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Enhanced photo catalytic activity of alkaline treated carbon dots/g-C₃N₄

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Abstract— The photocatalytic activity of bulk graphitic carbon nitride (g-C₃N₄) is limited by the high recombination of electron-hole pairs. A lot of efforts have been performed to enhance the photocatalytic performance of g-C₃N₄ (g-CN). For example, 1) increase visible light absorption by doping foreign element; 2) promote the separation of photo generated electron-hole pairs by surface functionalization or coupling g-CN with another semiconductor. 3) Increase specific surface area by the introduction of mesoporous g-CN. 4) Shorten the photo generated electron-hole mobility distance by exfoliated g-CN. Previous research showed that the loading carbon dots have been achieved to improve the photocatalytic activity of g-CN because the particles can act as electron trapping site to inhibit the recombination of photo induced charges and expanding the light absorbing region. In recent years, alkaline treatment was adapted to modify the morphology of g-CN, and it is very effective on the photocatalytic performance. However, alkaline treatment has not been utilized carbon dots loading on the g-CN. In this work, novel carbon dots and g-CN composite photo catalysts which were adapted alkaline treatment were synthesized. The composite samples were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), nitrogen-adsorption, UV-Vis diffuse reflectance spectra (DRS), photoluminescence spectra (PL), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Photocatalytic activity of alkaline treated carbon dots modified g-CN (C/g-CN) was evaluated by photocatalytic hydrogen production under visible irradiation ($\lambda \geq 420$ nm). In a conclusion, we successfully synthesized the novel alkaline treated C/g-CN composite. The highest photocatalytic hydrogen evolution rate for 0.5 wt% alkaline treated C/g-CN was approximately 480 $\mu\text{mol/g}\cdot\text{h}$, which was about 48 times higher than that of pure g-CN.

Index Terms— Photo catalyst, g-C₃N₄, Carbon dots, Hydrogen, Visible light.

I. INTRODUCTION

Recently, energy shortage has been concerned all over the world because fossil fuels which are most used energy resource will be vanished in the future. Therefore, developing new energy resources are very important [1]. Photocatalytic hydrogen production is one of the most promising methods to produce clean energy. Nowadays, graphitic carbon nitride (g-C₃N₄) has attracted attention as a visible light responsive photo catalyst [2]. However, the photocatalytic activity of g-C₃N₄ is limited by the high recombination rate of its photo generated charge carriers [3].

To enhance the photocatalytic activity of g-CN, a lot of efforts were carried out, for example, For example, (1) increase visible light absorption by doping foreign element, (2) promote the separation of photo generated electron-hole pairs by surface functionalization or coupling g-CN with another semiconductor, (3) increase specific surface area by the introduction of mesoporous g-CN, and (4) shorten the photo generated electron-hole mobility distance by exfoliated g-CN [4]. Previous our report showed the loading carbon dots on the g-C₃N₄ is very effective on enhanced photocatalytic activity of g-C₃N₄ because carbon dots can act as electron reservoirs to inhibit the recombination of electron-hole pairs. Also, those particles made the light absorbing region of g-C₃N₄ expanding [5]. Recently, alkaline treatment was adapted to modify the morphology of g-CN, and it is very effective on the photocatalytic performance [6]. However, alkaline treatment has not been utilized carbon dots loading on the g-CN.

In this work, to enhance the photocatalytic activity of g-C₃N₄, novel carbon dots and g-C₃N₄ composite photo catalysts were synthesized by calcination process followed by alkaline treatment. Those composites were evaluated by the photocatalytic hydrogen production under visible light ($\lambda \geq 420$ nm) and characterized by some instrumental analysis.

A. Preparation of carbon dots

All chemicals were reagent-grade and used without further purification. Firstly, 3.6 g of glucose was dissolved in distilled water (40 mL) to form a clear solution, then 40 mL of concentrated HCl solution was dropped into the solution of glucose. Afterward, the mixture solution was transferred into a 100 mL Teflon liner followed by hydrothermal treatment at 180 °C for 6 h. After hydrothermal reaction, the black precipitates were centrifuged and get brown carbon dots solution.

B. Preparation of C/ g-CN

Carbon dots and g-CN composite photo catalysts were prepared by two step calcination of the mixture of carbon dots and melamine. Before calcination, 5 mL of carbon dots suspension in ethanol was added into 3 g of melamine, and then ethanol was evaporated. This obtained ingredient was calcined 650 °C for 3 h. Pure g-CN was prepared by above calcination condition excluding adding carbon dots suspension.

C. Preparation of base treated photo catalysts

Base treatment was performed following method. Firstly, 90 mL NaOH aqueous solution (0.1 M) was dropped into the 1.0 g photo catalyst. After that, this solution was transferred into 100 mL Teflon liner followed by hydrothermal treatment at 110 °C for 18 h. After that, this solution was washed and removed supernatant by using centrifuge. Precipitate was dried and we got base treated photo catalysts. To confirm the optical base treatment condition, we changed temperature, times and base concentration of base treatment. Also we checked the optical loading amount of base treated C/ g-CN. The samples loading carbon dots 0.2, 0.35, 0.5, 1.0, 2.0 wt% were named as 0.2, 0.35, 0.5, 1.0, 2.0 BtCCN, respectively. Pure g-CN, base treated g-CN, C/ g-CN were defined g-CN, BtCN and CCN respectively.

D. Characterization of synthesized samples

Physicochemical measurement of the samples were characterized by XRD (RIGAKU, Ultima IV, FT-IR (Perkin Elmer, Spectrum 100), XPS (Ulvac PHI, Quantera SXM), nitrogen-sorption (Microtrac BEL, BELSORP-mini II), DRS (SHIMADZU, UV 2450), PL (SHIMADZU, RF-5300PC), SEM (HITACHI, S-4000), and TEM (JEOL, JEM-1011).

E. Evaluation of photo catalytic activity

The pyrex column vessel reactor (inner volume: 123 mL) was used for the photocatalytic H₂ production from aqueous solution (40 mL) containing 10 vol% triethanolamine (TEA) as a sacrificial donor. 2 wt% Pt loaded on the surface of the photo catalyst by the in situ photo deposition method using H₂PtCl₆. Before irradiation, N₂ gas was bubbled into the reaction solution for 30 min to remove a dissolved O₂. Typically, 40 mg of the photo catalyst was added into the reaction solution. A 300 W Xe lamp with a UV cut filter ($\lambda < 420$ nm) was applied as a light source. The concentration of H₂ production from the aqueous TEA solution was analyzed by GC with TCD. Fig. 1 shows the photo reactor for photo catalytic hydrogen production as a follow.

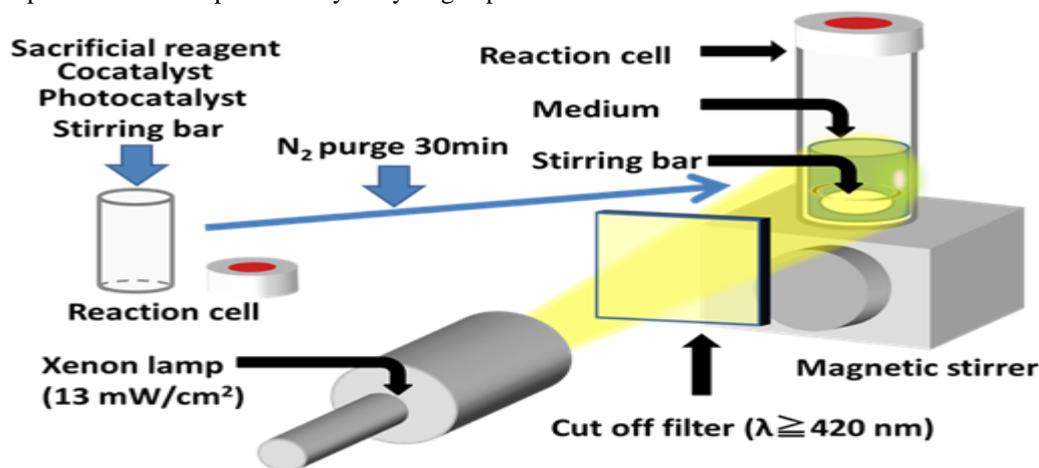


Fig. 1: Photo reactor for photo catalytic hydrogen production experiments

A. Structural and chemical characterizations

The structures of the as-synthesized g-CN, CCN and 0.5 BtCCN were characterized by XRD and two distinct peaks are exhibited in all XRD patterns in Fig. 2. The strongest peaks at $2\theta = 27^\circ$ are due to the interlayer-stacking of aromatic systems as in graphite, indexed as (0 0 2) peaks [7]. It is observed that (0 0 2) peaks were broadened and the intensity of these peaks decreased after the alkaline hydrothermal treatment, reflecting that the alkaline hydrothermal treatment could reduce the grain size of g-CN. And it has been reported that small grain size enhance the photocatalytic activity because of increased restive sites as well as the promoted electron-hole separation efficiency [8]. Moreover, the (0 0 2) peaks in treated samples broadened toward lower 2θ value indicate an increasing of the average inter-layer distance. Additionally, lower peaks at $2\theta = 13.1^\circ$, indexed to (1 0 0) plane corresponding to the in-plane structural packing motif [7], are not observed remarkable variations. These results illustrate that the stacked g-CN layers were peeled by the alkaline hydrothermal treatment, but the in-plane structure is retained after the treatment.

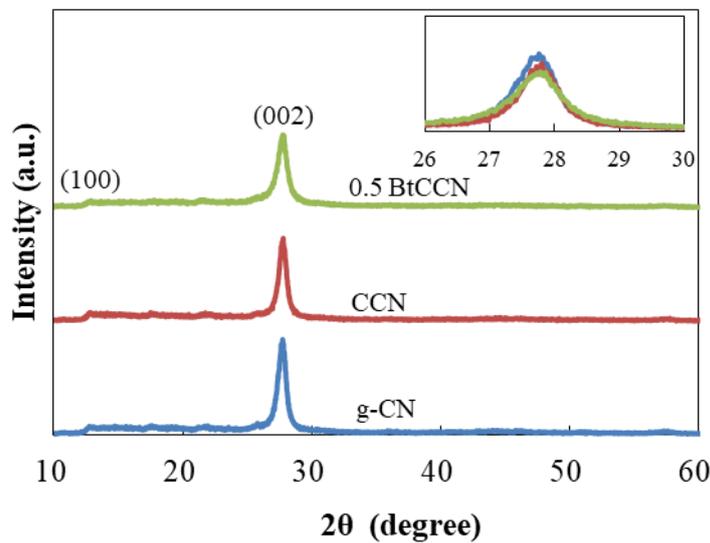


Fig. 2: XRD patterns of g-CN, CCN and 0.5 BtCCN.

Fig. 3 shows the nitrogen adsorption-desorption isotherms of the as-synthesized g-CN, CCN and 0.5BtCCN. The nitrogen adsorption-desorption isotherms with typical Type IV behavior indicates the presence of porous structure [9]. It is believed that the hierarchical porous structure could possess larger light-harvesting capacity and provide more reactive sites for photocatalytic reactions [10]. Through Barret-Joyner-Halender (BJH) method, the pore size distributions (Fig. 3 inset) of g-CN, CCN, and BtCCN were obtained. Especially, the pore size distribution of 0.5 BtCCN was high relatively around 10 nm.

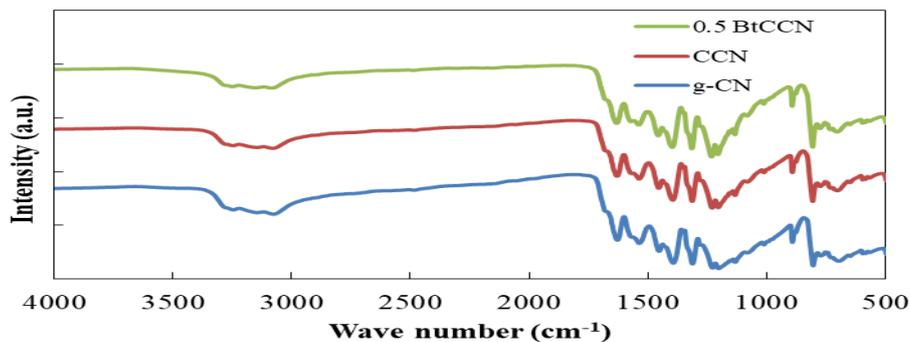


Fig. 3: Nitrogen adsorption-desorption isotherms and BJH plots of g-CN, CCN and 0.5 BtCCN

The structural keeping can be confirmed by the unchanged absorption bands at $1600\text{--}1200\text{ cm}^{-1}$ and 810 cm^{-1} , respectively, corresponding to the stretching vibrations of CN heterocycles and the characteristic breathing mode of s-triazine in FT-IR spectra (Fig. 4) [6].

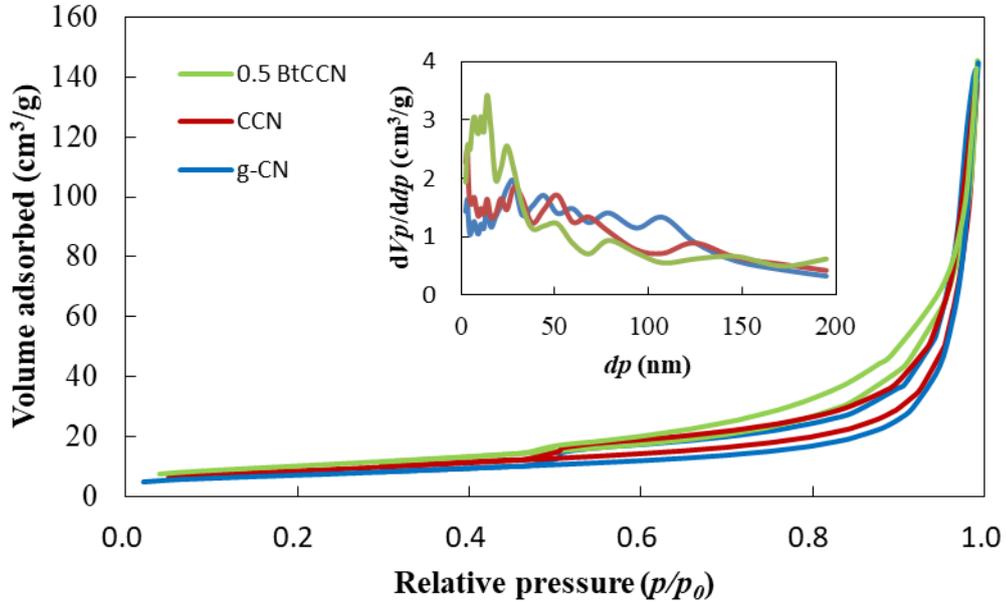


Fig. 4: FT-IR spectra of g-CN, CCN and BtCCN.

Fig. 5 displays the SEM images of the morphology and the microstructure of the as-synthesized g-CN, CCN and 0.5 BtCCN. Fig. 5a and b indicate the layered, stacked texture and the smooth surface morphology of the as-synthesized bulk g-CN. By contrast, BtCCN, as shown in Fig. 5c, exhibits small fragmented particles with abundant irregular porous structures on their surface. The differences of shape and morphology demonstrate that the alkaline treatment could not only break the bulk g-CN into small fragments, but yield some hole-shaped defects on the surface as well. These phenomena may result from the partial decomposition of unstable defective region on the partly imperfect polymer-like structure of the as-synthesized bulk g-CN under the condition of alkaline solution and appropriate temperature [11]. Therefore, it is inferred that the NaOH solution could be applied to the modification of g-CN that would bring about fragmented. Moreover, the presence of small fragmented g-CN particles instead of large bulk ones accords well with the result from XRD analysis that the grain size of g-CN decreases after the treatment.

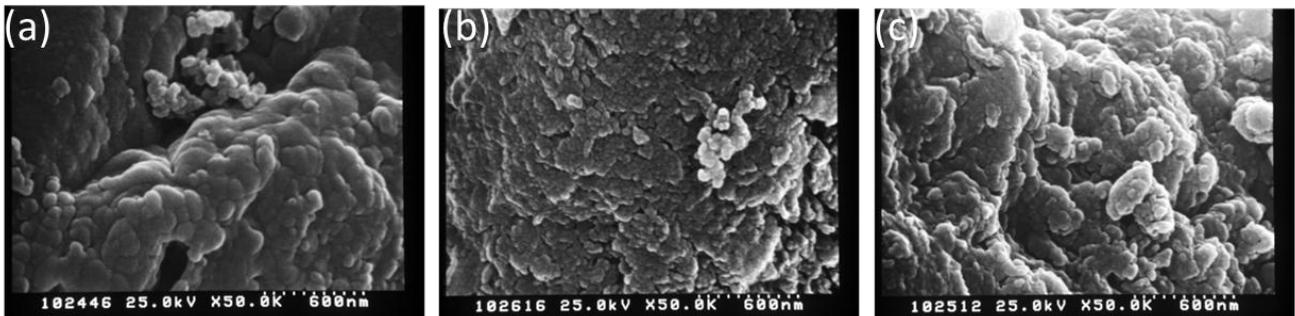


Fig. 5: SEM images of (a) g-CN, (b) CCN and (c) 0.5 BtCCN.

The morphology of g-CN, CCN and 0.5 BtCCN were further observed by TEM technology (Fig. 6), where some nanobelt-like particles with size of several hundred nanometers were revealed [6]. However, nanobelt-like particles of 0.5 BtCCN were shorter than those of g-CN and CCN. It implied that the stacked layers of g-CN were

peeled by alkaline treatment. In addition, the mottled pattern of black was observed TEM images of CCN and 0.5 BtCCN. It represented the existence of carbon dots.

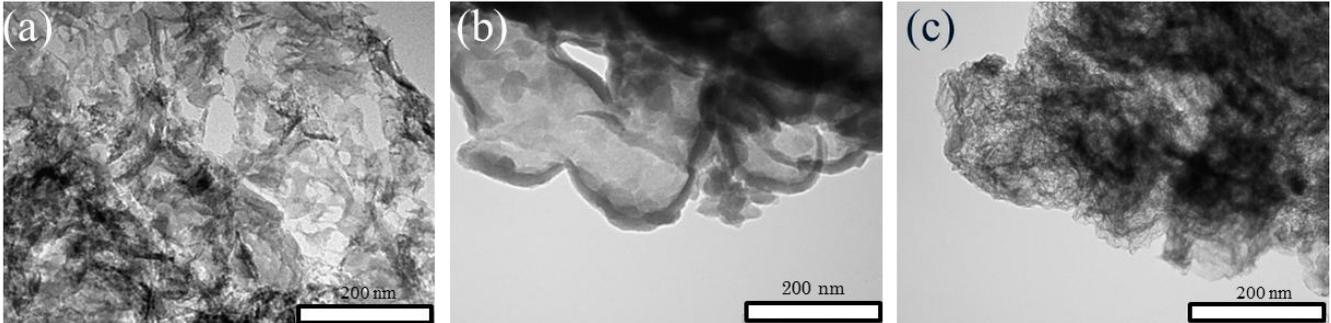


Fig. 6: TEM images of g-CN, CCN and 0.5 BtCCN.

In addition, XPS is used to investigate the chemistry environment of surface elements, as shown in Fig. 7. The elements of C, N and O were detected in the survey spectrum (Fig. 7a). The C 1s spectra of g-CN and BtCN (Fig. 7b) depicts two peaks located at the binding energies of 284 eV and 288 eV that are respectively attributed to the existence of sp² C-C bonds and the sp²-hybridized C (N-C=N) in the aromatic skeleton rings of g-CN. The similar spectra indicates the preservation of CN heterocycles after the alkali treatment [12]. Their N 1s spectra can be divided into three peaks (Fig. 7c), 398 eV related to C-N=C groups, 399 eV corresponding to N-(C)₃ units, 400 eV attributed by N-H bonds [13–16] and 404 eV involved in π-π* conjugation. The relative contents of these three N species are listed in Fig. 7d. An evident change in the relative content of N-(C)₃ and N-H after the alkaline treatment is ascribed to the hydrolysis of N-(C)₃ bonds.

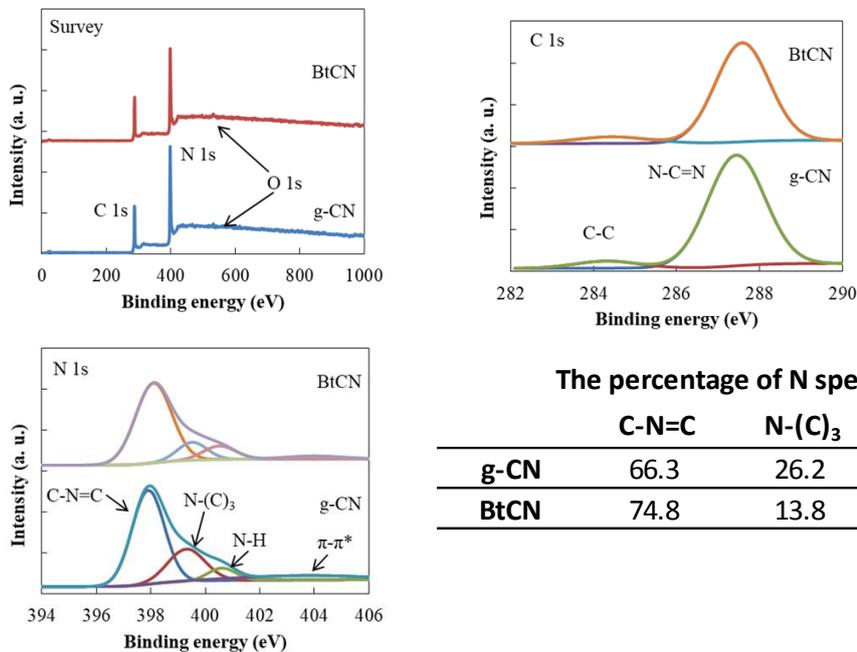


Fig. 7: (a)-(c) XPS survey, C1s, N1s and N1s spectra of g-CN and BtCN and (d) the percentage of different N species of g-CN and BtCN.

The optical absorption properties of the resultant samples were examined using DRS spectra (Fig. 8). g-CN exhibited an intrinsic absorption edge at around 460 nm, with a calculated band gap of about 2.70 eV according to the Kubelka–Munk function [17]. After loading with carbon dots, the absorbed wavelength region expanded. On the other hand, the band gap energy of 0.5 BtCCN (approximately 2.98 eV) was higher than that of g-CN. This

phenomenon was attributed to the fact that quantum confinement effect related to the decreased particle size of g-CN by alkaline treatment.

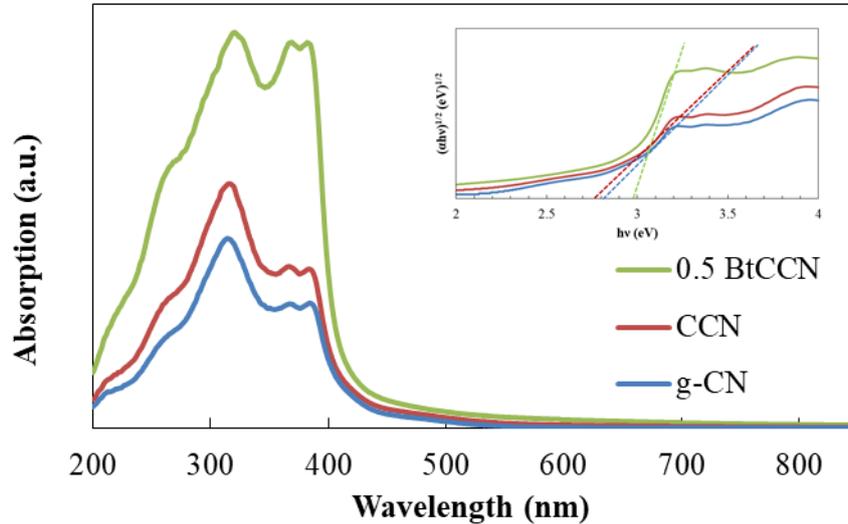


Fig. 8: DRS spectra and tauc plots (inset) of g-CN, CCN and 0.5 BtCCN.

The photoluminescence (PL) spectra of the obtained samples have been obtained for investigating their charge separation and recombination behavior, as displayed in Fig. 9. Compared with g-CN, CCN exhibits reduced PL intensity, suggesting that less charge recombination occurred in CCN. This result implies that the coupling with Carbon dots plays a role in suppressing the recombination of the photo generated carriers [18]. Moreover, after alkaline treatment, the PL intensity decreased. It implied alkaline treatment provided to inhibit the recombination of photo generated charges.

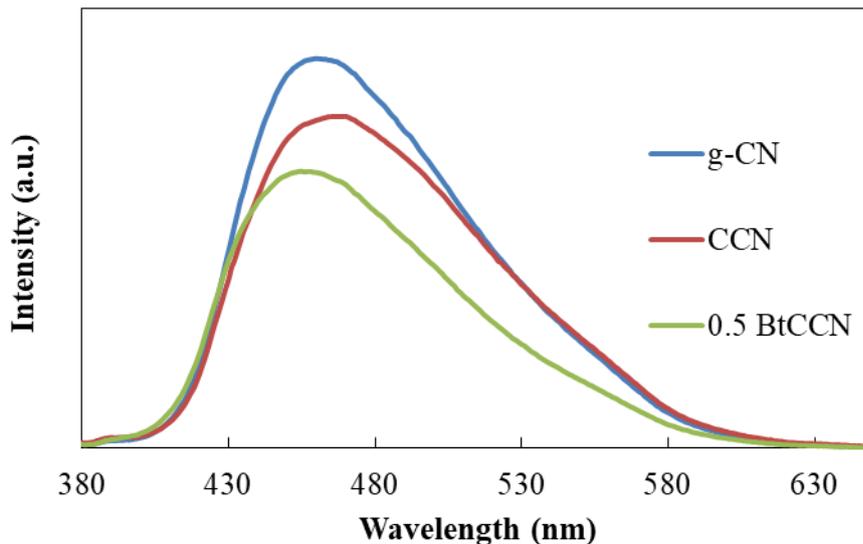


Fig. 9: Photoluminescence spectra of g-CN, CCN and 0.5 BtCCN (excited at 350 nm).

B. Evaluation of photocatalytic activity

Fig. 10 shows the photocatalytic activity of all samples. The photocatalytic hydrogen production rate of pure g-CN was only 10 $\mu\text{mol/g} \cdot \text{h}$. However, the rate of 0.5 BtCCN was 480 $\mu\text{mol/g} \cdot \text{h}$ which was 48 times higher than that of

pure g-CN (Fig 10). Furthermore, we performed the photocatalytic hydrogen production in case of changing the loading amount of carbon dots and the base treatment time, concentration and temperature respectively (Fig. 11). As the results, the optical loading amount of carbon dots was 0.5 wt%, the optical base treatment condition is 18 h, 0.1 M NaOH, and 110 °C.

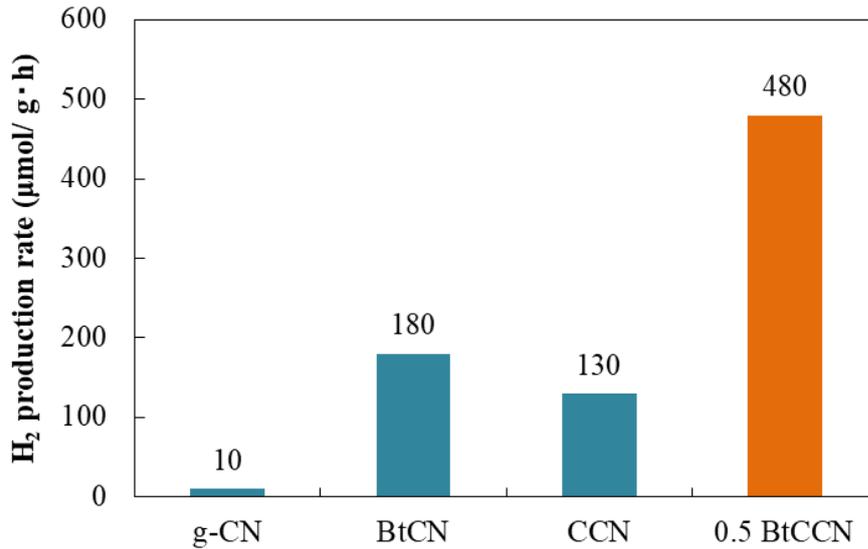


Fig. 10: Effect of alkaline treatment over photo catalysts.

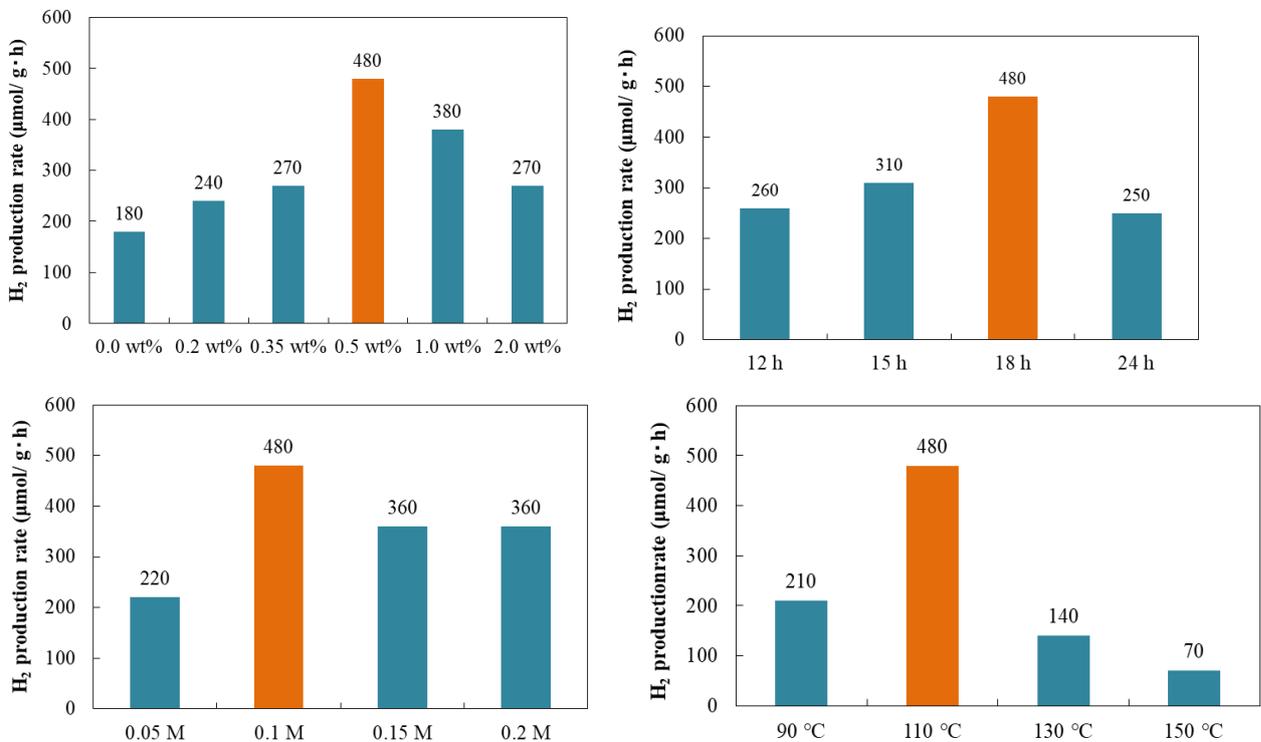
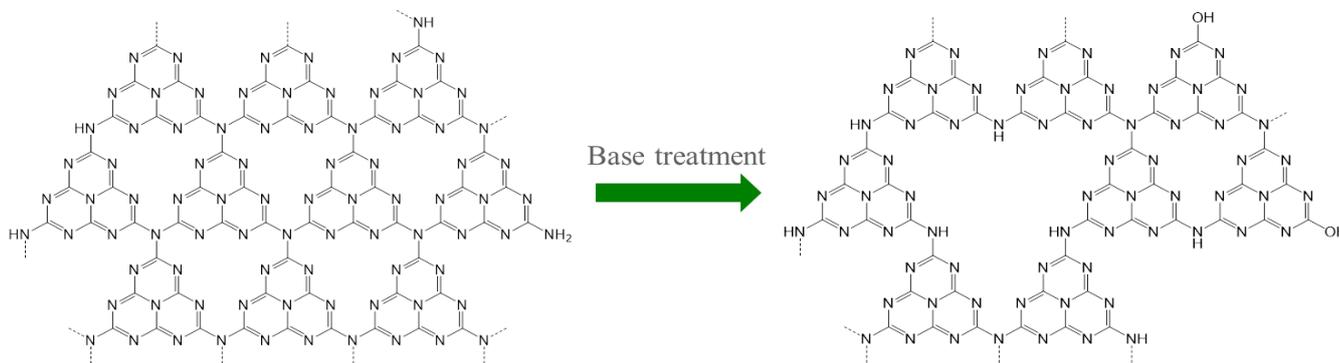


Fig. 11: (a) Effect of loading amount of carbon dots over photo catalysts. (b), (c), (d) Effect of base treatment time, base concentration and time on the photocatalytic activity of 0.5 BtCCN, respectively.

C. Alkaline treatment mechanism

According to the literatures, the layered framework of g-CN is mainly composed of tri-s-triazine with heterocyclic

nitrogen atoms at the edge of each layer. Both the bridge nitrogen atom, which connected two tri-s-triazine units, and terminal nitrogen atom are H- bonding motifs. Meanwhile, the conjugated layers are stacked together by weak van der Waals interactions to form graphite-like structure [19]. The exfoliation of g-CN in alkaline solution is based on the specific structure features of g-CN, as shown in Scheme 1. Two possible reactions would occur [20]. One is the weak hydrogen bonding between OH⁻ and -NH₍₂₎ groups present at the bridged or terminal site of each g-CN layer. The other is the electrophilic substitution between OH⁻ and heterocyclic carbon atoms connected with the terminal -NH₂, leading to the replacement of partial -NH₂ groups by OH⁻. As a result, the surface of g-CN layer would be eroded gradually by alkali solution, which, in the meantime permeate into the interlayer of the rocks. Whatever reaction happened, the originally neutral g-CN nanosheets would become somewhat negatively charged. The van der Waals interactions between layers would be destroyed and thus cause the total delamination.



Scheme 1: Pseudo base treatment mechanism.

IV. CONCLUSION

Novel carbon dots and g-CN composite photo catalysts which were adapted alkaline treatment were successfully synthesized. The highest photocatalytic hydrogen evolution rate for 0.5 BtCCN was approximately 480 $\mu\text{mol/g}\cdot\text{h}$, which was about 48 times higher than that of pure g-CN. The improved photocatalytic activity was attributed to the fact that carbon dots acted electron reservoirs to trap the electrons for promoting charge separation and light harvesters to enhance the visible light absorption. Furthermore, alkaline treatment made shorten the photo generated electron-hole mobility distance by exfoliated g-CN.

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