



CN/iodine-doped CN homojunction powder catalysts with excellent visible-light photocatalytic properties

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ABSTRACT

Although carbon nitride (CN) catalyst has great attraction, the relatively low separation efficiency of photogenerated carriers leads to its unsatisfactory photocatalytic performance. Herein, CN/iodine-doped CN (CN/CNI) homojunction powder catalysts were fabricated via a facile water-bath combined with in-situ sintering method. The optimized CN/CNI-40% catalyst with a proper CN content shows prominent visible-light ($\lambda > 420$ nm) photocatalytic performance and stability. Its photocatalytic conversion ratio for Rhodamine B (RhB) is 5.1, 2.7, 3.0 time higher than that of CN, CNI and CNI-R (reference sample), respectively. Its photocatalytic H₂ evolution rate is 5.8, 2.1, 2.2 time higher than that of CN, CNI, CNI-R, respectively. And its photocatalytic CH₄ generation rate is 4.9, 3.5, 3.6 time higher than that of CN, CNI, CNI-R, respectively. This remarkably improved activity was mainly caused by the synergistic effect of CN and CNI, which can contribute to the excellent absorption performance in the 442–591 nm regions and the efficient separation of photoinduced electron-hole pairs provided by the well-matched band structures and homojunction interfaces between CN and CNI. The probable mechanism of remarkably improved photocatalytic property was also investigated. This study offers a novel and rational avenue to synthesize cheap and high-efficiency multifunctional photocatalysts applied in environmental and energy fields.

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1. Introduction

With the global economy development, energy exhaustion and environmental pollution have been two main problems that human faced in the 21st century. Due to the advantages of mild reaction conditions and environment friendly, semiconductor photocatalysis technology has shown broad application prospects in the field of CO₂ photoreduction, pollutant degradation and organic photosynthesis [1–6]. However, the synthesis of stable, inexpensive and highly efficient photocatalytic materials is still the key to restrict the practical application of photocatalytic technology. Among numerous photocatalytic materials, the polymeric graphite-like carbon nitride (CN) is regarded as a promising material, owing to its structural stability, easy preparation, suitable energy band [7–10]. However, the intriguing CN visible-light

photocatalyst possesses still some shortcomings of relatively small specific surface area, poor visible-light ($\lambda > 420$ nm) absorption property and relatively high recombination rate of photoinduced carriers, resulting in an unsatisfactory photocatalytic efficiency, which has greatly inhibited its practical application [11–15].

In the past ten years, using non-metal (boron, sulfur, phosphorus, etc.) doped CN was used as one of idea ways to improve the photocatalytic property of monomer CN [16–26]. For example, the co-doping with carbon (C), phosphorus (P) of CN enhanced the photocatalytic H₂ production by enhancing the separation efficiency of electrons and holes [20]. Boron, phosphorus co-doped CN nanocomposite was used as an efficient visible-light-driven catalyst for both CO₂ reduction and pollutant control [21]. Iodine-doped CN (CNI) photocatalysts showed highly efficient activities for H₂ production and pollutant treatment, owing to the absorption performance enhancement of visible-light irradiation and the separation efficiency improvement of photoinduced carriers [22–25], but there is still much room for improvement.

In addition, the synthesis of CN heterojunction materials by combining CN and proper semiconductor has also been used as an effective tool to improve the photocatalytic performance of CN [27–33]. For example, owing to the effective separation of photoinduced carriers,

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the CH₄ evolution rate of CN/Sn₂S₃-DETA heterostructure catalyst is obviously higher than that of CN [27]. Besides, the CN/Bi₂MoO₆ heterojunction facilitated the separation and transfer of photogenerated carriers, showing a higher photocatalytic H₂ production performance than CN under visible-light irradiation [30]. However, there are some differences of lattice matching among different semiconductors for these CN heterojunction materials, which affects the transmission and separation of photoinduced carriers from the heterojunction interface to a certain extent.

Our research have shown that the conduction band (CB), valence band (VB) of CNI is -1.13 eV, $+1.53$ eV versus Normal Hydrogen Electrode (NHE), respectively, and there is a very good band structure matching between CN (CB, VB is -0.92 eV and $+1.78$ eV, respectively) and CNI. Obviously, extremely matched band structure offers a vital chance to fabricate CN/CNI homojunction semiconductors.

Herein, making full use of the topology-induced band offset and the almost same characteristics of lattice matching, electronic affinity and work function between CN and CNI, a novel CN/CNI homojunction catalyst was fabricated by a facile synthetic route. Compared with CN or CNI, the photocatalytic performance of CN/CNI catalyst was greatly improved under visible-light irradiation. In particular, the CN/CNI-40% catalyst with an optimized CN content indicated an excellent photocatalytic property, and its degradation ratio for RhB, H₂ evolution rate, CO₂ reduction rate is respectively 3.0, 2.2, 3.6 time higher than that of CNI-R (reference sample) with the highest photocatalytic activity in the literature (Adv. Mater. 2014, 26, 805–809). This study provides a facile strategy to fabricate stable, cheap and highly active multifunctional materials.

2. Experiments

2.1. Synthesis of catalysts

Synthesis process for one-step calcination of iodine-doped CN (CNI-O) is as follows. 2.0 g dicyandiamide and 1.0 g ammonium iodine were mixed by 15 mL deionized water with stirring, evaporating water molecules at 80 °C, then CNI-O precursors were calcined by a muffle furnace at 823 K reaction for 4.0 h. For comparative study, an iodine-doped CN reference sample (CNI-R) with the highest activity in the literature (Adv. Mater. 2014, 26, 805–809) [22] was also synthesized. Pure CN was obtained by the same way at the absence of ammonium iodine.

The CN/CNI catalysts were synthesized by mixing and sintering CNI-O (2.0 g) with different amounts of dicyandiamide. For example, CN/CNI-20% was obtained by grinding the mixture of CNI-O (2.0 g) and dicyandiamide (0.2 g) for 0.5 h, and subsequently calcined at 823 K reaction for 4.0 h to yield final catalyst. The other CN/CNI catalysts were also prepared by the same method, using 0.4 g or 0.6 g of dicyandiamide, and denoted as CN/CNI-40% and CN/CNI-60%, respectively. CNI (CNI-T) was obtained by secondary calcination of CNI-O at 823 K reaction for 4.0 h. Based on our previous research, 0.4 g dicyandiamide at 823 K reaction for 4.0 h can produce 0.1 g CN. Therefore, CN/CNI-40% (physical mixture) was obtained by grinding the mixture of CNI (2.0 g) and CN (0.1 g) for 1.0 h.

2.2. Characterizations

Fourier transformation infrared spectroscopy was measured on a Bruker Equinox 55 spectrometer with KBr pellets in the 500–3000 cm⁻¹ region. Scanning electron microscopy was measured by Carl Zeiss Sigma 500. The characterization processes of valence band X-ray photoelectron spectroscopy, X-ray powder diffraction, UV-Vis diffuse reflectance spectra, X-ray photoelectron spectroscopy, photoluminescence and photoelectrochemistry reference to this document [22,23].

2.3. Activity measurements

The activities of catalysts were evaluated by the photocatalytic degradation of Rhodamine B (RhB) (60 mL, 10 mg/L) solution, and 300 W Xe lamp ($\lambda > 420$ nm) was used as light source and the amount of photocatalyst was 0.1 g. To ensure the adsorption equilibrium of solution and catalyst, the mixed solution was magnetically stirred for 0.5 h before illumination. About 4.0 mL mixed solution was extracted and centrifuged at fixed time, and then was analyzed by a TU-1901 spectrophotometer. The change of total organic carbon (TOC) in the CN, CNI, CNI-R, CN/CNI-40% catalytic system was measured via a TOC (Shimadzu TOC-L CSH) monitoring system.

The evaluation of photocatalytic H₂ evolution references to this document [23]. The photocatalytic reduction of carbon dioxide (CO₂) into CH₄ reaction was performed in a Pyrex glass vessel, and Pt loading on catalysts was prepared by a photo-deposition method [34]. Then, 50 mg disperse catalyst was located at the bottom of a Pyrex glass cell, connecting with a closed system. The reaction system volume is ~230 mL. The reaction setup was vacuum-treated after several times, CO₂ gas with high purity was followed into the reaction setup to reach an ambient pressure. And then, 2.0 mL H₂O was injected into the reactor by a liquid syringe. Next, the reactor was stored under dark for 2.0 h, to reach the adsorption-desorption equilibrium. Finally, the reaction was irradiated by a 300 W Xe lamp ($\lambda > 420$ nm). At a given interval, from the reaction cell, 0.5 mL gaseous product was continually extracted, in order to check the concentration of CH₄ by using a gas chromatograph (Shimadzu, GC-2014, Ar carrier) during irradiation.

3. Results and discussion

3.1. Characterization

X-ray diffraction (XRD) results in Fig. 1A confirmed that CN, CNI, CN/CNI catalysts were crystalline and consisted of a typical graphite-like structure of CN, which was indicated by the diffraction peaks at 2θ angles of 27.4° and 13.0°, corresponding to the (002) and (100) crystal faces of layered CN [35,36]. At 27.4° and 13.0°, there was a strong and weak diffraction peak, were indexed to the inter-layer stacking and in-plane structural packing of conjugated aromatic systems, respectively [37]. It was found that no other diffraction peak was observed among CN, CNI and CN/CNI catalysts.

The functional group and structure of CNI, CN, CN/CNI catalysts were studied by fourier transformation infrared (FTIR) spectroscopy, and the results were shown in Fig. 1B. The absorption bands of these catalysts were found at about 805 and 1200–1700 cm⁻¹, belonging to the tri-s-triazine units and the aromatic C–N heterocycles of CN [38,39]. These FTIR results, together with the XRD analyses, indicated that the crystalline structure of CN was not changed after iodine doped.

The morphology of the CN, CNI and CN/CNI-40% catalysts was studied by scanning electron microscopy (SEM). As depicted in Fig. 2a, pure CN exhibited a large number of aggregated thick layers structures. Compared with CN, more micro-pores of small diameter size were observed on CNI surface (Fig. 2b). This change in microstructure probably was a result of NH₃ release by pyrolysis, which was induced by a sufficient doped with iodine at CN surfaces [22,23]. As described in Fig. 2c, after introducing CN, the CN/CNI-40% catalyst showed integrated morphology of pure CN and CNI together, suggesting the formation of CN/CNI homojunction catalyst. The element mapping images of the corresponding region shown in Fig. 2d, e, and f can further prove that the CN and CNI were coexistent and nearly homogeneously distributed in the CN/CNI-40% catalyst.

X-ray photoelectron spectroscopy (XPS) was used to reveal the surface component and interaction between CNI and CN in their homojunction catalysts. Fig. 3 depicted the XPS profiles of CNI, CN and CN/CNI-40% catalysts, where carbon (C) and nitrogen (N) elements were observed in these catalysts and iodine (I) element was detected

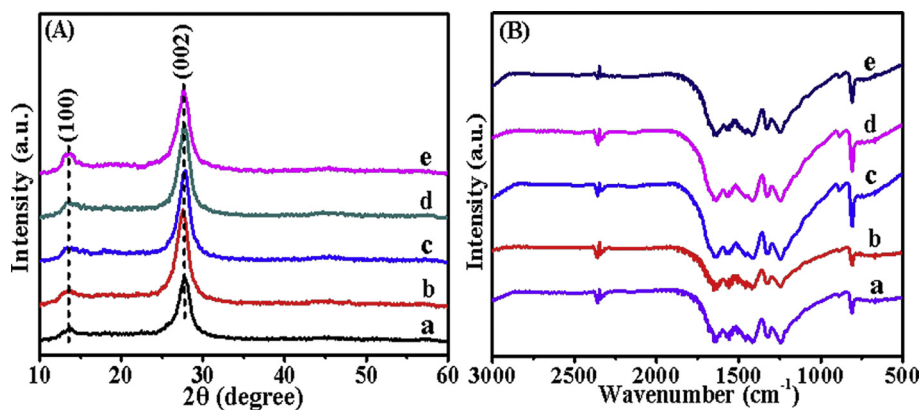


Fig. 1. (A) XRD and (B) FTIR patterns of (a) CN, (b) CN/CNI-20%, (c) CN/CNI-40%, (d) CN/CNI-60% and (e) CN catalysts.

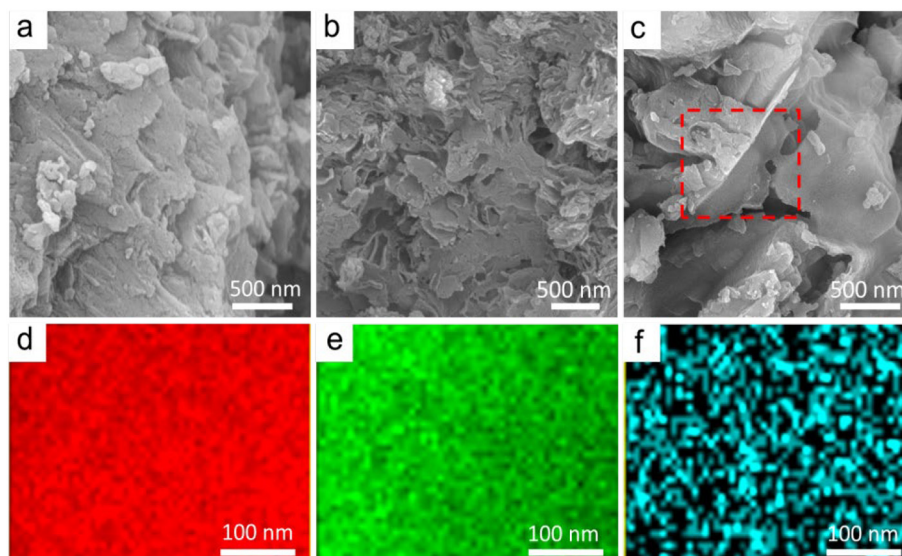


Fig. 2. SEM images of (a) CN, (b) CNI, (c) CN/CNI-40% and corresponding elemental mapping of (d) C, (e) N, (f) I in the CN/CNI-40% catalyst.

in CNI and CN/CNI-40% catalysts, indicating the successful formation of CN/CNI homojunction catalysts. The C 1 s XPS spectrum (Fig. 3A) could be deconvoluted into two peaks, the peak at 284.6 eV was attributed to carbon impurities, the peak at 288.2 eV was attributed to an sp^2 -bonded carbon (C—N=C) [40]. The N 1 s XPS spectrum (Fig. 3B) could be deconvoluted into three peaks at 398.8, 399.7, and 401.1 eV, which were ascribed to sp^2 -bonded nitrogen in N-containing aromatic rings (C—N=C), the tertiary nitrogen N-(C)₃ groups and the amino groups (C—N—H), respectively [41,42]. The I 3d XPS spectrum (Fig. 3C) could be deconvoluted into four peaks at 621.2, 621.9, 632.9, and 633.8 eV, corresponding to the I 3d_{5/2}, I 3d_{5/2}, I 3d_{3/2}, I 3d_{3/2}, respectively. The peaks at 621.2 and 621.9 eV were associated with the I⁺, which were oxidation products of I⁻ during the reaction process [22]. However, in the CN/CNI-40% catalyst, the C 1 s peak binding energy (288.4 eV), the N 1 s peaks binding energy (398.9, 399.9, and 401.2 eV) and the I 3d peaks binding energy (621.4, 622.2, 633.2, and 634.0 eV) were respectively higher than that of the CN or CNI catalysts. This result not only confirmed the existence of iodine in the homojunction catalyst, but also reflected an intermolecular interaction between CN and CNI in their hybrid catalysts.

3.2. Activity and stability

The visible-light ($\lambda > 420$ nm) photocatalytic properties for degradation organic pollutant Rhodamine B (RhB) over the CN, CNI, CNI-R

and CN/CNI catalysts were investigated, and the results were shown in Fig. 4A. Blank test in the lack of any catalyst was tested by same reaction conditions, which was barely decomposed without photocatalyst (only 4.5% removal) after being irradiated 4.0 h, indicating RhB direct photo-induced self-decomposition is negligible. The degradation ratio of CN, CNI, CNI-R was about 18%, 34%, 30% after 4.0 h, respectively. It was found that the synergistic effect of CN and CNI in their homojunction catalysts played a main role in improving catalytic efficiency. CN contents change from 20% to 60%, the activity of CN/CNI catalysts firstly increases, then decreased, and the highest photocatalytic activity was obtained by the CN/CNI-40% catalyst with the optimization content of CN, demonstrating that the combination of CN with CNI can exhibit superior catalytic activity towards RhB degradation. Furthermore, nearly 92% of RhB can be degraded by the CN/CNI-40% catalyst after an irradiation of 4.0 h, about 5.1, 2.7, 3.0 time as high as that of CN, CNI, CNI-R, respectively, confirming that CN/CNI-40% homojunction catalyst possesses an excellent property in degradation dye pollutants. The TOC removal efficiency was also studied (Fig. 4B), and the TOC removal efficiency was 35%, 44%, 47% and 71% for the CN, CNI-R, CNI and CN/CNI-40%, respectively, after 12 h photocatalytic reaction, indicating that massive intermediate products were oxidized and the CN/CNI-40% homojunction catalyst had excellent mineralizing ability.

The excellent photocatalytic H₂ evolution performance of CN, CNI, CNI-R and CN/CNI catalysts were evaluated (Fig. 5A), and CN, CNI and CNI-R shows a little activity, while the activity of CN/CNI homojunction

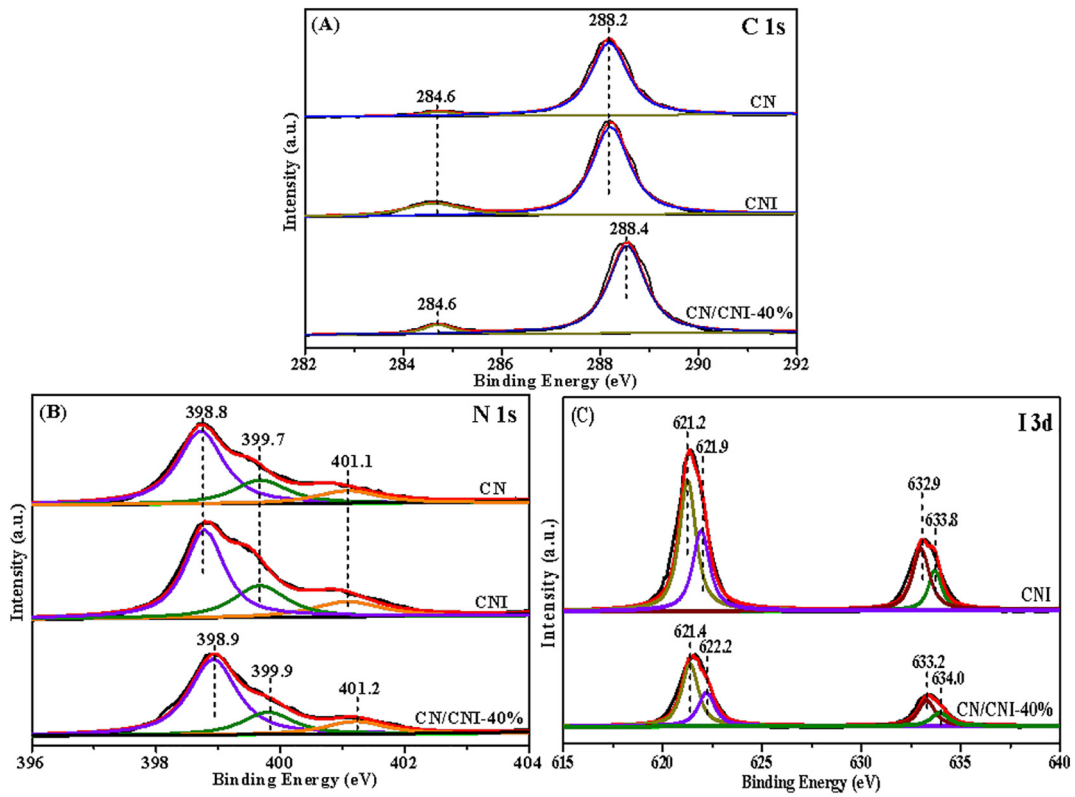


Fig. 3. XPS spectra of (A) C 1s, (B) N 1s and (C) I 3d peaks in CNI, CN/CNI-40% and CN catalysts.

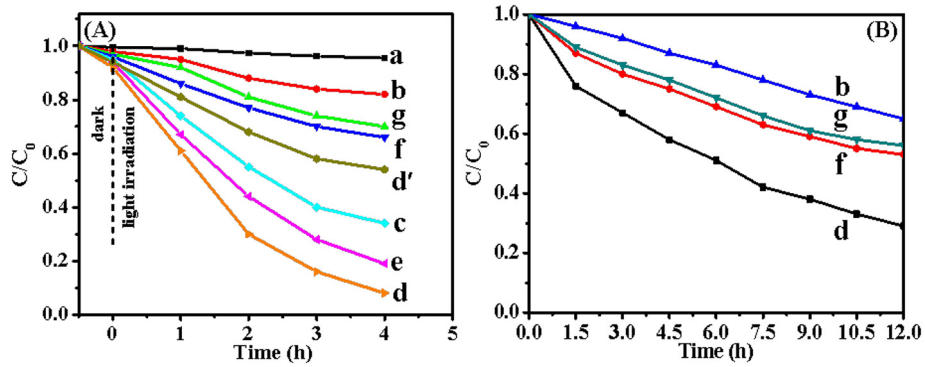


Fig. 4. (A) RhB degradation and (B) TOC removal for (a) blank, (b) CN, (c) CN/CNI-20%, (d) CN/CNI-40%, (d') CN/CNI-40% (physical mixture), (e) CN/CNI-60%, (f) CNI, (g) CNI-R catalysts under visible-light irradiation ($\lambda > 420$ nm).

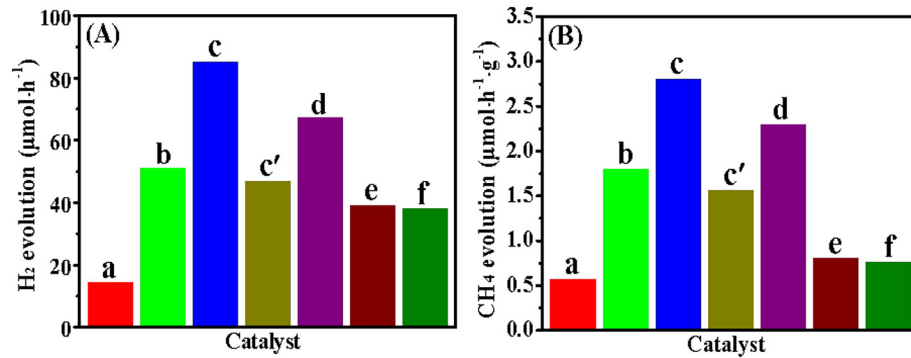


Fig. 5. (A) photocatalytic H₂ evolution rates and (B) photocatalytic CH₄ evolution rates for (a) CN, (b) CN/CNI-20%, (c) CN/CNI-40%, (c') CN/CNI-40% (physical mixture), (d) CN/CNI-60%, (e) CNI, and (f) CNI-R catalysts under visible-light irradiation ($\lambda > 420$ nm).

catalysts is significantly enhanced, further demonstrating the important role of homojunction. Also, we notice that the photocatalytic efficiency for H₂ evolution of CN/CNI catalysts follows the same order as photodegradation of RhB. Remarkably, the as-prepared CN/CNI-40% homojunction catalyst showed H₂ generation rate (85 μmol·h⁻¹), which was 5.8, 2.1, 2.2 time higher than that of CN, CNI and CNI-R, respectively.

To further study the performance of CN/CNI homojunction catalysts, the reduction of CO₂ to CH₄ was also carried out (Fig. 5B). In comparison with CN, CNI, or CNI-R, all of the CN/CNI homojunction catalysts show significantly enhanced CO₂ reduction rates, with an order of CN < CNI-R < CNI < CN/CNI-20% < CN/CNI-60% < CN/CNI-40%. These results further lead us to conclude that the homojunction of CN/CNI is very important in improving the activity. Moreover, optimized CN/CNI-40% catalyst showed CO₂ reduction rate of 2.8 μmol·h⁻¹·g⁻¹, which was 4.9, 3.5, 3.6 time higher than that of CN, CNI, CNI-R, respectively. Notably, these results of the CN/CNI homojunction catalysts on the photoreduction CO₂ was in accordance with the photocatalytic degradation RhB and photocatalytic H₂ evolution in Fig. 4A and Fig. 5A.

Moreover, in order to further prove the role of homojunction of CN/CNI, the photocatalytic properties of physical mixture CN/CNI-40% were also tested (Figs. 4A and 5). RhB degradation ratio, H₂ production rate, CH₄ production rate of physical mixture CN/CNI-40% was obviously lower than that of the in-suit CN/CNI-40% homojunction catalyst, strongly suggesting that there was a synergistic effect between CN and CNI in the homojunction catalyst.

It is well known, stability of catalyst affects its application. Therefore, the photocatalytic repeatability was also evaluated by reusing the CN/CNI-40% homojunction catalyst (Fig. 6). After three cycles, there was no significant change in RhB degradation, H₂ evolution and CO₂ reduction over the CN/CNI-40% homojunction catalyst, implying that it has good stability.

3.3. Activity enhancement mechanism

The reasons of remarkably enhanced photocatalytic activity over the CN/CNI-40% homojunction catalyst are analyzed as follows. As we all know, the photocatalytic performance is usually influenced by the crystallinity, morphology, pore volume, specific surface area and band structure of catalysts. Compared with CNI, the specific surface area (Table 1), crystallinity (Fig. 1), pore volume (Table 1) and morphology (Fig. 2) of CN/CNI-40% showed a little change, implying that these factors were not keys for improving the activity. Therefore, visible-light absorption

Table 1
Physicochemical properties of CN, CNI and CN/CNI catalysts.

Sample	Specific surface area (m ² /g)	Pore volume (cm ³ /g)
CN	7	0.02
CNI	19	0.04
CN/CNI-20%	26	0.06
CN/CNI-40%	30	0.07
CN/CNI-60%	23	0.06

property, electron-hole separation of CN/CNI-40% might be two important factors for the improving catalytic property.

Optical properties for CN, CNI and CN/CNI catalysts were investigated (Fig. 7). Compared with CN or CNI, the CN/CNI catalysts extended a red shift and exhibited a stronger photo-absorption property in 442–591 nm regions, demonstrating the interaction between CN and CNI in the heterojunction may contribute to the narrowing of the band gap, which was contributed to the modified electronic structures of the photocatalyst matrix [10,26]. Meanwhile, the optical absorption properties and band gap structure of the CN/CNI homojunction catalysts could be very well controlled via tuning CN content. Furthermore, higher or lower CN content resulted in a lower absorption performance compared to that of CN/CNI-40% catalyst, implying that the suitable CN concentration will cause an optimized generation of charge carriers under light illumination and the interaction of CN and CNI could result in the strongest photoresponse among the CN/CNI as-synthesized catalysts.

The valence band X-ray photoelectron spectroscopy (VB XPS) was used to further research the influence of iodine-doped CN on positions of the valence band (VB). Fig. 8 showed VB XPS of CN and CNI catalysts. It can be known that the VB of CN and CNI was +1.78 eV, +1.53 eV, respectively. Combined with the Kubelka-Munk-transformed reflectance spectra (Fig. 7B), it can infer that the conduction band (CB) of CN and CNI was -0.92 eV, -1.13 eV, respectively. Obviously, CNI possessed a more negative CB compared to that of CN, indicating that CNI had a stronger reduction ability for photogenerated charge carriers [43].

Fig. 9 recorded the photoluminescence (PL) spectra of CN, CNI, CN/CNI-20%, CN/CNI-40%, CN/CNI-60% catalysts. The three catalysts have a very strong similar emission band in the range of 400–600 nm, ascribed to the band-to-band transitions of CN [44,45]. The PL peaks of CN/CNI-20%, CN/CNI-40% and CN/CNI-60% weaken significantly in comparison with the CN or CNI. Among them, the PL peak of CN/CNI-40% was the weakest, implying that the recombination of charge carriers was greatly

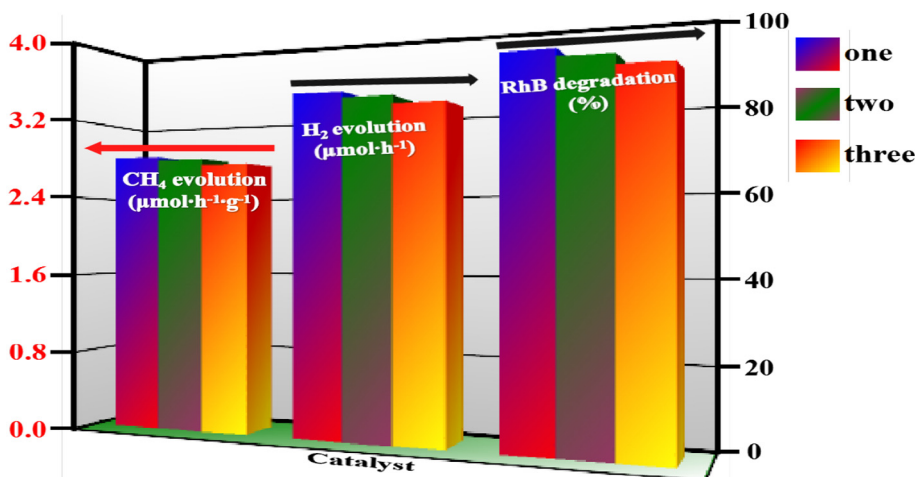


Fig. 6. Stability test of RhB degradation, H₂ evolution and CH₄ evolution for CN/CNI-40% recycling three times under visible-light irradiation ($\lambda > 420$ nm).

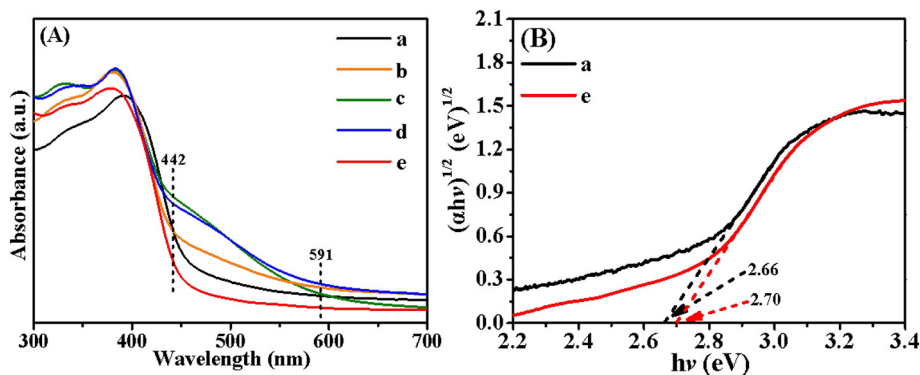


Fig. 7. (A) UV-Vis DRS and (B) Kubelka-Munk-transformed reflectance spectra of (a) CNI, (b) CN/CNI-20%, (c) CN/CNI-40%, (d) CN/CNI-60% and (e) CN catalysts.

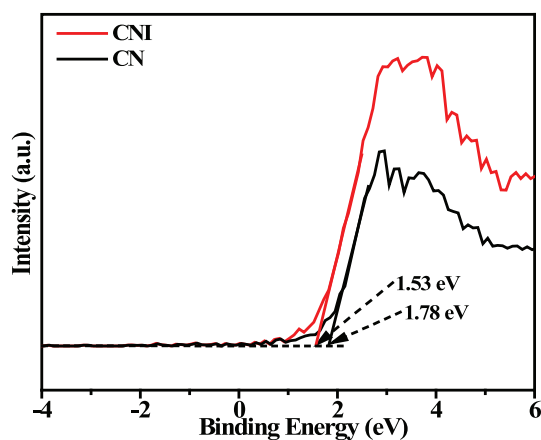


Fig. 8. XPS valence band (VB) spectra of CN and CNI catalysts.

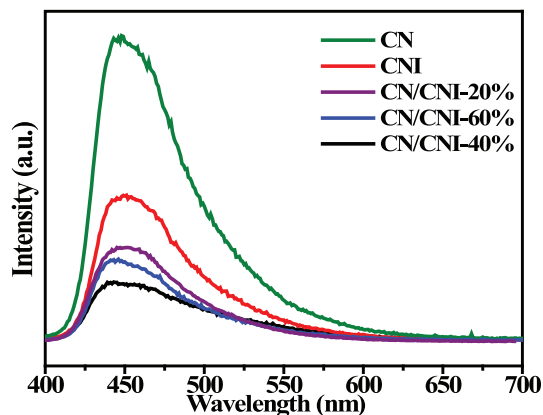


Fig. 9. PL spectra of CN, CNI, CN/CNI-20%, CN/CNI-40% and CN/CNI-60% catalysts.

inhibited for CN/CNI-40% homojunction catalyst. This result suggested that the homojunction of CNI and CN can significantly improve the separation efficiency of electron-hole pairs, which is useful to improve the activities.

Electrochemical Impedance Spectroscopy (EIS) measurement is also an effective mean of investigating the resistance of charge transfer and the separation efficiency of photoinduced carriers. Fig. 10A showed EIS Nyquist plots for CN, CNI and CN/CNI-40% catalysts. It is well known that a smaller arc of an EIS Nyquist plot implies a smaller resistance of charge transfer on electrode surface

[46]. Obviously, a decreased diameter of the EIS radius was observed for CN/CNI-40% compared to CN or CNI, showing a reduced electronic impedance and an improved charge mobility. In addition, transient photocurrent response measurements were carried out to further explore the transfer and separation of charge carriers. As shown in Fig. 10B, although CN, CNI and CN/CNI-40% catalysts showed a rapid response to light either off or on, the induced transient photocurrent density of CN/CNI-40% was 5.1, 1.9 time higher than that of CN or CNI, respectively. And the highest current density and smallest resistance of the CN/CNI-40% electrode verified the synergistic effect between the CN and CNI in the formation of homojunction catalyst. And the photocurrent is steady during five light-dark current cycles. Generally speaking, a higher photocurrent reflected a better separation ability of the photogenerated charges in the material [42]. Therefore, we can expressly figure out that the CN/CNI-40% illustrates an increased separation efficiency of the photoinduced carriers in homojunction catalyst as compared to individual CN and CNI.

Taken the above results and discussions together, we get a conclusion that the synergistic interaction between CN and CNI in their homojunction catalysts, especially for CN/CNI-40%, can result in an increased transfer and separation of interfacial charge carriers. Thus, enlarged light absorption property and accelerated separation/transport ability of photogenerated charges are mainly responsible for the enhanced reaction efficiency for CN/CNI catalysts.

Based on the above analysis, an activity enhancement proposed mechanism was presented for CN/CNI (Fig. 11). Photogenerated electrons-holes (Eq. (1)) of CN and CNI photocatalysts can be excited simultaneously by visible-light irradiation. According to theoretical calculation and previously reported results [47–49], there is a matching band structure between CN and CNI (Fig. 11). Due to the very well matched positions, CN/CNI homojunction could drive electron (e^-) migration from CNI to CN by conduction band offset, whereas the hole (h^+) can flow from CN to CNI by the valence band offset. As a result, electrons-hole pairs were effectively separated via using this technique, which was also supported by elevated photocurrent (Fig. 10B) and decreased photoluminescence intensity (Fig. 9) of CN/CNI. This causes an increase of photocatalytic performances over the CN/CNI catalysts.

However, the photocatalytic activities of CN/CNI homojunction catalysts have a close relationship with the composite proportion, and lower or higher CN concentration is inconvenient to increase the activity. With CN content increases from 20% to 40%, the CN/CNI catalysts produce a homogeneous dispersion process, which will promote the separation of electron-holes based on their matching electronic structure, thus resulting in enhanced catalytic performance. After that, excessive CN may block the active site on the CN/CNI contact interfaces and subsequently decrease the interfacial interaction of CN and CNI, causing a decreased photocatalytic activity. Therefore, the activity of CN/CNI

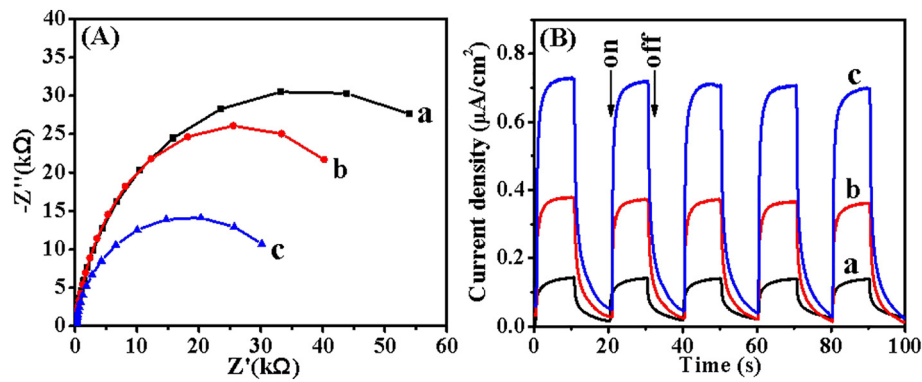


Fig. 10. (A) Electrochemical impedance spectroscopy and (B) transient photocurrent responses ($\lambda > 420$ nm) for (a) CN, (b) CNI and (c) CN/CNI-40% catalysts.

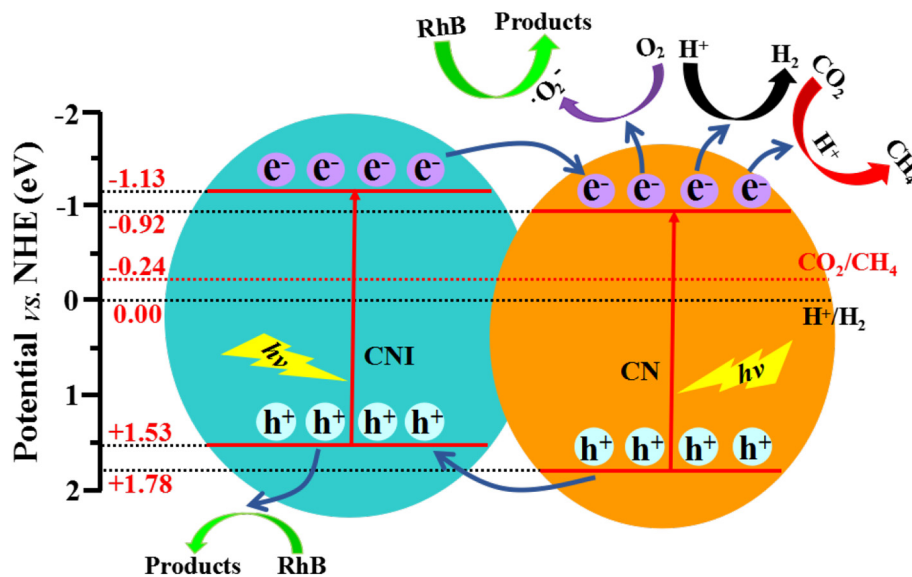


Fig. 11. The generation, transportation, and separation of visible-light-induced charge carries over the CN/CNI homojunction catalysts.

catalysts firstly increased and then decreased with increasing CN concentration, which results in the optimal photocatalytic performance of the CN/CNI-40% homojunction catalyst.



To study the role of $\cdot\text{OH}$, $\cdot\text{O}_2^-$, h^+ and H_2O_2 radicals in RhB degradation process, various scavengers were added in RhB reaction system [50,51], we found the degradation efficiency of RhB was significantly decreased from 92% to 28.5% and 45.8%, after addition benzoquinone (BQ) or ammonium oxalate (AO), respectively. While it was almost invariable in the presence of isopropanol (IPA) and catalase (CAT), as shown in Fig. 12. This, of course, gave a strong argument in favor of the contribution of both $\cdot\text{O}_2^-$ and h^+ as main active species in RhB reaction system for CN/CNI homojunction catalysts, while the $\cdot\text{OH}$ and H_2O_2 play mirror

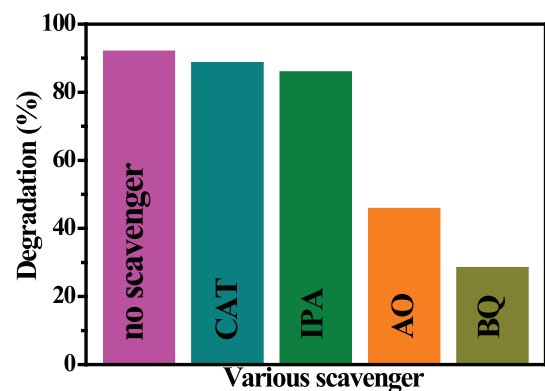


Fig. 12. Effect of scavengers for RhB in the CN/CNI-40% photocatalytic system under visible-light irradiation ($\lambda > 420$ nm) for 4 h.

contribution to it [52]. Therefore, we proposed Eqs. (1)–(6) to describe the possible photocatalytic degradation RhB, H_2 evolution and CO_2 reduction process of the catalysts. In the process of photocatalytic CO_2 reduction, when the CN/CNI photocatalyst is irradiated by visible light with the greater energy than the E_g (band-gap energy) of CN and CNI, the e^- (electron) in the VB of CNI and CN is excited to their CB, leading to the generation of h^+ (hole) in their VB. Then the band alignment

between them can not only drive the e^- in CNI to transfer towards the CN, but also drive the h^+ in CN transfer towards the CNI by valence band offset. The h^+ would react with the surface-adsorbed water molecules or hydroxyl groups to form $\cdot OH$ and $\cdot O_2^-$ radicals, along with H^+ . Meanwhile, CO_2 would react with H^+ and e^- to produce CH_4 [53,54].

4. Conclusions

In summary, the novel CN/CNI homojunction catalysts were fabricated by a facile synthetic route. The optimized CN/CNI-40% catalyst with an appropriate CN content showed an excellent photocatalytic activity and stability, and its RhB degradation ratio, H_2 evolution rate, CO_2 reduction rate was 3.0, 2.2, 3.6 time higher than that of CNI-R (reference sample), respectively. The remarkably enhanced activity of CN/CNI-40% was mainly ascribed to the strengthened visible-light (442–591 nm) absorption performance and efficient separation of photogenerated carriers. Overall, these results indicated that highly efficient CN/CNI catalysts have great potentialities as a cheap multifunctional material applied in energy and environment fields in the near future.

Declaration of Competing Interest

None.

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