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Article

Controllable photochemical synthesis of amorphous Ni(OH)₂ as hydrogen production cocatalyst using inorganic phosphorous acid as sacrificial agent

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ABSTRACT

Loading of cocatalysts can effectively inhibit the recombination of photogenerated carriers in photocatalysts and greatly improve the photocatalytic hydrogen production rate. Cocatalysts can be deposited at the outlet points of electrons using a photochemical method, which is beneficial for the following photocatalytic hydrogen production reaction. H₂PO₂⁻ has been used in the photochemical reduction of transition metals because of its special properties. However, the particles formed in the presence of H₂PO₂⁻ are very large and highly crystalline, which may inhibit the activity of photocatalysts. In this study, we designed a new method for synthesizing photocatalysts by photodeposition using some other phosphates, aiming to prepare controllable weakly crystalline and small-size cocatalysts to improve the hydrogen production activity. The cocatalyst prepared using H₂PO₃⁻ as an inorganic sacrificial agent has an amorphous structure and an average size of about 10 nm. The optimal photocatalytic hydrogen production rate of the obtained Ni(OH)₂/g-C₃N₄ (4.36 wt%) is 13707.86 μmol·g⁻¹·h⁻¹, which is even higher than the activity of Pt-4.36 wt%/g-C₃N₄ (11210.93 μmol·g⁻¹·h⁻¹). Mechanistic studies show that loading of Ni(OH)₂ can efficiently accelerate the separation and transfer efficiency of photogenerated charge carriers.

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1. Introduction

With the growing environmental pollution and energy crisis, it is urgent to develop sustainable energy resources. Hydrogen is considered to be one of the most promising energy resources that can replace fossil energy [1]. Photocatalytic water splitting

for hydrogen production is an environmentally friendly approach that involves transforming solar energy to hydrogen energy. The n-type semiconductor material graphitic carbon nitride C₃N₄ (g-C₃N₄) is widely used as a light-absorbing material for photocatalytic hydrogen production. However, the photogenerated electron-hole pairs of pure g-C₃N₄ recombine

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rapidly and the photocatalytic activity is very low. The loading of cocatalysts is an efficient way to improve the rate of photocatalytic hydrogen production by effectively inhibiting the recombination of the photogenerated carriers. Over the years, various cocatalysts have been developed, including noble metals (Pt [2–4], Pd [5,6]), transition metals (Fe [7], Co [8], Ni [9–11], Cu [12,13]), and their compounds (Co₂P [14–17], Ni₃P [18–21], NiS [22–27], MoSe₂ [28], MoS₂ [29,30], Ni(OH)₂ [31–35]).

The task of a cocatalyst is to transfer electrons and holes to the corresponding reactants. So, in addition to the matching energy levels between the cocatalyst and the light-absorbing material, the location of the cocatalyst is also important. The cocatalysts prepared by conventional methods are distributed randomly. However, it has been proved by Li and Yu's Group that photochemical methods can deposit cocatalysts at the outlet points of electrons and holes [36–39], which is beneficial for the next reaction. Using a photodeposition method, an oxidizing cocatalyst can be prepared by photochemical oxidation, and a reductive cocatalyst can be prepared by photochemical reduction. The photochemical method is commonly used to reduce noble metal cocatalysts, but it is still a novel method for preparing non-noble metals [40]. Since the photochemical method is lacking in the regulation of components, we tried to develop a relatively accurate and controllable photodeposition method. From previous research, it is known that H₂PO₂[−] can play an important role in the process of photodeposition, forming a variety of different composite photocatalysts which can reduce hydrogen production, such as Ni/g-C₃N₄ [9], Ni₃P/g-C₃N₄ [18], and Ni(OH)₂/g-C₃N₄/WO₃ [31]. However, the particles formed in the presence of H₂PO₂[−] are very large and highly crystalline, which may inhibit the activity of photocatalysts because the more perfect the crystal is, the fewer defects and active sites are present on the surface of the cocatalyst. The synthesis of position-matched transition metal cocatalysts with weak crystallization is still challenging. Therefore, we aim to synthesize some weakly crystalline and small-size cocatalysts to improve the hydrogen production activity.

We carefully analyzed the role of sodium hypophosphite, and concluded that it mainly acts as a reducing agent and a sacrificial agent during photodeposition. The reducing property of H₂PO₂[−] is so strong that the reduction rate in photodeposition is very fast, while the high-valence phosphate has a weaker reducing ability, which is beneficial for slowing down the rate of reduction to form weakly crystalline cocatalysts. In this work, we designed a photochemical synthesis route using H₂PO₃[−] as the sacrificial agent, NiCl₂ as the nickel source and g-C₃N₄ as the light-absorbing material. The results confirm that our supposition is reasonable, because the photocatalytic hydrogen evolution reaction (HER) activity of the composite photocatalyst prepared by H₂PO₃[−] is very prominent. Through various characterizations, it was confirmed that the product is Ni(OH)₂/g-C₃N₄. The Ni(OH)₂ content can be adjusted by changing the irradiation time.

2. Experimental

2.1. Chemicals

All reagents, including thiourea (CH₄N₂S, 99%), nickel chloride hexahydrate (NiCl₂·6H₂O, 98%), triethanolamine (TEOA, C₆H₁₅NO₃, 78%), phosphorous acid (H₃PO₃, 99%), sodium hypophosphite monohydrate (NaH₂PO₂·H₂O, 98%~103%), sodium phosphate dibasic anhydrous (Na₂HPO₄, 99%), chloroplatinic acid hexahydrate (H₂PtCl₆·6H₂O, 37% Pt basis) and sodium hydroxide (NaOH, 96%), were purchased from Sinopharm Chemical Reagent Co. Ltd. and used without further purification.

2.2. Preparation of g-C₃N₄ nanosheet

The g-C₃N₄ nanosheet was prepared by a modified method using thiourea as the starting material [9,41]. Thiourea (20 g) was heated to 550 °C with a ramp rate of 2 °C min^{−1} and maintained at this temperature for 2 h in air. After cooling to room temperature, the yellow bulk was ground into a fine powder and heated at 500 °C for another 2 h in an open porcelain crucible. A white powder of g-C₃N₄ nanosheet was finally obtained with a yield of about 1%.

2.3. Synthesis of Ni(OH)₂/g-C₃N₄ composite

The Ni(OH)₂/g-C₃N₄ composite was prepared by a photochemical deposition method. First, 20 mg of g-C₃N₄, 1 mL of NiCl₂ (0.1 M), 1 mL of H₃PO₃ (0.7 M), and 8 mL of water were mixed. Before use, the pH of H₃PO₃ was adjusted to neutral by adding 10 mL of H₃PO₃ (2 M) and 11.5 mL of NaOH (3 M) into 7.1 mL of H₂O. After sonication for 10 min, pure nitrogen was used to purge the mixed system from air for 40 min. Subsequently, the mixture was illuminated under UV-vis light (300 W Xe lamp). Then the precipitate was collected by centrifugation, washed with distilled water and ethyl alcohol, and dried under flowing N₂. The obtained products were named as Ni(OH)₂-T/g-C₃N₄, where *T* represents the illumination time (min).

2.4. Photocatalytic hydrogen production

The reaction was performed in a closed flask using a 300 W Xenon lamp with an AM 1.5G filter as the light source. The lamp was 8 cm away from the reaction solution. The prepared Ni(OH)₂/g-C₃N₄ composite photocatalyst (5 mg) was dispersed in 10 mL of aqueous solution (including 20 vol% TEOA) with sonication for 10 min. The mixed system was purged with pure nitrogen gas for 1 h to remove air. The produced hydrogen was measured by gas chromatography (GC-7920, argon as carrier gas).

The quantum yields (Q.Y.) was measured using a 300 W Xe lamp with a 400 nm (± 5 nm) band-pass filter, and calculated by the following equation:

$$\begin{aligned} \text{Q.Y. (\%)} &= \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100\% \\ &= \frac{\text{number of evolved H}_2 \text{ molecules} \times 2}{\text{number of incident photons}} \times 100\% \end{aligned}$$

The optical power density, measured by a radiometer (CEL-NP2000), was $44.86 \text{ mw}\cdot\text{cm}^{-2}$ and the irradiation area was 6.28 cm^2 , corresponding to the number of incident photons (5.67×10^{17} photons per s).

2.5. Photoelectrochemical experiments

Photocurrent tests were carried out to explore the role of $\text{Ni}(\text{OH})_2$ in enhancing the separation efficiency of photogenerated charges in a three-electrode system. It was performed on an electrochemical workstation with Pt foil ($1 \times 1 \text{ cm}$) as the counter electrode and Ag/AgCl (0.222 V vs. a normal hydrogen electrode (NHE)) as the reference electrode. The working electrode was prepared as follows [9]: 10 mg of the $\text{Ni}(\text{OH})_2/\text{g-C}_3\text{N}_4$ sample was dispersed in 100 mL of isopropanol with sonication for 3 h. Then, 10 mg of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was added into the above suspension to form a homogeneous solution with sonication for another 1 h. Subsequently, fluorine-doped tin oxide (FTO) glass as the cathode and a Pt wire as the anode were immersed in the solution at 1 cm below the liquid level. Electrophoretic deposition was performed at 160 V for 1 min, and then the working electrode was dried in a oven at 40°C for 1 h. For comparison, pure $\text{g-C}_3\text{N}_4$ was treated by the same method to prepare the working electrode.

2.6. Characterization

X-ray diffraction (XRD) patterns obtained with a D2 PHASER X-ray diffractometer (Bruker AXS, German) were used to explore the composition and phases of the samples. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were collected using a JEM-2100 transmission electron microscope (JEOL, Japan) to analyze the size and lattice fringe. The selected area electron diffraction (SAED) patterns, TEM-energy-dispersive X-ray spectroscopy (EDX) and EDX mapping results were collected by field emission TEM on Tecnai G2 F30. X-ray photoelectron spectroscopy (XPS) analysis was conducted using an ESCALAB 250 Xi X-ray photoelectron spectrometer (Thermo, USA), with $\text{Al } K_\alpha$ as the excitation source ($h\nu = 1484.6 \text{ eV}$). The content of $\text{Ni}(\text{OH})_2$ was measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, PerkinElmer 8300). UV-vis absorption spectra were recorded using a UV-3600 Plus spectrophotometer (Shimadzu, Japan). Fourier transform infrared (FT-IR) spectra were collected on a Nicolet 6700 infrared spectrometer (Thermal, USA) with a DLaTGS detector. A confocal microscopic Raman spectrometer (Renishaw InVia, England) was used to measure Raman spectra. Room temperature photoluminescence (PL) spectra with an excitation wavelength of 375 nm were measured on Cary Eclipse (Varian, USA). The time-resolved photoluminescence (TR-PL) was measured using a fluorescence spectrophotometer (Edinburgh Instruments, FLS980) with an excitation wavelength of 375 nm to measure the electronic lifetimes of the samples. The surface photovoltage (SPV) was measured using self-made equipment to study the charge features. Electrochemistry measurements were performed using a CHI660E electrochemical workstation (Chenhua Instruments

Table 1
Conditions of control experiments.

	g-C ₃ N ₄ /mg	NiCl ₂ (0.1M) /mL	H ₃ PO ₃ (0.7M) /mL	H ₂ O /mL	Irradia- tion time /min	Heating time /min	Stirring time /min
A	20	1	1	8	40	—	—
B	20	1	1	8	—	40	—
C	20	1	1	8	—	—	40
D	20	1	—	9	40	—	—
E	20	—	1	9	40	—	—
F	—	1	1	8	40	—	—

Co., China).

3. Results and discussion

3.1. Photochemical formation of $\text{Ni}(\text{OH})_2$

The control experiments were performed to study the influence of synthesis conditions on the formation of $\text{Ni}(\text{OH})_2/\text{g-C}_3\text{N}_4$. Table 1 shows the different synthesis conditions. All of the products except F were collected to test their photocatalytic hydrogen production activity. As shown in Fig. 1, sample A has a photocatalytic hydrogen production rate of $13707.86 \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, which is much higher than those of the other samples. This result indicates that only when $\text{g-C}_3\text{N}_4$, NiCl_2 , H_3PO_3 and irradiation are present at the same time, the $\text{Ni}(\text{OH})_2/\text{g-C}_3\text{N}_4$ composite photocatalyst with the highest hydrogen production rate can be obtained. We also compared the performance of catalysts synthesized with different phosphates and found that the catalyst prepared using H_3PO_3 has the best catalytic activity (Table S1 and Fig. S1).

The proposed photochemical synthesis route of $\text{Ni}(\text{OH})_2/\text{g-C}_3\text{N}_4$ is shown in Scheme 1, where $\text{g-C}_3\text{N}_4$ is used as the light-absorbing material. Under irradiation, $\text{g-C}_3\text{N}_4$ is excited to generate electrons and holes (Eq. (1)). Then, H_2O can react with the photogenerated electron. The produced H_2 has been observed by gas chromatography. Subsequently, Ni^{2+} in the solution reacts with the generated OH^- to form $\text{Ni}(\text{OH})_2$ (Eq. (2)). At the same time, H_2PO_3^- (+ III) is oxidized to H_2PO_4^- (+ V) by photogenerated holes (Eq. (3)).

Fig. 1. Photocatalytic HER activity of samples A, B, C, D and E, synthesized under conditions in Table 1.

Scheme 1. The proposed photochemical synthesis route of $\text{Ni(OH)}_2/\text{g-C}_3\text{N}_4$.

3.2. Structures and characterizations

TEM, HRTEM and SAED were used to characterize the morphology and structure of the samples. Fig. 2(a) and Fig. 2(b) are the TEM images of pure $\text{g-C}_3\text{N}_4$ and $\text{Ni(OH)}_2/\text{g-C}_3\text{N}_4$. Pure $\text{g-C}_3\text{N}_4$ appears to be a thin-layer, two-dimensional structure. Some Ni(OH)_2 particles with an average size of about 10 nm are dispersed on the surface of $\text{g-C}_3\text{N}_4$ in $\text{Ni(OH)}_2/\text{g-C}_3\text{N}_4$. In the HRTEM image of $\text{Ni(OH)}_2/\text{g-C}_3\text{N}_4$ (Fig. 2(c)), no lattice fringe is observed, indicating an amorphous structure of Ni(OH)_2 . As a comparison, the HRTEM images of samples synthesized with other phosphates were collected. They reveal that the sample

prepared with H_2PO_2^- has a size of 100~200 nm (Fig. S2(a)), and the size of sample synthesized by HPO_4^{2-} (Fig. S2(b)) is about 50 nm. Fig. 2(d) shows the SAED pattern of $\text{Ni(OH)}_2/\text{g-C}_3\text{N}_4$, in which a broad and diffused halo ring can be observed. This result corresponds to an amorphous morphology [32], which further supports the conclusion from HRTEM. EDX and TEM-EDX mappings were collected to investigate the elemental and spatial distribution of the atoms. The EDX mapping images (Fig. 2(e)) show that C and N are uniformly distributed in the $\text{g-C}_3\text{N}_4$ nanosheet, while O and Ni are uniformly present in the small nanoparticles, indicating that the Ni(OH)_2 nanoparticles exist in the $\text{g-C}_3\text{N}_4$ nanosheet. Meanwhile, all of the elements (C, N, O and Ni) were observed by TEM-EDX (Fig. S3). This result indicates that the high photocatalytic hydrogen production activity of $\text{Ni(OH)}_2/\text{g-C}_3\text{N}_4$ may be related to its small size and amorphous structure.

XRD patterns (Fig. S4) were collected to investigate the crystalline structure of pure $\text{g-C}_3\text{N}_4$ and $\text{Ni(OH)}_2/\text{g-C}_3\text{N}_4$. The two samples both show a weak peak at 13.1° and a sharp and strong peak at 28.0° , which belong to the feature diffraction peak of $\text{g-C}_3\text{N}_4$ [42,43], indicating that the loading of Ni(OH)_2 has not changed the structural features of $\text{g-C}_3\text{N}_4$. There is no obvious diffraction peak of Ni(OH)_2 in $\text{Ni(OH)}_2/\text{g-C}_3\text{N}_4$, proving the amorphous structure of Ni(OH)_2 indicated by the result of HRTEM.

The functional groups of samples can be confirmed by FT-IR (Fig. S5) and Raman (Fig. S6) spectroscopy. No obvious change is observed after the deposition of Ni(OH)_2 , indicating that the construction of $\text{g-C}_3\text{N}_4$ is not changed.

XPS was performed to investigate the composition and chemical status of $\text{Ni(OH)}_2/\text{g-C}_3\text{N}_4$. Fig. 3(a) shows the survey XPS spectra of $\text{Ni(OH)}_2/\text{g-C}_3\text{N}_4$ and the high-resolution XPS spectra of C 1s, N 1s and Ni 2p. The high-resolution C 1s spectrum (Fig. 3(b)) has two peaks at 288.37 and 285.02 eV, which can be attributed to the N-C=N and C-C/C=C groups, respectively. The N1s spectrum in Fig. 3(c) has three obvious peaks at 400.72, 399.20 and 398.63 eV. The main peak at 398.63 eV is a typical signal for the N-C=N group of triazine rings [33], while the peak at 399.20 eV is assigned to N(C)₃ groups. The last weak peak with a binding energy of 400.72 eV is attributed to amino functional groups. The binding energies of C 1s and N 1s are coincident with that of $\text{g-C}_3\text{N}_4$. In Fig. 3(d), the peaks of Ni 2p appear at 880.34, 874.61, 862.14 and 856.78 eV. The peaks at 874.61 and 856.78 eV are the typical signals of Ni 2p_{1/2} and Ni 2p_{3/2} in the Ni(OH)_2 phase [33]. The XPS spectra results indicate that the obtained product is $\text{Ni(OH)}_2/\text{g-C}_3\text{N}_4$.

3.3. Photocatalytic hydrogen production performance

The photocatalytic hydrogen production activities of the samples were examined. As shown in Fig. 4(a) and Fig. 4(b), pure $\text{g-C}_3\text{N}_4$ has a very low photocatalytic H_2 evolution rate of only $18.66 \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ due to the fast recombination of photogenerated carriers. With the loading of Ni(OH)_2 , the photocatalytic H_2 evolution rate is clearly increased. After loading a small amount of Ni(OH)_2 , the photocatalytic H_2 evolution rate is $3325.30 \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ for $\text{Ni(OH)}_2\text{-}20/\text{g-C}_3\text{N}_4$.

Fig. 2. TEM images of pure $\text{g-C}_3\text{N}_4$ (a) and $\text{Ni(OH)}_2/\text{g-C}_3\text{N}_4$ (b); HRTEM image (c) and SAED pattern (d) of $\text{Ni(OH)}_2/\text{g-C}_3\text{N}_4$; EDX mapping images (e) of C, N, O, Ni in $\text{Ni(OH)}_2/\text{g-C}_3\text{N}_4$.

Fig. 3. (a) The survey XPS spectra (a) of $\text{Ni}(\text{OH})_2/\text{g-C}_3\text{N}_4$; high-resolution XPS spectra of C 1s (b), N 1s (c) and Ni 2p (d).

$\text{Ni}(\text{OH})_2$ -40/g- C_3N_4 with an optimal weight ratio of 4.36 wt% (measured by ICP-AES) shows the highest photocatalytic activity of $13707.86 \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$. It is even higher than the activity of Pt-4.36 wt%/g- C_3N_4 ($11210.93 \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, Fig. 4(b)). These results demonstrate that $\text{Ni}(\text{OH})_2$ is an effective cocatalyst for g- C_3N_4 . However, when the irradiation time is prolonged further, the photocatalytic activity reveals a decrease, because excess $\text{Ni}(\text{OH})_2$ impedes light absorption and covers the active sites of g- C_3N_4 . The H_2 evolution quantum yield of $\text{Ni}(\text{OH})_2$ -40/g- C_3N_4 at 400 nm was determined to be about 0.78%. Furthermore, we explored the effect of the molar ratio of H_3PO_3 and NiCl_2 during photodeposition (Fig. S7). It is clear that when the molar ratio of H_3PO_3 and NiCl_2 is 7, the photocatalytic HER activity reaches the highest value. At the same time, the cocatalyst with small particles and low content has

higher atomic utilization when the molar ratio is 7, because the cocatalyst content increases as the ratio increases. Besides, different hole sacrificial agents were used in photocatalytic hydrogen production (Fig. S8). Among them, TEOA is the optimal sacrificial agent for $\text{Ni}(\text{OH})_2/\text{g-C}_3\text{N}_4$.

The stability of $\text{Ni}(\text{OH})_2/\text{g-C}_3\text{N}_4$ was tested in Fig. 4(c). During four cycles of photocatalytic hydrogen production, no obvious decrease of photocatalytic activity was observed, indicating its reasonable photocatalytic stability for 20 h. Subsequently, the XRD pattern (Fig. S9), FT-IR spectrum (Fig. S10), and Raman spectrum (Fig. S11) were collected to investigate the composition and structure of $\text{Ni}(\text{OH})_2/\text{g-C}_3\text{N}_4$ before and after photocatalysis. There is no obvious difference between the two samples. Additionally, TEM (Fig. S12(a)) and HR-TEM (Fig. S12(b)) of the sample after photocatalysis show a size of

Fig. 4. (a) Photocatalytic HER activity of $\text{Ni}(\text{OH})_2$ -T/g- C_3N_4 ($T = 10, 20, 30, 40, 50$ and 60 min); (b) Photocatalytic HER activity of g- C_3N_4 , $\text{Ni}(\text{OH})_2$ -4.36 wt%/g- C_3N_4 , and Pt-4.36 wt%/g- C_3N_4 ; (c) The stability test of $\text{Ni}(\text{OH})_2/\text{g-C}_3\text{N}_4$ for 20 h (four cycles). The system contained 5 mg of photocatalyst and 10 mL of 20 vol % TEOA aqueous solution and a 300 W Xe lamp with an AM 1.5G filter was used as the light source. The catalyst was washed after each cycle.

about 10 nm and an amorphous structure. These results indicate that the structure and morphology of the sample did not change during the reaction. The slight decrease of photocatalytic hydrogen production may be due to the loss of catalyst during washing.

3.4. Mechanism of enhanced photocatalytic activity by Ni(OH)₂

UV-vis diffuse reflectance spectroscopy was carried out to investigate the light-absorption performance of the samples. According to Fig. 5(a), Ni(OH)₂/g-C₃N₄ has a better light-absorption ability compared to pure g-C₃N₄, but the absorption edges of the pure g-C₃N₄ and Ni(OH)₂/g-C₃N₄ are both about 450 nm. The band gap of pure g-C₃N₄ is measured to be 2.8 eV (Fig. S13) [9,44–46], and that of Ni(OH)₂/g-C₃N₄ is also 2.8 eV (Fig. 5(b)). This result indicates that the loading of Ni(OH)₂ does not change the structure of g-C₃N₄. As shown in Fig. 5(c), the valence band of the sample is 1.8 eV [46], and the conduction band was evaluated to be −1.0 eV. Fig. 5(d) exhibits the H₂ evolution rate of Ni(OH)₂/g-C₃N₄ at different light wavelengths. The photocatalytic hydrogen production activity agrees well with the UV-vis diffuse reflectance spectrum of pure g-C₃N₄, indicating the cocatalyst role of Ni(OH)₂.

To investigate the separation and transfer efficiency of photogenerated charge carriers, PL spectra, TR-PL decay spectra, SPV spectra and the transient photocurrent density were investigated. As shown in Fig. 6(a), the PL spectra were collected to demonstrate the transfer of photogenerated electron-hole

pairs with an excitation wavelength of 375 nm. Pure g-C₃N₄ shows a strong peak in the PL spectrum, while the PL peak of Ni(OH)₂/g-C₃N₄ composites is much weaker than that of pure g-C₃N₄, suggesting that the recombination of electrons and holes in g-C₃N₄ is significantly inhibited by Ni(OH)₂. The TR-PL decay spectra (Fig. 6(b)) show that the average lifetimes of pure g-C₃N₄ and Ni(OH)₂/g-C₃N₄ are 5.45 and 5.06 ns, respectively. The lifetime of electrons in Ni(OH)₂/g-C₃N₄ is reduced compared to pure g-C₃N₄, indicating the accelerated separation and transfer efficiency of photogenerated charge carriers by the loading of Ni(OH)₂.

In addition, the SPV spectra (Fig. 6(c)) indicate that the photovoltage intensity of Ni(OH)₂/g-C₃N₄ is much higher than that of pure g-C₃N₄, confirming that the separation efficiency of photogenerated carriers from g-C₃N₄ is effectively enhanced by Ni(OH)₂. Moreover, both pure g-C₃N₄ and Ni(OH)₂/g-C₃N₄ have obvious positive photovoltage responses from 300 to 450 nm, further supporting the UV-vis result. The transient photocurrent response (Fig. 6(d)) shows that the photocurrent density of Ni(OH)₂/g-C₃N₄ is much higher than that of pure g-C₃N₄, indicating higher separation and transfer efficiency, in agreement with the above results.

Scheme 2 shows the proposed photocatalytic hydrogen production mechanism of Ni(OH)₂/g-C₃N₄. Under irradiation, g-C₃N₄ is excited to generate electrons and holes. Subsequently, the photogenerated electrons in the conduction band of g-C₃N₄ can be easily transferred to the cocatalyst Ni(OH)₂. These trapped electrons can further reduce H⁺ and lead to H₂ produc-

Fig. 5. (a) UV-vis diffuse reflectance spectra of pure g-C₃N₄ and Ni(OH)₂/g-C₃N₄; (b) Tauc plot of Ni(OH)₂/g-C₃N₄; (c) XPS spectrum of Ni(OH)₂/g-C₃N₄ for valence band offset determination; (d) UV-vis diffuse reflectance spectra of pure g-C₃N₄ and Ni(OH)₂/g-C₃N₄, and the H₂ evolution rate of Ni(OH)₂/g-C₃N₄ at different light wavelengths 400, 420, 450, 500, 550, 600 nm). The system contains 5 mg of photocatalyst, 2 mL of TEOA and 8 mL of water, and a 300 W Xe lamp with different bandpass filters was used as the light source.

Fig. 6. (a) PL spectra under an excitation wavelength of 375 nm; (b) TR-PL decay spectra excited at 375 nm; (c) SPV spectra of pure g-C₃N₄ and Ni(OH)₂/g-C₃N₄; (d) Transient photocurrent responses to on-off illumination of pure g-C₃N₄ and Ni(OH)₂-30/g-C₃N₄ at 0 V vs NHE.

tion. Additionally, the sacrificial agent TEOA is oxidized by the photogenerated holes left on the valence band of g-C₃N₄.

4. Conclusions

In conclusion, by precisely regulating the type of inorganic phosphates used, we successfully synthesized a weakly crystalline and small-size Ni(OH)₂ cocatalyst with an amorphous structure and an average size of about 10 nm. The photocatalytic hydrogen production activity of the prepared Ni(OH)₂/g-C₃N₄ was greatly improved compared to g-C₃N₄.

Scheme 2. Proposed photocatalytic hydrogen production mechanism of Ni(OH)₂/g-C₃N₄.

Based on various characterizations, we can attribute this ability to the loading of Ni(OH)₂, which accelerates the separation and transfer efficiencies of the photogenerated charge carriers. This article provides a unique reference for the precise photodeposition of transition metal cocatalysts, and is helpful to understand the function of inorganic sacrificial agents.

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Controllable photochemical synthesis of amorphous Ni(OH)₂ as hydrogen production cocatalyst using inorganic phosphorous acid as sacrificial agent

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The weak reducibility of H₂PO₃⁻ can slow down the rate of photodeposition to form a weakly crystalline and small-size Ni(OH)₂ cocatalyst with good photocatalytic hydrogen production activity.

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以无机亚磷酸为牺牲剂光化学法制备无定形Ni(OH)₂助催化剂用于光催化产氢

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摘要: 随着环境污染和能源危机的加剧, 发展可持续能源迫在眉睫. 氢气被认为是可以替代化石能源的最有前途的能源之一, 且光催化分解水产氢是一种可以将太阳能转化为氢能的环境友好的方法. n型半导体材料石墨C₃N₄ (g-C₃N₄)是一种被广泛用作光催化产氢的吸光材料, 然而, 纯g-C₃N₄的光生电子-空穴对会迅速重组, 其光催化活性非常低. 负载助催化剂能够有效抑制光生载流子的复合, 是提高光催化产氢速率的有效方法. 助催化剂的作用是将电子和空穴转移给相应的反应物, 因此除了助催化剂和光吸收材料之间的能级匹配之外, 助催化剂负载的位置也是非常重要的. 通过常规方法制备的助催化剂一般是随机分布的, 而光化学方法可以将助催化剂沉积在电子和空穴的出口处, 从而有利于下一步的光催化反应. 使用光化学沉积法, 可以通过光化学氧化制备氧化型助催化剂, 也可以通过光化学还原制备还原型助催化剂. 光化学法是还原贵金属助催化剂的一种常用方法, 但是对于制备非贵金属助催化剂来说, 它仍然是一种相对新颖的方法. 光化学法目前正处于发展阶段, 依然缺乏成分调控的手段, 因此我们致力于发展相对准确、可控的光沉积方法. H₂PO₂⁻由于其特殊的性质被用于光化学还原过渡金属, 然而, 在H₂PO₂⁻存在下形成的颗粒非常大且高度结晶, 这可能抑制光催化剂的活性. 本文设计了一种利用其他磷酸盐光沉积合成光催化剂的新方法, 旨在制备可控的弱结晶和小尺寸的助催化剂, 以提高产氢活性.

首先以不同磷酸盐为原料制备催化剂, 发现以H₂PO₃⁻为无机牺牲剂制得的催化剂的光催化产氢活性非常突出, 而且制得的催化剂具有无定形结构并且平均尺寸约为10 nm. 通过XRD, XPS等多种表征, 证实了该条件下得到的产物是Ni(OH)₂/g-C₃N₄. 同时, 通过设计对照实验, 发现在使用H₂PO₃⁻作为牺牲剂, NiCl₂作为镍源, g-C₃N₄作为光吸收材料条件下才能制得效果最好的催化剂. 然后对光沉时间, 原料添加量, 产氢牺牲剂等多组条件进行了优化, 得到最优的复合光催化剂Ni(OH)₂/g-C₃N₄ (4.36 wt%)的光催化产氢速率为13707.86 μmol·g⁻¹·h⁻¹, 甚至高于Pt-4.36 wt%/g-C₃N₄的活性(11210.93 μmol·g⁻¹·h⁻¹). 最后, 通过PL, TR-PL, SPV, I-V等多种表征对反应机理进行探究, 结果表明, 光催化产氢性能提升主要原因是Ni(OH)₂的负载可以有效提高光生电荷的分离和转移效率, 抑制光生电子对的重组.

关键词: 光催化; 光沉积; 产氢; 分解水; Ni(OH)₂/g-C₃N₄

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