



Full Length Article

In₂O₃/boron doped g-C₃N₄ heterojunction catalysts with remarkably enhanced visible-light photocatalytic efficiencies



Xiaoyan Jin^{a,1}, Qingmei Guan^{a,1}, Tong Tian^a, Huiquan Li^a, Yan Han^a, Fuying Hao^a, Yumin Cui^a, Wenyong Li^b, Yongfa Zhu^{a,c}, Yan Zhang^a

^a Anhui Provincial Key Laboratory for Degradation and Monitoring of Pollution of the Environment, School of Chemistry and Materials Engineering, Fuyang Normal University, Fuyang 236037, PR China

^b Anhui Province Key Laboratory of Environmental Hormone and Reproduction, Biology and Food Engineering School, Fuyang Normal University, Fuyang 236037, PR China

^c Collaborative Innovation Center for Regional Environmental Quality, Tsinghua University, Beijing 100084, PR China

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ABSTRACT

Novel In₂O₃/boron doped graphite-like carbon nitride (In₂O₃/g-C₃N₄B) heterojunction catalysts were successfully fabricated via a facile water-bath combined with calcination method. The resulting 5% In₂O₃/g-C₃N₄B catalyst with a proper In₂O₃ and B content exhibits excellent visible-light photocatalytic activities. Its conversion ratio for tetracycline hydrochloride (TH) and nitric oxide (NO) is 2.0, 1.9 times higher than that of In₂O₃, g-C₃N₄, g-C₃N₄B, g-C₃N₄B-R (reference sample), respectively. And its CH₄ evolution rate is 9.0, 3.6, 2.2, 2.5 times higher than that of In₂O₃, g-C₃N₄, g-C₃N₄B, g-C₃N₄B-R, respectively. The remarkably enhanced photocatalytic properties are mainly attributed to the result that an appropriate boron and In₂O₃ modified the g-C₃N₄ promoted the efficient separation and transfer of photoinduced electrons and holes from the heterojunction interface by the band alignment between In₂O₃ and g-C₃N₄B. The probable mechanism on the activity enhancement was also discussed. Moreover, 5% In₂O₃/g-C₃N₄B shows good activity stability as evidenced by three recycling reactions. This work offers some useful insights to design and fabricate other highly efficient and stable g-C₃N₄-based heterojunction multifunctional materials for energy conversion and environmental restoration applications in the near future.

1. Introduction

Two dimensional (2D) graphitic carbon nitride (g-C₃N₄) photocatalytic material, as a promising organic semiconductor for H₂ production, pollutants treatment and CO₂ reduction, has caused remarkable attention recently because of its unique optical and electronic properties that are very important in photocatalysis, non-toxicity and convenient synthetic routes [1–8]. However, for the g-C₃N₄ with a band gap (E_g) of ~2.7 eV, the poor photocatalytic efficiency induced by the quick recombination of photo-induced electrons and holes limits its practical applications [9–17].

To perfect the photocatalytic material, a great quantity of studies were committed to enhance the efficient separation of charge carriers. Among them, element doping [18–24] and heterojunction construction [25–31] are two promising means to enhance the performance of g-C₃N₄. It is acknowledged that boron (B) is an attractive non-metal dopant into g-C₃N₄ due to similar atomic size to carbon atom and its

electron-deficient property. For example, Zou et al. [32] synthesized a kind of boron-doped g-C₃N₄ catalyst, it shows a significantly improved performance in photo-degradation of organic dyes, in which carbon atoms in the ring were substituted via boron, forming π -bonded heterocyclic structure. Afterwards, a series of photocatalytic reactions with B-doped g-C₃N₄ for hydrogen production [23], CO₂ reduction [33] and UO₂²⁺ reduction [34] were investigated, all of which showed the excellent photocatalytic performances.

In addition, the heterojunction construction of combining different semiconductors with the appropriate band edges has become another significant method to restrain the electron-hole recombination of g-C₃N₄. Many works described that the separation of photo-induced carriers was promoted by coupling various metal oxide semiconductors with g-C₃N₄ [15,25,29,35–37]. Among these metal oxide semiconductors, In₂O₃ (a direct E_g of 3.6 eV; an indirect E_g of 2.8 eV) is a very potential material for realizing the activity enhancement of g-C₃N₄. For example, Cao et al. [38] has synthesized In₂O₃/g-C₃N₄

E-mail addresses: huiquanli0908@163.com (H. Li), liwenyong@aliyun.com (W. Li), zhuyf@tsinghua.edu.cn (Y. Zhu).

¹ X. Jin and Q. Guan contributed equally to this work.

heterojunction by heating $\text{In}(\text{Ac})_3$ and $\text{g-C}_3\text{N}_4$ in autoclave and demonstrated effective charge separation on the heterointerface. Recently, a kind of ternary composite photocatalyst by coupling two metal oxides semiconductor (TiO_2 and In_2O_3) with $\text{g-C}_3\text{N}_4$ was synthesized and high visible-light photocatalytic activity was exhibited [39].

Naturally, a novel design is proposed that boron doping and the introduction of In_2O_3 to $\text{g-C}_3\text{N}_4$ occur simultaneously. Whether the synergistic effect is more excellent? Motivated by the above concerns, in the present work the heterostructured $\text{In}_2\text{O}_3/\text{g-C}_3\text{N}_4\text{B}$ catalysts were prepared through a facile water-bath calcination method, and the information of morphology, structure and optical property of $\text{In}_2\text{O}_3/\text{g-C}_3\text{N}_4\text{B}$ catalysts was studied. The activities of $\text{In}_2\text{O}_3/\text{g-C}_3\text{N}_4\text{B}$ catalysts were researched by tetracycline hydrochloride (TH) degradation and nitric oxide (NO) conversion, and carbon dioxide (CO_2) reduction. Based on experimental outcomes, the probable mechanism of activity improvement for the $\text{In}_2\text{O}_3/\text{g-C}_3\text{N}_4\text{B}$ catalysts was discussed.

2. Experiments

2.1. Catalysts synthesis

$\text{In}_2\text{O}_3/\text{g-C}_3\text{N}_4\text{B}$ catalysts were fabricated via a simple water-bath combined with calcination method. Boron doped $\text{g-C}_3\text{N}_4$ ($\text{g-C}_3\text{N}_4\text{B}$) was prepared as follows: 2.0, 4.0, 10, or 20 mg sodium tetraphenylboron ($\text{C}_{24}\text{H}_{20}\text{BNa}$) and 10 g urea were dissolved into distilled water (10 mL), followed by stirring under 353 K for 5.0 h, and then the product was calcined under 823 K for 2.0 h. After cooled naturally, yellow product was grounded to obtain a powder sample. The synthesized B-doped $\text{g-C}_3\text{N}_4$ catalysts are denoted as $\text{g-C}_3\text{N}_4\text{B-x}$, and x is the mass (mg) of $\text{C}_{24}\text{H}_{20}\text{BNa}$ introduced into the precursor solution. For comparative study, a boron doped $\text{g-C}_3\text{N}_4$ reference sample ($\text{g-C}_3\text{N}_4\text{B-R}$) with the highest activity in the literature (Angewandte Chemie International Edition, 2013, 52, 1735–1738) [40] was also synthesized. To prepare the $\text{In}_2\text{O}_3/\text{g-C}_3\text{N}_4\text{B}$ composites, 0.01 g, 0.05 g, 0.10 g and 0.20 g of In_2O_3 nanocrystals (commodity) and 1.0 g of the as-synthesized $\text{g-C}_3\text{N}_4\text{B-4}$ were added into 10 mL absolute methanol, respectively. The resultant mixtures were ultrasonically treated for 5 min and then dried under 60 °C water-bath temperature. After being calcined at 723 K for 3 h, a series of $\text{In}_2\text{O}_3/\text{g-C}_3\text{N}_4\text{B}$ catalysts with different weight concentration of In_2O_3 , were denoted as 1%, 5%, 10% and 20% $\text{In}_2\text{O}_3/\text{g-C}_3\text{N}_4\text{B}$, respectively. The Pt loading on catalysts was prepared by a photo-deposition method [41].

2.2. Catalysts characterization

The crystalline phases of catalysts were analyzed by using a Bruker D8 X-ray diffractometer. The specific surface area of catalysts were measured by an ASAP2020 HD88 instrument at 77 K. Transmission electron microscopy (TEM) and higher-magnification transmission electron microscopy (HRTEM) images of catalysts were collected by a JEOL JEM2100F microscope. The X-ray photoelectron spectroscopy of catalysts was measured by a Thermo Scientific K-Alpha spectrometer. At 400 nm excitation wavelength, the photoluminescence spectroscopy was obtained by a CARY Eclipse fluorescence spectrophotometer. The electron paramagnetic resonance spectra were recorded by a Bruker model A300 spectrometer. Using BaSO_4 as the reference, the UV-Vis diffuse reflection spectroscopy (DRS) was done at a Varian Cary 500 Scan. Electrochemical measurements of $\text{g-C}_3\text{N}_4$, $\text{g-C}_3\text{N}_4\text{B}$ and 5% $\text{In}_2\text{O}_3/\text{g-C}_3\text{N}_4\text{B}$ samples were also carried out by following the steps of this reference [42].

2.3. Activity evaluation

Activity evaluation experiments were carried out under visible-light ($\lambda > 420$ nm) irradiation, by adding 200 mg photocatalysts into 40 mL of 5.0 mg/L tetracycline hydrochloride (TH) solution. In order to

establish an adsorption–desorption equilibrium, the solution was magnetically stirred for 0.5 h in the dark. After different irradiation time, the concentration of TH solution was measured by using a spectrophotometer (TU-1901). The change of total organic carbon (TOC) of 5% $\text{In}_2\text{O}_3/\text{g-C}_3\text{N}_4\text{B}$ reaction process was measured by using a TOC analysis system (Shimadzu TOC-L CSH).

NO conversion was studied by a flow reactor system under visible-light ($\lambda > 420$ nm) irradiation for 4 h. The photocatalyst (0.1 g) was uniformly coated onto a dish with a diameter of 8.0 cm, and then it was dried at 80 °C. Initial NO concentration is 400 ppb, and its flow rate is 3 L/min. After attaining the equilibrium of adsorption–desorption, the Xe arc lamp was turned on, and the concentration of NO was continually measured by a chemiluminescence NO analyzer.

The photocatalytic reduction of carbon dioxide (CO_2) into methane (CH_4) reaction was performed as follows. Typically, the disperse photocatalyst (50 mg) of small glass cell bottom was located in a Pyrex glass cell bottom, connected with a closed system. The reaction system volume was ~230 mL. After vacuum-treating the reaction setup for three times, the high purity CO_2 gas entered into the reaction setup to attain an ambient pressure, and the system air was replaced by CO_2 . And then, the reactor was injected into 2.0 mL H_2O by a liquid syringe. Next, the reactor was placed in darkness for 2.0 h to reach an adsorption-desorption equilibrium. Finally, the reactor was irradiated under $\lambda > 420$ nm. Within a given time interval, the reaction cell was continually extracted gaseous product (0.5 mL) to check CH_4 concentration by a Shimadzu gas chromatograph (GC-2014, Ar carrier) during irradiation.

3. Result and discussion

3.1. Composition, morphology, and structure of catalysts

The crystalline phases of pure $\text{g-C}_3\text{N}_4$, $\text{g-C}_3\text{N}_4\text{B}$, 1% $\text{In}_2\text{O}_3/\text{g-C}_3\text{N}_4\text{B}$, 5% $\text{In}_2\text{O}_3/\text{g-C}_3\text{N}_4\text{B}$, 10% $\text{In}_2\text{O}_3/\text{g-C}_3\text{N}_4\text{B}$, 20% $\text{In}_2\text{O}_3/\text{g-C}_3\text{N}_4\text{B}$ and pure In_2O_3 samples were shown in Fig. 1. All the patterns except pure In_2O_3 show characteristic diffraction peak of $\text{g-C}_3\text{N}_4$ at about $2\theta = 27.4^\circ$, which is ascribed to (0 0 2) reflection of the interlayer stacking peak of conjugated aromatic systems [43]. Meanwhile, from the XRD patterns in Fig. 2, it can be noticed that $\text{g-C}_3\text{N}_4$ diffraction peak (0 0 2) intensity decreased with the increasing B content, but the B-doping process did not change its crystal structure. It can be also observed from Fig. 1 that the diffraction peaks at 21.5° , 30.5° , 35.6° , 51.0° are perfectly indexed to the (2 1 1), (2 2 2), (4 0 0), (4 4 0) crystal planes in the cubic In_2O_3 (JCPDS No. 00-006-0416), respectively. Obviously, the diffraction peaks of In_2O_3 are strengthened gradually with increasing In_2O_3 amount at the expense of those of $\text{g-C}_3\text{N}_4\text{B}$, confirming that the co-

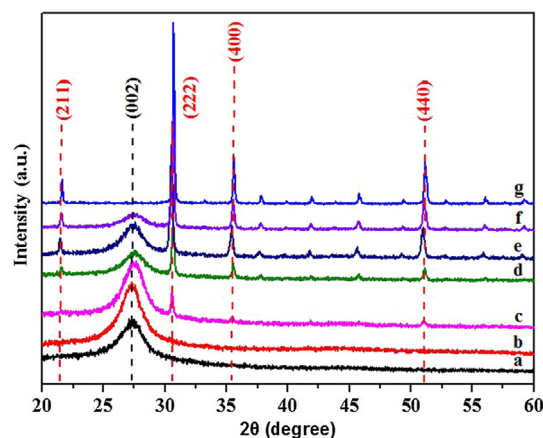


Fig. 1. XRD patterns of (a) $\text{g-C}_3\text{N}_4$, (b) $\text{g-C}_3\text{N}_4\text{B}$, (c) 1% $\text{In}_2\text{O}_3/\text{g-C}_3\text{N}_4\text{B}$, (d) 5% $\text{In}_2\text{O}_3/\text{g-C}_3\text{N}_4\text{B}$, (e) 10% $\text{In}_2\text{O}_3/\text{g-C}_3\text{N}_4\text{B}$, (f) 20% $\text{In}_2\text{O}_3/\text{g-C}_3\text{N}_4\text{B}$ and (g) In_2O_3 samples.

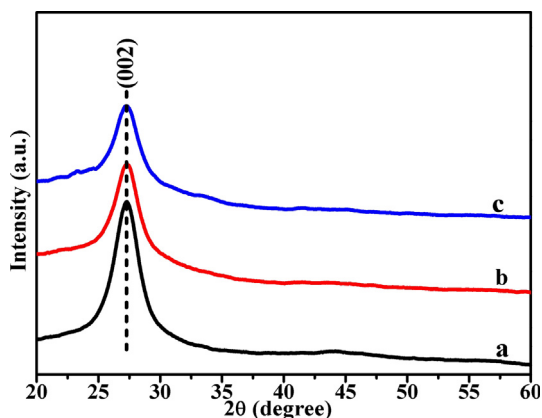


Fig. 2. XRD patterns of (a) g-C₃N₄B-2, (b) g-C₃N₄B-4, (c) g-C₃N₄B-10 samples.

existence of both In₂O₃ and g-C₃N₄B crystalline phases of In₂O₃/g-C₃N₄B samples. No other characteristic peaks are detected in the In₂O₃/g-C₃N₄B samples, suggesting that no impurity species were formed in addition to g-C₃N₄B and In₂O₃.

The results of specific surface area for g-C₃N₄, g-C₃N₄B, In₂O₃, and In₂O₃/g-C₃N₄B samples were displayed in Table 1, and it can be seen that the g-C₃N₄B (78–94 m²/g) and In₂O₃/g-C₃N₄B samples (83–91 m²/g) show a higher specific surface area than that of g-C₃N₄ (46 m²/g) or In₂O₃ (37 m²/g), which is beneficial for enhancing the photoactivity of g-C₃N₄B and In₂O₃/g-C₃N₄B samples.

The morphologies of g-C₃N₄, g-C₃N₄B, In₂O₃, In₂O₃/g-C₃N₄B samples were shown in Fig. 3. It can be noticed that the g-C₃N₄ sample shows a layered platelet-like shape [44] (Fig. 3A) and the g-C₃N₄B sample possesses a thin, silk-like hybrid nanostructure [40] (Fig. 3B). TEM images of pure In₂O₃ nanoparticles and In₂O₃/g-C₃N₄B hybrid samples were shown in Fig. 3C and Fig. 3D, respectively. It can be seen that many dark In₂O₃ nanoparticles tightly aggregates on the surface of g-C₃N₄B, corroborating that In₂O₃/g-C₃N₄B heteroarchitectures are successfully constructed. In addition, the HRTEM images (Fig. 4) of In₂O₃ and 5% In₂O₃/g-C₃N₄B samples revealed the existence of In₂O₃ nanocrystals, and the lattice fringes with d spacing of 0.294 nm could be assigned to the (2 2 2) crystal plane of cubic In₂O₃ [38].

These In₂O₃/g-C₃N₄B heterostructures were further also characterized by X-ray photoelectron spectroscopy. In the g-C₃N₄ and g-C₃N₄B samples, the C 1s XPS spectrum (Fig. 5A) could be deconvoluted into two peaks, the peak at 284.6 eV is attributed to carbon impurities, the peak at 287.9 eV is attributed to an sp²-bonded carbon (C–C=N) [40,45]. The N 1s XPS spectrum (Fig. 5B) could be deconvoluted into three peaks at 398.4, 399.6, and 400.7 eV, which are ascribed to sp²-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

Table 1

The specific surface areas, pore sizes and pore volumes data of the as-prepared catalysts calculated by BET and BJH methods.

Sample	Specific surface area (m ² /g)	Pore size (nm)	Pore volume (cm ³ /g)
g-C ₃ N ₄	46	26.7	0.216
g-C ₃ N ₄ B-2	78	25.9	0.532
g-C ₃ N ₄ B-4	94	27.4	0.561
g-C ₃ N ₄ B-10	85	26.3	0.541
1% In ₂ O ₃ /g-C ₃ N ₄ B-10	91	26.6	0.552
5% In ₂ O ₃ /g-C ₃ N ₄ B-10	89	27.6	0.548
10% In ₂ O ₃ /g-C ₃ N ₄ B-10	87	26.5	0.545
20% In ₂ O ₃ /g-C ₃ N ₄ B-10	83	26.1	0.538
In ₂ O ₃	37	3.8	0.091

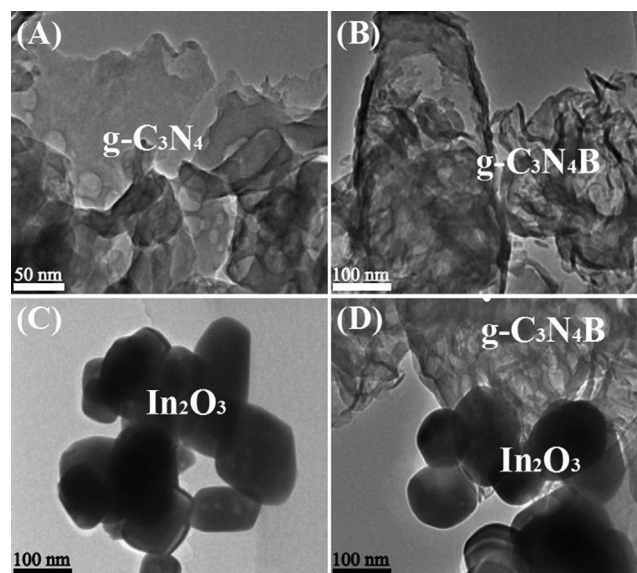


Fig. 3. TEM images of (A) g-C₃N₄, (B) g-C₃N₄B, (C) In₂O₃ and (D) 5% In₂O₃/g-C₃N₄B.

[40,45]. However, in the 5% In₂O₃/g-C₃N₄B sample, the C 1s peak binding energy (288.1 eV) and the N 1s peaks binding energy (398.7, 400.2, and 401.0 eV) are respectively higher than that of the g-C₃N₄ or g-C₃N₄B sample, which are mainly attributed to the intense interaction between In₂O₃ and g-C₃N₄B or the heterojunction formation in the In₂O₃/g-C₃N₄B sample, showing a consistency with the result of the above XRD and TEM analyses. As can be observed from Fig. 6A, an obvious B 1s XPS peak with a binding energy of ~191.6 eV is seen for g-C₃N₄B and 5% In₂O₃/g-C₃N₄B samples, corresponding to the coordination of N–B–N [40]. In Fig. 6B, the In 3d_{5/2} and 3d_{3/2} signals of In₂O₃ and 5% In₂O₃/g-C₃N₄B samples are at 444.4 eV and 451.9 eV originating from In³⁺ [38,46].

The optical performance of g-C₃N₄, g-C₃N₄B, In₂O₃, In₂O₃/g-C₃N₄B samples was shown in Fig. 7A. Comparing with g-C₃N₄, the photo-absorption ability of g-C₃N₄B is stronger and the absorption edge extends towards visible-light region, as is also reported previously by Yan et al [32]. The light absorption threshold of pure In₂O₃ is 450 nm, corresponding to ~2.8 eV band gap (Fig. 7C), which is consistent with the band gap of the In₂O₃ reported in literature [46]. Compared to g-C₃N₄ and g-C₃N₄B, the absorption band edges of In₂O₃/g-C₃N₄B photocatalysts are obviously blue-shifted with the increase of In₂O₃ content (Fig. 7A), leading to an increase in band gap energy (Fig. 7B). Moreover, the light absorption range of In₂O₃/g-C₃N₄B is between the single phases of In₂O₃ and g-C₃N₄B, indicating a strong interaction between In₂O₃ and g-C₃N₄B produced a synergistic effect in the In₂O₃/g-C₃N₄B photocatalyst [4], which is favorable to promote the separation and migration of the photogenerated charges, thus improving photocatalytic activity.

3.2. Activity and stability

The activities of g-C₃N₄, In₂O₃, g-C₃N₄B and In₂O₃/g-C₃N₄B catalysts with different In₂O₃ weight percentage were evaluated by the degradation test of tetracycline hydrochloride (TH) (Fig. 8A). From Fig. 8A, one can see that there is almost no change of TH concentration under λ > 420 nm light irradiation for 3.0 h in a lack of catalyst, showing that TH self-photodegradation can be ignored. Compared with g-C₃N₄, all the three B-doped g-C₃N₄ catalysts display better photocatalytic activity (Fig. 9). After 3 h irradiation, the TH degradation ratio of g-C₃N₄B-4 is 44.7%, which is 1.5 times that of g-C₃N₄. When In₂O₃ is used as the photocatalyst, only ~25% of TH is degraded after 3 h,

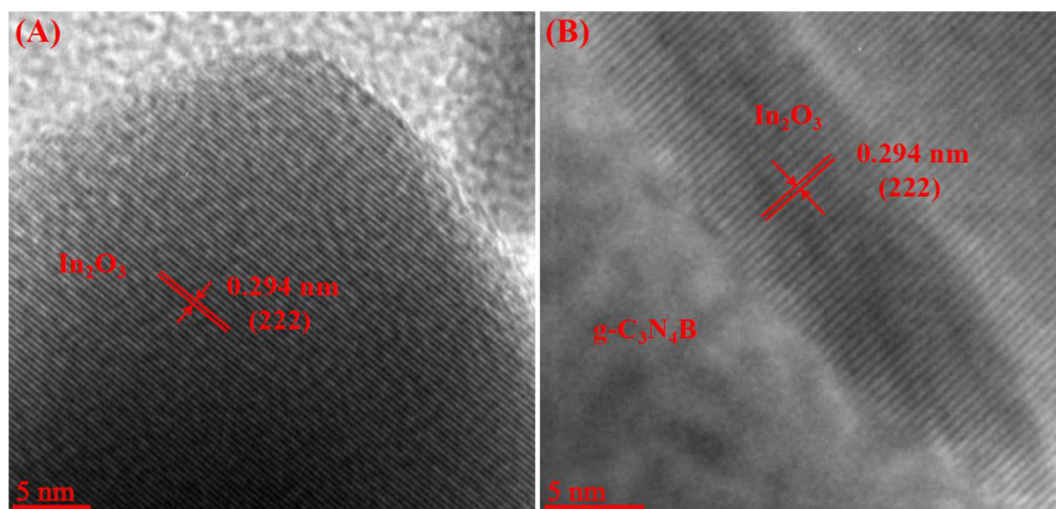


Fig. 4. HRTEM images of (A) In_2O_3 and (B) 5% $\text{In}_2\text{O}_3/\text{g-C}_3\text{N}_4\text{B}$.

showing a poor photocatalytic property. Although $\text{g-C}_3\text{N}_4\text{B-4}$ exhibits the better photodegradation activity compared with the undoped $\text{g-C}_3\text{N}_4$, only less than $\sim 45\%$ of TH is degraded. In Fig. 8A, it can also be observed that the higher photodegradation performance of TH is observed in the presence of $\text{In}_2\text{O}_3/\text{g-C}_3\text{N}_4\text{B}$ heterojunction catalysts relative to $\text{g-C}_3\text{N}_4\text{B-4}$, which significantly varies with the different amount of In_2O_3 , showing an order of 5% $\text{In}_2\text{O}_3/\text{g-C}_3\text{N}_4\text{B} > 10\%$ $\text{In}_2\text{O}_3/\text{g-C}_3\text{N}_4\text{B} > 20\%$ $\text{In}_2\text{O}_3/\text{g-C}_3\text{N}_4\text{B} > 1\%$ $\text{In}_2\text{O}_3/\text{g-C}_3\text{N}_4\text{B}$. It is noteworthy that 5% $\text{In}_2\text{O}_3/\text{g-C}_3\text{N}_4\text{B}$ possesses the best photocatalytic activity towards degradation of TH among all as-prepared catalysts and approximately 90% of TH is removed after 3 h irradiation.

The mineralization of TH in an aqueous solution was measured by monitoring the change of TOC in the reaction process by 5% $\text{In}_2\text{O}_3/\text{g-C}_3\text{N}_4\text{B}$ as a representative catalyst. It is noticed that the TOC of TH is degraded by 77%, after $\lambda > 420$ nm light irradiation for 6 h (Fig. 10), implying that TH degradation over the 5% $\text{In}_2\text{O}_3/\text{g-C}_3\text{N}_4\text{B}$ catalyst probably produces a large amount of CO_2 and H_2O .

Another typical nitric oxide (NO) pollutant was also used as a representative to investigate the activity of $\text{In}_2\text{O}_3/\text{g-C}_3\text{N}_4\text{B}$ catalysts. As shown in Fig. 8B, the concentration of NO is almost unchanged in the absence of photocatalyst, implying that the oxidation by NO itself is negligible. It can be observed from Fig. 8B, the conversion ratio of NO is low over pure In_2O_3 or $\text{g-C}_3\text{N}_4$ catalysts. Interestingly, the $\text{g-C}_3\text{N}_4\text{B}$ and $\text{In}_2\text{O}_3/\text{g-C}_3\text{N}_4\text{B}$ catalysts show significantly higher activity than that of In_2O_3 or $\text{g-C}_3\text{N}_4$. Further observation indicates that the activity of

$\text{In}_2\text{O}_3/\text{g-C}_3\text{N}_4\text{B}$ catalysts highly depended on the amount of incorporated In_2O_3 . The photocatalytic efficiency for NO conversion shows a same trend to that of HT degradation with the increase of In_2O_3 content in $\text{In}_2\text{O}_3/\text{g-C}_3\text{N}_4\text{B}$ catalysts.

In addition, the CO_2 photocatalytic reduction into CH_4 reaction was also performed to evaluate the activity of In_2O_3 , $\text{g-C}_3\text{N}_4$, $\text{g-C}_3\text{N}_4\text{B}$, and $\text{In}_2\text{O}_3/\text{g-C}_3\text{N}_4\text{B}$ catalysts, using Pt as a cocatalyst. Fig. 8C indicates the CH_4 production rates for Pt loaded In_2O_3 , $\text{g-C}_3\text{N}_4$, $\text{g-C}_3\text{N}_4\text{B}$, and $\text{In}_2\text{O}_3/\text{g-C}_3\text{N}_4\text{B}$ heterojunction photocatalysts. It can be observed that the activity for CH_4 evolution displays a similar tendency to that of HT and NO conversion with the increase of In_2O_3 content in $\text{In}_2\text{O}_3/\text{g-C}_3\text{N}_4\text{B}$ catalysts. The photocatalytic CH_4 evolution rate ($4.8 \mu\text{mol h}^{-1} \text{g}^{-1}$) of 5% $\text{In}_2\text{O}_3/\text{g-C}_3\text{N}_4\text{B}$ is 9.0, 3.6, 2.2 and 2.5 times higher than that of In_2O_3 , $\text{g-C}_3\text{N}_4$, $\text{g-C}_3\text{N}_4\text{B}$ and $\text{g-C}_3\text{N}_4\text{B-R}$ (reference sample), respectively, further confirming the synergistic effect of In_2O_3 and $\text{g-C}_3\text{N}_4\text{B}$ in photocatalytic reaction. During the photocatalytic CO_2 conversion reaction, 5% $\text{In}_2\text{O}_3/\text{g-C}_3\text{N}_4\text{B}$ also shows a better photocatalytic performance on hydrogen production, and the average hydrogen production rate on 5% $\text{In}_2\text{O}_3/\text{g-C}_3\text{N}_4\text{B}$ is $15.7 \mu\text{mol g}^{-1} \text{h}^{-1}$, being almost 9.5-, 5.8-, 3.5- and 4.1- times superior to that for In_2O_3 ($1.65 \mu\text{mol g}^{-1} \text{h}^{-1}$), $\text{g-C}_3\text{N}_4$ ($2.71 \mu\text{mol g}^{-1} \text{h}^{-1}$), $\text{g-C}_3\text{N}_4\text{B}$ ($4.43 \mu\text{mol g}^{-1} \text{h}^{-1}$) and $\text{g-C}_3\text{N}_4\text{B-R}$ ($3.86 \mu\text{mol g}^{-1} \text{h}^{-1}$), respectively. Moreover, to emphasize the importance of good interconnection between $\text{g-C}_3\text{N}_4\text{B}$ and In_2O_3 for $\text{In}_2\text{O}_3/\text{g-C}_3\text{N}_4\text{B}$ heterojunction catalysts, 5% $\text{In}_2\text{O}_3/\text{g-C}_3\text{N}_4\text{B}$ (physical mixture) was also measured for CO_2 photo-reduction (Fig. 8C).

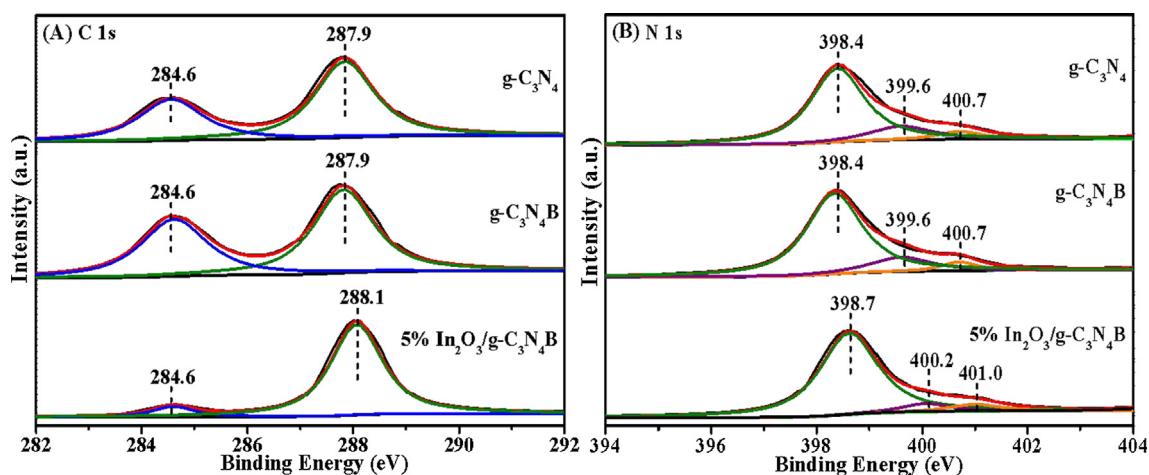


Fig. 5. XPS spectra of C 1s (A) and N 1s (B) for $\text{g-C}_3\text{N}_4$, $\text{g-C}_3\text{N}_4\text{B}$ and 5% $\text{In}_2\text{O}_3/\text{g-C}_3\text{N}_4\text{B}$.

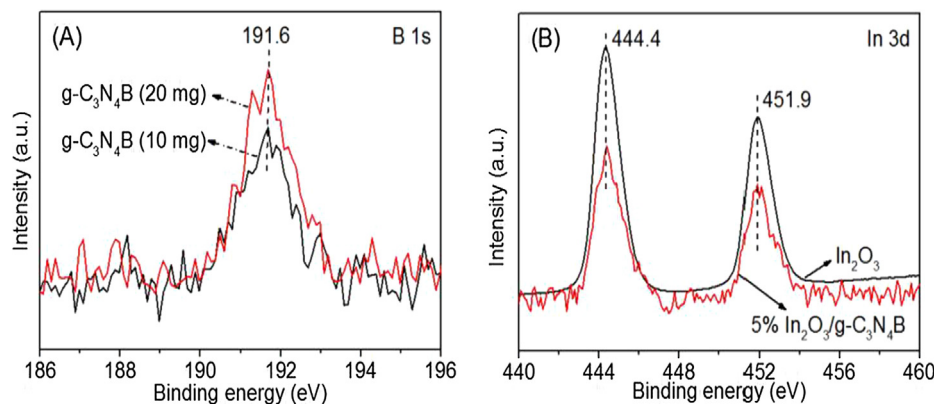


Fig. 6. XPS spectra of B 1s (A) for g-C₃N₄B prepared by using 10 and 20 mg C₂₄H₂₀BNa as a precursor, respectively; XPS spectra of In 3d (B) for In₂O₃ and 5% In₂O₃/g-C₃N₄B samples.

Obviously, the CH₄ evolution rate of 5% In₂O₃/g-C₃N₄B (physical mixture) is lower than that of the 5% In₂O₃/g-C₃N₄B heterojunction catalyst, showing the merit of hybridization.

The stability of 5% In₂O₃/g-C₃N₄B was also studied by recycling the catalyst for TH degradation, NO conversion, and CO₂ photocatalytic reduction into CH₄ under $\lambda > 420$ nm light irradiation. It can be clearly seen in Fig. 11 that there was no obvious deactivation on the activity after three consecutive runs, and the crystal structure of 5% In₂O₃/g-C₃N₄B remained no change after TH degradation, NO conversion and CH₄ evolution (Fig. 12), indicating the excellent stability of 5% In₂O₃/g-C₃N₄B catalyst.

3.3. Scavenger in TH degradation

To elucidate the photocatalytic mechanism of In₂O₃/g-C₃N₄B catalysts, the active species of HT photodegradation process were studied by trapping experiments. Three different quenchers, AO (ammonium oxalate), IPA (isopropanol), and BQ (benzopinone) were employed as h⁺ (hole), ·OH (hydroxyl radical) and ·O₂⁻ (superoxide radical) scavenger [42,47], respectively. In Fig. 13, a slight variation with the addition of IPA in the TH degradation efficiency is observed, indicating that hydroxyl radical is not crucial activity species in TH degradation process. However, TH degradation is suppressed by the AO and BQ addition, implying that hole and superoxide radical play an important roles in TH degradation. Furthermore, an obvious decrease of TH

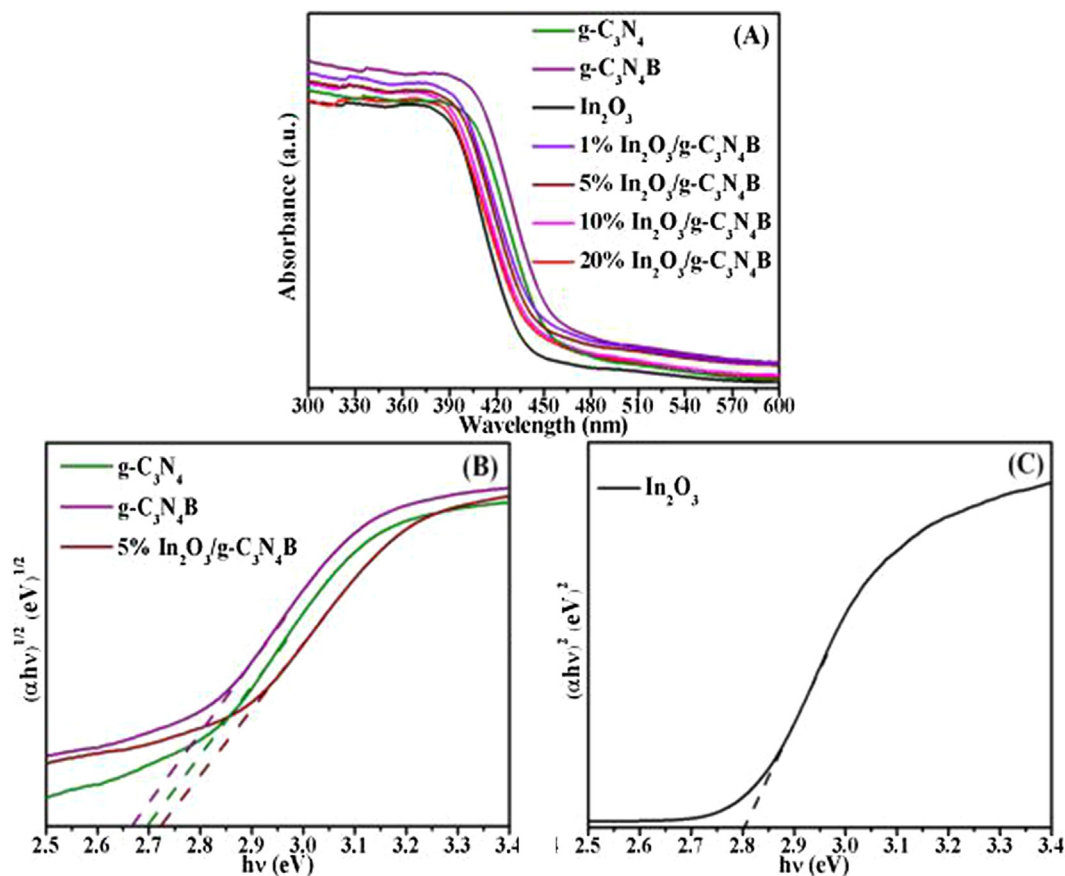


Fig. 7. (A) UV-Vis DRS of g-C₃N₄, g-C₃N₄B, 1% In₂O₃/g-C₃N₄B, 5% In₂O₃/g-C₃N₄B, 10% In₂O₃/g-C₃N₄B, 20% In₂O₃/g-C₃N₄B, In₂O₃; Kubelka-Munk-transformed reflectance spectra of (B) g-C₃N₄, g-C₃N₄B, 5% In₂O₃/g-C₃N₄B and (C) In₂O₃.

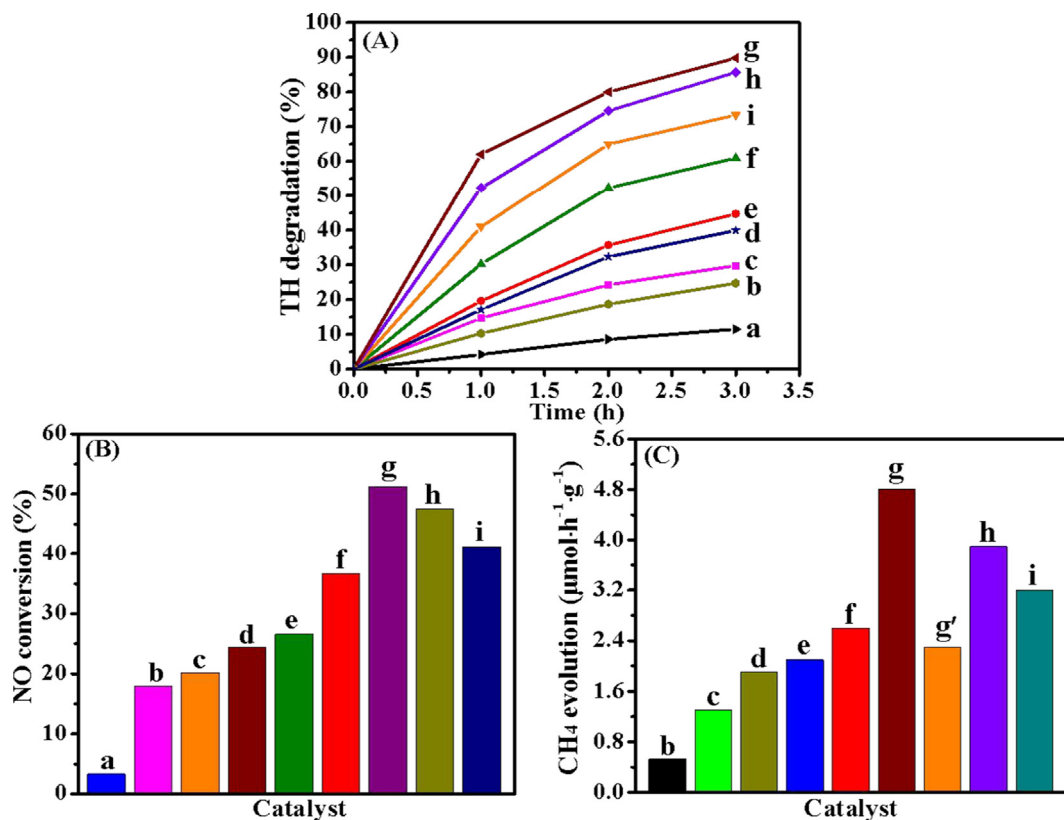


Fig. 8. Photocatalytic activity of TH degradation (A), NO conversion (B) and CH₄ evolution (C) for (a) blank, (b) In₂O₃, (c) g-C₃N₄, (d) g-C₃N₄B-R (reference sample), (e) g-C₃N₄B, (f) 1% In₂O₃/g-C₃N₄B, (g) 5% In₂O₃/g-C₃N₄B, (g') 5% In₂O₃/g-C₃N₄B (physical mixture), (h) 10% In₂O₃/g-C₃N₄B, (i) 20% In₂O₃/g-C₃N₄B catalysts.

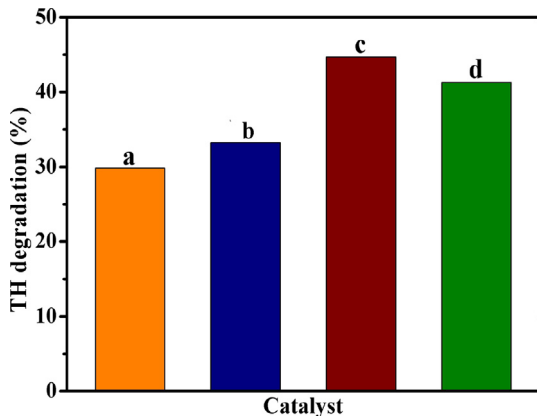


Fig. 9. The photocatalytic degradation of tetracycline hydrochloride (TH) for g-C₃N₄, (b) g-C₃N₄B-2, (c) g-C₃N₄B-4, and (d) g-C₃N₄B-10 catalysts under visible light irradiation ($\lambda > 420$ nm) for 3 h.

degradation ratio can also be observed in N₂ atmosphere, showing that oxygen (O₂) can mainly act as e⁻ (electron) traps to produce superoxide radical ([•]O₂⁻).

Therefore, the reactions of TH photodegradation are proposed in Eqs. (1)–(4):

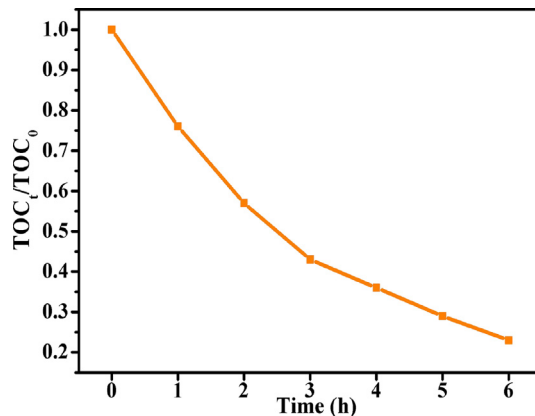
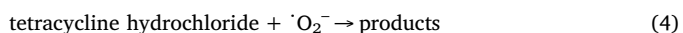
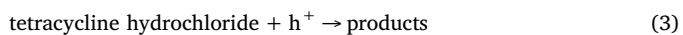
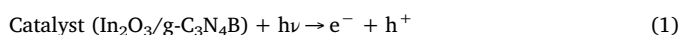


Fig. 10. Evolution of TOC during the course of photocatalytic degradation of tetracycline hydrochloride (TH) for 5% In₂O₃/g-C₃N₄B catalyst under visible light irradiation.

3.4. Photocatalytic activity enhancement mechanism of In₂O₃/g-C₃N₄B

In g-C₃N₄ framework, the boron (B) doping enhanced its light absorption and reduced its band gap, as shown in Fig. 7. Moreover, the surface boron sites can serve as Lewis acids [40], improving the separation efficiency of photo-induced electron-hole pairs, and promoting the surface reactivity. Hence, a proper B-doping resulted in an obvious activity enhancement of g-C₃N₄ (Fig. 8).

Based on the above results, the activity enhancement of In₂O₃/g-C₃N₄B catalysts may mainly originate from the synergism of nonmetal boron, cubic In₂O₃ and 2D g-C₃N₄, and the formation of heterojunctions between In₂O₃ and g-C₃N₄B.

Compared with 20% In₂O₃/g-C₃N₄B (83 m²/g), the 5% In₂O₃/g-

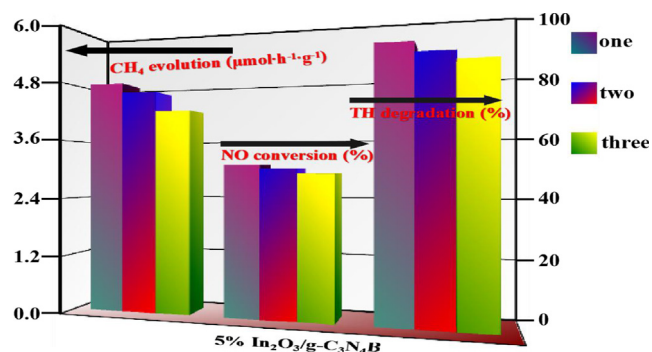


Fig. 11. Stability test of TH degradation, NO conversion and CH₄ evolution for 5% In₂O₃/g-C₃N₄B recycling three times under visible-light irradiation ($\lambda > 420$ nm).

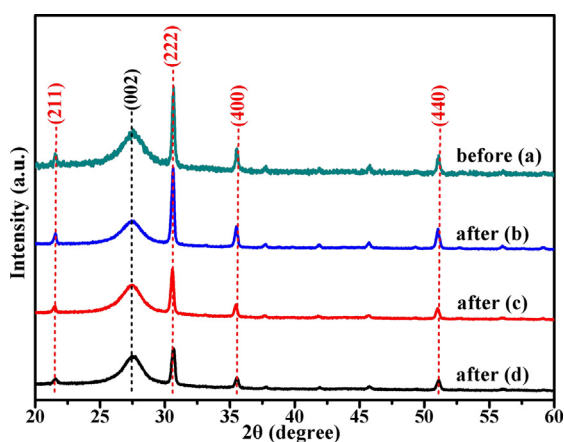


Fig. 12. XRD patterns of 5% In₂O₃/g-C₃N₄B before (a) and after TH degradation (b), NO conversion (c) and CH₄ evolution (d).

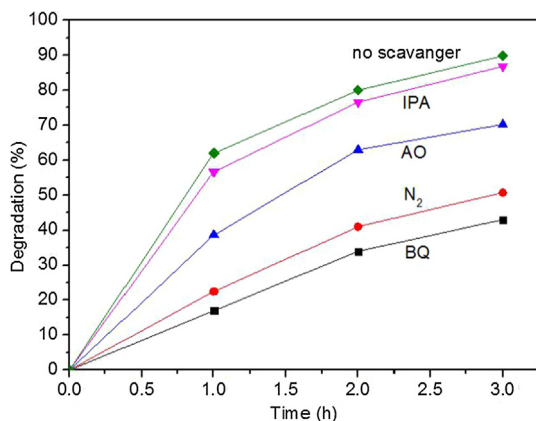


Fig. 13. The influence of various scavengers on the visible-light photocatalytic activity of 5% In₂O₃/g-C₃N₄B towards the degradation of TH.

C₃N₄B (89 m²/g) catalyst has comparable specific surface areas and similar optical absorption (Fig. 7), but its photocatalytic activities in the photocatalytic conversion of TH and NO, and photocatalytic reduction of CO₂ (Fig. 8) three aspects are obviously higher than those of 20% In₂O₃/g-C₃N₄B, implying that there is another crucial factor influencing its photocatalytic property. Therefore, the separation efficiency of photo-generated carriers might play a crucial role in influencing the activity of catalysts. For the sake of revealing the charge separation on the interfaces of In₂O₃/g-C₃N₄B, the band potentials of g-C₃N₄B and In₂O₃ were investigated.

The photocatalytic performance is generally believed to be tightly

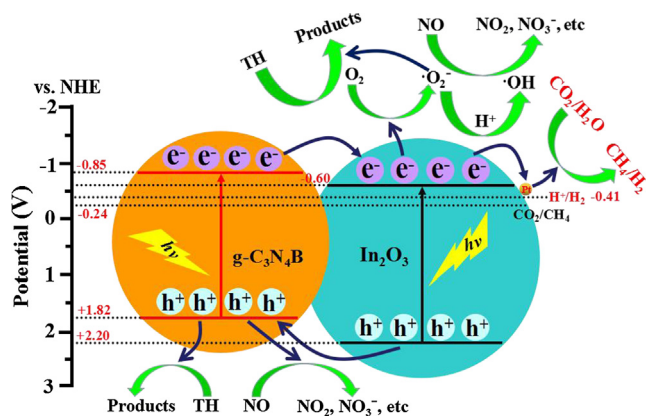


Fig. 14. The generation, transportation, and separation of visible-light-induced charge carries over the In₂O₃/g-C₃N₄B catalyst.

related to the redox potential and band structure of catalysts. Therefore, the activity enhancement mechanism for In₂O₃/g-C₃N₄B heterojunction catalyst may be reasonably explained by the scheme depicted in Fig. 14. According to theoretical calculation and previous reports [33,38,42,48,49], the top valence band potential (E_{VB}) and bottom conduction band potential (E_{CB}) for g-C₃N₄B and In₂O₃ are about +1.82 and -0.85 V, +2.20 and -0.60 V (vs. NHE), respectively. This indicates that the valence band top potential of In₂O₃ is more positive than that of g-C₃N₄B, whereas the conduction band bottom position of g-C₃N₄B is more negative than that of In₂O₃. When the In₂O₃/g-C₃N₄B photocatalyst is irradiated by visible light with the greater energy than the E_g (band-gap energy) of In₂O₃ and g-C₃N₄B, the e⁻ (electron) in the VB of In₂O₃ and g-C₃N₄B is excited to their CB, leading to the generation of hole in their VB. Then the band alignment between them can not only drive the photo-generated electrons in g-C₃N₄B to transfer towards the In₂O₃, but also drive the photo-induced holes in In₂O₃ transfer towards the g-C₃N₄B by valence band offset. Due to noble metal Pt can act as a superior acceptor and trapping site for photo-excited electrons, the photoinduced electrons would quickly transfer to the loaded Pt metal and then excited state electron can be quickly transfer to absorbed CO₂, forming the 'CO₂⁻ radical [50–52]. Meanwhile, the H⁺ react with the excited electrons and form 'H radicals. Finally, 'CO₂⁻ and 'H radicals react with each other to produce CH₄ [51,52]. Thus the photo-generated electron-hole pairs will be separated effectively by an interface formed in the heterostructure, leading to the activity improvement eventually. Moreover, the phenomenon was also confirmed by below-mentioned photoluminescence spectroscopy (Fig. 15A), photocurrent tests and EIS (electrochemical impedance spectroscopy) results (Fig. 16). The photo-generated electrons gathered in the conduction band of In₂O₃ principally react with the surface hydroxyls and adsorbed oxygen (O₂) molecules, to ultimately form ·OH (hydroxyl radicals) and ·O₂⁻ (superoxide radicals) reacting with the surface pollutants (TH, NO) of In₂O₃. At the same time, the corresponding photo-generated holes in the valence band of g-C₃N₄B can oxidize its surface pollutants (TH, NO) directly. And the possible reaction path is also shown in Fig. 14. Consequently, the heterojunction construction in the In₂O₃/g-C₃N₄B catalyst promoted the efficient separation of photo-generated electrons and holes, accelerating the photocatalytic reaction.

Photoluminescence (PL) emission spectroscopy is commonly performed to further verify the enhanced photo-excited charge separation efficiency [53]. The photoluminescence emission spectra of g-C₃N₄, g-C₃N₄B, 5% In₂O₃/g-C₃N₄B catalysts recorded under an excitation wavelength of 400 nm are presented in Fig. 15A. As can be observed, the peak positions of three catalysts are almost same, suggesting that there is no new photoluminescence with the introduction of boron and In₂O₃. The PL intensity of g-C₃N₄ is the highest among them, representing the high recombination probability of excited electrons and holes. Upon

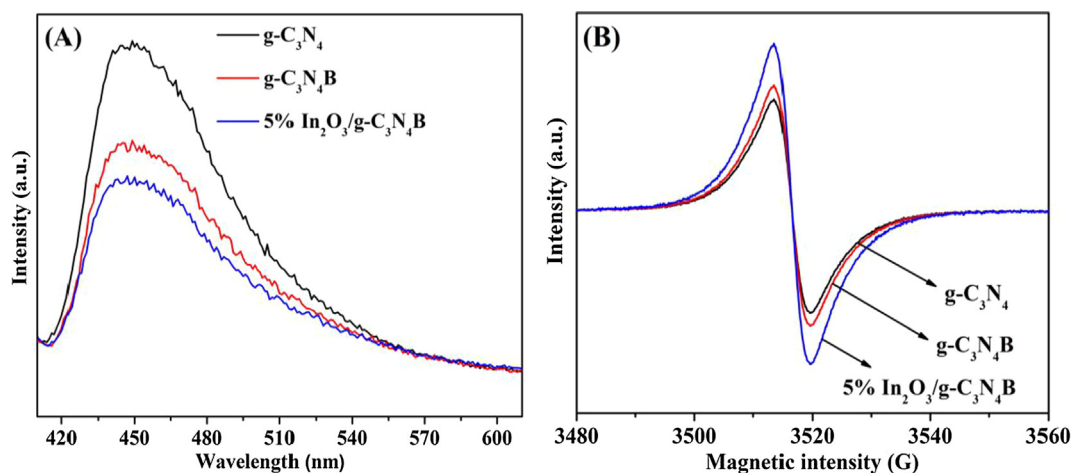


Fig. 15. PL(A) and EPR (B) spectra of g-C₃N₄, g-C₃N₄B and 5% In₂O₃/g-C₃N₄B catalysts.

doping boron into g-C₃N₄ the PL intensity obviously decreased, which is in accordance with the reported result [32]. It should be noted that the 5% In₂O₃/g-C₃N₄B catalyst exhibits the lowest emission intensity, implying that the charge separation is greatly enhanced due to the cooperative effect of In₂O₃ and boron.

Fig. 15B shows the EPR (electron paramagnetic resonance) spectra of g-C₃N₄, g-C₃N₄B, 5% In₂O₃/g-C₃N₄B catalysts. A Lorentzian line was centered at $g = 2.0034$ that can be seen, suggesting that the unpaired electrons were formed in π -conjugated aromatic rings of carbon nitride [54]. Obviously, this Lorentzian line is heightened after In₂O₃/g-C₃N₄B heterojunction formation, presumably owing to π electrons redistribution in the 5% In₂O₃/g-C₃N₄B catalyst by band offsets [42]. Therefore, through the optimization of electronic band structure, the heterojunction formation between In₂O₃ and g-C₃N₄B is advantageous to the separation and migration of electron-hole pairs.

Fig. 16A shows the EIS (electrochemical impedance spectroscopy) of g-C₃N₄, g-C₃N₄B, 5% In₂O₃/g-C₃N₄B catalysts under $\lambda > 420$ nm light irradiation. Obviously, the Nyquist plot diameter shows an order of g-C₃N₄ > g-C₃N₄B > 5% In₂O₃/g-C₃N₄B, validating that the joint action of In₂O₃, B and g-C₃N₄ promotes the 5% In₂O₃/g-C₃N₄B catalyst with a smaller electronic resistance. Moreover, the response results of transient photocurrent in Fig. 16B also supported the above outcomes. Under $\lambda > 420$ nm light irradiation, in contrast to both g-C₃N₄ and g-C₃N₄B, the 5% In₂O₃/g-C₃N₄B heterojunction catalyst exhibits a remarkably enhanced photocurrent density, which is 1.64 and 1.30 times higher than that of g-C₃N₄ and g-C₃N₄B, respectively. This result confirms that the more efficient charge migration and separation of 5% In₂O₃/g-C₃N₄B than that of g-C₃N₄ or g-C₃N₄B [55–58], which is also consistent with the results of photoluminescence emission spectroscopy

(Fig. 15A).

Therefore, the photocatalytic activity of In₂O₃/g-C₃N₄B catalysts firstly increases with the increase of In₂O₃ content (Fig. 8). However, when In₂O₃ amount is > 5% in the In₂O₃/g-C₃N₄B catalyst, excess In₂O₃ might result in a decrease in the interface area between In₂O₃ and g-C₃N₄B, which is disadvantageous to the separation and transfer of photo-induced electron-hole pairs [38]. As a consequence, the In₂O₃/g-C₃N₄B catalyst with a suitable In₂O₃ content (weight percents of 5%) shows the highest photocatalytic activity among all catalysts.

4. Conclusions

In₂O₃/g-C₃N₄B heterojunction catalysts were prepared by a simple synthetic route. The 5% In₂O₃/g-C₃N₄B catalyst with a proper In₂O₃ and B content possesses excellent photocatalytic properties in TH and NO oxidation, and CO₂ reduction. Moreover, the possible mechanism on the enhanced activity of 5% In₂O₃/g-C₃N₄B was also discussed in detail. In addition, 5% In₂O₃/g-C₃N₄B shows enough catalytic stability. This work has provided some important information in environment and energy applications of such a multifunctional heterojunction catalyst with excellent photocatalytic performance.

Declaration of Competing Interest

The authors declare that there is no conflict of interest.

Acknowledgements

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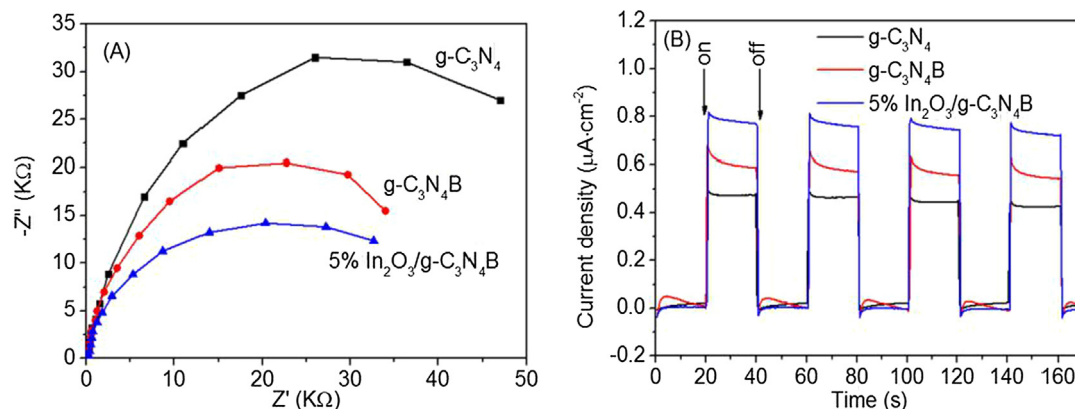


Fig. 16. Electrochemical impedance spectroscopy (A) and transient photocurrents (B) over g-C₃N₄, g-C₃N₄B and 5% In₂O₃/g-C₃N₄B catalysts.

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