A Convenient Method to Prepare Novel Alkali Metal Potassium
Doped Carbon Nitride Photocatalyst with Tunable Band Structure

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A novel alkali metal ion K^+ doped carbon nitride photocatalyst with a tunable band structure was prepared using dicyandiamide monomer and potassium hydrate as precursor. X-ray diffraction, UV-visible, FT-IR and XPS were used to characterize the prepared catalysts. The valence band and conduction band potentials were obviously altered by changing the potassium concentration. Besides, the addition of potassium inhibited the crystal growth of graphitic carbon nitride and increased the separation rate of photogenerated electrons and holes. The visible-light-driven Rhodamine-B photodegradation performance was significantly improved after K^+ doping. The possible doping site and influence mechanism of potassium concentration on photocatalytic performance was proposed.

Keywords: g-C₃N₄, Potassium doping, Tunable band structure, Visible light.

INTRODUCTION

Nowadays, energy and environmental crisis are the great problems for all the countries in the world. With outstanding virtues, including non-pollution and inexhaustible supply, solar light is considered as one of the most promising candidate to resolve the energy crisis and environmental problems. However, low energy conversion efficiency still restricts its practical application. Recently, a metal-free visible-light photocatalyst graphitic carbon nitride (g-C₃N₄) has attracted intensive interest for its many promising applications. The g-C₃N₄ has a moderate band gap (2.7 eV), high chemical and thermal stability as well as fascinating electronic property. However, the rapid photo-generated electron-hole pair recombination leads to the low activity in practical applications[1,2].

Several routes have been developed to solve this problem[3-6], preparation of porous[7] g-C₃N₄, protonating by strong acids[8] and designing composite with other semiconductors[9]. Among those strategies, doping is one of the most convenient and effective method. Yan *et al*.[3] prepared B doped g-C₃N₄ and suggested that the enhanced degradation performance of Rhodamine-B was due to the improvement of dye adsorption and light absorption ability. Zhang *et al*.[4] synthesized phosphorus doped g-C₃N₄ using ionic liquid [Bmim]PF₆ as phosphorus source. The obtained material exhibited significantly improved electrical conductivity and photocurrent. Noble metal, such as Pt, Pd and Ag, is an effective dopant to trap the

photogenerated electrons, thus improve the separation rate of photogenerated electrons and holes. Bu *et al*.[5] prepared Ag-modified carbon nitride and found that the separation efficiency was significantly improved, thus enhanced the photoelectric conversion performance. Chang *et al*.[6] synthesized Pd/mpg-C₃N₄ and used for photodegradation of bisphenol A. They found that most of Pd presented as Pd⁰ state which acted as electron traps, leading to the improved separation efficiency and photocatalytic performance. However, the high price of noble metal inhibits their practical application.

Because of the active chemical properties, alkali metals are widely used in the catalytic reaction[10-12]. Salinas *et al*.[10] prepared potassium-supported TiO₂ catalysts for transesterification reaction. Chu *et al*.[11] prepared halogen-free K⁺-modified CuOₓ/SBA-15 and used 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*.[12] reported the modification effect of K⁺ on N₂O reduction by alkanes or alkenes over Pd/γ-Al₂O₃ catalysts. However, little attention has been given to the investigation of the influence of alkali metal on the promotion of photocatalytic activity[13,14]. Grzechulska *et al*.[13] 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 follows 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[14]. Calcination

leads to the formation of $K_{4-4x}Ti_xO_2$ in which x value is regarded as 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. In this work, a novel K^+ doped carbon nitride photocatalyst with a tunable band structure was prepared for the first time. The photocatalytic activity was evaluated in the photocatalytic degradation of Rhodamine-B under visible light. The effects of doping on the structural property, optical property and photocatalytic performance of as-prepared catalysts were discussed in this work.

EXPERIMENTAL

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 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 CNK(x), where x stands for the KOH concentration. When 10 mL deionized water or 10 mL NH$_4$OH (0.05 M) was used to replace 10 mL KOH (0.05 M) following the same procedure as in the synthesis of CNK (0.05), the product is denoted as neat g-C$_3$N$_4$ or CNOH (0.05), respectively. For comparison, as-prepared g-C$_3$N$_4$ 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-C$_3$N$_4$/KOH.

X-ray diffraction patterns of the prepared samples were recorded on a Rigaku D/max-2400 instrument using CuK$_\alpha$ radiation (λ = 1.54 Å). UV-visible spectroscopy measurement was carried out on a JASCO V-550 model UV-visible spectro-photometer, using BaSO$_4$ as the reflectance sample. Fourier transform infrared spectra (FT-IR) were obtained on a Nicolet 20DXB FT-IR spectrometer. 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 K$_\alpha$ radiation as the exciting source. The binding energies were calibrated by referencing the C 1s peak (284.6 eV) to reduce the sample charge effect.

Rhodamine-B was selected as the model compound to evaluate the photocatalytic performance of the prepared g-C$_3$N$_4$ based catalysts in an aqueous solution under visible light irradiation. 0.05 g catalyst was dispersed in 200 mL aqueous solution of Rhodamine-B (10 ppm) in an ultrasound generator for 10 min. The suspension was transferred into a self-designed glass reactor and stirred for 0.5 h in darkness to achieve the adsorption equilibrium. In the photoreaction under visible light irradiation, 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 NaNO$_2$ solution. All runs were conducted at ambient pressure and 30 °C. At given time intervals, 4 mL suspension was taken and immediately centrifuged to separate the liquid samples from the solid catalyst. The concentrations of Rhodamine-B before and after reaction were measured by UV-Visible spectrophotometer at a wavelength of 550 nm.

RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of as-prepared g-C$_3$N$_4$ and CNK(x). The patterns of g-C$_3$N$_4$ and CNK(x) exhibit two peaks at 13.1 and 27.3°, corresponding to (100) and (002) crystal planes of g-C$_3$N$_4$ (JCPDS 87-1526)[15]. These two peaks show gradually decreased intensity with the increasing potassium concentration, which suggests that the crystal growth of graphitic carbon nitride is inhibited by introduction of potassium. No peak for potassium related species is observed in the pattern of CNK(x). Whereas, an obvious shift toward a lower 2θ value is observed for all the CNK(x) catalysts. This is probably due to that potassium doped into interstitial sites of in-planar g-C$_3$N$_4$ which enlarged the interlayer spacing.
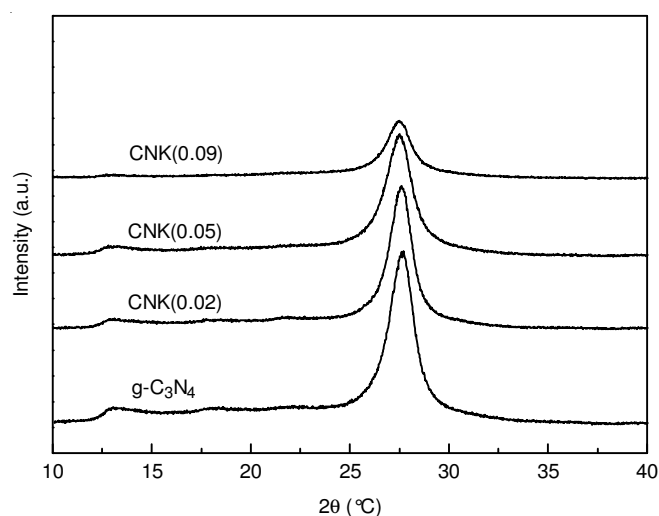

Fig. 1. XRD patterns of as-prepared g-C$_3$N$_4$ and CNK(x)

FT-IR spectra result of as-prepared g-C$_3$N$_4$ based catalysts (Fig. 2) shows that the peak at 1640 cm^{-1} was attributable to C-N stretching vibration modes, while the 1400-1200 cm^{-1} to aromatic C-N stretching. The band near 3200 and 800 cm^{-1} are attributed to out-of-plane bending modes of C-N hetero-cycles and stretching vibration of N-H bond, associated with uncondensed amino groups[16]. For CNK(x), all the characteristic
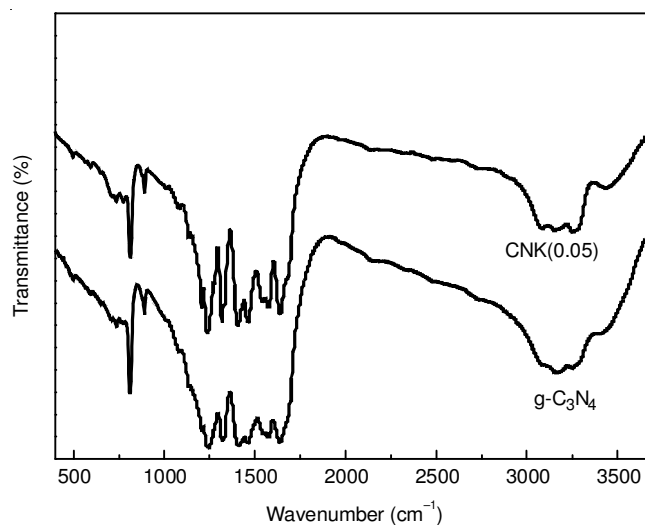

Fig. 2. FT-IR spectra of as-prepared g-C$_3$N$_4$ and CNK(0.05)

vibrational peaks of g-C_3N_4 were observed. The vibrations of K-related group were not observed, suggesting that the framework of g-C_3N_4 is not changed after K doping.

The optical absorption of as-prepared g-C_3N_4 based catalysts was measured using UV-visible diffuse reflectance spectra. As presented in Fig. 3, the main absorption edge of g-C_3N_4 occurs at about 460 nm. The band gap energy of g-C_3N_4 estimated with the Kubelka-Munk function is about 2.65 eV, which is in good agreement with the value reported in previous literature[17]. In the case of CNK(x), the obvious red shifts of the absorption band are observed. However, no obvious difference between g-C_3N_4 and g-C_3N_4/KOH was shown. This suggests that the existence form of potassium species in g-C_3N_4/KOH and CNK(x) is different. The band gap energy decreased to 2.6, 2.57 and 2.52 eV for CNK (0.02), CNK (0.05) and CNK (0.09). This indicated that potassium concentration strongly influences the optical property and band structure of as-prepared g-C_3N_4 based catalysts. Ma *et al.*[18] calculated the electronic structure of phosphorus doped g-C_3N_4 using first-principles. They found that isolated P 3p orbital was localized below the bottom of the conduction band in the host g-C_3N_4, thus decreased the band gap energy. Similarly, after potassium doping, an isolated atomic orbital of dopant may locate in the g-C_3N_4 band gap, or orbital hybridization occurs between dopant orbital and molecular orbital of g-C_3N_4, leading to the altered position of valence band and conduction band.
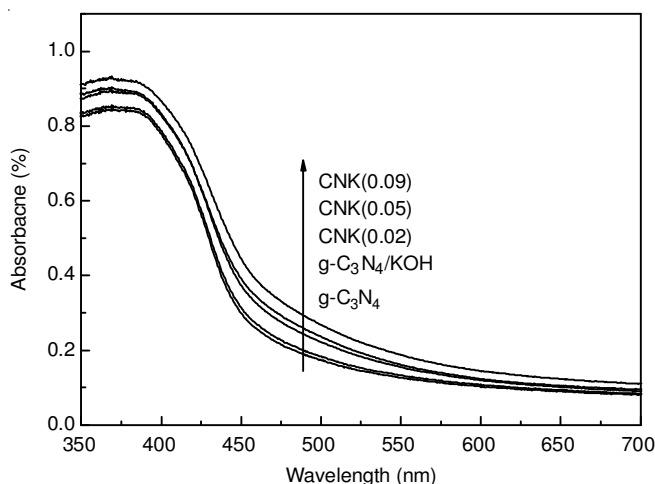

Fig. 3.   UV-visible diffuse reflectance spectra of as-prepared g-C_3N_4 based catalysts

X-ray photoelectron spectroscopy (XPS) measurements were performed to explicate the valence states of various species. Fig. 4 displays the XP spectra of as-prepared g-C_3N_4 based catalysts in the region of K 2p (a) and valence band XPS (b). As shown in Fig. 4a, the binding energy of g-C_3N_4/KOH in K 2p region was located at 292.7 eV, which should be attributed to the K-O group[19]. In the case of CNK (0.05), a obvious shift to lower binding energy (0.2 eV) was observed. Besides, the calculation result of surface elemental concentration determined by XPS reveals that K concentration in CNK (0.05) was 1.46 wt. %, which is close to the ICP result (1.35 wt. %). In the case of g-C_3N_4/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. For g-C_3N_4/KOH,

K species mainly exists on the surface. Whereas K could be doped into g-C_3N_4 lattice in the formation of K-N bond during the polycondensation process, leading to the uniform dispersion in the bulk of CNK (0.05). Moreover, K doping could influence the chemical environments of both N and K atoms. The lone electron pair of nitrogen causes the electron-rich structure of g-C_3N_4. Therefore, K could be coordinated to N ligands and stabilized by the lone electron pair. The similar structure such as Fe doped g-C_3N_4 has been reported[20]. Thus, the electron density increased for K atoms, leading to the binding energy shifts (Fig. 4a). It is known that the lone pair electron of nitrogen plays an important role in the electronic structure of carbon nitride[21]. The doping of K could influence the electron density of N atoms, thus altered the electronic structure and band gap of carbon nitride. As for the doping site of potassium, the probably situation is interstitial sites. The ionic radius of K is much larger than that of C and N, the substitutional doping should not occur. Besides, the maximum in-planar distance of nitride pores is 0.71 nm[22], which is adequate to accommodate the K ions. Summarizing the above results, the possible doping site of K ions in CNK(x) is as shown in Fig. 5.

To further investigate the influence of K doping on the relative positions of the conduction band and valence band, the valence band XP spectra was employed to determine the
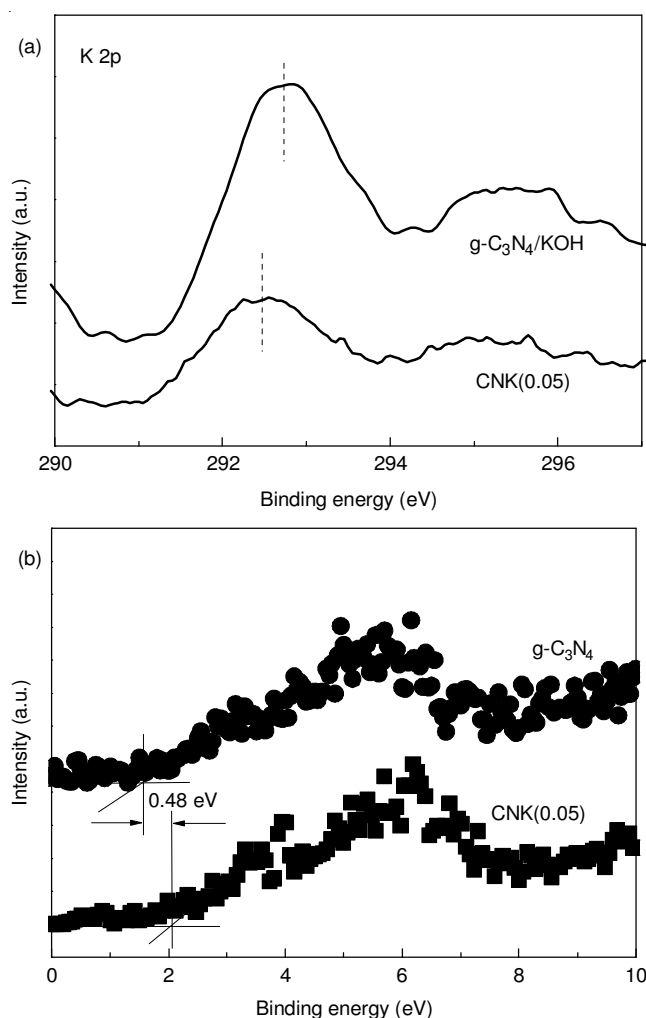

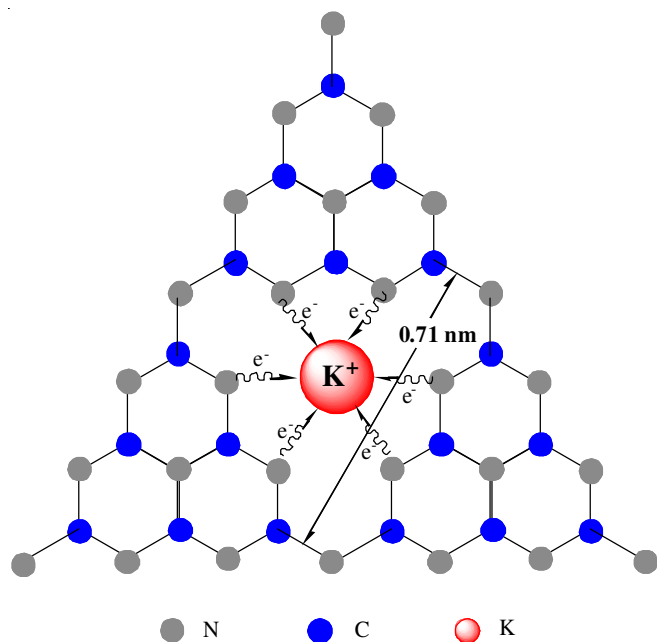Fig. 4.   XP spectra of as-prepared g-C_3N_4 based catalysts in the region of K 2p (a) and valence band XPS (b)

Fig. 5. Possible doping site of K ions in CNK(x)

electronic structure (Fig. 4b). Compared with the spectrum of g-C_3N_4, an obvious shift (0.48 eV) is shown in CNK (0.05), which should be attributed to the K atoms doped into g-C_3N_4 lattice. The valence band of g-C_3N_4 and CNK (0.05) locate at +1.56 and +2.04 eV, respectively. Combined with the UV-visible result, the optical conduction band potentials of g-C_3N_4 and CNK (0.05) locate at -1.09 and -0.53 eV, respectively. The valence band and conduction band potentials of other K doped g-C_3N_4 catalysts were calculated and shown in Fig. 6. Obviously, the conduction band and valence band positions were obviously altered with increasing the potassium concentration. The conduction band and valence band potentials could be tuned from -1.09 and +1.56 eV to -0.31 and +2.21 eV, respectively by controlling the K concentration. Such tunable conduction band and valence band potentials are beneficial to form the heterojunction with other semiconductors to meet different application demands.
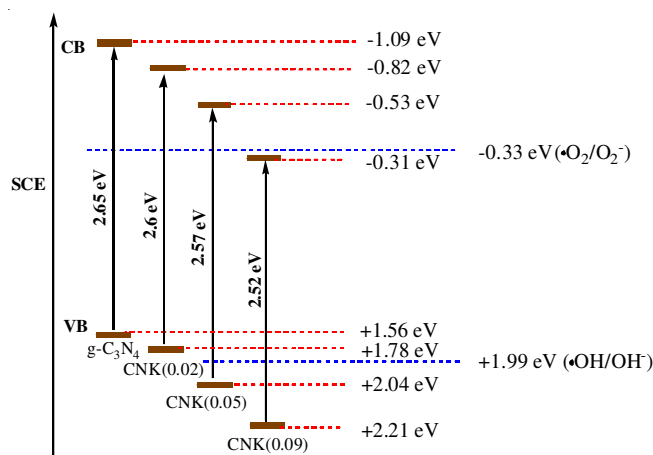

Fig. 6. Band gap structures of as-prepared g-C_3N_4 and CNK(x)

Fig. 7a shows the photocatalytic performances of as-prepared g-C_3N_4 based catalysts in the degradation of Rhodamine-B under visible light irradiation. CNK(x) catalysts show clearly

higher activity than that of g-C_3N_4. Whereas, as shown in Fig. 8, g-C_3N_4/KOH and CNOH (0.05) exhibit almost the same photocatalytic activities as g-C_3N_4. This hints two points. First of all, the existence form of potassium species in g-C_3N_4/KOH and CNK(x) is different, which is consistent with UV-visible result. Secondly, the improved activity is not attributed by the alkali treatment but by the K doping. The photocatalytic activity enhanced gradually with increasing the K concentration from 0.02 to 0.05. CNK (0.05) showed much higher photocatalytic activity than that of other potassium doped catalysts. When the K concentration beyond 0.05, the activity decreased remarkably. The reaction rate constant k was obtained by assuming that the reaction followed first order kinetics[23]. Fig. 7b displays that a linear relationship is established when -ln (C/C_0) is plotted against t (reaction time). The rate constant k can be calculated by the slope of the line. The results indicated that the rate constant k were 0.0017, 0.0074, 0.011 and 0.0037 min^{-1} for g-C_3N_4, CNK (0.02), CNK (0.05) and CNK (0.09). CNK (0.05) shows the highest rate constant, which is 6.4 times higher than that of g-C_3N_4.

Conclusion

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-C_3N_4 exhibited smaller grain size and

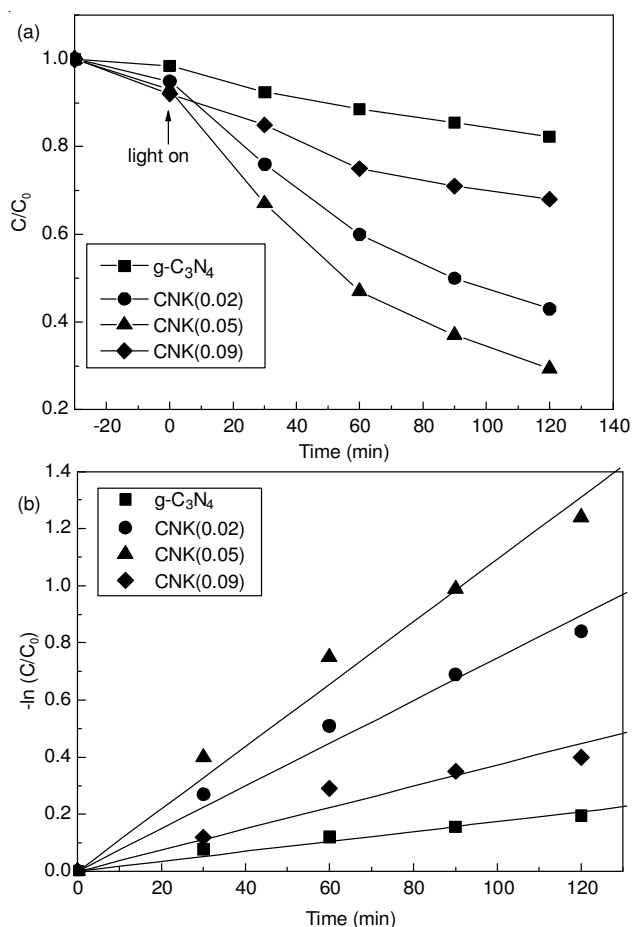Fig. 7. Photocatalytic performances of as-prepared g-C_3N_4 based catalysts (a) and plot of -ln (C/C_0) against reaction time (b) in the degradation of Rhodamine-B under visible light irradiation
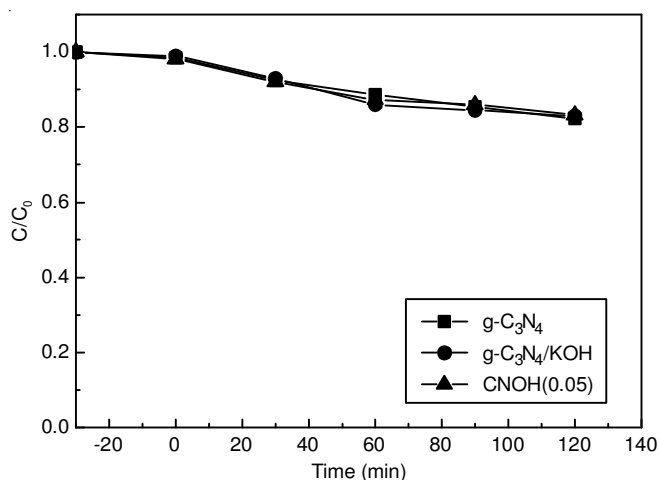
Fig. 8. Photocatalytic performances comparison of as-prepared g-C₃N₄, g-C₃N₄/KOH and CNOH (0.05)

narrower band gap energy. The contrast experiment results indicated that those changes are not caused by the alkalization treatment but by potassium doping. The conduction band and valence band potentials of as-prepared CNK(x) were obviously altered by changing the potassium concentration. Potassium could be coordinated to N ligands, stabilized by the lone electron pair and doped in interstitial sites. The photodegradation performance of Rhodamine-B was significantly improved after potassium doping under visible light. The improved activity is not attributed by the alkali treatment but by the K doping. CNK (0.05) shows the highest rate constant, which is 6.4 times higher than that of g-C₃N₄.

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