Non-Noble-Metallic Cocatalyst Ni₂P Nanoparticles Modified Graphite-Like Carbonitride with Enhanced Photocatalytic Hydrogen Evolution under Visible Light Irradiation

Peng Zhang^{1,2}, Jiquan Wang^{1,*}, Yuan Li², Lisha Jiang², Zhuangzhuang Wang², Gaoke Zhang^{2,*}

¹ Hubei Province Engineering Consulting Co, Ltd., Wuhan 430061, China.

² School of Resources and Environmental Engineering, Wuhan University of Technology, Wuhan 430070, China.

Abstract: Energy crisis has become a serious global issue due to the increasing depletion of fossil fuels; therefore, it is crucial to develop environmentally friendly and renewable energy resources, such as hydrogen (H₂), to replace fossil fuels. From this viewpoint, photocatalytic H₂ production is considered as one of the most promising technologies. Noble metal platinum (Pt) can be applied as an efficient cocatalyst for improving the H₂ production performance of photocatalytic systems; however, its high cost limits its further application. Thus, the development of novel, high-activity, and low-cost cocatalysts for replacing noble metal cocatalysts is of great significance for use in photocatalytic H₂ evolution techniques. Herein, we successfully synthesized a Ni₂P/graphite-like carbonitride photocatalyst (Ni₂P/CN) using a conjugated polymer (SCN)_n as precursor for enhanced photocatalytic H₂ production under visible light illumination. Various characterization techniques, including optical and photoelectronic chemical tests, were used to investigate the structural composition, morphology, and light adsorption ability of these materials. X-ray diffraction, Fourier transform infrared spectroscopy (FT-IR), and X-ray photoelectron spectroscopy results showed that Ni₂P/CN nanocomposites with good crystal structure were obtained. Scanning electron microscopy and transmission electron microscopy results revealed that the Ni₂P/CN samples had a typical two-dimensional layered structure, and the Ni₂P nanoparticles were uniformly loaded on the surface of the CN to form a non-noble metal promoter. UV-Vis diffuse reflectance spectra results demonstrated that the loading of Ni₂P nanoparticles effectively enhances the adsorption capacity of CN to visible light. Photoluminescence spectroscopy and photocurrent (PL) results suggested that Ni₂P loading to CN is beneficial for promoting the migration and separation efficiency of photogenerated carriers. Photocatalytic H₂ production was conducted under visible light irradiation with triethanolamine as a sacrificial agent. The results suggest that the Ni₂P/CN composite photocatalysts exhibit excellent photocatalytic reduction performance. In particular, the H₂ evolution rate of the optimal Ni₂P/CN nanocomposite is 623.77 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$, which is higher than that of CN modified by noble metal Pt, i.e., 524.63 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$. In conclusion, Ni₂P nanoparticles are homogeneously attached to the surface of CN, and a strong interfacial effect exists between them, thereby forming an electron transfer tunnel that greatly inhibits the recombination of photoinduced carriers and promotes the migration of electrons from CN to Ni₂P. In addition, a possible photocatalytic mechanism is proposed based on the experiments and characterizations. This work has profound significance for developing non-noble metal cocatalysts for the substitution of noble metal cocatalysts for high-efficiency photocatalytic H₂ evolution.

Key Words: Cocatalyst; Ni₂P; Photocatalytic hydrogen evolution; Interfacial effect, Visible light

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*Corresponding authors. Emails: 441780131@qq.com (J.W.); gkzhang@whut.edu.cn (G.Z.).

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非贵金属助剂 Ni_2P 修饰类石墨碳氮化物光催化剂增强可见光光催化产氢性能

张鹏^{1,2}, 王继全^{1,*}, 李源², 姜丽莎², 王壮壮², 张高科^{2,*}

¹ 湖北省工程咨询股份有限公司, 武汉 430061

² 武汉理工大学资源与环境工程学院, 武汉 430070

摘要: 随着化石燃料的日益枯竭, 能源危机已经成为一个严重的全球性问题。开发氢气等环境友好型的可再生能源来替代化石燃料已迫在眉睫。光催化水解制氢被认为是解决这一问题最有效的技术之一, 贵金属(如Pt)可以作为助催化剂提高光催化体系的制氢性能, 但高昂的成本限制了该技术的进一步应用。因此, 开发新型、高性能、低成本的非贵金属助催化剂以替代贵金属助催化剂, 对于将光催化产氢技术付诸实践具有重要意义。在此, 我们以共轭聚合物(SCN)_n为前驱体成功地合成了 Ni_2P /类石墨碳氮化物光催化剂($\text{Ni}_2\text{P}/\text{CN}$), 在可见光照射下具有优异的光催化产氢性能。使用各种表征技术、光学和光电化学测试研究了这些材料的结构组成、形貌特征以及光学性质。X射线衍射(XRD)、傅里叶变换红外光谱(FT-IR)和X射线光电子能谱(XPS)结果表明了合成的 $\text{Ni}_2\text{P}/\text{CN}$ 纳米复合材料具有良好的晶体结构。扫描电镜(SEM)和透射电镜(TEM)结果显示, $\text{Ni}_2\text{P}/\text{CN}$ 样品具有典型的二维层状结构, Ni_2P 纳米颗粒均匀地负载在CN表面。紫外-可见漫反射光谱(DRS)结果表明, 负载 Ni_2P 纳米颗粒有效地增强了CN对可见光的吸收能力。光致发光光谱(PL)和光电流测试结果表明, Ni_2P 的负载有利于促进光生载流子的迁移和分离效率。光催化产氢实验是在可见光照射下进行的, 以三乙醇胺为牺牲剂。结果表明, $\text{Ni}_2\text{P}/\text{CN}$ 复合光催化剂具有良好的光催化还原性能。性能最优的 $\text{Ni}_2\text{P}/\text{CN}$ 复合材料产氢效率达到了 $623.77 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$, 优于以贵金属Pt作助催化剂的CN样品的产氢效率($524.63 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$)。此外, 通过一系列表征、光学以及光电化学测试的分析表明, Ni_2P 纳米粒子均匀地附着在CN的表面上, 并且它们之间存在很强的界面效应, 从而形成了抑制光生载流子重组并促进电子迁移的电子传输通道, 促进电子从CN迁移至 Ni_2P 。此外, 根据实验和表征, 提出了一种可能的光催化机理。这项工作对于非贵金属取代贵金属作为光催化产氢助剂的发展具有重要意义。

关键词: 助催化剂; Ni_2P ; 光催化产氢; 界面效应; 可见光
中图分类号: O643

1 Introduction

Owing to the gradually depletion and unsustainable nature of global fossil energy, the development of clean and sustainable energy for the substitution of traditional fossil energy is of great urgency and indispensable for our world. Therefore, looking for an ideal technique for clean energy evolution is of great significance. Among various energy conversion techniques, photocatalytic hydrogen (H_2) evolution is one of the most promising technologies to resolve the fossil energy shortage problem and has received more and more attention in the past decade¹⁻⁴. However, a single photocatalyst is hardly utilized to directly conduct H_2 evolution experiment owing to its rapid recombination efficiency of photoinduced electron-hole pairs and usually needs to get additive support from the cocatalyst which usually possesses superior electrons trapping ability⁵⁻⁸. To date, many researches about cocatalyst selection in photocatalytic H_2 evolution are over relied on noble-metal cocatalyst such as platinum (Pt). The expensive cost and easy back reaction with O_2 and H_2 to produce H_2O of noble-metal cocatalyst largely restrict the practical utilization of H_2 evolution technique in industry. Therefore, developing non-noble metallic cocatalysts with high efficiency and low price is pivotal for the practical utilization of this technique. So far, several transition metal phosphides, including Co_2P , FeP , MoP and Ni_2P , have been

investigated as promising non-noble metallic cocatalysts to substitute for noble metal cocatalysts⁹⁻¹². Among them, Ni_2P is excellent for its superior electron trapping ability which can effectively inhibit the recombination of photoinduced carriers. Therefore, Ni_2P may be a promising non-noble metallic cocatalyst for photocatalytic H_2 evolution^{13,14}.

Graphite-like carbonitride, a semiconductor driven by visible light, has attracted much attention as a promising photocatalyst mainly owing to its controllable surface, low cost, excellent chemical stability and nontoxicity¹⁵⁻¹⁷. Nevertheless, it is usually difficult to achieve a satisfying photocatalytic efficiency by only using graphite-like carbonitride due to the insufficient light adsorption and rapid recombination of photoinduced carriers. Various strategies were therefore investigated to modify graphite-like carbonitride such as metallic/non-metallic heteroatom doping^{18,19}, modifying with defects²⁰, microstructure regulation²¹ and construction of heterojunction²². Especially, cocatalyst modification on the surface of graphite-like carbonitride is considered to be an ideal strategy for boosting photocatalytic H_2 production via rapidly transferring interfacial electrons, minimizing the recombination of photoinduced charges, and offering effectively active sites.

Considering the numerous merits of Ni_2P , we successfully introduced Ni_2P nanoparticles on the surface of graphite-like

carbonitride (CN)²³. The Ni₂P/CN nanocomposites exhibit apparently enhanced photocatalytic H₂ evolution performance than that of single CN. Especially, the H₂ evolution performance of the optimal sample is better than that of CN supported by Pt nanoparticles, indicating Ni₂P is indeed a promising non-noble metallic cocatalyst. The structures, morphologies, optical and photoelectronic properties of as-prepared nanomaterials were investigated by various characterization techniques. These characterizations demonstrate Ni₂P nanoparticles are uniformly attached on the surface of CN and a strong synergistic effect exists between Ni₂P and CN, thus forming an electron transfer channel that can greatly improve the charge separation. Moreover, based on the trapping experiments and analyses of characterizations, a possible photocatalytic H₂ evolution mechanism is proposed. This work offers new insight for synthesizing novel photocatalysts decorated by non-noble metallic cocatalyst such as Ni₂P for photocatalytic H₂ evolution.

2 Experimental and computational section

2.1 Materials preparation

Potassium thiocyanate (KSCN, $\geq 98.5\%$), potassium persulfate ((NH₄)₂S₂O₈, $\geq 99.5\%$), nickel dichloride hexahydrate (NiCl₂·6H₂O, $\geq 98.0\%$) and sodium hypophosphite monohydrate (NaH₂PO₂·H₂O, $\geq 98.0\%$) were purchased from Sinopharm Chemical Reagent Co., Ltd. All of the reagents were analytical grade without further purified.

2.2 Synthesis of Ni₂P/CN samples

Firstly, KSCN and (NH₄)₂S₂O₈ with a molar ratio of 2 : 1.5 were ground in an agate mortar. After grinding for 1 h in the fume cupboard, the precursor conjugated polymer (SCN)_n was rinsed with deionized water for 4 times and dried to obtain solid powders²⁴. Subsequently, the solid powder was heated to 500 °C for 2 h with a rate of 5 °C·min⁻¹. Ultimately, CN photocatalyst was obtained by cooling naturally to room temperature.

Ni₂P/CN composites were prepared by mixing the nickel salt, sodium hypophosphite, pristine CN and heating them in nitrogen (N₂) atmosphere. Typically, 10 mg NiCl₂·6H₂O was dissolved into 5 mL of deionized water. Then, 150 mg as-prepared CN was mixed into the above solution. After that, this mixture was stirred for 1 h, followed by ultrasonication for another 1 h. Subsequently, 50 mg NaH₂PO₂·H₂O was dissolved into the previous mixture. The whole mixed solution was again stirred and sonicated for 1 h each and dried in a vacuum oven. The dried solid was then heated at a rate of 5 °C·min⁻¹ up to 200 °C for 1 h under N₂ atmosphere in a tube furnace and cooled down to ambient temperature. The obtained solid was washed 4 times by ethanol and deionized water, the Ni₂P/CN composite with the mass ratio of 2% (w, mass fraction) was fabricated after dried at 60 °C for 8 h. Composites with various loading amounts of Ni₂P nanoparticles (1% (w), 3% (w), 5% (w)) were denoted as 1% (w) Ni₂P/CN, 3% (w) Ni₂P/CN, 5% (w) Ni₂P/CN.

2.3 Characterization

The structure and crystallinity of the as-prepared photocatalysts were investigated by X-ray diffraction (XRD,

D/MAX-RB, Japan) analysis under the experimental situation of 40 kV and 50 mA. A Fourier transform infrared spectroscopy (FT-IR, Thermo Nicolet, American) was used to study the chemical bonds of these composite samples. X-ray photoelectron spectroscopy (XPS) analyses were performed on a PHI Quantera II system (American) with a monochromatic Mg Ca source to study the chemical states and valence band. All binding energies were referenced to the C 1s peak at 284.5 eV. UV-Vis diffuse reflectance spectra (DRS) analyses were performed via a Shimadzu UV 2550 (Japan) spectrometer with the BaSO₄ powder as the substrate. Scanning electron microscopy (SEM, JSM-5610LV, American) and transmission electron microscopy (TEM, JEM-2100F, American) were applied to observe the morphology of these samples. And photoluminescence (PL) emission spectra measurements were tested via a fluorescence spectrophotometer (RF-5301PC, Shimadzu, Japan).

2.4 Photocatalytic measurements

The photocatalytic H₂ evolution experiments were performed in a 400 mL three-necked Pyrex flask at room temperature. Four 3 W 420 nm LED lamps were employed as the visible light source to trigger the reaction of photocatalytic H₂ generation. Typically, 20 mg of the as-prepared sample was dispersed in 100 mL aqueous solution containing 10% (volume fraction) of triethanolamine (TEOA) and the dispersion was sonicated for 5 min. Additionally, a control experiment that moderate amount H₂PtCl₆ was added to make sure the pristine CN loaded with 1% (w) Pt by photodeposition route was performed. Before each reaction, the photocatalytic system was bowled with N₂ for 15 min to pull out the air completely. Finally, photocatalytic H₂ generation was evaluated by a gas chromatograph (Shimadzu GC-2014C, Japan, with N₂ as carrier gas), and 200 μ L of the gaseous sample was detected at regular intervals (30 min).

3 Results and discussion

3.1 Sample characterizations

The XRD results of pristine CN and Ni₂P/CN composites with various Ni₂P loading amounts were demonstrated in Fig. 1. The two peaks at 13.0° and 27.8° indicate that both pristine CN

Fig. 1 XRD patterns of pristine CN and Ni₂P/CN composites with different Ni₂P contents (1% (w), 2% (w), 3% (w), 5% (w)).

and $\text{Ni}_2\text{P}/\text{CN}$ composites present similar structural characteristics of graphite-like carbonitride. Meanwhile, peaks of $\text{Ni}_2\text{P}/\text{CN}$ composites at 40.8° , 44.6° , 47.3° , 54.2° , 54.9° and 66.2° matched with the characteristic peaks of Ni_2P [JCPDS 03-0953]²⁵. The peaks of Ni_2P in 1% (w) $\text{Ni}_2\text{P}/\text{CN}$ composite are not apparently observed in comparison with other composites, which is attributed to low loading concentration and highly dispersed Ni_2P nanoparticles. With further increasing loading concentration, the peaks corresponding to Ni_2P can be gradually observed, indicating the successful introduction of Ni_2P to CN. Furthermore, no other impurity peaks are found in XRD spectra, confirming $\text{Ni}_2\text{P}/\text{CN}$ composites were successfully synthesized.

The FT-IR analyses (Fig. 2) indicate that the pristine CN backbones are retained after Ni_2P nanoparticles hybridization. For the pristine CN and $\text{Ni}_2\text{P}/\text{CN}$ composite samples, the characteristic peak at 807 cm^{-1} originates from the unique vibration characteristic of the triazine ring unit. Furthermore, there is a wide absorption band in the region between 1200 cm^{-1} and 1700 cm^{-1} , which can be corresponded to the representative stretching vibration modes of $\text{C}-\text{N}$ and $\text{C}=\text{N}$ ²⁶. Besides, the absorption band between 2850 cm^{-1} and 3450 cm^{-1} includes residual $\text{N}-\text{H}$ components and $\text{O}-\text{H}$ bands, which are related to uncooled amino groups and water molecules adsorbed on the surface. The results confirm that there is no variation in the

Fig. 2 FT-IR spectra of pristine CN and $\text{Ni}_2\text{P}/\text{CN}$ composites with different Ni_2P contents (1% (w), 2% (w), 3% (w), 5% (w)).

stretching and bending vibrations of CN on Ni_2P nanoparticles loading, which is consistent with XRD analysis^{27–29}.

The XPS measurements of pristine CN and 2% (w) $\text{Ni}_2\text{P}/\text{CN}$ were performed to further study the elemental composition and chemical valence of the photocatalysts. As depicted in Fig. 3a, the $\text{C } 1s$ orbitals of pristine CN and 2% (w) $\text{Ni}_2\text{P}/\text{CN}$ can be fitted to two peaks, and their binding energies can be detected at 284.5 eV and 288.1 eV, which can be matched to the C source adsorbed on the sample surface and the $\text{N}-\text{C}=\text{N}$ bond position in the graphite-like carbon nitride structure^{30,31}. Meanwhile, the $\text{N } 1s$

Fig. 3 XPS spectrum of pristine CN and 2% (w) $\text{Ni}_2\text{P}/\text{CN}$: (a) $\text{C } 1s$ region, (b) $\text{N } 1s$ region, (c) $\text{Ni } 2p$ region of 2% (w) $\text{Ni}_2\text{P}/\text{CN}$, (d) $\text{P } 2p$ region of 2% (w) $\text{Ni}_2\text{P}/\text{CN}$.

region of pristine CN and 2% (w) Ni₂P/CN involved four contributions in Fig. 3b. The analytical peaks are detected at 398.6 eV, 399.5 eV, 400.8 eV and 404.2 eV, which corresponded to C—N=C, C₃—N, C₂—N—H, and π -excitation, respectively^{32,33}. It is noteworthy that the N 1s peak of C₃—N in 2% (w) Ni₂P/CN located at 399.3 eV decreases by 0.2 eV compared to that in CN, implying the combination of chemical bonds between Ni₂P nanoparticles and CN layer to form N—Ni bond. Fig. 3c indicates that the Ni 2p region of the 2% (w) Ni₂P/CN can be fitted to four peaks, which can be detected at 855.7, 861.8, 873.5 and 881.8 eV. It shows that there are nickel elements in Ni₂P in the valence state of Ni²⁺^{34,35}. Furthermore, the P 2p region of 2% (w) Ni₂P/CN was shown in Fig. 3d, the peak at 129.5 eV can be attributed to metal—P bonds in Ni₂P, the peak at 133.1 eV is ascribed to oxidized and unreduced phosphate in air^{36,37}. These results further affirm the formation of Ni₂P in the Ni₂P/CN composites.

To investigate the optical properties of pristine CN, as well as Ni₂P/CN composites, UV-Vis measurement was carried out and the spectra were displayed in Fig. 4. The pristine CN expresses weak light absorption in the visible light region. Besides, Ni₂P/CN composites have better light absorption ability than pristine CN, and the absorption intensity of Ni₂P/CN composites in the region of visible light becomes stronger with the increasing amount of Ni₂P. Furthermore, the Ni₂P/CN composites exhibit a few redshifts of the absorption edge comparing to the pristine CN, indicating the Ni₂P/CN composites possess a wider adsorption range of visible light, which is beneficial to H₂ evolution by generating more photoinduced charge carriers.

The morphologies of the synthesized photocatalysts were observed by SEM and TEM techniques. Fig. 5a,b are the SEM images of pristine CN and 2% (w) Ni₂P/CN, respectively. It can be observed that the two photocatalysts were composed *via* the aggregation of nanoparticles with irregular morphology, and the morphology of the 2% (w) Ni₂P/CN composite after secondary

Fig. 4 UV-Vis absorption spectra of pristine CN and Ni₂P/CN composites with different Ni₂P contents (1% (w), 2% (w), 3% (w), 5% (w)).

calcination did not change significantly. In order to verify the loading status of Ni₂P nanoparticles, the morphological characteristics of 2% (w) Ni₂P/CN composite was further observed by TEM technology. The TEM images of 2% (w) Ni₂P/CN in Fig. 5c–e clearly demonstrated that Ni₂P nanoparticles were homogeneous distribution on the surface of CN. Especially, the size of Ni₂P nanoparticles ranging from 10 to 50 nm, which is beneficial to enhance the active space area and facilitate electron transport.

3.2 Photocatalytic performance

The photocatalytic H₂ generation activities of pristine CN, Ni₂P/CN and Pt/CN composites were measured with TEOA as a scavenger under visible light illumination. As is revealed in Fig. 6a, pristine CN showed little photocatalytic H₂ evolution (only trace H₂ can be detected) without noble metal loading. Interestingly, Ni₂P/CN composites presented a much superior H₂ evolution to pristine CN so that loading Ni₂P nanoparticles could significantly promote the photocatalytic performance of CN. For 1% (w) Ni₂P/CN and Pt/CN, the H₂ generation rates are 159.66 and 524.63 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$, respectively in Fig. 6b. The highest H₂ generation rate of 623.77 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ was achieved when using

Fig. 5 The SEM images of (a) pristine CN and (b) 2% (w) Ni₂P/CN, the TEM images (c–e) of 2% (w) Ni₂P/CN.

Fig. 6 (a) Time course of H₂ generation performance and (b) H₂ generation rate of pristine CN, Pt/CN and Ni₂P/CN composites with different Ni₂P contents (1% (w), 2% (w), 3% (w), 5% (w)). (c) Cyclic H₂ evolution curve of 2% (w) Ni₂P/CN composite under 420 nm visible light in 10% (volume fraction) TEOA solution and (d) XRD patterns of 2% (w) Ni₂P/CN composite before and after the photocatalytic H₂ evolution for 4 times.

2% (w) Ni₂P/CN composite, despite being more naturally abundant and less price, it is superior to Pt/CN. Nevertheless, as the Ni₂P loading content is further increased more than 2% (w), the H₂ generation gradually decreased but still significantly stronger than the pristine CN, which may be due to excessive Ni₂P covers the active sites on the surface of CN and prevents CN from absorbing incident light³⁸.

The stability and durability of photocatalyst are also essential for practical application. Therefore, we used 2% (w) Ni₂P/CN as a representative sample to measure the stability of as-prepared composites for photocatalytic H₂ generation, and the results are depicted in Fig. 6c. It is pretty clear that the 2% (w) Ni₂P/CN composite could maintain an efficient and stable photocatalytic

property in long-term reaction for four cycles usage. Moreover, XRD analysis confirmed the unchanged basic structure of 2% (w) Ni₂P/CN before and after four cycles photocatalytic H₂ production experiment (Fig. 6d). This further supports the stability and durability of Ni₂P as a non-noble metal cocatalyst, which can be used to improve the ability of photocatalytic H₂ evolution.

3.3 Mechanism for enhanced photocatalytic performance

The PL measurements of pristine CN and 2% (w) Ni₂P/CN were carried out to investigate the separation efficiency and recombination process of photoinduced carriers³⁹. As revealed in Fig. 7a, the peak value of the fluorescence spectrum of 2% (w)

Fig. 7 (a) PL spectra of pristine CN and 2% (w) Ni₂P/CN ($E_x = 315$ nm), (b) the photocurrent response curve of pristine CN and 2% (w) Ni₂P/CN.

Fig. 8 Mechanism for photocatalytic H₂ evolution from water over Ni₂P/CN composite.

Ni₂P/CN composite is lower than that of pristine CN, illustrating that the recombination rate of photoinduced carriers is hindered impressively with Ni₂P nanoparticles loading. Moreover, the absorption peak of 2% (w) Ni₂P/CN composite shifted from 432 nm to 435 nm compared with pristine CN because of the addition of Ni₂P nanoparticles, which was more conducive to the transfer of photoinduced carriers from CN to Ni₂P. Additionally, the photocurrent response was measured as well in Fig. 7b. It is clearly observed that pristine CN showed pretty low photocurrent response and photocurrent density, but 2% (w) Ni₂P/CN composite presented much higher photocurrent density than pristine CN. The increased photocurrent intensity indicates the enhanced migration efficiency of photoinduced charge carriers, thus finally promoting the photocatalytic efficiency of H₂ production⁴⁰.

On the basis of the results above, the enhanced photocatalytic H₂ generation performance may be attributed to the effective interfacial charge transfer from CN to the Ni₂P (Fig. 8)^{41,42}. As a cocatalyst, Ni₂P mainly plays two roles: (1) reducing the charge recombination effect after charge separation, and (2) promoting the surface chemical reaction of pristine CN. The facilitated electrons in Ni₂P cocatalyst would reduce H⁺ into H₂, while holes on CN can oxidize the sacrificial electron donor TEOA.

4 Conclusions

In conclusion, Ni₂P/CN photocatalysts were successfully synthesized by solid-phase grinding, ultrasonic mixing and calcination method. Ni₂P nanoparticles can be served as an active and highly stable free-noble metal cocatalyst under visible light irradiation to enhance the photocatalytic H₂ evolution efficiency of pristine CN. The optimized H₂ production rate is 623.77 μmol·h⁻¹·g⁻¹ for 2% (w) Ni₂P/CN composite, which is pretty higher than that of Pt/CN composite. The improvement of photocatalytic performance is mainly ascribed to the effective transfer of charge from CN to Ni₂P, which inhibits the recombination of photoinduced electron-hole pairs in CN. Most significantly, the long-term stability and excellent performance of continuous H₂ evolution under visible light irradiation promote the practical application of the system made of free-noble metal elements as cocatalyst.

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