TOPICAL REVIEW

Alkali/alkaline-earth metal intercalated g-C₃N₄ induced charge redistribution and optimized photocatalysis: status and challenges

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Abstract

Limited by the intrinsic graphitic sp²-hybridized array of tri-s-triazine repeating units and inert stack of layers, the insertion of intercalant between layers of graphitic carbon nitride (CN) could be an effective way to strengthen the van der Waals force between adjoining layers and induce the charge redistribution in CN for the improvement of photocatalysis. This review summarizes the latest progress related to the design and construction of alkali/alkaline-earth metal intercalated CN, including (a) single alkali/alkaline-earth metal intercalated CN, (b) alkali/alkaline-earth metal and non-metallic species co-intercalated CN, (c) alkali/alkaline-earth metal intercalated and surface modification co-functionalized CN. The promotion mechanism of each classification will be critically discussed, namely alkali/alkaline-earth metal intercalated CN-induced charge redistribution facilitates the adsorption and activation of reactants, accelerates the separation efficiency of photogenerated carriers, and optimizes the reaction pathway. Also, the influence on band structure and optical property has been discussed with the intercalation of alkali/alkaline-earth metal. Finally, this mini-review highlights crucial issues that should be addressed in future research.

1. Introduction

Ever since the 1970s, the increasing challenges in energy demands and environmental concerns due to the consumption of fossil fuels have raised awareness of a potential global crisis. Thus, developing cutting-edge science and technology has been pursued to overcome the obstacle for effective energy conversion and environmental protection [1–4]. Among various renewable energy projects, semiconductor photocatalysis as a feasible technology that can be harvested by the inexhaustible and clean solar energy has gained considerable interdisciplinary attention for its diverse potential in energy and environmental applications [5–11].

Since the landmark event of photocatalytic water splitting using TiO₂ electrodes under ultraviolet light was ignited by Fujishima and Honda in 1972 [12], extensive research has been carried out on traditional semiconductor photocatalysts to address the energy shortages and environmental threats. Recently, great efforts have been made to design visible-light-responsive novel photocatalysts for effective utilization of the solar spectrum that comprises a large fraction of visible light (ca. 43%) [13–18]. In 2009, a metal-free polymeric photocatalyst graphitic carbon nitride (CN) was first reported by Wang et al for photocatalytic H₂ evolution, which potentially shifted the research exploration from inorganic compound to artificial conjugated polymer semiconductors [19]. Afterwards, CN became an alternative and attractive photocatalyst in view of its facile synthesis, appealing electronic structure, high physicochemical stability, and ‘earth-abundant’ nature [19–24].
However, practical applications of bare CN are still hindered by several obstacles and shortcomings. The intrinsic graphitic sp²-hybridized array of tri-s-triazine repeating units and an inert stack of layers give rise to a high recombination rate of charge carriers and low electrical conductivity [25–28]. Thus, several modifications of bare CN, including microstructure design, element doping, copolymerization and construction of heterojunctions have been conducted to optimize the photocatalytic performance. Considering the polymeric and layered stacking feature of CN, it provides the advantage that the surface chemistry and internal electronic structure could be easily modulated at atomic-level for the enhancement of photocatalytic performance [24, 29]. Generally, intercalation could endow layered material with controllable physical properties, such as the conductivity of layered graphite can be adjusted from insulating to conducting by the insertion of intercalant between layers [30]. Therefore, the layered CN with a large interlayer space of 0.326 nm allows the intercalation of heteroatom to strengthen the van der Waals (vdW) force between adjoining layers and induce the charge redistribution in CN [31], which is beneficial to facilitate the separation of charge carriers and thus optimize the photocatalysis.

Even though numerous studies on the doping of anions and cations have been proposed, the heteroatoms are usually introduced in plane of CN. The doping of anions such as B, C, O, F, P, S, I preferentially substitute the C/N atoms on the heptazine units of CN because of the difference of electronegativity [32–39]; and also, the doped metal cations like Fe, Cu, Zn, Ni would be easily captured in the large nitrogen pots in the plane of CN, which can be ascribed to the strong interactions between the cations and the negatively charged nitrogen atoms due to lone pairs of electrons in the nitrogen pots of CN [24, 40–43]. Therefore, the introduced heteroatoms between neighboring layers should be carefully taken into account. Alkali/alkaline-earth metal could be a feasible candidate to be intercalated into the adjacent layer of CN since the relatively large but appropriate atomic radius of alkali/alkaline-earth metal is more suitable to be intercalated into the interlayer instead of the conjugated plane of CN. Xiong et al firstly demonstrated that K atoms tend to be intercalated into the CN interlayer whereas Na atoms with smaller radius are inclined to be doped into the conjugated plane [27]. Since then, comprehensive study based on alkali/alkaline-earth metal intercalated CN is increasingly proposed. The intercalation of alkali/alkaline-earth metal into the interlayer of CN has become an effective way to extend the π-conjugated system, bridge the interlayer, and thus induce the charge redistribution of CN, aiming to accelerate the adsorption and activation of reactants, the separation of charge carriers, and the optimization of photocatalysis.

However, alkali/alkaline-earth metal intercalated CN induced charge redistribution and promoted photocatalysis are not thoroughly discussed thus far. To the best of our knowledge, there is no review article hitherto which critically presents the rational design and construction of alkali/alkaline-earth metal intercalated CN. Therefore, it has spurred our enormous interest in further underlining the advancements of alkali/alkaline-earth metal intercalated CN. We herein present a comprehensive and updated review on the construction strategy of intercalated CN and the core principles of photocatalytic enhancement. The functionalization of CN includes alkali/alkaline-earth metal intercalated CN (section 2), alkali/alkaline-earth metal and non-metallic species co-intercalated CN (section 3), alkali/alkaline-earth metal intercalated and surface modification co-functionalized CN (section 4). The introduction of a heteroatoms induced charge redistribution and corresponding promotion mechanism have also been discussed in-depth, such as facilitated adsorption and activation of reactant, accelerated separation efficiency of photogenerated carriers, and even optimized reaction pathways (figure 1). Besides, we have compared and explained the influence on band structure and optical property by the intercalation of alkali/alkaline-earth metal. We are confident that this comprehensive review is timely not only to highlight the advancements in this rapidly progressing research field, but also to inspire new concepts and present a good reference to engineer CN-based and two-dimensional photocatalysts for energy and environmental applications.

2. Enhanced photocatalysis on alkali/alkaline-earth metal intercalated g-C₃N₄

Even though several literatures reported that the introduction of alkali/alkaline-earth metal in CN could improve the photocatalytic performance, the position of doped atoms, promotion mechanism, and the influence of other congener alkali elements with similar electronic structure on photocatalytic performance have not been revealed clearly [31, 44–47]. Recent studies on alkali/alkaline-earth metal intercalated CN are summarized in table 1. The first comprehensive study with theoretical and experimental proofs was reported by Xiong et al in 2016 [27]. Further, Li et al developed alkalis (K, Rb, Cs) intercalated in CN, and unravelled the key role of interlayer electron transfer direction and particular promotion mechanism [48]. The alkali species could suppress random charge transfer in the planes of CN and enable the electrons to directionally migrate between adjacent layers. The intercalation of alkali/alkaline-earth metal induces the charge redistribution in CN, which is beneficial to accelerate the adsorption and activation of
Figure 1. Schematic illustration of alkali/alkaline-earth metal intercalated CN induced charge redistribution and optimized photocatalysis.

Table 1. Summary of the recent studies on alkali/alkaline-earth metal intercalated CN.

| Samples               | Reaction                  | Activity                                      | Ref.  |
|-----------------------|---------------------------|-----------------------------------------------|-------|
| K-intercalated CN     | NO removal                | 36.80% (degradation rate)                     | [27]  |
| K-intercalated CN     | NO removal                | 36.80% (degradation rate)                     |       |
| Rb-intercalated CN    | NO removal                | 48.23% (degradation rate)                     | [48]  |
| Cs-intercalated CN    | NO removal                | 43.27% (degradation rate)                     |       |
| Sr-intercalated CN    | NO removal                | 53.10% (degradation rate)                     |       |
| Ca-intercalated CN    | NO removal                | 54.78% (degradation rate)                     |       |
| Ca-intercalated CN    | Degradation of RhB dye    | ~75% (degradation rate)                       |       |
| Sr multi-site doped CN| NO removal                | 55.00% (degradation rate)                     |       |
| Li-intercalated CN    | Degradation of RhB dye    | 0.028 min$^{-1}$ (photocatalytic efficiency)  | [53]  |
| Li-intercalated CN    | Degradation of RhB dye    | 0.007 min$^{-1}$ (photocatalytic efficiency)  |       |
| K-intercalated CN     | Hydrogen production       | 919.5 mol h$^{-1}$ g$^{-1}$ (13.1 times higher than CN) | [54]  |
| Li/Na/K-intercalated CN| Hydrogen production      | Vacuum condition: AQY = 37%, air condition: AQY = 4.9% | [55]  |
| Ba-intercalated CN    | Tetracycline elimination  | 91.94% (degradation efficiency)               | [56]  |
| K-intercalated CN     | Degradation of RhB dye    | 0.03698 min$^{-1}$ (photocatalytic rate constant, 8.3 times higher than CN) | [57]  |

reactants, the separation of charge carriers, and even the optimization of reaction pathways for the enhancement of photocatalysis.

2.1. Accelerated separation efficiency of photogenerated carriers

During a photocatalytic reaction, the successful migration of charge carriers to the reactant molecules determines the subsequent processes. Once spatial separation is realized, the ignited charge carriers are migrated to the surface of the photocatalyst for initiating the reduction and oxidation processes, aiming to the photocatalytic conversion of reactants. However, it is noteworthy that the photocatalyst is chemically active only when the photogenerated electron–hole pair is consumed simultaneously before the recombination occurs in a fraction of nanoseconds.

Limited by the intrinsic character, random charge transfer in the planes of CN and the inert stack of layers gives rise to a high recombination rate of charge carriers. The intercalation of heteroatom could be an efficient way to induce the charge redistribution in CN and also strengthen the vdW force between adjoining layers for the spatial separation of charge carriers and thus the improvement of photocatalysis. Xiong et al developed CN doped with Na and K atoms, and demonstrated that the photocatalytic performance of K-doped CN (CN–K) was superior to Na-doped CN (CN–Na) [27]. According to the DFT calculation, there
was a static coulomb interaction between Na/K and N nearest to them after the introduction of heteroatoms. K atoms tended to intercalate into the CN interlayer and the charge of upper layer N (C) atoms and lower layer C (N) atoms close to the intercalated K atoms increased, forming a funnel-like three-dimensional structure (figure 2(a)). K atoms could chemically bond with atoms at the adjacent layers to form charge delivery channels and bridge the layers, which induced the charge redistribution and extended the π conjugated system to accelerate the charge carrier transfer between neighbouring layers and thus enhance the photocatalytic performance. However, Na atoms existing in the caves of the CN plane resulted in the increase of in-planar electron density (figure 2(b)), which led to a high recombination rate of the charge carrier and thus a decrease of performance. The quenched PL intensity (figure 2(e)), increased photocurrent response (figure 2(f)), and prolonged lifetime of charge carriers (figure 2(g)) also demonstrated that intercalated K atoms promoted the charge transfer and separation. Thus, the introduction of heteroatoms between adjacent layers of CN steers the random carriers and then induces the interlayer delivery of carriers to promote the separation efficiency.

Besides, Zhou et al modified CN using multi-site Sr-doping with simultaneous N atom replacement (CNSr0.05), cavity padding, and intercalation, and further demonstrated that intercalation was the best doping site to improve the separation efficiency of electron and hole pairs [52]. The PL intensity of CNSr0.05 was obviously lower than that of CN (figure 3(a)), the circular arc radius on the EIS Nyquist plot of CNSr0.05 was significantly smaller than that of pure CN (figure 3(b)), and the intensity of the photocurrent was enhanced (figure 3(c)), suggesting that the introduction of Sr atoms could improve the separation efficiency of electron and hole pairs. Further, the promotion mechanism was confirmed by theoretical simulation. According to the electron density distribution of CN, it could be found that the replacement of N atoms and cavity padding had no effect on the electron transfer (figures 3(e)–(g)), however, the intercalation of Sr could form an interlayer electron channel (figure 3(h)). The intercalary Sr atom induced channel links two adjacent layers of CN and then facilitated the migration of carriers from one layer to another layer, which was beneficial to the separation of photogenerated carriers for the optimization of performance [52].

Several similar research results that intercalated alkali/alkaline-earth metal induced charge redistribution in CN and then accelerated the separation efficiency of photogenerated carriers have also been reflected [53, 55, 57]. Liu et al indicated that the separation efficiency of charge carriers was improved by the
introduction of K, which was attributed to the static electricity deriving from intercalated K atoms controlling the directional flow of charge carriers [57]. Zeng et al developed alkali-metal-atoms intercalated CN (K, Na, Li co-intercalated CN) for efficient overall water splitting and verified that intercalated alkali-metal-atoms bridged the adjacent layers of CN, which boosted the interlayer transportation of charge and then accelerated the separation of the charge carrier [55]. Even though alkali/alkaline-earth metal intercalated CN induced the charge redistribution and promoted the separation efficiency of charge carriers to optimize the photocatalytic performance, the difference of congenerelementshas been neglected and the promotion mechanism of photocatalytic efficiency should be further revealed to conduct the effective design and fabrication of 2D photocatalysts.

Li et al found that Rb intercalated CN (CN–Rb) improved the photocatalytic efficiency of CN, significantly exceeding that of bare and the other alkali K/Cs-intercalated CNs (CN–K/CN–Cs). The transfer direction of electrons was firstly confirmed and also the difference of congeneralkalineelementswas further clarified, which advanced the explanation of the promotion mechanism. As shown in figure 4(a), the electrostatic potential of the second layer (L2) was significantly increased after the introduction of alkalis.
Figure 4. Analysis of electron delivery. (a) Electrostatic potential; (b) electronic location function; and (c) charge difference distribution between metal atoms and CN layers (charge accumulation is in blue and depletion is in yellow, the isosurfaces are set to 0.005 eV Å\(^{-3}\), brown, blue, purple, red and green spheres depict C, N, K, Rb and Cs atoms, respectively). Reproduced from [48] with permission of The Royal Society of Chemistry.

(K, Rb, Cs), and a further increase of potential in L1 was acquired in CN–Rb and CN–Cs. Compared with CN–K, the electron migration in the direction of L1 → L2 → L3 by the one-way transmission manner after the intercalation of Rb and Cs. The unspecific electrostatic potential difference between L1 and L2 of CN–K resulted in a random interlayer electron delivery, thus increasing the potential possibility of charge carrier recombination. Besides, stronger covalent interactions between Rb/Cs and adjacent N atoms were confirmed by the electronic location function and the charge difference distribution (figures 4(b) and (c)), which indicated that the covalence mainly exists between the alkali and L2 and thus provided a more solid interlayer channel for directional electron transfer in CN–Rb and CN–Cs than in CN–K. The directional electron delivery via a one-way transmission manner could further boost charge separation, thus contributing to much higher photocatalytic performance of CN–Rb/CN–Cs than CN–K [48].

The intercalary heteroatoms steer the random intralayer carriers and also strengthen the vdW force between adjoining layers, thus realizing the directional electron delivery via a vertical channel between CN layers. Therefore, the intercalation of alkali/alkaline-earth metal is an effective way to facilitate the migration of carriers from one layer to another layer, which is beneficial to the separation of photogenerated electrons and holes. Nevertheless, the ignited charge carriers initiate subsequent reduction and oxidation processes and need to be further explored for the sake of revealing the promotion mechanism, which could conduct the fabrication of highly efficient 2D photocatalysts.

2.2. Optimized reactant activation and reaction pathway

The heterogeneous photocatalysis involves successive procedures of reactant adsorption, photoactivated reaction, and product desorption occurring at the catalyst surface [58–60]. Thus, the adsorption and activation of reactants is the prerequisite condition for subsequent photogenerated carrier-initiated reactions and then the separation efficiency of electron and hole pairs has a great effect on the formation of radicals participating in redox reaction. Generally, the introduction of heteroatoms could induce the charge redistribution, contributing to the transform of electrons from a delocalized state to a localized state for the formation of localized excess electrons (e\(^{-}\)\(_{ex}\)). The generation of e\(^{-}\)\(_{ex}\) is beneficial to accelerate the adsorption and activation of reactants and facilitate subsequent chemical reactions, thus elevating the photocatalytic performance.

Dong et al developed Sr-intercalated CN (CN–5Sr) to realize the electron localization, which promoted the activation of reactants and intermediates, as well as the charge separation and transfer for the optimization of photocatalytic activity and selectivity in oxidizing NO into target products (NO\(_2\)\(^{-}\) and NO\(_3\)\(^{-}\)) [49]. According to the charge difference distribution between Sr atoms and CN layers, randomly distributed electrons on the surface layer were localized to Sr atom and formed a local region with high electron density, and then e\(^{-}\)\(_{ex}\) could directionally transfer to the sublayer via the Sr-mediated electronic channel (figures 5(a) and (b)). The localized electrons provided more possibility for the adsorption and activation of reactants and intermediates. Besides, prolonged lifetime of charge carriers in CN–5Sr verified that the formation of electron localization and the interlayered electrons transfer channel effectively inhibited the recombination of carriers (figure 5(e)). Therefore, the facilitated activation of reactants and the accelerated separation of charge carriers jointly promoted the formation of reactive oxygen species (ROS) participating in photocatalytic pollutant removal, which was well reflected by the enlarged O–O bond length, increased adsorption energy, and stronger signals of light-induced DMPO–O\(_2\)\(^{–}\) on CN–5Sr (figures 5(f) and (g)).

Also, Li et al constructed an interlayer channel between CN layers by the intercalation of Ca to induce the formation of e\(^{-}\)\(_{ex}\) and besides, further demonstrated the function of e\(^{-}\)\(_{ex}\) [50]. The e\(^{-}\)\(_{ex}\) prefer to be captured by
Figure 5. (a), (b) Charge difference distribution between Sr atoms and CN layers; charge accumulation is in blue and depletion in yellow; carried electrons for (c) pristine CN and (d) CN–Sr; (e) ns-level time-resolved fluorescence spectra surveyed at room temperature; (f) DMPO ESR spectra in dark and under visible-light (λ ≥ 420 nm) for 15 min in methanol dispersion, respectively for (g) ·O₂⁻; ((g), up) charge difference distribution of optimized O₂ adsorption between O₂ and CN layers (charge accumulation is in blue and depletion in yellow with the isosurfaces set to 0.005 eV Å⁻³); ((g), down) electronic location function of optimized O₂ adsorption; (h) design diagram for localized excess electrons that decrease the reaction activation energies and increase the photocatalysis efficiency. Reprinted from [49, 50], Copyright (2018), with permission from Elsevier.

Figure 6. Calculated results for ROS generation and reaction pathways: charge difference density distribution of (a) O₂@CN, (b) 4O₂@CN, (c) O₂@CN–Ca, and (d) 4O₂@CN–Ca; calculated CI–NEB reaction pathways for NO photo-oxidation by (e) ·O₂⁻ and (f) ·OH. Charge accumulation and depletion are in blue and yellow, respectively; the isosurfaces are all set to 0.005 eV Å⁻³; blue, green, red, and gold spheres represent N, C, Ca, and O atoms respectively; negative values for $E_{ads}$ indicate heat release. Reprinted from [50], Copyright (2018), with permission from Elsevier.

reactants [61, 62], which dominantly contributes to reinforced reactant activation and ROS generation [63]. Then it directly initiates the photocatalytic reaction, which reduces the reaction activation energies and increases the reaction rates of elementary reactions, hence overcoming the rate-determining step for more efficient pollutant conversion and target product generation [5, 64]. According to the calculation of adsorption and activation of one O₂ molecule and multiple O₂ molecules (figures 6(a)–(d)), more intense charge transfer was observed between O₂ (one O₂ molecule and multiple O₂ molecules) and CN–Ca than between O₂ (one O₂ molecule and multiple O₂ molecules) and CN [50]. Besides, O₂ molecules on CN–Ca were more easily activated to form ROS–H (ROS with high oxidative capability, ROS–L: ROS with low activity), which could directly participate in the photooxidation reaction and overcome the rate-determining step of elementary reactions for the improvement of photocatalysis (figure 5(h)). The calculation of ROS-driven reaction pathways show that activation Energy ($\Delta E_a$) and reaction energies ($\Delta E_r$) of CN–Ca were much lower than that of pristine CN (figures 6(e) and (f)), which indicated that promoted activation of reactants could reduce the energy barrier for a chemical reaction.
Similarly, adsorbed intermediates and products and corresponding adsorption energies have been monitored and calculated by combined in situ DRIFTS and DFT simulation, revealing the function on the intercalation of Sr in CN layers [49]. As shown in the tendency of species evolution (figure 7(a)), the adsorption and transformation of NO, intermediates cis-N$_2$O$_2$ and trans-N$_2$O$_2$ were all greatly boosted on CN–5Sr in the NO adsorption process, indicating that doped Sr promoted the adsorption and activation of NO. During the irradiation process (figure 7(b)), two target products NO$_2^-$ and NO$_3^-$ were greatly increased as well, which implied that the promoted activation of reactants significantly improved the selectivity during photocatalytic oxidation of NO into target products. According to DFT calculations (figure 7(c)), the energy profile clearly demonstrated that the whole NO→cis-N$_2$O$_2^-$→trans-N$_2$O$_2^-$→NO$_2^-$→NO$_3^-$ processes were exothermic reactions and all energy were favourable in comparison with pristine CN, indicating that the intermediates could be transformed into the target products more smoothly.

The intercalation of alkalis induces the charge redistribution and fabricates a vertical channel between adjacent layers for directional electron delivery, contributing to promote the formation of e$^-$ex and suppress the random transfer of charge carriers. Correspondingly, the accelerated activation of reactants and the facilitated separation efficiency of photogenerated carriers has been realized to promote the generation of ROS, which could optimize the reaction pathway to elevate the photocatalytic performance. Meanwhile, considering the remarkable effects on the activation of reactants and the separation of carriers after the introduction of alkali/alkaline-earth metal, the controllable doping content and co-intercalation should be taken into account to further enhance the overall photocatalysis efficiency.

3. Enhanced photocatalysis on alkali/alkaline-earth metal and non-metallic species co-intercalated g-C$_3$N$_4$

Even though the fabrication of the directional electron delivery channel by intercalating alkali/alkaline-earth metal in CN promotes the photocatalytic performance, the accelerated accumulation of charge carriers in one layer would inevitably lead to the recombination of carriers. Alkali/alkaline-earth metal and non-metallic species co-intercalated CN have been proposed to address this challenge and further improve the photocatalytic performance. It is found that co-doped alkali/alkaline-earth metal and non-metallic species could function as interlayer dual channels to relieve the accumulation of carriers in one layer, and thus inhibit the recombination of carriers.

Correctly, the intercalated alkali/alkaline-earth metal and non-metallic species can not only bridge the adjacent layers but also be served as the cations and anions to regulate the separate transfer of electrons and holes. Xiong et al used KCl as the doping precursor to introduce K and Cl ions into the interlayer of CN (CN–KCl) [65]. As shown in the charge redistribution of CN (figure 8(b)), K atoms donated electrons to the
Figure 8. Charge difference distribution of (a) CN–K and (b) CN–KCl (the isosurface is 0.01 e Å$^{-3}$); (c) the electrostatic potential of CN, CN–K and CN–KCl; (d) photocurrent responses, (e) EIS spectra, (f) the ns-level time-resolved fluorescence spectra and (g) the photoluminescence spectra of the as-obtained samples. Reproduced from [65] with permission of The Royal Society of Chemistry.
upper N atoms and were then ionically bonded with them, and in contrast the upper and lower atoms donated electrons to the Cl atoms and were chemically bonded to the Cl atoms. The K atoms were accommodated as cations, while the Cl atoms served as anions, indicating that K and Cl ions could separately behave as transport paths for electrons and holes. Therefore, K and Cl ions coexisting in the interlayer of CN might function as a dual channel for electrons and holes transfer respectively, which induced the charge redistribution and simultaneously inhibited the inevitable recombination of carriers in single-channel transportation. Also, the average electrostatic potential of the CN layers from L3 to L1 showed a stepwise increase by the co-doping of K and Cl (figure 8(c)). The interlayer electrical field drove excited electrons to transfer from L1 to L2, then to L3, and inversely, holes transferred in the opposite direction, from L3 to L2, and then to L1. The introduction of KCl lowered the barrier of charge transfer between the adjacent layers, and thus contributed to the highly efficient separation of charge carriers. As shown in the experimental characterization, increased photocurrent density (figure 8(d)), smaller arc radius in the electrochemical impedance spectrum (figure 8(e)), prolonged lifetime (figure 8(f)) and lower PL intensities (figure 8(g)) also reflected the enhanced separation efficiency of photogenerated electrons and holes.

Furthermore, apart from the construction of interlayer dual channels for the separate transfer of electron and hole, interlayer circuit by co-doping alkali/alkaline-earth metal and non-metallic species also could be an efficient way to inhibit the recombination of carriers in single-channel transportation. As reported by Cui et al, an interlayer bioriented electron transportation channel in CN by co-doping K and NO$_3^-$ species (CN–KN) between neighbouring layers was crafted to balance the charge distribution, which significantly decreased the recombination of charge carrier [66]. As shown in charge difference distribution (figure 9(b)), K atoms could chemically bond with N (C) atoms to bridge the neighbouring layers and form interlayer electron delivery channels (the electron delivery direction was from L1 to L2), also, N (C) atoms (in L2) close to the interbedded NO$_3^-$ could donate electrons to NO$_3^-$, resulting in the formation of another vertical electron transportation channel via NO$_3^-$ species (the electron delivery direction was from L2 to L1). The
interlayer bioriented electron transportation channels significantly reduced the energy barriers for electron transfer between adjacent layers. Thus, the inevitable recombination of carriers caused by the accumulation of electrons in one layer through single-channel transportation was precluded, and thus the separation and transportation efficiency of carriers was boosted, as evidenced by the prolongation of radiative lifetime and the quenching of PL peaks.

Therefore, the intercalated alkali/alkaline-earth metal and non-metallic species as interlayer dual channels could effectively relieve the accumulation of carriers in one layer. Further, Zhang et al constructed a modified CN (K and Cl co-interlayered and OH group decorated CN, AKCN), and demonstrated that the charge balance can be reached in co-intercalated CN by calculating the absolute value about the difference of electron distribution [67]. The presence of doped K atoms induced the anisotropic electron density redistribution, and a relatively large number of electrons were accumulated on the first layer ($-2.34$ e of layer charge) than on the second one ($-0.99$ e of layer charge) (figure 10(a)). Further, the additional doping of Cl atoms made the electron distribution more balanced between the layers (figure 10(b)). Therefore, the K-induced electron density polarization could be counterbalanced by Cl and thus the $|\Delta q|$ ($|\Delta q|$ represents the absolute value of the difference of the electron distribution between the first and second layer) were decreased from 1.35 e of K-doped CN to 0.16 e of KCl-doped CN. When the hydroxyl (OH) group was additionally introduced in AKCN, the OH group was preferably bonded to the surface carbon, inducing an outstanding electron depletion region around the OH group on the first layer (figure 10(c)). The introduction of OH groups further decreased the $|\Delta q|$ from 0.16 e to 0.06 e, contributing to the charge transfer between adjacent layers, simultaneously addressing the accumulation of charge in one layer and alleviating the recombination of carriers.

Correspondingly, the ideal efficiency (about 100% quantum efficiency of $\text{H}_2\text{O}_2$ generation) of AKCN implied that the photogenerated charge carriers in AKCN were efficiently separated to realize the selective reduction of $\text{O}_2$ to $\text{H}_2\text{O}_2$, as evidenced by the highest photocurrent, smallest arc radius in Nyquist plot analysis, the highly enhanced interfacial charge transfer on AKCN by measuring the $\text{Fe}^{3+/2+}$ shuttle-mediated photocurrent, higher open-circuit voltage and slower photovoltage decay. Meanwhile, the presence of the OH group induced the charge distribution over different atoms and thus achieved the local polarization (figures 10(d) and (e)), which accelerated the adsorption and activation of reactants. The synergistic improvement of spatial charge separation and local polarization between the interlayers and in-plane was critical for the ideal efficiency of AKCN. Therefore, the improvement strategies of photocatalysis are to optimize the charge distribution for accelerated reactant activation and the spatial charge separation for the inhibition of excessive accumulation of charge carriers in one layer.
Table 2. Summary of the recent studies on alkali/alkaline-earth metal intercalated and surface modification co-functionalized CN.

| Samples                              | Intralayer                      | Interlayer | Reaction       | Activity                  | Ref.   |
|--------------------------------------|---------------------------------|------------|----------------|---------------------------|--------|
| K-incorporated amino-rich carbon      | Amino group/ carbon defects      | K intercalation | CO$_2$ conversion | Five-fold enhancement    | [69]   |
| nitride                              |                                 |            |                |                           |        |
| O/Ba co-functionalized amorphous      | O surface decoration             | Ba         | NO removal     | 55.77%                    | [68]   |
| carbon nitride                       |                                 | intercalation |                |                           |        |
| O, K-functionalized CN                | O surface decoration             | K         | NO removal     | 45.00%                    | [70]   |
| PO$_4$/K co-functionalized carbon     | Phosphate groups surface        | K         | NO removal     | 35.20%                    | [71]   |
| nitride                              | decoration                      | intercalation |                |                           |        |
| B/K co-doping carbon nitride with     | B doping/Nitrogen vacancies      | K         | CO$_2$ conversion | 5.93 μmol g$^{-1}$ CH$_4$; | [72]   |
| nitrogen vacancies                    |                                 |            |                | 3.16 μmol g$^{-1}$ CO    |        |
| (after 5 h)                          |                                 |            |                |                           |        |
| Sulphur/potassium co-doped graphitic  | S doping                        | K         | H$_2$ evolution | 1962.10 μmol g$^{-1}$ h$^{-1}$ | [73]   |
| carbon nitride                       |                                 |            |                |                           |        |
| K/halogen binary-doped graphitic      | F doping                        | K         | H$_2$ evolution | 1039 μmol g$^{-1}$ h$^{-1}$ | [74]   |
| carbon nitride                       |                                 |            |                |                           |        |
| KOH/KCl modified GCN                 | OH group                        | K/Cl intercalation | Glucose oxidation and diox | Near 100% apparent | [67]   |
|                                     |                                 |            | oxygen reduction | quantum efficiency | (2019) |        |
| g-C$_3$N$_4$ with alkali Zn$^{2+}$    | Zn doping                       | K         | Photodynamic therapy (PDT) | 45.16% (release rate of ROS) | [75]   |
| and K$^+$ modification               |                                 |            |                |                           |        |

4. Enhanced photocatalysis on alkali/alkaline-earth metal intercalated and surface modification co-functionalized g-C$_3$N$_4$

Recently, surface modification and alkali/alkaline-earth metal intercalated co-functionalized g-C$_3$N$_4$ have been developed to further facilitate the charge redistribution and alleviate the inevitable recombination of carriers in one layer (table 2). The introduction of hetero atoms/species or vacancies in plane and the intercalation of alkali/alkaline-earth metal between adjacent layers induce the intralayer charge localization and bridge the adjacent layers, respectively, which suppresses random migration of electrons in plane and strengthens the Coulomb interactions between layers. Therefore, the co-functionalized strategy could realize the charge redistribution, spatial charge separation and most importantly make the electron distribution more balanced in CN, thus improving the activation of reactants and the separation efficiency of charge carriers for the optimization of photocatalytic performance.

4.1. Alkali/alkaline-earth metal intercalated and surface decoration co-functionalized g-C$_3$N$_4$

As shown in figure 10, the presence of OH group in-plane induced the charge redistribution over different atoms, which further balanced the distribution of electron in CN and thus alleviated the excessive accumulation of charge carriers in one layer. Also, the decoration of OH group induced the localization of charge to facilitate the adsorption and activation of reactants. Therefore, the intercalation of alkali/alkaline-earth metal and simultaneously the intralayer decoration of hetero atoms/species is an efficient way to balance the charge distribution, accelerating the spatial charge separation and optimizing the photocatalytic reaction. Similarly, Ran et al synthesized the phosphate/potassium co-functionalized carbon nitride via a one-step in situ co-pyrolysis of thiourea and potassium phosphate [71]. The surface modification with phosphate groups and the interlayer incorporation with potassium significantly promoted the activation of O$_2$, NO and H$_2$O on the catalyst surface and facilitated the separation of carriers, contributing to the enhancement of photocatalytic performance.

Apart from the decoration of functional groups, the surface modification by heteroatoms-doped is another conventional approach. Considering the limitation of intrinsic graphitic sp$^2$-hybridized array of tri-s-triazine repeating units and the inert stack of layers in CN, the construction of intralayer electronic trapping/converging districts and interlayer electronic mediators was proposed by Cui et al [68]. An O/Ba co-functionalized amorphous carbon nitride (O–ACN–Ba) was designed and synthesized. The intralayer
electronic trapping districts inducing by O species promoted the convergence of delocalized intralayer electrons and the interlayer electronic trapping mediators (intercalated Ba atoms) bridged adjacent CN layers to direct the transfer of photogenerated electron (figures 11(a)–(c)). The modification of CN modulated the random migration of electrons in planes and weak Coulomb interactions between layers and then induced the charge redistribution, promoting the adsorption and activation of reactants, achieving elongated lifetime of photogenerated carriers, and thus accelerating the generation of abundant ROS to participate in photocatalytic reaction (figures 11(d) and (e)). The unique electronic structure of O–ACN–Ba enabled highly enhanced photocatalytic NO removal efficiency and suppressed the generation of toxic intermediate (figure 11(f)).

Generally, the introduction of heteroatoms has an effect on the electronic structure and energy band configuration of photocatalyst, which influences the subsequent photocatalytic reaction. Thus, it is important to further explore the function of inner structure optimization and explain the promotion mechanism. Li et al further found that once O ‘adjuster’ atoms were introduced into a layer of CN, a van der Waals heterostructure was established between the O-modified CN layer (OCN) and adjacent CN sublayer, and meanwhile, interlayer charge flow could be expedited via intercalated elemental K, which served as a ‘mediator’ to strengthen the interlayer vdW interaction (scheme 1(a)) [70]. According to the calculated total density of states of CN and OCN layers, OCN band structure was adjusted by the O adjustor atoms, leading to a band-offset between the OCN layer and the CN sublayer and thus indicating the formation of internal van der Waals heterostructures (IVDWHs). Furthermore, the band-offset between CN and OCN layers allowed light-generated hole migration to OCN layer and electron transfer to CN sublayer to achieve a spatial charge carrier separation, which suppressed the accumulation of carriers in one layer and addressed the inevitable recombination (scheme 1(c)).

By comparing the electronic structures of pristine CN and OCN–K–CN, the potential energies of the OCN layer and CN sublayer in OCN–K–CN were significantly increased after the incorporation of O and K, which provided the driving force for electron transfer from the OCN layer to the CN sublayer through the interlayer K channel (figures 12(a) and (b)). Correspondingly, the local charge distribution in the OCN layer
was altered and thus induced the accumulation of electrons around the O adjuster atoms, and the interlayer electron transfer was strengthened with the introduction of O adjuster atoms, which reinforced the internal vDW force to effectively facilitate the interlayer charge flow and accelerate the separation of electron–hole pairs (figures 12(c)–(f)). The expedited spatial charges separation thus promoted the generation of abundant ROS for the highly efficient photocatalytic performance.

The surface decoration in layered materials not only induces the charge redistribution to facilitate the activation of reactants, but also makes a difference between surface layer and sublayer to establish an inner heterostructure for the directional charge transfer. Meanwhile, the intercalation of alkali/alkaline-earth metal served as a ‘mediator’ to strengthen the interlayer interaction and realize the spatial charge carrier separation, which greatly suppressed the accumulation of charge carriers in one layer and thus addressed the inevitable recombination. The intrinsic defect of CN could be well remedied by the co-functionalization of alkali/alkaline-earth metal intercalated and surface decoration.

4.2. Alkali/alkaline-earth metal intercalated and intralayer modification co-functionalized g-C₃N₄

Considering the intrinsic graphitic sp²-hybridized array of tri-s-triazine repeating units and the inert stack of layers, multiple dopants (intralayer and interlayer co-doping) provides an approach to overcome the intrinsic shortcomings of CN. The intralayer and interlayer co-doping could realize the comprehensive modification of the electronic structure and thus make the charge distribution more balanced, achieving the spatial separation of carriers to optimize photocatalysis. Bi et al fabricated S/K co-doped CN photocatalysts for hydrogen evolution [73]. The binary-doped S and K atoms offered more electrons to the band gap in comparison with pure CN, and simultaneously the intercalation of the K atom bridged the adjacent layers for interlayer charge transfer, contributing to the separation and transport of photogenerated carriers for the efficient photocatalytic hydrogen evolution. Also, halogen and potassium binary-doped graphitic carbon nitride (named as X–K–C₃N₄, X=F, Cl, Br, I) photocatalysts were synthetized via simply one pot thermal polymerization method [74]. F–K–C₃N₄ showed the highest H₂ evolution rate and stability, which was attributed to the synergistic effect of the intralayer C–F bond, the C≡N triple bond and the interlayer K junction promoting the separation and transfer of carriers.

 Elemental doping is one of the appealing strategies to modulate the physicochemical properties, but the fact that introduced heteroatoms would lead to the distortion of crystal lattice cannot be ignored. Wu et al developed a Zn and K co-doped water-soluble carbon nitride (MCN) as a PDT photosensitizer for cancer therapy and confirmed that the introduction of Zn and K atoms caused the distortion of CN layers and thus the lattices were tilted to a certain extent to balance the distortion, which enhanced the coupling in layer-to-layer and therefore regulated the electronic structure of CN [75]. Based on the DFT calculation, Zn atoms tended to occupy the vacancy of π−π conjugate planes while K atoms occupied the spaces between
adjacent CN layers (figure 14(b)). The sp² orbitals were partially opened due to the broken symmetry when Zn and K atoms were introduced, as shown in differential charge density distribution (figure 13(c)). Therefore, the electrons of the sp² orbital would transfer to the p orbital for the expansion of π conjugate electron system, and also bond with the outer electrons of doped metal atoms to enhance the stability of metal atoms in the system. Besides, a stronger ionic bond between Zn atoms and CN atoms at the edge of holes and the covalent bond between K atoms and the adjacent layers were reflected by the electron localization function (figures 13(e) and (f)). The π–π conjugate electron system was immensely extended, and the electrons were rapidly shifted through the bridge of K atoms, which was beneficial to the transmission of the photogenerated carriers in different MCN layers. Correspondingly, the dramatically decreased PL peak intensity and the longer lifetime of charge carriers of MCN well demonstrated that the co-doping of Zn or K atoms could hinder the annihilation of carriers (figures 14(g) and (h)). Also, the distinctly smaller semicircle radius of impedance and $R_\text{ct}$ reflected a remarkable promotion on interfacial transfer efficiency of carriers, which thus boosted the generation of ROS and enhanced the therapeutic effect of PDT (figures 14(i)–(l)).

Besides, aiming to modify the electronic structure, vacancy-engineering is proven to be a promising approach and shows high efficiency in forming active sites, which is beneficial to balance the charge distribution and thus facilitate the separation of the charge carriers for the improvement of photocatalytic performance. Sun et al synthesized an amino-rich carbon nitride photocatalyst with incorporated K and carbon defects (K–AUCN) for photocatalytic CO$_2$ conversion [69]. The enriched basic amino groups contributed to improved CO$_2$ fixation and activation, and importantly the incorporated potassium (K$^+$) among the disordered layers and the accompanied carbon defects as electron promoters facilitated the separation and transfer of photogenerated carriers. The optimized sample exhibited a more-than-five-fold enhancement in CO$_2$ photocatalytic conversion under simulated sunlight compared to pristine CN.
It is worth noting that the synergetic effect of multiple modification greatly improves the performance but the respective roles also need to be further confirmed, which could direct the rational design of the inner structure for the targeted optimization. Wang et al proposed a new synthesis strategy of rational co-doping of B, K elements in line with the controllable introduction of N vacancies (N_v) into CN (KBH–C_3N_4), aiming to compensate the drawback of single element doping [72]. The modified KBH–C_3N_4 achieved 161% and 527% increases for the production of CH_4 and CO respectively, compared with pristine CN during photocatalytic CO_2 reduction. The enhancement of performance was attributed to the synergetic effects that the multiple modifications constructed the electron-rich surface and tailored the electronic structure to significantly facilitate the adsorption and activation of CO_2 and accelerate the separation charge carriers.

Experimental and theoretical characterization has been employed to demonstrate that co-doping of B, K elements in line with controllable introduction of N_v play their primary role to elevate the performance. According to the CO_2-TPD profiles (figure 14(a)), CO_2 uptake ability increased with the introduction of B, K dopant and N_v, and the promoting effects were in the order of N_v > B > K. Also, as shown in the theoretical
simulation of CDD, both Nv and B induced charge redistribution (electron-rich environment) at their adjacent atoms and it was worth noting that the electron accumulation caused by Nv was stronger than B doping (figures 14(b)–(d)), which explained the facts that Nv exhibited superior enhancement on CO2 uptake than B doping. After the calculation of CO2 adsorption on the optimal site of KBH–C3N4, it reflected a spontaneous process with the adsorption energy of −0.361 eV, which was four times as much as the pristine one. Also, the total charge (Δq) further demonstrated that there were more electrons (0.23 e−) transferred from KBH–C3N4 to CO2 than pristine CN (0.02 e−). Therefore, the introduction of Nv greatly induced the charge redistribution and promoted the accumulation of electrons to accelerate the activation of CO2 to participate in following conversion reactions. Besides, the CDD plots of KBH–C3N4 illustrated the existence of K and significantly accelerated the spatial electron distribution, especially for the adjacent layers, and the Δq of intercalated K atom was −1.55. The charge analyses also illustrated that B dopant with a Δq (electron transfer) of −2.10 which donated ~0.8 more electron than the C atom in the pristine CN, and N atoms as the Lewis basic sites showing Δq of 1.37 gained ~0.3 more electron than the N at the same site in pristine CN. According to the orbital plots (figure 14(g)), the HOMO and LUMO in KBH–C3N4 were not adjacent but localized mainly at N and C atoms of different layers of CN, which was benefit to the electron/hole separation and ensured a relative long carrier lifetime. Therefore, intercalated K bridged the adjacent layers and facilitated the electron transfers between the layers; intralayer doped B and N, rearranged the electron and molecular orbitals spatial distributions, and correctly B helped to maintain a high reduction potential and compensated the drawbacks of the K, and also N, narrowed the bandgap and significantly enhanced the CO2 adsorption.
Figure 15. UV–vis spectra (a) and the estimated band gaps (b) of CN and the K-intercalated CN samples, VB XPS (c), and schematic illustration of the band gap structure of CN and CN–K5 (d); (e) UV–vis spectra, (f) estimated bandgaps, (g) calculated adsorption spectra, and (h) the density of states of CN, CN–K, CN–Rb and CN–Cs, with the Fermi level set to 0 eV. Reproduced from [48] with permission of The Royal Society of Chemistry; Reprinted with permission from [27]. Copyright (2016) American Chemical Society.

Therefore, the synergistic effect on the introduction of heteroatoms/species or vacancies in plane and the intercalation of alkali/alkaline-earth metal between adjacent layers could alleviate the intrinsic shortcomings of CN. Surface modification and alkali/alkaline-earth metal intercalated co-functionalized CN make the electron distribution more balanced in CN to realize the expedited spatial charge separation, which facilitates the adsorption and activation of reactants and improves the separation efficiency of charge carriers for the optimization of photocatalytic performance.

5. Optimization of light absorption and band structure of g-C_3N_4 via alkali/alkaline-earth metal intercalation

Photocatalysis is essentially dependent on the band structure and optical property of photocatalyst, which enables the electron excitation for subsequent photocatalytic redox reaction. The intercalated alkali/alkaline-earth metal atoms are bonded with the adjacent C or N atoms and thus lead to the expansion of the crystal lattice, correspondingly, the band gap and the band edge position would be influenced [27, 48, 49, 52, 53, 57].

As shown in figures 15(a) and (b), K-intercalated CN samples showed enhanced visible absorption and the absorption edges undergo red shifts, confirming that the bandgap could be narrowed by introducing K atoms into CN interlayers. Also, it is obvious that the valence band (VB) and conduction band (CB) position downshift over CN-K5, which indicated K-intercalated CN samples possess enhanced oxidation ability of VB holes relative to pristine CN. Li et al also revealed that K/Rb/Cs-intercalated CN exhibited red shifts both in UV–vis spectra and calculated adsorption spectra (figures 15(e)–(g)) [48], and as the total density of states suggested, alkali-doped CN displayed narrowed band gaps and the VB and CB edges of the alkali-doped CN downshifted in comparison with pristine CN (figure 15(h)). According to the experimental characterization and theoretical simulation [27, 48–50], alkali-doped CN displays narrowed band gaps and the VB and CB edges of the alkali-doped CN downshift in comparison with pristine CN. The introduction of alkali metal atoms regulates the light adsorption and make photocatalysts absorb more photons, which is easier to ignite the photocatalytic reaction. Also, the downshifted band structure endowed a stronger oxidation ability to the valence hole participating in the photocatalytic oxidation reaction.

The intercalation of atoms led to the distortion of the tri-s-triazine CN layers and the expansion of the interlayer distance, and inducing the charge distributions to be changed from the relative uniform state to the un-uniform state [31]. The charge separation was thus featured with the electrons confined in the intercalated region while the holes are in the far intercalated region. As reported by Wang et al, the HOMO and LUMO of CN were quite localized and in coplanar relation, which was responsible for the high recombination rate [72]. However, the HOMO and LUMO in KBH–C_3N_4 were not adjacent but localized mainly at N and C atoms of different layers of CN to realize the charge redistribution, contributing to the efficient separation of carriers. Also, the co-doping of K and Cl induced the charge redistribution and narrowed the bandgap [65]. According to the layer-projected density of states of KCl doped CN, the VBs of
Figure 16. (a) TDOS of CN, CN–K, Cl doped g-C₃N₄ (CN–Cl) and CN–KCl; (b) CN–KCl layer-projected DOS; (c) UV–vis spectra of prepared samples. Reproduced from [65] with permission of The Royal Society of Chemistry.

the first and second CN layers downshifted, and upshifted for the third CN layer (figure 16(b)). Notably, the bandgap of the second CN layer was narrower than that of the first CN layer, meaning that the second CN layer could be more easily excited by light to yield charge carriers and simultaneously the enlarged bandgap of first layer was beneficial for enhancing the lifetime of the charge carriers. Furthermore, the Cl 3p and K 3s mainly contributed to the top of VB and the bottom of CB between L1 and L2, respectively, which could act as a local hub for hole acceptors/donors and electron transfer. Therefore, the intercalated K and Cl ions broaden the visible light absorption and also might function as a dual channel for electrons and holes transfer, respectively, realizing the optimization of photocatalytic performance.

The intercalation of heteroatoms induces the expansion of the crystal lattice to influence the electronic structure and energy band configuration of CN, which subsequently could optimize the charge distribution to facilitate reactant activation and adjust the light absorption range and electron excitation to improve subsequent photocatalytic redox reaction. Therefore, it is an efficient way to engineer the intrinsic structure of CN-based and even two-dimensional photocatalysts for the enhancement of overall photocatalysis efficiency.

6. Conclusion and perspectives

This mini review summarizes the latest research efforts on the construction strategy of alkali/alkaline-earth metal intercalated CN and the core principles of photocatalytic enhancement. The introduction of heteroatoms induces the charge redistribution in CN, contributing to (a) the adsorption and activation of the reactant, (b) the spatial charge separation, and (c) the optimization of the reaction pathway, and therefore realizing the highly efficient photocatalytic performance. This review inspires new concepts and presents a good reference to engineer CN-based photocatalysts and even 2D materials for energy and environmental applications.

Despite the impressive advancement made in the past few years, there are still some challenges that face the development of alkali/alkaline-earth metal intercalated CN. In previous research, a first-principle calculation based on density functional theory has been employed to investigate the structural, electronic, and thermodynamic properties of reactants and photocatalysts at atomic or unit-cell levels, however, (a) experimental techniques still need to be utilised to intuitively reveal the position of introduced hetero species and the information of coordination environment; (b) in situ observations are also highly desirable to obtain a true picture of photocatalytic processes, including the charge redistribution, the adsorption and activation of reactants, and the transfer of charge carriers. (c) Additionally, the exact reaction mechanism still remains doubtful and unresolved to date, and thus the experimental investigation of reaction pathways is vital to elucidate the fundamental enhancements and further optimization of the photoactivity in the future. With that successful accomplishment in years to come, it is expected the breakthrough can take place in the near future.

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**References**

[1] Baxter J, Bian Z, Chen G, Danielson D, Dresselhaus M S, Fedorov A G, Fisher T S, Jones C W, Maginn E and Kortshagen U 2009 Nanoscale design to enable the revolution in renewable energy Energy Environ. Sci. 2 559–88

[2] Tong H, Ouyang S, Bi Y, Umezawa N, Oshikiri M and Ye J 2012 Nano-photocatalytic materials: possibilities and challenges Adv. Mater. 24 229

[3] Kondratenko E V, Mul G, Baltrusaitis J, Larrazabal G O and Pérez-Ramírez J 2013 Status and perspectives of CO2 conversion into fuels and chemicals by catalytic, photocatalytic and electrocatalytic processes Energy Environ. Sci. 6 3112–35

[4] Zhang X, Fevre M, Jones G O and Zou Z 2018 Catalysis as an enabling science for sustainable polymers Chem. Rev. 118 839–85

[5] Hoffmann M R, Martin S T, Choi W and Bahnemann D W 1995 Environmental applications of semiconductor photocatalysis Chem. Rev. 95 69–96

[6] Zou Z, Ye J, Sayama K and Arakawa H 2001 Direct splitting of water under visible light irradiation with an oxide semiconductor photocatalyst Nature 414 625

[7] Yoon T P, Ishay M A and Du J 2010 Visible light photocatalysis as a greener approach to photochemical synthesis Nat. Chem. 2 527

[8] Kubacka A, Fernández-García M and Colón G 2012 Advanced nanoarchitectures for solar photocatalytic applications Chem. Rev. 112 1555–614

[9] Lan Y, Liu Y and Ren Z 2013 Mini review on photocatalysis of titanium dioxide nanoparticles and their solar applications Nano Energy 2 1031–45

[10] Kim D, Sakimoto K K, Hong D and Yang P 2015 Artificial photosynthesis for sustainable fuel and chemical production Cheminform 46 3259

[11] Mamaghani A H, Haghighat F and Lee C-S 2017 Photocatalytic oxidation technology for indoor environment air purification: the state-of-the-art Appl. Catal. B 203 247–69

[12] Fujishima A and Honda K 1972 Electrochemical photolysis of water at a semiconductor electrode Nature 238 37–8

[13] Yan S, Luo W, Li Z and Zou Z 2010 Progress in research of novel photocatalytic materials Mater. China 1 003

[14] Lang X, Chen X and Zhao J 2013 Heterogeneous visible light photocatalysis for selective organic transformations Chem. Soc. Rev. 42 473–86

[15] Cheng C, Ma W and Zhao J 2010 Semiconductor-mediated photodegradation of pollutants under visible-light irradiation Chem. Soc. Rev. 39 4206–19

[16] Liu J, Liu Y, Liu N, Han Y, Zhang X, Huang H, Lifshitz Y, Lee S-T, Zhong J and Kang Z 2015 Metal-free efficient photocatalyst for stable visible water splitting via a two-electron pathway Science 347 970–4

[17] Marzo L, Pagire S K, Reiser O and König B 2018 Visible-light photocatalysis: does it make a difference in organic synthesis? Angew. Chem., Int. Ed. 57 10034–72

[18] Prithushmi M, Habibi-Yanghieh A and Rahim Pouran S 2018 Review on the criteria anticipated for the fabrication of highly efficient ZnO-based visible-light-driven photocatalysts J. Ind. Eng. Chem. 62 1–25

[19] Wang X, Mela K, Thomas A, Takanahe K, Xin G, Carlsson J M, Domen K and Antonietti M 2009 A metal-free polymeric photocatalyst for hydrogen production from water under visible light Nat. Mater. 8 76–80

[20] Wang X, Blechert S and Antonietti M 2012 Polymeric graphitic carbon nitride for heterogeneous photocatalysis ACS Catal. 2 1596–606

[21] Liang Q, Huang Z-H, Kang F and Yang Q-H 2015 Facile synthesis of crystalline polymeric carbon nitride with an enhanced photocatalytic performance under visible light ChemCatChem 7 2897–902

[22] Schwinghammer K, Tuffy B, Mesch M B, Wirthier E, Martineau C, Taulle F, Schnick W, Senker J andLotsch B V 2013 Triazine-based carbon nitrides for visible-light-driven hydrogen evolution Angew. Chem., Int. Ed. 52 2435–9

[23] Martin D J, Reardon P J, Monie S J A and Tang J 2014 Visible light-driven pure water splitting by a nature-inspired organic semiconductor-based system J. Am. Chem. Soc. 136 12568–71

[24] Ong W J, Tan L L, Ng Y H, Yong S T and Chai S P 2016 Graphitic carbon nitride (g-C3N4)-based photocatalysts for artificial photosynthesis and environmental remediation: are we a step closer to achieving sustainability? Chem. Rev. 116 7139

[25] Pannier S, Ganguly P, Nair B N, Peer A M and Warrier K G K 2017 CO2→C=N4 n-p nano-heterojunctions for the simultaneous degradation of a mixture of pollutants under solar irradiation Environ. Sci. Nano 4 212–21

[26] Kang Y, Yang Y, Yin L-C, Kang X, Wang L, Liu G and Cheng H M 2016 Selective breaking of hydrogen bonds of layered carbon nitride for visible light photocatalysis Adv. Mater. 28 6471–7

[27] Xiong T, Cen W, Zhang Y and Dong F 2016 Bridging the g-C3N4 interlayer for enhanced photocatalysis ACS Catal. 6 2462–72

[28] Ye C, Li J X, Li Z, Li X B, Fan X B, Zhang L P, Chen B, Ting C H and Wu L Z 2015 Enhanced driving force and charge separation efficiency of protonated g-C3N4 for photocatalytic O2 evolution ACS Catal. 5 6973–9

[29] Maeda K, Wang X, Nishihara Y, Lu D, Antonietti M and Domen K 2009 Photocatalytic activities of graphitic carbon nitride powder for water reduction and oxidation under visible light J. Phys. Chem. C 113 4940–7

[30] Dresselhaus M S and Dresselhaus G 2002 Intercalation compounds of graphite Adv. Phys. 51 1–186

[31] Gao H, Yan S, Wang J, Huang Y A, Wang P, Li Z and Zou Z 2013 Towards efficient solar hydrogen production by intercalated carbon photocatalyst Phys. Chem. Chem. Phys. 15 18077–84

[32] Zhang G, Zhang M, Ye X, Qin X, Lin S and Wang X 2014 iodine modified carbon nitride semiconductors as visible light photocatalysts for hydrogen evolution Adv. Mater. 26 803–9

[33] Wang Y, Li H, Yao J, Wang X and Antonietti M 2011 Synthesis of boron doped polymeric carbon nitride solids and their use as metal-free catalysts for aliphatic C–H bond oxidation Chem. Sci. 2 446–50
[34] Huang Z F, Song J, Pan L, Wang Z, Zhang X, Zou J J, Mi W, Zhang X and Wang J 2015 Carbon nitride with simultaneous porous network and O-doping for efficient solar-energy-driven hydrogen evolution Nano Energy 12 646–56
[35] Zha Y P, Ren T Z and Yuan Z Y 2015 Mesoporous phosphorus-doped g-C3N4 nanostuctures with superior photocatalytic hydrogen evolution performance ACS Appl. Mater. Interfaces 7 16850–6
[36] Hu S, Ma L, You J, Li F, Fan Z, Wang F, Liu D and Gui J 2014 A simple and efficient method to prepare a phosphorus modified g-C3N4 visible light photocatalyst RSC Adv. 4 21657–63
[37] Feng L J et al 2014 Nanoporous sulfur-doped graphitic carbon nitride microcolds: a durable catalyst for visible-light-driven H2 evolution Int. J. Hydrog. Energy 39 15373–9
[38] Hong J, Xia X, Wang Y and Xu R 2012 Mesoporous carbon nitride with in situ sulfur doping for enhanced photocatalytic hydrogen evolution from water under visible light J. Mater. Chem. 22 15006–12
[39] Wang Y, Di Y, Antonietti M, Li H, Chen X and Wang X 2010 Excellent visible-light photocatalysis of fluorinated polymeric carbon nitride solids Chem. Mater. 22 5119–21
[40] Pan H, Zhang Y W, Shenoy V B and Gao H 2011 Ab initio study on a novel photocatalyst: functionalized graphitic carbon nitride nanotube ACS Catal. 1 99–104
[41] Gao H, Yan S, Wang J and Zou Z 2014 Ion coordination significantly enhances the photocatalytic activity of graphitic-phase carbon nitride Dalton Trans. 43 8178–83
[42] Hu S, Ma L, You J, Li F, Fan Z, Lu G, Liu D and Gui J 2014 Enhanced visible light photocatalytic performance of g-C3N4 photocatalysts co-doped with iron and phosphorus Appl. Surf. Sci. 311 164–71
[43] Ding Z, Chen X, Antonietti M and Wang X 2011 Synthesis of transition metal-modified carbon nitride polymers for selective hydrocarbon oxidation ChemSusChem 4 274–81
[44] Zhang J, Hu S and Wang Y 2014 A convenient method to prepare a novel alkali metal doped carbon doped carbon nitride photocatalyst with a tunable band structure RSC Adv. 4 62912–9
[45] Hu S, Li F, Fan Z, Wang F, Zhao Y and Lv Z 2015 Band gap-tunable potassium doped graphitic carbon nitride with enhanced mineralization ability Dalton Trans. 44 1084–92
[46] Wu M, Yan J-M, Tang X N, Zhao M and Jiang Q 2014 Synthesis of potassium-modified graphitic carbon nitride with high photocatalytic activity for hydrogen evolution ChemSusChem 7 2655–68
[47] Zhang M, Bai X, Liu D, Wang J and Zhu Y 2015 Enhanced catalytic activity of potassium-doped graphitic carbon nitride induced by lower valence position Appl. Catal. B 164 77–81
[48] Li J, Cui W, Sun Y, Chu Y, Cen W and Dong F 2017 Directional electrons delivery via vertical channel between g-C3N4 layers promoting the photocatalysis efficiency J. Mater. Chem. A 5 9358–64
[49] Dong X A, Li J, Xing Q, Zhou Y, Huang H and Dong F 2018 The activation of reactants and intermediates promotes the selective photocatalytic NO conversion on electron-localized Sr-intercalated g-C3N4 Appl. Catal. B 232 69–76
[50] Li J, Dong X A, Sun Y, Gao J, Chu Y, Lee S C and Dong F 2018 Tailoring the rate-determining step in photocatalysis via localized excess electrons for efficient and green solar energy Appl. Catal. B 239 187–95
[51] Islam M M, Tentu R D, Ali M A and Basu S 2018 Enhanced visible-light-driven activity of sodium-, calcium- and aluminium-inserted g-C3N4 Chem. Select 3 11241–50
[52] Zhou M, Dong G, Yu F and Huang Y 2019 The deep oxidation of NO was realized by Sr multi-site doped g-C3N4 via photocatalytic method Appl. Catal. B 256 117825
[53] Zhang W, Zhang Z, Choi S H and Yang W 2019 Facile enhancement of photocatalytic efficiency of g-C3N4 by Li-intercalation Catal. Today 321 322 67–73
[54] Sun S, Li J, Cui J, Gou X, Yang Q, Jiang Y, Liang S and Yang Z 2019 Simultaneously engineering K-doping and exfoliation into graphitic carbon nitride (g-C3N4) for enhanced photocatalytic hydrogen production Int. J. Hydrog. Energy 44 778–87
[55] Zeng Z, Quan X, Yu H, Chen S, Choi W, Kim B and Zhang S 2019 Alkali-metal-oxides coated ultrasmall Pt sub-nanoparticles loading on intercalated carbon nitride: enhanced charge interlayer transportation and suppressed backwash reaction for overall water splitting J. Catal. 377 72–80
[56] Bui T S, Bansal P, Lee B K, Mahvelati-Shamsabadi T and Soltani T 2020 Facile fabrication of novel Ba-doped g-C3N4 photocatalyst with remarkably enhanced photocatalytic activity towards tetracycline elimination under visible-light irradiation Appl. Surf. Sci. 506 (NewYork:Wiley)
[57] Heitbaum M, Glorius F and Escher I 2010 Asymmetricheterogeneouscatalysis
[58] Tryba B, Toyoda M, Morawski A W, Nonaka R and Inagaki M 2007 PhotocatalyticactivityandOHradicalformationonTiO2Chem. Rev. 110 351–60
[59] Bui T S, Bansal P, Lee B-K, Mahvelati-Shamsabadi T and Soltani T 2020 Facile fabrication of novel Ba-doped g-C3N4 photocatalyst with remarkably enhanced photocatalytic activity towards tetracycline elimination under visible-light irradiation Appl. Surf. Sci. 506 144184
[60] Liu Y, Tian J, Wang Q, Wei L, Wang C and Yang C 2020 Enhanced visible light photocatalytic activity of g-C3N4 via the synergistic effect of K atom bridging doping and nanosheets formed by thermal exfoliation Opt. Mater. 99 105959
[61] Mael B I 1996 Principles of Adsorption and Reaction on Solid Surfaces (New York: Wiley)
[62] Heitbaum M, Glorius F and Escher I 2010 Asymmetric heterogeneous catalysis Angew. Chem., Int. Ed. 45 4732–62
[63] Zhang Z and Yates J J 2012 Band bending in semiconductors: chemical and physical consequences at surfaces and interfaces Chem. Rev. 112 5520
[64] Le N Q and Schweigert I V 2017 Modeling electronic trap states at interfaces between anatase nanoparticles J. Phys. Chem. C 121 14254–60
[65] Sevriu M, Hao X, Daniel B, Pavelec J, Novotny Z, Parkinson G S, Schmid M, Kresse G, Franchini C and Diebold U 2014 Charge trapping at the step edge of TiO2: atom (101) Angew. Chem. Int. Ed. 53 43–52
[66] Nosaka Y and Nosaka A Y 2017 Generation and detection of reactive oxygen species in photocatalysis Chem. Rev. 117 11302–36
[67] Tryba B, Toyoda M, Morawski A W, Nomaka R and Inagaki M 2007 Photocatalytic activity and OH radical formation on TiO2 in the relation to crystallinity Appl. Catal. B 71 163–8
[68] Xiong T, Wang H, Zhou Y, Sun Y, Cen W, Huang H, Zhang Y and Dong F 2018 KCl-mediated dual electronic channels in layered g-C3N4 for enhanced visible light photocatalytic NO removal Nanoscale 10 8066–74
[69] Cui W, Li J, Cen W, Sun Y, Lee S C and Dong F 2017 Steering the interlayer energy barrier and charge flow via bioriented transportation channels in g-C3N4: enhanced photocatalysis and reaction mechanism J. Catal. 352 351–60
[70] Zhang P, Sun D, Cho A, Weon S, Lee S, Lee J, Han J, Kim D-P and Choi W 2019 Modified carbon nitride nanosyme as bifunctional glucose oxidase-peroxidase formetal-freebioinspiredcascadephotocatalysis Nat. Commun. 10 940
[71] Cui W, Li J, Sun Y, Wang H and Dong F 2018 Enhancing ROS generation and suppressing toxic intermediate production in photocatalytic NO oxidation on O/Be co-functionalized amorphous carbon nitride Appl. Catal. B 237 938–46
[72] Sun Z et al 2017 Enriching CO2 activation sites on graphitic carbon nitride with simultaneous introduction of electron-transfer promoters for superior photocatalytic CO2-to-fuel conversion Adv. Sustain. Syst. 1 1700003
[73] Li J, Zhang Z, Cui W, Wang H, Cen W, Johnson G, Jiang G, Zhang S and Dong F 2018 The spatially oriented charge flow and photocatalysis mechanism on internal van der Waals heterostructures enhanced g-C3N4 ACS Catal. 8 8376–85
[71] Ran M, Chen P, Li J, Cui W, Li J, He Y, Sheng J, Sun Y and Dong F 2019 Promoted reactants activation and charge separation leading to efficient photocatalytic activity on phosphate/potassium co-functionalized carbon nitride Chin. Chem. Lett. 30 875–80
[72] Wang K, Fu J and Zheng Y 2019 Insights into photocatalytic CO$_2$ reduction on C$_3$N$_4$: strategy of simultaneous B, K co-doping and enhancement by N vacancies Appl. Catal. B 254 270–82
[73] Bi J, Zhu L, Wu J, Xu Y, Wang Z, Zhang X and Han Y 2019 Optimizing electronic structure and charge transport of sulfur/potassium co-doped graphitic carbon nitride with efficient photocatalytic hydrogen evolution performance Appl. Organomet. Chem. 33 e5163
[74] Zhu Q H, Chen Z, Tang L N, Zhong Y, Zhao X F, Zhang L Z and Li J H 2019 K and halogen binary-doped graphitic carbon nitride (g-C$_3$N$_4$) toward enhanced visible light hydrogen evolution Int. J. Hydrog. Energy 44 27704–12
[75] Wu Y et al 2020 Tunable water-soluble carbon nitride by alkali-metal cations modification: enhanced ROS-evolving and adsorption band for photodynamic therapy Appl. Catal. B 269 118848