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Article

C-I codoped porous g-C₃N₄ for superior photocatalytic hydrogen evolution

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ABSTRACT

Porous C-I codoped carbon nitride materials were synthesized by in-situ codoping with iodized ionic liquid followed by post-thermal treatment in air. The effects of doping content of C-I codoping with different amounts of ionic liquid on the structural, optical and photocatalytic properties of the samples were investigated. Characterization results show that more compact interlayer sacking can be achieved by post-thermal treatment. Combined with C-I codoping by insertion of ionic liquids, much enlarged surface area but optimized *sp*² conjugated heterocyclic structure can be found in the catalysts. Optical and energy band analysis results evidence that the light absorptions especially in visible light region are significantly improved. Although the band gap of porous C-I codoped samples enlarge because of the generation of porous, the negatively shifted conduction band position thermodynamically supplies stronger motivation for water reduction. Photoelectricity tests reveal that the photo-induced electron density was increased after C-I codoping modification. Also, the recombination rate of electron-hole pairs is remarkably inhibited. The catalysts with moderate C-I codoping content perform sharply enhanced photocatalytic H₂ evolution activity under visible light irradiation. A H₂ evolution rate of 168.2 μmol/h was achieved and it was more than 9.8 times higher than pristine carbon nitride. This study demonstrates a novel non-metal doping strategy for synthesis and optimization of polymer semiconductor with gratifying photocatalytic H₂ evolution performance from water hydrolysis.

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1. Introduction

Hydrogen (H₂), a kind of clean energy, is regarded as an ideal substitute for fossil fuels, which is nonrenewable and the combustion products are harmful for the environment. One of the most promising ways to produce H₂ energy is to split water into H₂ by photocatalytic process, because photocatalysis technology could realize the conversion and utilization of abundant solar energy [1]. Semiconductor-based photocatalyst materials with high activity and good stability are the core of

photocatalytic process and great influence photocatalytic efficiency. To date, substantial research efforts have focused on developing a variety of visible-light responded photocatalysts, in order to extend the utilization of visible light in solar spectrum [2,3].

Relative to inorganic semiconductors, organic polymers usually contain no or few metal elements, possess abundant synthetic materials, and easy to realize processing modification. Based on these advantages, polymers with comparative band gaps have been developed and applied in photocatalytic

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reactions for H_2 evolution, such as heptazine-based microporous polymer networks (HMPs) and covalent triazine-based frameworks (CTFs) [4,5]. Graphitic carbon nitride ($g\text{-C}_3\text{N}_4$), an old but novel polymer semiconductor has been considered as a promising photocatalytic material. With appropriate band gap (~ 2.7 eV) and energy band positions ($E_{CB} = -1.3$ V and $E_{VB} = 1.4$ V, vs NHE at pH = 7), it can thermodynamically suitable for water reduction into H_2 [6]. However, the lower electron transport properties determines that a mass of works are still needed to modify and improve the photocatalytic performance of $g\text{-C}_3\text{N}_4$ semiconductors.

To address the inherent limitations, so many strategies have been applied to modify physicochemical structures of $g\text{-C}_3\text{N}_4$, such as semiconductor coupling, copolymerization, nanostructured design, and non-metal doping [7–19]. Doping is one of the most effective and convenient methods among these strategies. Non-metal doping is an effective way not only can improve charge separation due to electronegativity difference of atoms, but also keep non-metallic properties of semiconductor. For this, doping nonmetals by O, B, P and S could expand the visible-light response and adjust the energy band positions so as to improve the photoactivities [20–23]. In addition to the common single non-metal doping, codoping strategies with metal and nonmetal elements or multiple nonmetal elements have potential to develop high-performance $g\text{-C}_3\text{N}_4$ -based photocatalysts [24,25]. Choi et al. [26] prepared potassium (K) and phosphate (P) codoped carbon nitride (CN) framework from in situ incorporation method. The obtained catalyst exhibited a high apparent quantum yields (8.0 % at 420 nm) for H_2 production, and was about 25 times from those of bare CN. Liu et al. [27] prepared P-O codoped $g\text{-C}_3\text{N}_4$ from hydrothermal synthesis assisted by dissolution-precipitation process. Increases anoxic photocatalytic RhB degradation constants by approximately 27 times under visible light was achieved. In our previous work [28,29], boron (B) and fluorine (F) codoped $g\text{-C}_3\text{N}_4$ was prepared from direct calcination, and the precursors were mixed by imidazole tetrafluoroborate ionic liquid. The separated doping state by B and F in skeleton and surface of catalyst significantly improved the electronic properties of pristine $g\text{-C}_3\text{N}_4$, hence got much enhanced photocatalytic H_2 production rate.

Carbon (C) and iodine (I) are well known species to improve electrical conductivity and light absorption properties of semiconductors [30]. Up to now, although C and I doped $g\text{-C}_3\text{N}_4$ photocatalysts have been explored, little work has been done on the C and I codoped $g\text{-C}_3\text{N}_4$, and the effects of the codoping on its electronic structure, band gap, and photocatalytic activity for H_2 evolution have not been investigated yet [31–33]. In this work, porous C-I codoped $g\text{-C}_3\text{N}_4$ photocatalysts were synthesized via two-step methods including thermal polymerization of a mixture of dicyandiamide (DCDA), urea and 1-ethyl-3-methylimidazolium iodide ([Emim]I), then post-thermal treated in air. The characteristics of the codoped materials were analyzed and the results show that the post-thermal activation and codoped C-I both play important role in the enhancement of photocatalytic H_2 evolution activity,

the former of which contributes to the compact conjugate accumulation and the latter improves visible light response and charge transport. This work might provide feasible route for developing visible-light nanostructured $g\text{-C}_3\text{N}_4$ photocatalysts for efficient H_2 production from water reduction.

2. Experimental

2.1. Catalyst preparation

All of the materials were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and used as received without further purification.

C-I codoped $g\text{-C}_3\text{N}_4$ was synthesized as follows: 4.0 g of dicyandiamide (DCDA), 4.0 g of urea and measurable 1-ethyl-3-methylimidazolium iodide ([Emim]I) were dissolved in H_2O with vigorous stirring, and then the resulting solution was evaporated to dryness at 80 °C. The solid mixtures were placed into covered porcelain crucibles and direct calcined at 550 °C in a muffle furnace for 2 h with a ramp rate of 5 °C/min. The process yield was about 31.7%. The obtained samples were denoted as $CN I_x$. Then, the $CN I_x$ products were taken into open porcelain crucibles and further calcined at 550 °C for 2 h. The samples were denoted as $CN I N_x$ and the process yield was about 59.6% to $CN I_x$. Here, x refers to the used mass of [Emim]I (g).

2.2. Catalyst characterization

The following specific analysis methods were used to test the performance of the sample. X-ray diffraction (XRD) patterns were collected on a Bruker D8 Advance diffractometer with $Cu K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). Scanning electron microscope with energy-dispersive X-ray spectroscopy analysis (EDS) was performed using a Nova NanoSEM 230 instrument. Nitrogen adsorption-desorption isotherms were collected at -196 °C using a Micromeritics ASAP 2020 surface area and porosity analyzer. X-ray photoelectron spectroscopy was made using a Thermo ESCALAB250Xi spectrometer with $Mg K\alpha$ radiation as the excitation source. Ultraviolet-visible (UV-Vis) diffuse reflectance spectroscopy (DRS) was performed on a Varian Cary 500 Scan UV-visible system. The photoluminescence (PL) emission spectra were recorded on an QuantaMasterTM fluorescence spectrometer. The electrochemical experiments were taken on a CHI660D workstation. The working electrode was prepared on a fluorine-doped tin oxide (FTO) transparent conductive film glass. Electrochemical measurements were performed in a typical three electrode cell, using a Pt piece and calomel electrode as counter electrode and reference electrode, respectively. The electrolyte was 0.2 mol/L Na_2SO_4 aqueous solution.

2.3. Photocatalytic tests

Photocatalytic activity tests were evaluated by the photocatalytic hydrogen evolution from water under visible light irradiation ($\lambda > 400$ nm). Reactions were carried out in a

Pyrex top-irradiation reaction vessel connected to a glass closed gas system. In each experiment, 50 mg of photocatalyst powder was dispersed in an aqueous solution (100 mL) containing triethanolamine (10 vol%) as a sacrificial electron donor. 3 wt% Pt was loaded on the surface of the catalyst by in situ photodeposition method using H_2PtCl_6 . The reaction solution was evacuated several times to remove air completely prior to irradiation under a 300 W xenon-lamp (CEL-HXF300). The wavelength of the incident light was controlled by applying appropriate cut-off filters. The temperature of the reaction solution was maintained at 6 °C by the flow of cooling water during the reaction. The evolved gases were analyzed by gas chromatography equipped with a thermal conductive detector (TCD) and a 5 Å molecular sieve column, using nitrogen as carrier gas.

3. Results and discussion

3.1. Morphology and structure characterizations

The morphology of the CNI and CNIN samples was investigated by SEM observations and the results were shown in Fig. 1. Clearly, without participation of ILs, the obtained bulk sample CNI_0 features typical dense slate-like lamellar agglomerates. For $\text{CNI}_{0.2}$, the laminar particles became smashed to small pieces, suggesting that the incorporated ILs decomposed during the synthesis process and caused disorder degree of conjugated plane of CN materials due to particle fragmentation and size reduction. In the meantime, there are

significant fractured slice can be seen in CNIN_0 after post-thermal treatment, derived from the further thermal decomposition of unpolymerized CN fragments. By conjunct effects of ILs incorporation and recalcination, the $\text{CNIN}_{0.2}$ possesses unconsolidated porous accumulation, which is important for increased surface contact in heterogeneous catalytic reaction.

EDS elements analysis for $\text{CNIN}_{0.2}$ is inserted in Fig. 1(d). In addition to C, N and O, which were regular necessary in $\text{g-C}_3\text{N}_4$, I was also observed. SEM elements mapping images for C, N, O and I also confirmed the existence of indine. The relative element contents (wt%) of prepared samples were analyzed and shown in Fig. 1. Although few iodine can be found uniformly distributed in CNI samples synthesized from ILs doping, and with the increase of ILs mass used, the iodine contents in corresponding products apparent increased. After post-thermal treatment, the volatilization of some I was inevitable, and the content reduced. Moreover, the content of C also increases with the increase amount of used ILs after secondary heat-treatment. The increased C content resulted from high-carbon ILs. These results could identify that C-I codoped $\text{g-C}_3\text{N}_4$ products were prepared from iodized ionic liquid as dopant source. From previous reports, single C doped and I doped could improve the optical absorption and electronic property, hence in favour of the improvement of photocatalytic performance of $\text{g-C}_3\text{N}_4$ [28,29]. Therefore, the C-I co-doped samples could show predictable optimized structure and photocatalytic properties.

Fig. 2 shows XRD patterns of pristine CNI_0 and post-thermal treated C-I Co-doped ($\text{g-C}_3\text{N}_4$) graphitic carbon nitride samples. Two characteristic peaks of graphite-like carbon nitride were observed in all samples. The small peaks at about 13.1° corresponded to (100) in-planar repeat tri-s-triazine units and the strong peaks around 27.4° corresponded to (002) interlayer reflection of $\text{g-C}_3\text{N}_4$ [34,35]. Compared with pure $\text{g-C}_3\text{N}_4$, there was no obvious change in the (001) diffraction peak of samples doped with iodide-containing liquids, indicating that there was no change in the interplanar spacing. As shown in Fig. 2(b), the (002) peak shifts from 27.4° of CNI_0 to 27.5° of CNIN_0 , reflecting the XRD d -spacing changes from 0.325 nm for CNI_0 to 0.324 nm for CNIN_0 , also the peak intensity was enhanced obviously. It indicates an optimized compactness and higher polymerization degree due to improved post-polycondensation, which could strongly avails the charge transport in organic semiconductors [36]. With the increasing content of inserted ILs, the (002) peaks for CNIN slightly lower but no shift. That is to say, more defects occurred after co-doped by C and I, but no significant change for the lamellar stacking characteristic, which is consistent with the morphology observation.

Increased porosity is of great concern for heterogeneous photocatalysis. The textural properties of CNI and CNIN samples were analyzed using a nitrogen adsorption-desorption spectrometer. The isotherms and the Barrett-Joyner-Halenda (BJH) pore size distributions were shown in Fig. 3. The isotherm of the samples shows type IV with H3 hysteresis loops, and the adsorption branch of nitrogen isotherms shows a sharp increase at high relative pressures, proving the existence of

Fig. 1. Typical SEM micrographs of CNI_0 (a), $\text{CNI}_{0.2}$ (b), CNIN_0 (c), $\text{CNIN}_{0.2}$ (d) samples, EDS spectrum and elements mapping images of $\text{CNIN}_{0.2}$.

Fig. 2. XRD patterns of CNI and CNIN samples.

Fig. 3. N₂ adsorption-desorption isotherms (a) and the corresponding BJH pore-size distribution (b) of different samples.

mesopores. The surface areas measured by the BET technique for CNIN₀ is 37.3 m²/g, about 2 times higher than that of CNI₀, because of the post-thermal decomposition effect. However, the surface area of CNI_{0.2} (13.8 m²/g) slight decrease, which may resulted from the heteroatomic doping. It is expected that the surface area for CNIN_{0.2} increased to 54.4 m²/g, nearly 4 times to that of CNI_{0.2}. The increased surface area of CNIN_{0.2} may resulted from intensive decomposition of CNI_{0.2}, which possessed lower degree of polymerization than CNI₀ due to heteroatomic doping. Additionally, the pore-size distribution curves of all samples are wide around pore diameters of 10–50 nm, indicating the co-existence of meso- and macropores. Obviously, the pore volumes of samples treated by secondary calcination and doping increased. The results show that the increase of surface area and porosity for C-I co-doped samples could increase the surface active sites, hence improve photocatalytic performance. From the comparison results, post-thermal treatment is more crucial to enlarge porosity. Heteroatomic co-doping realized by ILs inserting take no obvious affect for the texture of CN catalysts. Although CNIN_{0.2} has no significant increase in the absorption of visible light compared with CNI₀, the increased specific surface area adds more active sites for

surface catalytic reaction. So the increase of porous properties plays important role in optimizing the photocatalytic performance. Nevertheless, microstructure photoelectric property changes could not be ignored, which are equal or more important for photocatalysis.

To further reveal the microstructure and the chemical environment of surface elements, X-ray photoelectron spectra (XPS) were characterized and shown. Fig. 4(a) shows XPS scan spectra of CNIN_{0.2} and signals for C, N, O and I can be detected. The high resolution spectra for I 3d are shown in Fig. 4(b). I 3d region can be fitted into four peaks in the spectrum around 617.5, 618.7, 629.1 and 630.8 eV. The two peaks about 629.1 eV (I 3d_{3/2}) and 617.5 eV (I 3d_{5/2}) show the existence of I⁻, while the other two weaker peaks at 621.6 (I 3d_{5/2}) and 633.1 eV (I 3d_{3/2}) indicate the oxidation state of doped iodine I⁵⁺ during the reaction process [33,37,38]. The high-resolution C 1s and N 1s XPS spectra were also analyzed. The mainly carbon species centered at 284.6, 286.3 and 288.1 eV are assigned to C–C, C–O and N-containing aromatic ring (N–C=N), respectively [39]. The N1s spectrum of CNIN_{0.2} is deconstructed into three peaks located at 398.6, 400.0 and 401.0 eV, which are assigned to sp²-hybridized nitrogen (N1) in triazine rings (C–N=C), tertiary

Fig. 4. Survey (a) and high-resolution XPS spectra of I 3d (b), C 1s (c) and N 1s (d) of CNIN_{0.2}.

nitrogen N₂-(C)₃ groups (N2) and amino functions carrying hydrogen (C-N-H, N3) [40].

To further investigate the influence of post-thermal treatment and C-I codoping modification, the surface elements chemical states of CNI₀, CNIN₀ and CNIN_{0.2} from XPS were parsed and summarized in Table 1. Clearly, the molar ratio of C/N increase. The raised C content on one hand signifies N deficiency, which is inevitable, on the other hand, states C doping dating from decomposition of carbon-rich ILs, proved by remarkable increased molar ratio of C1/C3 [41,42]. More importantly, the increased N1/N2 after post-thermal treatment and C-I co-doping indicates much optimized in plane heterocyclic *sp*² conjugate structure. Meanwhile, the decreased N3/N1 values confirms the reduction of surface amino group. These results coincidently confirm that the C-I co-doping modification did not change the basic skeleton, but optimize *sp*² aromatic ring polymerization structure. It is a significant factor and favorable for photocatalytic hydrogen production [43].

Table 1

XPS spectral analysis results of CNI and CNIN samples.

Sample	C/N	C1/C3	N3/N1	N1/N2
CNI ₀	0.69	0.05	0.21	3.7
CNIN ₀	0.75	0.08	0.13	4.2
CNIN _{0.2}	0.79	0.23	0.12	6.3

3.2. Photocatalytic H₂ evolution

The photocatalytic activity of prepared samples were evaluated by H₂ evolution in a conventional closed-circulation system under visible light irradiation ($\lambda > 400$ nm). Fig. 5(a) shows the photocatalytic H₂ evolution of samples using triethanolamine and 3wt% of chloroplatinic acid as electron donors and co-catalysts, respectively. It can be observed that compared to CNI₀ (17.0 $\mu\text{mol/h}$), the H₂ evolution rate for CNI samples modified by C-I codoping first increase, and then decrease which is restrained by excess C content, and CNI_{0.2} shows the best performance for 30.1 $\mu\text{mol/h}$. More significantly, the H₂ production over CNIN samples after post-thermal treatment was sharply enhanced, following the same trend that increase first and then decrease. The H₂ evolution rate achieved of CNIN_{0.2} is as high as 168.2 $\mu\text{mol/h}$, which is more than 5.5 times higher than CNI_{0.2} and 2.7 times higher than CNIN₀.

Fig. 5(b) shows the H₂ evolution performance of CNI₀, CNIN₀ and CNIN_{0.2} under different wavelength of light illumination. The order of H₂ evolution rate is CNIN_{0.2} > CNIN₀ > CNI₀ regardless of the wavelength of illumination, which further confirms that C-I co-doping and post-thermal treatment jointly promote the photocatalytic performance of CN catalysts. When

Fig. 5. H₂ production of CNI and CNIN under 400 nm light irradiation (a) and different wavelength ranges (b).

the incident wavelength extends from visible to ultraviolet region, the H₂ production rate of all samples was enhanced. It is according to photoresponse of CN samples and confirms the photocatalytic reaction progress. Interestingly, the advantages for H₂ generation over CNIN_{0.2} is more significant in visible light, especially $\lambda > 420$ nm. Therefore, optimized visible-light absorption can be speculated for CNIN samples. In addition, the energy band structure, electronic properties and photoelectric response were investigated to illustrate the enhanced photocatalytic H₂ evolution activity.

In order to evaluate the stability and reusability of the CNIN photocatalyst, H₂ production catalyzed by CNIN_{0.2} was carried out cycled for four times under visible light ($\lambda > 400$ nm). As shown in Fig. 6, under continuous illumination, the amount of H₂ release shows an approximate linear. In addition, after four consecutive cycle's reactions, almost negligible deactivation could be observed, indicating that CNIN_{0.2} has good H₂ generation stability under visible light irradiation.

3.3. Light absorption and electronic properties of samples

Fig. 6. Stability test of H₂ evolution for CNIN_{0.2} photocatalyst under visible-light irradiation ($\lambda > 400$ nm).

The optical absorption of the samples was elucidated by UV-Vis diffuse reflection spectra (DRS), as shown in Fig. 7. Post-thermal treatment caused a slight blue shift in the spectrum for CNIN₀ due to quantum size effect. For CNIN samples, band edges redshift can be found, and the corresponding band gaps (E_g) from Tauc plot for CNIN_{0.2} and CNIN₀ are 2.81 and 2.82 eV, respectively. Compared to CNI₀, although the band gap enlarges, the effect of C-I codoping remedied this shortage. On the other hand, the absorption sideband of CNIN samples is larger than CNI₀ (shown in Fig. 7(a)), which are derived from C-I codoping expounded in the aforementioned contents. Beyond this, enhanced light absorption, especially in visible light region (450–700 nm) was observed and gradually improve with the increased C-I doping content. The enhanced visible light absorption is beneficial for the photocatalytic reaction proved by H₂ evolution test. Compared with CNI₀ and CNI_{0.2}, the absorption capacity and response range of visible light increased, indicating that C-I doping could in favor of the photocatalytic performance of the catalyst. From previous reports, C and I doping are all conducive to enhance the light absorption of CN materials, but from above-mentioned results, the doping amount of I is much lower than C, so the improved light absorption is mainly due to C doping.

Mott-Schottky analysis has been employed to determine the semiconductor type and flat potential of prepared samples. Fig. 7(c) gives Mott-Schottky curves of CNI₀, CNIN₀ and CNIN_{0.2} samples measured at 800 Hz. It can be seen that the plot slopes are positive for all samples, indicating n-type behavior for all samples. The plot of CNIN₀ and CNIN_{0.2} show bigger slope than that of CNI₀, indicating higher electron donor density for the former catalysts. It is helpful for promoting photocatalytic performance because of increased electrical conductivity and mobility of charge carriers [44]. The flat potentials for CNI₀, CNIN₀ and CNIN_{0.2} samples are −1.35, −1.37 and −1.40 eV vs SCE, respectively. Therefore, the conduction band (CB) of samples are deduced since the CB potentials of n-type semiconductors are close to the flat band potentials [45]. Combined with the E_g values gained from UV-Vis plot, the band positions of these samples are exhibit in Fig. 7(d). According to the thermal dynamics

Fig. 7. UV-Vis spectra (a), Kubelka-Munk spectra (b), Mott-Schottky curves (c) and the band positions (d) of doped carbon nitride.

principle of photocatalytic water for H_2 evolution, C-I codoped $\text{CNIN}_{0.2}$ sample with negative shifted CB has higher H_2 evolution power.

3.4. Primary factors to enhanced activity

In addition to band gap structure, the effects of C-I co-doping

and post-thermal treatment on the charge transfer property change of the catalysts were also investigated. Fig. 8(a) gives the room temperature steady-state PL emission spectra of samples excited at 400 nm. All samples exhibit broad emission peaks in the range of about 470 nm, which can be attributed to the band-band PL phenomenon with the light energy approximately equal to the band gap energy of g- C_3N_4 . Compared with

Fig. 8. Steady-state PL (a) and PL decay spectra (b) of samples.

Fig. 9. (a) Electrochemical impedance spectroscopy, (b) Transient photocurrent response and (c) Electrochemical Mott-Schottky plots for CNi₀, CNIN₀ and CNIN_{0.2} samples.

CNi₀, the PL intensity of CNIN₀ raise. It may be resulted from the increased defects which could became recombination centers. After modification by C-I co-doping, the PL intensity of both CNi and CNIN samples significantly reduced, and gradually decreases with increasing doping amount, indicating that C-I co-doping inhibit the recombination of photo-generated charges, lower the disadvantages of increased defects.

It is well known that a longer charge carrier lifetime usually implies a better photocatalytic activity because of higher participation possibility of carriers in photocatalytic reactions. Calculated results of time-resolved transient PL spectroscopy (Fig. 8(b)) shows that the average lifetime of the excited charge carriers in the case of CNIN_{0.2} is 5.203 ns, whereas CNi₀ and CNIN₀ exhibit average lifetimes of 0.671 and 4.762 ns, respectively. These fitting data solidly corroborate that the lifetimes of charge carriers in CNIN_{0.2} is significantly lengthened by the combinative post-thermal treatment and C-I codoping.

Fig. 9(a) displays the transient photocurrent responses of CNi₀, CNIN₀ and CNIN_{0.2} with several on-off cycles. CNIN_{0.2} produces significant higher photocurrent than that of CNi₀ and CNIN₀, verifies the results of PL. It is a good indication of the improved mobility of the photo-excited charge carriers. First, it is attributed to the close-grained layer stacking and optimized *sp*² conjugate structure, which can shorten the diffusion length of charge migration and promote electron relocalization on the surface. Secondly, heteroatomic doping by C and I both beneficial to the improvement of carrier transmission in semiconductors. The photocurrent response has a slight attenuation might due to the less stability of iodine in the electrochemical process.

The above PL and photocurrent techniques highlight the high separation and transfer efficiency of photo-generated electron-hole pairs in CNIN_{0.2} upon light irradiation. In order to inspect the capacity to shuttle and convey charge carriers to the targeted reactive sites, EIS measurement were carried out under dark. Fig. 9(b) gives the EIS Nyquist plots. Among these samples, CNIN_{0.2} shows the smallest diameter, suggesting its lowest resistance for interfacial charge transfer.

The interrelation of several structure parameters of CNi and CNIN samples with H₂ evolution rate (HER) was summarized and listed in Table 2. It can be found that enlarged surface area, negative shifted conduction band position and optimized separation/transfer efficiency of photo-induced carriers all give push to the enhanced photocatalytic H₂ evolution activity over C-I codoped porous carbon nitride.

4. Conclusions

Porous C-I co-doped g-C₃N₄ materials (CNIN) were successfully prepared through post-thermal treat and doped by iodized ionic liquid co-polymerization. The secondary calcination makes for higher degree of polymerization, more porous and larger surface area. Synergistic with C-I co-doping modification, light absorption response of the prepared catalysts were much enhanced for prepared catalysts, especially in visible-light region. Compared to pristine g-C₃N₄, although the band gaps of C-I codoped porous CNIN materials enlarged, the improved reduction potential due to negative shifted conduction band position provides powerful impetus for the H₂ production from water photolysis. In addition, the faster transfer and lower recombination rate of photo-induced carriers for CNIN samples renders much enhanced photocatalytic H₂ evolution rate under visible light irradiation. The CNIN_{0.2} with moderate C-I doping content shows best photocatalytic activity (168.2 μmol/h), which is nearly 5.5 times higher than merely C-I doped CNi_{0.2} and 2.7 times higher than post-thermal treated porous CNIN₀. This is an easily-operated route for preparation non-metallic

Table 2

Structure parameters and H₂ evolution activities of CNi and CNIN samples.

Sample	C (wt%)	I (wt%)	BET (m ² /g)	E _g (eV)	E _{CB} (V)	PL life (ns)	HER (μmol/h)
CNi ₀	37.3	—	14.6	2.75	-1.35	0.671	17.0
CNiN ₀	39.2	—	37.3	2.82	-1.37	4.762	61.4
CNi _{0.2}	40.7	0.11	13.8	2.74	-1.36	2.303	30.1
CNiN _{0.2}	44.5	0.08	54.4	2.81	-1.40	5.203	168.2

doped porous CN-based polymer semiconductors using ILs as dopant source, and the photocatalytic properties of samples could be convenient modified and enhanced.

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Graphical Abstract

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C-I codoped porous g-C₃N₄ for superior photocatalytic hydrogen evolution

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C-I co-doped porous g-C₃N₄ synthesized from two-step thermal polymerization method was demonstrated as a stable photocatalyst for H₂ evolution under visible light irradiation.

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C-I共掺杂多孔g-C₃N₄光催化分解水制氢

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摘要: 氢气是一种可替代传统燃料的理想清洁能源, 利用光催化技术分解水制氢是制取氢气的有效途径之一。无机半导体光催化材料具有较高的活性和稳定性, 且原料丰富, 易加工改性。目前针对光催化技术的应用, 大量的研究工作都集中在开发可见光响应光催化剂, 以提高对可见光的利用率。同时, 非金属聚合物半导体因其特殊的光电性质, 在光催化应用研究中越来越受到关注, 如庚嗉基微孔聚合物(HMP)和共价三嗉基骨架(CTF)。石墨相碳化氮(g-C₃N₄)是一种典型非金属二维聚合物半导体, 被认为是一种非常有价值的光催化材料。然而, 其较低的光生电子的传输效率限制了其实际应用, 因此诸多研究对g-C₃N₄的物理化学结构进行优化, 如半导体耦合、共聚合、纳米结构设计和掺杂。非金属掺杂是一种有效的方法, 由于原子电负性差异引起的电荷分离可有效改善载流子传输效率, 且保持半导体的非金属性质。通过O, B, P和S等掺杂可以扩大可见光响应范围, 并调节能带位置以改善光催化活性。除了常见的单一非金属掺杂, 金属和非金属元素或多非金属元素共掺杂的办法同样可提高g-C₃N₄的光催化性能。

本工作通过两步法对双氰胺、尿素和碘化1-乙基-3-甲基咪唑的混合物直接热聚合, 合成C-I共掺杂的多孔g-C₃N₄, 其在可见光照射下表现出较高的产氢活性和稳定性。采用X射线衍射(XRD)、X射线光电子能谱(XPS)、荧光光谱(PL)和电化学实验等方法对多孔掺杂g-C₃N₄结构进行详细表征和分析。在助催化剂Pt和电子牺牲剂(三乙醇胺)存在的条件下, 采用可见光(>400 nm)照射分解水产氢的方法评价其光催化活性。结果表明, 后热处理和碘离子液掺杂对g-C₃N₄材料的结构和性能具有较大影响。C-I共掺杂和后热处理使催化剂产物颗粒尺寸减小, 形成多孔片层状紧密堆积, 比表面积和孔隙率显著增加, 吸收带边发生蓝移。后热处理使样品层间距减小, 聚合度增加, 有利于电荷传输, C-I共掺杂后出现更多的缺陷, 但没有改变其层状堆积的特性。XPS结果表明, 样品中碘元素以I⁻和I³⁺的形式存在, 改性后催化剂C/N比明显增加, sp²芳环N含量增加, 表面氨基含量降低, 表明后热处理和C-I共掺杂没有改变多孔g-C₃N₄的基本骨架, 共轭结构更加完善。PL和光电流结果表明, 改性后样品的PL强度均显著降低, 并且随着掺杂量的增加而逐渐降低, 表明共掺杂可抑制光生电荷的复合。电化学测试结果表明, 后热处理和C-I共掺杂的样品界面电荷转移电阻降低, 导电率和电荷迁移率增加, 从而有助于提高光催化性能。光解水产氢性能测试表明, 后热处理和C-I共掺杂有利于催化剂产氢速率的提高, 改性后CNIN_{0.2}的产氢速率达168.2 μmol/h, 是纯氮化碳的9.8倍。经过多次循环测试, 其产氢性能保持稳定而没有显著下降, 表明其产氢稳定性较好。

关键词: 多孔氮化碳; C-I共掺杂; 后热处理; 光催化; 产氢

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