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Article

In situ construction of protonated g-C₃N₄/Ti₃C₂ MXene Schottky heterojunctions for efficient photocatalytic hydrogen production

Haotian Xu ^a, Rong Xiao ^a, Jingran Huang ^a, Yan Jiang ^{a,#}, Chengxiao Zhao ^b, Xiaofei Yang ^{a,b,c,*}^a School of Materials Science & Engineering, Jiangsu University, Zhenjiang 212013, Jiangsu, China^b College of Science, Institute of Materials Physics and Chemistry, Nanjing Forestry University, Nanjing 210037, Jiangsu, China^c Key Laboratory for Photonic and Electronic Bandgap Materials, Ministry of Education, School of Physics and Electronic Engineering, Harbin Normal University, Harbin 150025, Heilongjiang, China

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ABSTRACT

Converting sustainable solar energy into hydrogen energy over semiconductor-based photocatalytic materials provides an alternative to fossil fuel consumption. However, efficient photocatalytic splitting of water to realize carbon-free hydrogen production remains a challenge. Heterojunction photocatalysts with well-defined dimensionality and perfectly matched interfaces are promising for achieving highly efficient solar-to-hydrogen conversion. Herein, we report the fabrication of a novel type of protonated graphitic carbon nitride (PCN)/Ti₃C₂ MXene heterojunctions with strong interfacial interactions. As expected, the two-dimensional (2D) PCN/2D Ti₃C₂ MXene interface heterojunction achieves a highly improved hydrogen evolution rate (2181 μmol·g⁻¹) in comparison with bulk g-C₃N₄ (393 μmol·g⁻¹) and protonated g-C₃N₄ (816 μmol·g⁻¹). The charge-regulated surfaces of PCN and the accelerated charge transport at the face-to-face 2D/2D Schottky heterojunction interface are the major contributors to the excellent hydrogen evolution performance of the composite photocatalyst.

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1. Introduction

Over the past few decades, the increasingly severe energy crisis and the need for environmental remediation have become important challenges facing human society [1–5]. Clean hydrogen has emerged as an ideal new energy source to replace traditional fossil fuels. The photochemical splitting of water using sustainable solar energy is a new technology to produce hydrogen. In this method, semiconductor photocatalysts are excited after absorbing photons of specific energies and generate reductive electrons and oxidative holes that in-

duce redox reactions [6–10]. Therefore, an effective semiconductor must have a suitable band gap (2–2.5 eV) and a matched band position for the activation of water splitting under light illumination [11,12]. Moreover, it is also essential that the semiconductor be earth-abundant and not generate secondary pollution.

Recently, various semiconductor-based photocatalysts have been employed as hydrogen-producing catalysts for water splitting; in particular, graphitic carbon nitride (g-C₃N₄) has long been regarded as one of the most promising candidates for photocatalytic hydrogen production owing to its tunable elec-

* Corresponding author. E-mail: xiaofei.yang@njfu.edu.cn

Corresponding author. E-mail: jiangy@ujs.edu.cn

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tronic structure and good chemical stability [13–16]. However, g-C₃N₄ has inherent drawbacks, such as low specific surface area, poor charge transport capacity, and a high electron-hole pair recombination rate, which leads to a low efficiency of hydrogen production [17–21]. Therefore, follow-up treatment of pristine g-C₃N₄ is essential to enhance its catalytic activity. For example, minor element doping, especially doping with non-metal elements, can result in defect energy levels, which can improve its light absorption properties and promote effective charge separation. Morphology regulation can also significantly increase its specific surface area and reactive sites [22–25]. Surface functionalization is another approach for the modification of g-C₃N₄. Protonation (*i.e.* acid pretreatment) is a functionalizing approach that can convert the negative charges on the surface of g-C₃N₄ into positive charges and adjust its electronic bandgap and ionic conductivity, thus improving its hydrogen generation performance [26–31]. In addition to the optimization of g-C₃N₄ alone, the fabrication of composite systems is also a common method to enhance photocatalytic capacity [32–37]. The introduction of co-catalysts such as noble metals, transition metal phosphides, graphene, and carbon materials has also been explored for the acceleration of charge separation and interfacial charge transport [38–40]. Transition metal carbides (MXenes) obtained from the etching and exfoliation of MAX materials (Ti₃AlC₂) are a new family of 2D materials that has attracted attention for their excellent structural stability, tunable surface terminations, and metal conductivity. Thus, 2D MXenes can act as excellent electron transport media for enhancing the photocatalytic performance of catalysts [41–45].

Inspired by the aforementioned achievements, we designed and synthesized PCN/2D Ti₃C₂ MXene heterojunctions and investigated their use as photocatalysts for efficient visible-light-responsive hydrogen production. The as-prepared PCN/MXene composite photocatalysts exhibit a significantly enhanced hydrogen generation rate. In particular, when 20 mg of the co-catalyst MXene is added, the hydrogen production efficiency of the optimal sample PCN-20 is 2181 $\mu\text{mol}\cdot\text{g}^{-1}$, which is 5.5-fold and 2.7-fold greater than that of pure CN and PCN. The morphology, light absorption, and photoelectrochemical properties of the composites were studied. The protonated g-C₃N₄, which has an optimized lamellar structure, is integrated with 2D MXene nanosheets to form a close interfacial contact, and the optimal sample PCN-20 shows significantly improved photoelectrochemical properties that facilitate charge carrier separation and interfacial migration due to the synergistic effect of the protonation of g-C₃N₄ and its hybridization with MXene. The findings in this work provide insights for optimization and performance improvement of semiconductor photocatalysts.

2. Experimental

2.1. Synthesis of g-C₃N₄

Pristine g-C₃N₄ (CN) was calcined by a previously reported thermal polymerization method in a tube furnace [46–49]. Spe-

cifically, 5 g of dicyandiamide (DCDA) was placed in a semi-closed ceramic crucible with a cover, heated to 550 °C at a moderate rate of 5 °C·min⁻¹, and then maintained at this temperature for 4 h under a N₂ atmosphere. Subsequently, the sample was cooled naturally to room temperature, and the obtained yellow product was ground into a fine powder and collected.

2.2. Synthesis of MXene nanosheets

MXene was prepared using the precursor Ti₃AlC₂ (MAX). In a typical synthesis, 50 mL of HF (40%) was gently poured into a beaker, after which 5 g of MAX was slowly added to the beaker using a long spoon. The mixed suspension was then gently stirred at room temperature for 3 h, washed repeatedly with DI water, and centrifuged at high speed until the pH value of the solution was close to neutral. After being dried in an oven at 60 °C overnight, the HF-etched sample (5 g) was exfoliated to give ultrathin MXenes in 100 mL dimethyl sulfoxide (DMSO) using continuous low-speed stirring for 24 h. The exfoliated MXenes were then washed with deionized water repeatedly to remove the excess DMSO. The washed MXene was placed in 150 mL of water under an argon atmosphere for 2 h, then centrifuged for one hour and dried at 60 °C overnight to obtain a black powder (MXene).

2.3. Protonation of g-C₃N₄

The yellow powder CN (3 g) was ultrasonically dispersed in 100 mL of hydrochloric acid (0.4 mol·L⁻¹) at room temperature for 2 h, and then magnetically stirred for a further 4 h. The centrifuged product (PCN) was washed to neutrality with deionized water and then dried *in vacuo* at 60 °C overnight.

2.4. Synthesis of the PCN/MXene nanocomposite photocatalyst

The PCN/MXene composites were synthesized as follows. First, the appropriate amount of PCN was dispersed in 30 mL of deionized water and subjected to 3 h of ultrasonic treatment. The desired quantity of the MXene sample (10, 20, or 40 mg) was ultrasonically dispersed in 20 mL of DI water for 3 h. Then the two dispersion systems were mixed by stirring overnight to obtain the PCN and MXene composites. The composites PCN-*x* (*x* = 10, 20, or 40) collected after centrifugation and washing were dried *in vacuo* at 60 °C overnight and ground into fine powders.

2.5. Characterization

The morphologies of the obtained products were examined by a FEI Nova Nano 450 scanning electron microscope (SEM). The crystal structures of the materials were analyzed using an UltimaIV X-ray diffractometer (Cu K α radiation, ranging from 5° to 50° at a scan rate of 5°·min⁻¹). Fourier transform infrared (FT-IR) spectra of the as-prepared samples were recorded using a Nicolet Model Nexus 470 spectrometer. Their light-harvesting properties were measured by UV-visible spec-

troscopy on a Shimadzu UV2450 spectrometer from 200 nm to 800 nm. The photoelectrochemical behavior of the catalysts was recorded using a CHI660B electrochemical analyzer with a standard three-electrode system. Photoluminescence (PL) emission measurements were carried out using a QuantaMaster™ 40 instrument with an excitation wavelength of 385 nm.

2.6. Photocatalytic hydrogen production

Photocatalytic hydrogen evolution experiments were performed in a gas-tight circulation system (CEL-SPH2N-D9, CEAU Light, China) with a Pyrex top-irradiation reaction vessel. A 300 W Xe lamp (CEL-HXF 300, CEAU Light, China) was used as the visible-light source (> 420 nm). Typically, 10 mg of the photocatalyst was dispersed in 50 aqueous solution containing 5 mL of triethanolamine (TEOA) by sonication for 8 min. Continuous stirring was employed in order to obtain well-dispersed mixtures and balanced illumination. The hydrogen evolution performance was monitored by online gas chromatography (GC-7920) with N_2 protection. The apparent quantum efficiency (AQE) was calculated according to the method reported in a previous study: $AQE = 2 \times \text{number of evolved } H_2 \text{ molecules} / \text{number of incident photons} \times 100\%$.

3. Results and discussion

The PCN/MXene composites were synthesized by electrostatic-driven interactions, as shown in Fig. 1. First, the cambium-like MXene obtained by etching MAX with HF was intercalated by DMSO molecules, which facilitated the disaggregation of the nanosheets with negative surface charges by ultrasonic treatment. CN synthesized by traditional thermal polymerization has been demonstrated to have a negatively charged surface, which would not be conducive to electrostatic self-assembly with MXene. Therefore, CN was protonated using a dilute hydrochloric acid solution to modify its surface charge. The zeta potentials of CN, PCN, and MXene were measured to be -9.5 , 27.3 , and -11.4 mV, respectively (Fig. S1). The different charges of MXene and PCN were conducive to electrostatic interaction between PCN and MXene [50,51].

To verify the formation of composites between PCN and MXene, the PCN-20 composite containing a moderate amount of MXene was chosen for investigation. The morphological characteristics and elemental distribution of CN, PCN, and the

composite PCN-20 were investigated by SEM and elemental mapping analysis. As shown in Fig. 2a, the pure CN powder consisted of large bulk particles with slightly smooth surfaces and significant agglomeration. After four hours of protonation, rugged surfaces were observed (Fig. 2b). This clearly indicates that the treatment changes the surface morphology of CN by protonation. Ti_3C_2 nanosheets were prepared by etching the precursor Ti_3AlC_2 (Fig. S2a) with hydrofluoric acid. The etched MXene after the delamination and ultrasonication processes showed micro-sized 2D structures constructed of large and thin nanosheets (Fig. 2c). The composite PCN-20 exhibited a smooth surface (Fig. 2d). Moreover, EDS coupled with elemental mapping images demonstrated the uniform dispersion of the elements Ti, N, and C (Fig. 2e), indicating the homogeneous assembly of PCN and MXene in PCN-20.

The microstructures of the samples and the thickness of the nanoparticles were further determined by atomic force microscope (AFM) analysis. As shown in Fig. 3a, in the AFM image of MXene, a large nano-sheet can be observed, which is consistent with the microscopic morphology seen by SEM. The corresponding height cutaway view shows that the thickness of the nanosheet is about 2.3 nm (Fig. 3b), implying that ultrathin layered MXene nanosheets were successfully prepared. In Fig. 3c, it can be observed that the AFM image of PCN shows a two-dimensional sheet structure, and its corresponding thickness is about 3.4 nm (Fig. 3d).

XRD patterns and FTIR spectra were obtained to determine the compositions and chemical states of CN, PCN, MXene, and PCN-20. As shown in Fig. S2b, after the etching treatment with HF, the element Al was removed from Ti_3AlC_2 . As expected, the most intense diffraction peak in the precursor Ti_3AlC_2 , which was located at 39° (2θ), disappeared, and the (002) peak of the as-synthesized Ti_3C_2 shifted to lower angle, indicating that the layered Ti_3AlC_2 had been successfully transformed into thin

Fig. 1. Synthesis flow chart for the PCN/MXene composites.

Fig. 2. SEM images of CN (a), PCN (b), and MXene nanosheets (c); SEM image and corresponding elemental mapping images of the composite PCN-20 (d, e).

Fig. 3. AFM images (a, b) and height cutaway view of MXene and PCN nanosheets (c, d).

Ti_3C_2 nanosheets. In Fig. 4a, two obvious diffraction peaks located at 13° and 27.5° were detected, which were indexed to the (100) plane, which corresponds to the in-plane packing of heptazine units, and the (200) plane, which originates from the characteristic stacking of conjugated aromatics, respectively [52]. After treatment with hydrochloric acid, the characteristic diffraction peaks of PCN appeared at the same positions, suggesting that the typical layered structure of polymeric $\text{g-C}_3\text{N}_4$ was well maintained. However, the composite PCN-20 showed

only the characteristic diffraction peaks of graphene-like carbon nitride because the content of MXene in the composite was too low to produce detectable signals. The functional groups evolved were further analyzed using FT-IR spectroscopy. As shown in Fig. 4b, the strong peaks at 3440 and 1635 cm^{-1} in the FT-IR spectrum of MXene were assigned to the stretching vibrations of the OH and C=O groups, and the peak at 1393 cm^{-1} was attributed to O-H group bending. For CN, PCN, and PCN-20, the peaks located at 810 cm^{-1} originated from the breathing mode of the aromatic heterocycle in tri-s-triazine, and the peaks in the range $1240\text{--}1642\text{ cm}^{-1}$ were ascribed to stretching vibrations of heterocycles (C-N/C=N). Furthermore, the broad peak at around 3200 cm^{-1} was assigned to unconjugated terminal amino groups [14,53,54].

To uncover the effects of the 2D MXene nanosheets on the photocatalytic hydrogen evolution reaction (HER) performance of the composites, the hydrogen production performances of pure CN, PCN, and PCN- x composites loaded with different amounts of MXene ($x = 10, 20$, and 40 mg) were evaluated under a standard solar simulator. As can clearly be observed in Fig. 5a, in the absence of a Pt co-catalyst, the hydrogen production of PCN increased when the content of MXene was increased to 20 mg , but further increase of the MXene content suppressed hydrogen production, which implies that MXene played a critical role in enhancing the hydrogen generation performance of PCN. PCN-20 split water into hydrogen at a rate of approximately $2181\text{ }\mu\text{mol}\cdot\text{g}^{-1}$ under light illumination for 3 h with a quantum efficiency of 8.6% at 420 nm (Fig. S3); this efficiency was remarkably higher than that of CN or PCN. Moreover, PCN-20 still exhibited stable H_2 evolution after five cycles

Fig. 4. XRD patterns (a) and FT-IR spectra (b) of PCN-20, PCN, CN, and MXene.

Fig. 5. Hydrogen production (a) of CN, PCN, and PCN- x ($x = 10, 20, 40$); five hydrogen production cycles using the composite PCN-20 (b).

Fig. 6. UV-vis diffuse reflectance spectra of MXene, CN, PCN, and PCN-20 (a); Optical bandgaps of CN and PCN (b); Mott-Schottky plots of CN and PCN (c); Schematic illustration of the band structures of CN and PCN (d).

(Fig. 5b), clearly indicating that PCN-20 can serve as an effective photocatalyst for H_2 production. In addition, comparison of the photocatalytic H_2 evolution results for the protonated g-C₃N₄/Ti₃C₂ MXene photocatalysts with those of previously reported hydrogen-evolving photocatalysts in the literature are shown in Table S1 in the Supporting Information.

To understand the nature of the outstanding photocatalytic properties of PCN-20, UV-visible spectroscopy and electrochemical measurements were carried out. Fig. 6a presents the absorption enhancement of PCN-20 above 500 nm, which occurs because MXene is a full-spectrum absorber. The corresponding Tauc plots are shown in Fig. 6b. PCN exhibits a narrower band energy of 2.41 eV, which is conducive to the capture of more visible-light photons [55,56]. The positive slopes of the Mott-Schottky plots (Fig. 6c) correspond to the typical n-type characteristics of CN and PCN, and the flat-band potentials were calculated to be roughly -0.71 and -0.56 V for CN and PCN, respectively. The flat-band potentials above were based on Ag/AgCl, and should be corrected to the normal hy-

drogen electrode (NHE) potentials via the equation [57,58]. $E_{fb} = E_{Ag/AgCl} + 0.059 \times pH + E^0_{Ag/AgCl}$, where $E_{Ag/AgCl}$ refers to the flat band potential measured for the above sample. The pH of the electrolyte BaSO₄ (1 mol·L⁻¹) is around 5.9, and $E^0_{Ag/AgCl}$ is 0.197 eV. Therefore, the NHE potentials of CN and PCN were calculated to be -0.17 and -0.02 eV. It is well-known that the conduction band (CB) minimum of an n-type semiconductor is generally 0.3 eV more negative than E_{fb} [59,60], thus the CB values of CN and PCN were determined to be -0.47 and -0.32 eV, respectively. Based on the expression $E_v = E_g + E_c$, the valence bands (VBs) of CN and PCN were calculated to be 2.06 and 2.09 eV, respectively (Fig. 6d).

The electron-hole separation efficiency and electron transfer capability of CN, PCN, and PCN-20 were revealed by investigating their photoelectrochemical properties, namely, their photocurrent and electrochemical impedance responses. The steady and transient photocurrent responses under visible light illumination for CN, PCN, and PCN-20 during on-off cycles of illumination were measured (Fig. 7a). The photocurrent of

Fig. 7. (a) Transient photocurrent responses and (b) EIS Nyquist plots of CN, PCN, and PCN-20 in 1 mol·L⁻¹ Na₂SO₄ aqueous solutions under visible light irradiation.

Fig. 8. Photoluminescence spectra (a) and photoluminescence decay curves of CN (b), PCN (c), and PCN-20 (d).

the PCN electrode was obviously larger than that of CN, indicating that the electron-hole pair separation efficiency was improved in protonated carbon nitride [61]. Moreover, the composite PCN-20 demonstrated the highest photocurrent intensity, possibly because the surface recombination of the photoinduced electrons and holes was significantly suppressed by the 2D MXene nanosheets with high electrical mobility. The kinetics of the HER at the interface were subsequently studied by EIS measurements (Fig. 7b), in which the semicircle diameter of PCN-20 was found to be much smaller than that of the control groups CN and PCN, implying decreased electron transfer resistance for PCN-20.

Photoluminescence (PL) spectroscopy has been regarded as an effective tool to reveal the separation and recombination rates of photogenerated charge carriers in excited photocatalysts. The main peak in the PL spectra of CN, PCN, and PCN-20 (Fig. 8a) appeared at 455 nm, but the emission intensity of PCN was much weaker than that of CN. Moreover, PCN-20 showed the weakest emission, corresponding to restrained electron-hole recombination; this result was in good agreement with the above photocurrent results and electrochemical impedance responses [56,62]. Using the fitting function $y = A_1 \times \exp(-x/\tau_1) + y_0$, the fluorescence life-times of PCN-20, PCN, and CN were calculated to be 2.79, 3.00, and 3.38 ns, respectively (Fig. 8b–8d), indicating more nonradiative transfer of photogenerated charge carriers and better charge transport in PCN-20.

On the basis of the results presented above, a diagram depicting the photocatalytic HER in the 2D/2D MXene/PCN heterojunctions is given in Fig. 9. The negatively charged MXene nanosheets are closely integrated with the protonated PCN through electrostatic interactions, forming an effective interface. In essence, the high-conductivity MXene acts as a co-catalyst in the composite PCN-20. Typically, photogenerated electrons move from the VB to CB under simulated solar light,

Fig. 9. Charge-transfer progress in the 2D/2D MXene/PCN system during photocatalytic H₂ evolution under visible light.

simultaneously creating positively-charged holes in the VB of PCN. Given the excellent metal conductivity of MXene, the electrons in CB of modified PCN can be transferred rapidly to the MXene surface and accumulate at the active sites, which promotes charge separation and speeds the reduction of protons to H₂.

4. Conclusions

In summary, we have described the protonation of nano-structured g-C₃N₄ by treatment with hydrochloric acid. The obtained protonated carbonitride (PCN) demonstrates not only altered surface morphology but also increased absorption in the visible light range via adjustment of the band gap width. From the photocurrent and PL measurements, it can be seen that the modified PCN is able to improve the efficiency of electron separation and also minimize the electron-hole recombination, providing more photogenerated electrons for hydrogen production under illumination, which increases the hydrogen production performance. Additionally, highly efficient PCN/MXene composite materials can be prepared by loading a new non-metallic co-catalyst, MXene, on PCN. The plot of hydrogen production demonstrated an initial increase in the hydrogen production with a further slight decay in hydrogen generation. The optimal amount of MXene for the best performance of PCN is around 20 mg, with this composite showing the highest hydrogen production rate of 2181 $\mu\text{mol}\cdot\text{g}^{-1}$. Pure CN loaded with the same amount of MXene demonstrated the same pattern of improvement in hydrogen production. Our findings reveal that as-synthesized MXene-containing PCN heterojunctions could be applied as cost-effective, highly efficient photocatalysts for converting solar energy into clean chemical fuel, laying a foundation for the scalable synthesis and broader applications of g-C₃N₄-based materials.

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Graphical Abstract

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In situ construction of protonated g-C₃N₄/Ti₃C₂ MXene Schottky heterojunctions for efficient photocatalytic hydrogen production

Haotian Xu, Rong Xiao, Jingran Huang, Yan Jiang*, Chengxiao Zhao, Xiaofei Yang*
*Jiangsu University; Nanjing Forestry University;
 Harbin Normal University*

In addition to the protonation of graphitic carbon nitride, conductive 2D MXene was introduced as a co-catalyst to further accelerate electron-hole separation and interfacial charge transport for improved hydrogen production.

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原位构筑质子化氮化碳/碳化钛光催化制氢肖特基异质结

徐浩添^a, 肖蓉^a, 黄靖然^a, 姜燕^{a, #}, 赵呈孝^b, 杨小飞^{a, b, c, *}

^a江苏大学材料科学与工程学院, 江苏镇江212013

^b南京林业大学理学院材料物理与化学研究所, 江苏南京210037

^c哈尔滨师范大学光电带隙材料教育部重点实验室, 黑龙江哈尔滨150025

摘要: 氢气因其具有高燃烧热、可再生性以及燃烧产物无污染等优势被认为是一种绿色可再生能源, 是取代化石燃料的候选能源之一。然而, 如何利用自然界中丰富的太阳能和水资源实现光分解水制氢的关键在于开发高效的光催化剂。在尺寸明确、能级带隙匹配的纳米材料间进行完美的界面复合(异质结构筑)是实现高效太阳能-氢能转换的最佳途径。石墨相氮化碳(CN)材料因其电子结构可调 and 化学性能稳定等特性被光催化界所关注。然而, 氮化碳材料较弱的电学性能如电荷传输能力差及电子-空穴对复合率高导致其表现出较低的光催化制氢效率。基于此, 我们用盐酸对氮化碳进行质子化处理, 使材料表面电荷发生改变, 从而实现氮化碳的电子带隙调节和电导率提升。在此基础上, 将二维碳化钛原位负载于质子化的氮化碳(PCN)纳米片表面构筑肖特基结。PCN纳米片与碳化钛纳米片间的良好界面接触促进了电荷在材料界面上传输, 进而加速了氮化碳材料的电荷分离, 实现了氮化碳光催化剂活性的提升。

Zeta电位测试结果显示, CN和PCN的表面电位分别为−9.5和27.3 mV, 表明质子化处理可以有效改变材料表面电荷, 并促其与碳化钛纳米片进行静电组装。该结果进一步得到了扫描电子显微镜(SEM)和原子力显微镜(AFM)的证实。改变表面电荷使氮化碳材料的能带宽度由2.53 eV (CN)减小到2.41 eV (PCN), 增强了可见光区吸收。同时, PCN的光电流密度提升了约4倍, 电子阻抗和激发态电子的辐射复合都显著降低。将PCN与碳化钛复合制得复合材料(PCN-x, x = 10, 20, 40), 实验结果表明5 g的PDN最佳负载碳化钛的量为20 mg (PCN-20)。在标准太阳模拟器的可见光区(> 420 nm), 复合材料PCN-20的光催化水分解产氢量可达2181 $\mu\text{mol} \cdot \text{g}^{-1}$, 是CN催化剂的约5.5倍, PCN的2.7倍, 并且经过5次产氢循环后PCN-20仍具有稳定的氢气释放速率。以上结果表明, 氮化碳材料可以通过质子化处理以及适量的碳化钛复合实现光催化产氢性能的提升, 其中碳化钛在体系中起助催化剂的作用。该研究结果可为其他半导体光催化剂的性能优化以及非贵金属助催化剂的研究提供新思路。

关键词: 氮化碳; 碳化钛; 杂化; 肖特基异质结; 质子化; 光催化产氢

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*通讯联系人. 电子信箱: xiaofei.yang@njfu.edu.cn

#通讯联系人. 电子信箱: jiangy@ujls.edu.cn

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