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Biomass Photoreforming for Hydrogen Production over Hierarchical 3DOM TiO$_2$-Au-CdS

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Abstract: Photocatalytic hydrogen production is a promising route to the provision of sustainable and green energy. However, the excess addition of traditional electron donors as the sacrificial agents to consume photogenerated holes greatly reduces the feasibility of this approach for commercialization. Herein, considering the abundant hydroxyl groups in cellulose, the major component of biomass, we adopted glucose (a component unit of cellulose), cellobiose (a structure unit of cellulose) and dissolving pulp (a pretreated cellulose) as electron donors for photocatalytic hydrogen production over a TiO$_2$-Au-CdS material. The well-designed ternary TiO$_2$-Au-CdS possesses a hierarchical three-dimensional ordered macroporous (3DOM) structure, which not only benefits light harvesting but can also facilitate mass diffusion to boost the reaction kinetics. As expected, the fabricated photocatalyst exhibits considerable hydrogen production from glucose (645.1 µmol·h$^{-1}$·g$^{-1}$), while the hydrogen production rates gradually decrease with the increased complexity in structure from cellobiose (273.9 µmol·h$^{-1}$·g$^{-1}$) to dissolving pulp (79.7 µmol·h$^{-1}$·g$^{-1}$). Other gaseous components such as CO and CH$_4$ are also produced, indicating the partial conversion of biomass during the photoreforming process. This work demonstrates the feasibility of sustainable hydrogen production from biomass by photoreforming with a rational photocatalyst design.

Keywords: biomass; photoreforming; hydrogen production; 3DOM; TiO$_2$-Au-CdS

1. Introduction

With the increasing global pressure of energy depletion and environmental issues, it is urgent to develop sustainable processes for green energy generation [1]. Photocatalytic hydrogen production using solar energy as the driving force and abundant water as the hydrogen source has emerged as an extremely promising alternative [2,3]. Since the successful demonstration of solar-driven water splitting for hydrogen production, its photocatalytic activity has been constantly increasing [4–6]. The basic processes of photocatalytic hydrogen production involve the following steps. First, photons with enough energy are absorbed to activate semiconductor photocatalysts to generate electron–hole pairs. Second, the photogenerated electrons and holes migrate to the surface of the photocatalyst, during which process surface and bulk recombination happen. Third, the electrons on the photocatalyst’s surface trigger a proton reduction reaction for hydrogen production [7,8]. It can be foreseen that improving the light absorption ability and reducing the combination of photogenerated electrons and holes should benefit the hydrogen production and solar-to-hydrogen efficiency.

The formation of a heterojunction by combining two separated semiconductors with suitable bandgap structures has been proven to be an efficient strategy to realize the spatial separation of photogenerated electrons and holes, thereby enhancing the photocatalytic quantum yield [9]. For example, introducing CdS onto the surface of TiO$_2$ not only extends...
the light absorption from UV to visible light but also improves the lifetime of photogenerated electrons with the formation of a typical type-II heterojunction [10], which could not only take the advantages of TiO$_2$ in chemical stability, cost effectiveness and non-toxicity but also address the intrinsic disadvantages of TiO$_2$ in terms of limited light utilization and the high recombination of charge carriers. However, the interfacial impedance at the contact interface of CdS and TiO$_2$ greatly hinders the smooth transfer of the photogenerated charge carriers. The introduction of metals with higher working functions between CdS and TiO$_2$ to bridge the charge transfer channel has also been proven to be a feasible strategy to improve quantum efficiency [11]. This formed Schottky junction sometimes acts to simultaneously enhance light absorption with some typical metals such as Au, Cu, and Ag, etc. The localized surface plasmon resonance (LSPR) effect endows the photocatalyst with further enhanced visible light absorption, and the hot electrons produced also help to produce hydrogen [12]. In terms of light harvesting, the catalyst morphology design is another important approach to significantly improve the incident light absorbance. In photocatalysts, the presence of a hierarchical three-dimensional ordered macroporous (3DOM) structure also stands out due to the slow photon effect and the multiple scattering of incident light [13–15].

Although our previous works already proved the positive effect of a 3DOM structure and a TiO$_2$-Au-CdS heterojunction on enhancing the photocatalytic performance for hydrogen production, the addition of excess sacrificial agents (such as Na$_2$S/Na$_2$SO$_3$ and methanol, etc.) to consume photogenerated holes in a timely manner heavily reduces the sustainability of photocatalytic hydrogen production [11,13,16]. Alternatively, biomass with abundant reductive functional groups (hydroxyl, aldehyde, etc.) could theoretically act as an electron donor to replace the traditional sacrificial agent for photocatalytic hydrogen production [17,18]. Some investigations have already demonstrated the feasibility of hydrogen production from the biomass photoreforming process [19–25]. However, the currently achieved activity is still far from the state-of-art efficiency achieved by using traditional sacrificial agents [26]. This is due to the complex structure and components of biomass, which lead to extremely slow reaction kinetics. From this point of view, the inter-connected hierarchical 3DOM structure is expected to hold superior advantages, as it can greatly facilitate mass diffusion [27,28].

Herein, we demonstrate biomass photoreforming for hydrogen production by using 3DOM TiO$_2$-Au-CdS as a photocatalyst and saccharides as electron donors. The photocatalyst is prepared by a colloidal template method with polystyrene spheres as the template and isopropyl titanate as the precursor of TiO$_2$. Gold nanoparticles (Au NPs) and CdS are sequentially introduced to form the final ternary photocatalyst. Enhanced visible light absorbance is realized due to the LSPR effect and intrinsic bandgap of CdS. Combining the advantages of a heterojunction for charge separation, the well-designed photocatalyst exhibits an excellent hydrogen production rate (645.1 $\mu$mol·h$^{-1}$·g$^{-1}$) from a glucose solution. The activity of photocatalytic hydrogen generation gradually decreases when cellobiose (273.9 $\mu$mol·h$^{-1}$·g$^{-1}$) and dissolving pulp (79.7 $\mu$mol·h$^{-1}$·g$^{-1}$) with more complex structures compared to glucose are used as the electron donor. Along with hydrogen generation, the biomass photoreforming also produces CO and CH$_4$ from the substrates. Control experiments demonstrated that acidic conditions are more beneficial for hydrogen production while the substrate oxidation is still the rate-limiting step. The present work provides a good example of how to boost hydrogen production from biomass photoreforming by rationally designing a hierarchically porous photocatalyst.

2. Results and Discussion

Figure 1 illustrates the general photocatalyst preparation process. Polystyrene spheres were first synthesized via a surfactant-free emulsion polymerization method. The obtained polystyrene spheres were assembled into a colloidal template with a typical opal structure. The precursor containing isopropyl titanate penetrated and filled the voids of the colloidal template via a sol-gel process [29,30]. The polystyrene spheres were then removed after
calcination, during which process TiO$_2$ with a high crystallinity was formed. Figure 1 shows a typical scanning electron microscopy (SEM) image of the 3DOM structure at a high magnification. Then, gold nanoparticles (Au NPs) were deposited onto the surface of the 3DOM TiO$_2$ by the sodium citrate reduction method. Finally, CdS with a typical hexagonal phase was introduced by chemical bath deposition. A typical SEM image clearly shows the preservation of the 3DOM structure after the introduction of Au NPs and CdS.

The catalyst morphology and component distribution were then investigated by SEM and transmission electron microscopy (TEM). The hierarchical 3DOM structure could clearly be observed in a backscattered electron (BSE) image, while the Au NPs exhibited a uniform distribution in the 3DOM framework (Figure 2a). This indicated that the 3DOM structure was kept after the introduction of Au NPs and CdS. The Au NPs had a diameter of around 20 nm, and the 3DOM structure was mainly constructed by numerous TiO$_2$ nanocrystals of around 10 nm (Figure 2b). The crystallinity and intimate contact of the three components can be identified using high resolution transmission electron microscopy (HR-TEM) (Figure 2c). The Au NPs are partially covered by CdS, which could enhance significantly the dual roles of Au NPs in this ternary photocatalyst. The part of the Au covered by CdS could construct the charge transfer channels between CdS and TiO$_2$, while exposed Au would enhance visible light absorption by the LSPR effect to provide additional hot electrons. The selected area electron diffraction (SAED) pattern further reveals the presence of these three material components in the photocatalyst (Figure 2d).

The crystal structure and crystallinity of 3DOM TiO$_2$-Au-CdS were then investigated by X-ray diffraction (XRD) (Figure 3a). The results clearly show the typical peaks of the anatase phase of TiO$_2$, which were obtained after calcination at 550 °C, while the shoulder peak at around 28.2° (2 theta) revealed the hexagonal phase of CdS (Figure 3a). Typical peaks for Au NPs were not observed in the XRD pattern, which is mainly due to the low content of Au in the composite material (0.65 wt% as determined by ICP). In order to further reveal the presence of Au in the as-prepared photocatalyst, X-ray photoelectron spectroscopy (XPS) was performed (Figure 3b). The two peaks detected at 83.1 eV and 86.7 eV were ascribed to Au 4f7/2 and Au 4f5/2, with splitting energies of 3.0 eV and an area ratio of 4:3, revealing the metallic state of the Au NPs (Figure 3b) [31–33].
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The light absorption of the as-fabricated 3DOM TiO$_2$-Au-CdS and each of the components were investigated by UV-vis spectroscopy (Figure 4). Due to the large bandgap of TiO$_2$ (anatase, 3.2 eV) and the narrow bandgap of CdS (2.4 eV), the composite can theoretically absorb both UV and visible light. The light absorbance spectrum shows the typical absorption edges at around 380 nm and 517 nm (Figure 4a), which are attributed to the intrinsic band gaps of 3.26 eV and 2.40 eV for TiO$_2$ and CdS [13]. Due to the localized surface plasmon resonance (LSPR) effect of Au NPs, the as-fabricated photocatalyst also exhibits light absorbance at wavelengths longer than 520 nm. The LSPR of gold NPs of 20 nm is typically centered at 520 nm (Figure 4b) [34]. The red shift of LSPR in the composite is due to the strong electromagnetic coupling of Au with TiO$_2$ and CdS [11]. Considering
all of the above characterization results, we can conclude that the 3DOM TiO$_2$-Au-CdS material with extended light absorption was successfully prepared as expected.

![Figure 4](image_url)

**Figure 4.** UV-vis light apparent absorbance spectrum of (a) 3DOM TiO$_2$-Au-CdS and (b) individual TiO$_2$, Au, and CdS.

The performance of the prepared 3DOM TiO$_2$-Au-CdS was evaluated in photocatalytic hydrogen production from glucose, cellobiose, and dissolving pulp, respectively. It should be noticed that glucose is the component unit of cellulose, cellobiose is the structure unit of cellulose (as it has the typical $\beta$-1,4-glycosidic linkage), and dissolving pulp is the typically pretreated cellulose in industry [35]. It is noteworthy that the reaction was performed at room temperature without any way to control the reaction temperature. The pH was not controlled (about pH~7), and the reaction was performed with stirring. The photocatalytic hydrogen production in Figure 5a exhibits an almost linear relation with the reaction time, with glucose as the electron donor showing the highest hydrogen production after 5 h of reaction. For the disaccharide of cellobiose, the photocatalytic hydrogen production was reduced, and it further decreased when dissolving pulp was used as the substrate. These results clearly reveal that the structural complexity and molecular size of substrates greatly affect photocatalytic hydrogen production performance, which is mainly attributed to the reduced accessibility of substrates to the photocatalyst surface. Along with H$_2$, CO and CH$_4$ were also observed during the photoreforming process, indicating the further conversion of the substrates and their intermediates in subsequent reactions. Interestingly, glucose and cellobiose showed a similar amount of CO over 3DOM TiO$_2$-Au-CdS (Figure 5b). Meanwhile, for the production of CH$_4$, the performances were similar for cellobiose and dissolving pulp (Figure 5c). The photocatalytic rates for the generation of gaseous products are summarized in Figure 5d. In total, 645.1 $\mu$mol h$^{-1}$ g$^{-1}$, 273.9 $\mu$mol h$^{-1}$ g$^{-1}$, and 79.7 $\mu$mol h$^{-1}$ g$^{-1}$ of hydrogen production were achieved when glucose, cellobiose and dissolving pulp were used as the electron donors, respectively. The theoretical amounts of H$_2$, CO or CH$_4$ from glucose should be 1 mmol, respectively. However, the detected H$_2$, CO or CH$_4$, even after an 8-h reaction, was much lower than the theoretical values, indicating the low substrate conversion into gaseous products, or the partial conversion of these substrates into other liquid chemicals. The apparent quantum yield of 3DOM TiO$_2$-Au-CdS was investigated under 450 nm monochromatic light in the presence of cellobiose and Na$_2$S/Na$_2$SO$_3$ as the sacrificial agents. Cellobiose is the structural unit of cellulose, which was chosen as the model to show that our photocatalyst also had the ability to produce hydrogen with certain quantum efficiency from the cellulose model component. The calculated apparent quantum yield in the case of Na$_2$S/Na$_2$SO$_3$ as the sacrificial agent was 6.9%, which is similar to our previous investigation [16]. When the sacrificial agent was switched to cellobiose, the apparent quantum yield significantly decreased to 0.05%, further demonstrating the slow kinetic process of biomass photoreforming [36]. It can be
confirmed that the H₂ was from water in presence of Na₂S/Na₂SO₃ as the sacrificial agent; this is more complicated regarding the source of the hydrogen in the presence of glucose, cellobiose and dissolving pulp, as these substrates also contain hydrogen atoms.

The hydrogen production is triggered by the proton reduction reaction of photogenerated electrons. In a neutral condition, the produced hydrogen is mainly from glucose and water; in an acidic aqueous solution, the presence of free hydrogen ions has more reactivity to generate hydrogen [37,38]. Herein, it could be foreseen that acidic conditions with a higher concentration of protons should be more beneficial for hydrogen production. The reaction was then investigated using different pH values in the reaction solution, which was just controlled and measured at the beginning of the photocatalytic reaction. As expected, Figure 6a clearly shows that acidic conditions contribute to hydrogen production. The highest hydrogen production rate was achieved at pH = 1 with 4648 µmol·h⁻¹·g⁻¹. However, the pH values have a negligible effect on the production of CO and CH₄. The CO and CH₄ production is probably due to the oxidation reaction of substrates caused by the photogenerated holes. The photocatalytic activity from glucose was compared with the same concentration of isopropanol, which is the typical electron donor for hydrogen production (Figure 6b). This shows that H₂ (2050 µmol·h⁻¹·g⁻¹) and CH₄ (1812 µmol·h⁻¹·g⁻¹) were significantly enhanced when the substrate was changed from glucose to isopropanol, indicating that glucose has less access to the photocatalyst than isopropanol, or that the C-X bonds in glucose are more recalcitrant. In summary, the current results demonstrate the feasibility of photocatalytic hydrogen production by using biomass to substitute traditional sacrificial agents. However, further improvements in photocatalytic efficiency must be pursued in order to increase biomass conversion.
3. Experimental Section

3.1. Materials

All of the reagents in the experiments were of analytical grade, and were commercially available: methanol (CH$_3$OH, 99.8%, CAS number: 67-56-1, catalog number: 179337-1L), titanium (IV) isopropoxide (TTIP, C$_{12}$H$_{28}$O$_4$Ti, 97%, CAS number: 546-68-9, catalog number: 205273-100ML), sodium hydroxide (NaOH, 98%, CAS number: 1310-73-2, catalog number: S5881-500G), hydrochloric acid (HCl, 37%, CAS number: 7647-01-0, catalog number: 320331-500ML), potassium persulfate (K$_2$S$_2$O$_8$, 99%, CAS number: 7727-21-1, catalog number: 216224-100G), trisodium citrate (C$_6$H$_{5}$Na$_3$O$_7$, 99%, CAS number: 6132-04-3, catalog number: S4641-500G), chloroauric acid (HAuCl$_4$, 50% Au basis, CAS number: 27988-77-8, catalog number: 50790-1G), sodium sulfide nonahydrate (Na$_2$S·9H$_2$O, 98%, CAS number: 1313-84-4, catalog number: 642045-100G), and sodium sulfite (Na$_2$SO$_3$, 98%, CAS number: 7757-83-7, catalog number: S0505-250G) were purchased from Aldrich Industrial Co., Ltd. (Wuxi, China), and were used without any further purification.

3.2. 3DOM TiO$_2$-Au-CdS

In total, 1 mL hydrochloric acid was mixed with 5 mL methanol. Then, 5 mL TIPT was added dropwise at room temperature, with stirring. Next, 2 mL DI water was added dropwise to prepare the precursor of TiO$_2$. A polystyrene colloidal template was prepared according to our previous reports [11,13]. In total, 5 g dried polystyrene colloidal template was placed in a Buchner funnel with a filter paper (pore size: 30–50 μm) and the prepared precursor was added while a vacuum was applied to the Buchner funnel. After 8 h to achieve the complete hydrolysis of the precursor in the voids, a fresh precursor was again added into the Buchner funnel, and this process was repeated three times. After air-drying the mixture of precursor and template at ambient conditions, the three dimensionally ordered macroporous (3DOM) TiO$_2$ could be obtained after calcination in a muffle furnace at 300 °C for 2 h, 400 °C for 2 h and 550 °C for 2 h using a heating rate of 2 °C/min in static air conditions. It is noteworthy that there is a glass transition temperature (300 °C) of polystyrene spheres, and the precursor should be partially crystallized in order to maintain the three dimensionally ordered macroporous structure. The 400 °C temperature was intended was to remove the organic polystyrene spheres, and 550 °C was used to achieve a good crystallinity. In total, 0.2 mL of 1% HAuCl$_4$ solution and 0.5 g of 3DOM TiO$_2$ were

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**Figure 6.** (a) Photocatalytic gas production with different pHs; (b) comparison of the gas production between glucose and isopropanol. Reaction conditions: 10 mg photocatalyst, 15 mL 2 g/L aqueous solution with glucose or isopropanol, and a 300 W xenon lamp.
mixed with 100 mL water in a two-necked flask. Then, the mixture was heated to boiling, with stirring. In total, 1.5 mL trisodium citrate solution (10 g/L) was added rapidly to the boiling solution in order to reduce the HAuCl$_4$ to gold nanocrystals, and another 1.5 mL trisodium citrate solution was added rapidly after 15 mins to promote the growth of the gold nanocrystals into nanoparticles. The overall mixture was stirred for another 1 h in the boiling condition and cooled down to room temperature. A purple 3DOM TiO$_2$-Au sample was obtained after filtration, then washed three times with DI water (20 mL in each washing process) and dried in a static-air oven at 60 $^\circ$C overnight. Au NPs in solution for UV-vis characterization were prepared by the same process without the addition of 3DOM TiO$_2$. In total, 100 mg 3DOM TiO$_2$-Au was immersed into 20 mL of 0.05 M Cd(NO$_3$)$_2$ aqueous solution in a 100 mL beaker with magnetic stirring for 0.5 h, and then 20 mL 0.05 M Na$_2$S solution was added dropwise. The suspension was stirred for another 2 h at room temperature before filtration, washed with 50 mL DI water, and dried in a static-air oven in a plastic petri dish at 60 $^\circ$C overnight to obtain the final 3DOM TiO$_2$-Au-CdS photocatalyst. Pure CdS for UV-vis characterization was also prepared by the same process without the addition of 3DOM TiO$_2$-Au.

3.3. Characterization

The crystalline phase was determined by power X-ray diffraction (XRD) with a D8 ADVANCE instrument (Bruker, Berlin, Germany) at 40 kV, 40 mA, and equipped with a Cu anode X-ray tube (Cu K$_\alpha$ X-rays, $\lambda = 1.54056$ Å). The morphology was observed using a field-emission scanning electron microscope (SEM, S-4800, Hitachi, Tokyo, Japan) and a transmission electron microscope (TEM, FEI Talos, Waltham, MA, USA). X-ray photoelectron spectroscopy (XPS) was performed on an Escalab 250Xi (Thermo Scientific, Waltham, MA, USA) to check the chemical state of Au NPs. The UV-vis light diffuse reflectance spectrum was recorded on a SHIMADZU (Kyoto, Japan) UV–Vis spectrophotometer in the range of 200–800 nm, with BaSO$_4$ as the reference.

3.4. Photocatalytic H$_2$ Generation

The photoreactor used was home-made; it can found in our previous work [12]. In total, 10 mg of the photocatalyst was added into 15 mL of a 2g/L solution with different substrates (glucose, cellobiose, dissolving pulp, isopropanol). The suspension was sonicated and degassed for 0.5 h before the photocatalytic reaction using a vacuum pump (VEVOR 12CFM, VEVOR, Shanghai, China). A 300 W xenon lamp (Excelitas Tech., Mississauga, ON, Canada) was used as the light source, and the spectrum was in the range of 300 nm to 1100 nm, which was the simulated solar light. It is noteworthy that the reaction was performed at room temperature without any way to control the reaction temperature. The pH was not controlled, and the reaction was performed with stirring. A bandpass filter with 450 nm (DT450, Perfectlight, Beijing, China) was used to provide the monochromatic 450 nm light. The gas products were collected with a syringe, and were quantified periodically using a gas chromatograph (GC, Agilent 7890B, Santa Clara, CA, USA) with a thermal conductivity detector (TCD). The reaction was performed at room temperature without any way to control the reaction temperature.

4. Conclusions

In summary, a 3DOM TiO$_2$-Au-CdS composite was successfully prepared using a colloidal template method, and this photocatalyst showed the ability to absorb both UV and visible light due to the intrinsic bandgap structures of TiO$_2$ and CdS. Besides this, the LSPR effect of Au NPs also contributed to the visible light absorbance with a wavelength longer than 520 nm. The as-fabricated photocatalytic exhibited good performance for hydrogen production by the photoreforming of biomass substrates such as glucose, cellobiose and dissolving pulp. Specifically, 645.1 $\mu$mol·h$^{-1}$·g$^{-1}$ H$_2$ was obtained from glucose photoreforming, along with some other gaseous products (CO and CH$_4$). The photocatalytic performance decreased when the substrates were changed to more complex
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cellulbiose and dissolving pulp. Although the accessibility of biomass to the photocatalyst is less ideal than that of isopropanol, this present work demonstrates the feasibility of sustainable hydrogen production through a biomass photoreforming process.

**Author Contributions:** X.Y. and N.Z. performed the experiment and drafted the original version. H.Z. contributed to the data analysis and characterizations. H.Z. and J.H. reviewed and revised the manuscript. J.H. and I.D.G. supervised this project and provided funding. All authors have read and agreed to the published version of the manuscript.

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