Preparation and Photocatalytic Water Splitting Hydrogen Production of Titanium Dioxide Nanosheets

Fuying Li,1,2 Yin Huang,1 Hongling Peng,1 Yu Cao,1 and Yu Niu1,2

1College of Resources and Chemical Engineering, Sanming University, Sanming 365004, China
2Collaborative Innovation Center of 2011 Clean Coal Gasification Technology, Sanming 365004, China

Correspondence should be addressed to Yu Niu; niuyu200704@163.com

Received 27 December 2019; Revised 29 February 2020; Accepted 16 March 2020; Published 5 August 2020

Copyright © 2020 Fuying Li et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

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 reflectance 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,
TiO$_2$ 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 TiO$_2$ nanomaterials are different from those of conventional TiO$_2$ materials. Among the differences, TiO$_2$ 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 TiO$_2$ 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 TiO$_2$ nanosheets with controlled morphology prepared via a hydrothermal calcining method [20–22] was proposed.

2. Experimental Part

2.1. Preparation of TiO$_2$ Nanosheets. The preparation process of TiO$_2$ 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 for 20 min. Full contact was made with the hydrothermal solution. After ultrasonic treatment, the precipitate was magnetically stirred for a period of time. To convert the fluorinated TiO$_2$ nanosheets to fluorine-free TiO$_2$ 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 H$_2$Ti$_3$O$_7$·nH$_2$O 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 TiO$_2$.

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 pattern of the TiO$_2$ 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 H$_2$Ti$_3$O$_7$·nH$_2$O was still present in the sample after calcination at 300°C. The above observation indicates that the sample gradually changed to anatase TiO$_2$ 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 TiO$_2$. The peaks characteristic of anatase for the sample that was calcined at 500°C are 2θ = 25.1°, 37.6°, 48.0°, 53.8°, 55.0°, and 62.7° (A, JCPDS 21-1272) all appeared. These indicate that the crystal form of the prepared TiO$_2$ 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 TiO$_2$ 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
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 TiO₂ 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 TiO₂ nanosheets prepared at different calcination temperatures. TiO₂ is an n-type semiconductor material. The light absorption threshold of anatase TiO₂ 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 (\(\lambda_g\)). 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 TiO₂ (300°C)<TiO₂ (500°C)<TiO₂.
(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 μmol/h. For the hydrogen production efficiency of the samples calcined at 300°C and 500°C, the values were only 58 μmol/h and 62 μmol/h, respectively, which were even less than the photocatalytic hydrogen production efficiency of granular nano-P25 (80% anatase-and 20% rutile-mixed TiO2), which is 76 μmol/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 TiO2 samples. Compared to the lamellar structure, the granular aggregates contained hydrates and bulk anatase crystal phase TiO2. 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 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 TiO2 (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. TiO2 calcined at 300°C had highly agglomerated particles with poor crystal quality that were partly in the form of hydrate (H2Ti3O7 · nH2O), and the hydrogen production efficiency of the photolysis of water was low. TiO2 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
as a result of the lamellar structure morphology and the 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.

Acknowledgments

This study received financial support from the Outstanding Youth Program Foundation of Fujian (No. 201752), the Key Project Young Natural Science of Fujian Provincial University (No. JZ160478), the Natural Science Foundation of Fujian Province (No. 2019J01818), the Resources and Environment Monitoring and Sustainable Management and Utilization of Fujian Provincial Key Laboratory (No. ZD1804), the University Student Innovation of Fujian (No. 20171311036), and the Collaborative Innovation Center of Clean Coal Gasification Technology of Fujian (Nos. XK1401 and XK1403).

References

[1] R. Miandad, M. Rehan, O. K. M. Ouda et al., “Waste-to-hydrogen energy in Saudi Arabia: challenges and perspectives,” in Biohydrogen Production: Sustainability of Current Technology and Future Perspective, pp. 237–252, Springer, 2017.
[2] B. Zohuri, “Hydrogen energy technology, renewable source of energy,” in Hybrid Energy Systems, pp. 135–179, Springer, Cham, 2018.
[3] J. Ren, D. Xu, H. Cao, S. Wei, L. Dong, and M. E. Goodsite, “Sustainability Decision Support Framework for the Prioritization of Hydrogen Energy Systems,” in Hydrogen Economy, pp. 225–276, Springer, 2017.
[4] A. Fujishima and K. Honda, “Electrochemical photolysis of water at a semiconductor electrode,” Nature, vol. 238, no. 5358, pp. 37–38, 1972.
[5] E. Zhang, “Photocatalytic hydrogen evolution from water splitting using semiconductors: advance, challenge and prospects,” Chinese Journal of Inorganic Chemistry, vol. 33, no. 2, pp. 177–209, 2017.
[6] W. Liu, Y. Xu, W. Zhou et al., “A facile synthesis of hierarchically porous TiO₂ microspheres with carbonaceous species for visible-light photocatalysis,” Journal of Materials Science & Technology, vol. 33, no. 1, pp. 39–46, 2017.
[7] V. K. Gupta, A. Fakhri, M. Azad, and S. Agarwal, “Synthesis and characterization of Ag doped ZnS quantum dots for enhanced photocatalysis of Strychnine as a poison: charge transfer behavior study by electrochemical impedance and time-resolved photoluminescence spectroscopy,” Journal of Colloid and Interface Science, vol. 510, pp. 95–102, 2018.
[8] M. Baek, E. J. Kim, S. W. Hong, W. Kim, and K. Yong, “Environmentally benign synthesis of CuInS₂/ZnO heteronanorods: visible light activated photocatalysis of organic pollutants in water and study of its mechanism,” Photochemical and Photobiological Sciences, vol. 16, no. 12, pp. 1792–1800, 2017.
[9] X. Zeng, Z. Wang, G. Wang et al., “Highly dispersed TiO₂ nanocrystals and WO₃ nanorods on reduced graphene oxide: Z-scheme photocatalysis system for accelerated photocatalytic water disinfection,” Applied Catalysis B: Environmental, vol. 218, pp. 163–173, 2017.
[10] L. Peng, Y. Xiao, X. L. Wang, D. W. Feng, H. Yu, and X. T. Dong, “Realization of visible light photocatalysis by wide band gap pure SnO₂ and study of In₂O₃ Sensitization porous SnO₂ Photocatalysis catalyst,” ChemistrySelect, vol. 4, no. 29, pp. 8460–8469, 2019.
[11] A. Singh and A. S. K. Sinha, “Synthesis and characterization of CdS-based ternary composite for enhanced visible light-driven photocatalysis,” Journal of Physics and Chemistry of Solids, vol. 120, pp. 123–132, 2018.
[12] Q. Du and Q. Gao, “Template-free synthesis of mesoporous α-Fe₂O₃nanoflowers with short charge-carrier diffuse distance for superior photocatalysis,” Materials Technology, vol. 32, no. 12, pp. 724–728, 2017.
[13] N. H. Karam, N. R. Iber, and A. H. al-Dujaili, “A new series of triazine-core based mesogenic derivatives: synthesis, characterization and mesomorphic study,” Molecular Crystals and Liquid Crystals, vol. 675, no. 1, pp. 39–48, 2019.
[14] J. Liu, J. Feng, J. Gui et al., “Metal@semiconductor core-shell nanocrystals with atomically organized interfaces for efficient hot electron-mediated photocatalysis,” Nano Energy, vol. 48, pp. 44–52, 2018.
[15] I. Daou, N. Moukrad, O. Zegaoui, and F. Rhazi Filali, “Antimicrobial activity of ZnO-TiO₂ nanomaterials synthesized from three different precursors of ZnO: influence of ZnO/TiO₂ weight ratio,” Water Science and Technology, vol. 77, no. 5, pp. 1238–1249, 2018.
[16] C. Chen, X. Xin, J. Zhang et al., “Few-layered MoS2 Nanoparticles loaded TiO2 Nanosheets with Exposed (001) Facets for enhanced photocatalytic activity,” *Nano*, vol. 13, no. 11, article 1850129, 2018.

[17] L. Ma, Y. Zhu, X. Li, C. Yang, P. Han, and G. Song, “The architecture of carbon fiber-TiO2 nanorods hybrid structure in supercritical water for reinforcing interfacial and impact properties of CF/epoxy composites,” *Polymer Testing*, vol. 66, pp. 213–220, 2018.

[18] L. Zhong, X. Li, R. Liu, X. Wei, and J. Li, “A visible-light-driven photoelectrochemical molecularly imprinted sensor based on titanium dioxide nanotube arrays loaded with silver iodide nanoparticles for the sensitive detection of benzoyl peroxide,” *The Analyst*, vol. 144, no. 10, pp. 3405–3413, 2019.

[19] H. Fu, L. Yang, D. Hu et al., “Titanium dioxide nanoheterostructure with nanoparticles decorating nanowires for high-performance photocatalysis,” *International Journal of Hydrogen Energy*, vol. 43, no. 22, pp. 10359–10367, 2018.

[20] Y. Zhao, Y. Zhao, R. Shi et al., “Tuning oxygen vacancies in ultrathin TiO2 Nanosheets to boost photocatalytic nitrogen fixation up to 700 nm,” *Advanced Materials*, vol. 31, no. 16, article 1806482, 2019.

[21] T. Shi, Y. Duan, K. Lv et al., “Photocatalytic oxidation of acetone over high thermally stable TiO2 nanosheets with exposed (001) facets,” *Frontiers in Chemistry*, vol. 6, p. 175, 2018.

[22] M. L. Grilli, M. Yilmaz, S. Aydogan, and B. B. Cirak, “Room temperature deposition of XRD-amorphous TiO2 films: investigation of device performance as a function of temperature,” *Ceramics International*, vol. 44, no. 10, pp. 11582–11590, 2018.

[23] S. R. Sowmya, G. M. Madhu, and M. Hashir, “Studies on nanoengineered TiO2 Photo catalyst for effective degradation of dye,” *IOP Conference Series: Materials Science and Engineering*, vol. 310, no. 1, article 012026, 2018.

[24] A. Casu, A. Lamberti, S. Stassi, and A. Falqui, “Crystallization of TiO2 nanotubes by in situ heating TEM,” *Nanomaterials*, vol. 8, no. 1, p. 40, 2018.

[25] M. Ek, I. Beinik, A. Bruix, S. Wendt, J. V. Lauritsen, and S. Helveg, “Step edge structures on the anatase TiO2 (001) surface studied by atomic-resolution TEM and STM,” *Faraday Discussions*, vol. 208, pp. 325–338, 2018.

[26] W. Zhang, J. Yang, and C. Li, “Role of thermal treatment on sol-gel preparation of porous cerium titanate: characterization and photocatalytic degradation of ofloxacin,” *Materials Science in Semiconductor Processing*, vol. 85, pp. 33–39, 2018.

[27] S. R. Mirrakoon, M. Mehdi, and M. Galedari, “Photocatalytic degradation of diazinon under visible light using TiO2/Fe2O3 nanocomposite synthesized by ultrasonic-assisted impregnation method,” *Separation and Purification Technology*, vol. 175, pp. 418–427, 2017.

[28] J. Y. Do, S. Choi, K. Nahm, S. K. Kim, and M. Kang, “Reliable hydrogen production from methanol photolysis in aqueous solution by a harmony between In and Zn in bimetallic zinc indium sulfide,” *Materials Research Bulletin*, vol. 100, pp. 234–242, 2018.