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A comparison study of alkali metal-doped g-C₃N₄ for visible-light photocatalytic hydrogen evolution

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ABSTRACT

Photocatalytic hydrogen production based on semiconductor photocatalysts has been considered as one of the most promising strategies to resolve the global energy shortage. Graphitic carbon nitride (g-C₃N₄) has been a star visible-light photocatalyst in this field due to its various advantages. However, pristine g-C₃N₄ usually exhibits limited activity. Herein, to enhance the performance of g-C₃N₄, alkali metal ion (Li⁺, Na⁺, or K⁺)-doped g-C₃N₄ are prepared via facile high-temperature treatment. The prepared samples are characterized and analyzed using the technique of XRD, ICP-AES, SEM, UV-vis DRS, BET, XPS, PL, TRPL, photoelectrochemical measurements, photocatalytic tests, etc. The resultant doped photocatalysts show enhanced visible-light photocatalytic activities for hydrogen production, benefiting from the increased specific surface areas (which provide more active sites), decreased band gaps for extended visible-light absorption, and improved electronic structures for efficient charge transfer. In particular, because of the optimal tuning of both microstructure and electronic structure, the Na-doped g-C₃N₄ shows the most effective utilization of photogenerated electrons during the water reduction process. As a result, the highest photocatalytic performance is achieved over the Na-doped g-C₃N₄ photocatalyst (18.7 μmol/h), 3.7 times that of pristine g-C₃N₄ (5.0 μmol/h). This work gives a systematic study for the understanding of doping effect of alkali metals in semiconductor photocatalysis.

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1. Introduction

In the fields of renewable energy development and environmental remediation, the conversion of solar energy into clean chemical fuels by semiconductor photocatalysts has been a popular strategy worldwide [1–7]. Various kinds of semiconductors, including oxides, sulfides, and nitrides, have been investigated as active photocatalysts in the past decades [8–13]. However, the greatest restriction on their practical application

is currently the low energy conversion efficiency of photocatalysis. One possible solution is to develop highly efficient photocatalytic materials that can trigger hydrogen production in the visible-light region.

Recently, intense interest has been focused on the metal-free semiconductor graphitic carbon nitride (g-C₃N₄) [14,15]. This material exhibits potentially desirable photocatalytic activity because of its band gap of roughly 2.7 eV, allowing visible absorption, and the distinct redox ability of the photoinduced

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electrons and holes [16,17]. Moreover, polymeric g-C₃N₄ possesses extended π -conjugated layer networks, and the convenient thermal polymerization synthesis allows for its large-scale preparation and structural modification [18,19]. Nevertheless, g-C₃N₄ still shows low activity for photocatalytic H₂ evolution, suffering from the limited ability to utilize sunlight below 450 nm and high recombination rate of photoinduced electron-hole pairs [20,21]. To date, various modification strategies have been explored to optimize this promising material for better performance [22–31]. Among them, band gap engineering through element doping has proven an effective approach to improve the photocatalytic activity of g-C₃N₄. Introducing impurities at the atomic level has been demonstrated to extend the light absorption region, modify the band structure, and generate electron/hole traps for charge separation [32–37]. In particular, Li, Na, and K have been recognized as effective doping additives into the inner structure of g-C₃N₄ [38–41]. However, few comparison studies have investigated the differences among g-C₃N₄ photocatalysts doped with various alkali metals, which has limited our understanding of their effects.

Herein, we present a comparison study of g-C₃N₄ doped with different alkali metal ions (Li⁺, Na⁺, and K⁺) for photocatalytic H₂ evolution. Detailed analysis of optical absorption, intrinsic band structure, and charge transfer are carried out to investigate the positive effects of doping metal ions in g-C₃N₄ matrices for visible-light photocatalytic activity.

2. Experimental

2.1. Preparation of photocatalysts

Pristine g-C₃N₄ was prepared in the conventional manner by heating melamine precursor at 550 °C for 2 h in air with a heating rate of 5 °C min⁻¹, and denoted as CN. To synthesize alkali metal-doped g-C₃N₄, the obtained g-C₃N₄ powder (500 mg) was dispersed in 15 mL deionized water containing 15 mg MOH (where M represents Li, Na, or K). Then the mixture was stirred for 1 h and heated to 100 °C to remove water. The uniformly mixed solid was further ground and calcined at 600 °C for 1 h under N₂ atmosphere in a tube furnace, followed by washing with diluted HCl solution to remove the excess alkali metal ions and washing with deionized water several times until pH = 7. The resulting products were labeled as Li-CN, Na-CN, and K-CN, respectively. For comparison, the as-prepared g-C₃N₄ was also calcined without adding any MOH, and the as-obtained sample was denoted as C-CN.

2.2. Characterization

The doping amounts of alkali metal ions in the products were measured by inductively coupled plasma atomic emission spectrometry (ICP-AES, Optima 4300 DV, Perkin Elmer). The X-ray diffraction (XRD) patterns were recorded on a D/Max-RB X-ray diffractometer with Cu-K α radiation at a slow-scan rate of 0.005° (2 θ) s⁻¹. Scanning electron microscopy (SEM) and elemental mapping images were obtained on a scanning electron microscope (FESEM, JSM 7500F). UV-visible diffuse reflectance

spectra were investigated on a UV-vis spectrophotometer (UV2600, Shimadzu) using a BaSO₄ reference. Nitrogen adsorption-desorption isotherms were analyzed by a BET analyzer (Micromeritics ASAP 3020, USA). Chemical states and valence band spectra were collected by X-ray photoelectron spectroscopy (XPS, VG ESCALAB 210). An Al-K α excitation source was employed and the C 1s peaks (284.8 eV) were referenced for all binding energies. Photoluminescence (PL) emission spectra were examined on a Hitachi F-7000 fluorescence spectrophotometer under the excitation wavelength of 350 nm. Both the excitation and emission slits were 5.0 nm in width and the voltage was 400 V. Time-resolved photoluminescence (TRPL) decay curves were measured on a fluorescence lifetime spectrophotometer (FLS920, Edinburgh Instruments, UK) excited at 360 nm.

2.3. Photocatalytic H₂ production

Photocatalytic H₂ production reactions were performed at room temperature in a three-neck vessel, of which the three openings were sealed with rubber plugs and tubes. A 350 W Xe lamp with a UV cutoff filter ($\lambda > 400$ nm) was used as the light source. Typically, 50 mg photocatalyst powder was dispersed in 80 mL aqueous solution containing 10 vol% triethanolamine as scavenger. All samples were loaded with 1 wt% Pt by photodeposition for 30 min. The reaction system was evacuated for 30 min before light irradiation to ensure anaerobic conditions. The amount of evolved H₂ was detected using a GC-14C gas chromatograph (Shimadzu, Japan, TCD) with N₂ carrier gas and a 5 Å molecular sieve column.

2.4. Photoelectrochemical measurements

Electrochemical impedance spectra (EIS) and photocurrent responses were tested on a CHI 660D electrochemical workstation (Chenhua Instruments, Shanghai, China) with a traditional three-electrode system. This system included the prepared sample as the working electrode, a Pt wire as the counter electrode, and a Ag/AgCl electrode as the reference electrode. A Na₂SO₄ aqueous solution (0.5 mol·L⁻¹) was used as the electrolyte and a low-power LED (3 W, 420 nm) was used as the visible-light source. The potential was set as 0.5 V for photocurrent measurement. The working electrode was prepared by grinding 50 mg photocatalyst, 20 mg polyethylene glycol (PEG, $M_w = 20000$), together with 2 mL ethanol to form a slurry. The obtained slurry was coated onto a 2 cm × 1.2 cm fluorine-doped tin oxide (FTO) glass substrate and then annealed at 450 °C for 30 min in a muffle furnace.

3. Results and discussion

Fig. 1(a) displays the XRD patterns of g-C₃N₄ and modified g-C₃N₄. All g-C₃N₄ samples show two diffraction peaks at ca. 13.1° and 27.4°, which are typical of g-C₃N₄ graphitic stacking layers, and are similar for each sample. Specifically, the former peak corresponds to an in-plane structure repeating with the distance of the in-plane cavity between three tri-s-triazine

Fig. 1. XRD patterns (a) and slow-scan XRD patterns (b) of g-C₃N₄, modified C-CN, and M-CN.

units, i.e. 0.68 nm, while the latter (strong) peak is assigned to the interplanar stacking of g-C₃N₄ [42–44]. These peak intensities are weakened for the metal ion-doped g-C₃N₄, indicating a decreased crystallinity degree from Li-CN to K-CN. This implies that the in-plane structure may be partially fragmented into smaller crystallites in the doped samples. Such distortion of g-C₃N₄ usually leads to the formation of defects and band-structure changes. The slow-scan XRD patterns were then measured in the range of 25°–30° and are shown in Fig. 1(b). It is clearly seen that after heating at the higher temperature of 600 °C, the dominant (002) peak of g-C₃N₄ shifts to the higher angle of 27.6°, which reflects a higher degree of stacking order and a narrower interlayer distance, resulting from the layer compaction of g-C₃N₄ [45,46]. Meanwhile, in the XRD patterns of metal-doped g-C₃N₄, the (002) diffraction peak gradually shifts back toward a lower 2θ value, from 27.6° to 27.4°, with

the successive introduction of Li, Na, and K. This indicates that successively larger interlayer distances are created by the interstitial doping of those three ions into the structure [47]. Clearly, larger atom sizes induce larger interlayer distances. It is probable that the metal ions are incorporated into nano-sized cavities, where they coordinate with the electron-donating N-containing functional groups of g-C₃N₄ [36]. The elemental mapping images of the samples, shown in Fig. 2, reveal the existence of C and N in all cases, as well as Na or K in the corresponding samples; however, the Li content in Li-CN is beyond the detection limit of this method. It can be seen that the metal ion species are uniformly distributed within the g-C₃N₄ matrix. The doping concentrations of Li, Na, and K measured by ICP-AES are 0.118, 0.052, and 0.059 mol% for Li-CN, Na-CN, and K-CN, respectively.

The BET specific surface areas and pore structures were al-

Fig. 2. SEM images and elemental mapping images of Li-, Na-, and K-doped g-C₃N₄.

Fig. 3. Nitrogen adsorption-desorption isotherms of pristine g-C₃N₄ and modified g-C₃N₄.

Table 1

Physicochemical parameters of pristine g-C₃N₄ and modified g-C₃N₄.

Sample	S_{BET} /(m ² g ⁻¹)	V_{pore} /(cm ³ g ⁻¹)	D_{pore} /nm	Metal doping /mol%	Band gap /eV
CN	10	0.06	27	—	2.74
C-CN	35	0.22	25	—	2.52
Li-CN	15	0.10	27	0.118	2.48
Na-CN	28	0.15	22	0.052	2.42
K-CN	21	0.12	23	0.059	2.39

so investigated to clarify the structural variation among the samples. From the nitrogen adsorption-desorption isotherms in Fig. 3, it can be seen that all the g-C₃N₄ photocatalysts show a type IV isotherm and H3 hysteresis loops, indicating the formation of slit-like mesopores from aggregated g-C₃N₄ plates. The data listed in Table 1 reveal that post-calcination g-C₃N₄ has a much higher specific surface area and larger pore volume than pristine g-C₃N₄, suggesting that high temperature increases the porosity of g-C₃N₄ [46]. However, the BET specific surface areas of Li-CN, Na-CN, and K-CN are 15, 28, and 21 m²g⁻¹, respectively, i.e. they are reduced compared with that of C-CN. This is possibly attributed to the treatment of the g-C₃N₄ sur-

face with basic reagents (MOH) after heat treatment, resulting in the destruction and collapse of the pore structure [48]. Note that Na-CN shows the highest specific surface area among the metal-doped samples. Generally, a larger S_{BET} provides more active sites and facilitates light absorption for enhanced photocatalytic activity [49,50].

UV-vis diffuse reflectance spectra of M-CN and pristine g-C₃N₄ were collected to investigate their light absorption properties. The corresponding band gaps were obtained by plotting $(\alpha h\nu)^2$ against photon energy ($h\nu$) (Fig. 4(b)) and are listed in Table 1. Fig. 4(a) shows a steep rise in absorption intensity from 452 nm to the ultraviolet region for pristine g-C₃N₄, which represents a relatively narrow band gap of ~2.74 eV. In comparison, the absorption edge of C-CN is red-shifted and the band gap is calculated to be even smaller, 2.52 eV. The narrowed band gap results from the small-size effect of the decreased particle sizes as well as the increased degree of condensation for high-temperature-treated g-C₃N₄ [45]. An additional absorption shoulder also appears near 500 nm, which can be assigned to the $n-\pi^*$ transitions occurring in a π -conjugated system [51]. This is another effect of the high-temperature treatment: the increased layer condensation causes structural distortions, which increases the number of lone-pair electrons on the N-containing groups at the edges of localized regions of g-C₃N₄. These N-containing groups with high electron density are basic in nature and behave as active sites to accommodate metal ions by electrostatic interaction or complexation [51–53]. Hence, the post-treatment at high temperature facilitates the metal doping process. Moreover, the absorption edges of the alkali metal-doped samples exhibit even greater shifts to longer wavelengths and the corresponding band gaps decrease to 2.48, 2.42, and 2.39 eV for Li-CN, Na-CN, and K-CN, respectively. This result demonstrates that alkali metal ions were successfully doped into the g-C₃N₄ matrix with the aid of high-temperature treatment. The resulting decreased band gaps should endow the M-CN catalysts with a better ability to harvest visible light, thus increasing their photocatalytic activities.

The chemical states of C and N and the presence of dopant

Fig. 4. UV-vis diffuse reflectance spectra (a) and corresponding band gaps obtained by plots of $(\alpha h\nu)^2$ vs. photon energy ($h\nu$) (b) of pristine g-C₃N₄ and modified g-C₃N₄.

Fig. 5. High-resolution XPS spectra in the regions of C 1s (a), N 1s (b), Li 1s (c), Na 1s (d), K 2p (e) and valence band spectra (f) of pristine g-C₃N₄ and modified g-C₃N₄.

elements in the g-C₃N₄ samples were analyzed by XPS, as shown in Fig. 5. The two dominant peaks at 284.8 and 287.9 eV in the C 1s region correspond to typical C-C graphitic carbon and *sp*²-hybridized C atoms (N=C-N) in the g-C₃N₄ aromatic structure, respectively. The high-resolution N 1s XPS of all g-C₃N₄ samples can be fitted to three characteristic peaks located at 398.3, 399.5, and 400.8 eV. They are assigned to *sp*²-hybridized N atoms (C=N-C), N-(C)₃ in the tri-s-triazine rings, and terminal amino functional groups (NH₂ and NH), respectively [54,55]. All the C 1s and N 1s spectra are in accordance with the typical chemical states and bonding forms of C and N in g-C₃N₄. Note that no obvious shift of the C 1s and N 1s binding energies is observed for the C-CN sample in comparison with pristine g-C₃N₄. However, the alkali metal-treated g-C₃N₄ show a positive shift, by 0.2–0.4 eV, of the corresponding C 1s and N 1s binding energies. Such a shift reveals the formation of an interaction, presumably chemical coordination, between the doped ions and g-C₃N₄ aromatic rings.

The Li 1s, Na 1s, and K 2p peaks appearing at 55.3, 1071.4, and 292.6 eV are attributed to metal-N bonding, and all are lower in energy than that of the relevant alkali salts with M-O bonding (56.0, 1072.1 and 292.9 eV, respectively) [39,41,48]. This result suggests that during high-temperature calcination, the triazine units in g-C₃N₄ became partially disordered, and the nitrogen atoms with increased lone-pair electron density (see above) had a strong coordination affinity toward the metal ions. This caused the formation of strong (high-energy) N-bridging covalent bonds between the N-containing groups and metal ions [47,56]. In this way, the metal doping changed

the electron density around the N atoms, subsequently altering the electronic structure and band gap of g-C₃N₄.

The valence band spectra were thus measured for all samples to determine the relative valence band positions. As shown in Fig. 5(f), the energies of the valence bands gradually increased from CN, through C-CN, to metal-doped g-C₃N₄. Combined with the band gaps calculated from the UV-vis spectra, the valence band energies allowed us to obtain the electronic structures and relative band positions of the prepared photocatalysts, as depicted in Fig. 6. Both post-calcinated and doped g-C₃N₄ show narrower band gaps, more positive valence bands,

Fig. 6. Band structures of g-C₃N₄ and doped g-C₃N₄.

Fig. 7. Comparison of hydrogen evolution rates for pristine g-C₃N₄ and modified g-C₃N₄ under visible-light irradiation.

and less negative conduction band positions than pristine g-C₃N₄, allowing for more efficient visible-light utilization and charge excitation, while still providing enough energy for water reduction. Consequently, these materials should show improved visible-light photocatalytic performance for hydrogen production.

The photocatalytic hydrogen production performances of the as-prepared g-C₃N₄ samples were evaluated under visible-light ($\lambda > 400$ nm) irradiation. In the absence of photocatalysts or light irradiation, no product was detected in the system. From Fig. 7, it can be seen that all the modified g-C₃N₄ catalysts show enhanced photocatalytic activities in comparison with pristine g-C₃N₄ (5.0 $\mu\text{mol/h}$). Importantly, the introduction of alkali metal ions into g-C₃N₄ significantly raises the H₂ production rates, exceeding that of post-calcinated g-C₃N₄. Especially, Na-CN has the highest photocatalytic activity (18.7 $\mu\text{mol h}^{-1}$), which is more than three times and two times that of pristine g-C₃N₄ and C-CN, respectively.

As mentioned above, the modification of g-C₃N₄ led to increased specific surface areas and broadened visible-light absorption, both of which contribute to the enhanced photocatalytic activities. To obtain an in-depth understanding of the photocatalytic process, the charge transfer dynamics was fur-

Table 2

Fitted lifetimes and their percentages of as-prepared g-C₃N₄ samples.

Samples	τ_1 (ns)	A_1 (%)	τ_2 (ns)	A_2 (%)
CN	2.23	63.38	8.12	36.62
C-CN	1.57	63.95	7.82	36.05
Li-CN	1.43	69.72	7.24	30.28
Na-CN	1.32	75.16	6.83	24.84
K-CN	1.26	80.60	6.31	19.40

ther investigated by PL, TRPL analysis, and photoelectrochemical measurements.

The PL spectrum of pristine g-C₃N₄ shown in Fig. 8(a) displays a strong characteristic peak near 445 nm, which can be assigned to its band-to-band emission. All the modified g-C₃N₄ photocatalysts have similar but highly quenched PL peaks at about 465 nm, indicating successful suppression of the recombination of photogenerated charge carriers. Particularly, the sharply decreased PL intensity for C-CN can be ascribed to the structural distortion. The inset of Fig. 8(a) shows that the intensity was further decreased after doping with metal ions from Li-CN to K-CN. This suppression of PL by metal doping can be attributed to two causes: the presence of slight defects and the introduction of impurity levels between the gaps, both of which benefit charge transfer and reduce the recombination rate of photoinduced electron-hole pairs [57,58]. This tuning of the electronic structures occurs to different degrees for different metal ions, so that the PL intensities vary among Li⁺, Na⁺, and K⁺-doped g-C₃N₄.

The lifetimes of charge carriers were calculated by analyzing the TRPL spectra (Fig. 8(b)), which were fitted with bi-exponential decay kinetics. The results are listed in Table 2. As can be seen, both the lifetime components (τ_1 and τ_2), representing radiative and non-radiative processes, respectively, are shortened after the high-temperature and doping treatments, consistently with the above-mentioned suppression of PL. This further confirms that the recombination of charge carriers is successfully retarded in modified g-C₃N₄ because of the distortion of the microstructures and the alteration of the electronic structures, which generate defects and impurity levels for trapping charge carriers [57,59].

Photoelectrochemical measurements, including transient

Fig. 8. PL (a) and TRPL (b) spectra of pristine g-C₃N₄ and modified g-C₃N₄.

Fig. 9. Transient photocurrent responses (a) and EIS spectra (b) of pristine g-C₃N₄ and modified g-C₃N₄ under visible light.

photocurrent responses and electrochemical impedance spectra, were further conducted to determine the charge transfer efficiency. As shown in Fig. 9(a), all the photocatalysts show prominent photocurrent responses and maintain relatively good stability through repeated cycling runs, suggesting their ability to efficiently transfer photogenerated electrons to an external circuit under visible-light irradiation [60]. The photocurrent intensity of C-CN is slightly higher than that of CN because of the broader light utilization and increased photogenerated charge separation of the former. Meanwhile, the three M-CN samples show considerably increased current intensities, among which Na-CN exhibits the highest value, nearly 7 times that of CN. These results agree well with the photocatalytic activities.

Similarly, the EIS spectra also provide information about the recombination/separation of electrons and holes [61–63]. In Fig. 9(b), the smaller arc radii for C-CN and M-CN relative to CN represent better conductivity or more efficient electron transfer under visible light, which is consistent with the above results. It is noted that the sample with the best performance in retarding charge recombination, according to the PL and TRPL spectra, is K-CN, while the sample with the best performance in promoting charge transfer, based on the photoelectrochemical measurements, is Na-CN. This difference implies that the utilization of photogenerated charge carriers should be more effective for Na-doped g-C₃N₄ during the water splitting process. The K-doped sample undergoes the most favorable change in the electronic structure of g-C₃N₄ among all samples, and thus exhibits the lowest recombination rate of photogenerated charge carriers. However, the conduction band of K-CN is also shifted to the least negative energy among all samples. As a result, under visible-light irradiation, the electrons in the conduction band of K-CN show the reduced ability to reduce protons for H₂ evolution.

Therefore, based on the above discussion, it can be deduced that the improved visible-light photocatalytic hydrogen evolution by metal ion-doped g-C₃N₄ originates from two causes: the optimization of the microstructures for a high specific surface area, and the optimization of the electronic structures for fast charge transfer and effective charge utilization.

4. Conclusions

g-C₃N₄ samples doped with alkali metal ions (Li⁺, Na⁺, and K⁺) are successfully synthesized by high-temperature assisted calcination. The doped photocatalysts exhibit larger specific surface areas, narrower band gaps, and more efficient charge-carrier transfer, all of which greatly enhance their photocatalytic hydrogen production performances under visible light. Among the metal ion-doped g-C₃N₄ photocatalysts, the Na-doped g-C₃N₄ shows the highest photocatalytic activity, because the electronic structure and redox potentials are tailored optimally for the effective utilization of photogenerated electrons during the water reduction process. This work provides a protocol for the optimization of the doping method to design efficient photocatalysts.

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Graphical Abstract

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A comparison study of alkali metal-doped g-C₃N₄ for visible-light photocatalytic hydrogen evolution

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Alkali metal ion-doped graphitic carbon nitride shows enhanced visible-light photocatalytic activity for hydrogen production because of the increased specific surface areas, decreased band gaps, and improved electronic structures.

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碱金属掺杂的石墨相氮化碳在可见光光催化制氢中的比较研究

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摘要: 利用半导体光催化技术将太阳能转化为清洁化学能源是解决能源危机和环境问题的最有潜力的途径之一。过去几十年, 许多半导体包括氧化物、硫化物和氮化物均表现出光催化活性。然而, 半导体光催化的实际应用仍然受制于其较低的太阳能转化效率。解决上述问题的方法之一是发展高效的可见光光催化制氢材料。近年来, 石墨相氮化碳(g-C₃N₄)作为一种聚合物半导体材料, 受到了光催化研究人员的广泛关注。g-C₃N₄具有可见光吸收能力、合适的导带价带位置、良好的热稳定性和化学稳定性, 且制备方法简单和结构易调控, 是一种极具潜力的光催化制氢材料。然而g-C₃N₄仍然仅能吸收波长450 nm以下的光, 且其光生电子和空穴极易复合, 因而光催化制氢效率较低。目前, 研究人员采用了多种改性方法来增强g-C₃N₄的光催化性能, 其中通过元素掺杂进行能带结构调控是一种非常有效的策略。而碱金属原子(Li, Na和K)被认为可有效进入g-C₃N₄的内部结构, 通过引入缺陷来拓宽g-C₃N₄的光吸收范围和提高光生电荷的分离效率。不过到目前为止, 尚未见系统的比较研究来深入理解不同碱金属元素掺杂的g-C₃N₄在可见光光催化制氢中的性能差异。

本文采用X射线衍射(XRD)、氮气吸附-脱附测试、紫外可见漫反射光谱(UV-vis DRS)、时间分辨荧光光谱(TRPL)、X射线光电子能谱(XPS)、光电化学测试和光催化制氢测试等表征和测试手段比较研究了不同碱金属元素掺杂的g-C₃N₄在结构、光学性质、能带结构、电荷转移能力和光催化性能等方面的差异。XRD结果表明, 碱金属掺杂可导致g-C₃N₄的层间距离增大, 且碱金属原子半径越大, g-C₃N₄的层间距离越大。氮气吸附-脱附测试结果表明, 碱金属掺杂可提高g-C₃N₄的比表面积, 其中Na掺杂的最高。UV-vis DRS和XPS谱结果表明, 依Li, Na, K的顺序, 碱金属掺杂导致g-C₃N₄带隙逐渐变窄, 使得可见光吸收能力逐渐增强, 且其导带和价带位置逐渐下移。TRPL和光电化学测试结果显示, 碱金属掺杂有效抑制了g-C₃N₄的光生载流子复合和促进了光生载流子的转移, 其中Na掺杂的g-C₃N₄的光生载流子利用效率最高。可见光光催化制氢实验表明, 碱金属掺杂显著提升了g-C₃N₄的光催化性能, 其中以Na掺杂的g-C₃N₄性能最佳, 其产氢速率(18.7 μmol h⁻¹)较纯的g-C₃N₄ (5.0 μmol h⁻¹)可提高至3.7倍。由此可见, g-C₃N₄的掺杂改性是一个对其微结构和能带结构的优化调控过程, 最终获得最优的光催化性能。

关键词: 石墨相氮化碳; 碱金属掺杂; 光催化制氢; 可见光; 电荷转移

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