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Band gap-tunable potassium doped graphitic carbon nitride with enhanced mineralization ability

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A band gap-tunable potassium doped graphitic carbon nitride with enhanced mineralization ability was prepared using dicyandiamide monomer and potassium hydrate as precursor. X-ray diffraction (XRD), N2 adsorption, UV-Vis spectroscopy, Fourier transform infrared spectra (FT-IR), Scanning electron microscopy (SEM), Photoluminescence (PL) and X-ray photoelectron spectroscopy (XPS) were used to characterize the prepared catalysts. The CB and VB potentials of graphitic carbon nitride could be tuned from -1.09 and +1.56 eV to -0.31 and +2.21 eV by controlling the K concentration. Besides, the addition of potassium inhibited the crystal growth of graphitic carbon nitride, enhanced the surface area and increased the separation rate of photogenerated electrons and holes. The visible-light-driven Rhodamine B (RhB) photodegradation and mineralization performances were significantly improved after potassium doping. The possible influence mechanism of potassium concentration on photocatalytic performance was proposed.

Introduction

Nowadays, due to the significant energy and environmental crises, looking for new energy resources and strategies for pollution degradation become much more important. With outstanding virtues, including non-pollution and inexhaustible supply, solar energy is considered as one of the most promising candidates to resolve these problems. However, the low efficiency of the energy conversion still restricts its practical application. Recently, a metal-free visible-light photocatalyst graphitic carbon nitride (g-C3N4) has attracted intensive interest for its promising applications in splitting water to produce H2 decomposition of organic pollutants and organic synthesis. That attributes to the energy level with other semiconductor, thus is beneficial for the tunable band structure of g-C3N4 is convenient to match the and fascinating electronic property of g-C3N4. However, the rapid increase of the energy conversion still restricts its practical application. Because of the active chemical properties, alkali metals are widely used in the catalytic reaction. Salinas et al. prepared potassium-supported TiO2 catalysts for transesterification reaction. Chu et al. prepared halogen-free K+-modified CuO/SBA-15 for propylene epoxidation by molecular oxygen. They suggested that Cu(I) on the surface modified by K+ was responsible for the epoxidation. Pekridis et al. reported the modification effect of K+ on N2O reduction by alkanes over Pd/γ-Al2O3 catalysts. Qu et al. reported the effects of alkali metal on the toluene catalytic oxidation over the manganese oxide supported on SBA-15. They found that the catalysts, with K/Mn in the range of 0.15/1~0.18/1, exhibited better performances in the catalytic oxidation of toluene. However, little attention has been given to the investigation of the influence of alkali metal on the promotion of photocatalytic activity. Grzechulska et al. added a series of alkali to crystallized TiO2 slurry to prepare alkali metal modified TiO2 catalysts. The result of photocatalytic decomposition of oil indicated that the activity followed the order: TiO2/KOH > TiO2/Ca(OH)2 > TiO2/Ba(OH)2 > TiO2 (anatase). Chen et al. prepared K+-doped TiO2 by the sol-gel method and thermal treatment. Calcination leads to the formation of K4Ti3O7, which x value corresponds to promoters of photoactivity. K+ doping reduced recombination of the e− and h+ pair, enhanced the interfacial charge transfer, and improved reactants adsorption on the catalyst. Besides, the appropriate K+ concentration could reduce crystal size, increase surface area and raise the crystal transition temperature.

In addition to superior catalytic performance, the
mineralization ability in the degradation process is a key issue impeded the practical application of photocatalysts. The photocatalytic degradation of organic compound is a complex process, and many intermediate products are produced, especially when the initial substrate is complicated. Many intermediate products are more harmful to human health than the initial pollutant, thus thorough decomposition of the pollutant is necessary. In this work, a band gap-tunable potassium doped graphitic carbon nitride with enhanced mineralization ability was prepared for the first time using dicyandiamide monomer and potassium hydrate as precursor. The photocatalytic activity and stability were evaluated in the photocatalytic degradation of RhB under visible light. The effects of doping on the structural property, optical property and photocatalytic performance of as-prepared catalysts were discussed in detail.

Experimental

Preparation and characterization

In a typical experiment, 2 g dicyandiamide was dispersed into 10 ml deionized water under stirring. Then 10 ml KOH solution (0.02, 0.05, 0.07 and 0.09 M) was added. The obtained suspension was heated to 100 °C to remove the water. The solid product was dried at 80 °C in oven, followed by milling and annealing at 520 °C for 2 h (at a rate of 5 °C·min⁻¹). The obtained product was denoted as K(x)-CN, where x corresponds to the KOH concentration. When 10 ml deionized water or 10 ml NH₂OH (0.05 M) was used to replace 10 ml KOH (0.05 M), following the same procedure as the synthesis of K(0.05)-CN, two products of g-C₃N₄ and OH(0.05)-CN can be obtained. For comparison, as-prepared g-C₃N₄ was dispersed into 10 ml KOH (0.05 M). The obtained suspension was stirred for 10 h, and heated to 100 °C to remove the water. The solid product was dried and denoted as g-C₃N₄/KOH.

XRD patterns of the prepared samples were recorded on a Rigaku D/max-2400 instrument using Cu-Kα radiation (λ = 1.54 Å). The scan rate, step size, voltage and current was 0.05 °/min, 40kV and 30 mA, respectively. UV-vis spectroscopy measurement was carried out on a JASCO V-550 model UV-vis spectrophotometer, using BaSO₄ as the reflectance sample. Fourier transform infrared spectra (FT-IR) were obtained on a Nicolet 20DXB FT-IR spectrometer. Nitrogen adsorption was measured at -196 °C on a Micromeritics 2010 analyzer. All the samples were outgassed at 393 K for 3 h before the measurement. BET surface area (S_BET) was calculated according to the adsorption isotherm. The morphology of prepared catalyst was observed by using a scanning electron microscope (SEM, JSM 5600LV, JEOL Ltd.). ICP was performed to determine the actual K concentration on a Perkin-Elmer Optima 3300DV apparatus. XPS measurements were conducted on a Thermo Escalab 250 XPS system with Al Kα radiation as the exciting source. Curve fits were made using CasaXPS, while the relative sensitivity factors and asymmetry functions were taken from the PHI ESCA handbook. The binding energies were calibrated by referencing the C 1s peak (284.6 eV) to reduce the sample charge effect. Photoluminescence (PL) spectra were measured at room temperature with a fluorospectrophotometer (FP-6300), using Xe lamp as excitation source.

Photocatalytic Reaction

RhB was selected as the model compound to evaluate the photocatalytic performance of the prepared g-C₃N₄ based catalysts in an aqueous solution under visible light irradiation. In 200 ml aqueous solution of RhB (10 ppm), 0.05 g catalyst was dispersed and the solution was left in an ultrasound generator for 10 min. The suspension was transferred into a self-designed glass reactor, stirred for 30 min in darkness to achieve the adsorption equilibrium. In the photoreaction, the suspension was exposed to a 250 W high-pressure sodium lamp with main emission in the range of 400-800 nm and air was bubbled at 130 ml/min through the solution. The UV light portion of sodium lamp was filtered by 0.5 M NaNO₂ solution. All runs were conducted at ambient pressure at 30 °C. At given time intervals, 4 ml suspension was taken and immediately centrifuged to separate the liquid phase from the solid catalyst. The concentrations of RhB before and after reaction were measured by UV-Vis spectrophotometer at wavelength of 550 nm.

Results and discussion

Fig. 1 shows the XRD patterns of as-prepared g-C₃N₄ and K(x)-CN. The patterns of g-C₃N₄ and K(x)-CN exhibit two peaks at 13.1° and 27.3°, corresponding to (100) and (002) crystal planes of g-C₃N₄ (JCPDS 87-1526). These two peaks show gradually decreased intensity with increasing the potassium concentration, which suggests that the crystal growth of graphitic carbon nitride inhibited by introduction of potassium. No peak for potassium related species is observed in the pattern of K(x)-CN. Whereas, the obvious shifts toward a lower 2θ value are observed for all the K(x)-CN catalysts. This is probably because potassium doped into interstitial sites of in-planar g-C₃N₄, which enlarged the interlayer spacing. In Fig. S1, no peak shift in the pattern of g-C₃N₄/KOH and OH(0.05)-CN is shown by comparing with g-C₃N₄. This hints two kinds of information. First of all, the existence form of potassium species in g-C₃N₄/KOH and K(0.05)-CN is different. Secondly, such lattice distortion shown in Fig. 1 is not caused by the alkalization treatment but by potassium doping.

![Fig. 1 XRD patterns of as-prepared g-C₃N₄ and K(x)-CN.](image-url)

FT-IR spectra of as-prepared g-C₃N₄ based catalysts (Fig. S2) show that the peak at 1640 cm⁻¹ is attributed to C-N stretching vibration modes and the peaks in the range of 1200–1400 cm⁻¹ is for the stretching of aromatic C-N. The bands near 800 and 3200...
cm$^{-1}$ attribute to out-of-plane bending modes of C-N heterocycles and stretching vibration of N-H bond, associating with uncondensed aminogroups.\(^\text{22}\) For K(x)-CN, all the characteristic vibrational peaks of g-C$_3$N$_4$ are observed. The vibrations of K-related group are not observed, suggesting that the framework of g-C$_3$N$_4$ is not changed after doping.

Fig. 2 $N_2$ adsorption-desorption isotherms of g-C$_3$N$_4$ and K(0.05)-CN.

Fig. 3 UV-Vis diffuse reflectance spectra of as-prepared g-C$_3$N$_4$ based catalysts.

Nitrogen adsorption and desorption isotherms were measured to characterize the specific surface area of as-prepared g-C$_3$N$_4$ based catalysts (Fig. 2). Both g-C$_3$N$_4$ and K(x)-CN show a type IV isotherm with H3 hysteresis loop, suggesting the presence of mesopores. The hysteresis loop in the low pressure range (0.4<$P/P_0$<0.9) is associated with the intra-aggregated pores. The high-pressure hysteresis loop (0.9<$P/P_0$<1) is related to the larger pores formed between secondary particles. The BET specific surface areas ($S_{BET}$) of g-C$_3$N$_4$, K(0.02)-CN, K(0.05)-CN, K(0.07)-CN and K(0.09)-CN are calculated to be 8.9, 18.8, 26.9, 29.2 and 30.8 m$^2$·g$^{-1}$, respectively. This increased $S_{BET}$ is probably due to potassium doping inhibited the crystal growth of graphitic carbon nitride, leading to the formation of more secondary particles. Such large $S_{BET}$ is favorable to the photocatalytic performance because it can promote adsorption, desorption and diffusion of reactants and products.\(^\text{23}\)

The optical absorption of as-prepared g-C$_3$N$_4$ based catalysts were measured using UV-Vis diffuse reflectance spectra. The band gaps are estimated from the tangent lines in the plots of the square root of the Kubelka-Munk functions against the photon energy (Fig. S3).\(^\text{24}\) As presented in Fig. 3, the main absorption edge of g-C$_3$N$_4$ occurs at ca. 460 nm. The band gap for g-C$_3$N$_4$ is about 2.65 eV, which is in good agreement with the value reported in previous literature.\(^\text{25}\) In the case of K(x)-CN, the obvious red shifts of the absorption band are observed. However, no obvious difference among g-C$_3$N$_4$, g-C$_3$N$_4$/KOH and OH(0.05)-CN is shown in Fig. S4. This hints two kinds of information. First of all, the existence form of potassium species in g-C$_3$N$_4$/KOH and K(x)-CN is different, which is consistent with XRD pattern. Secondly, such shift of absorption band is not caused by the alkalization treatment but by potassium doping. The inset in Fig. 3 reveals that pure g-C$_3$N$_4$ is light yellow in color. The color of K(x)-CN gradually deepens with increasing the potassium concentration. The band gap energy decreases to 2.6, 2.57, 2.55 and 2.52 eV for K(0.02)-CN, K(0.05)-CN, K(0.07)-CN and K(0.09)-CN, respectively. This indicates that potassium doping has a strong influence on the optical property and band structure of as-prepared g-C$_3$N$_4$ based catalysts. After potassium doping, an isolated atomic orbital of dopant may locate in the g-C$_3$N$_4$ band gap or orbital hybridization occurs between dopant orbital and molecular orbital of g-C$_3$N$_4$, leading to the altered potential of VB and CB.

Fig. 4 SEM images of g-C$_3$N$_4$ (A), K(0.05)-CN (B, C) and elemental mapping image of K (D).

The morphologies of the representative samples were examined by using SEM analysis. Fig. 4C indicates as-prepared g-C$_3$N$_4$ based catalyst with a large number of irregular particles. Those particles exhibit layer structure that is similar to its analogue graphite (Fig. 4A and B). The size of layered structure of K(0.05)-CN is obviously decreased compared with g-C$_3$N$_4$. This indicates that potassium doping could inhibit crystal growth of graphitic carbon nitride, which is consistent with the XRD result. The elemental mapping image shown in Fig. 4D indicates that potassium is homogenously distributed in the whole host of g-C$_3$N$_4$. The potassium concentration obtained by ICP is 0.68,
C 3N4 in both N 1s and C 1s regions can be fitted with three contributions. The peak at 287.9 eV corresponds to sp²-hybridized carbon in N=C-N coordination, which connected with three neighboring N atoms in one double and two single bonds. In the case of K(0.05)-CN, a slight shift to lower binding energy is observed in N 1s but not in C 1s region compared with that of g-C3N4. This is probably due to higher electronegativity of N atoms, leading to the formation of strong interaction with doped potassium. The electrons of potassium could be transferred to nitrogen, which caused the increasing electron density of N atoms.

Fig. 5c shows that the binding energy of g-C3N4/KOH in K 2p region is located at 292.7 and 295.5 eV, which should be attributed to the 2p3/2 and 2p1/2 in K-O group. In the case of K(0.05)-CN, a obvious shift to lower binding energy (0.2 eV) is observed. Besides, the calculation result of surface elemental concentration determined by XPS reveals that K concentration in K(0.05)-CN is 1.46 wt.%, which is close to the ICP result (1.35 wt.%). In the case of g-C3N4/KOH, this value is 3.3 wt.%, much higher than that of ICP result (1.39 wt.%). This is probably due to the different existence form of K species in two samples. In the case of g-C3N4/KOH, K species mainly exists on the surface. Whereas K could be doped into g-C3N4 lattice in the formation of K-N bond during the polycondensation process, leading to the uniform dispersion in the bulk of K(0.05)-CN. Moreover, because the electronegativity of N atoms is lower than O atoms, the electron density of potassium in K-N bond should be higher than that in K-O group, leading to the binding energy difference (Fig. 5c).

In Fig. 5a and b, the spectra of g-C3N4 in both N 1s and C 1s regions can be fitted with three contributions. For N 1s region (Fig. 5a), three contributions located at 398.2, 399.3 and 400.4 eV are assigned to the sp² hybridized aromatic nitrogen atoms bonded to carbon atoms (C=N=C), tertiary nitrogen N=C(C) groups linking structural motif and nitrogen atoms bonded to three carbon atoms in the aromatic cycles. In Fig. 5b, the component at 284.6 eV corresponds to C-C originates from pure graphitic carbon presumably formed during minor decomposition of the carbon nitride. The peak at 285.8 eV corresponds to C=N or C≡N, which could be ascribed to defect containing sp²-hybridized carbon atoms present in g-C3N4 pores.28 The peak at 287.9 eV corresponds to sp²-hybridized carbon in N=C-N coordination, which connected with three neighboring N atoms in one double and two single bonds.29

Fig. 6: The possible doping site of K ions in K(x)-CN.
To further investigation the influence of K doping on the relative positions of the CB and VB, the VB XP spectra was employed to determine the electronic structure (Fig. 5d). Compared with the spectrum of g-C3N4, an obvious shift (0.48 eV) is shown in K(0.05)-CN, which could be attributed to the K doping. The VB potentials of g-C3N4 and K(0.05)-CN locate at +1.56 and +2.04 eV. Combined with the UV-Vis results, the optical CB potentials of g-C3N4 and K(0.05)-CN locate at -1.09 and -0.53 eV. The VB XP spectra of K(0.02)-CN, K(0.07)-CN and K(0.09)-CN are shown in Fig. S6. Their VB and CB potentials are also calculated and shown in Fig. 7. Obviously, the CB and VB positions obviously alters after K doping. Their VB and CB potentials are beneficial to the forming of the heterojunction with other semiconductor in order to meet different application demands.

Fig. 7 Band gap structures of as-prepared g-C3N4 and K(x)-CN.

PL is a highly sensitive technique used to provide information on charge separation/recombination of photoinduced charged carriers. In general, the lower PL intensity, the higher separation rate of photogenerated electron-hole pairs. Fig. 8 shows the PL spectra of as-prepared g-C3N4 based catalysts under the excitation wavelength of 380 nm at room temperature. For g-C3N4, the broad PL band is around 465 nm, which is attributed to the band-band PL phenomenon with the energy of light approximately equal to the band gap of g-C3N4. Such band-band PL signal is attributed to excitonic PL, which mainly results from the n-π* electronic transitions involving lone pairs of nitrogen atoms in g-C3N4. In the case of K(x)-CN, the shape of the curves are similar to that of g-C3N4, whereas the peak intensities decrease sharply. Such increased separation rate of photogenerated electrons-holes pairs in K(x)-CN catalysts could improve the visible light utilization, thus is beneficial to the photocatalytic performance. No essential difference in PL curves among g-C3N4/KOH, OH(0.05)-CN and K(0.05)-CN is observed, indicating those two modification methods did not improve the separation rate of photogenerated electrons-holes pairs. This result not only confirms the different existence form of K species between K(0.05)-CN and g-C3N4/KOH, but also suggests that such increased separation rate of electron-hole pairs for K(x)-CN is not caused by the alkalinization treatment but by K doping. K doping gives rise to distortion in the lattice structure of g-C3N4. That caused the increased surface energy, leading to the reduced recombination rate of electron-hole pairs, enhancing the interfacial charge transfer rate.

Fig. 8 PL spectra of as-prepared g-C3N4 based catalysts.

Fig. 9 Photocatalytic performances of as-prepared g-C3N4 based catalysts (a) and plot of -ln(C/C0) against reaction time (b) in the degradation of RhB under visible light irradiation.

Fig. 9a shows the photocatalytic performances of as-prepared g-C3N4 based catalysts in the degradation of RhB under visible light irradiation. Before the light on, the RhB adsorption abilities of K(x)-CN catalysts are enhanced, which is probably due to the larger SBET. Control experiment results indicate that the RhB degradation performance could be ignored in the absence of either irradiation or photocatalyst, indicating that RhB is degraded via photocatalytic process. Fig. S7 shows that g-C3N4/KOH and OH(0.05)-CN exhibit almost the same photocatalytic activity as g-C3N4. Whereas K(x)-CN catalysts show clearly higher activities than that of g-C3N4 (Fig. 9a). This is probably due to the synergistic effect caused by the K doping which improved the SBET, decreased the band gap energy and enhanced the separation rate of photogenerated electron-hole pairs. The photocatalytic activity enhances gradually with increasing the K concentration from 0.02 to 0.05. K(0.05)-CN and K(0.07)-CN show much higher photocatalytic activity than that of other potassium doped catalysts. When the K concentration beyond 0.07, the activity decrease remarkably. The possible reason is discussed (see below). The reaction rate constant k is obtained by assuming that the reaction followed first order kinetics. Fig. 9b displays that a linear relationship is established when -ln(C/C0) is plotted against t (reaction time). The rate constant k can be calculated by the slope of the curve. The results indicate that the rate constant k are 0.0017, 0.0074.
0.011, 0.010 and 0.0037 min⁻¹ for g-C3N4, K(0.02)-CN, K(0.05)-CN, K(0.07)-CN and K(0.09)-CN, respectively. K(0.05)-CN shows the highest rate constant, which is 6.4 times higher than that of g-C3N4.

Fig. 10 Degradation rate, mineralization rate and mineralization ratio comparison of as-prepared g-C3N4 based catalysts.

The mineralization ability of prepared catalysts to RhB molecules was evaluated by monitoring the changes of TOC in the reaction systems. Fig. 10 shows the degradation rate, mineralization rate and mineralization ratio comparison of as-prepared g-C3N4 based catalysts. Mineralization ratio, which represents the mineralization ability, is equal to the ratio of the mineralization rate to the degradation rate. Obviously, the mineralization rates of as-prepared g-C3N4 based catalysts show a similar variation trend to the degradation rate. However, the mineralization ratio increases evidently with increasing the KOH concentration. Zhang et al. prepared TCNQ-g-C3N4 organic conjugative hybridized photocatalysts. In this investigation, potassium doping can alter the band structure of as-prepared g-C3N4 based catalysts, thus improve the mineralization ability.

The catalytic stability test of as-prepared K(0.05)-CN was carried out (Fig. S8). The results indicate that no obvious decrease in RhB degradation performance is observed after three cycles. The XPS curves of fresh and reused K(0.05)-CN reveal that the chemical state of potassium element is not changed (Fig. S9). Moreover, ICP result displays that the potassium concentration is 1.33 wt.% in reused K(0.05)-CN which is very close to the fresh catalyst (1.35 wt.%). Therefore, it is deduced that the as-prepared K(0.05)-CN is stable. However, the ICP result indicates that the potassium concentration of used g-C3N4/KOH decreases sharply to 0.44 wt.%, probably due to that KOH dissolved into the solution. To confirm this point, the pH values of K(0.05)-CN and g-C3N4/KOH suspension were measured by a pH meter. The results show that the suspension of K(0.05)-CN is almost neutral (pH=7.17). In the case of g-C3N4/KOH, the pH value is 9.25, much higher than that of K(0.05)-CN.

Fig. 11 Influence of various scavengers on the visible light photocatalytic activity of g-C3N4, K(0.05)-CN and K(0.09)-CN.

The hole and free radical trapping experiments were carried out to clarify the reaction mechanism and the active species generated during the reaction process. In this investigation, EDTA-2Na, tert-butyl alcohol (t-BuOH) and 1,4-benzoquinone (BQ) are used as the hole (h⁺), hydroxyl radical (•OH) and superoxide radical (•O2-) scavenger, respectively. Fig. 11 shows the influence of various scavengers on the visible light photocatalytic activity of g-C3N4, K(0.05)-CN and K(0.09)-CN. For g-C3N4, the photodegradation rate of RhB only decreases slightly after the addition of t-BuOH, but sharply when BQ is added. This indicates that the main active species is not hydroxyl radicals but •O₂⁻ in the current photocatalytic systems. In theory, the CB and VB position of g-C3N4 are -1.12 V and +1.57 V, respectively. The redox potentials of •OH/OH⁻ and O₂/•O₂⁻ are +1.99 V and -0.33 V, as shown in Fig. 7. Obviously, the reduction potential of CB electrons in g-C3N4 is more negative than the redox potential of O₂/•O₂⁻ which can reduce O₂ to form •O₂⁻, whereas the VB holes in g-C3N4 are not positive enough to generate •OH. This theoretical result is consistent with our experiment results. In the presence of EDTA-2Na, the degradation rate is increased obviously, which is completely different from previous results. Zhang et al. prepared C60N4/Bi4Nb5O15 heterojunction catalyst for 4-CP photodegradation. The photodegradation rate decreased significantly after the addition of EDTA-2Na, indicating the photogenerated holes were the main active species in their system. In this study, although the redox potential of RhB is reported to be 1.43 V, which is higher than the VB of g-C3N4 (Fig. 7), the direct photogenerated holes oxidation did not occur. On the contrary, the addition of EDTA-2Na to trap the h⁺ could promote the separation rate of electron-hole pairs, leading to the increased photocatalytic performance. In the case of K(0.05)-CN, the activity decreases obviously when each scavenger is added, suggesting both •OH and •O2⁻ are the main active species in this photocatalytic system. This is due to the change of VB and CB positions after potassium doping. The VB potential is +2.04 eV, more positive than the redox potential of •OH/OH⁻. Therefore, •OH could trap the h⁺ to form •OH, which is responsible for RhB degradation. For K(0.09)-CN, the VB and CB potentials are +2.21 and -0.31 eV, as shown in Fig. 7. The CB potential decreases obviously, even lower than that of redox potential of O₂/•O₂⁻. Therefore, when BQ is added, only slight decrease in activity is observed. Moreover, the addition of EDTA-2Na and BuOH remarkably decrease the activity confirms that the main active species is •OH in this photocatalytic system. Because the
positions of VB and CB of K(x)-CN are obviously altered after potassium doping. Both OH and O2 could be formed in K(0.05)-CN and K(0.07)-CN systems (Fig. 7). Therefore, it is reasonable that K(0.05)-CN and K(0.07)-CN show much higher activities than that of other potassium doped catalysts.

To further prove the effectiveness of alkali metal modification, we used this approach to synthesize sodium doped g-C3N4 catalysts. The preparation method is same as that of K(x)-CN but using NaOH instead of KOH. Fig. S10 indicates that the photocatalytic activities increase obviously after sodium doping. From the color of as-prepared sodium doped g-C3N4 catalysts, the band structure could also be altered by sodium doping. These results prove that alkali metal modification is a facile and flexible approach for the synthesis of carbon nitride photocatalyst with a tunable band structure. Such tunable band structure of g-C3N4 is beneficial for the forming of heterojunction with other semiconductor for different application demands.

Conclusions

A novel alkali metal potassium doped carbon nitride photocatalyst with a tunable band structure was prepared using dicyandiamide monomer and potassium hydrate as precursor. Potassium doped g-C3N4 exhibited smaller grain size, larger S BET, narrower band gap energy and better separation rate of photogenerated electrons and holes. The contrast experiment results indicated that those changes are not caused by the anodization treatment but by potassium doping. The CB and VB potentials of as-prepared K(x)-CN were obviously altered by increasing the potassium concentration. The RhB photodegradation and mineralization abilities under visible light were significantly improved after potassium doping. Because of the regulating effect of potassium doping on band structure, both OH and O2 could be formed in K(0.05)-CN and K(0.07)-CN system, leading to their activities much higher than that of other potassium doped catalysts. K(0.05)-CN shows the highest rate constant, which is 6.4 times higher than that of g-C3N4. Moreover, K(0.05)-CN exhibited stable catalytic activity and chemical structure. Sodium doped g-C3N4 catalysts prepared by the similar method also exhibited the tunable band structure and improved photocatalytic performance.

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Notes and references