Hierarchical Heterostructure of ZnO@TiO2 Hollow Spheres for Highly Efficient Photocatalytic Hydrogen Evolution

Yue Li 1, Longlu Wang 2*, Jian Liang 1, Fengxian Gao 1, Kai Yin 2 and Pei Dai 1

Abstract

The rational design and preparation of hierarchical nanoarchitectures are critical for enhanced photocatalytic hydrogen evolution reaction (HER). Herein, well-integrated hollow ZnO@TiO2 heterojunctions were obtained by a simple hydrothermal method. This unique hierarchical heterostructure not only caused multiple reflections which enhances the light absorption but also improved the lifetime and transfer of photogenerated charge carriers due to the potential difference generated on the ZnO–TiO2 interface. As a result, compared to bare ZnO and TiO2, the ZnO@TiO2 composite photocatalyst exhibited higher hydrogen production rate up to 0.152 mmol h⁻¹ g⁻¹ under simulated solar light. In addition, highly repeated photostability was also observed on the ZnO@TiO2 composite photocatalyst even after a continuous test for 30 h. It is expected that this low-cost, nontoxic, and readily available ZnO@TiO2 catalyst could exhibit promising potential in photocatalytic H₂ to meet the future fuel needs.

Keywords: ZnO, TiO2, Hollow sphere, Hierarchical, Heterojunction, Hydrogen production

Background

Hydrogen (H₂), one of the most important clean and sustainable energy, has been regarded as a promising alternative energy for meeting future fuel needs [1–5]. Since the discovery of photoelectrochemical (PEC) water-splitting system by Fujishima and Honda in the 1970s [6], the production of H₂ based on TiO2 semiconductor photocatalysts using sunlight has attracted increasing attention. However, the practical application of single bare TiO₂ in the industry is still a challenge due to the high-rate recombination of photogenerated electrons and holes at the surface of TiO₂ results in a low quantum efficiency. To date, many efforts have been made to design TiO₂-based composite photocatalysts to solve the above issues, such as coupling with another semiconductor, doping transition metal ions or nonmetal atoms, and so on [7–9]. In particular, the formation of semiconductor–semiconductor heterojunctions with matching band potentials is an effective way to prevent the charge recombination and increase the lifetime of the charge carriers [10–12].

Among the various semiconductors, ZnO is also extensively studied because of its identical properties of TiO2 with non-toxicity, cheapness, high efficiency, and chemical stability [13, 14]. Since the conduction band (CB) and valence band (VB) of ZnO lie above those of TiO₂, the photogenerated electrons in ZnO will be transferred to TiO₂ once a heterojunction was formed between TiO₂ and ZnO. This kind of ZnO@TiO2 composite heterojunction will benefit for the separation of photogenerated electron–hole pairs, thus leading more electrons accumulated on the TiO₂ which will react with H₂O to generate H₂ [15–17].

In addition to the above we have discussed, geometric shapes and morphologies of the photocatalysts also heavily influence the hydrogen evolution reaction (HER) performance [18–20]. It is has been reported that the diffractions on the hollow spheres and the multiple reflections due to the shell structure would enhance the effectiveness of light utilization [21]. For example, Li’s group prepared hydrogenated cage-like titania hollow spheres exhibited much higher HER activities than solid structure [22]. Beyond that, the spherical hollow structures have the advantages...
of large specific surface area, reduced transport lengths for charge carriers, and good chemical and thermal stability, which all contribute to the excellent photocatalytic ability [23]. However, most of the research has focused on the preparation of composite hollow spheres by doping transition element, such as Ce–ZnO [24], Ni–ZnO [25], Ag–TiO2 [26], Au–TiO2 [27], and so on. To the best of our knowledge, few studies reported on the synthesis of closed, complete, and intact hollow spheres composed of mixed metal oxides porous particles. Even so, most of these composites are applied in photocatalytic degradation of organic pollutants but not in the photocatalytic hydrogen production.

In this paper, we reported a facile method to synthesize hierarchically porous ZnO@TiO2 composite hollow microspheres and applied them in the photocatalytic H2. The hollow spheres enhanced the light absorption by multiple reflections, at the same time, the lifetime and transfer rate of photogenerated charge carriers were also improved due to the potential difference generated on the ZnO–TiO2 interface. The result showed that the ZnO@TiO2 composite photocatalyst exhibited enhanced H2 evolution rate, compared to the bare ZnO and TiO2. In addition, the mechanism of the photocatalytic H2 on the ZnO@TiO2 composite hollow spheres was discussed in detail.

Methods

Synthesis of the Hierarchical ZnO@TiO2 Hollow Spheres

The preparation of ZnO@TiO2 composites was based on a very facile one-step template-free hydrothermal method at ambient conditions. In a typical procedure, 0.015 mol of Ti(SO4)2, 0.015 mol of Zn(NO3)2·6H2O, 0.015 mol of NH4F, and 0.06 mol of CO(NH2)2 were added to a beaker with 50 mL deionized water. After stirring for 60 min, the mixture solution was transferred into a Teflon-lined stainless steel autoclave and heated in an electric oven at 180 °C for 12 h. After that, the white precipitate was thoroughly washed with ethanol four times and then dried at 60 °C for 12 h to obtain ZnO@TiO2 heterostructures. For comparison, bare TiO2 and ZnO were prepared under the same conditions.

Synthesis of Pt–ZnO@TiO2 Samples

In a typical synthesis process of Pt–ZnO@TiO2 samples, the ZnO@TiO2 hollow spheres were put into a container containing 10 vol% triethanolamine and H2PtCl6 solution. Then, the system was bubbled with nitrogen for 30 min to remove the air. Finally, the Pt was in situ photodeposited on the ZnO@TiO2 hollow spheres under a full arc light irradiation (λ > 300 nm) for 2 h. The Pt content can be tuned by the concentration of H2PtCl6 and the reaction time, which was determined by inductively coupled plasma (ICP, PE5300DV).

Characterization

The morphology of ZnO@TiO2 heterostructures was characterized via field emission scanning electron microscope (FESEM, Hitachi, Japan), transmission electron microscopy (TEM, Tecnai F20), high-angle annular dark field scanning TEM (STEM, Tecnai F20), and high-resolution TEM (HRTEM, Tecnai F20). The energy-dispersive X-ray spectroscopy (EDS) mapping images were captured on a Tecnai G2 F20 S-TWIN atomic resolution analytic microscope. The crystal phase properties of the samples were characterized using an X-ray diffractometer with Cu–K radiation (XRD, M21X, MAC Science Ltd., Japan). The BET specific surface areas were measured on Belsorp-mini II analyzer (Japan).

Photoelectrochemical Measurements

Photocurrent studies were performed on a CHI 660D electrochemical workstation, using a three-electrode configuration where fluorine-doped tin oxide (FTO) electrodes deposited with the samples as working electrode, Pt as counter electrode, and a saturated calomel electrode.
(SCE) as reference. The electrolyte was 0.35 M/0.25 M Na2S–Na2SO3 aqueous solution. For the fabrication of the working electrode, 0.25 g of the sample was grinded with 0.06 g polyethylene glycol (PEG, molecular weight 20,000) and 0.5 mL ethanol to make a slurry. Then, the slurry was spread onto a 1 × 4 cm FTO glass by the doctor blade technique and then allowed to dry in air. A 300 W xenon arc lamp served as a simulated solar light irradiation source (Perfectlight, PLS-SXE 300C, Beijing, China). The incident light intensity was tuned to be 100 mW/cm² measured by NOVA Oriel 70260 with a thermodetector.

Photocatalytic Hydrogen Production Tests

Photocatalytic hydrogen production experiments were performed in a sealed quartz flask at ambient temperature and under atmospheric pressure. A 300 W xenon arc lamp (Perfect light, PLS-SXE 300C, Beijing, China) was used as the light source to trigger the photocatalytic reaction. The evolved H₂ were collected and online-analyzed by a H₂-solar system (Beijing Trusttech Technology Co., Ltd.) with a gas chromatogram equipped with a thermal conductivity detector (TCD), 5A molecular sieve column, and nitrogen as the carrier gas. All photocatalytic experiments over 100 mg photocatalyst were performed in an aqueous solution containing H₂O (80 mL) and alcohol (20 mL). Prior to irradiation, the system was deaerated by bubbling nitrogen for 15 min. During the photocatalytic reaction, the reactor was tightly sealed to avoid gas exchange.

Results and Discussion

The size and morphology of the as-prepared ZnO@TiO₂ hollow spheres were displayed in Fig. 1. Figure 1a shows the sample has a uniform spherical morphology with a mean diameter about 1.45 μm according to the nanoparticle size distribution (inset of Fig. 1a). Figure 1b reveals a single broken sphere, indicating that the prepared sample is a hollow structure composed of small particles. TEM image was further used to confirm the structure of the ZnO@TiO₂ hollow spheres. The color change of the ZnO@TiO₂ spheres at the center and the outside realm was dark and bright, respectively, confirming the ZnO@- TiO₂ spheres were hollow structure (Fig. 2a). A high-magnified view in Fig. 2b also depicts the surface of the hollow spheres was rough which were constructed by nanoparticles subunits, as a result in the formation of the hierarchical heterostructure of ZnO@TiO₂ hollow spheres. The elemental maps in Fig. 2(d–f) were used to confirm the elemental distribution in the ZnO@TiO₂
hollow spheres. It can be seen that the Zn, Ti, and O were uniformly distributed in ZnO@TiO$_2$ hollow spheres.

HRTEM images in Fig. 3 verified the heterojunction structure of ZnO@TiO$_2$ hollow spheres. The selected areas in Fig. 3a marked by white square were magnified in Fig. 3b–d, corresponding to ZnO, TiO$_2$, and ZnO@TiO$_2$ heterojunction. The lattice spacing distances of 0.28 and 0.35 nm were corresponding to the (100) planes of wurtzite ZnO and (101) planes of the anatase TiO$_2$, respectively, as shown in Fig. 3b, c. Figure 3d shows a clear transition from wurtzite ZnO phase to anatase TiO$_2$ phase, which confirmed the heterojunction was formed at the interface between ZnO and TiO$_2$. Such heterojunction structure can greatly promote the photoexcited electron transfer for enhanced photocatalytic activity.

The pore structure properties of ZnO, TiO$_2$, and ZnO@TiO$_2$ samples were further determined by the N$_2$ adsorption–desorption isotherms and corresponding Barrett–Joyner–Halenda (BJH) pore size distribution plots (Fig. 4). All the samples showed a type IV isotherm.

All the measurement was carried out under a simulated solar light irradiation source with intensity of 100 mW/cm$^2$.
with a hysteresis loop at a high relative pressure ($P/P_0 > 0.7$), demonstrating the existence of mesoporous structures according to International Union of Pure and Applied Chemistry (IUPAC) classification. The inset of Fig. 4 is BJH pore size distribution plots, which further indicated that all the samples have the mesoporous structures. Meanwhile, the calculated BET surface areas of the ZnO@TiO$_2$ microsphere was about 102 m$^2$ g$^{-1}$, which was much larger than that of ZnO (23 m$^2$ g$^{-1}$) and TiO$_2$ (35 m$^2$ g$^{-1}$). It can be concluded the introduction of ZnO into TiO$_2$ to form the ZnO@TiO$_2$ hollow spheres could increase the surface areas greatly, although all the samples have the mesoporous structures. The higher surface areas of ZnO@TiO$_2$ hollow spheres would provide more sites for enhanced catalytic H$_2$ performance.

The photocatalytic ability of the as-prepared samples was evaluated by photocurrent and photocatalytic H$_2$ tests. As shown in Fig. 5a, the ZnO@TiO$_2$ hollow spheres yielded the highest photocurrent density of 3.38 mA/cm$^2$, which was more than 2.61, 2.17 times higher than that of ZnO and TiO$_2$, respectively. These results mean the stronger ability of producing charge carriers and improved separation efficiency of ZnO@TiO$_2$ hollow spheres. As excepted, the hydrogen production rate of ZnO@TiO$_2$ hollow spheres reached to 0.152 mmol h$^{-1}$ g$^{-1}$, higher than the 0.039 mmol h$^{-1}$ g$^{-1}$ of ZnO and 0.085 mmol h$^{-1}$ g$^{-1}$ of TiO$_2$ (Fig. 5b). Pt, as a very high-efficiency noble metal cocatalyst, has been widely used for H$_2$ evolution reaction in the reported literature [8, 11]. A series of Pt–ZnO@TiO$_2$ with different Pt contents were prepared and compared in Fig. 5c. It was shown that the loading of Pt onto ZnO@TiO$_2$ hollow spheres could significantly enhance the H$_2$ evolution activity and the sample with 1.5 at % Pt exhibiting the highest H$_2$ evolution rate. Figure 5d shows that the ZnO@TiO$_2$ hollow spheres still retained its original photocatalytic activity without noticeable degradation in the five reaction cycles for 30 h, which demonstrates the exceptional photocatalytic stability.

A photocatalytic mechanism was proposed for the improved HER activity of the ZnO@TiO$_2$ hollow spheres, as shown in Fig. 6. Under simulated solar light irradiation, the electrons of both ZnO and TiO$_2$ were excited from their valence bands (VB) to their conduction bands (CB). Since the conduction band (CB) and valence band (VB) of ZnO were more positive than those of TiO$_2$, the photogenerated electrons transferred from ZnO to TiO$_2$ through the intimate interfacial contacts [16]. Then, the more accumulated electrons on the TiO$_2$ reacted with H$_2$O for generating H$_2$ for the higher photocatalytic H$_2$ rate (as shown on the right of Fig. 6). At the same time, the photogenerated holes in the VB of TiO$_2$ migrated to ZnO, which were trapped by the sacrificial agent to keep the thermodynamical balance. Additionally, the hierarchical hollow spheres benefit for light scatter and multiple reflections among ZnO@TiO$_2$ composite photocatalyst, which would enhance the effectiveness of light utilization [10, 21, 22]. Thus, more free electrons and holes would be generated due to the increased effective photon path length [21, 22], leading to a higher HER efficiency (as shown in the left of Fig. 6).

**Conclusions**

In summary, the hierarchical heterostructure of ZnO@TiO$_2$ hollow spheres has been successfully prepared via a simple hydrothermal method. Compared to bare ZnO and TiO$_2$, the ZnO@TiO$_2$ composite photocatalyst exhibited high hydrogen production rated up to 0.152 mmol h$^{-1}$ g$^{-1}$ under simulated solar light. It is believed that hierarchical heterostructure increased the surface area which proving more active sites for effective
HER and simultaneously improved the lifetime and transfer of photogenerated charge carriers due to the potential
difference generated on the ZnO–TiO₂ interface. Moreover, the ZnO@TiO₂ composite photocatalyst
exhibited good durability even after being reused five
times. This work demonstrated a good prospect for photocatalytic H₂ evolution from water based on the
rational use and preparation of high activity, inexpensive, and chemical stability of ZnO and TiO₂.

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Authors’ Contributions
The concept was developed by WLL and LY. This manuscript was written by
LY and WLL. The experiment and the data analysis were carried out by G FY,
WLL, and LY. The preparation of samples is performed by LJ, DP, and YT. The
characterization of samples are made by YK and G FY. All authors read and
approved the final manuscript.

Competing Interests
The authors declare that they have no competing interests.

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Author details
1 School of Materials and Chemical Engineering, Henan University of
Engineering, Zhengzhou 451191, Henan, People’s Republic of China.
2 State Key Laboratory of Chemo/Biosensing and Chemometrics, Hunan University,
Changsha 410082, People’s Republic of China.

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