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Article

Highly enhanced visible-light photocatalytic hydrogen evolution on g-C₃N₄ decorated with vopc through π - π interaction

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ABSTRACT

Photocatalytic H₂ evolution reactions on pristine graphitic carbon nitrides (g-C₃N₄), as a promising approach for converting solar energy to fuel, are attractive for tackling global energy concerns but still suffer from low efficiencies. In this article, we report a tractable approach to modifying g-C₃N₄ with vanadyl phthalocyanine (VOPc/CN) for efficient visible-light-driven hydrogen production. A non-covalent VOPc/CN hybrid photocatalyst formed via π - π stacking interactions between the two components, as confirmed by analysis of UV-vis absorption spectra. The VOPc/CN hybrid photocatalyst shows excellent visible-light-driven photocatalytic performance and good stability. Under optimal conditions, the corresponding H₂ evolution rate is nearly 6 times higher than that of pure g-C₃N₄. The role of VOPc in promoting hydrogen evolution activity was to extend the visible light absorption range and prevent the recombination of photoexcited electron-hole pairs effectively. It is expected that this facile modification method could be a new inspiration for the rational design and exploration of g-C₃N₄-based hybrid systems with strong light absorption and high-efficiency carrier separation.

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1. Introduction

Nowadays, the energy crisis and global warming problems caused by fossil fuel combustion are becoming more and more serious issues, and are two major challenges hindering the long-term and sustainable development of human civilizations [1,2]. In view of the above problems, the development of environmentally friendly and renewable technologies for green energy production is an urgent task. Ever since the landmark event of photoelectrochemical water splitting on TiO₂ electrodes was reported by Fujishima et al. in 1972 [3], photocata-

lytic technology has been considered as an effective and sustainable technology to solve the global energy issue [3,4]. Especially, photocatalytic H₂ production has gained considerable interdisciplinary attention due to high-specific-energy-efficient, non-polluting, and storable hydrogen energy [5]. In the photocatalytic hydrogen production process, not only is clean and inexhaustible solar energy required as a driving force, but a suitable semiconductor as the photocatalyst is required as well. Until now, many traditional materials, like transition-metal-based oxides [6], sulfides [7], selenides [8], etc., have been studied for photocatalytic hydrogen production. In addi-

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tion to these traditional materials, polymeric semiconductor-based materials like graphitic carbon nitrides (g-C₃N₄) have also received increasing attention as a new family of promising photocatalysts for photocatalytic H₂ generation.

The state-of-the-art g-C₃N₄ was found to perform photocatalytic water splitting under visible light in 2009 [9], potentially shifting the search hotspot for photocatalysts from inorganic semiconductors to more abundant organic/polymeric ones. As a metal-free polymeric material, g-C₃N₄ possesses a two-dimensional (2D) planar structure with a π -conjugated electronic system, a moderate optical band gap (≈ 2.7 eV), and good physical and chemical stability [10]. These allow its direct use as a heterogeneous catalyst in the activation of carbon dioxide (CO₂) and other organic reactions [11,12], and as a photocatalyst for the splitting of water into hydrogen gas [13–15]. In spite of the advantages mentioned above, the photocatalytic hydrogen evolution activity of pure g-C₃N₄ is not always noticeable due to the fast recombination of photogenerated electron-hole pairs in the bulk or on its surface. Thus, the transfer and separation of the charge carriers would be key factors in improving the photocatalytic performance of g-C₃N₄. To date, many attempts have been made to modify the physical and electron structures of g-C₃N₄, for example, integrating with other semiconductors [16–23], doping with metal or nonmetal elements [24–26], or surface modification [27–30].

Among the various strategies, modification with organic molecules has been identified as an effective and feasible route to promote the separation of photoinduced electron-hole pairs [31,32]. From this viewpoint, we have previously designed organic molecule-g-C₃N₄ photocatalysts for H₂ production. We have found that hydrogen bonds or π - π interactions can form between the molecule and planar aromatic structure of g-C₃N₄ [33,34]. The driving force among them could facilitate the transfer and separation of photoinduced electron and hole (e⁻/h⁺) pairs, leading to higher photocatalytic hydrogen production. In addition, functionalizing g-C₃N₄ through means of π - π non-covalent interactions can preserve its electronic structure. Therefore, we can design more efficient g-C₃N₄-based photocatalysts through π - π interactions for enhancing photo-generated charge transfer and even expanding the photore-sponse range of graphitic carbon nitride.

Phthalocyanines (Pc) make up a class of macrocyclic molecules with an intrinsic planar 18- π conjugated network [35,36]. It has excellent optical and electrochemical properties, especially its intrinsic absorption in the 600–800 nm range, which is usually referred to as the Q-band and is responsible for the characteristic intense blue color of the materials [37]. Therefore, it is beneficial to immobilize phthalocyanine molecules on g-C₃N₄ through π - π stacking interactions for photocatalysis due to the conjugated two-dimensional electron system of g-C₃N₄. Recently, a series of phthalocyanines, including magnesium phthalocyanine (MgPc) and zinc phthalocyanine (ZnPc) derivatives, has been used to sensitize g-C₃N₄ and has showed enhanced photocatalytic hydrogen production [38,39]. However, the utilization of vanadyl phthalocyanine (VOPc) is rarely reported. According to the literature, the LUMO and HOMO positions of VOPc are -1.29 and $+0.71$ eV, respectively, which are

well matched with the energy bands of g-C₃N₄ [9,40].

Hence, we report that g-C₃N₄ decorated with VOPc molecules via a simple ultrasonic method facilitates H₂ production from water under visible-light irradiation. The obtained VOPc/CN photocatalyst showed a broader spectral responsive range (460–800 nm) compared to that of pure g-C₃N₄ (<460 nm). More importantly, the π - π interaction between VOPc and the planar aromatic structure of g-C₃N₄ could speed up the interfacial charge transfer rate. As a result, the VOPc/CN photocatalyst exhibited significantly enhanced photocatalytic activity for H₂ production under visible-light irradiation in comparison to pure g-C₃N₄. This work demonstrates that phthalocyanine has a promising application for photocatalytic hydrogen production systems that can utilize solar radiation more efficiently.

2. Experimental

2.1. Chemicals

Urea ($\geq 99\%$) and triethanolamine (TEOA, $\geq 78\%$) were purchased from Sinopharm Chemical Reagent. Vanadyl phthalocyanine (VOPc, $\geq 98\%$) was bought from J&K Chemical Reagents Ltd. Hexahydrate (H₂PtCl₆·6H₂O, $\geq 37\%$ Pt basis) was bought from Aldrich. All chemical reagents were used without further purification. Double-distilled water used in the whole experimental process was purified through an SZ-93A auto-double distillation apparatus (Ya Rong Corp., Shanghai, China).

2.2. Preparation of photocatalysts

In a typical synthesis, 4.0 g of urea was added to an alumina crucible with the cover and then heated in a muffle furnace under an air atmosphere at a rate of 5 °C min⁻¹ to 550 °C, and kept at this temperature for 4 h. After cooling to room temperature naturally, the resulting yellow powders were milled and collected for further use.

2.3. Characterization

The crystal structures of the samples were investigated using X-ray diffraction (XRD, MXPAHF, Japan) at room temperature with Cu K α radiation ($\lambda = 1.541$ Å). The acceleration voltage and applied current were 40 kV and 20 mA, respectively. Transmission electron microscopy (TEM) images, high-resolution transmission electron microscopy (HRTEM) images, and energy-dispersive X-ray spectroscopy (EDX) elemental mapping analyses were obtained on a JEOL JEMARF200F atomic resolution analytical microscope with a spherical aberration corrector. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet Magana-IR 750 spectrometer in the 400 to 4000 cm⁻¹ range. X-ray photoelectron spectroscopy (XPS) patterns were acquired with a Thermo ESCALAB 250 system. The UV-vis diffuse reflectance spectra over a range of 200–800 nm were recorded by a Shimadzu spectrophotometer (Model 2501 PC). The UV-vis absorption spectra of aqueous solutions were obtained using a Shimadzu

UV-2510 spectrophotometer. The steady-state photoluminescence (PL) of the photocatalyst was measured on a fluorescence spectrophotometer (JY Fluorolog-3-Tau) at room temperature. The time-resolved photoluminescence (TRPL) measurements were performed using a fluorescence detector (QM400-TM, Photo Technology International, USA). N_2 adsorption-desorption isotherms were measured at 77 K by an adsorption instrument (Micromeritics ASAP 2010 system) and the Brunauer-Emmett-Teller (BET) specific surface area (S_{BET}) was calculated using a multi-point BET method.

Photoelectrochemical tests were done at a CHI 760E electrochemical workstation (Chenhua Instrument Company, Shanghai, China) based on a standard three-electrode system composed of Ag/AgCl as the reference electrode, Pt wire as the counter electrode, and indium-tin oxide (ITO) glass as the working electrode. Na_2SO_4 solution (0.5 mol/L) was used as the electrolyte. The $g-C_3N_4$ and VOPc/CN electrodes were prepared by depositing suspensions made of $g-C_3N_4$ or VOPc/CN and water (the concentration of $g-C_3N_4$ and VOPc/CN was 2 mg mL^{-1}) onto ITO glass, respectively.

2.4. Photocatalytic hydrogen production

The experiments on H_2 evolution from water splitting were carried out in an outer top-irradiation gas-closed Pyrex glass system (500 mL) with a 300-W xenon lamp (Perfect Light, PLS-SXE300C, Beijing) equipped with a cut-off filter ($\lambda \geq 420$ nm). Typically, 50 mg of $g-C_3N_4$ powder and 2 mg of VOPc were dispersed in 100 mL of a water solution containing 10% triethanolamine (TEOA) as the sacrificial electron donor. Then, 1 wt% Pt, as a co-catalyst to boost H_2 generation, was loaded onto the surface of the catalyst by in situ photodeposition of $H_2PtCl_6 \cdot 6H_2O$. Before the photocatalytic reaction, the solution was evacuated for 1 h in order to remove air completely. To eliminate any thermal effects, the temperature of the reaction solution was maintained at 10 °C by a flow of cooling ethylene glycol. The amount of hydrogen evolved from photocatalytic water splitting was measured by an on-line gas chromatograph (GC1120, Shanghai Sunny Hengping Limited, HTCD), and N_2 was used as the carrier gas. To get an accurate amount of the generated H_2 , an average value from three measurements was adopted.

The apparent quantum yields (AQYs) for H_2 evolution were measured with irradiation under different monochromatic light (irradiated by a 300-W Xe lamp using a band-pass filter of $\lambda \pm 5$ nm for 420, 450, 500, 550, and 600 nm) under the same photocatalytic reaction conditions. The AQY was calculated according to the following equation:

$$\begin{aligned} \text{AQY (\%)} &= \frac{\text{Number of reacted electrons}}{\text{Number of incident photons}} \times 100\% \\ &= \frac{\text{Number of evolved } H_2 \text{ molecules} \times 2}{\text{Number of incident photons}} \times 100\% \end{aligned}$$

3. Results and discussion

The photocatalyst of $g-C_3N_4$ was prepared by directly heat-

ing urea at 550 °C for 4 h in an air flow. Vanadyl phthalocyanine modified $g-C_3N_4$ hybrid photocatalysts (VOPc/CN) were obtained via an ultrasonic method in solution. The crystalline phases of VOPc, $g-C_3N_4$, and the 4 wt%-VOPc/CN photocatalysts were analyzed by XRD and shown in Fig. S1. The VOPc/CN hybrid photocatalyst exhibits similar peaks to those of $g-C_3N_4$, indicating that the introduction of VOPc does not change the crystal phase or electronic structure of $g-C_3N_4$. There was no characteristic peak of VOPc molecules from the VOPc/CN photocatalyst. This fact might be due to the loading amount of VOPc being relatively low for detection and the highly dispersed VOPc molecules on the surface of $g-C_3N_4$. In addition, the morphology of $g-C_3N_4$ nanosheets does not change after modification by VOPc (Fig. S2). The successful hybridization of VOPc molecules with $g-C_3N_4$ was proved through EDX (Fig. S3), elemental mapping (Fig. S3), FT-IR spectra (Fig. S4), and XPS patterns (Fig. S5). In Fig. S3, we can see that C, N, V, and O elements are distributed homogeneously all over the whole sample; as depicted in Figs. S4 and S5, there were obvious peaks of VOPc from the VOPc/CN composite, indicating the successful introduction of VOPc molecules into $g-C_3N_4$.

As we all know, the optical absorption properties of materials have a great influence on their photocatalytic performance, and more strong light absorption usually leads to higher photocatalytic H_2 evolution activity. To investigate the optical properties of VOPc, $g-C_3N_4$, and the as-prepared 4 wt%-VOPc/CN photocatalysts, the UV-vis diffuse reflectance spectra (DRS) of the samples were recorded using a Shimadzu UV-2510 spectrophotometer. It can be seen from Fig. 1(a) that pristine $g-C_3N_4$ has an absorption edge of 460 nm, which can be assigned to a band gap of 2.70 eV [9]. Compared to pristine $g-C_3N_4$, the VOPc/CN hybrid photocatalyst exhibits a much broader absorption band throughout the visible/near-IR light region from 400 to 800 nm due to the introduction of VOPc molecules. The excellent UV-visible light absorption properties of the VOPc/CN hybrid photocatalyst are extremely beneficial to photocatalytic H_2 production. Moreover, it is worth noting that the characteristic absorption band of VOPc in VOPc/CN shows a red shift of about 37 nm relative to that of pure VOPc molecules. The apparent bathochromic shift reflects the efficient interaction between the VOPc and $g-C_3N_4$, which is known as a π - π stacking interaction [41,42]. A schematic of the π - π interaction between $g-C_3N_4$ and VOPc is illustrated in Fig. 1(b). It is well known that VOPc molecules, which have a delocalized π -electron conjugation system, could interact with $g-C_3N_4$ aromatic frameworks through π - π interactions. On one hand, this non-covalent interaction would not disturb the physical properties of either material; on the other hand, it could promote the separation of the photogenerated hole-electron pairs.

The charge carrier dynamics, especially the charge carrier separation and recombination rates of the photoexcited electron-hole pairs, have a direct influence on the photocatalytic performances of materials [43]. To study the charge carrier dynamics of the photocatalysts, we measured the steady-state PL emission spectra of $g-C_3N_4$ and the as-prepared VOPc/CN hybrid composite with an excitation wavelength of 315 nm and they are depicted in Fig. 2(a). The PL intensity of the VOPc/CN

Fig. 1. (a) The UV-vis absorption spectra of VOPc, g-C₃N₄, and 4 wt%-VOPc/CN photocatalysts. (b) Molecular flattening of VOPc adsorbed on the g-C₃N₄ sheet.

composite shows an obvious decrease at approximately 450 nm compared to that of pure g-C₃N₄, suggesting that the recombination of photogenerated charge carriers is efficiently suppressed after the incorporation of VOPc, and thus, the non-radiative decay process from the excitation status of g-C₃N₄ is promoted [44]. In addition, time-resolved PL spectroscopy provided additional insight into the charge recombination and the transfer process between VOPc molecules and g-C₃N₄. As shown in Fig. 2(b), the average lifetime of an electron for pure g-C₃N₄ is about 0.31 ns, while the lifetime for the VOPc/CN hybrid photocatalyst is longer (1.11 ns). Generally speaking, the longer lifetime of the electrons means some photoinduced charge carriers undergo rapid transfer between g-C₃N₄ and VOPc, and suppression of electron-hole recombination [45]. Both the steady-state PL quenching and time-resolved PL spectroscopy results confirmed that the introduction of VOPc molecules can efficiently decrease electron-hole recombination; this demonstrates that the VOPc/CN hybrid may be an appealing photocatalyst for H₂ generation.

The transfer and generation of the photoexcited charge carriers were investigated by transient photocurrent responses on a photoelectrochemical test device with visible-light irradiation ($\lambda \geq 420$ nm). As shown in Fig. 2(c), the photocurrent responses of g-C₃N₄ and the VOPc/CN composite were examined under several on/off visible-light irradiation cycles. It is clearly seen that the VOPc/CN composite exhibits a much higher photocurrent than a bare g-C₃N₄ sample, indicating that the VOPc/CN composite possesses enhanced charge separation under visible-light irradiation, resulting in higher photocatalytic performance in water splitting [7]. In addition, EIS of the samples was employed to study the charge transfer resistance. As displayed in Fig. 2(d), the VOPc/CN composite exhibits a smaller semicircle at the intermediate frequency compared to that of pure g-C₃N₄. In general, a semicircle at a high frequency characterizes the process of charge transfer, and a smaller arc radius implies efficient separation of photogenerated electron-hole pairs and a fast interface charge migration process [46]. Obviously, the VOPc/CN composite exhibits a smaller semicircle than that of the pure g-C₃N₄ electrode, implying that introduction of VOPc could make the separation and migration of photogener-

ated electron-hole pairs more efficient. Taken together, the photoelectrochemical test result is in good accordance with the results of steady-state PL and time-resolved PL, demonstrating that the introduction of VOPc molecules into g-C₃N₄ is favorable for boosting photocatalytic H₂ production.

The photocatalytic activities of the VOPc/CN catalysts were studied through the water reduction reaction for hydrogen evolution under visible-light ($\lambda \geq 420$ nm) illumination using TEOA as the scavenger agent. The H₂ evolution rates of each sample were an average value from three measurements. The results plotted in Fig. 3(a) show that the photocatalytic activity of g-C₃N₄ alone is relatively low (11.21 $\mu\text{mol h}^{-1}$), which is probably the result of intrinsically rapid charge recombination [47]. As expected, upon introducing VOPc molecules into g-C₃N₄, an obvious increase in photocatalytic H₂ generation activity was observed, suggesting a positive effect of VOPc molecules on g-C₃N₄ for photocatalytic H₂ production. By increasing the percentage of VOPc, the photocatalytic H₂ evolution rate could be increased gradually. The highest H₂ production rate was 65.52 $\mu\text{mol h}^{-1}$ when the content of VOPc molecules was 4 wt%, and this value exceeds that of pure g-C₃N₄ by a factor of 6. The VOPc content has a significant influence on the photocatalytic activity of g-C₃N₄; the hydrogen evolution rate decreases sharply when further increasing the amount of VOPc molecules. For example, when the amount of VOPc was 6 wt%, the average H₂ evolution rate dramatically decreased to 27.08 $\mu\text{mol h}^{-1}$. This is likely due to the following. (1) A suitable amount of VOPc could cause strong coupling that facilitates charge transfer, and then promotes the separation of photo-generated electron-hole pairs; excess CBV²⁺ could cover the surface active sites of g-C₃N₄, subsequently lowering interfacial charge transfer and photocatalytic activity [48]. (2) The phenomenon could be ascribed to the “shielding effect” [49]; the existence of the excess VOPc in the VOPc/CN composite will partially block the light absorption of g-C₃N₄ and the hole scavengers, and thus lead to reduced photocatalytic activity for hydrogen evolution. A similar phenomenon has also been found in other previous research for photocatalytic systems [33,50]. From the BET data in Fig. S6, we can see that the S_{BET} surface area of the 4 wt%-VOPc/CN composite is 81 m² g⁻¹,

Fig. 2. (a) The steady-state PL spectra of g-C₃N₄ and VOPc/CN, (b) time-resolved PL spectra measured at room temperature for g-C₃N₄ and VOPc/CN solid solutions (excitation at 315 nm and probe at 400 nm); Transient photocurrent response (c) and EIS Nyquist plots (d) for g-C₃N₄ and VOPc/CN composite under visible-light irradiation ($\lambda \geq 420$ nm, $[\text{Na}_2\text{SO}_4] = 0.5$ mol/L).

Fig. 3. (a) Comparison of the photocatalytic activities of VOPc/CN catalysts with different weight ratios of VOPc and 1 wt% Pt as co-catalyst; (b) wavelength-dependent apparent quantum yield for the photocatalytic hydrogen evolution reaction over VOPc/CN. Reaction conditions: 50 mg of photocatalyst, solvent (100 mL, H₂O/TEOA = 9:1 (vol/vol)), and a 300-W xenon lamp equipped with a cut-off filter ($\lambda \geq 420$ nm) as light source at 10 °C.

which is smaller than that of g-C₃N₄ (101 m² g⁻¹). The corresponding pore size distribution of the sample showed almost no change after introducing VOPc molecules. The results imply that the introduction of VOPc molecules has little effect on the corresponding pore size distribution of g-C₃N₄, but negatively affects the specific surface area of g-C₃N₄. Thus, introducing a suitable content of VOPc is very important to optimize the photocatalytic hydrogen production activity of VOPc/CN com-

posites.

AQYs of the 4 wt%-VOPc/CN hybrid for photocatalytic hydrogen evolution were measured under irradiation with different monochromatic light ($\lambda = 420, 450, 500, 550$, and 600 ± 5 nm), which is often used to distinguish whether the present H₂ generation process is driven by photoexcited charge carriers or not [51]. From Fig. 3(b), we can observe that the highest AQY of 6.29% was obtained for the 4 wt%-VOPc/CN hybrid at 420

Table 1

A comparison of photocatalytic H₂ evolution rates obtained for VOPc/CN and other systems.

Photocatalyst	Light source	H ₂ evolution (μmol h ⁻¹ g ⁻¹)	Ref.
NiS/g-C ₃ N ₄	λ > 420 nm (350 W Xe)	593.6	[20]
Ni ₁₂ P ₅ /g-C ₃ N ₄	λ > 420 nm (350 W Xe)	126.61	[21]
g-C ₃ N ₄ /Ni ₂ P	λ ≥ 420 nm (300 W Xe)	82.5	[51]
VOPc/CN	λ ≥ 420 nm (300 W Xe)	1310.4	This work

nm. In addition, AQY decreases with an increase in the incident light wavelength, which is consistent with the UV-vis absorption spectrum of VOPc/CN. This revealed that the harvested visible photons dominated the driving force for the present reaction [52]. In addition, the photocatalytic activity of the 4 wt%-VOPc/CN hybrid was compared with those from previous reported works (Table 1) [20,21,53]. Notably, the as-prepared VOPc/CN exhibits high photocatalytic activity for H₂ evolution under visible-light irradiation.

The stability as well as the recycling behavior are very important issues for photocatalytic materials in terms of practical application. In order to confirm the persistence of VOPc/CN, we performed cycling tests on 4 wt%-VOPc/CN under the same experimental conditions (Fig. 4). The results show that there is no significant deactivation in terms of H₂ evolution activity after 20 h of visible-light illumination, suggesting that the VOPc/CN hybrid material has favorable stability and can be a promising photocatalyst towards H₂ generation processes.

Based on the above-mentioned experimental results and discussion, a possible mechanism for visible-light-induced H₂ production over the VOPc/CN photocatalyst was proposed and is shown in Scheme 1. The VOPc (*E_g* = 2 eV) can absorb the photons with energies above 2 eV, which could enhance the light absorption at λ < 460 nm, in addition to harvesting the

Fig. 4. Time course for photocatalytic hydrogen production over 4 wt%-VOPc/CN with visible-light illumination (λ ≥ 420 nm). Reaction conditions see Fig. 3.

Scheme 1. Proposed mechanism of electron-hole transport and photocatalytic activity of the VOPc/CN photocatalyst under visible-light irradiation (λ ≥ 420 nm).

light at longer wavelengths (λ > 460 nm) [40]. According to previous literature, the LUMO and HOMO positions of VOPc are −1.29 and +0.71 eV, respectively, and the conduction band (CB) and valence band (VB) energy levels of g-C₃N₄ are −1.1 and +1.6 eV, respectively [9,40,54,55]. In the VOPc/CN structure, the LUMO position of VOPc is lower than the CB of g-C₃N₄, while its HOMO value is higher than the VB of g-C₃N₄; therefore, the photoinduced electrons on the LUMO of VOPc can be directly transferred to the CB of g-C₃N₄ and the photogenerated holes in the VB of g-C₃N₄ can spontaneously migrate to the HOMO of VOPc. Therefore, the probability of electron-hole recombination can be reduced because of the well-matched band potentials.

The photogenerated electrons from the intrinsic excitation of g-C₃N₄ and the injected electrons from the excited VOPc molecules are trapped by the loaded Pt co-catalyst for photocatalytic H₂ production. At the same time, the separated holes remaining at VOPc are scavenged by accepted electrons from TEOA, so that the VOPc and g-C₃N₄ can be regenerated for cyclic utilization. As a result, the photogenerated electrons and holes are spatially separated between VOPc and g-C₃N₄, reducing the recombination probability significantly and resulting in the enhanced photocatalytic hydrogen production activity of g-C₃N₄. The VOPc molecules not only serve as a dye sensitizer to enhance the visible light utilization efficiency but also enhance the separation and transfer of photogenerated charges in g-C₃N₄, leading to greatly improved photocatalytic activity for g-C₃N₄.

4. Conclusions

In summary, we presented a simple method to prepare vanadyl phthalocyanine/graphitic carbon nitride (VOPc/CN) hybrid photocatalysts for H₂ generation in aqueous solution with TEOA as a sacrificial electron donor. The VOPc molecules

can easily hybridize with g-C₃N₄ through strong π - π stacking interactions, which do not have much influence on the electronic properties of g-C₃N₄. The introduction of VOPc molecules can extend the spectral response region to longer than 460 nm; at the same time, it can retard charge recombination, thus resulting in significantly improved photoactivity for H₂ production. When the amount of VOPc molecules was 4 wt%, the developed VOPc/CN hybrid photocatalyst exhibited the highest photocatalytic activity, with a H₂ evolution rate of 65.52 $\mu\text{mol h}^{-1}$, which is nearly 6 times higher than that of bare g-C₃N₄ (11.20 $\mu\text{mol h}^{-1}$), and a high AQY of 6.29% at 420 nm. This study offers a way to develop a new class of visible-light-driven hybrid materials with high photocatalytic performance.

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Highly enhanced visible-light photocatalytic hydrogen evolution on g-C₃N₄ decorated with vopc through π - π interaction

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This work describes a novel system of molecule-grafted g-C₃N₄ through π - π interactions between VOPc and g-C₃N₄ aromatic frameworks. The introduction of VOPc can extend the spectral response region to longer than 460 nm and retard charge recombination, thus resulting in significantly improved photoactivity for H₂ production.

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π - π 作用下的VOPc/g-C₃N₄用于有效提升可见光光催化制氢性能

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摘要: 近年来, 随着全球科学技术的进步和工业的不断发展, 人们的经济生活水平有了极大的提高, 但同时也造成能源短缺和环境污染问题, 成为21世纪制约经济和社会进一步发展的严重瓶颈, 因此开发和研究环保和可再生的绿色能源技术是一项紧迫任务. 自首次报道用二氧化钛为电极、采用光电化学分解水制氢之后, 光催化分解水制氢引起了人们极大的兴趣, 并被认为是缓解全球能源问题的最有希望的解决方案之一. 其中, 实现有效的太阳能制氢生产中最关键因素是设计稳定、高效和经济的光催化剂, 并且能够利用可见光区进行工作(入射到地球上46%的太阳光谱是可见光). 聚合物石墨相氮化物(g-C₃N₄)作为一种对可见光响应的新型无机非金属半导体光催化剂, 被认为是一种“可持续”有机半导体材料, 目前已并被广泛应用于各种光催化反应中. 但是由于其光生电子-空穴在动力学上具有相对较大的复合速率, 单纯g-C₃N₄的光催化活性远远达不到人们的要求. 因此, 应该尽可能的提高电荷转移动力学来抑制g-C₃N₄中光生电荷的复合, 从而提高光生电荷从g-C₃N₄转移至反应位点的迁移速率. 在前期研究的基础上, 本文利用钒氧酞菁(VOPc)分子通过 π - π 相互作用以修饰g-C₃N₄的表面和电子结构, 从而提高其光生电子-空穴的分离效率, 最终极大提升其可见光光催化制氢性能.

本文采用紫外可见光谱(UV-vis), 高分辨透射电镜(HRTEM), 傅里叶变换红外光谱(FT-IR), X-射线能谱(XPS), 稳态光致发光光谱(PL), 时间分辨光致发光光谱(TRPL), 光电流和阻抗等一系列表征手段研究了VOPc/g-C₃N₄(VOPc/CN)复合催化剂的结构和性质. FT-IR, XPS及mapping等结果表明, VOPc分子已经成功引入到g-C₃N₄表面且未对其晶相、电子结构及其纳米片结构产生显著影响; UV-vis结果显示, VOPc分子成功引入并通过非共价键的 π - π 作用连接. 总之, 引入VOPc分子即拓展了催化剂对可见光的响应区域, 又有利于光生载流子的传递和光生电子-空穴对的有效分离. 当引入4 wt%的VOPc分子时, VOPc/CN复合光催化剂的产氢速率增加至65.52 $\mu\text{mol h}^{-1}$, 420 nm处的量子效率高达6.29%, 是单纯g-C₃N₄的6倍. 此外, 该催化剂在可见光下连续照射反应20 h后, 其光催化活性几乎没有降低, 表现出良好的光化学稳定性. 由于两者

LUMO和HOMO轨道之间的良好匹配,在光催化过程中光生电子-空穴在VOPc和g-C₃N₄之间实现了空间分离,有效阻止了光生电子-空穴对的复合,因而g-C₃N₄光催化制氢性能显著提升.

同时对比了利用NiS和NiPx做助剂的g-C₃N₄的可见光光催化制氢性能.结果显示,VOPc/CN复合光催化剂具有较好的光催化性能.总之,本文通过一种简单、经济、有效的方法将两种新兴的功能材料有机地复合在一起,用于可见光照射下高效光催化制氢,为以后合理地开发用于太阳能转换的更为高效经济的材料提供了一个新的思路.

关键词: VOPc/g-C₃N₄; π - π 作用; 可见光催化; 制氢; 电荷分离效率

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