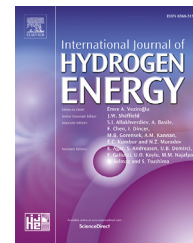




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A facile dissolution strategy facilitated by H₂SO₄ to fabricate a 2D metal-free g-C₃N₄/rGO heterojunction for efficient photocatalytic H₂ production

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ABSTRACT

A 2D g-C₃N₄(pPCN)/rGO heterojunction for photocatalytic hydrogen production is fabricated by a facile dissolution strategy facilitated by H₂SO₄. The bulk g-C₃N₄ (CN) can be directly exfoliated into ultrathin protonated g-C₃N₄ (PCN) nanosheets under the assistance of H₂SO₄, and PCN can be further modified by rGO in a dissolved state under the electrostatic self-assembly process. The nanocomposite exhibits a large surface area (146.47 m²/g) and intimate contact interfaces between pPCN and rGO due to the specific synthesis method. Based on the DRS, PL and photoelectrochemical analyses, the introduction of rGO can greatly improve the light absorption and photogenerated charge carrier separation and transfer of g-C₃N₄. The optimal pPCN/2 wt% rGO nanocomposite shows an efficient photocatalytic H₂ evolution rate of 715 μmol g⁻¹ h⁻¹ under visible light irradiation, which is 2.6 and 13 times higher than those obtained on pPCN and CN. In addition, a photocatalytic mechanism over a 2D pPCN/rGO heterojunction is proposed. This work offers a new effective strategy for fascinating g-C₃N₄-based nanocomposites with promising hydrogen generation.

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Introduction

Photocatalytic water splitting for hydrogen evolution has been regarded as one of the most promising and sustainable strategies for solar energy utilization [1–3]. During the past few years, a multitude of semiconductors have been explored as water splitting photocatalytic materials [4–7]. However, most

of them suffer from problems of high cost, non-earth abundant, toxicity, poor stability or low efficiency. Thus, explorations and searches for low-cost and environmentally friendly metal-free semiconductor photocatalysts with highly efficient and stable performance are still greatly desirable. Recently, a graphitic carbon nitride (g-C₃N₄) metal-free polymer has become a rising star in photocatalytic water splitting due to its excellent chemical and thermal stabilities, visible-light

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response, appropriate electronic band gap, environmental friendliness, low cost and abundance in raw materials [8–12]. However, the photocatalytic efficiency of bulk $g\text{-C}_3\text{N}_4$ is still limited in terms of its practical requirements because of the high recombination rate and poor transfer ability of photo-generated charge carriers. Consequently, multifarious modification strategies have been developed to greatly optimize the photocatalytic performance of $g\text{-C}_3\text{N}_4$, such as chemical doping [13–15], the use of special morphologies and structures including mesoporous structures and ultrathin two-dimensional nanosheets [16–20], surface functionalization [21,22], co-catalyst and carbon material loading [23–26], and heterojunction construction [27–31].

Among these modification strategies, the construction of a metal-free $g\text{-C}_3\text{N}_4$ -based heterojunction system has become a new research hotspot in the field of photocatalytic water splitting. The use of the especially appealing 2D/2D metal-free nanocomposite obtained by combining $g\text{-C}_3\text{N}_4$ with graphene or reduced graphene oxide (rGO), which can act as an excellent support material and as an electron collector and transporter to enhance the electron density within the photocatalyst, is a good strategy to boost the performance of $g\text{-C}_3\text{N}_4$ [32–34]. The traditional preparation method for $g\text{-C}_3\text{N}_4/\text{rGO}$ heterojunctions involves hydrothermal methods [35–37], in situ chemical synthesis by calcination [38,39] and sonochemical approaches [40]. However, the thermochemical method requires a high temperature, and the concentration of rGO in the heterojunction is difficult to control. In addition, calcination easily causes aggregation of the rGO nanosheet, which is detrimental to the interfacial contact between $g\text{-C}_3\text{N}_4$ and rGO. Furthermore, the negative surface charges of both $g\text{-C}_3\text{N}_4$ and rGO weaken the interactions of the $g\text{-C}_3\text{N}_4/\text{rGO}$ composite in the sonochemical method, resulting in poor photocatalytic performance. Very recently, protonation of $g\text{-C}_3\text{N}_4$ by strong mineral acids has been of particular interest to improve the properties [41–44], which can afford a positive surface charge, modify the solubility/dispersibility, enhance the surface area and adjust the electronic structure of $g\text{-C}_3\text{N}_4$. Inspired by this, a new synthetic strategy for 2D/2D $g\text{-C}_3\text{N}_4/\text{rGO}$ heterojunction photocatalysts via a sonication-assisted electrostatic self-assembly technique has been developed [45–47], resulting in enhanced visible-light photocatalytic performance in comparison to pure $g\text{-C}_3\text{N}_4$. However, this strategy usually requires strong ultrasonic exfoliation processing for $g\text{-C}_3\text{N}_4$ and GO, a protonation process for $g\text{-C}_3\text{N}_4$ by acid pretreatment, a heating reaction for the electrostatic self-assembly of protonated $g\text{-C}_3\text{N}_4$ and GO, and a reduction reaction of GO to form a $g\text{-C}_3\text{N}_4/\text{rGO}$ composite. The entire process is complex, has low yields and has high energy costs, and the size of the protonated $g\text{-C}_3\text{N}_4$ is still large. Most importantly, the synthesis of $g\text{-C}_3\text{N}_4/\text{rGO}$ heterojunctions by all the above-mentioned methods involves solid-solid contact in the composite process, and homogeneous and intimate interfacial contact remains the biggest problem in the heterojunction. Therefore, a new synthetic strategy for obtaining highly efficient $g\text{-C}_3\text{N}_4/\text{rGO}$ or other $g\text{-C}_3\text{N}_4$ -based heterojunction photocatalysts is of great significance.

In this work, a novel dissolution-precipitation strategy under the assistance of H_2SO_4 was developed for the

fabrication of 2D $g\text{-C}_3\text{N}_4/\text{rGO}$ nanosheet heterojunction photocatalysts. Bulk $g\text{-C}_3\text{N}_4$ was dissolved in concentrated H_2SO_4 without destroying its structure, which not only afforded positive polarity on the surface but also promoted the exfoliation of $g\text{-C}_3\text{N}_4$ from bulk to ultrathin $g\text{-C}_3\text{N}_4$ nanosheets directly. Then, the dissolved protonated $g\text{-C}_3\text{N}_4$ was composited with rGO dispersion liquid with molecular level contact by electrostatic self-assembly. The as-synthesized 2D/2D $g\text{-C}_3\text{N}_4/\text{rGO}$ nanocomposites exhibited significantly enhanced visible-light photocatalytic H_2 evolution performance in comparison to pure $g\text{-C}_3\text{N}_4$. As far as we know, the dissolution of $g\text{-C}_3\text{N}_4$ still remains a challenge, and this is considered to be the first report on the development of $g\text{-C}_3\text{N}_4$ -based heterojunctions via a dissolution-precipitation strategy for photocatalytic hydrogen production, which can achieve exfoliation, protonation and combination in only one process. Meanwhile, the technique is highly efficient, with low energy consumption and easy operation.

Experimental section

Fabrication of precipitated protonated $g\text{-C}_3\text{N}_4$ (pPCN)

Bulk $g\text{-C}_3\text{N}_4$ was first synthesized according to our previously reported procedures [29,47]. Typically, 5 g melamine was placed into a crucible and heated in a muffle furnace at $550\text{ }^\circ\text{C}$ for 3 h. After cooling naturally, the resultant yellow powders were collected as $g\text{-C}_3\text{N}_4$ (CN). For the PCN/ H_2SO_4 solution, 1 g obtained CN was mixed with 20 mL sulfuric acid by continuously stirring at $100\text{ }^\circ\text{C}$ for 2 h. The mixture gradually turned into a clear pale yellow solution to obtain the dissolved protonated $g\text{-C}_3\text{N}_4$ (PCN), the concentration of PCN was approximately 50 mg/mL. Subsequently, 2 mL PCN/ H_2SO_4 solution was added to 20 mL DMF, after cooling to room temperature, and excess deionized water was gradually added to precipitate PCN until no more precipitates formed. After that, the obtained pPCN was collected by vacuum suction filtration, washed with deionized water sufficiently until neutral, and dried at $60\text{ }^\circ\text{C}$.

Fabrication of pPCN/rGO nanocomposites

Graphene oxide (GO) was synthesized from powdered flake graphite by a modified Hummers' method in our previous work [47]; then, a certain amount of GO was dispersed in DMF at 1 mg/mL. An appropriate GO-DMF solution was added to the above-obtained PCN/ H_2SO_4 -DMF solution to form a homogeneous mixture solution. Then, excess deionized water was gradually added to precipitate PCN-GO until no more precipitates formed. In the process, the DMF solution served as the solvent and buffering agent for the drastic precipitation reaction. After that, the obtained pPCN/GO was collected by vacuum suction filtration and washed with deionized water sufficiently until neutral. pPCN/rGO was synthesized by irradiation under a 300 W Xe lamp for 2 h. The final precipitates were centrifuged and washed repeatedly with water. Finally, the obtained precipitate was dried at $60\text{ }^\circ\text{C}$ for 12 h. When preparing pPCN/rGO with different rGO contents, the products were denoted as pPCN/xwt% rGO, where x represents the weight fractions of rGO in the composites and $x = 1, 2$ and 4. A

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