



Improvement of the photocatalytic hydrogen production activity of g-C₃N₄ by doping selenides as cocatalysts

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ABSTRACT

Carbon nitride is emerging as leading candidate for photocatalyst which enables one to use light to drive hydrogen production reactions. However, noble-metal such as Pt was adopted to be effective co-catalyst to increase the activity of g-C₃N₄ in most reactions which is costly. Herein, a novel g-C₃N₄-based photocatalyst with NiSe₂ and CoSe₂ as cocatalysts (abbreviated as CN-CoNiSe) in absence of noble-metal applied in photocatalytic hydrogen production was devised with a lamellar structure through a calcination process of the mixture of Ni²⁺ doped ZIF-67 and g-C₃N₄ for the first time in this work. The optimum photocatalytic activity in hydrogen evolution for CN-CoNiSe photocatalysts with a Ni²⁺ doped ZIF-67 mass content in precursors of 5 wt% (854.1 μmol g⁻¹ h⁻¹) was up to 87.4 times as high as that of pure g-C₃N₄ (9.77 μmol g⁻¹ h⁻¹). The greatly improved photocatalytic activity of CN-CoNiSe photocatalysts was mainly attributed to the synergistic effect of NiSe₂, CoSe₂ and g-C₃N₄, which leads to enhanced charge transfer and separation rate based on the results of electrochemical experiments and photoluminescence.

1. Introduction

Spontaneously solar-driven water splitting to produce H₂ in the existence of photocatalyst is a highly promising pathway towards a clean and renewable energy supply in the future [1–11]. To increase the efficiency of hydrogen production, developing an efficient and stable photocatalyst which is able to accomplish maximum hydrogen evolution is meaningful [12–14]. Graphitic carbon nitride (g-C₃N₄) has elicited ripples of excitement in the research communities as the next generation photocatalyst, due to its facile synthesis, appealing electronic band structure, high physicochemical stability, and earth-abundant nature [15–19]. However, the efficiency of g-C₃N₄ is still limited due to the high recombination rate of photogenerated electron–hole pairs [20]. Thus, it still remains challenging to construct g-C₃N₄-based photocatalysts which carry efficient charge transfer and separation to drive hydrogen evolution reactions [21]. For further practical application of solar-driven water splitting, introducing co-catalysts is an auspicious solution that can promote water molecules adsorption, charge separation and transfer, and photocatalytic stability [7,22,23].

To improve the photocatalytic hydrogen production activity of g-

C₃N₄-based photocatalysts, proper pick of co-catalysts which can not only improve the charge separation by capturing electrons or holes, but also favor the transfer of electron is vital [24]. Pt is an excellent catalyst for the hydrogen evolution reaction, but its practical use is hindered by its high price and rarity [25–28]. The developed transition metal selenides systems, such as CoSe₂, NiSe₂, benefiting from their faster transformation efficiency of adsorbed H atoms into hydrogen and providing active sites of pyrite catalysts, are reported to be suitable water splitting catalysts [29–34]. Besides, compared with the other chalcogenides such as O and S, Se has a larger ionic radius with lower electronegativity, leading to the weak attraction to the outer electrons of cobalt, contributing to a promoted redox reaction rate [35]. Meanwhile, simple procedure and appropriate precursors should be chosen deliberately, aimed at obtaining efficient and stable cocatalysts easily. Based on the point above, zeolitic imidazolate frameworks (ZIFs), as an important branch of metal organic frameworks MOFs synthesized by coordinating transition metals (Zn²⁺, Co²⁺) with imidazole ligands can be candidate for constructing photocatalyst or cocatalyst incorporated with g-C₃N₄ which has not been mentioned in previous reports [36–39]. Additionally, MOF-derived materials, such as ZIF-67 derivation cobalt

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selenide have been successfully applied in the field of electrocatalysis and electrochemistry [34,40–42]. The corresponding results show that the metal sites in MOF-derived materials can be stabilized and reinforced because of the accompanied surface coating in the calcination process which consists of carbon or metal oxide nanoparticles [34,43,44]. Thus, ZIF-67, which is rich in carbon, nitrogen and transition metals, easily prepared and very cost-effective, could be ideal solid-phase precursors for the synthesis of cocatalysts [36]. Further, we envisaged that the introduction of the transition metal selenides, in the form of nickel selenide and cobalt selenide would greatly enhance the ability of hydrogen evolution of $g\text{-C}_3\text{N}_4$. In addition, the intimately combination of co-catalysts on a semiconductor support is quite beneficial for charge separation, since the electron can be transferred faster.

Herein, we design a $g\text{-C}_3\text{N}_4$ -based photocatalyst by rationally introducing NiSe_2 and CoSe_2 as co-catalysts derived from Ni^{2+} doped ZIF-67 on $g\text{-C}_3\text{N}_4$ support for hydrogen evolution via a calcination process. Specifically, the calcination temperature of synthesizing CN-CoNiSe was set as 350°C which is above the melting point of Se and below the decomposition temperature of $g\text{-C}_3\text{N}_4$. Owing to melt mixing method used in the formation of the $g\text{-C}_3\text{N}_4$ -based photocatalyst, NiSe_2 , CoSe_2 and $g\text{-C}_3\text{N}_4$ can be well connected and dispersed uniformly [45]. With the cocatalysts combined intimately, the electron-hole pairs activated by light would be easily dissociated and transferred into the active sites to participate in hydrogen evolution reactions. The as-obtained photocatalyst exhibited remarkable H_2 production activities of $854.1\ \mu\text{mol h}^{-1}\ \text{g}^{-1}$ in the absence of noble metal, outperforming $g\text{-C}_3\text{N}_4$ obviously.

2. Experimental

2.1. Photocatalysts preparation

Bulk $g\text{-C}_3\text{N}_4$ can be simply prepared by the thermal condensation of melamine. In a typical fabrication, melamine in a crucible was kept at 550°C for 4 h and then cooled to room temperature. Thus, the yellow $g\text{-C}_3\text{N}_4$ was obtained. ZIF-67 was synthesized by a facile method according to previous publications [46]. Cobalt nitrate hexahydrate, 2-methylimidazole (2-Hmim) and methanol were mixed in a molar ratio of 1: 40: 1100 (Co/2-Hmim/methanol) following with vigorous agitation and ultrasonic dispersing for 1 h at room temperature. The dispersions were centrifuged at 8000 rpm for 5 min, washed with methanol to remove excess soluble ions for at least 5 times, and dried. The obtained precipitate was dispersed in methanol, then added into $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ methanol solution with a molar ratio of 1:1. Afterwards, the mixture was for ultrasonic dispersing 0.5 h. The dispersions were centrifuged at 8000 rpm for 5 min, washed with methanol to remove excess soluble ions for at least 3 times, and dried in drying cabinet at 60°C overnight. After volatilization of the methanol, Ni^{2+} doped ZIF-67 was obtained. And then it was crushed for further use.

Ni^{2+} doped ZIF-67, $g\text{-C}_3\text{N}_4$ and Se powder were milled in a mortar for 15 min. Then, the mixture mentioned above was placed in a quartz boat in pipe furnace. The precursor was directly heated to 350°C and kept for 2 h in a flowing 60 mL/min N_2 . The product was put into mortar, grinding into fine powder for further use. Through this method, samples with different Ni^{2+} doped ZIF-67 to $g\text{-C}_3\text{N}_4$ weight ratios (i.e., 2.5, 5, 10 and 12.5 wt% Ni^{2+} doped ZIF-67/ $g\text{-C}_3\text{N}_4$) were obtained and labelled as CN-CoNiSe2.5, CN-CoNiSe5, CN-CoNiSe10 and CN-CoNiSe12.5, respectively. Additionally, the mass ratio of Se powder to Ni^{2+} doped ZIF-67 is 1:1. For comparison, $\text{CoSe}_2/g\text{-C}_3\text{N}_4$ was prepared, following a similar procedure to that of CN-CoNiSe.

2.2. Characterizations of photocatalysts

The composition, structure and texture properties of the materials were investigated by Fourier transform infrared (FTIR) spectra (Spectrum 100), X-ray powder diffraction (XRD) patterns (Bruker D8 X-

ray diffractometer), X-ray photoelectron spectroscopy (XPS) (Kratos-AXIS ULTRA DLD apparatus), scanning electron microscopy (SEM) micrographs (Hitachi S-4800), transmission electron microscopy (TEM) experiment (JEM-2100 electron microscope). Optical properties were also studied by diffuse reflectance UV–vis spectroscopy (Lambda 35 spectrometer), photoluminescence spectrum (SPEX Fluorolog-3 spectrofluorometer).

The electrochemical impedance spectra (EIS), Mott-Schottky plot and photocurrent-time (I-T) profiles was recorded on the CHI660E electrochemical workstation with a standard three-electrode cell at room temperature. The electrolyte was 0.1 M Na_2SO_4 solution. ITO glasses dipping with catalysts as working electrode, an Ag/AgCl reference electrode and a Pt counter electrode were used. The powder was fabricated onto ITO glass substrate electrodes via the uniformly dispersed by mixing catalyst with alcohol solutions for 30 min and dried for 24 h. Calomel electrode and 0.5 M sulphuric acid aqueous solution were used in linear sweep voltammetry.

2.3. Photocatalytic experiments

Light driven H_2 evolution reactions were conducted in a closed gas circulation and evacuation system fitted with a top window Pyrex cell (CEAULIGHT CEL-SPH2N). Prior to light irradiation, the system was vacuumed for 0.5 h to remove air with vacuum bump. In a typical reaction, 30 mg of photococatalyst was dispersed in 50 mL of 20 vol% triethanolamine (TEOA) aqueous solution. Then the solution was irradiated with a 300 W Xe lamp ($\lambda > 320\ \text{nm}$) under vigorous stirring. Meanwhile, the photoreaction temperature was kept at 6°C . The hydrogen evolved was determined by a GC112A gas chromatograph with TCD detector.

3. Results and discussion

The morphology of as-synthesized particles is detected by scanning electron microscopy (SEM). The SEM image (Fig. S1a) exhibits the ZIF-67 rhomb dodecahedron with an average size of 300 nm was synthesized. After Ni^{2+} doping, the surface of the resulting crystal became irregular (Fig. S1b). It can be inferred that the add of $\text{Ni}(\text{NO}_3)_2$ contributes to the generation of protons from the hydrolysis of Ni^{2+} ions which can etch part of the ZIF-67 particles [46]. On the basis of that, the Co^{2+} ions are partially released from ZIF-67. Meanwhile, the Co^{2+} ions co-precipitate with Ni^{2+} ions to form the Ni^{2+} doped ZIF-67 particles. The PXRD pattern of the as-synthesized sample of Ni^{2+} doped ZIF-67 is identical to that of its simulated pattern of ZIF-67 from X-ray single crystal (Fig. S2), confirming the successful synthesis of Ni^{2+} doped ZIF-67. Even if Ni^{2+} was introduced, the basic structure of ZIF-67 remained. This phenomenon coincided well with the results obtained by Fourier transform infrared spectrometer (FTIR) spectra (Fig. S3). The strongest XRD peak (Fig. S4) at 27.4° (002) is a characteristic inter-planar stacking peak of conjugated aromatic systems of $g\text{-C}_3\text{N}_4$ [47]. Another distinct peak (100) at 13.0° can be attributed to an in-planar structural packing motif [48]. The FT-IR spectrum (Fig. S5) also displays two significant absorptions in the $900\text{--}1800\ \text{cm}^{-1}$ region possibly resulting from the vibration characteristics of the s-triazine ring units and heptazine heterocyclic ring units, and $3100\text{--}3300\ \text{cm}^{-1}$ indicating an N-H bending mode, respectively, representative of $g\text{-C}_3\text{N}_4$ [49–51]. Additionally, thermogravimetric analysis (TGA) exhibits the excellent thermal stability of the as-synthesized $g\text{-C}_3\text{N}_4$ (Fig. S6).

Fig. 1a shows the XRD patterns of the as-synthesized photocatalysts CN-CoNiSe, which show weaker pronounced diffraction peaks at 27.4° and 13.0° than $g\text{-C}_3\text{N}_4$ because of the doping of cocatalysts [52], indicating that the basic structure of $g\text{-C}_3\text{N}_4$ was not destroyed [24]. This is consistent with the observation from FT-IR spectra in Fig. 1b, in which there are two significant absorptions. Besides, weak CoSe_2 and NiSe_2 peaks can be observed in the XRD patterns for all the calcined CN-CoNiSe with different additions of Ni^{2+} doped ZIF-67 in the precursors

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