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Communication

3D flower-like heterostructured $\text{TiO}_2/\text{Ni}(\text{OH})_2$ microspheres for solar photocatalytic hydrogen production

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ABSTRACT

$\text{TiO}_2/\text{Ni}(\text{OH})_2$ core-shell microspheres were synthesized by a facile strategy to obtain a perfect 3D flower-like nanostructure with well-arranged $\text{Ni}(\text{OH})_2$ nanoflakes on the surfaces of TiO_2 microspheres; this arrangement led to a six-fold enhancement in photocatalytic hydrogen evolution. The unique p-n type heterostructure not only promotes the separation and transfer of photogenerated charge carriers significantly, but also offers more active sites for photocatalytic hydrogen production. A photocatalytic mechanism is proposed based on the results of electrochemical measurements and X-ray photoelectron spectroscopy.

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Titanium dioxide (TiO_2) has been considered as one of the most promising photocatalysts over the past few decades because of its availability, low cost, photostability, and non-toxicity [1–7]. However, the large binding energy of the excitons (130 meV) and the relatively fast electron-hole recombination severely limit its photon-to-electricity conversion efficiency and, consequently, the photocatalytic performance [8–15]. Loading a cocatalyst is a simple and facile way of promoting the separation and transfer of photogenerated charge carriers. Much effort has recently been devoted to seeking low-cost transition-metal cocatalysts, besides the conventional noble metals. Ni compounds such as NiO, NiS, and $\text{Ni}(\text{OH})_2$ are the most promising candidates [16–22]. Yoshikawa et al. [23] reported that NiO nanoparticles can largely enhance photocatalytic hydrogen production over mesoporous TiO_2 . Xu et al.

[24] showed that NiS is highly efficient in promoting photocatalytic hydrogen production over CdS nanoparticles. $\text{Ni}(\text{OH})_2$ has received more attention owing to the controllable shapes and hydrogen evolution properties [25–30]. Furthermore, as a p-type semiconductor, $\text{Ni}(\text{OH})_2$ is also an ideal host material for fabricating p-n type heterostructures at the interfaces of oxide semiconductors, where the formed internal electric field is able to efficiently separate the charge carriers, consequently leading to enhancements in the photon-to-electricity conversion efficiency and solar photocatalytic hydrogen evolution and production [16,31].

In this work, we report a solvothermal approach combined with oil-bath-based chemical synthesis to prepare a 3D flower-like $\text{TiO}_2/\text{Ni}(\text{OH})_2$ core-shell heterostructure, through which a six-fold increase in hydrogen production is obtained.

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Fig. 1. FESEM images (a and b), TEM and HRTEM images (c and d), and the mapping images (e–h) of $\text{TiO}_2@\text{Ni}(\text{OH})_2$ samples. The insert image in Fig. 1a shows the FESEM images of TiO_2 microspheres.

First, anatase (TiO_2) microspheres were prepared via the solvothermal pathway reported in the literature [32], and then, 50 mg of the as-prepared TiO_2 microspheres was dispersed in 200 mL of deionized (DI) water and stirred for 30 min. Afterwards, 2.5 mmol of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 2.5 mmol of hexamethylenetetramine, and 0.25 mmol of citric acid trisodium salt dehydrate were well dissolved in the above dispersion and continuously stirred at room temperature for 1 h. The resulting solution was then heated at 363 K in an oil-bath for 12 h with slow stirring. After the growth of $\text{Ni}(\text{OH})_2$ on TiO_2 , the products were separated by centrifugation, and washed several times with DI water and ethanol. The 3D flower-like $\text{TiO}_2@\text{Ni}(\text{OH})_2$ samples were finally obtained after being dried at 333 K for 12 h.

The morphology and structure of the as-prepared $\text{TiO}_2@\text{Ni}(\text{OH})_2$ microspheres were characterized by field-emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) analyses. The TiO_2 microspheres show uniform morphology and sphere sizes of ca. 1–2 μm , based on the insert image shown in Fig. 1a. Fig. 1a

and 1b show the typical FESEM images of the as-prepared $\text{TiO}_2@\text{Ni}(\text{OH})_2$ samples that exhibit a perfect 3D flower-like nanostructure with well-arranged $\text{Ni}(\text{OH})_2$ nanoflakes on the surfaces and well-knit core-shell morphologies. However, there are no obvious lattice fringes in the HRTEM image, indicating that the $\text{Ni}(\text{OH})_2$ nanosheets exhibit weak crystallinities (Fig. 1c and 1d). From the HAADF-STEM image and the corresponding EDS mapping spectra (Fig. 1e–1h), homogeneous distributions of elemental Ni and Ti in the shell layer and the core, respectively, are observed, confirming the perfect formation of the core-shell heterostructure. Meanwhile, the loading of $\text{Ni}(\text{OH})_2$ was ca. 18.47%, calculated based on the atomic ratio of Ni to Ti (4.64:23.77), which was determined from the EDS mapping results.

The crystal structure and composition of the as-prepared samples were analyzed by powder XRD, as shown in Fig. 2a. The dominant peaks, centered at 33.4° and 59.7° , correspond to the diffraction peaks of (101) and (110) that are indexed to the characteristic peaks of $\text{Ni}(\text{OH})_2$ standard (JCPDS no. 38-0715) [33]. All the peaks of the as-prepared TiO_2 indicate that the sample contains the pure tetragonal anatase phase (JCPDS no. 21-1272). After enwrapping the $\text{Ni}(\text{OH})_2$ nanosheet shells on the surface of the TiO_2 substrate, the intensities of the characteristic diffraction peaks obviously decreased, and two new diffraction peaks, centered at 33.4° and 59.7° and attributed to $\text{Ni}(\text{OH})_2$, can be observed, which confirmed the successful synthesis of $\text{TiO}_2@\text{Ni}(\text{OH})_2$. In order to investigate the change in the optical properties, the UV-vis diffuse reflectance spectroscopy (UV-vis DRS) patterns of the TiO_2 , $\text{Ni}(\text{OH})_2$, and $\text{TiO}_2@\text{Ni}(\text{OH})_2$ samples were examined, as shown in Fig. 2b. Pristine TiO_2 shows bandgap absorption at ca. 380 nm, corresponding to a bandgap energy of ca. 3.2 eV. It is notable that upon enwrapping the $\text{Ni}(\text{OH})_2$ shells, the photoresponse of TiO_2 significantly extends up to the visible-light region. As for the $\text{TiO}_2@\text{Ni}(\text{OH})_2$ samples, the absorptions observed in the region ca. 600–800 nm and at ca. 450 nm can be assigned to the $\text{Ni}(\text{II})$ d - d transition and the direct interfacial charge transfer (IFCT) that occurs from the VB of TiO_2 to that of $\text{Ni}(\text{II})$ [34]. Fig. 3 shows the N_2 adsorption/desorption isotherms and pore-size distribution curves of the TiO_2 and $\text{TiO}_2@\text{Ni}(\text{OH})_2$ samples. The special surface area of the $\text{TiO}_2@\text{Ni}(\text{OH})_2$ samples is $111.24 \text{ m}^2 \text{ g}^{-1}$, which is attributed to their flower-like structures with ra-

Fig. 2. (a) XRD patterns and (b) UV-vis absorption spectra of $\text{Ni}(\text{OH})_2$, $\text{TiO}_2@\text{Ni}(\text{OH})_2$, and TiO_2 samples.

Fig. 3. N_2 adsorption-desorption isotherms and pore-size distribution curves of the TiO_2 and $TiO_2@Ni(OH)_2$ samples.

dially aligned nanosheets, and is much higher than that of the TiO_2 microspheres ($49.4838 \text{ m}^2 \text{ g}^{-1}$). After enwrapping the $Ni(OH)_2$ shells on the TiO_2 surface, the pore size is *ca.* 7.35 nm, as obtained from the pore-size distribution curves. These results demonstrate that the $Ni(OH)_2$ shells offer more active sites for photocatalytic hydrogen production.

All the as-prepared photocatalysts were evaluated in terms of their photocatalytic hydrogen production capabilities. The photocatalytic hydrogen evolution experiments were performed in a relatively evacuated system by using an external glass reaction cell. In a typical experiment, 0.1 g of the photocatalyst and 0.5 g of EDTA- Na_2 , used as a sacrificial reagent, were suspended in 100 mL of an aqueous solution subjected to magnetic stirring and the temperature of the glass reaction cell was maintained at about 278 K by circulating water. Fig. 4a shows the variations in the amounts of hydrogen evolved over $Ni(OH)_2$, TiO_2 , and $TiO_2@Ni(OH)_2$ samples that were stimulated through solar irradiation. The separated $Ni(OH)_2$ photocatalyst shows a small hydrogen production activity ($3.66 \text{ } \mu\text{mol}$ within 6 h, or $0.61 \text{ } \mu\text{mol g}^{-1} \text{ h}^{-1}$). The amount of hydrogen evolved in the case of the TiO_2 photocatalyst is *ca.* $31.8 \text{ } \mu\text{mol}$ within 6 h, corresponding to a rate of $5.3 \text{ } \mu\text{mol g}^{-1} \text{ h}^{-1}$, whereas a six-fold enhancement ($205.8 \text{ } \mu\text{mol}$ within 6 h, or $34.3 \text{ } \mu\text{mol g}^{-1} \text{ h}^{-1}$) is

Fig. 5. Results of the cycling experiments on the photocatalytic hydrogen production of $TiO_2@Ni(OH)_2$.

achieved over the $TiO_2@Ni(OH)_2$ sample. It is noteworthy that the rate of hydrogen evolution reveals a gradually increasing trend, suggesting that an activation process is involved in the reaction system. This will be discussed in detail in the section on reaction mechanism. In order to further understand the role of the $Ni(OH)_2$ cocatalyst, a reference experiment was carried out as shown in Fig. 4b. $TiO_2@NiO$ sample displays a much higher hydrogen evolution rate ($10.3 \text{ } \mu\text{mol g}^{-1} \text{ h}^{-1}$) than pristine TiO_2 , suggesting that the NiO -based material is a favorable cocatalyst for hydrogen production. In order to eliminate the effect of the separated Ni^{2+} , 100 μL of 10 mg mL^{-1} aqueous $Ni(NO_3)_2$ was added into the reaction system. Remarkably, the added Ni^{2+} did not change the photocatalytic hydrogen production rate. In this system, it is possible that the added Ni^{2+} precludes the dissolution of Ni^{2+} from the $Ni(OH)_2$ nanosheets, which can promote the hydrogen evolution. These results confirm that the enhancement in the amount of photocatalytic hydrogen produced can be attributed to the role of the $Ni(OH)_2$ cocatalyst and the unique core-shell nanostructure. Fig. 5 shows the results of the cycling experiments performed for the $TiO_2@Ni(OH)_2$ photocatalyst, over which hydrogen is produced under the stimulation of solar irradiation. It clearly indicates that the $TiO_2@Ni(OH)_2$ photocatalyst does not reveal a noticea-

Fig. 4. (a) H_2 evolution and (b) photocatalytic H_2 production rate of the as-prepared samples.

Fig. 6. (a) Transient photocurrent curves and (b) Nyquist plots of $\text{TiO}_2@(\text{Ni}(\text{OH})_2)_2$ and TiO_2 samples.

ble deactivation even after four cycling tests for 24 h, implying a high stability. It was calculated that the apparent quantum yield (AQY) of the $\text{TiO}_2@(\text{Ni}(\text{OH})_2)_2$ sample for photocatalytic hydrogen evolution is ca. 0.356%, which is a six-fold enhancement compared to that (0.055%) of the bare TiO_2 sample. The AQY was calculated as $\text{AQY} = \text{number of reacted electrons/number of incident photons} \times 100\%$, or $\text{AQY} = \text{number of evolved H}_2 \text{ molecules} \times 2/\text{number of incident photons} \times 100\%$.

The overall irradiance of the Xe lamp used was 150 mW cm^{-2} , and the irradiated area was 38.47 cm^{-2} . The irradiance of the Xe lamp was measured by using a light intensity meter (ILT950).

The transient photocurrent of $\text{TiO}_2@(\text{Ni}(\text{OH})_2)_2$ was recorded to investigate the interfacial electronic interaction occurring between the $\text{Ni}(\text{OH})_2$ shell and the TiO_2 core. Fig. 6a shows the transient photocurrent curves of the $\text{TiO}_2@(\text{Ni}(\text{OH})_2)_2$ and TiO_2 photoelectrodes with several on-off cycles of the intermittent solar irradiation in 0.2 mol L^{-1} aqueous Na_2SO_4 solution. Upon illumination, the $\text{TiO}_2@(\text{Ni}(\text{OH})_2)_2$ photoelectrode shows a strong photocurrent response (ca. 6.5 μA), which is nearly 520 times higher than that of TiO_2 (ca. 12.2 nA); this confirms that the unique p-n type heterostructure and the $\text{Ni}(\text{OH})_2$ cocatalyst can promote the separation of the photogenerated charge carriers and accelerate the interfacial reaction. After several on-off cycles, there is no obvious decay in the photocurrent, further indicating the high stability of $\text{TiO}_2@(\text{Ni}(\text{OH})_2)_2$. Nyquist plots of $\text{TiO}_2@(\text{Ni}(\text{OH})_2)_2$ and TiO_2 were obtained from EIS measurements to characterize the intrinsic electronic transport properties; a simple Randles circuit model was used for fitting the data (Fig. 6b). The elements $R_{\text{ct,bulk}}$ and C_{bulk} are related to the bulk resistance and bulk capacitance corresponding to the charge transfer from the semiconductor to the electrolyte [35]. $\text{TiO}_2@(\text{Ni}(\text{OH})_2)_2$ reveals a smaller radius ($R_{\text{ct,bulk}} = 1.9 \text{ k}\Omega$) than TiO_2 ($R_{\text{ct,bulk}} = 2.5 \text{ k}\Omega$), indicating its stronger charge-transfer ability, which is in agreement with the results obtained based on their activities.

To reveal the chemical state of the elemental Ni, high-resolution XPS was carried out on the $\text{TiO}_2@(\text{Ni}(\text{OH})_2)_2$ sample before (TN-1) and after (TN-2) the photocatalytic reaction; the obtained patterns are shown in Fig. 7. For the TN-1 sample, the measured binding energies of $\text{Ni } 2p_{3/2}$ and $\text{Ni } 2p_{1/2}$

are equal to 855.6 and 873.1 eV, respectively. On the other hand, after the photocatalytic reaction proceeded for 4000 s, the spectrum of TN-2 is significantly changed. The binding energy of $\text{Ni } 2p_{3/2}$ shifts to 854.8 eV, indicating the formation of NiO, which is in good agreement with the results presented in other reports [36]. One possible explanation is that the photo-generated electrons transfer from the CB of TiO_2 to the CB of $\text{Ni}(\text{OH})_2$ and partially reduce the Ni^{2+} to Ni^0 atoms. However, these Ni atoms are unstable in air and are easily oxidized. Therefore, it is not surprising that NiO is observed in the TN-2 sample after the photocatalytic reaction. The unchanged binding energy of $\text{Ni } 2p_{1/2}$ indicates that $\text{Ni}(\text{OH})_2$ still exists in the TN-2 sample.

Based on the XPS patterns and the gradually increasing trend observed for the photocatalytic hydrogen rate, a possible mechanism has been proposed, as shown in Fig. 8. Since the potential of Ni^{2+}/Ni ($E^0 = -0.23 \text{ V}$) is slight lower than the CB energy level of TiO_2 and owing to the driving force of the electric field that is developed internally in the unique p-n type heterostructure, the photogenerated electrons will be easily transferred to $\text{Ni}(\text{OH})_2$ from the CB of TiO_2 . Therefore, when the TiO_2 sphere was irradiated by simulated solar light, the photogenerated electrons were rapidly transferred to the surface of the $\text{Ni}(\text{OH})_2$ cocatalyst, where the electrons were partially used to reduce the hydrogen protons (process I shown

Fig. 7. XPS patterns of TN-1 and TN-2 samples.

Fig. 8. The proposed photocatalytic oxidation-reduction reaction mechanism.

in Fig. 8); the remaining electrons were utilized in the reduction of Ni^{2+} (process II).

In summary, this work demonstrated the fabrication of a p-n type $\text{TiO}_2@\text{Ni}(\text{OH})_2$ core-shell heterostructure to achieve a six-fold increase in hydrogen production and provided some useful guidance for the design and synthesis of nanostructured photocatalysts in the domain of photocatalysis and photoelectrocatalysis.

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Graphical Abstract

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3D flower-like heterostructured $\text{TiO}_2@\text{Ni}(\text{OH})_2$ microspheres for solar photocatalytic hydrogen production

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We report a solvothermal approach combined with an oil-bath-based chemical synthesis to prepare a 3D flower-like $\text{TiO}_2@\text{Ni}(\text{OH})_2$ core-shell heterostructure, which results in a six-fold enhancement in the hydrogen production rate.

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三维花状Ni(OH)₂包裹TiO₂微米球用于光催化产氢

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摘要: TiO₂具有合适的能带位置以及成本低、无毒、稳定性高等优点,但由于大的激子结合能(130 meV)以及电子-空穴复合严重,其光催化性能和效率较低。目前,负载助催化剂是一种比较有效的提高TiO₂光催化效率的方法。助催化剂可通过抑制电子与空穴的复合、降低激子结合能、提高界面电子传输速率来提高光催化性能。寻求新型、廉价、高效产氢的助催化剂是当前光催化研究的热点。

近年来, Ni(OH)₂由于具有多变的形貌以及一定的光催化性能而被人们关注。并且Ni(OH)₂本身就是p型光催化剂,可与主体材料复合形成p-n异质结材料,其中由异质结形成的内建电场可起到促进电子与空穴分离的作用。基于此,本文采用简单的合成方法制备出新颖的三维花状Ni(OH)₂包裹TiO₂纳米结构微球,通过X射线衍射仪(XRD)、扫描电镜(SEM)和透射电镜(TEM)等表征手段确定了目标产物被成功合成,并采用光催化产氢为探针反应研究了其光催化性能。结果表明, Ni(OH)₂包裹TiO₂纳米材料的产氢速率比纯TiO₂纳米材料提高了5倍。

通过紫外-可见漫反射吸收光谱(DRS)与一系列对比实验发现, Ni(OH)₂拓宽了TiO₂的吸收光谱范围,催化活性的提高确实来源于引入的Ni(OH)₂。氮气吸附脱附等温线和孔径分布分析表明, Ni(OH)₂壳的引入增大了催化剂的比表面积并且带来介孔,证实三维花状的纳米片界面为光催化产氢提供了更多的活性位点。电化学表征结果进一步证明,这种独特的p-n异质结促进了电子与空穴的分离和转移。基于元素分析和产氢活性结果,我们提出了可能的反应机理。

关键词: 三维花状核壳微球; 二氧化钛; 氢氧化镍; 光催化产氢

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