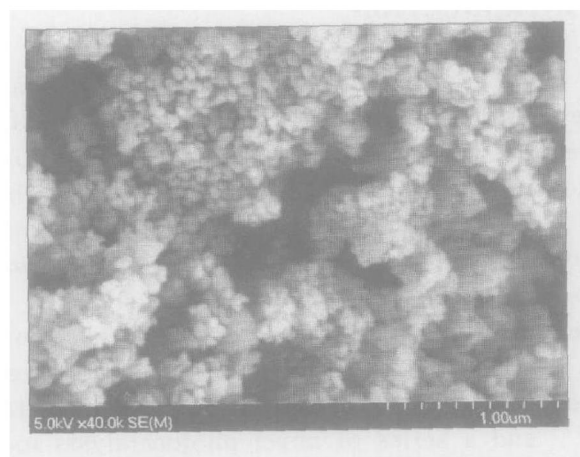


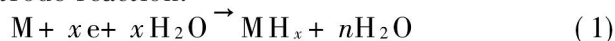
Fig. 3 SEM image of as-prepared SrTiO_3 oxide

SrTiO_3 oxide. The mean size of SrTiO_3 oxide is 100–200 nm. However, the aggregation of particles is also observed.

3.2 Photoelectrochemical properties

Fig. 4 shows the cyclic voltammogram curves of $\text{SrTiO}_3/\text{HSA}$ electrode. The scanning rate was $5\text{ mV}/\text{s}$ and the HSA electrode was not activated by electrochemical charging/discharging cycle before light irradiation. As shown in Fig. 4, the cyclic voltammogram behavior exhibits great difference under the light irradiation. When the xenon

light irradiates on the surface of electrode, the cathodic reduction peak current increases fast as the potential shifts to negative direction, indicating that the light irradiation can remarkably improve the reduction current of water. Considering the electrode reaction:



the additional part of the reduction current may be ascribed to the photogenerated electrons which react with water to produce hydrogen atom.

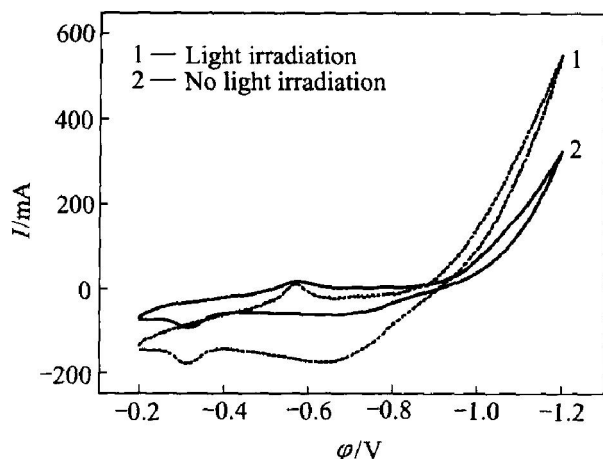


Fig. 4 Cyclic voltammogram curves of SrTiO₃/HSA electrode

Fig. 5 shows the potential change as a function of the photocharging time for SrTiO₃/HSA electrode. For comparison, the result of the HSA electrode modified with SrTiO₃ prepared by sol-gel method was also presented. The results indicate that the potential of SrTiO₃/HSA electrode all rises quickly with the increase of photocharging time, and then tends to a constant value. The potential plateaus of about -0.9 V and -0.8 V (vs Hg/HgO) appear for the two electrodes separately. The initial potential is about -0.52 V and -0.45 V for the two electrodes respectively. At the first stage of light irradiation, the potential of SrTiO₃/HSA electrode modified with SrTiO₃ prepared by sol-gel method rises more quickly, however, the potential plateau of SrTiO₃/HSA electrode modified with SrTiO₃ prepared by direct hydrolysis-precipitation method is higher.

The discharge curves for the two SrTiO₃/HSA electrodes are shown in Fig. 6. The discharge capacity of the SrTiO₃/HSA electrode modified with SrTiO₃ prepared by hydrolysis-precipitation method is about 54 min, but that of the electrode modified with SrTiO₃ prepared by sol-gel method is only about 10 min. This result indicates that the higher the photocharging potential plateau, the larger the discharge capacity. Compared with the results of Akuto et al.^[10], the electrodes prepared by hydrolysis-precipitation method can obtain higher charging potential. The effect of the photocatalyst

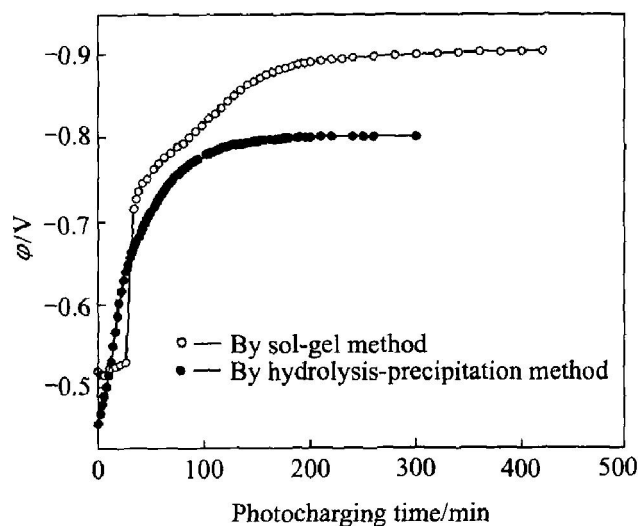


Fig. 5 Change of electrode potential with photocharging time for SrTiO₃/HSA electrode

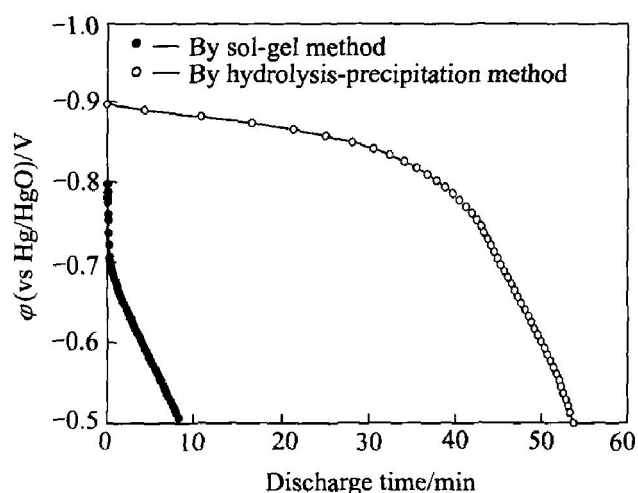


Fig. 6 Discharge curves of SrTiO₃/HSA electrodes (Discharge current: 6 mA/g)

on the photoelectrochemical properties is very remarkable and worth further investigation.

3.3 Surface observation

Fig. 7 depicts the morphologies of SrTiO₃/HSA electrodes modified with SrTiO₃ prepared by hydrolysis-precipitation method after photocharging process. Fig. 7(a) shows the morphology of the HSA electrodes prepared by dry powder cool compression technique without additives, in which the traces observed on the surface of HSA electrode represent the rolling direction. After 400 min photocharging and electrochemical discharge process, a large amount of crevice and microcracks with the mean size of 200 nm occur on the surface of HSA electrode. Especially, these cracks usually distribute near the SrTiO₃ powder.

Considering the photocharging process, the following reactions can take place on the surface of

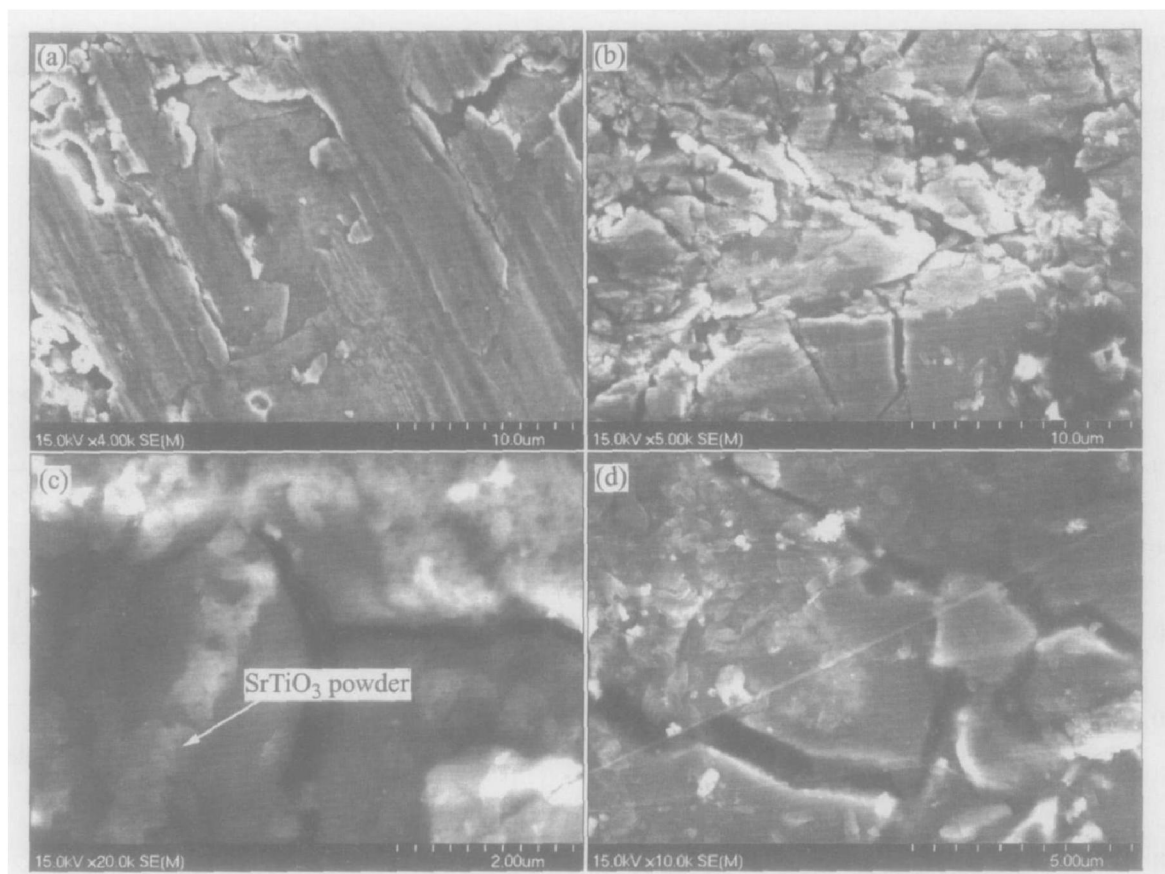
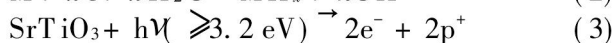
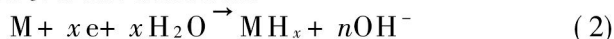


Fig. 7 Morphologies of SrTiO₃/HSA electrodes after photocharging
 (a) —HSA electrode prepared by dry powder cool compression technique without additives;
 (b)–(d) —After photocharging for 400 min

SrTiO₃/HSA electrode:



During the photocharging process, the photo-generated electrons excited into the conduction band transfer to the hydrogen storage alloy. As a result, the electrons react with water to produce hydrogen atom, and the produced H atom can be absorbed by the electrode to form hydride. Thus, a large amount of microcracks occur on the surface of the electrode, which are caused by the formation of hydride in the bulk of electrode.

4 CONCLUSIONS

Perovskite-type SrTiO₃ powders were prepared by using strontium acetate, tetrabutyl titanate and sodium hydroxide via direct hydrolysis-precipitation process. AB₅-type hydrogen storage alloy (HSA) electrodes modified with SrTiO₃ powders were prepared and the photoelectrochemical characteristics of the as-prepared electrodes were investigated.

1) The current of reduction peak increases remarkably under the light irradiation. The obvious photochargeable properties are obtained for the hydrogen storage alloy modified with Perovskite-type SrTiO₃ powders.

2) During photocharging process, the potential of the electrode quickly shifts to negative direction and a potential plateau appears. HSA electrode modified with SrTiO₃ powders prepared by direct hydrolysis-precipitation process causes a higher potential of about -0.90 V (vs Hg/HgO) by the light irradiation.

3) SEM observation discloses that a large amount of microcracks occur on the surface of the electrode after photocharging process, which are caused by the formation of hydride in the bulk of electrode.

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