Article

Synthesis of Durian-like TiO$_2$@CdS Core-Shell Structure and Study on H$_2$ Generation Properties

Dongping Li $^{1,2,*}$, Zeheng Chen $^{1,2}$, Xin Wang $^{1,2,*}$, Zhenhong Zhong $^{1,2}$, Chunjun Chen $^3$ and Mengling Wu $^4$

$^1$ The School of Material Science & Chemical Engineering, Harbin University of Science & Technology, Harbin 150040, China
$^2$ Heilongjiang Provincial Key Laboratory of CO2 Resource Utilization and Energy Catalytic Materials, Harbin 150040, China
$^3$ Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China
$^4$ School of Materials Science and Engineering, Nanjing Institute of Technology, Nanjing 211167, China
$^*$ Correspondence: huagong0003@163.com (D.L.); wangxin01208163.com (X.W.)

Abstract: Novel durian-like TiO$_2$@CdS core-shell particles were synthesized through a solvothermal method in ethylenediamine solution and the obtained nanocomposites were characterized by scanning electron microscopy (SEM), powder X-ray diffraction (XRD), and transmission electron microscopic (TEM) techniques. It can be seen from the characterization that the synthesized core-shell structured particles show uniform size. The possible formation mechanism of TiO$_2$@CdS core-shell particles is also presented schematically. CdS grows on the TiO$_2$ surface in the form of nanorods, turning the TiO$_2$@CdS composite particles into durian-like structures. The durian-like TiO$_2$@CdS core-shell particles prepared in the experiment can overcome the disadvantages of TiO$_2$ and CdS, respectively. They not only produce a higher yield of H$_2$ than pure TiO$_2$; the durian-like TiO$_2$@CdS nanostructures formed at 180$^\circ$C for 16 h produced 2.5 times as much H$_2$ as did TiO$_2$, also showing enhanced stability as compared with pure CdS.

Keywords: TiO$_2$; CdS nanorods; core-shell structure; H$_2$ generation

1. Introduction

In recent years, photocatalysis via titanium dioxide (TiO$_2$) has been widely investigat...
Cadmium sulfide (CdS) which is an important II–VI semiconductor (\(E^* = 2.42\) eV (515 nm) at room temperature) with many excellent physical and chemical properties \[22\], has been used as a light-harvesting sensitizer to improve the photoelectric properties of TiO\(_2\) because of its appropriate direct energy band gap. Recently, TiO\(_2\)/CdS composite materials have attracted great interest. They could compensate the disadvantages of the individual components based on some synergistic effects, such as efficient charge separation and migration, expanded visible light response, and improved photostability \[23−25\]. Cao et al., prepared TiO\(_2\)/CdS core-shell nanorod arrays with visible light activity by a two-step method. This increased the probability of electron–hole separation and extended the range of the TiO\(_2\) photoresponse from ultraviolet to visible regions \[26\].

Many fundamental properties of semiconductor materials are dependent on the size and shape of their particles. Controlling the relevant size and shape would provide opportunities for tailoring properties of materials and offer possibilities for observing attractive and useful physical phenomena \[27\]. Therefore, materials engineering in nanometer-scale has attracted much attention in optics, electronics, magnetics, catalysis, and ceramics \[28–32\]. In this paper, TiO\(_2\)/CdS core-shell particles, with CdS nanorods as shell layers and TiO\(_2\) nanoparticles as the corresponding core units, were successfully fabricated, in order to overcome the disadvantages of both TiO\(_2\) and CdS, thus gaining better optical and electric performances. To the best of our knowledge, this is the first report on TiO\(_2\)/CdS core-shell particles with a durian-like surface structure.

2. Results and Discussion

2.1. SEM and TEM Characterizations

SEM and TEM techniques were employed to characterize the morphology of the TiO\(_2\)/CdS particles obtained with different reaction times. As shown in Figure 1a, the commercially available TiO\(_2\) nanoparticles with diameters of about 100 nm have a smooth surface. After adding a CdCl\(_2\) solution, SC(NH\(_2\))\(_2\), H\(_2\)NCH\(_2\)CH\(_2\)NH\(_2\) and conducting continuous heating for 8 h, we find the surface of TiO\(_2\) is no longer smooth due to the formation of a TiO\(_2\)/CdS composite (Figure 1b). With an extended heating time (16 h), we observe the formation of durian-like TiO\(_2\)/CdS particles (Figure 1c) with various nanorods on the TiO\(_2\) surface, with a diameter of 50 nm. We further used TEM to characterize the TiO\(_2\)/CdS particles. As shown in Figure 1d, the clear contrast between the core and the shell indeed proves that the CdS nanorods coat the surface of the TiO\(_2\) nanoparticles. Furthermore, as shown in Figure 2 and Table 1, the ratio of S:Cd is ca. 1:1. The results of EDX basically indicate that the surface rods are CdS.

Table 1. The EDX data of Weight % and Atomic % of S and K Element in the sample.

| Element | Weight % | Atomic % |
|---------|----------|----------|
| S K     | 23.25    | 51.50    |
| Cd L    | 76.75    | 48.50    |
| Totals  | 100.00   | 100.00   |

Based on the above observations, we can conclude that the reaction time played a crucial role in controlling the durian-like morphology of the TiO\(_2\)/CdS. With the help of ethylenediamine, the CdS grows into a rod-like structure on the surface of the TiO\(_2\) particles forming durian-like TiO\(_2\)/CdS particles (Figure 1c), as further confirmed by TEM (Figure 1d).

2.2. XRD Characterization

The powder XRD patterns of the TiO\(_2\), TiO\(_2\)/CdS and CdS samples prepared with different reaction times are shown in Figure 3. A typical diffraction peak located at \(2\theta = 25.3^\circ\) is attributed to the (101) crystal planes of the anatase-phase TiO\(_2\) (JCPDS no. 21-1272). The peaks at 26.5\(^\circ\) and 28.2\(^\circ\) observed in the XRD of TiO\(_2\)/CdS and CdS particles are attributed to (002) and (101) crystal planes of hexagonal CdS. If the reaction time lasts longer, the
(002) diffraction peak of the TiO$_2$@CdS samples becomes both stronger and narrower, as shown in Figure 3 (TiO$_2$@CdS, 16 h). The unusual (002) diffraction peak indicates that the sample (TiO$_2$@CdS, 16 h) is preferentially orientated along the $c$ axis. The rod shape is confirmed by SEM and TEM photographs. In addition, the typical diffraction peak located at $2\theta = 25.3^\circ$ of anatase-phase TiO$_2$ is weak which can be explained by the thick coating of CdS on the surface of TiO$_2$. This result is also verified by the TEM photograph.

![Figure 1. SEM and TEM image. (a) SEM image of TiO$_2$; (b) SEM image of TiO$_2$@CdS formed at 180 °C for 8 h; (c) SEM image of durian-like TiO$_2$@CdS nanostructure formed at 180 °C for 16 h; (d) TEM image of a durian-like TiO$_2$@CdS core-shell nanostructure formed at 180 °C for 16 h.]

![Figure 2. The EDX data of Weight % and Atomic % of S and Cd elements in the sample.]

2.3. The Formation Mechanism of TiO$_2$@CdS Core-Shell Particles

The possible formation mechanism of TiO$_2$@CdS core-shell particles is depicted schematically in Figure 4. The first step is to link the Cd$^{2+}$ to the TiO$_2$ surface through inorganic grafting which is achieved by impregnating TiO$_2$ nanoparticles in a CdCl$_2$ solution. In the second step, the addition of SC(NH$_2$)$_2$ promotes generation of CdS on the surface of the TiO$_2$ nanoparticle, which is used as the seed. In the third step, CdS grows in the
form of nanorods on the surface of TiO₂ with the help of ethylenediamine, which turns the composite particle into a durian-like structure.

**Figure 3.** XRD patterns of the anatase-phase TiO₂ and TiO₂@CdS particles.

**Figure 4.** Schematic process for durian-like TiO₂@CdS core-shell structure.
2.4. Photocatalytic Reaction for H$_2$ Generation

In order to verify the photocatalyst activity of the TiO$_2$@CdS particles, the photocatalytic hydrogen evolution ability under light irradiation was studied, and the results are shown in Table 2. We find that the efficiency of H$_2$ generation in the produced hybrid materials increases in the order TiO$_2$ < TiO$_2$@CdS (8 h) < durian-like TiO$_2$@CdS (16 h) with a maximum H$_2$ generation rate of 1065 $\mu$mol·h$^{-1}$·g$^{-1}$ for the durian-like TiO$_2$@CdS core/shell particles (16 h). This is two times larger than the activity of bare TiO$_2$ particles. The yield of H$_2$ of durian-like TiO$_2$@CdS (16 h) is higher than that of TiO$_2$@CdS (8 h). The results indicate that the durian-like TiO$_2$@CdS particles have better photocatalytic activity than TiO$_2$ particles since the CdS nanorod can expand the visible light response and improve charge separation and migration. The yield of H$_2$ of pure CdS is higher than that of durian-like TiO$_2$@CdS (16 h), but pure CdS is less stable, as suggested by a color change from yellow to black. The color of the hybrid materials TiO$_2$@CdS is not changed during the photocatalytic reaction.

Table 2. H$_2$ generation rate of different samples.

| Sample         | H$_2$ Generation Rate, $\mu$mol·h$^{-1}$·g$^{-1}$ |
|----------------|-----------------------------------------------|
| TiO$_2$        | 400                                           |
| TiO$_2$@CdS (8 h) | 588                                          |
| TiO$_2$@CdS (16 h) | 1065                                         |
| CdS            | 3550                                          |

Additionally, the reproducibility experiments have been performed. The H$_2$ generation rate of durian-like TiO$_2$@CdS (16 h) decreased to 800 $\mu$mol·h$^{-1}$·g$^{-1}$ after four cycle reaction (see the Figure 5). In contrast, the H$_2$ generation rate of pure CdS dropped to 400 $\mu$mol·h$^{-1}$·g$^{-1}$ in the second cycle reaction. Meanwhile, the SEM experiments of both CdS and durian-like TiO$_2$@CdS after photocatalytic reaction have also been performed (Figure 6). The results indicated that the particle size of durian-like TiO$_2$@CdS slightly changed as compared with the pure CdS. In addition, no obvious change was observed before and after catalysis in the XRD of the TiO$_2$@CdS (Figure 6e). Thus, the reproducibility of H$_2$ generation rate of durian-like TiO$_2$@CdS is basically good. Compared with the state-of-the-art catalysts, the activity and stability of TiO$_2$@CdS is comparable.

![Figure 5. The diagram of H$_2$ generation rate of TiO$_2$@CdS four cycle reaction.](image)

From the above results, we can observe that the activity of H$_2$ generation over TiO$_2$@CdS was higher than that of the TiO$_2$, and the stability of TiO$_2$@CdS was better than that of CdS. Thus, we can assume that the charged species can be separated over the
composites, and photocorrosion is severely inhibited. Hence, we can assume that a typical Z-scheme mechanism was occurring over the TiO$_2$@CdS. Under simulated sunlight illumination, both TiO$_2$ and CdS can be excited to produce photoinduced electrons and holes. The photoinduced electrons in CdS tend to keep in the CB of CdS, and the photoinduced holes in TiO$_2$ remain in the VB of TiO$_2$. Meanwhile, the photoinduced electrons in the CB of TiO$_2$ combine with the photoinduced holes in VB of CdS (Figure 6f). Thus, the holes over the CdS can be reduced, and the photooxidation reaction may occur on the surface of TiO$_2$ rather than the CdS. Therefore, the carriers can be separated and photocorrosion can be inhibited. In addition, the photo-current responses of CdS, TiO$_2$@CdS and TiO$_2$ were tested to gain a deeper understanding of the efficacy of photoexcited charge separation. As shown in Figure 6g, we can observe that the photocurrent intensity of TiO$_2$@CdS (16 h) was higher than that of TiO$_2$, indicating more effective charge separation in TiO$_2$@CdS (16 h). Although the CdS exhibited the highest photocurrent, the H$_2$ generation rate of pure CdS dropped seriously.

![Figure 6.](image)

**Figure 6.** (a) SEM image of pure CdS, (b) SEM image of pure CdS after reaction, (c) SEM image of TiO$_2$@CdS, (d) SEM image of TiO$_2$@CdS after reaction, (e) XRD patterns of TiO$_2$@CdS before and after the reaction, (f) Illustration of the photocatalytic mechanism, (g) The photocurrent measurements over TiO$_2$, CdS and TiO$_2$@CdS (16 h).

### 3. Materials and Methods

#### 3.1. Subsection

All chemicals were commercially purchased and used without purification. The source of reagents that we used: TiO$_2$ (Tianjin No.3 Chemical Reagent Factory, Tianjin, China), CdCl$_2$ (Tianjin GuangFu Science and Technology Development Co., Ltd., Tianjin, China), thiourea (Tianjin Zhiyuan Chemical Reagent Co., Ltd., Tianjin, China), ethylenediamine (Tianjin Zhiyuan Chemical Reagent Co., Ltd., Tianjin, China) and Ethanol (Tianjin TianLi Chemical Co., Ltd., Tianjin, China).

#### 3.2. Preparation of TiO$_2$@CdS Core-Shell Particles

These particles were synthesized by a solvothermal method [33,34]. The commercial anatase-phase TiO$_2$ nanoparticles (1 g, 0.013 mol) were added to dilute nitric acid (10 mL, 1 mol·L$^{-1}$) with ultrasound for 4 h, and were collected and washed with distilled water to neutral. The final products were dried at 80 °C for 4 h in a vacuum box. The obtained TiO$_2$ (0.1 g) nanoparticles and 5 mL of an aqueous solution of CdCl$_2$ (1 mol·L$^{-1}$) were added to a beaker with a capacity of 100 mL and were stirred magnetically for 4 h at room temperature. 5 mL of a thiourea solution (1.5 mol·L$^{-1}$) and the mixture described above were added to a teflon-lined stainless steel autoclave with a 25 mL capacity. The autoclave was filled with 10 mL ethylenediamine solution up to about 80% of the total volume. The solution was
stirred and treated with ultra-sound. The autoclave was maintained at 180 °C for 8–16 h and then allowed to cool to room temperature. Yellow precipitates were collected and washed with ethanol and distilled water to remove residues of organic material. The final products were dried at 80 °C for 4 h in a vacuum box. The pure CdS was prepared by the same method without TiO₂.

3.3. Characterization of TiO₂@CdS Core-Shell Particles

The morphologies of the TiO₂ nanoparticles and durian-like TiO₂@CdS core-shell particles were characterized by scanning electron microscopy (SEM, SU8020) and transmission electron microscopy (TEM, JEM-2100). To facilitate the investigation of the detailed surface morphology of TiO₂@CdS, no conductive metal layer such as Au, Pd/Au, Cr, or carbon layer was coated on the sample surface. The samples were further analyzed with a Bruker D8 Avance X-ray diffractometer (XRD) using Ni-filtered Cu Kα radiation at 40 kV and 40 mA in the 2θ range of 20–80°, with a scan rate of 0.02° per second.

3.4. Photocatalytic Experiment

Photocatalytic reactions of hydrogen production by water splitting were conducted in a gas-closed system with a side irradiation Pyrex cell. An aluminum alloy shell was employed outside the Pyrex cell to reflect and gather the visible light originating from Xe lamp. A water cycling system was used to maintain the reaction temperature.

Photocatalyst powder (10 mg) was dispersed in a solution (2 mL) containing 0.35 mol·L⁻¹ Na₂S and 0.25 mol·L⁻¹ Na₂SO₃. After being evacuated and flushed by N₂ gas for over 10 min, the photocatalysts were irradiated by visible light (λ ≥ 300 nm) from a 300 W Xe lamp for 4 h. The amount of H₂ gas was determined using a gas chromatograph (Bruker GC-4890, using column type TDX01).

4. Conclusions

In summary, novel durian-like TiO₂@CdS core-shell particles were synthesized through a solvothermal method in ethylenediamine solution. As demonstrated, CdS coated the surface of the TiO₂ material. The reaction time plays a crucial role in controlling the nucleation and growth of crystallites; with a prolonged reaction time, CdS gradually forms a rod shape, which effectively enhances visible light absorption and possesses a high electron affinity. The durian-shaped TiO₂@CdS composite not only produced a higher yield of H₂ than pure TiO₂, but also possessed an enhanced stability as compared with the pure CdS. Therefore, the durian-like TiO₂@CdS core-shell particles might be a good catalyst for application in photocatalysis.

Author Contributions: Conceptualization, Z.C. and D.L.; methodology, Z.C. and X.W.; software, C.C.; investigation, D.L. and Z.Z.; data curation, X.W.; writing—original draft preparation, Z.C.; writing—review and editing, D.L., Z.C., X.W., Z.Z., C.C. and M.W. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: Not applicable.

Acknowledgments: The authors thank the Harbin University of Science & Technology and Chinese Academy of Sciences for experimental and technical support.

Conflicts of Interest: The authors declare no conflict of interest.

References
1. Ge, M.; Cao, C.; Huang, J.; Li, S.; Chen, Z.; Zhang, K.-Q.; Al-Deyab, S.S.; Lai, Y. A review of one-dimensional TiO₂ nanostructured materials for environmental and energy applications. J. Mater. Chem. A 2016, 4, 6772–6801. [CrossRef]
2. Pelaez, M.; Nolan, N.T.; Pillai, S.C.; Seery, M.K.; Falaras, P.; Kontos, A.G.; Dunlop, P.S.M.; Hamilton, J.W.J.; Byrne, J.A.; O’Shea, K. A review on the visible light active titanium dioxide photocatalysts for environmental applications. Appl. Catal. B Environ. 2012, 125, 331–349. [CrossRef]
3. Rempel, A.A.; Valeeva, A.A.; Vokhminstev, A.S.; Weinstein, I.A. Titanium dioxide nanotubes: Synthesis, structure, properties and applications. *Russ. Chem. Rev.* 2021, 90, 1397–1414. [CrossRef]

4. Falletta, E.; Bianchi, C.L.; Morazzoni, F.; Polissi, A.; Di Vincenzo, F.; Bellobono, I.R. Tungsten Tioxide and Its TiO₂ Mixed Composites for the Photocatalytic Inactivation of Bacteria (*Escherichia coli*). *Catalysts* 2022, 12, 822. [CrossRef]

5. Bergamontii, L.; Graiff, C.; Bergonzì, C.; Potenza, M.; Reverberi, C.; Ossiprandi, M.C.; Lottici, P.P.; Bettini, R.; Elviri, L. Photodegradation of Pharmaceutical Pollutants: New Photocatalytic Systems Based on 3D Printed Scaffold-Supported Ag/TiO₂ Nanocomposite. *Catalysts* 2022, 12, 580. [CrossRef]

6. Yu, J.; Caravaca, A.; Guillard, C.; Vernoux, P.; Zhou, L.; Wang, L.; Lei, J.; Zhang, J.; Liu, Y. Carbon Nitride Quantum Dots Modified TiO₂ Inverse Opal Photonic Crystal for Solving Indoor VOCs Pollution. *Catalysts* 2021, 11, 464. [CrossRef]

7. Xiao, T.; Chen, Y.; Liang, Y. Ni(II) Tetra(4-carboxylphenyl)porphyrin-Sensitized TiO₂ Nanotube Array Composite for Efficient Photocatalytic Reduction of CO₂. *J. Phys. Chem. C* 2022, 126, 9742–9752. [CrossRef]

8. Liu, J.; Liu, B.; Ren, Y.; Yuan, Y.; Zhao, H.; Yang, H.; Liu, S. Hydrogenated nanotubes/nanowires assembled from TiO₂ nanoflakes with exposed {111} facets: Excellent photo-catalytic CO₂ reduction activity and charge separation mechanism between (111) and (111) polar surfaces. *J. Mater. Chem. A* 2019, 7, 14761–14775. [CrossRef]

9. Appadurai, T.; Subramaniam, C.M.; Kuppusamy, R.; Karazhanov, S.; Subramanian, B. Electrochemical Performance of Nitrogen-Doped TiO₂ Nanotubes as Electrode Material for Supercapacitor and Li-Ion Battery. *Molecules* 2019, 24, 2952. [CrossRef]

10. Li, H.; Wang, S.; Wang, M.; Gao, Y.; Tang, J.; Zhao, S.; Chi, H.; Zhang, P.; Qu, J.; Fan, F.; et al. Enhancement of Plasma-Induced Photocatalytic Water Oxidation over Au/TiO₂ with Lithium Intercalation. *Angew. Chem. Int. Ed.* 2022, 61, e202204272. [CrossRef]

11. Nam, Y.; Lim, J.H.; Ko, K.C.; Lee, J.Y. Photocatalytic activity of TiO₂ nanoparticles: A theoretical aspect. *J. Mater. Chem. A* 2019, 7, 13833–13859. [CrossRef]

12. Al Qarnì, F.; Alomair, N.A.; Mohamed, H.H. Environment-Friendly Nanoporous Titanium Dioxide with Enhanced Photocatalytic Activity. *Catalysts* 2019, 9, 799. [CrossRef]

13. Yang, B.; Ma, Z.; Wang, Q.; Yang, J. Synthesis and Photoelectrocatalytic Applications of TiO₂/ZnO/Diotomite Composites. *Catalysts* 2022, 12, 268. [CrossRef]

14. Cai, M.; Cao, S.; Zhuo, Z.; Wang, X.; Shi, K.; Cheng, Q.; Xue, Z.; Du, X.; Shen, C.; Liu, X.; et al. Fabrication of Ni₂P Cocatalyzed CdS Nanorods with a Well-Defined Heterointerface for Enhanced Photocatalytic H₂ Evolution. *Catalysts* 2022, 12, 417. [CrossRef]

15. Gao, X.-F.; Sun, W.-T.; Hu, Z.-D.; Ai, G.; Zhang, Y.-L.; Feng, S.; Li, F.; Peng, L.-M. An Efficient Method To Form Heterojunction CdS/TiO₂ Photocathodes Using Highly Ordered TiO₂ Nanotube Array Films. *J. Phys. Chem. C* 2009, 113, 20481–20485. [CrossRef]

16. Kang, X.; Chaperman, L.; Galeckas, A.; Ammar, S.; Mammeri, F.; Norby, T.; Chatzitakis, A. Water Vapor Photoelectrolysis in a Solid-State Photoelectrochemical Cell with TiO₂ Nanotubes Loaded with CdS and CdSe Nanoparticles. *ACS Appl. Mater. Int. 2021, 13, 46875–46885. [CrossRef]

17. Pal, S.; Taurino, A.; Catalano, M.; Liciulli, A. Block Copolymer and Cellulose Templated Mesoporous TiO₂-SiO₂ Nanocomposite as Superior Photocatalyst. *Catalysts* 2022, 12, 770. [CrossRef]

18. Irfan, R.M.; Tahir, M.H.; Maqsood, M.; Lin, Y.; Bashir, T.; Iqbal, S.; Zhao, J.; Gao, L.; Haroon, M. CoSe as non-noble-metal cocatalyst integrated with heterojunction photosensitizer for inexpensive H₂ production under visible light. *J. Catal.* 2020, 390, 196–205. [CrossRef]

19. Pan, Z.; Wang, R.; Li, J.; Iqbal, S.; Liu, W.; Zhou, K. Fe₂P nanoparticles as highly efficient freestanding co-catalyst for photocatalytic hydrogen evolution. *Int. J. Hydrogen Energy* 2018, 43, 5337–5345. [CrossRef]

20. Kim, H.-I.; Kim, J.; Kim, W.; Choi, W. Enhanced Photocatalytic and Photoelectrochemical Activity in the Ternary Hybrid of CdS/TiO₂/WO₃ through the Cascadal Electron Transfer. *J. Phys. Chem. C* 2011, 115, 9797–9805. [CrossRef]

21. Lv, Z.; Wang, Y.; Liu, Y.; Wang, J.; Qin, G.; Guo, Z.; Zhang, C. NiB as a Substitute for the Pt Cocatalyst in CdS with Enhanced Visible-Light Photocatalytic H₂ Production. *J. Phys. Chem. C* 2022, 126, 9041–9050. [CrossRef]

22. Jie, J.S.; Zhang, W.J.; Jiang, Y.; Meng, X.M.; Li, Y.Q.; Lee, S.T. Photoconductive Characteristics of Single-Crystal CdS Nanoribbons. *Nano Lett.* 2006, 6, 1887–1892. [PubMed]

23. Zhang, J.; Cai, P.; Lin, J. Modulation of the Band Bending of CdS by Fluorination to Facilitate Photoinduced Electron Transfer for Efficient H₂ Evolution over Pt/CdS. *J. Phys. Chem. B* 2022, 126, 7896–7902. [CrossRef]

24. Du, Y.-e.; Niu, X.; He, X.; Hou, K.; Liu, H.; Zhang, C. Synthesis and Photocatalytic Activity of TiO₂/CdS Nanocomposites with Co-Exposed Anatase Highly Reactive Facets. *Molecules* 2021, 26, 6031. [CrossRef] [PubMed]

25. Guo, N.; Wang, C.; Bao, W.; Zeng, Y.; Yu, H. Hollow TiO₂@CdS nanosphere: Interface construction for spatial charge separation and higher charge transfer efficiency. *J. Environ. Chem. Eng.* 2021, 9, 106211. [CrossRef]

26. Cao, C.; Hu, C.; Shen, W.; Wang, S.; Tian, Y.; Wang, X. Synthesis and characterization of TiO₂/CdS core–shell nanorod arrays and their photoelectrochemical property. *J. Alloys Compd.* 2012, 523, 139–145. [CrossRef]

27. Kim, M.R.; Kang, Y.-M.; Jang, D.-J. Synthesis and Characterization of Highly Luminescent CdS@ZnS Core–Shell Nanorods. *J. Phys. Chem. C* 2007, 111, 18507–18511. [CrossRef]

28. Chen, S.; Peng, Y.; Li, C.; Hou, Z. The co-decorated TiO₂ nanorod array photoanodes by CdS/CdSe to promote photoelectrochemical water splitting. *Int. J. Hydrogen Energy* 2021, 46, 32055–32068. [CrossRef]

29. Dang, W.; Xu, K.; Zhang, L.; Qian, Y. Fabrication of multilayer 1D TiO₂/CdS/ZnS with high photocatalytic performance and enhanced stability. *J. Alloys Compd.* 2021, 866, 161329. [CrossRef]
30. Revathi, M.; Jeyakumari, A.P. Fabrication of TiO$_2$/CdS heterostructure photoanodes and optimization of light scattering to improve the photovoltaic performance of dye-sensitized solar cells (DSSCs). *J. Mater. Sci. Mater. Electron.* 2021, 32, 11921–11930. [CrossRef]

31. Devaraji, P.; Gao, R.; Xiong, L.; Jia, X.; Huang, L.; Chen, W.; Liu, S.; Mao, L. Usage of natural leaf as a bio-template to inorganic leaf: Leaf structure black TiO$_2$/CdS heterostructure for efficient photocatalytic hydrogen evolution. *Int. J. Hydrogen Energy* 2021, 46, 14369–14383. [CrossRef]

32. Lu, Y.; Yi, G.; Zhou, H.; Liu, J.; Zhang, H.; Lu, L.; An, L. Arrays of needle-like TiO$_2$/CdS nanorod heterostructure photoelectrodes with enhanced photoelectrochemical properties fabricate by pulsed laser deposition. *Vacuum* 2021, 184, 109985. [CrossRef]

33. Yang, J.; Zeng, J.-H.; Yu, S.-H.; Yang, L.; Zhou, G.-e.; Qian, Y.-t. Formation Process of CdS Nanorods via Solvothermal Route. *Chem. Mater.* 2000, 12, 3259–3263. [CrossRef]

34. Ye, C.; Meng, G.; Wang, Y.; Jiang, Z.; Zhang, L. On the Growth of CdS Nanowires by the Evaporation of CdS Nanopowders. *J. Phys. Chem. B* 2002, 106, 10338–10341. [CrossRef]