

SiO₂ Carrier Dispersed Perovskite for Solar Thermal Decomposition of H₂O

Aiping Deng

College of Materials and Chemical Engineering, Pingxiang University, Pingxiang 337055, China
 dap258@163.com

In this paper, the photocatalytic decomposition of composite catalysts for hydrogen production was investigated from two aspects of the preparation of the catalyst and the photocatalytic reaction system. The catalyst preparation conditions which affect the photocatalytic hydrogen production activity was considered, which include the doping amount of SiO₂, effect of perovskite complex, catalyst preparation temperature and preparation time. In the photocatalytic reaction system on the hydrogen production activity, the effects of catalyst dosage and sacrificial agent concentration on the hydrogen production rate were investigated, respectively. The methods and materials provided herein can utilize high-temperature heat generated by solar focusing as a source of energy and H₂O as a starting material, which can stably and rapidly produce H₂ at a lower reduction temperature compared to the reported results.

1. Introduction

Photoelectrochemical hydrogen production is the use of special chemical batteries, and this battery consists of a photoanode and cathode (Binder et al., 2010). The photoanode is typically a semiconductor material that is excited by light to generate electron-hole pairs, and the photoanode and cathode form a photo electrochemical cell (Jaojaruek et al., 2009). Under the action of the electrolyte, the light generated by the light-emitting anode in the semiconductor conduction band flows to the cathode through the external loop, and the ammonia ion in the water receives the electrons from the cathode to generate ammonia gas. Perovskite solar cells are generally composed of a transparent conductive substrate, a carrier transport layer, a perovskite layer, and a metal electrode. The perovskite layer absorbs photons to generate electron-hole pairs (Michel et al., 2016). Since the exciton binding energy of the perovskite material is very small, the exciton binding energy of CH₃NH₃PbI₃ is only 19 ± 3 meV and can be separated into free carriers at room temperature. And then the generated free carriers are transmitted by the transmission layer material, and are collected again by the electrode to form a current to the external circuit to do work to complete the entire photoelectric conversion process (Otto et al., 2014). The working process of perovskite battery can be divided into the following steps: (i) exciton generation and separation; (ii) free carrier transport; (charge) carrier collection and current generation; which is also accompanied by (iv) carrier recombination process (Qian and Huang, 2011).

The mechanism of semiconductor photocatalytic decomposition of water to hydrogen can be explained by the energy band theory of semiconductors, which is composed of a low-energy valence band filled by electrons and an empty high band gap (Conduction band, CB) consisting of a band gap. There is a difference in energy between the top of the valence band and the bottom of the conduction band. The difference is called the band gap semiconductor, also known as band gap can (Razmara et al., 2016). When the light source impinges on the surface of perovskite, in which the amount of photon energy is greater than or equal to the perovskite bandgap energy, the electrons in the perovskite valence band undergo photon excitation transition to the conduction band level. And thus in the perovskite, the valence band and the conduction band are formed with photogenerated holes with positive charges (h⁺) and photoelectrons with negative charges (e⁻) respectively: TiO₂ + hv → h⁺ + e⁻. Photo-generated holes have oxidizing property and photo-generated electrons have reduction property (Shin et al., 2015). From the schematic diagram of photocatalytic reaction mechanism, we can see the specific reaction process of photogenerated electron and hole in the catalyst system (Zalba et al., 2003).

2. Experiments

2.1 Reagents and instruments

Table 1: Experimental reagents

Reagent name	Molecular	Specification	Manufacturer
Four butyl titanate	Ti(OC ₄ H ₉) ₄	Analysis	Tianjin light complex Fine Chemical Research Institute
Thiourea	H ₂ NCSNH ₂	Analysis	Tianjin Xin Bote Chemical Co. Ltd.
Sulphuric acid	H ₂ SO ₄	Analysis	Tianjin Yaohua chemical reagents Co., Ltd.
Anhydrous ethanol	CH ₃ CH ₂ OH	Analysis	Tianjin Hengxing Chemical Reagent Co. Ltd.
Hydrochloric acid	HCl	Analysis	Tianjin Yaohua chemical reagents Co., Ltd.
Sodium nitrate	NaNO ₃	Analysis	Tianjin Hengxing Chemical Reagent Co. Ltd.
Potassium Permanganate	KMnO ₄	Analysis	Tianjin kwangfu Chemical Reagent Co. Ltd.
Hydrogen peroxide	H ₂ O ₂	Analysis	Tianjin Guangfu Yu Reagent Co., Ltd.

Table 2: Experimental instruments

Instrument name	Model	Manufacturer
Gas chromatograph	GC-112A	Shanghai Precision Scientific Instruments Co., Ltd.
Mercury lamp	500W	Chengdu Nanpu optoelectronic Co., Ltd.
Photocatalytic reactor	-	Harbin Asia Pacific Glass Instrument Plant
High pressure reactor	HZ5-100L	Shanghai Leici Instrument Factory
Electronic balance	ALC-210.4	Beijing sartorius Instrument System Co. Ltd.
Electrothermal constant temperature dryness box	GZX-9070MBE	Shanghai Bo Xun Industrial Co., Ltd. medical equipment factory
Bi-directional magnetic heating agitator	78-2	Jiangsu Jintan Rong Hua Instrument Manufacturing Co., Ltd.
Ultrasonic cleaner	KQ-250B	Kunshan Ultrasonic Instrument Co., Ltd.
Electrothermal constant temperature water bath	HHS	Shanghai Bo Xun Industrial Co., Ltd. medical equipment factory

2.2 Experimental methods

SiO₂ doped perovskite composite catalysts are prepared by hydrothermal synthesis. Specific steps are as follows: Weigh a certain amount of the prepared perovskite and add it to 60 mL of absolute ethanol, sonicated 1 h, and give a brown black suspension. 12 mL of tetrabutyl titanate was slowly added dropwise to the suspension. Stir for 1 h to obtain a mixture A, and a certain amount of thiourea was added to the mixture A. Stirring was continued for 1 h to obtain a mixture B, and 1.6 mL of HCl was added dropwise to the mixture B for 30 min. And continue stirring for 30 min to obtain a mixed solution C, and the mixed solution C is transferred to a 100 mL hydrothermal reactor, sealed, and incubated at 180 °C. For a certain period of time, cooled at room temperature, separated by suction filtration, and washed with water. The filter cake was washed three times, and the filter cake was dried in an oven at 80 °C and ground. The resulting product was a SiO₂-doped perovskite composite catalyst. According to the above method, pure perovskite with different SiO₂ doping amount and composite catalysts prepared by different hydrothermal temperatures and hydrothermal time were prepared in this paper. Photocatalytic decomposition of water experiments were proceeded in a closed quartz reactor, and the reactor specific structure is shown in Figure 1. The light source is 500 W high-pressure mercury lamp (use sodium nitrite solution to filter out the wavelength below 400nm UV Light in interlayer). The hydrogen system consists of photocatalyst, sacrificial agent and water. A certain amount of prepared photocatalyst was added to a mixture of water and sacrificial agent methanol (total volume of 300 mL). The reaction solution was sonicated for 15 min, and then all moved into the quartz reactor. In the photocatalytic decomposition process, nitrogen was introduced into the reactor for about 30 min prior to the start of the water hydrogen reaction to remove dissolved oxygen in the water and other possible impurity gases. The amount of hydrogen produced by the catalyst was determined by gas chromatography. The chromatographic conditions were as follows: the carrier gas was N₂, the packing of the separation column

was 13X molecular sieve, and the detector was a TCD thermal conductivity detector with a column temperature of 80 °C and a detection chamber temperature of 80 °C.

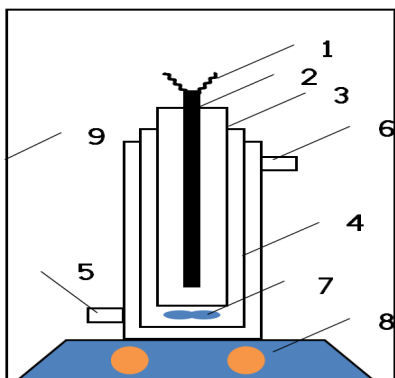


Figure 1: The system of hydrogen production for photocatalytic splitting water

1-electrode line, 2-light source, 3-quartz tube, 4-condensate water jacket, 5-condensate outlet, 6-condensate inlet, 7-magneton, 8-magnetic stirrer, 9-radiation shield

3. Test results and analysis

3.1 X-ray diffraction analysis

Figure 2 shows the XRD patterns of SiO₂-dispersed perovskite at different hydrothermal synthesis temperatures. The doping of SiO₂ and the composite with perovskite did not change the crystal form of TiO₂, and still belong to anatase TiO₂. When hydrothermal temperature is 150 °C and 180 °C, with the increase of hydrothermal temperature, the diffraction peak of TiO₂ intensified and the absorption peak became sharper, which indicates that the orderliness of the crystals inside the sample was improved and the degree of crystallinity was getting better.

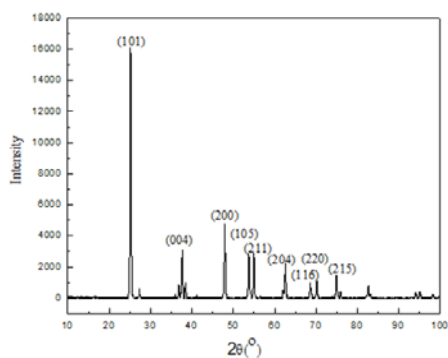


Figure 2: XRD pattern of SiO₂ dispersed H₄GaW₁₂O₄₀ / TiO₂ substrate

However, when the hydrothermal temperature reaches 210 °C, the crystal phase structure of SiO₂ in the composite catalyst is dominated by rutile phase, and the characteristic diffraction peak of rutile phase appears, which shows that with the further increase of catalyst preparation temperature, high temperature and high-pressure environment has reached the phase transition conditions of perovskite. In the (e) curve, the $2\theta = 24.0^\circ$, absorption peak corresponds to the (002) characteristic diffraction peak of perovskite, whereas in (c) and (d), since the content of SiO₂ in the composite catalyst is small and the perovskite is at 24. The intensity of the diffraction peak is relatively weaker, resulting in the (002) diffraction peak peculiar to perovskite being covered by the diffraction peak of TiO₂ at 25.4° . Based on the Scherrer formula, the average particle size of SiO₂ in the perovskite composite catalyst is about 14 nm.

3.2 Catalyst preparation process of photolysis of hydrogen production rate

According to the above, thiourea was the sulfur source, ethanol as solvent, and tetra butyl titanite as titanium source. Use water-solvothermal method to prepare different SiO₂ doping amount of titanium dioxide photocatalyst. According to the same hydrogen system conditions, investigate the effect of different amount of SiO₂ doping to hydrogen production rate of photolysis water, and the results shown in Figure3:

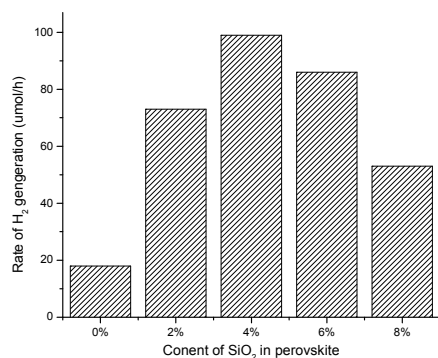


Figure 3: The effect of SiO₂ doping on the perovskite photocatalytic decomposition of hydrogen production rate

Figure 3 shows the effect of SiO₂ doping on the photocatalytic decomposition rate of perovskite photocatalytic hydrogenation. The results show that the photocatalytic activity of the prepared samples increases first and then decreases with the increase of SiO₂ doping ratio. The best ratio of SiO₂ doping is obtained. When the doping amount of SiO₂ is 4.0 at%, the maximum rate of hydrogen production by photolysis water is 101.3 $\mu\text{mol} \cdot \text{h}^{-1}$. This is because a proper amount of SiO₂ doping into the crystal lattice of titanium dioxide forms a new impurity level between the conduction band of the titania and the valence band, which narrows the band gap of the TiO₂ so as to enhance the absorption of the photocatalyst in the visible light region degree of utilization. However, when the amount of SiO₂ doping is too large, it is not obvious to increase the absorption of the photocatalyst in the visible light region. On the contrary, excessive amount of SiO₂ becomes a new recombination center of electrons and holes, which reduces the lifetime of carriers and decreases photocatalytic activity.

With the prolongation of the preparation time, the rate of photocatalytic hydrolysis of the composite catalyst increased first and then decreased. It can be seen that when the preparation time is 8 h, the photocatalytic activity is the highest and the hydrogen production rate is 145.6 mol/h. The reason is probably that in the initial stage of water solvent thermal reaction, the nucleation stage is slowly formed. With the prolongation of reaction time, the growth of crystal nucleus can be promoted, and the nucleation is well developed. Good nucleation can improve the photocatalytic activity of the catalyst. As a further extension of the preparation time, the reactant in the reaction system of basic consumption is the main material transport process between nuclei. The grains size increases gradually, and with the process of grain size increases, the grain defect concentration decreased, which results the decrease of catalytic activity of the particle itself, thereby reducing the hydrogen production rate. In the hydrothermal synthesis process of composite catalyst, based on the doping amount of 4 at% of SiO₂, different perovskite composite amount of SiO₂-TiO₂ photocatalytic decomposition of hydrogen production rate was investigated, the results are shown in figure 4:

From the figure 4, it can be seen that the proper amount of perovskite can increase the photocatalytic decomposition rate of aquatic hydrogen. With the perovskite composite catalyst content increasing, the photocatalytic activity will first show a gradual increase in the trend, which may probably because: 1) perovskite has good conductivity, which can rapidly lead by the excited electron to reduce the recombination probability of photogenerated electrons and holes, so that photogenerated electrons are widely used for hydrogen production and improve the photocatalytic activity; 2) the perovskite has good absorbance, and the sp² hybridized carbon atoms containing in graphene bonded to form a large π bond, can effectively respond to visible light; 3) the specific surface area of perovskite is large, and when it is compounded with SiO₂-TiO₂, the specific surface area of the catalyst is increased, and the surface active sites of the catalyst are increased, thereby increasing the hydrogen production rate of the catalyst. According to the principle of photocatalytic decomposition of water to hydrogen, it can be seen that when the light source excites the catalyst, photogenerated electrons and holes are rapidly recombined, thus a large amount of photogenerated electrons are consumed, resulting in the decrease of the photoelectron utilization rate. In order to improve the utilization

of photo-generated electrons, a suitable electron donor or sacrificial agent is usually added to the reaction system because the sacrificial agent can inevitably consume holes, thereby promoting the separation of electrons and holes and increasing the photo-generated electron utilization ratio. In order to investigate the effect of methanol concentration (volume fraction) on the photocatalytic decomposition rate of aquatic hydrogen production, methanol was chosen as the sacrificial agent. The optimal catalyst was selected and the dosage of catalyst was 0.6 g and the total reaction volume was 300 mL. The reaction time is 2 h. Change the concentration of methanol for photocatalytic reaction experiments, and determine the hydrogen content by gas chromatography, and the experimental results are shown in Figure 5:

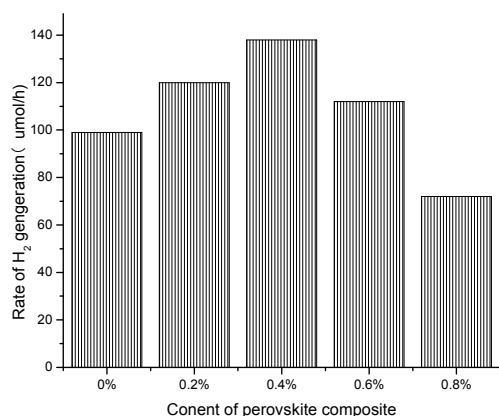


Figure 4: Effect of perovskite composite amount on hydrogen evolution rate of water by photocatalytic decomposition

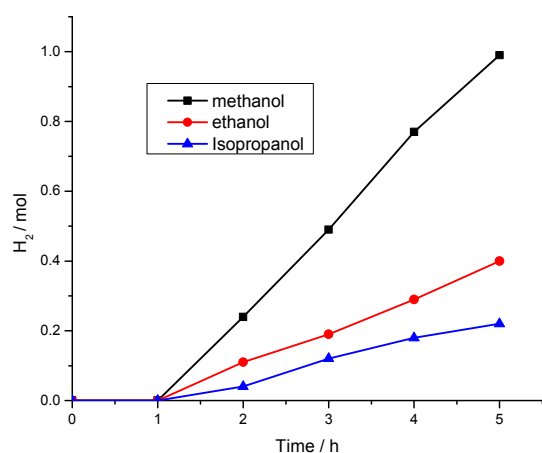


Figure 5: Production of hydrogen at different sacrificial reagents versus time (perovskite)

4. Conclusions

In this paper, photocatalytic decomposition of water was carried out on the prepared composite photocatalyst, and the photocatalytic activity of the catalyst under different preparation conditions was investigated. The effects of hydrogen production system on the hydrogen production activity of the photocatalyst were investigated. The specific results are as follows: The effect of SiO₂ doping on the rate of hydrogen production by photolysis was investigated. The results show that the SiO₂ doping ratio has the best value. When SiO₂ doping ratio is 4.0 at%, the photocatalytic activity of SiO₂ doping TiO₂ catalyst is the highest, and hydrogen production rate of 101.3 μmol · h⁻¹. The effects of photocatalytic hydrogen production on the rate of hydrogen production by photolysis were investigated. The results showed that photocatalytic activity of the photocatalytic hydrogenation catalyst was higher when the amount of catalyst was 0.6 g and the volume concentration of sacrificial agent methanol was 10% highest.

Acknowledgments

2017 Pingxiang City Science and Technology Project (2017GY007, 2017GY004), Key Research and Development Project of Jiangxi Province(20071BBE50049), 2015 Pingxiang City Science and Technology Support Program project (Research and Development of Animation Rendering Service Platform in the Central Region Based on Cloud Computing).

References

- Binder A., Seipenbusch M., Kasper G., 2010, Sintering of Pd Catalyst Particles on SiO₂-TiO₂ Carrier Particles of Different Mixing Ratios, *J.phys.chem.c*, 114(17), 7816-7821, DOI: 10.1021/jp100763q
- Jaojaruek K., Kumar S., 2009, Numerical simulation of the pyrolysis zone in a downdraft gasification process, *Bioresource Technology*, 100(23), 6052-6058, <https://doi.org/10.1016/j.biortech.2009.06.052>
- Michel B., Mazet N., Neveu P., 2016, Experimental investigation of an open thermochemical process operating with a hydrate salt for thermal storage of solar energy: local reactive bed evolution, *Applied Energy*, 180, 234-244, DOI: 10.1016/j.apenergy.2016.07.108
- Otto K., Acik I.O., Krunks M., Tõnsuaadu K., Mere A., 2014, Thermal decomposition study of H₂AuCl₄ · 3H₂O and AgNO₃ as precursors for plasmonic metal nanoparticles, *Journal of Thermal Analysis & Calorimetry*, 118(2), 1065-1072, DOI: 10.1007/s10973-014-3814-3
- Qian K., Huang W., 2011, Au-Pd alloying-promoted thermal decomposition of PdO supported on SiO₂ and its effect on the catalytic performance in CO oxidation, *Catalysis Today*, 164(1), 320-324.
- Rahimi A.N., Mustafa M.F., Zaine M.Z., Ibrahim N., Ibrahim K.A., Hamid M.K.A., 2017, Hydrocarbon Mixture Fractionation Direct Sequence Retrofitting and Feed Condition Sensitivity Analysis, *Chemical Engineering Transactions*, 56, 787-792
- Razmara Z., Rezvani A.R., Saravani H., 2016, Fischer-Tropsch reaction over a Co₂-Ni-Mn/SiO₂ nanocatalyst prepared by thermal decomposition of a new precursor, *Chemical Papers*, 2016, 1-8.
- Shin D., Banerjee D., 2015, Enhanced thermal properties of SiO₂ nanocomposite for solar thermal energy storage applications, *International Journal of Heat & Mass Transfer*, 84, 898-902.
- Ștefănescu M., Dippong T., Stoia M., Ștefănescu O., 2008, Study on the obtaining of cobalt oxides by thermal decomposition of some complex combinations, undispersed and dispersed in SiO₂ matrix, *Journal of Thermal Analysis & Calorimetry*, 94(2), 389-393.
- Zalba B., Jos M.M., Cabeza L.F., Mehling H., 2003, Review on thermal energy storage with phase change: materials, heat transfer analysis and applications, *Applied Thermal Engineering*, 23(3), 251-283.