



Amorphous nickel pyrophosphate modified graphitic carbon nitride: an efficient photocatalyst for hydrogen generation from water splitting

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ABSTRACT

A noble-metal-free amorphous Ni₂P₂O₇ modified g-C₃N₄ nanocomposite (a-Ni₂P₂O₇/g-C₃N₄) has been successfully prepared by a facile calcined process. The experimental results suggest that a-Ni₂P₂O₇/g-C₃N₄ displays the enhanced visible light absorption and improved charge separation relative to pristine g-C₃N₄, and shows smaller particle sizes and more negative conduction band edge potential than that of the crystalline Ni₂P₂O₇ modified g-C₃N₄ nanocomposite (c-Ni₂P₂O₇/g-C₃N₄), resulting in large amount of active sites and enhanced reduction capacity. The resultant a-Ni₂P₂O₇/g-C₃N₄ is evaluated as an excellent catalyst for photocatalytic hydrogen (H₂) generation under visible light irradiation, whose H₂ generation rate is almost 5 and 37 times higher than that of c-Ni₂P₂O₇/g-C₃N₄ and pristine g-C₃N₄, respectively, even better than that of Pt/g-C₃N₄. The improved activity of a-Ni₂P₂O₇/g-C₃N₄ is mainly ascribed to the good visible light utilization, efficient electron-hole pairs' separation and transfer, small particle sizes and high reduction ability of electron.

1. Introduction

The overusing of fossil fuels has made negative impact on the environment in the past years. Many efforts have been done to explore the environmental-benign energy to replace the traditional fuels. As a sustainable approach for new energy sources, photocatalytic hydrogen (H₂) generation utilizing solar energy from water splitting has attracted much attention [1,2]. Undoubtedly, the development of highly efficient and stable photocatalysts, especially on using earth-abundant semiconductors for H₂ generation from water splitting under visible light irradiation, is highly desired but remains a big challenge from the practical point of view [3,4].

Recently, graphitic carbon nitride (g-C₃N₄), which is composed of extremely abundant elements, has been regarded as one of the most promising photocatalysts for solar conversion, owing to its appealing chemical stability, environment friendliness, and capability of visible-light harvesting with band gap energy of 2.7 eV [5,6]. Unfortunately, g-C₃N₄ still faces a long way to meet the practical requirements on account of its fast recombination of photo-induced electrons and holes. Hence, in order to improve its photocatalytic efficiency, several methods have been employed, such as increasing surface area [7], protonation and polymerization [8], loading with co-catalysts [9], etc. Modifying noble metals, such as Pt [10], Ag [11] and Au [12], on g-

C₃N₄ can efficiently improve the separation of electron-hole pairs. However, these noble metals are scarce and expensive, which is the serious barrier for their large scale application. Most recently, some very important non-noble metal-based materials, especially for Ni-based compounds, such as NiS [13], Ni₂P [14,15], Ni(OH)₂ [16], and NiO [17] have been reported as the excellent co-catalysts for photocatalytic H₂ generation. However, to the best of our knowledge, the use of non-precious Ni-based amorphous pyrophosphates for photocatalytic H₂ generation is rarely reported. Amorphous materials hold the high concentrations of unsaturated coordinative sites and the isotropic structures, and this usually makes the activities of its being superior to those of the crystalline ones [18,19]. On the other hand, development of synthesis method to obtain amorphous photocatalysts, not crystalline ones, is highly desired. Therefore, pursuit of high-effective, low-cost and non-noble amorphous co-catalysts to fabricate novel structure and further increase the activity of g-C₃N₄ to H₂ generation from water splitting is highly desirable and valuable.

Herein, as a proof-of-concept experiment, the amorphous nickel pyrophosphate (a-Ni₂P₂O₇) modified g-C₃N₄ (a-Ni₂P₂O₇/g-C₃N₄) has been successfully synthesized by calcining a mixture of g-C₃N₄ and NiNH₄PO₄·H₂O for the first time. Compared with the pristine g-C₃N₄, a-Ni₂P₂O₇/g-C₃N₄ displays the advanced visible light utilization and improved charge separation. Furthermore, the increased amount of

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active sites and robust reduction ability of electron can also be obtained relative to crystalline $\text{Ni}_2\text{P}_2\text{O}_7$ modified $\text{g-C}_3\text{N}_4$ ($\text{c-Ni}_2\text{P}_2\text{O}_7/\text{g-C}_3\text{N}_4$), which is contributed to the better photocatalytic activity for H_2 generation from water splitting under visible light irradiation, and is even superior to $\text{Pt/g-C}_3\text{N}_4$.

2. Experimental section

2.1. Chemicals

Urea (H_2NCONH_2 , Sinopharm Chemical Reagent Co., Ltd., $\geq 99\%$), triethanolamine (TEOA, $(\text{HOCH}_2\text{CH}_2)_3\text{N}$, Sinopharm Chemical Reagent Co., Ltd., $\geq 78\%$), chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, Sinopharm Chemical Reagent Co., Ltd., $\geq 37\%$ Pt basis), ammonia ($\text{NH}_3 \cdot \text{H}_2\text{O}$, Beijing Chemical Works, 25.0–28.0%), ethylene glycol ($\text{HOCH}_2\text{CH}_2\text{OH}$, Sinopharm Chemical Reagent Co., Ltd., $\geq 99\%$), nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Sinopharm Chemical Reagent Co., Ltd., $\geq 98.5\%$), sodium dihydrogen phosphate dehydrate ($\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$, Sinopharm Chemical Reagent Co., Ltd., $\geq 99\%$), sodium carbonate (Na_2CO_3 , Beijing Chemicals Works, $\geq 99\%$), anhydrous ethanol ($\text{CH}_3\text{CH}_2\text{OH}$, Beijing Chemical works, $\geq 99.7\%$) and sodium sulfate anhydrous (Na_2SO_4 , Beijing Chemicals Works, $\geq 99\%$). Nafion solution (5 wt.%, Dupont). Ultrapure water with the specific resistance of $18.2 \text{ M}\Omega \cdot \text{cm}$ was obtained by reverse osmosis followed by ion-exchange and filtration.

2.2. Preparation of graphitic carbon nitride ($\text{g-C}_3\text{N}_4$)

The $\text{g-C}_3\text{N}_4$ was synthesized by directly heating urea in a muffle furnace at 600°C for 4 h with a heating rate of $0.5^\circ\text{C min}^{-1}$. The as-prepared yellow powder was obtained and then grinded.

2.3. Preparation of ammonium nickel phosphate ($\text{NiNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$) precursor

The precursor was obtained by a one-step solvothermal process [20]. Typically, ethylene glycol (10 mL) was added into the concentrated $\text{NH}_3 \cdot \text{H}_2\text{O}$ (10 mL) with stirring for 5 min to form an uniform mixture. Then, Na_2CO_3 (5 mL, 1 M), NaH_2PO_4 (7.5 mL, 1 M), and $\text{Ni}(\text{NO}_3)_2$ (5 mL, 1 M) were gradually added to the above liquid one by one at intervals of 5 min, and the final mixture was stirred for 1 h with the bright blue color. After that, the above mixed solution was transferred to a 50 mL Teflon-lined stainless-steel autoclave, which was later maintained at 170°C for 24 h. And then, the autoclave was cooled down to room temperature, and the precipitate was collected and washed with distilled water for three times and ethanol for once. The as-synthesized product was dried in vacuum at 60°C overnight.

2.4. Preparation of amorphous (a-) and crystalline (c-) $\text{Ni}_2\text{P}_2\text{O}_7$

The $\text{a-Ni}_2\text{P}_2\text{O}_7$ was synthesized by calcining precursor of $\text{NiNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ in a muffle furnace at 500°C for 2 h with a heating rate of 2°C min^{-1} , and $\text{c-Ni}_2\text{P}_2\text{O}_7$ was obtained by the similar method but changing the calcining temperature to 600°C .

2.5. Preparation of $\text{a-Ni}_2\text{P}_2\text{O}_7/\text{g-C}_3\text{N}_4$ and $\text{c-Ni}_2\text{P}_2\text{O}_7/\text{g-C}_3\text{N}_4$

Typically, the $\text{a-Ni}_2\text{P}_2\text{O}_7/\text{g-C}_3\text{N}_4$ was obtained as follows: firstly, $\text{NiNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ (48 mg) and $\text{g-C}_3\text{N}_4$ (400 mg) were ultrasonicated in ethanol (40 mL) for 30 min, and then magnetic stirred for 1 h. Secondly, the obtained mixture was washed by distilled water and dried at 60°C for 10 h. After that, the as-prepared solid sample was grinded and put into an alumina crucible and calcined at 500°C for 2 h with a heating rate of 2°C min^{-1} to get the $\text{a-Ni}_2\text{P}_2\text{O}_7/\text{g-C}_3\text{N}_4$ with 12 wt.% of initial content of $\text{NiNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$. The various loading contents of $\text{a-Ni}_2\text{P}_2\text{O}_7$ on $\text{g-C}_3\text{N}_4$ were also obtained by only changing the initial adding

content of $\text{NiNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ (5, 8 and 15 wt.%). For comparison, the crystalline $\text{c-Ni}_2\text{P}_2\text{O}_7/\text{g-C}_3\text{N}_4$ (12 wt.%) was also synthesized by the similar method by altering the calcined temperature from 500 to 600°C .

2.6. Characterizations

Wide angle X-ray diffraction (XRD) measurements were performed on a Rigaku D/max-2500pc X-ray diffractometer with $\text{Cu K}\alpha$ irradiation ($\lambda = 1.5406 \text{ \AA}$) by a scan rate of 4° min^{-1} . Transmission electron microscope (TEM) analyses were performed using a JEOL JEM-2010 microscope (accelerating voltage = 200 kV). X-ray photoelectron spectroscopy (XPS) analyses were performed using an ESCALAB MK II (Vacuum Generators) spectrometer using $\text{Al K}\alpha$ radiation (300 W). All binding energies were referenced to the C 1s peak at 284.6 eV of the surface adventitious carbon. Ultraviolet photoelectron spectroscopy (UPS) measurements were performed with an unfiltered He I (21.22 eV) gas discharge lamp at a total instrumental energy resolution of 100 meV. Ultraviolet-visible diffuse reflectance spectra (UV-vis DRS) were recorded on a Shimadzu UV-3600 spectrophotometer using the same amount of photocatalysts, in which BaSO_4 was used as the background. The photoluminescence (PL) spectra were detected on a Hitachi F-4500 fluorescence spectrophotometer with an excitation wavelength of 360 nm. Time-resolved photoluminescence (TRPL) spectra were recorded on a FLSP920 fluorescence lifetime spectrophotometer (Edinburgh, Instruments, UK) at an excitation wavelength of 360 nm. Fourier transform infrared spectroscopy (FTIR) of the samples were tested on a NEXUS-670 spectrometer at room temperature.

All electrochemical and photoelectrochemical tests were performed on a typical three-electrode system in 0.5 M Na_2SO_4 solution (PH = 6.8) on a CHI760E electrochemical workstation at room temperature using Ag/AgCl as the reference electrode, Pt mesh as the counter electrode, and catalyst films as the working electrodes. The photocurrent measurements were performed at an applied potential of 0 V versus Ag/AgCl (vs. Ag/AgCl) under visible light irradiation. A 300 W Xe lamp (CEL-HXF 300, $320 < \lambda < 2500 \text{ nm}$) equipped with a cut off filter ($\lambda > 420 \text{ nm}$) was served as the light source. The electrochemical impedance spectroscopy (EIS) was determined over the frequency range from 0.01 to 100,000 Hz with an alternating current (AC) amplitude of 10 mV at the open circuit voltage in dark.

2.7. Photocatalytic activity for H_2 generation

Reactions were carried out in a Pyrex top-irradiation reaction vessel connected to a glass closed gas system. H_2 generation was achieved by dispersing 100 mg of photocatalyst ($\text{a-Ni}_2\text{P}_2\text{O}_7/\text{g-C}_3\text{N}_4$ with different initial adding contents of $\text{NiNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ (5, 8, 12 and 15 wt.%), $\text{c-Ni}_2\text{P}_2\text{O}_7/\text{g-C}_3\text{N}_4$ (12 wt.%) and pure $\text{g-C}_3\text{N}_4$) in aqueous solution (100 mL) containing 10 vol.% of TEOA as a sacrificial electron donor. The reaction system was degassed to remove air absolutely prior to irradiation under the Xe lamp (300 W) with a 420 nm cut off filter to remove the ultraviolet (UV) light. During the reaction, the temperature of the reaction solution was maintained at 8°C by a flow of cooling water. The evolved gas was detected by gas chromatography (GC7900) equipped with a thermal conductive detector (TCD), using N_2 as the carrier gas.

2.8. Photocatalytic stability

The stability experiment was operated as below: the H_2 generation reaction was firstly tested for 3 h by using the method mentioned above. After that, all the H_2 generated in the gas system was removed completely. Then, the photocatalytic reaction was continued for another 3 h. As a result, the above reaction was performed three times (9 h in total).

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