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Z-scheme N-doped $\text{K}_4\text{Nb}_6\text{O}_{17}/\text{g-C}_3\text{N}_4$ heterojunction with superior visible-light-driven photocatalytic activity for organic pollutant removal and hydrogen production

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ARTICLE INFO

Article history:

Received 26 February 2020

Accepted 9 April 2020

Published 5 January 2021

Keywords:

Photocatalysis

 $\text{K}_4\text{Nb}_6\text{O}_{17}$ $\text{g-C}_3\text{N}_4$

Z-scheme

Heterojunction

ABSTRACT

A simple calcination method was employed to prepare a Z-scheme N-doped $\text{K}_4\text{Nb}_6\text{O}_{17}/\text{g-C}_3\text{N}_4$ (KCN) heterojunction photocatalyst, in which the electronic structure of $\text{K}_4\text{Nb}_6\text{O}_{17}$ was regulated by N-doping, and $\text{g-C}_3\text{N}_4$ was formed both on the surface and within the interlayer spaces of $\text{K}_4\text{Nb}_6\text{O}_{17}$. The KCN composite showed profoundly improved photocatalytic activity for both H_2 generation and RhB degradation compared to its counterparts. This improved performance was attributed to the synergistic effects of N-doping, which broadened its light harvesting ability, and heterojunction formation, which increased the charge separation rate. The relatively low BET specific surface area of the KCN composite had little effect on its photocatalytic activity. Based on ESR spectroscopy studies, $\cdot\text{O}_2^-$, $\cdot\text{OH}$, and h^+ are the main active species in the photocatalytic degradation of RhB. Thus, it is reasonable to propose a Z-scheme photocatalytic mechanism over the KCN composite, which exhibits the dual advantages of efficient charge separation and high redox ability. Our work provides a simple approach for constructing large-scale Z-scheme heterojunction photocatalysts with high photocatalytic performance.

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1. Introduction

Photocatalysis has been widely investigated, and is generally considered to be one of the “green” approaches for solving the problems of environmental pollution and energy shortages [1]. Various semiconductor photocatalysts, such as layered

niobate, polymeric carbon nitride ($\text{g-C}_3\text{N}_4$), perovskite materials, TiO_2 , and MoS_2 , have been carefully constructed and applied in organic dye degradation, H_2 generation, and CO_2 reduction [2–5]. Among these semiconductor photocatalysts, the typical layered compound $\text{K}_4\text{Nb}_6\text{O}_{17}$, which contains NbO_6 units connected by bridging oxygen atoms [6], has been investigated

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This work was supported by the National Natural Science Foundation of China (51902282 and 11474246), China Postdoctoral Science Foundation (2018M632283), Joint Open Fund of Jiangsu Collaborative Innovation Center for Ecological Building Material and Environmental Protection Equipments and Key Laboratory for Advanced Technology in Environmental Protection of Jiangsu Province (JH201819), and Open Project of Key Laboratory for Ecological-Environment Materials of Jiangsu Province

DOI: 10.1016/S1872-2067(20)63608-7 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 42, No. 1, January 2021

extensively for photocatalytic applications because of its appealing electronic band structure, easy structural modification, and favorable charge transfer capacity [7–9]. However, pure $\text{K}_4\text{Nb}_6\text{O}_{17}$ presents some drawbacks, such as a narrow light-response range and a high recombination rate of its photogenerated charge carriers, which restrict its practical applications. Thus, it is necessary to develop $\text{K}_4\text{Nb}_6\text{O}_{17}$ -based photocatalysts with high activity via broadening its light harvesting ability and improving its charge separation rate.

Various modification methods, such as doping, morphological design, and heterojunction formation, have been employed to enhance the photocatalytic activity of $\text{K}_4\text{Nb}_6\text{O}_{17}$. For instance, Zhou *et al.* [10] developed a simple UV-light photoreduction method to synthesize Nb^{4+} -self-doped $\text{K}_4\text{Nb}_6\text{O}_{17}$ microspheres. Their improved photocatalytic activity was attributed to the synergistic effects of self-doping, which significantly widened their absorption ability in the visible-light/near-infrared-light region, and their large specific areas, which increased the reaction active sites. Furthermore, metal sulfides have been introduced on the surface of $\text{K}_4\text{Nb}_6\text{O}_{17}$ to construct heterojunction composites, leading to improved photocatalytic activity [11, 12]. However, the limited contact area between the two components may be not a benefit for the separation of charge carriers. For comparison, metal sulfides were intercalated into the interlayer spaces of $\text{H}_4\text{Nb}_6\text{O}_{17}$ to construct layered heterojunction composites via a two-step proton-exchange reaction/sulfurization process [13–15]; the resulting composites exhibited high photocatalytic activity. The interfacial contact area between the metal sulfides and $\text{H}_4\text{Nb}_6\text{O}_{17}$ could be greatly increased by the appropriate use of the interlayer spaces, resulting in enhanced electron-hole pair separation efficiency and thus high photocatalytic activity.

The metal-free and visible-light-driven photocatalyst graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) has been widely studied, and is even regarded as a next-generation photocatalyst in view of its “Earth-abundant” nature, facile synthesis, appropriate band position, and high physicochemical stability [16–18]. Importantly, nitrogen-rich precursors, such as melamine and urea, have been applied not only for the preparation of $\text{g-C}_3\text{N}_4$ by thermal polymerization, but also for elemental doping. For example, our group synthesized layered N-doped $\text{KTiNbO}_5/\text{g-C}_3\text{N}_4$ composites using melamine as the raw material. The wide-band-gap semiconductor KTiNbO_5 was doped with N atoms to enhance its visible-light response, and two-layered $\text{g-C}_3\text{N}_4$ nanosheets were formed within the interlayer spaces of N- KTiNbO_5 [19]. However, the redox ability of this typical type-II N-doped $\text{KTiNbO}_5/\text{g-C}_3\text{N}_4$ heterojunction was profoundly reduced due to the efficient transfer of photogenerated electrons/holes to less negative conduction band and positive valence band positions, respectively [20]. Z-scheme photocatalytic systems have been widely investigated due to their dual advantages of high redox ability and efficient charge separation [21–25]. Thus, it is necessary to construct Z-system $\text{K}_4\text{Nb}_6\text{O}_{17}$ -based photocatalysts with higher redox ability.

To the best of our knowledge, this work represents the first time that a Z-system layered N-doped $\text{K}_4\text{Nb}_6\text{O}_{17}/\text{g-C}_3\text{N}_4$ composite has been constructed using a facile calcination method.

The $\text{K}_4\text{Nb}_6\text{O}_{17}$ layers were doped with nitrogen atoms to achieve visible-light response through the creation of doping energy levels, and $\text{g-C}_3\text{N}_4$ was formed exclusively as single layers both on the surface and within the interlayers of N-doped $\text{K}_4\text{Nb}_6\text{O}_{17}$. The structure, morphology, chemical states, and visible-light photocatalytic activity of the resulting samples in RhB degradation and H_2 generation have been studied and discussed in detail. Moreover, a possible Z-scheme photocatalytic mechanism was proposed based on the experimental results.

2. Experimental

2.1. Preparation of $\text{K}_4\text{Nb}_6\text{O}_{17}/\text{g-C}_3\text{N}_4$ composites

All reagents in this experiment were of analytical grade and were used without further purification. Bulk $\text{K}_4\text{Nb}_6\text{O}_{17}$ was prepared by a two-step solid-state reaction as follows [26]. A mixture of K_2CO_3 and Nb_2O_5 with a molar ratio of 2.1:3.0 was fully ground, and then calcinated at 800 °C and 1000 °C for 5 h each, with an intermediate grinding step.

To prepare the $\text{K}_4\text{Nb}_6\text{O}_{17}/\text{g-C}_3\text{N}_4$ (denoted as KCN) composite, 1.0 g of $\text{K}_4\text{Nb}_6\text{O}_{17}$ was mixed with 3.0 g of melamine and fully ground, and then heated at 500 °C for 5 h at a heating rate of 2.5 °C/min in a covered crucible. The mass of the resulting KCN composite was 2.08 g. As the mass of $\text{K}_4\text{Nb}_6\text{O}_{17}$ (1.0 g) was found to decrease to 0.96 g after thermal treatment at 500 °C for 5 h, the mass percentage of $\text{g-C}_3\text{N}_4$ in the KCN composite was calculated to be 53.8 wt%. To investigate the role of N doping, 1.0 g of $\text{K}_4\text{Nb}_6\text{O}_{17}$ was also mixed with 3.0 g of melamine and subjected to a process similar to that used for preparing KCN, except for a covered crucible. The resulting solid sample was denoted as Me- $\text{K}_4\text{Nb}_6\text{O}_{17}$. Additionally, pure $\text{g-C}_3\text{N}_4$ was prepared using the same process without the addition of $\text{K}_4\text{Nb}_6\text{O}_{17}$.

Details of the characterization techniques and photocatalytic tests for RhB degradation and H_2 generation are given in the supporting information.

3. Results and discussion

SEM and TEM images were obtained to investigate the morphology of the as-prepared samples. Pure $\text{g-C}_3\text{N}_4$ exhibits a sheet-like structure with serious aggregation (Fig. 1a), indicating the existence of graphite planes stacked along the *c*-axis in [27]. As shown in Fig. 1b, a typical layered structure and smooth surface are clearly visible in the image of the synthesized $\text{K}_4\text{Nb}_6\text{O}_{17}$. After combining $\text{K}_4\text{Nb}_6\text{O}_{17}$ with $\text{g-C}_3\text{N}_4$, the resulting KCN composite (Fig. 1c) also shows a layered structure, but with a rough surface due to the introduction of amorphous $\text{g-C}_3\text{N}_4$ on the surface of $\text{K}_4\text{Nb}_6\text{O}_{17}$ to form a heterojunction structure, which is beneficial for the effective separation of photogenerated charge carriers [28,29].

The TEM images of KCN (Fig. 1d and 1e) confirm the maintenance of the layered structure with some shadowed areas on the overlapping sheets, which was ascribed to the formation of $\text{g-C}_3\text{N}_4$ on the surface of $\text{K}_4\text{Nb}_6\text{O}_{17}$. In the HRTEM image of KCN (Fig. 1f), a clear boundary line is visible, illustrat-

Fig. 1. SEM images of (a) g-C₃N₄, (b) K₄Nb₆O₁₇, and (c) the KCN composite. (d, e) TEM and (f, g) HRTEM images, and (h) EDS profile of the KCN composite. (i) STEM-HAADF image of the combined elements and (j–n) the distribution of the elements C/N/O/K/Nb on the KCN composite.

ing that amorphous g-C₃N₄ was connected to and combined with the K₄Nb₆O₁₇ sheets. In Fig. 1g, the fringes show a marked lattice spacing of 0.32 nm, which originated from the (0100) facet of K₄Nb₆O₁₇ based on the crystallographic symmetry, further confirming the formation of a heterojunction structure between amorphous g-C₃N₄ and K₄Nb₆O₁₇. Additionally, the K₄Nb₆O₁₇ layers were doped in-situ with nitrogen atoms to produce visible-light-responsive N-doped K₄Nb₆O₁₇ during the formation of g-C₃N₄ from nitrogen-rich melamine.

The EDS profile of KCN in Fig. 1h consists of C, N, O, K, Nb, and Cu peaks (from the copper grid matrix), providing indirect evidence for the coexistence of both K₄Nb₆O₁₇ and g-C₃N₄. Furthermore, the scanning transmission electron microscopy-high-angle annular dark-field (STEM-HAADF) and EDS images of KCN are shown in Fig. 1i–1n. It can be clearly observed that the elements C, N, O, K, and Nb are uniformly dispersed in KCN. This indicates that a thin layer of g-C₃N₄ was deposited on the surface of K₄Nb₆O₁₇. Based on the strong K and Nb signals, it is reasonable to conclude that the thickness of covering layer g-C₃N₄ is suitable and that component of N-doped K₄Nb₆O₁₇ can be generated under visible-light irradiation.

Figure 2a shows the TG curves of K₄Nb₆O₁₇, Me-K₄Nb₆O₁₇, g-C₃N₄, and the KCN composite. For pure K₄Nb₆O₁₇, the weight loss (ca. 6.5 wt%) was assigned to the dehydration of water within the interlayer spaces and the collapse of the layers [30]. Compared to K₄Nb₆O₁₇, Me-K₄Nb₆O₁₇ exhibited a slightly lower weight loss value (ca. 5.8 wt%), while that of the KCN composite was 55.4 wt%, indicating that no g-C₃N₄ phase was formed over Me-K₄Nb₆O₁₇. Based on the full decomposition of g-C₃N₄ below 700 °C, the mass percentage of g-C₃N₄ in KCN was estimated to be approximately 48.9 wt%, which is close to the calculated value above (53.8 wt%).

The XRD patterns of the samples were used to investigate

their structure and crystallinity, and are shown in Fig. 2b. All the peaks of K₄Nb₆O₁₇ can be indexed to the standard PDF card (JCPDS, No. 53-0780), indicating the formation of a pure orthorhombic K₄Nb₆O₁₇ phase [10]. For pure g-C₃N₄, the low-intensity peak at $2\theta = 12.7^\circ$ was assigned to the (100) plane, which can be associated with repeated in-plane tri-s-triazine units [31]. Moreover, the strong peak at $2\theta = 27.4^\circ$, indexed to the (002) plane, was attributed to the stacking of a conjugated aromatic system [32, 33].

Even after being heated with melamine in a covered crucible, the characteristic peaks of K₄Nb₆O₁₇ remained almost unchanged in the KCN composite, indicating the maintenance of its crystal structure. However, the intensity of the peaks for KCN decreased profoundly in comparison to those of pure K₄Nb₆O₁₇, owing to the introduction of g-C₃N₄. A new weak peak at $2\theta = 5.75^\circ$ ($d = 1.55$ nm) related to K₄Nb₆O₁₇ ($2\theta = 9.40^\circ$, $d_{040} = 0.94$ nm) can be clearly observed for KCN, while this new peak cannot be found in the XRD pattern of Me-K₄Nb₆O₁₇ (Fig. S1). The increased gallery height, which was attributed to the introduction of g-C₃N₄, was calculated to be 0.61 nm. As the thickness of single-layer g-C₃N₄ is ~ 0.325 nm [34], it is reasonable to conclude that only single-layered g-C₃N₄ nanosheets are formed within the interlayer spaces of N-doped K₄Nb₆O₁₇ due to the confinement effect. Importantly, the (040) plane is also retained in KCN with a relatively high intensity. As the formation of intercalated g-C₃N₄ nanosheets proceeds from the exterior to the interior, the g-C₃N₄ nanosheets cannot fully intercalate into the central position of N-doped K₄Nb₆O₁₇ due to the strong resistance of the formed g-C₃N₄ nanosheets themselves. Moreover, the formation of single-layered g-C₃N₄ nanosheets within the interlayer spaces of N-doped K₄Nb₆O₁₇ with an ordered alternating layer structure can greatly increase the contact area between the two components, which plays a

Fig. 2. (a) TG curves, (b) XRD patterns, and (c) UV-visible diffuse reflectance and (d) FT-IR spectra of the as-prepared samples.

key role in efficient charge transfer across the interface.

The optical absorption performance of K₄Nb₆O₁₇, Me-K₄Nb₆O₁₇, g-C₃N₄, and the KCN composite were investigated using UV-visible diffuse reflectance spectra in Fig. 2c [35]. Pure K₄Nb₆O₁₇ shows only UV-light absorption ability, and a sharp absorption edge can be observed at ~350 nm owing to its intrinsic band gap absorption [36,37]. The light absorption of the KCN composite was broadened to a certain extent compared to those of K₄Nb₆O₁₇ and g-C₃N₄ in both the UV and visible light regions. Noteworthily, Me-K₄Nb₆O₁₇ shows a clear visible light response due to N doping. Thus, in addition to the N doping resulting from the pyrolysis of melamine, the main reason for the widened light absorption of KCN was the introduction of the narrow-band-gap semiconductor g-C₃N₄. Additionally, the bandgap values (Fig. S2) of K₄Nb₆O₁₇, KCN, g-C₃N₄, and Me-K₄Nb₆O₁₇ were estimated to be 3.65, 2.68, 2.78, and 2.84 eV, respectively. The KCN composite (2.68 eV) has a decreased bandgap value relative to that of g-C₃N₄ (2.78 eV), which was attributed to the combined effects of N doping, heterojunction formation, and a possible quantum size effect [38].

The FT-IR spectra of K₄Nb₆O₁₇, g-C₃N₄ and KCN are shown in Fig. 2d. In that of K₄Nb₆O₁₇, the bands in the range 400–1000 cm⁻¹ were attributed to the vibrations of octahedral NbO₆ in K₄Nb₆O₁₇ [39]. The framework of KCN is similar to that of g-C₃N₄, indicating that the signals mainly originated from the g-C₃N₄ formed in the KCN composite. The band at 807 cm⁻¹ was assigned to the characteristic breathing vibration of triazine units [40]. Additionally, the bands from 1200 to 1700 cm⁻¹ were associated with the skeletal stretching of C–N heterocycles [41–43]. It should be noted that no bands characteristic of

g-C₃N₄ are visible in the spectrum of Me-K₄Nb₆O₁₇ (Fig. S3), indicating the widened light absorption region in Me-K₄Nb₆O₁₇ was due to N doping alone.

The surface composition and chemical states of the as-prepared samples were determined using XPS measurements [38]. As shown in Fig. 3a, the survey spectrum of K₄Nb₆O₁₇ demonstrates the presence of the elements of Nb, O, and C. The observed carbon peak was assigned to adventitious hydrocarbon for calibration. Compared to the spectrum of K₄Nb₆O₁₇, the KCN composite shows distinct nitrogen and carbon signals, which may be due to the introduction of g-C₃N₄ in KCN.

As shown in Fig. 3b, two typical peaks at 206.6 (Nb 3d_{5/2}) and 209.4 eV (Nb 3d_{3/2}) are observed in the Nb 3d spectrum of K₄Nb₆O₁₇, which were attributed to the Nb⁵⁺–O bond [10]. After being combined with g-C₃N₄ in KCN, these peaks are profoundly shifted toward higher binding energies (206.8 and 209.6 eV), confirming the existence of strong interfacial interactions between K₄Nb₆O₁₇ and g-C₃N₄. This interfacial interaction may have originated from electron transfer and delocalization between the two components [19]. Furthermore, the spin-orbit separation value between Nb 3d_{5/2} and Nb 3d_{3/2} is 2.8 eV for both K₄Nb₆O₁₇ and KCN, indicating the exclusive presence of Nb⁵⁺ [44,45].

As shown in Fig. 3c, the O 1s spectrum of K₄Nb₆O₁₇ can be deconvoluted into two peaks at 530.1 and 531.0 eV, which were assigned to the lattice oxygen of niobium and surface-adsorbed oxygen species, respectively [46]. For KCN, the deconvoluted O 1s peaks exhibited distinct shifts relative to their positions in pure K₄Nb₆O₁₇, to 530.0 and 531.7 eV, further

Fig. 3. (a) XPS survey and XPS profiles of (b) Nb 3d, (c) O 1s, and (d) N 1s of the as-prepared samples.

confirming the presence of interfacial interactions between K₄Nb₆O₁₇ and g-C₃N₄. Notably, KCN shows two new peaks at 530.7 and 532.8 eV, which were attributed to O–N, C–O, and N–C–O species in the lattice of the introduced g-C₃N₄, respectively [47].

The N 1s spectrum of g-C₃N₄ (Fig. 3d) shows three characteristic peaks at 401.1, 399.8, and 398.6 eV, which were ascribed to C–N–H, N–(C)₃, and C=N–C groups, respectively [48, 49]. Three characteristic peaks similar to those observed for g-C₃N₄, (400.2, 399.9, and 398.8 eV) are also observed in the KCN spectrum with a slight shift, further confirming the formation of g-C₃N₄ and the presence of interfacial interactions between the two components. Me-K₄Nb₆O₁₇ shows a distinct N 1s signal with an N content of 0.89 at% (Fig. S4), which origi-

nated from the atomic β-N introduced by N doping [50].

The photocatalytic H₂-generation performance of the as-prepared samples was investigated under visible light irradiation using triethanolamine (TEOA) as the hole scavenger. As shown in Fig. 4a, pure K₄Nb₆O₁₇ shows no evident H₂ production due to the fact that it can only be excited under ultraviolet light. After N doping, Me-K₄Nb₆O₁₇ shows slightly enhanced photocatalytic activity for H₂ evolution (~1.30 μmol/h), indicating that N doping alone does not significantly enhance the photocatalytic activity. The photocatalytic H₂ production rate of the pure g-C₃N₄, which is a typical visible-light-driven photocatalyst, was measured to be 8.24 μmol/h. The photocatalytic H₂ production rate of KCN is profoundly improved in comparison, with a value of ~16.91 μmol/h, which is approximately 2.1

Fig. 4. (a) Rate of H₂ production on K₄Nb₆O₁₇, Me-K₄Nb₆O₁₇, g-C₃N₄, and KCN; (b) Cycling test of photocatalytic H₂ production over the KCN composite under visible light. (Reaction conditions: 100 mg photocatalyst in 200 mL of an aqueous solution containing 10 vol% TEOA and 2 wt% Pt.)

times higher than that of pure g-C₃N₄. These results suggest that the synergistic effects of N doping and heterojunction formation can greatly enhance the photocatalytic activity of K₄Nb₆O₁₇. Moreover, the KCN composite (Fig. 4b) shows excellent stability for H₂ production, with no distinct decrease in performance after four cycles.

RhB was chosen as the target pollutant for evaluation of the photocatalytic activity due to its structural stability under visible light irradiation (Fig. 5a) [51]. Using pure K₄Nb₆O₁₇, only ~15% of the RhB concentration was degraded within 60 min under visible light due to the self-sensitization oxidation. After N doping, the obtained Me-K₄Nb₆O₁₇ exhibits enhanced photocatalytic activity for the degradation of RhB under visible light due to the visible-light response induced in K₄Nb₆O₁₇ by tuning of its electronic structure through N doping. The KCN composite shows profoundly improved photocatalytic activity compared to Me-K₄Nb₆O₁₇ and g-C₃N₄, which was attributed to the synergistic effects of N-doping and heterojunction formation.

As shown in Fig. 5b, the KCN composite shows high adsorption ability for RhB solution, with a ~30% concentration reduction within 30 min in the dark. Under visible light, the characteristic absorption band of RhB at ~554 nm is greatly reduced due to the destruction of the conjugated structure, with complete decolorization within 60 min. Additionally, a remarkable blue-shift of the main absorption band is also apparent, which was attributed to the step-by-step de-ethylation of RhB.

For the KCN composite, the changes in the TOC during adsorption and visible-light photodegradation were measured in order to reflect the degree of mineralization of RhB, and are provided in Fig. 5c. After 30 min of adsorption and 60 min of

photodegradation, a TOC removal rate of approximately 87.9% is achieved in the presence of the KCN composite, demonstrating a high degree of mineralization. Thus, the KCN composite is an efficient photocatalyst that can significantly mineralize RhB solution under visible light.

Generally, the stability and reusability of a photocatalyst is a key factor in its practical applications. Only a slight reduction in the photocatalytic efficiency of KCN (Fig. 5d) is observed after four repeated runs due to the inevitable loss of sample during each rinsing and collection process. Additionally, the crystal structure of KCN was studied after four cycles of photodegradation. The XRD patterns (Fig. S5a) show that the position of the characteristic peaks is almost unchanged, while their intensity showed some change. As shown in Fig. S5b, the FT-IR spectra of the samples before and after photodegradation do not exhibit any significant changes. These results indicate that the KCN composite has relatively good structural stability and reusability in the removal of RhB under visible light.

The PL technique can provide significant information on the transfer, separation, and recombination processes of photo-generated electron-hole pairs [52,53]. Generally, higher PL intensities correspond to more rapid recombination rates for the photogenerated electron-hole pairs, leading to low photocatalytic activity. As shown in Fig. 6a, pure K₄Nb₆O₁₇ exhibits the highest emission intensity with a broad peak at ~425 nm, indicating severe recombination of the photoexcited carriers. Me-K₄Nb₆O₁₇ exhibits lower emission intensity than K₄Nb₆O₁₇, indicating that N doping facilitates separation of the photogenerated electron-hole pairs. A broad PL emission peak at 460 nm can be clearly observed for g-C₃N₄, owing to the radiative re-

Fig. 5. (a) Visible-light photocatalytic degradation rate of RhB solution over different samples. (b) UV-vis spectral changes. (c) TOC removal (relative to C_0) and (d) photocatalytic degradation stability of RhB over KCN under visible-light irradiation.

Fig. 6. (a) PL spectra and (b) time-resolved PL decay spectra of the as-prepared samples.

combination of the electron-hole pairs [40]. The KCN composite shows a distinct decrease in emission intensity, suggesting that remarkable enhancement of the separation of photogenerated electron-hole pairs was achieved through the combined effects of N doping and heterojunction formation.

To gain deeper insight into the recombination process of photo-induced charge carriers, the ns-level time-resolved photoluminescence (TRPL) spectra of $g-C_3N_4$ and KCN were measured and are shown in Fig. 6b. The fluorescence decay curves were fitted using the biexponential model below (Eq. 1):

$$R(t) = B_1 \exp(-t/\tau_1) + B_2 \exp(-t/\tau_2) \quad (1)$$

where B_1 and B_2 represent the weight factor, and τ_1 and τ_2 are the fluorescence lifetimes. Compared to those of pure $g-C_3N_4$ ($\tau_1 = 0.98$ ns, $A_1 = 83\%$; $\tau_2 = 5.23$ ns, $A_2 = 17\%$), both the short and long lifetimes of KCN ($\tau_1 = 1.29$ ns, $A_1 = 91\%$; $\tau_2 = 6.30$ ns, $A_2 = 9\%$) are profoundly prolonged. The corresponding average lifetime, calculated based on the previous work [54,55], is increased from 3.18 ns ($g-C_3N_4$) to 6.20 ns (KCN), indicating that the synergistic effects of N doping and heterojunction formation via $g-C_3N_4$ incorporation can efficiently facilitate charge separation, suppress charge recombination, and prolong the lifetime of the photogenerated charge carriers, thus enhancing photocatalytic activity.

Electron spin resonance (ESR) using DMPO or TEMPO as free radical trapping agents is commonly employed to investigate the role of active species [56]. All ESR experiments (Fig. 7) for the KCN composite were performed in the dark and under visible light irradiation with an interval time of 30 seconds. As shown in Fig. 7a, four characteristic DMPO- $\bullet O_2^-$ peaks are observed in the KCN photocatalytic system under visible light,

while no signals are seen under dark conditions, indicating that the generated $\bullet O_2^-$ radicals played a key role in this photocatalytic degradation system. In Fig. 7b, DMPO- $\bullet OH$ signals with a characteristic relative intensity of 1:2:2:1 are clearly visible, confirming the contribution of the active species $\bullet OH$ to the enhancement of the photocatalytic activity. Moreover, strong characteristic TEMPO- h^+ peaks are observed in the dark (Fig. 7c) [57]. After visible light irradiation, the intensity of the characteristic TEMPO- h^+ signals gradually decreases, validating the formation of h^+ . Thus, it can reasonably be concluded that $\bullet O_2^-$, $\bullet OH$, and h^+ act as the main active species in improving the photocatalytic performance.

Photocurrent and electrochemical impedance spectroscopy (EIS) measurements were employed to study the kinetics of charge transfer in depth [58]. The transient photocurrent responses of the different samples shown in Fig. 8a were measured in an on-and-off cycling mode. The KCN composite evidently shows higher photocurrent intensity than those of $K_4Nb_6O_{17}$, $Me-K_4Nb_6O_{17}$, and $g-C_3N_4$, which was attributed to the effective transfer and separation of the photo-generated charge carriers at the interface between the two components. The transfer process of the charge carriers was investigated using the EIS Nyquist plots shown in Fig. 8b. The plot of KCN exhibits an evidently smaller arc radius than those of $K_4Nb_6O_{17}$, $Me-K_4Nb_6O_{17}$, and $g-C_3N_4$, demonstrating the generation and migration of photogenerated charge carriers in the KCN composite. Benefiting from both N-doping and heterojunction formation, the KCN composite shows the most effective light harvesting, charge carrier production, and electron-hole pair separation, which enhance its visible-light-driven photocatalytic

Fig. 7. ESR spectra of a KCN dispersion in the dark and under visible light irradiation: (a) DMPO- $\bullet O_2^-$, (b) DMPO- $\bullet OH$, and (c) TEMPO- h^+ .

Fig. 8. (a) Transient photocurrent responses and (d) electrochemical impedance spectra of $\text{K}_4\text{Nb}_6\text{O}_{17}$, $\text{Me-K}_4\text{Nb}_6\text{O}_{17}$, $\text{g-C}_3\text{N}_4$, and the KCN composite.

activity. It should be mentioned that the gradual drop in the photocurrent that can be observed for KCN composite is mainly caused by the peeling of the photocatalyst from the FTO electrode.

As shown in Fig. S6a, the KCN composite ($9.9 \text{ m}^2/\text{g}$) shows a slight increase in BET surface area compared to pure $\text{K}_4\text{Nb}_6\text{O}_{17}$ ($5.6 \text{ m}^2/\text{g}$). The pore size distribution curves of $\text{K}_4\text{Nb}_6\text{O}_{17}$ and KCN (Fig. S6b) demonstrate their very small surface areas and negligible pores. Thus, the BET specific surface area has little effect on their photocatalytic activities. Based on the above analyses, the enhanced visible-light-driven photocatalytic activity of RhB degradation and H_2 production over the KCN composite was mainly attributed to the synergistic effects of the broadened light harvesting ability due to N-doping and effective charge generation/separation due to heterojunction formation. Thus, it is crucial to understand the migration channel of charge carriers in order to reveal the photocatalytic mechanism. For the KCN composite, two possible photocatalytic mechanisms, *i.e.*, a Z-scheme system and a type-II heterojunction, were proposed; schematic illustrations of charge transfer via each of these mechanisms is shown in Fig. 9.

From their VB-XPS profiles (Fig. S7), the valence band (VB) potentials of $\text{g-C}_3\text{N}_4$ and $\text{K}_4\text{Nb}_6\text{O}_{17}$ can be estimated as +1.60 and +3.41 eV, respectively. By combining these with their bandgap values, the VB and conduction band (CB) potentials were calculated to be (+1.6/−1.18 eV) for $\text{g-C}_3\text{N}_4$ and (+3.41/−0.24 eV) for $\text{K}_4\text{Nb}_6\text{O}_{17}$. It has been reported that impu-

rity energy levels can be formed above the VB potential via N doping [59]. As the bandgap energy of $\text{Me-K}_4\text{Nb}_6\text{O}_{17}$ is 2.84 eV, it is reasonable to conclude that the potential of the N 2p state is +2.60 eV. According to the Nernst equation, the CB and VB potentials of $\text{g-C}_3\text{N}_4$ and $\text{K}_4\text{Nb}_6\text{O}_{17}$ can be converted to (+1.36/−1.42 V vs NHE, pH = 7) and (+3.17/−0.48 V vs NHE, pH = 7), and that of the formed N 2p state in $\text{K}_4\text{Nb}_6\text{O}_{17}$ to +2.36 V (vs NHE, pH = 7) [60]. Thus, the $\text{g-C}_3\text{N}_4$ and N-doped $\text{K}_4\text{Nb}_6\text{O}_{17}$ components can be excited under visible-light irradiation.

In a type-II heterojunction system, the generated electrons in the CB of $\text{g-C}_3\text{N}_4$ would migrate to the CB of N-doped $\text{K}_4\text{Nb}_6\text{O}_{17}$, while the holes from N 2p states of N-doped $\text{K}_4\text{Nb}_6\text{O}_{17}$ would migrate to the VB of $\text{g-C}_3\text{N}_4$ across the intimate interface of the well-aligned straddling band structures due to the potential difference. Finally, the photogenerated electrons and holes would gather around the CB of the N-doped $\text{K}_4\text{Nb}_6\text{O}_{17}$ and the VB of $\text{g-C}_3\text{N}_4$. As the potentials of $\text{OH}^-/\cdot\text{OH}$ (+1.99 V vs. NHE) and $\text{H}_2\text{O}/\cdot\text{OH}$ (+2.27 V vs. NHE) are more positive than the VB edge potential of $\text{g-C}_3\text{N}_4$, the accumulated holes would not be able to react with $\text{H}_2\text{O}/\text{OH}^-$ to produce $\cdot\text{OH}$ radicals, which is inconsistent with the DMPO- $\cdot\text{OH}$ results.

In a Z-scheme photocatalytic system involving the KCN composite, the electrons in the CB of $\text{g-C}_3\text{N}_4$ would react with O_2 molecules to generate $\cdot\text{O}_2^-$ radicals due to the potential of $\text{O}_2/\cdot\text{O}_2^-$ (−0.046 V vs. NHE) [61]. Some of the accumulated holes in the N 2p states of N-doped $\text{K}_4\text{Nb}_6\text{O}_{17}$ could react with $\text{H}_2\text{O}/\text{OH}^-$ to produce $\cdot\text{OH}$ radicals, and thus combine with the

Fig. 9. Schematic of the two possible photocatalytic mechanisms, *i.e.*, the Z-scheme system and type-II heterojunction, for charge-transfer in the KCN composite under visible light. The energy levels of $\text{K}_4\text{Nb}_6\text{O}_{17}$ and $\text{g-C}_3\text{N}_4$ in the KCN composite are referenced to the normal hydrogen electrode (NHE) at pH 7.

remaining holes for the mineralization of the RhB molecules. Based on the ESR results, the charge separation and migration in the KCN heterojunction should be assigned to the Z-scheme photocatalytic mechanism. Thus, for photocatalytic H_2 generation over the KCN composite, the electrons in the CB of g-C₃N₄ will transfer easily to the co-catalyst Pt to generate H_2 , and the positive holes in the N 2p states can oxidize the sacrificial reagent (TEOA). Since the N-doped K₄Nb₆O₁₇ and g-C₃N₄ exhibit matched band structures and a strong electronic interaction, the formation of Z-scheme photocatalytic system in KCN can result in highly efficient interfacial charge transfer and thus boost photocatalytic performance.

4. Conclusions

In this work, a Z-scheme N-doped K₄Nb₆O₁₇/g-C₃N₄ (KCN) heterojunction photocatalyst was synthesized by a simple calcination method in which the electronic structure of K₄Nb₆O₁₇ was regulated by N doping. The formed g-C₃N₄ accounted for ~50 wt.% in the KCN composite, and was located on the surface and within the interlayer spaces of N-doped K₄Nb₆O₁₇ due to the space-confinement effect. The KCN composite shows a relatively small BET specific surface area (9.9 m²/g) and negligible pores, which had little effect on its photocatalytic activity. The KCN composite exhibits profoundly enhanced visible-light-driven photocatalytic activity in both H_2 generation (~16.91 μ mol/h) and RhB degradation, which was attributed mainly to the synergistic effects of N-doping, which broadened its light harvesting ability, and heterojunction formation, which increased the charge separation rate. In particular, the formation of only single-layered g-C₃N₄ nanosheets within the interlayer spaces of the N-doped K₄Nb₆O₁₇ can greatly increase the contact area between the two components, which is beneficial for efficient charge transfer across the interface. Based on

ESR spectroscopy, the active species $\bullet O_2^-$, $\bullet OH$, and h^+ play the main roles in the photocatalytic degradation of RhB. Based on these results and the well-matched band structures of N-doped K₄Nb₆O₁₇ and g-C₃N₄, it is reasonable to propose a Z-scheme photocatalytic mechanism for the KCN composite, which has the dual advantages of efficient charge separation and high redox ability, resulting in high photocatalytic activity. Our work may provide a simple approach for constructing large-scale Z-scheme heterojunction photocatalysts with high photocatalytic performance.

Conflicts of Interest

The authors declare no conflict of interest.

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Graphical Abstract

Chin. J. Catal., 2021, 42: 164–174 doi: 10.1016/S1872-2067(20)63608-7

Z-scheme N-doped K₄Nb₆O₁₇/g-C₃N₄ heterojunction with superior visible-light-driven photocatalytic activity for organic pollutant removal and hydrogen production

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Z-scheme N-doped K₄Nb₆O₁₇/g-C₃N₄ composite shows improved photocatalytic activities for H_2 generation and RhB degradation due to the synergistic effects of the broadened light harvesting ability by N-doping and the efficient charge separation by heterojunction.

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高可见光催化降解污染物和产氢活性的Z型N-掺杂K₄Nb₆O₁₇/g-C₃N₄异质结

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摘要: 随着人口增长和全球工业化进程加快, 人们饱受环境污染和能源短缺问题的困扰。半导体光催化技术作为一种高

效、可持续、环境友好、有潜力的新技术,在环境净化和能源开发方面有着广阔的应用前景. 到目前为止,人们已开发出多种半导体光催化剂,并广泛应用于污染物降解、氢气制备和二氧化碳还原等领域. 其中,化合物 $\text{K}_4\text{Nb}_6\text{O}_{17}$ 具有典型的层状结构、合适的电子能带结构、结构易改性以及良好的电荷传输性能等特点,在光催化领域得到了广泛研究. 然而,单纯 $\text{K}_4\text{Nb}_6\text{O}_{17}$ 仍存在光响应范围窄、光生载流子复合率高等问题,限制了 $\text{K}_4\text{Nb}_6\text{O}_{17}$ 的进一步应用. 因此,需要对 $\text{K}_4\text{Nb}_6\text{O}_{17}$ 进行改性,拓宽其光吸收范围,提高其光生载流子分离效率,从而提高其光催化活性.

本研究通过简单焙烧法制备Z型N-掺杂 $\text{K}_4\text{Nb}_6\text{O}_{17}/\text{g}-\text{C}_3\text{N}_4$ (KCN)异质结光催化剂,其中石墨相氮化碳($\text{g}-\text{C}_3\text{N}_4$)在复合材料中质量比约为50%. 层状 $\text{K}_4\text{Nb}_6\text{O}_{17}$ 层板的电子结构通过N掺杂进行调控,拓宽其光响应范围,使其具有可见光响应;同时,形成的 $\text{g}-\text{C}_3\text{N}_4$ 位于N-掺杂 $\text{K}_4\text{Nb}_6\text{O}_{17}$ 的外层以及内层空间,在这两种组分之间形成异质结,有利于提高光生载流子的分离效率. 荧光光谱、时间分辨荧光光谱和光电化学测试表明,N掺杂和异质结的形成有利于增强光生电子-空穴对的传输和分离效率. 通过在可见光照射下降解罗丹明B(RhB)和产氢来评估材料的光催化性能. 相比 $\text{g}-\text{C}_3\text{N}_4$ (8.24 $\mu\text{mol/h}$)和 $\text{Me}-\text{K}_4\text{Nb}_6\text{O}_{17}$ (~1.30 $\mu\text{mol/h}$), KCN复合材料光催化产氢效率(~16.91 $\mu\text{mol/h}$)得到了极大提高,并显示出极好的光催化产氢稳定性能. 对于光催化降解RhB体系, KCN复合材料也显示出较好的光催化活性和稳定性,并能很好地将RhB矿化. 鉴于KCN复合材料具有较小的比表面积(9.9 m^2/g)且无孔结构,认为比表面积对光催化活性影响较小. 因此,与单组分相比, KCN复合材料光催化产氢和RhB降解活性都得到了极大提高,活性的增强主要归功于N掺杂和异质结形成的协同效应,其中N掺杂可以拓宽光捕获能力,异质结形成可提高电荷载流子的分离效率. 电子自旋共振(ESR)谱表明,在KCN降解RhB体系中,超氧自由基($\cdot\text{O}_2^-$)、羟基自由基($\cdot\text{OH}$)和空穴(h^+)作为主要活性物质都参与了反应. 结合实验结果可以推测KCN复合材料满足了Z型光催化体系,该体系具有高效的光生载流子分离效率和较高的氧化还原能力.

关键词: 光催化反应; $\text{K}_4\text{Nb}_6\text{O}_{17}$; $\text{g}-\text{C}_3\text{N}_4$; Z型光催化剂; 异质结

收稿日期: 2020-02-26. 接受日期: 2020-04-09. 出版日期: 2021-01-05.

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基金来源: 国家自然科学基金(51902282和11474246); 中国博士后科学基金(2018M632283); 江苏省生态建材与环保装备协同创新中心暨江苏省新型环保重点实验室联合开放基金(JH201819); 江苏省生态环境材料重点实验室开放课题.

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