

Full Length Article

Cobalt-doped graphitic carbon nitride photocatalysts with high activity for hydrogen evolution



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ABSTRACT

Cobalt-doped graphitic carbon nitride (Co–CN) was synthesized by one-step thermal polycondensation using cobalt phthalocyanine (CoPc) and melamine as precursors. The π – π interaction between melamine and CoPc promotes cobalt doping into the framework of g-C₃N₄. The prepared samples were carefully characterized and the results demonstrated that Co-doped graphitic carbon nitride inhibited the crystal growth of graphitic carbon nitride (CN), leading to larger specific surface area (33.1 m² g^{−1}) and abundant Co–N_x active sites, narrower band gap energy and more efficient separation of photogenerated electrons and holes. 0.46% Co–CN exhibited higher hydrogen evolution rate (28.0 μ mol h^{−1}) under visible light irradiation, which is about 3.0 times of that over the pure CN and about 2.2 times of that over cobalt-doped CN using CoCl₂ · 6H₂O as a cobalt source. This study provides a valuable strategy to modify CN with enhanced photocatalytic performance.

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1. Introduction

As one of the most abundant elements on the Earth, hydrogen holds promise to replace traditional fossil energy in the future [1]. Although hydrogen can be generated from biomass, natural gas, or coal gasification, only hydrogen derived from water splitting can provide a sustainable, secure and clean energy system without environmental pollution [2–4]. Photocatalytic hydrogen evolution reaction (HER) is one of the ideal channels for developing clean and sustainable hydrogen energy [5]. Since Fujishima and Honda firstly reported photocatalytic water splitting using TiO₂ as a catalyst in 1972 [6], numerous efforts have been devoted to seeking highly efficient photocatalysts. Metal oxide photocatalysts, such as TiO₂ and SnO₂, have been widely studied in dye-sensitized solar cells [7], degradation of organic dyes in wastewater treatment [8–11], hydrogen production from water splitting [12], gas sensing [13] and so on. However, these metal oxide catalysts show low response to visible light region due to their wide band gap, some of which can only be excited by ultraviolet light.

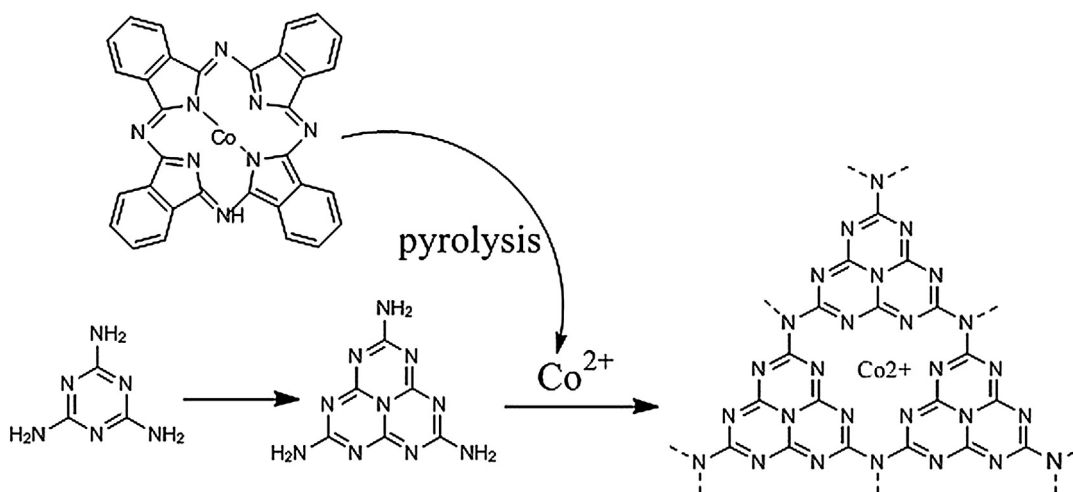
Metal-free photocatalyst, π -conjugated graphitic carbon nitride (g-C₃N₄) has aroused increasing concern for its promising applications in hydrogen production from water splitting due to its appropriate band position [14]. In addition, the nontoxic g-C₃N₄

with visible light response also possesses high thermodynamic and chemical stability as well as outstanding electronic properties [15]. Nevertheless, the photocatalytic performance of bulk g-C₃N₄ is low due to the fast recombination of photogenerated electron and hole pairs, low specific surface area, few adsorption and active sites [16]. To solve these problems, many attempts have been devoted to improving the photocatalytic activity of g-C₃N₄, such as nonmetal doping [17–19], metal doping [20,21], morphology control [22–24], modification with conductive materials [25,26], coupling with other semiconductors [27–31]. Among these strategies, doping is one effective and convenient way to tune electronic structures of g-C₃N₄ in order to promote its photocatalytic efficiency. Zn-doped g-C₃N₄ was reported to exhibit significantly improved hydrogen evolution rate. Modification of g-C₃N₄ induced more electron-hole pairs by extending the optical absorption range, thus providing more electrons for hydrogen evolution. Meanwhile, g-C₃N₄ can be regarded as a Lewis base and filled with abundant nitrogen lone-pair electrons, which can coordinate with transitional metals to construct metal–N active sites in the covalent polymeric framework [32]. Inspired by the unique structural features of chlorophyll and protohemin, in which the metal centers (Mg and Fe) are coordinated with the nitrogen atoms through metal–N bond, modification of g-C₃N₄ through introducing metal into g-C₃N₄ framework has been reported for hydrogen evolution and oxygen reduction reaction [33,34].

Metal phthalocyanine is two-dimensional 18 π -electron aromatic porphyrin synthetic analogues with a metal atom located

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Scheme 1. Schematic illustration of preparation of cobalt-doped $g\text{-C}_3\text{N}_4$.

at the central cavity. The π - π conjugate system of metal phthalocyanine can produce strong π - π stacking interaction with carbon material, facilitating the attachment of metal phthalocyanine particles onto the surfaces of carbon material [35–38].

In this study, the mixture of melamine and CoPc was calcined at high temperature, and then cobalt-doped $g\text{-C}_3\text{N}_4$ catalysts were obtained after thermal polymerization of melamine accompanying with pyrolysis of CoPc. In such a process, cobalt was introduced into the $g\text{-C}_3\text{N}_4$ cavities. The π - π interaction between melamine and CoPc results in tight combination of CoPc with melamine, which is beneficial to cobalt doping into $g\text{-C}_3\text{N}_4$. A possible cobalt doping path is presented in Scheme 1. The melamine formed melem by deamination and then formed tri-s-triazine by thermal condensation, in which the Co^{2+} derived from the pyrolysis of CoPc was simultaneously doped into the $g\text{-C}_3\text{N}_4$ cavities. The hydrogen evolution activity and stability of photocatalyst was evaluated in the photocatalytic hydrogen production under visible light irradiation. Compared with pure CN, the as-synthesized Co-CN showed much higher hydrogen evolution rate, due to its larger specific surface area, abundant accessible Co-N_x active sites, decreased band gap energy and efficient separation of photo-generated electrons and holes.

2. Experimental section

2.1. Materials and reagents

Cobalt phthalocyanine (CoPc, 95%) and chloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, Pt \geq 37.5%) were purchased from Aladdin Industry Corporation. Phthalocyanine was purchased from J & K Scientific Ltd. Melamine ($\text{C}_3\text{H}_6\text{N}_6$, 98%) and cobaltous chloride 6-hydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 99.0%) were obtained from Tianjin Kemiou Chemical Reagent Co. Ltd. (Tianjin, China). *N,N*-Dimethylformamide (DMF, 99.5%) was supplied by Jiangsu Qiangsheng Chemical Co. Ltd. (Jiangsu, China). Triethanolamine (TEOA, 85%) was purchased from Tianjin Fuyu Fine Chemical Co. Ltd. (Tianjin, China). All of these chemicals were used without further purification. Deionized water was generated from pure water system (GWA-UN, Beijing, China).

2.2. Preparation of photocatalysts

To prepare Co-CN, a certain amount of CoPc was dissolved in 100 mL *N,N*-dimethylformamide (DMF) and then 2 g melamine was added. After being ultrasonicated for 30 min, the obtained solution was being stirred at 80 °C until the DMF solvent was completely

evaporated. The obtained CoPc/melamine hybrid was dried at 60 °C for 6 h and then put in a 30 mL covered crucible. The crucible was placed into a tube furnace and heated at a heating rate of 3.0 °C/min to 550 °C, and maintained for 4 h. After cooling, the final products were collected and ground into powders. Herein, a series of Co-CN powders with Co contents from 0.06% to 0.50% were synthesized (labeled as x% Co-CN, x is the Co element/CN mass percentage). For comparison, pure CN was prepared in the absence of CoPc, while Co-doped CN (labeled as Co-CN(CoCl_2)) was prepared using $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ instead of CoPc as a cobalt source under the same experimental conditions. In addition, samples were also prepared using a certain amount of phthalocyanine or the mixture of phthalocyanine and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ instead of CoPc by the same process for comparison. The products were named as CN(Pc) and Co-CN(Pc + CoCl_2), respectively.

2.3. Characterization

The phase composition and structure of the samples were analyzed using an X-ray diffractometer (XRD, Bruker GADDS diffractometer, with Cu K α radiation). The morphology of the as-prepared samples was observed by scanning electron microscopy (SEM, Merlin, Zeiss). UV-vis diffuse reflectance spectroscopy (DRS) absorption spectra were recorded on a UV-vis spectrometer (Hitachi U-3010) using BaSO_4 as a reference. Fourier transform infrared spectra (FTIR) of the samples were taken using an IR Affinity-1 FTIR spectrometer. The photoluminescence spectra were recorded on a fluorescence spectrophotometer (F-4500, Hitachi) at room temperature under excitation of 315 nm light. The X-ray photoelectron spectroscopy (XPS) was conducted using X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250X1, USA) to analyze the surface composition of the samples. The solid-state ^{13}C nuclear magnetic resonance (NMR) measurement was performed on a Bruker Avance III HD 400 spectrometer. The Brunauer-Emmett-Teller (BET) surface area was measured by N_2 adsorption using a static volume method with a specific surface analysis instrument (Beishide, 3H-2000PS1, China).

2.4. Photocatalytic activity of H_2 evolution

Photocatalytic H_2 -evolution experiments were performed in a gas-closed circulation system (Labsolar-III, Beijing Perfectlight Technology Co., Ltd, Beijing, China) with a top-irradiation quartz vessel. In a typical experiment, 50 mg of the as-prepared photocatalyst was dispersed in 100 mL mixed solution containing 90 mL

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