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Enhanced photocatalytic hydrogen production activity of highly crystalline carbon nitride synthesized by hydrochloric acid treatment

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ABSTRACT

Crystalline carbon nitride (CCN) prepared by a molten-salt method is attracting increased attention because of its promising properties and excellent photocatalytic activity. In this work, we further improve the crystallinity of CCN through synthesis by the molten-salt method under the action of aqueous hydrochloric acid (HCl) solution. Our results showed that the crystallinity of the as-prepared samples increased with increasing HCl concentration and reached the maximum value at 0.1 mol L⁻¹. This can be attributed to the removal of some potassium ions (K⁺) from the terminal amino groups of CCN by the aqueous HCl solution, which results in a release of the polymerization sites. As a result, the crystallinity of the as-prepared samples further increased. Moreover, the obtained 0.1 highly crystalline carbon nitride (0.1HCCN; treated with 0.1 mol L⁻¹ aqueous HCl solution) exhibited an excellent photocatalytic hydrogen evolution of 683.54 μmol h⁻¹ g⁻¹ and a quantum efficiency of 6.6% at 420 nm with triethanolamine as the sacrificial agent. This photocatalytic hydrogen evolution was 2 and 10 times higher than those of CCN and bulk carbon nitride, respectively. The enhanced photocatalytic activity was attributed to the improved crystallinity and intercalation of K⁺ into the xHCCN interlayer. The improved crystallinity can decrease the number of surface defects and hydrogen bonds in the as-prepared sample, thereby increasing the mobility of the photoinduced carriers and reducing the recombination sites of the electron-hole pairs. The K⁺ intercalated into the xHCCN interlayer also promoted the transfer of the photoinduced electrons because these ions can increase the electronic delocalization and extend the π-conjugated systems. This study may provide new insights into the further development of the molten-salt method.

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1. Introduction

Photocatalytic water splitting into hydrogen is considered as an ideal way to address the environmental and global energy problems because of the high energy density and zero pollution

characteristics of hydrogen [1–9]. Since the successful application of graphitic carbon nitride (g-C₃N₄) polymer in the field of photocatalysis in 2009 [10], this metal-free photocatalyst has attracted considerable attention because of its chemical stability, accessibility, low cost, and nontoxicity [11–17]. However,

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g-C₃N₄ obtained by conventional thermal polymerization of nitrogen-containing precursors presents an amorphous or semi-crystalline structure and a poor photocatalytic activity because the nitrogen-containing precursors are incompletely polymerized, which results in massive residual amino groups in the amorphous or semi-crystalline carbon nitrogen (CN) during the condensation process. Moreover, the abundance of hydrogen bonds in the amorphous or semi-crystalline CN framework increases the recombination centers for the charge carriers. These factors are the main cause of the moderate photocatalytic performance of g-C₃N₄. [18,19].

To address these issues, various strategies such as molten-salt method [20,21], microwave-assisted synthesis [22,23], and some other methods [24–28] have been proposed for the synthesis of crystalline carbon nitride (CCN). Among these, molten-salt method is widely used because it is convenient, environment friendly, and powerful [29]. At present, the CCN prepared by molten-salt method can be divided into two types: poly (triazine imides) (PTI) and poly (heptazine imides) (PHI). The photocatalytic activity of PHI is superior to that of PTI owing to the presence of a larger π -conjugated system in the heptazine unit, which is favorable for optical absorption and promotes the mobility of photoinduced carriers [30,31]. For instance, Zeng et al. [32] designed highly crystalline CCN with triazine (CCN_{PTI}) and heptazine subunits (CCN_{PHI}) by molten-salt method. As expected, the photocatalytic hydrogen evolution of CCN_{PHI} is considerably higher than that of CCN_{PTI} because of the low light-harvesting capability and limited extension of the aromatic rings of CCN_{PTI}. However, the intensity of the (002) facets of the prepared CCN_{PHI} is always lower than that of bulk carbon nitride (BCN) and its crystallinity is still not satisfactory [33], even if the prepared CCN_{PHI} shows a good photocatalytic activity. Moreover, the CCN prepared by molten-salt method contains a certain amount of K⁺ [34]. Most of the literature reports have pointed out that K⁺ can promote the photocatalytic activity of CCN, but no specific research on K⁺ has been carried out or reported.

In this work, we report a facile method to synthesize highly crystalline carbon nitride (HCCN) based on molten-salt method by aqueous HCl solution treatment. The obtained 0.1HCCN (under the treatment of 0.1 mol L⁻¹ aqueous HCl solution) exhibited optimum crystallinity and an appropriate concentration of K⁺, compared with those of the other samples. The excellent crystallinity can decrease the surface defects and hydrogen bonds in the as-prepared sample, which increases the mobility of the photoinduced carriers and reduces the recombination sites of the electron-hole pairs. Moreover, the K⁺ intercalated into the xHCCN interlayer also promote the transfer of photoinduced electrons because they can increase the electronic delocalization and extend the π -conjugated systems. Owing to these features, 0.1HCCN showed an excellent photocatalytic hydrogen evolution of 683.54 $\mu\text{mol h}^{-1} \text{g}^{-1}$ and a quantum efficiency of 6.6% at 420 nm with triethanolamine (TEOA) as the sacrificial agent. This represents a photocatalytic hydrogen evolution rate (HER) that is approximately 2 and 10 times higher than those of CCN and BCN, respectively.

2. Experimental

2.1. Materials

The melamine (C₃H₆N₆, 99%), HCl (36%–38%), KCl (99.5%), and LiCl (97%) used were of analytical grade and employed without further purification. Deionized water was used in all the experiments.

2.2. Sample preparation

CCN was synthesized in accordance with previous studies. In brief, 8 g of melamine was heated to 500 °C for 4 h at a rate of 12 °C min⁻¹ under air atmosphere. Subsequently, the light-yellow product (600 mg) obtained was ground with KCl (3.3 g) and LiCl (2.7 g) in a crucible. Then, the mixture was heated to 550 °C for 4 h at a rate of 5 °C min⁻¹ under N₂ atmosphere in a muffle furnace. The product was washed with boiling water and collected after drying overnight at 60 °C in an oven. The obtained sample was referred to as CCN. Finally, the obtained CCN (100 mg) was disposed with HCl solution (0.005, 0.01, 0.1, and 0.2 mol L⁻¹) and stirred for 1 h. The final products were washed with deionized water and collected after drying overnight at 60 °C in an oven. The products were labeled as xHCCN, where x refers to 0.005, 0.01, 0.1, and 0.2 (the concentration of the HCl solution in moles per liter).

2.3. Characterization

The XRD patterns were recorded on a D8-Advance diffractometer (Bruker, German) with nickel-filtered Cu K α radiation at a scan rate (2 θ) of 10° min⁻¹, an accelerating voltage of 40 kV, and a current of 40 mA. The TEM images were obtained using a Hitachi H-7650 (HITACHI, Japan) transmission electron microscope at an accelerating voltage of 200 kV, and HRTEM analysis was performed with a JEM-2100F (JEOL, Japan) microscope. The SEM images were recorded on an S-4800 (HITACHI, Japan) instrument. The UV-vis diffuse reflectance spectra (DRS) were obtained using a UV-vis spectrophotometer (Lambda 650s), and Teflon was used as the reflectance standard. The X-ray photoelectron spectroscopy (XPS) spectra were obtained with the help of a Leybold Heraeus–Shenyang SKL-12 X-ray photoelectron spectrometer, and Mg K α served as the excitation source. The electron paramagnetic resonance (EPR) spectra were obtained using a suitable spectrometer (Bruker, German) at room temperature. The time-resolved fluorescence decay spectra were recorded at room temperature on a fluorescence spectrophotometer (Edinburgh, FS5).

The photocatalytic H₂ productions of the obtained photocatalysts were measured in a 100 mL three-necked flask at atmospheric pressure and room temperature. A 350 W xenon arc lamp was utilized as the light source and aqueous 10% TEOA solution (by volume) was used as the sacrificial agent. The details of the steps involved are as follow. 20 mg of the samples were dispersed in 80 mL of the sacrificial agent by loading 3% platinum as the co-catalyst. The suspension solution of the mixture of photocatalysts was degassed with N₂ for

30 min to remove the remaining O₂ and air in the flask. After 1 h of illumination, 0.4 mL of gas was extracted, which was detected with a gas chromatograph (GC-2004C, Japan).

The wavelength-dependent HERs of TF samples were determined through a method similar to that of photocatalytic H₂ production, except for the xenon arc lamp being replaced with an LED equipped with different monochromatic lights. The averaged irradiation intensity of the different monochromatic lights realized by controlling the internal power was 80 mW cm⁻². QE was obtained using the Nether equation: $QE = \text{number of reacted electrons} \div \text{number of incident photons} \times 100\% = \text{number of evolved H}_2 \text{ molecules} \times 2 \div \text{number of incident photons} \times 100\%$.

The photocurrent curves and the electrochemical impedance spectroscopy (EIS) patterns were obtained by using a CHI660E (Shanghai Chenhua Limited, China) electrochemical analyzer with a three-electrode system that employs a platinum wire and Ag/AgCl as the counter and reference electrodes, respectively. The working electrodes were prepared glass electrodes with an effective area of ca. 1.0 cm². A 350 W xenon arc lamp and 0.5 mol L⁻¹ aqueous Na₂SO₄ solution were used as the light source and electrolyte, respectively.

The glass working electrode was synthesized as follows. A mixture of 0.02 g of the sample, 0.02 g of polyethyleneglycol, and 0.5 mL of ethanol was ground into a slurry. Doctor blade method was used to evenly coat the slurry onto a 2 cm × 1.2 cm fluorine-doped SnO₂-coated glass electrode. Finally, the obtained glass electrodes were dried at 100 °C for 60 min in an oven.

3. Results and discussion

3.1. Structure and morphology of the samples

The X-ray diffraction (XRD) patterns of the samples are shown in Fig. 1. For BCN, the peak at 27.8° (indexed as (002)) was assigned to the layered stacking of heptazine frameworks. The peak at 13.1° (indexed as (100)) was attributed to the in-plane structure [35–37]. However, two main peaks located at 8.1° and 28.3° were found for CCN. The former peak shifted to a lower angle, compared to those of BCN, because of the enlarged in-plane repeating motifs [38]. The latter peak shifted from 27.4° to 28.3°, which corresponded to a decreased inter-

layer distance [33]. In the case of xHCCN, the weak peak at 8.1° can be observed in all the samples and does not significantly change compared with that of CCN. However, the (002) peak intensity and position increased and shifted to a larger degree with an increase in the concentration of the aqueous HCl solution from 0.005 to 0.1 mol L⁻¹. This phenomenon indicated that the interlayer distance in xHCCN decreases with the increase in the concentration of the aqueous HCl solution from 0.005 to 0.1 mol L⁻¹, which can be attributed to the enhanced interaction between the layers. Interestingly, when the concentration of the HCl solution is up to 0.2 mol L⁻¹, the (002) peak intensity of 0.2HCCN decreases, compared with that of 0.1HCCN. This phenomenon may be attributed to destruction of the structure of the CN framework [39]. As a comparison, the XRD pattern of BCN obtained after treatment with aqueous HCl solution is displayed in Fig. S1. The sharply weakened (002) peak confirms the destruction of the structure of CN. Moreover, the full width at half maximum (FWHM) of the (002) peaks of CCN and xHCCN is narrower than that of BCN (Fig. 1b), which suggests high crystallinities of CCN and xHCCN. Moreover, the narrowest FWHM can be found in 0.1HCCN, which indicates that 0.1HCCN exhibits the highest crystallinity among these samples.

The chemical compositions of BCN, CCN, and xHCCN were further identified by FTIR spectroscopy. As shown in Fig. 2a, peaks at 3000–3500, 1200–1700, and 810 cm⁻¹ appear for BCN; these peaks are attributed to the terminal amino group, C–N stretching vibrations, and bending mode of heptazine, respectively [42–46]. The FTIR spectra of CCN and xHCCN are similar to that of BCN, which suggests that the molten-salt method and HCl treatment do not change the main structure of the CN framework. Further, a decrease in the intensity of the peak at 3000–3500 cm⁻¹ can be observed in the cases of CCN and xHCCN, compared with that in the case of BCN, which indicates that the ammonia content decreases in CCN and xHCCN. This result was further confirmed by the appearance of a new peak at 2150 cm⁻¹ for CCN and xHCCN that was ascribed to the existence of terminal cyano groups. Moreover, the formation of cyano groups can affect the light harvesting and charge separation, which are beneficial to the photocatalytic reaction of CCN and xHCCN [47,48].

The optical absorptions of BCN, CCN, and xHCCN were characterized based on their UV-vis DRS. As shown in Fig. 2b, all the samples reveal the typical absorption curve of semicon-

Fig. 1. (a) XRD patterns and (b) FWHMs of as-prepared BCN, CCN, and xHCCN.

Fig. 2. (a) FTIR spectra and (b) UV-vis DRS of as-prepared BCN, CCN, and xHCCN (inset shows the colors of BCN, CCN, and HCCN); (c) Time-resolved photoluminescence (PL) spectra of 0.01HCCN, 0.1HCCN, CCN, and BCN; (d) EPR spectra of BCN, CCN, and 0.1HCCN.

ductors. As expected, the optical absorption intensities of CCN and xHCCN were significantly higher than that of BCN, because of the crystallinity and the existence of cyano groups in CCN and xHCCN. This result matched well with the XRD and FTIR results. This finding is beneficial for the photocatalytic activity because a higher optical absorption can lead to a greater number of photons being utilized in the photocatalytic reaction. Moreover, the absorption edge of CCN exhibited a red shift in comparison with that of BCN, which may be attributed to the doping of K^+ in CCN during the preparation process. Moreover, the absorption edges of xHCCN displayed a blue shift, compared with that of CCN, because of the decreased K^+ contents of xHCCN during the HCl treatment. The bandgap energies were 2.7, 2.74, and 2.8 eV for CCN, BCN, and 0.1HCCN, respectively, and were estimated from the respective Tauc plots (Fig. S2). In fact, the bandgap slightly differed from that of xHCCN owing to the differences in the K^+ concentration and crystallinity.

The time-resolved fluorescence spectra were also obtained to confirm the efficiency of electron-hole pair separation and migration. As shown in Fig. 2c, BCN exhibits a slower PL decay, compared with those of CCN and xHCCN (where $x = 0.01$ and 0.1), which show similar decay rates. The radiative lifetimes

and the related parameters of the fitted decay spectra are listed in Table 1. The average lifetime of 16.487 ns for 0.1HCCN was notably shorter than those of BCN (19.819 ns) and CCN (16.571 ns). The reduced average lifetime of 0.1HCCN, which indicates effective migration of charge carriers, was very beneficial for photocatalytic reactions [49,50]. This result was further proven by the EPR spectra. As shown in Fig. 2d, three samples display a single peak centered at a g -value of 2.0034, which indicates the existence of unpaired electrons in the sp^2 carbon in the π -conjugated aromatic rings [51–53]. Notably, the peak intensity of 0.1HCCN was lower than that of BCN. The decreased lone-pair electron density may be attributed to the high crystallinity and low surface-defect density of 0.1HCCN [54]. In general, surface defects can be considered as recombination centers that limit carrier separation and thereby reduce the photocatalytic activity. These results confirmed that the separation and migration of charge carriers in 0.1HCCN are superior to those in BCN and CCN.

The morphologies of the as-prepared samples were investigated by SEM. As shown in Fig. 3, BCN exhibits a stacking layered structure, whereas CCN and xHCCN reveal nanorod structures. Notably, the nanorod structure of the xHCCN samples

Table 1

Fluorescence decay lifetimes and percentages of photoinduced carriers in pristine BCN, CCN, and 0.1 HCCN.

Sample	τ_1 /ns	A_1 /%	τ_2 /ns	A_2 /%	τ_3 /ns	A_3 /%	τ /ns
BCN	3.530	29.388	10.968	40.093	47.131	30.519	19.819
CCN	2.992	19.871	8.312	41.437	32.389	38.692	16.571
0.1HCCN	2.766	17.038	7.867	43.196	32.215	39.766	16.487

Fig. 3. SEM images of (a) BCN, (b) CCN, (c) 0.01HCCN, and (d) 0.1HCCN.

becomes clearer with an increase in the HCl concentration. The crystalline structure of the as-prepared samples was further confirmed by TEM. As shown in Fig. 4a and 4b, the nanorod structures of CCN and xHCCN can be observed using the TEM images. Lattice fringes of spacing 0.33 nm are clearly observed on CCN and xHCCN in Fig. 4c and 4d, which strongly supports the idea that their structure is crystalline. However, the lattice fringe of BCN is not observed in Fig. S3, which indicates that the structure of BCN is amorphous. These results well agreed with the XRD results, which revealed the planar diffraction distances.

The elemental compositions of 0.1HCCN and 0.01HCCN were obtained by XPS. As shown in Fig. 5a, 0.1HCCN and 0.01HCCN exhibit similar survey spectra. Obviously, carbon, nitrogen, oxygen, and potassium elements can be detected from the two curves. The additional oxygen atom signals originated from the absorbed H_2O or O_2 molecules [55]. The high-resolution XPS C 1s, N 1s, and K 2p spectra of 0.01HCCN and 0.1HCCN are shown in Figs. 5b–5d, respectively. Different peaks at 288.5, 286.4, and 284.8 eV can be observed in the high-resolution C 1s (Fig. 5b) spectrum that probably originat-

Fig. 4. (a, b) TEM and (c, d) HRTEM images of (a, c) CCN and (b, d) 0.1HCCN.

ed from the sp^2 bonds of the nitrogen-containing heptazine rings ($\text{N}=\text{C}=\text{N}$), cyano group, and adventitious carbon, respectively [56,57]. In the high-resolution N 1s spectrum of 0.01HCCN, four peaks are observed at 404.4, 401.6, 400.7, and 398.9 eV. The peaks at 404.4, 401.6, and 398.9 eV were attributed to the π excitation, tertiary nitrogen, and heptazine rings ($\text{C}=\text{N}=\text{C}$) (NC_3) [58], respectively, whereas the peak at 400.7 eV was assigned to the terminal amino groups [59]. In the high-resolution N 1s spectrum of 0.1HCCN, three similar peaks at 404.4, 401.6, and 398.9 eV can be observed. However, an obvious shift of the peak at 400.4 eV is observed relative to that of 0.01HCCN. The peak shift observed for the terminal amino groups indicates strong effects between the nitrogen and potassium atoms. K 2p peaks also appear in the sample spectra. As a comparison, the XPS spectrum of CCN was also recorded (Fig. S5). As shown in Fig. S5d and S5d, the K state is almost the same before and after the HCl treatment. These results may be attributed to the K^+ acting as charge compensators that replace the hydrogen ions in the terminal amino groups formed due to the breakage of the hydrogen bonds in BCN [60]. However, the concentration of K^+ changes from 2.63% in CCN to 0.81% in 0.01HCCN and 0.57% in 0.1HCCN owing to the instability of the terminal K–N, which proves that increasing the concentration of HCl can gradually decrease the concentration of K^+ . These results confirm that HCl treatment only changes the concentration of K^+ and not the structure of the sample.

3.2. Formation mechanism

Based on the above characterization results, a possible formation mechanism of xHCCN is shown in Fig. 6. The synthesis process was divided into three steps. In the first step (500 °C, 4 h), the melamine molecules polymerized to form heptazine nitride CN frameworks with massive hydrogen bonds and amino groups. In the second step (550 °C, 4 h), the solid KCl/LiCl mixture (melting point: 450 °C) melted to provide a liquid medium for heptazine CN. Under this condition, some of the K^+ acted as charge compensators to replace the hydrogen ions of the terminal amino groups that were formed due to the breakage of the hydrogen bonds in BCN. Another K^+ was doped into the heptazine interlayer, which resulted in the formation of CCN with a massive amount of K^+ . However, unsatisfactory crystallinity was observed in CCN when the K^+ in the terminal amino groups of CCN occupied some polymerization sites of the heptazine unit. In the last step (HCl treatment), under the influence of HCl, some of the K^+ in the terminal amino groups of CCN were removed and the polymerization sites released, which further enhanced the crystallinity of CCN.

3.3. Photoelectrochemical performances of the samples

Photoelectrochemical measurements were used to further investigate the separation and migration of the photogenerated carriers. The photocurrent curves of 0.01HCCN, 0.1HCCN, CCN, and BCN are shown in Fig. 7a. Among these samples, 0.1HCCN exhibited the highest photocurrent density owing to its high

Fig. 5. (a) XPS survey spectra, (b) C 1s, (c) N 1s, and (d) K 2p spectra of 0.01HCCN and 0.1HCCN. The XPS spectra show that the elemental compositions of 0.01HCCN and 0.1HCCN do not change, which suggest that the treatment with HCl does not change the structure of the samples. Only the concentration of K⁺ changes from 0.81% in 0.01HCCN to 0.57% in 0.1HCCN.

crystallinity and a suitable K⁺ doping concentration, which suggested the most efficient separation of photogenerated carriers. This result was further proven by EIS. Fig. 7b shows that 0.1HCCN exhibits the smallest semicircular Nyquist plot, compared with those of the other samples, which indicates enhanced photocatalytic activity.

3.4. Photocatalytic activities of the samples

The HERs were measured in TEOA (10 vol%) solution for 1 h light irradiation by loading 3% platinum as a co-catalyst. As shown in Fig. 8a, obviously, both CCN and xHCCN exhibit en-

hanced HERs compared with BCN. Moreover, in the case of xHCCN, the HER gradually increased with the increase in the aqueous HCl concentration from 0.005 to 0.1 mol L⁻¹. This finding was attributed to the excess amount of K⁺ in the 0.005HCCN sample, which occupied the polymerization and active sites of the photocatalytic reaction, which resulted in undesirable crystallinity and photocatalytic activity. However, with the increase in the concentration of the aqueous HCl solution, the polymerization and active sites of the photocatalytic reaction were gradually released, which led to increased crystallinity and number of active sites for the photocatalytic reaction. Consequently, the HER gradually increased from 0.005HCCN to 0.1HCCN. However, with the increase in the aqueous HCl concentration to 0.2 mol L⁻¹, the HER rapidly decreased, which probably resulted from an increase in the number of recombination centers of the photogenerated carriers caused by destruction of the structure of the CN framework. Among the xHCCN samples, the HER of 0.1HCCN was the highest at 683.54 $\mu\text{mol h}^{-1} \text{g}^{-1}$, which was higher than those of BCN and CCN by 2 and 10 times, respectively. The wavelength-dependent HER of 0.1HCCN was also determined by utilizing different monochromatic lights. Fig. 8b shows that the apparent quantum yield (AQY) was in line with the results obtained from the DRS. Under 420 nm monochromatic light irradiation, the AQY of 0.1HCCN was 6.6% when TEOA solution (10 vol%) was used as the sacrificial agent. Moreover, the sacrificial-dependent HER of 0.1HCCN was also determined. Four reagents, namely glycerinum, TEOA, ethane diamine, and lactic acid, were used as sacrificial agents to compare the photocatalytic activities, which are shown in Fig. 8c. Among these sacrificial agents, the HER_{TEOA} of 0.1HCCN is the highest, owing to the

Fig. 6. Possible synthesis process of HCCN by molten-salt method and aqueous HCl solution treatment. In the first step (500 °C, 12 °C min⁻¹), the melamine molecules polymerize to form heptazine nitride CN frameworks with a large number of hydrogen bonds and amino groups. In the second step (550 °C, 5 °C min⁻¹), CCN with a large amount of K⁺ is synthesized. In the last step (treatment with HCl), HCCN is obtained because some of the K⁺ in the CCN frameworks have been removed and the polymerization sites released, which further enhance the crystallinity of CCN.

Fig. 7. (a) Photocurrent curves and (b) EIS plots of 0.01HCCN, 0.1HCCN, CCN, and BCN. Both the photocurrent curves and EIS results indicate that 0.1HCCN exhibits the potential to realize an excellent photocatalytic activity.

Fig. 8. (a) HERs of the samples loaded with 3% platinum co-catalyst that were measured under 1 h light irradiation. TEOA/ H_2O (1:10 vol%) solution was chosen as the sacrificial agent; (b) Wavelength-dependent HER of 0.1HCCN under 1 h monochromatic light irradiation using TEOA/ H_2O (1:10 vol%) solution as the sacrificial agent and for 3% loading of platinum as a co-catalyst; (c) Results of photocatalytic activity tests of 0.1HCCN loaded with 3% platinum co-catalyst that were obtained with different sacrificial agents under 1 h light irradiation; (d) Results of photocatalytic stability tests of 0.1HCCN and CCN conducted using TEOA/ H_2O (1:10 vol%) solution as the sacrificial agent for 3% loading of platinum as the co-catalyst.

suitable chemical reactivity of TEOA. Finally, the stabilities of the HERs of 0.1HCCN and CCN were studied under 1 h light irradiation by performing four circulation operations in TEOA (10 vol%) solution after loading 3% platinum as the co-catalyst. As shown in Fig. 8d, the HERs of CCN and 0.1HCCN exhibit no obvious decay after four circulation operations, which indicate their satisfactory stabilities in the photocatalytic reactions.

3.5. Mechanism

Based on the above results, tentative mechanisms of the roles of BCN, CCN, and xHCCN in the photocatalytic reaction

were proposed. As shown in Fig. 9, under light irradiation, the samples are excited and produce free electrons and holes. In BCN sample, abundant intralayer hydrogen bonds and amino groups in the covalent CN framework and radiative charge carriers highly localized within each melon strand are observed, which lead to moderate intralayer transport of the photogenerated carriers [54,61]. As a result, massive recombination of the photogenerated electron-hole pairs occurs over the hydrogen bonds, and BCN exhibits a poor photocatalytic H_2 activity. In the case of CCN, the doping sites of K^+ are in the terminal amino groups and at the interlaminal positions. In primary CCN (i.e., no K^+ doping in CCN), the valence band (VB) edge

Fig. 9. Schematic of the tentative photocatalytic mechanisms of BCN, CCN, and HCCN. The BCN sample exhibits a moderate photocatalytic performance owing to the existence of hydrogen bonds. The photocatalytic performance of CCN is restricted because excess of active K^+ occupy the activity sites of the photocatalytic reaction. The xHCCN samples exhibit excellent photocatalytic activity owing to their excellent crystallinity and appropriate K^+ concentration, compared with those of the other samples.

covers all N2 atoms (Fig. S6), and the conduction band (CB) edge comprises C1, C2, N2, and N3. As a result, the bridging nitrogen (N1) atoms contribute little to the CB and VB edges, which suggests that the N1 atoms will not be excited to produce photoinduced electrons; thus, the transfer of the photoinduced electrons between the units of heptazine through the N1 atoms is restrained [62]. When K^+ are intercalated into the CCN interlayer, adjacent heptazine units can form delivery paths, increase the electronic delocalization, and extend the π -conjugated systems, which benefit charge-carrier transfer among the heptazine units [63]. However, the K^+ in the terminal amino groups occupy the polymerization sites of heptazine and the activity sites of the photocatalytic reaction [64]. As a result, CCN exhibits unsatisfactory crystallinity and photocatalytic H_2 activity. In the case of xHCCN, the K^+ in the terminal amino groups are removed with aqueous HCl solution. Thus, the crystallinity of xHCCN increases because of the release of the polymerization sites of heptazine, and the photocatalytic H_2 activity is enhanced owing to the increase in the number of activity sites for the photocatalytic reaction. Among the xHCCN, 0.1HCCN exhibits the highest photocatalytic H_2 activity owing to its excellent crystallinity and appropriate K^+ concentration, compared with those of the other samples.

4. Conclusions

We have successfully prepared a series of HCCN with an appropriate concentration of K^+ by molten-salt method. The improved crystallinity of the as-prepared samples can decrease the recombination sites of the electron–hole pairs and increase the mobility of the photoinduced carriers through decreases in the surface defects and hydrogen bonds. Moreover, the K^+ intercalated into the CCN interlayer also enhances the transfer of charge carriers because the former can increase the electronic delocalization and extend the π -conjugated systems. These features enable 0.1HCCN with the optimum crystallinity and the appropriate concentration of K^+ to be obtained; it exhibits an excellent photocatalytic hydrogen evolution of $683.54 \mu\text{mol}$

$\text{h}^{-1} \text{g}^{-1}$, which is 2 and 10 times those of CCN and BCN, respectively. A quantum efficiency of 6.6% was achieved at 420 nm by using TEOA as the sacrificial agent. This study may provide insights for further improving the light absorption and charge mobility of CCN.

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Graphical Abstract

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Enhanced photocatalytic hydrogen production activity of highly crystalline carbon nitride synthesized by hydrochloric acid treatment

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Highly crystalline carbon nitride, prepared by a molten-salt method with aqueous hydrochloric acid solution treatment, exhibited an enhanced photocatalytic H₂ production activity.

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盐酸处理制备高结晶氮化碳及其增强光催化产氢活性

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摘要: 由于氢气燃烧具有高能量和零污染的优点, 氢能一直被认为是解决环境污染和全球能源危机问题的新能源。而光催化剂可以将太阳能转化为氢能, 是目前制氢最理想的方式。近年来, 研究者的目光已经转向非金属光催化剂, 其中氮化碳光催化剂因其化学稳定性好、成本低和无毒性而备受关注。但是传统的利用含氮前驱体通过热聚合得到的氮化碳呈无定形或半结晶结构, 导致其光催化活性很差。而熔盐法制备的结晶氮化碳(CCN)则具有优异的光催化产氢性能。但是, 熔盐法得到的CCN依然没达到理想的结晶度。

在本文中, 我们用盐酸(HCl)洗涤处理熔盐法制备的产物, 进一步提高了CCN的结晶度。结果表明, 随着盐酸水溶液浓度的增加, 制备样品的结晶度增大, 在盐酸浓度为0.1 mol/L时, 样品结晶度达到最大值。这是因为盐酸水溶液可以去除CCN末端氨基中的一些钾离子, 导致聚合位点被释放, 所以进一步提高了样品的结晶度。而当盐酸浓度进一步提高到0.2 mol/L时, 氮化碳结构因为过高的盐酸浓度被破坏, 导致结晶度反而下降。以0.1 mol/L盐酸水溶液处理得到的0.1HCCN样品具有良好的光催化产氢性能, 在以三乙醇胺为牺牲剂时, 其光催化产氢速率达到 $683.54 \mu\text{mol h}^{-1} \text{g}^{-1}$, 在420 nm处的量子效率为6.6%, 光催化产氢速率分别是CCN和块状氮化碳的2倍和10倍。光催化活性的提高主要有两个原因: 样品结晶度的提高和钾离子嵌入xHCCN样品的中间层。其中, 样品结晶度的提高可以减少样品中的表面缺陷以及破坏结构中的氢键, 从而增加了光生载流子的迁移, 减少了电子空穴对的复合位点, 这都非常有利于光催化反应的进行。而插入到xHCCN中间层的钾也促进了光生电子的转移。这是因为桥连的氮原子(N1)并不会被激发产生光生电子, 因此抑制了光生电子在七嗪单元之间的迁移, 而插入到xHCCN中间层的K可以增加电子的离域性, 延长 π 共轭体系, 从而促进光生电子的转移, 进一步提高光催化产氢活性。本研究为熔盐法的进一步发展提供了新的思路。

关键词: 晶化氮化碳; 熔盐法; 光催化析氢; 钾离子; 盐酸水溶液

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