Research Article

Preparation and Photocatalytic Water Splitting Hydrogen Production of Titanium Dioxide Nanosheets

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Improving the efficiency of photocatalytic water splitting to produce hydrogen is currently a hot topic in research. TiO₂ nanosheets are a good carrier of photocatalytic materials and have become attractive materials in the new century because of their high active surface exposure characteristics and special morphology. Considering the advantages and disadvantages of conventional chemical and physical methods that are used for preparing TiO₂ nanosheets, an optimized scheme for the preparation of TiO₂ nanosheets via hydrothermal calcination was proposed. X-ray powder diffraction (XRD), scanning electron microscopy (SEM), and UV-visible diffuse reflection absorption spectra (DRS) were used to characterize the structure and morphology of the TiO₂ nanosheets, and differences in the photocatalytic water splitting hydrogen production activity of the different calcination temperatures were compared. The suitable calcination temperature of the TiO₂ nanosheets was 400°C, and the hydrogen production rate was 270 μmol/h, which indicated that the sheet structure was beneficial for improving the photocatalytic water splitting hydrogen production performance of the material. It is hoped that this work will support the regulation of the surface morphology and surface modification of nanomaterials.

1. Introduction

Negative effects of the rapid development of science and technology include deterioration of the ecological environment and depletion of the earth's resources. This has caused humanity to face two major problems, environmental pollution and an energy crisis. Renewable clean energy is undoubtedly an effective way to simultaneously solve environmental and energy problems. Since the 21st century, research on a variety of alternative types of energy (solar, biomass, water, wind, geothermal, tidal, hydrogen, and biogas) has been conducted. Great efforts have been made in this area of research [1]. Among the kinds of alternative energy, hydrogen energy has excellent characteristics, such as high energy, a wide combustion range, and good thermal conductivity. Hydrogen energy exists in three forms (gas, liquid, and solid), which is convenient for storage and transportation. The hydrogen combustion process and products are nonpolluting, and hydrogen is recognized as the most popular clean energy in

the world. Hydrogen can be produced by decomposing the most abundant water resources on earth, and thus, hydrogen energy is known as “the oil of the future” [2, 3]. However, the current production of hydrogen is mainly from burning fossil fuels or a high-energy consumption process, which is contrary to the environmentally friendly and sustainable development that people desire. In 1972, Fujishima and Honda discovered that water could be decomposed to produce hydrogen via the irradiation of a titanium dioxide electrode with sunlight; this brought the photocatalytic decomposition of hydrogen to produce hydrogen technology into the spotlight [4]. In the following decades, researchers have engaged in many discussions regarding the research and development of semiconductor materials and their mechanism of action, and this has promoted photocatalytic technology as a promising new method for producing hydrogen [5]. At present, most of the semiconductor photocatalytic materials that have been discovered are *n*-type semiconductors, such as TiO₂, ZnS, ZnO, WO₃, SnO₂, CdS, and Fe₂O₃. Among them,

TiO₂ is promising because of its strong oxidizing power and cheap availability and because it is nontoxic and harmless. It also has many advantages, such as being not easily prone to photocorrosion, and these advantages have been widely studied and used [6–12].

In recent years, semiconductor materials with nanostructures have shown significant advantages in terms of magnetic, superconductivity, optical, and thermodynamic properties [13, 14]. Therefore, the physical and chemical properties of TiO₂ nanomaterials are different from those of conventional TiO₂ materials. Among the differences, TiO₂ nanosheets provide more active centers, have a larger specific surface area than nanorods, and have better high active surface exposure than nanotubes, showing better catalytic performance [15–19]. The conventional methods for preparing TiO₂ nanosheets can be divided into two methods: physical methods (vapor condensation method, high-energy ball milling method, etc.) and chemical methods (sol-gel, liquid deposition, microemulsion, hydrothermal calcination, etc.). Nanosheets that are prepared via a simple method often have a disordered arrangement, and nanosheets that are produced via a complicated method have a low yield. Therefore, from a comprehensive analysis of the advantages and disadvantages of the common methods, an optimization scheme for preparing TiO₂ nanosheets with controlled morphology prepared via a hydrothermal calcining method [20–22] was proposed.

2. Experimental Part

2.1. Preparation of TiO₂ Nanosheets. The preparation process of TiO₂ nanosheets via hydrothermal calcination is shown as follows: At room temperature, 25 mL of tetrabutyl titanate and 2 mL of hydrofluoric acid were measured and mixed to obtain a transparent yellow solution. After ultrasonic treatment for 20 min, the mixtures were magnetically stirred for 20 min. Full contact was made with the hydrofluoric acid. The treated liquid was transferred to a hydrothermal reactor with a polytetrafluoroethylene liner, and the reactor was placed in a 180°C constant temperature incubator for hydrothermal treatment for 24 h. The reactor was allowed to cool naturally to room temperature, and then, it was centrifuged to isolate a white precipitate. To remove the hydrofluoric acid remaining on the white precipitate, the precipitate was placed in a suitable amount of deionized water and magnetically stirred for a period of time. After centrifugation, the supernatant was removed, and the above operation was repeated until the pH value of the supernatant obtained via centrifugation was ≈ 7 . To remove the remaining fat-soluble substances on the white precipitate, the precipitate was magnetically stirred in an appropriate amount of absolute ethanol for a period of time. To convert the fluorinated TiO₂ nanosheets to fluorine-free TiO₂ nanosheets, 0.1 mol/L of NaOH solution was used under magnetic stirring and then washed thoroughly with deionized water to remove the residual NaOH. The white precipitate was dried under a constant temperature of 80°C for 6 h to obtain the H₂Ti₃O₇ · nH₂O nanosheets. Finally, a resistance box was used for calcinations at different temperatures (300°C, 400°C, and 500°C (2 h)). The nanosheets were converted to anatase TiO₂.

2.2. Characterization of Samples. A Bruker D8 Advance X-ray powder diffractometer was used to analyze the crystal phase structure of the catalyst sample. A ZEISS SIGMA scanning electron microscope was used to observe the surface morphology. A Varian Cary 500 UV-visible diffuse reflection absorption spectrometer was used to measure the light absorption performance, and the DRS spectrum was observed.

2.3. Hydrogen Production Performance Test of Water Photolysis. Photocatalytic performance was evaluated using a vacuum glass circulation system, as shown in Figure 1. Deionized water (155 mL) and the catalyst sample (100 mg) were added to the photocatalytic reactor (250 mL) before the reaction. A sacrificial agent (5 mL of methanol) was added under magnetic stirring, and then, the reactor was connected to the system. A chiller was used to maintain the temperature of the reaction solution at 10°C to avoid thermal effects, and then, the entire reaction system was evacuated using a vacuum pump. An ultraviolet lamp was used as a light source, and an online sample was taken every half hour under an argon atmosphere. A gas chromatograph was used to measure the peak value of the hydrogen response signal, which was converted to the amount of hydrogen.

3. Results and Discussion

3.1. Crystal Phase of the Sample. Figure 2 shows an XRD spectrum of the TiO₂ nanosheets that were prepared at different calcination temperatures. As seen in the figure, the sample that was calcined at 300°C only showed the outline of the anatase phase. Also, the broad band between 2θ of 27° and 30°, which is neither anatase phase nor rutile, was more obvious. The broad diffraction peak of the phase indicates that the hydrate H₂Ti₃O₇ · nH₂O was still present in the sample after calcination at 300°C. The above observation indicates that the sample gradually changed to anatase TiO₂ at this temperature, but the crystal effect was relatively poor. The prepared samples showed good crystal peaks that were characteristic of anatase. Also, the broad band between 2θ of 27° and 30° disappeared, and the double peak of 2θ at about 70° also appeared. These observations indicate that after forging at 400°C, there was no hydrate in the fired sample and it had been converted into anatase TiO₂. The peaks characteristic of anatase for the sample that was calcined at 500°C are $2\theta = 25.1^\circ, 37.6^\circ, 48.0^\circ, 53.8^\circ, 55.0^\circ$, and 62.7° (A, JCPDS 21-1272) all appeared. These indicate that the crystal form of the prepared TiO₂ nanosheets was the most complete at this calcination temperature, consistent with previous studies [23–25].

3.2. Morphology of the Sample. Figure 3 shows the SEM images of the prepared TiO₂ nanosheets at different calcination temperatures. Observations from the SEM images of the morphology and structure of the samples [26, 27] showed that the morphologies of the samples that were prepared at different calcination temperatures were significantly different. As seen in Figure 3(a), the sample that was calcined at 300°C has a granular agglomerate and does not show a sheet structure. Figure 3(b) shows that the sample calcined at

FIGURE 1: Vacuum glass circulation system for photocatalytic performance evaluation.

FIGURE 2: XRD spectra of samples calcined at different temperatures.

400°C has a sheet structure. The structure and shape were relatively regular. As seen in Figure 3(c), the sheet structure of the sample calcined at 500°C disappeared and was transformed into a block structure. These observations show that the suitable calcination temperature for preparing TiO_2 with lamellar structure was 400°C.

3.3. Spectral Absorption Properties of the Sample. Figure 4 shows the ultraviolet-visible diffuse reflection absorption spectra of the TiO_2 nanosheets prepared at different calcination temperatures. TiO_2 is an *n*-type semiconductor material. The light absorption threshold of anatase TiO_2 is 380 nm, and the corresponding forbidden bandwidth (E_g) is 3.2 eV. The straight line segment of the DRS spectrum is extended to intersect the abscissa axis, and the intersection point is the absorption wavelength threshold (λ_g). The band gap can be obtained from $E_g = 1240/\lambda_g$ [28]. As seen in Figure 4, although the sample shows a weak redshift in the UV absorption band at 400 nm, it is clear that the absorption wavelength threshold exhibits an order of TiO_2 (300°C) < TiO_2 (500°C) < TiO_2

FIGURE 3: SEM images of samples at different calcination temperatures.

FIGURE 4: UV-visible diffuse reflection absorption spectrum of the sample.

(400°C), indicating that the band gap of the sample that was prepared via calcination at 400°C had the smallest width and relatively high light absorption capacity [29].

3.4. Activity Comparison of Samples. The photocatalytic hydrogen splitting hydrogen production performance of the samples was tested as described in Section 2.3. A comparison of the photocatalytic hydrogen splitting hydrogen production activity is shown in Figure 5. The hydrogen production efficiency of the sample calcined at 400°C was the highest. The hydrogen production reached 1.35 mmol in 5 h, and this was calculated as 270 $\mu\text{mol/h}$. For the hydrogen production efficiency of the samples calcined at 300°C and 500°C, the values were only 58 $\mu\text{mol/h}$ and 62 $\mu\text{mol/h}$, respectively, which were even less than the photocatalytic hydrogen production efficiency of granular nano-P25 (80% anatase and 20% rutile-mixed TiO_2), which is 76 $\mu\text{mol/h}$ [30].

Analysis of the combined XRD, SEM, and DRS characterization results showed that the complete anatase crystal form lamellar structure was conducive for improving the photocatalytic water and hydrogen production performance of the TiO_2 samples. Compared to the lamellar structure, the granular aggregates contained hydrates and bulk anatase crystal phase TiO_2 . These are not conducive to the production of hydrogen from the photolysis of water, and this may be because the granular and massive morphology greatly

FIGURE 5: Photocatalytic decomposition of water to produce hydrogen.

reduces the specific surface area of the sample and blocks the active surface [31, 32].

The multicycle performance of the samples calcined at 400°C is shown in Figure 6. After three cycles, the TiO_2 (400°C) sample still maintained good photohydrolytic hydrogen production activity, indicating that the sample had good photocorrosion resistance and sustained stability. After recycling, the hydrogen production efficiency of the photolyzed water was lower than that of the previous cycle, and this was because of loss during the sample recovery.

4. Conclusions

To optimize the hydrothermal calcination method, samples were prepared at calcination temperatures of 300°C, 400°C, and 500°C, and the samples were characterized via XRD, SEM, and DRS. The hydrogen production activity of the photocatalytic decomposition of water was also tested, and the experimental results were analyzed. An appropriate calcination temperature was selected. TiO_2 calcined at 300°C had highly agglomerated particles with poor crystal quality that were partly in the form of hydrate ($\text{H}_2\text{Ti}_3\text{O}_7 \cdot n\text{H}_2\text{O}$), and the hydrogen production efficiency of the photolysis of water was low. TiO_2 calcined at 500°C had a block structure, and this may have been because of the high temperature of the calcination. This resulted in a large reduction in the specific

FIGURE 6: Performance of the sample after multiple cycles.

surface area and greatly reduced the catalytic capacity. At a calcination temperature of 400°C, TiO₂ nanosheets with complete crystals, uniform grain distribution, and controllable morphology were prepared. The nanosheets had excellent photohydrolytic hydrogen production activity, and this may have been because of the increase in the specific surface area as a result of the lamellar structure morphology and the characteristics of the highly active exposed surface.

Data Availability

All data included in this study are available upon request by contacting the corresponding author.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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