



Full Length Article

Post-activation of in situ B–F codoped g-C₃N₄ for enhanced photocatalytic H₂ evolution

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ABSTRACT

Porous graphitic carbon nitride polymer (p-CN-BF) with enhanced photoproduction of H₂ from water was prepared by a two-step treatment process including in-situ Boron and fluorine codoping using [Emim]BF₄ as dopants followed by post-calcination in air. Several techniques were employed to characterize the modified structure and elucidate the doping state of B and F. It was shown that in-situ doping method is necessary for efficient doping of heteroatoms into the molecular composition of CN. The difference of doping state of B and F was that B doping primary existing in the inside skeleton of CN, but F doping merely presents in the surface layer. The inside doped B made for the enhanced visible light absorption and the production of uniform porous structure during post-sintering process. By the synergistic effect of B–F codoping and post-activation, p-CN-BF showed much enhanced photoelectron generation, transmission and separation, therefore, it performs high photocatalytic activity for H₂ evolution (351 μmol h⁻¹), which was 13 and 5 times higher than samples only modified by B–F codoping (CN-BF) or post-annealing (P-CN).

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1. Introduction

It is well known that over the last one hundred years, fossil fuel is the major driving force for economic and social development. However, the non-renewability of fossil fuel resources and accumulated environmental problems seriously limit its availability. So, the development of new alternatives especially green energy is urgent need to explore. Hydrogen (H₂), as a clean and efficient energy carrier, is receiving increasing attention all-over the world. Nowadays, hydrogen evolution from semiconductor photocatalytic technology driven by solar energy is considered to be a promising solution for sustainable energy sources [1,2]. In the past decades, substantial research efforts have been focused on developing semiconductor photocatalysts to produce H₂ by splitting of water [3–5]. Although a great number of impressive materials have been employed for hydrogen production, many shortcomings still need to solve in order to develop high-efficiency photocatalysts meeting the requirements of practical applications.

Graphitic carbon nitride (g-C₃N₄) polymer, an age-old material but possesses appealing unique physicochemical properties, has attracted great attention for H₂ production in water splitting. It is no doubt that g-C₃N₄ is a good sustainable candidate for H₂

production under visible light [6,7]. However, the photocatalytic activity of pristine g-C₃N₄ is non-competitive compared to other inorganic semiconductor, due to its small surface area and adverse charge transmission in polymer framework. Therefore, ceaseless methods and techniques have been proposed to enhance its photocatalytic activity since the first report, such as nanostructure design, heterostructure construction and electronic structure modulation [8–13].

Post-sintering technology is one of the most effective pathways to regulate and optimize the polymerized texture and surface activated for the g-C₃N₄ materials [14,15]. The thermal driving force can in principle promote the conjugated degree of tri-s-triazine units and enable fast charge transport due to improved connectivity of the ordered regions. Meanwhile, thermal exfoliation is an efficient route for g-C₃N₄ nanosheets synthesis [16,17]. The enlarged surface area and surface reconstruction resulting from lamellar nanosheets are highly conducive to enhance H₂ evolution due to the release of surface defects and favourable charge transfer from bulk to surface. From other point of view, enlarged band gap was usually induced into g-C₃N₄ after post-thermal treatment. The hypochromatic shift of absorption band edges sacrifices the harvesting of visible light in solar spectrum.

Throughout so many modified methods towards g-C₃N₄ semiconductor, elemental doping is one of the most effective approaches. Non-metal elements doping especially regarded as

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an important aspect, so as to regulate the electronic structure of $g\text{-C}_3\text{N}_4$ by atom substitution or chemical bonding. As a result, improved photocatalytic activity of doped $g\text{-C}_3\text{N}_4$ can be achieved deriving from the optimized bandgap shift and charge carrier transport. Up to now, various non-metal elements have been used for heteroatom doping of $g\text{-C}_3\text{N}_4$, such as O, P, I, N and S [18–22]. Photocatalytic activities over these doped materials were improved by the expanded visible-light response which affected the electronic properties, although the effects of formed surface states on the charge separation by introducing dopants were always neglected [23]. Multielement co-doping is an effective brightening strategies to overcome the charge confinement from single element doping by charge compensation effects. There are reports illustrate that Co-doped $g\text{-C}_3\text{N}_4$ by B–P, P–K, K–I and B–F etc. showed enhanced photocatalytic activity in CO_2 conversion, pollutant degradation and H_2 evolution [24–26]. During co-doping process, surface decoration and skeleton doping usually occurred simultaneously. However, the activity-enhanced mechanisms depending on surface or inside doping are not fully understood.

In the current work, B and F codoped $g\text{-C}_3\text{N}_4$ photocatalysts were synthesized via thermal polymerization of a mixture of dicyandiamide, urea and ionic tetrafluoroborate liquids. Further optimizations on the bulk and surface properties of doped materials are realized by post-thermal treatment. The characteristics of the codoped photocatalysts were analyzed, and the doping states of the B and F were elucidated. It was found that B substitute $\text{sp}^2\text{-N}$ and dominant skeleton doping of the heptazine units of CN material through in-situ thermal polymerization route. Nevertheless, C–F bonds formed from F doping only present in the surface layer of doped samples. The effect of inside and surface doping towards the crystal structure and photoelectric properties were investigated. The photocatalytic activity on H_2 evolution under visible light were also tested. The in-situ B–F codoped material post-activated by thermal treatment show gratifying performance in the H_2 production from water.

2. Experimental section

2.1. Sample preparation

Synthesis of pure $g\text{-C}_3\text{N}_4$ (CN): Mixed aqueous solution (20 mL) of Dicyandiamide (DCDA, 4 g) and urea (4 g) were stirred at 80°C to remove water. The obtained dry solid product was subjected to sintering at 550°C for 2 h in a muffle furnace in an alumina crucible with a cover for 2 h with a ramp rate of 5°C min^{-1} .

Synthesis of B–F codoped CN (CN-BF): 49.6 mg of Ionic Liquid (IL) 1-Ethyl-3-methylimidazolium Tetrafluoroborate ([Emin]BF₄) was dropwise added into the mixed solution of DCDA (4 g) and urea (4 g). Same as above mentioned process, after evaporated to dry, the obtained solid product was calcined at 550°C for 2 h.

Synthesis of post-activated of CN (p-CN) and B–F codoped CN (p-CN-BF): Pure CN and B–F codoped CN within alumina crucibles without covers were further calcined for 2 h to obtain post-activated products. As a contrast, non in situ post-activated CN (p'-CN-BF) was prepared as follows: 49.6 mg of EMIM was dropwise added into the aqueous dispersion with CN-BF obtained above. Similarly, after evaporating to dry of the mixture, the solid was pyrolyzed in an alumina crucible without a cover for 2 h.

2.2. Characterization

The products were characterized by X-ray diffraction (XRD-6000, Shimadzu) with $\text{Cu K}\alpha$ radiation and the scanning rate was 5° min^{-1} . The morphology of the samples were explored using a

Merlin Compact field-emission scanning electron microscope (FE-SEM, Carl Zeiss) and JEM-2010 high resolution transmission electron microscope (HR-TEM). Fourier transform infrared spectroscopy (FTIR) was recorded from KBr pellets in the range of $400\text{--}4000\text{ cm}^{-1}$ on a Thermo Nicolet FTIR apparatus. X-ray photoelectron spectroscopy (XPS) analysis was performed on the ESCALAB 250 photoelectron spectrometer (ThermoFisher Scientific) with Al K α (1486.6 eV) as the X-ray source setting at 100 W and a pass energy of 30 eV for high-resolution scan. N_2 adsorption-desorption isotherms were obtained using a Micromeritics ASAP 2010 sorptometer at 77 K, and the specific surface area was calculated by the Brunauer–Emmett–Teller (BET) method. UV–Vis diffuse reflectance spectra (DRS) were obtained by a UV–Vis spectrophotometer (UV-2550, Shimadzu) using BaSO_4 as reference. Steady Photoluminescence (PL) measurements were carried out by FS5 Spectrofluorometer with an excitation wavelength of 400 nm. And PL decay tests were performed on a QuantaMaster™ fluorescence spectrophotometer with an excitation wavelength of 337 nm. Photocurrent and EIS measurements were carried out on an electrochemical workstation (CHI660E) in a three-electrode-cell system: platinum wire as the counter electrode, saturated calomel electrode (SCE) as the reference electrode, while the FTO glass ($0.5 \times 0.5\text{ cm}^2$) covered with catalyst [27,28].

2.3. Photocatalytic H_2 production activity

The photocatalytic H_2 production experiments were carried out in a Pyrex top-irradiation reaction vessel connected to a glass closed gas system. The temperature of the reaction solution was maintained at 6°C by the flow of cooling water. A 300 W Xe arc lamp (CEL-HXF500, light irradiation intensity of about 190 mW cm^{-2}) was used as the light source. Typically, 50 mg of catalyst power was dispersed in 100 mL aqueous solution containing 10 vol% triethanolamine (TEOA) as sacrificial electron donor. 3 wt% Pt was loaded on the surface of the catalyst by in situ photodeposition method using H_2PtCl_6 as co-catalyst. Before irradiation, the system was evacuated several times to remove air completely. The evolved gases were analyzed by gas chromatography equipped with a thermal conductive detector (TCD), using nitrogen as the carrier gas.

3. Results and discussion

3.1. Structural features

The basic phase structure and crystallinity of the as-prepared materials were analyzed by XRD and FTIR. As shown in Fig. 1a, pure CN shows a diffraction peak at 27.4° , characterizing the graphitic interlayer stacking reflection of conjugated aromatic systems in (002) planes. After post-activated treatment, the (002) peak shifts from 27.6° of p-CN to 27.4° of CN, reflecting the XRD d-spacing changes from 0.326 nm for CN to 0.321 nm for post-activated p-CN. Plus the obvious enhanced peak intensity, it indicates an optimized structural compactness and degree of order in the π -stacks due to improved post-polycondensation, which strongly influences the charge transport in organic semiconductors [29]. For CN-BF, nearly no changes of XRD peak can be observed compared to CN. It illustrates that in situ B–F doping by ionic liquid does not change the polymeric structures of graphitic CN material, which is consistent with previous report [30]. However, the crystallinity of p-CN-BF decrease after post-calcination, different from pure CN. On the other hand, nearly no changes occur for p'-CN-BF. Therefore, we can infer that B–F heteroatoms are doped into the molecular skeleton of CN materials by in situ IL copolymerization. The intercalation of IL merely in the post-processing stage is adverse for the

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