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Article

Design of p-n homojunctions in metal-free carbon nitride photocatalyst for overall water splitting

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ABSTRACT

Two-dimensional (2D) carbon nitride (CN) photocatalysts are attracting extensive attention owing to their excellent photocatalytic properties. In this study, we successfully prepared CN materials with heterogeneous structures via hydrothermal treatment, high-temperature roasting, ball milling, sintering, and other processes. Benefitting from interface interactions in hybrid architectures, the CN photocatalysts exhibited high photocatalytic activity. The rate of hydrogen production using these CN photocatalysts reached $17028.82 \mu\text{mol h}^{-1} \text{g}^{-1}$, and the apparent quantum efficiency was 11.2% at 420 nm. The ns-level time-resolved photoluminescence (PL) spectra provided information about the time-averaged lifetime of fluorescence charge carriers; the lifetime of the charge carriers causing the fluorescence of CN reached 9.99 ns. Significantly, the CN photocatalysts displayed satisfactory results in overall water splitting without the addition of sacrificial agents. The average hydrogen and oxygen production rates were $270.95 \mu\text{mol h}^{-1} \text{g}^{-1}$ and $115.21 \mu\text{mol h}^{-1} \text{g}^{-1}$ in 7 h, respectively, which were promising results for the applications of the catalysts in overall water splitting processes. We investigated the high efficiency of the prepared CN photocatalysts via a series of tests (UV-vis diffuse reflectance spectroscopy, photocurrent response measurements, PL emission spectroscopy, time-resolved PL spectroscopy, and Brunauer-Emmett-Teller analysis). Furthermore, the Mott-Schottky plot and current-voltage curve were acquired via electrochemical tests. The fabricated CN photocatalyst had a small p-n junction in its heterogeneous structure, which further enhanced its photocatalytic efficiency. Therefore, this work can promote the development of CN photocatalysts.

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1. Introduction

Two-dimensional (2D) graphene-like carbon nitride (CN) photocatalysts have been recently receiving significant attention from researchers owing to their particularly good response to visible light, relatively large specific surface area, non-toxicity, low cost, and other advantages [1–10]. In 2009,

Wang et al. [11] successfully used block g-C₃N₄ as a photocatalyst in water splitting for the production of hydrogen. Subsequently, high-quality g-C₃N₄ or composite structures (metallic oxide/g-C₃N₄) were prepared via various methods [12–17]. For example, She et al. designed α-Fe₂O₃ nanosheets that could actively promote the exfoliation of g-C₃N₄, producing 2D hybrid structures that exhibited good photocatalytic efficiency in the

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production of hydrogen [18]. All these reports showed that g-C₃N₄ had numerous application prospects in the field of water splitting.

However, there are two difficulties encountered during the production of hydrogen. The first is that, like metal-free CN photocatalysts, metal-based composite CN materials are often prepared [19–27]. The second is the need to add a sacrificial agent in water splitting; otherwise, the effect of the catalyst is extremely low [28–33]. Therefore, these two issues limit the practical applications of CN to metal-free photocatalysts. In 2015, Kang's research group used carbon quantum dots with CN to conduct a full splitting water experiment via an all-metal-free photocatalyst without the use of precious metals and sacrificial agents for the first time; they proposed the two-electron channel phenomenon in Science [34]. Since then, there have been few major breakthroughs in the use of metal-free CN photocatalysts for the full splitting of water.

In our previous work, we investigated a lot of literature on CN. We found that almost all CN photocatalysts assumed n-type structures owing to specific ratios of carbon and nitrogen [35–41]. Generally, most researchers use p-type metal-based materials and n-type CN photocatalysts for the development of composites, which was inspired by the fundamental p-n junction principle applied in silicon solar cells. This structure can greatly improve the light-conversion efficiency of hybrid photocatalysts. For example, Sun et al. reported that a ZnO/g-C₃N₄ composite photocatalyst exhibited better photocatalytic activity than pure g-C₃N₄ [42]. However, the synthesis of p-type metal-free CN photocatalysts has rarely been reported. Therefore, we aimed to design a metal-free CN photocatalyst with a small p-n junction structure.

Recently, we prepared a new 2D CN-precursor organic material with a thickness of approximately 1 nm [43]. The carbon content of the prepared CN was higher than the nitrogen content, and the prepared material was a p-type CN semiconductor [43]. Thus, the prepared material could be compounded with conventional n-type CN semiconductor materials. A pure metal-free CN photocatalyst had a heterogeneous structure with a small p-n junction and was prepared after grinding and calcining. This type of non-metallic CN photocatalyst displayed superior photocatalytic effect (hydrogen production rate of 17028.82 $\mu\text{mol h}^{-1} \text{g}^{-1}$) than other pure CN photocatalysts under the same experimental conditions. The apparent quantum efficiency (AQE) was 11.2% at 420 nm. The ns-level time-resolved photoluminescence (PL) spectra provided information about the time-averaged lifetime of fluorescence charge carriers; the lifetime of the charge carriers causing the fluorescence of CN reached 9.99 ns. Significantly, the CN photocatalyst demonstrated satisfactory results in overall water splitting without the addition of sacrificial agents (the average hydrogen and oxygen production rates were 270.95 $\mu\text{mol h}^{-1} \text{g}^{-1}$ and 115.21 $\mu\text{mol h}^{-1} \text{g}^{-1}$, respectively, within the first 7 h).

We investigated the high efficiency of this CN photocatalyst via a series of tests (UV-vis diffuse reflectance spectroscopy, photocurrent response measurements, PL emission spectroscopy, time-resolved PL spectroscopy, and Brunauer-Emmett-Teller (BET) analysis). Furthermore, the

Mott-Schottky plot and current-voltage curve were acquired via electrochemical tests. The fabricated CN photocatalyst had a small p-n junction in its heterogeneous structure, which further enhanced its photocatalytic efficiency. Therefore, this work can promote the development of CN photocatalysts.

2. Experimental

2.1. Preparation

Analytical-grade ammonium fluoride, melamine, triethanolamine, and alcohol were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai). All reagents were used as received.

First, 5 g melamine as the raw material was heat-treated via hydrothermal synthesis at 180 °C for 24 h, filtered, and dried. Then, the material was transferred into a tubular furnace under the protection of high-purity argon at 550 °C for 1 h. Second, 5 g melamine was treated with 5 g ammonium fluoride at 180 °C for 24 h, filtered, and dried. The product was heat-treated in a tubular furnace under a protective nitrogen atmosphere at 550 °C for 1 h. Finally, we mixed two types of CN in equal proportions, grinded them, and transferred them to the tube furnace for quenching at 550 °C for 1 h at a heating rate of 5 °C/min (the protective gas was nitrogen). Then, the target material (CN) could be synthesized. The bulk melamine raw material was directly treated for 2 h in air at 550 °C in a contrast experiment.

2.2. Measurement of hydrogen and oxygen evolution

The photocatalytic reactions were carried out in a Pyrex reaction cell connected to a closed gas-circulation and evacuation system: (a) 0.05 g catalyst (1% Pt) was dispersed in 100 mL aqueous solution containing 20 mL triethanolamine as a sacrificial agent. Then, the suspension was thoroughly degassed and irradiated using a Xe lamp (300 W) equipped with an optical cut-off filter ($\lambda > 420 \text{ nm}$) to eliminate ultraviolet light. The temperature of the reactant solution was maintained at 279 K by flowing cooling water during the reaction. The amount of H₂ produced was analyzed using an online gas chromatograph. The activities of different catalysts were compared using the average rate of H₂ evolution in the first 7 h. The AQE was also measured under similar conditions using the following equation: $\text{AQE} = 2 \times \text{amount of hydrogen molecules evolved} / \text{number of incident photons} \times 100\%$. (b) 0.05 g catalyst (1% Pt) was dispersed in 100 mL aqueous solution. Then, the suspension was thoroughly degassed and irradiated using a Xe lamp (300 W) to eliminate ultraviolet light. The temperature of the reactant solution was maintained at 279 K by flowing cooling water during the reaction. The amount of H₂ and O₂ produced was analyzed using an online gas chromatograph.

2.3. Photoelectrochemical activity measurements

Photoelectrochemical test systems included a CHI660D workstation (Shanghai Chenhua, China) with a three-electrode configuration using the prepared samples as the working elec-

trodes, a Pt plate as the counter electrode, Ag/AgCl as the reference electrode, and a 300-W Xe lamp equipped with an optical cut-off filter ($\lambda > 420$ nm) as the light source. Na_2SO_4 was used as the electrolyte in an aqueous solution (0.5 M). The working electrodes were prepared as follows: 10 mg of the as-prepared CN was dispersed in absolute ethanol and the suspension was directly deposited onto a fluorine-doped tin oxide conductive glass plate and dried at 80 °C in a vacuum oven.

2.4. Material Characterization

Scanning electron microscopy (SEM) was performed with a Hitachi S-4800 microscope. Fourier-transform infrared spectroscopy was carried out with a Thermo-Nicolet Nexus 670 infrared (IR) spectrometer. X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance powder X-ray diffractometer using $\text{Cu } K\alpha$ radiation ($\lambda = 0.15406$ nm). UV-vis diffuse reflectance spectra were recorded on a Shimadzu UV-2550 spectrophotometer within a wavelength range of 300 nm to 800 nm. The PL spectra of the photocatalysts were recorded using an Edinburgh FLS920 spectrometer. X-ray photoelectron (XPS) measurements were carried out using the Thermo Fisher ESCALAB 250 monochromatized XPS spectrometer with Al ($K\alpha$) radiation as the probe and a 500-mm analysis spot size. The pressure of the base chamber was 2×10^{-9} mbar.

2.5. Theoretical analysis

We performed first-principles density-functional (DFT) theory calculations using the Vienna ab initio simulation package. The energy cut-off of the plane-wave basis set was 500 eV. A generalized gradient approximation in the form of Perdew-Burke-Ernzerhof for the electron exchange-correlation functional was employed to optimize the structure. The unit cell was repeated periodically along the x - and y -directions, while a vacuum space of approximately 15 Å was applied along the z -direction to avoid interaction between adjacent images. In the static self-consistent calculations, we adopted a $10 \times 10 \times 1$ Monkhorst-Pack k -point mesh for Brillouin zone sampling. All the atoms were fully relaxed without symmetry restrictions until the residual forces on each atom were smaller than 0.01 eV/Å.

3. Results and discussion

The flow diagram of the preparation of the CN photocatalyst with a heterogeneous structure is shown in Fig. 1. First, melamine was used as the raw material, and it was heat-treated under hydrothermal synthesis at 180 °C for 24 h, filtered, and dried. Then, the material was transferred into a tubular furnace under the protection of high-purity argon at 550 °C for 1 h. Second, melamine was treated with ammonium fluoride at 180 °C for 24 h, filtered, dried, and calcined (at 550 °C for 1 h) leading to CN. Finally, we mixed two types of CN in equal proportions, grinded them, and transferred them to the tube furnace for quenching at 550 °C for 1 h. Then, the target material (CN)

Fig. 1. Process flow diagram of the preparation of CN photocatalyst with a heterogeneous structure.

could be synthesized.

The morphology of different CN photocatalysts was observed via SEM. The nanotube-like type CN shown in Fig. 2(a) was synthesized based on the above method. The maximum length of the nanotubes was approximately 6 μm , and most of the nanotubes were distorted at high temperatures. The surface morphology of another type of CN, prepared via the second method mentioned above, is displayed in Fig. 2(b); the nanosheets exhibited a degree of distortion. The chiffon CN nanosheet is visible in the lower right corner of Fig. 2(b). When the two types of CN were mixed, ground, and roasted, lamellar CN with a heterogeneous structure was formed, as shown in Fig. 2(c). For comparison, ordinary $\text{g-C}_3\text{N}_4$ was prepared according to previous reports [44–49]. The block and unordered structure of ordinary $\text{g-C}_3\text{N}_4$ is shown in Fig. 2(d).

The IR spectra and XRD patterns of the photocatalysts are shown in Fig. 2(e) and 2(f). The IR spectra and XRD patterns of the three types of CN were very similar despite their varying shapes. The CN nanotubes had a weak N–H bond because the content of the NH_3 group in the sample was very low after water heat treatment ($3000\text{--}3500\text{ cm}^{-1}$) (Fig. 2(e)) [44–46]. The peaks at $1000\text{--}1450\text{ cm}^{-1}$ were caused by C–N stretching vibrations and the spectra of all three types of CN contained the same absorption peak. The peaks of the CN nanosheets at $1500\text{--}1700\text{ cm}^{-1}$ were different from the absorption peaks of other samples (CN nanotubes and this work-CN). This was because there were more C–C than C–N bonds in the CN nanosheets. Furthermore, the peak at 809 cm^{-1} was ascribed to the vibrational fingerprint of the C–NH–C units in the three types of CN [47–49]. The XRD patterns of the samples (Fig. 2(f)) showed that the peaks of the prepared CN nanosheets were different from those of the CN nanotubes and this work-CN because the CN nanosheets had fluorine ions in their structure. High-resolution XPS spectra of F1s are displayed in Fig. S1. Fluoride was present in the CN nanosheet and the amount of fluorine in the final product was so small that the XPS test could not detect it. The (002) and (001) crystal facets of the three types of CN were similar to those of CN_x (No. JCPDS 50-0664) from the bulk melamine raw material [50,51].

The yield and efficiency of the photocatalytic water splitting into hydrogen and oxygen under visible-light irradiation were

Fig. 2. SEM images of CN nanotubes (a), CN nanosheets (b), CN photocatalyst (c) with heterogeneous structure, and ordinary g-C₃N₄ photocatalyst (d); IR spectra (e) and XRD patterns (f) of photocatalysts.

used to evaluate the catalytic performance, as shown in Fig. 3. The efficiency of this work-CN catalyst in hydrogen evolution was much higher than those of the CN nanotubes, CN nanosheets, and g-C₃N₄ catalyst (Fig. 3(a)). Furthermore, the hydrogen-evolution rate of this work-CN was approximately 17028.82 μmol h⁻¹ g⁻¹ (Fig. 3(b)), and it was much higher than those of other CN photocatalysts under the same experimental conditions. Moreover, the AQE of this work-CN was 11.2%, 3.18%, and 0.23% at 420, 475, and 550 nm, respectively (Fig. 3(c)). The AQE value of 11.2% at 420 nm was satisfactory. Furthermore, the CN catalyst demonstrated good overall water splitting capability without the addition of sacrificial agents. The hydrogen and oxygen production rates were 270.95 and 115.21 μmol h⁻¹ g⁻¹, respectively, within the first 7 h (Fig. 3(d))

and 3(e)).

To evaluate the efficiency of this work-CN in photocatalytic hydrogen and oxygen production, the reaction was allowed to proceed for 70 h with intermittent evacuation every 7 h, as shown in Fig. 3(f). Continuous H₂ and O₂ evolution by CN was observed from the beginning of the reaction. The total evolution of H₂ and O₂ after 70 h was 12131 and 4895 μmol, respectively. The average hydrogen and oxygen production rates were 173.30 and 69.93 μmol h⁻¹ g⁻¹ in 70 h, respectively. Although the overall water splitting efficiency was lower than that of the first cycle (first 7 h), the 70-h average efficiency was significantly higher than those of the first cycle reported previously [34]. The decrease in the efficiency was due to the photocorrosion of the photocatalyst by simulated sunlight, which

Fig. 3. (a) Typical time course of H₂ production from aqueous solution (100 mL) containing triethanolamine (20 vol%) as a sacrificial electron donor and 50 mg of 1 wt% Pt-loaded catalyst under 300 W Xe lamp with an optical cut-off filter ($\lambda > 420$ nm); (b) Hydrogen evolution rates with different CN photocatalysts; (c) Wavelength dependent AQE by this work-CN; (d) H₂ and O₂ production from aqueous solution (100 mL) and 50 mg of 1 wt% Pt-loaded catalyst under 300 W Xe lamp; (e) H₂ and O₂ evolution rates based on this work-CN photocatalyst; (f) H₂ and O₂ evolution cycling curves of this work-CN photocatalyst.

Fig. 4. (a) UV-vis diffuse reflectance spectra of different CN photocatalysts; (b) Plot of $(AE_{\text{photon}})^2 \sim E_{\text{photon}}$; (c) Photocurrent response of samples to on-off cycles of illumination; (d) PL emission spectra.

was a problem with all photocatalysts and remains to be studied.

The optical absorptions of CN photocatalysts were analyzed via UV-vis, photocurrent response, and PL measurements, as depicted in Fig. 4. The band edges of different CN photocatalysts were positioned at approximately 435–450 nm (Fig. 4(a)). The absorption edge energy was 2.75–2.85 eV, as shown in Fig. 4(b). The E_g values of this work-CN, CN nanotubes, CN nanosheets, and g-C₃N₄ were approximately 2.75, 2.81, 2.85, and 2.83 eV, respectively. The photocurrent response was evaluated to measure the photogenerated electron-hole separation, as shown in Fig. 4(c) [52–54]. The transient photocurrent responses of different CN photocatalysts were recorded for several on-off cycles of irradiation. When simulated sunlight was shining, the photocurrent increased sharply, and it quickly returned to its dark current state when the light was turned off. As shown in Fig. 4(c), the photocurrents were stable and reproducible during several intermittent on-off irradiation cycles. The prepared CN exhibited satisfactory photocurrent response

compared to CN nanotubes, CN nanosheets, and g-C₃N₄, indicating that the recombination of the photogenerated charge carriers was greatly inhibited by the heterogeneous structure. The PL spectra of different CN photocatalysts are shown in Fig. 4(d); the heterogeneous structure decreased the recombination of the electron-hole pairs in comparison with the structures of the other CN photocatalysts.

Furthermore, time-resolved PL spectra were recorded on an FLS980 fluorescence spectrometer (Edinburgh Instruments) with excitation at 420 nm. The ns-level time-resolved PL spectra provided information about the time-averaged lifetime of fluorescence charge carriers (Fig. 5) [55–57]. The effective lifetime of charge carriers was 6.81 ns in the CN-nanotubes photocatalyst at 450 under 420 nm excitation, and the effective lifetime of the CN nanosheets charge carriers was 7.98 ns (Figs. 5(a) and 5(b)). However, the lifetime of the charge carriers causing fluorescence in this work-CN reached 9.99 ns, as shown in Fig. 5(c). The lifetime of the charge carriers in these three CN materials was higher than that of previously reported block CN

Fig. 5. ns-Level time-resolved PL spectra monitored at 450 nm under 420 nm excitation for CN nanotubes (a), CN nanosheets (b), and this work-CN (c).

Fig. 6. Typical nitrogen adsorption-desorption isotherms of different CN photocatalysts. (a) CN nanotubes; (b) CN nanosheets; (c) this work-CN; (d) g-C₃N₄.

materials [55–57].

The specific surface areas (BET) of different CN photocatalysts were further investigated using the nitrogen adsorption-desorption isotherms shown in Fig. 6. The surface area of the prepared CN reached 42.8 m² g^{−1}, which was more than 8.7 times that of g-C₃N₄ (4.9 m² g^{−1}). The surface area of CN nanotubes was 37.5 m² g^{−1} and that of CN nanosheets was 10.8 m² g^{−1}. The higher specific surface area of the prepared CN photocatalysts led to many more active sites [58,59].

Based on elemental analyses via the XPS spectra shown in Fig. 7, the C/N molar ratios of different CN photocatalysts were 2.86:1 (CN nanotubes), 0.87:1 (CN nanosheets) and 0.81:1 (this work-CN). The peaks in the N1s spectra (Fig. 7(b), (d), and (f)) were caused by *sp*² hybridizations (C–N–H, N(–C)₃, and C=N–C at approximately 400.4, 398.7, and 398.4 eV, respectively) [60].

Fig. 8. Optimized structures of C_{2.83}N (a) and C_{0.82}N (b); carbon atoms are gray and nitrogen atoms are blue. Electronic band structures of C_{2.83}N (c) and C_{0.82}N (d). The energy at the Fermi level was set to zero. (e, f) Mott-Schottky plots for determining CN nanotubes and nanosheets.

Moreover, the elemental analyzer was typically used to determine the molar ratio of C/N. The C/N molar ratios were 2.83:1 (CN nanotubes), 0.82:1 (CN nanosheets), and 0.78:1 (this work-CN). Because XPS is surface-sensitive technology, the carbon content of the prepared CN surface was low by roasting. Therefore, the results of the elemental analysis of C/N were relatively accurate [33,58].

Modeling and calculations based on the first principle are shown in Fig. 8, and they were performed in accordance with the C/N element ratio. When the C/N molar ratio was 2.83:1

Fig. 7. High-resolution XPS spectra of different CN photocatalysts. (a, c, e) C1s; (b, d, f) N1s.

Fig. 9. (a) Characteristic current-voltage curve of CN (this work). (b) Schematic diagram showing the production of hydrogen and oxygen, energy band structure, and electron-hole pair separation in this CN photocatalyst containing a p-n heterojunction.

(Fig. 8(a)), the Fermi level approached the valence band (Fig. 8(c)), indicating that CN might contain a p-type structure. When the molar ratio of C/N was 0.82:1 (Fig. 8(b)), the Fermi level approached the conduction band (Fig. 8(d)), suggesting that this CN might contain an n-type structure. Impedance spectroscopy at an alternating current frequency of 1 kHz afforded the Mott-Schottky diagrams shown in Fig. 8(e) and 8(f). The slope of the Mott-Schottky curve indicated the type of semiconductor to which the material belonged [60–63]. Generally, the slope of the curve of C_xN_y materials is positive; a positive slope suggests that the material is an n-type semiconductor. However, the CN nanotubes prepared in this way contained a p-type structure, and the slope of the Mott-Schottky curve was negative (Fig. 8(e)), which was a new discovery. Moreover, CN (nanosheets) containing an n-type structure were also prepared via the above method. As shown in Fig. 8(f), the Mott-Schottky curve of the n-type CN material had a positive slope with electrons as most carriers [64–66].

We attempted to prove that there was a small p-n junction structure in CN (this work) after compounding CN nanotubes (containing a p-type structure) and CN nanosheets (containing an n-type structure). The current-voltage curve of CN (this work) is shown in Fig. 9(a). When the reverse voltage was increased to the breakdown voltage value, the current instantly increased, indicating that the p-n junction contained in this CN was broken down, which is a typical p-n junction characteristic. Therefore, this CN photocatalyst contained a certain size of a p-n junction structure. As shown in Fig. 9(b), preparing a photocatalyst with a p-n heterojunction led to highly efficient charge collection and separation [67–69]. In this structure, there was an internal electric field, which could cause the photocatalyst to generate electrons and charges under very low light intensity [70–72]. The photogenerated electrons were transferred to the n-type CN conduction band and reduced with water to generate hydrogen. Additionally, the photogenerated charges shifted to the p-type CN valence band and were oxidized with water to convert into oxygen. Therefore, under the same light intensity, the CN photocatalyst that contained the p-n heterojunction could generate more electrons and holes, greatly improving its activity and efficiency. The photocatalytic efficiency of CN was much higher than those of CN nanotubes and nanosheets.

4. Conclusions

CN photocatalysts with heterogeneous structures were successfully synthesized via a clever design for the first time. Benefitting from the interface interactions in hybrid architectures, the CN photocatalysts exhibited high photocatalytic activity. The hydrogen production rate of these CN photocatalysts reached $17028.82 \mu\text{mol h}^{-1}\text{g}^{-1}$, the AQE was 11.2% at 420 nm, and the lifetime of the charge carriers causing the fluorescence of CN reached 9.99 ns. Significantly, the CN photocatalysts displayed satisfactory results in overall water splitting without the addition of sacrificial agents. The average hydrogen and oxygen production rates were 270.95 and $115.21 \mu\text{mol h}^{-1}\text{g}^{-1}$ in 7 h, respectively. Furthermore, the structural model was established and discussed via first principles, and the Mott-Schottky plot and current-voltage curve were fabricated via electrochemical tests. This CN photocatalyst had a small p-n junction in its heterogeneous structure, which further enhanced its photocatalytic efficiency. Therefore, this work can promote the development of CN photocatalysts.

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version.

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Graphical Abstract

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Design of p-n homojunctions in metal-free carbon nitride photocatalyst for overall water splitting

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In this work, we successfully prepared a CN material with a heterogeneous structure via a clever design for the first time. Benefiting from the interface interactions in hybrid architectures, the CN photocatalysts exhibited high photocatalytic activity.

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设计p-n同质结构实现碳氮光催化剂的全解水性能

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摘要: 非金属氮化碳(CN)因其独特的光催化性能而备受关注. 本文利用水热处理、高温烧结、高能球磨和烧结的方法成功制得一种具有混合结构的CN光催化剂. 先以三聚氰胺为原料进行水热处理(180 °C, 24 h), 过滤干燥后, 转移到高纯氩气保护下的管式炉中, 于550 °C处理1 h得到CN材料. 然后将CN用三聚氰胺和氟化铵水热180 °C处理24 h, 过滤、干燥、煅烧(550 °C, 1 h)得到第二种材料. 最后将其与CN材料按等比例混合, 经高能球磨研磨, 再于管式炉中在气氛保护下淬火, 得到最终催化剂样品. 由于这种结构的界面作用, 使CN光催化剂显示出了高的光催化活性. 它的产氢效果可以高达17028.82 $\mu\text{mol h}^{-1} \text{g}^{-1}$, 在420 nm光照下, 其光量子效率也达到11.2%. 随后, 采用纳秒级别的时间分辨荧光(PL)光谱测得其荧光寿命为9.9 ns. 有助于电子与空穴参与反应更有趣的是, 在不加牺牲剂时, 该光催化剂具有高效的全解水效果, 其产氢效率为270.95 $\mu\text{mol h}^{-1} \text{g}^{-1}$, 产氧效率为115.21 $\mu\text{mol h}^{-1} \text{g}^{-1}$, 有望实际用于全解水反应中. 另外, 通过紫外可见漫反射光谱, PL光谱和材料的比表面等测试来考察该CN光催化剂效果好的原因. 发现该材料具有更高比表面积有更多活性点参与反应. 同时, 通过电化学测试获得了肖特基曲线和电流-电压曲线, 发现该光催化剂里含有少量的pn结构, 这种结构使材料在弱光下也会产生光生载流子, 实际上它是起到光生载流子的激发作用, 即在相同光照下, 就会产生更多的光生载流子数量, 从而进一步提高了其催化效果. 因此, 本工作对优化碳氮光催化剂的催化效果有很好的指导意义.

关键词: 二维非金属光催化剂; 氮化碳; 全解水; 时间分辨光谱; 密度泛函理论; 多相结构

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