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Article

Ni-P cluster modified carbon nitride toward efficient photocatalytic hydrogen production

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ABSTRACT

Exploring low-cost cocatalyst to take over noble metal cocatalyst is still challenging in the field of photocatalytic proton reduction. Herein, Ni-P alloy clusters are anchored onto the surface of polymeric carbon nitride through a chemical plating method and serve as highly efficient and stable cocatalyst toward photocatalytic proton reduction. An effective role in promoting the charge separation and migration of the photocatalytic system is demonstrated for Ni-P clusters, which essentially enhance the photocatalytic H₂-production rate to a value of 1506 $\mu\text{mol h}^{-1} \text{g}^{-1}$. This performance is comparable to that of the benchmark of Pt-modified carbon nitride. This work highlights that the Ni-P alloy could be a potential alternative to noble metal cocatalyst in the photocatalytic reactions.

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1. Introduction

With increasing concerns of global energy shortage, it is realized urgent for the development of sustainable technology for producing renewable energy. One of the attractive approaches is the H₂ generation from proton reduction driven by semiconductor photocatalysis [1–5]. The choice of a high-performance and stable photocatalyst is critical in this approach. An ideal photocatalyst for this application must be qualified both thermodynamically and kinetically with a well-matched band gap to harvest a wide range of solar light, a negative enough position of conduction band to drive the proton reduction reaction, and sufficient reactive sites to accomplish the surface catalytic reactions [6–10]. Polymeric carbon nitride is a potentially hopeful candidate as it is chemically stable, absorbs visible light, and is economical in synthesis [11,12]. Nevertheless, the photocatalytic activity of pristine

carbon nitride is rather low because of the severe recombination of photoexcited electron and holes, which heavily restricts the electron transfer from the inner to the outmost surface, as well as the subsequent proton reduction reaction [13,14].

Several strategies could be applied to improve the ability of polymeric carbon nitride in photocatalytic proton reduction, such as crystallinity enhancement [15–17], elemental doping [18–22] and heterostructure construction [23–27], by extending the photoresponse range and accelerating the spatial separation of photoexcited charge carriers. Particularly, cocatalyst modification has attracted much interest because this strategy could not only boost the charge separation by capturing photoexcited charge carriers but also promote the surface catalytic process by reducing the overpotential [28,29]. Typical cocatalysts could be noble metals, e.g. Pt [30,31], Pd [32,33] and Au [34,35], but the high cost of them is unfavorable for practicable technological application. More and more attention have then

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been paid on the investigation of cocatalysts composed by earth-abundant elements such as Ni-based, Co-based, Cu-based, Mo-based and W-based materials [36–45], in order to find an efficient and economical photocatalytic system for solar-to-fuel conversion.

Herein, we describe the modification of polymeric carbon nitride by Ni-P alloy clusters via a chemical plating method. The resultant photocatalyst shows an effective charge separation and thus a stable and efficient activity toward photocatalytic hydrogen evolution, which is comparable to that of Pt modified carbon nitride as a benchmark. The study demonstrates that the Ni-P alloy clusters could be regarded as an alternative to noble metal cocatalysts in the photocatalytic applications.

2. Experimental

2.1. Sample preparation

Ni-P modified carbon nitride (labeled as NP-CN) was prepared through a chemical plating method. Firstly, the bulk carbon nitride (labeled as CN) was obtained by directly heating urea at 550 °C for 2 h in a muffle furnace. The heating rate is 5 °C/min. To evenly deposit the Ni-P alloy layer onto the surface of polymeric carbon nitride, 600 mg CN was initially sensitized in 200 mL stannous chloride solution ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, 1 g/L) for 15 min by sonication, and subsequently activated in 200 mL palladium chloride solution (PdCl_2 , 0.1 g/L) for 15 min by sonication. The sensitization and activation procedure was repeated for another time. Afterward, the mixture was filtered and the obtained powder was immersed in 100 mL solution containing 0.1 mol/L $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 0.3 mol/L $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$ and 1.0 mol/L DL-malic acid. Then, 10.6 g $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ was added into the mixture under continuous stirring. The pH value of the resultant suspension was adjusted to 2.0–3.0 by using 1 mol/L H_2SO_4 solution. The reaction was kept proceeding at 85 °C for 1 h. Finally, the NP-CN was obtained after washing the precipitates with deionized water for 5 times and drying in an oven at 80 °C overnight. The sensitized and activated CN without Ni-P modification was also used as a reference sample, which is denoted as CN1.

The chemical plating process follows the reaction equations shown below:

2.2. Characterization

X-ray diffraction (XRD) patterns were surveyed on a powder diffractometer (HZG41 B-PC) with $\text{Cu K}\alpha$ radiation. Morphology observation and EDS mapping were performed on a JSM-7500 F (JEOL, Japan) field emission scanning electron microscope (FESEM) and a JEM-2100F transmission electron microscope

(TEM, JEOL, Japan). The contents of Ni, P, and Pd were determined on a 4300DV inductively coupled plasma atomic emission spectrometry (ICP-AES). Nitrogen adsorption-desorption isotherms were analyzed on a Micromeritics ASAP 3020 nitrogen adsorption apparatus (USA). The photoluminescence (PL) spectra were recorded on an F-7000 fluorescence spectrophotometer (Hitachi, Japan) with a Xenon lamp as the excitation source. Time-resolved photoluminescence (TRPL) measurements were conducted on a FLS920 fluorescence lifetime spectrophotometer (Edinburgh Instruments, UK). Both excitation wavelength of PL and TRPL was 325 nm. A Shimadzu UV-vis spectrophotometer (UV-2600) was employed to measure the UV-visible diffuse reflectance spectra (DRS). Fourier transform infrared (FTIR) spectra were measured by a Nicolet iS50 FTIR Spectrometer (TMO, US). X-ray photoelectron spectroscopy (XPS) analysis were conducted using a VG ESCALAB 210 electron spectrometer with $\text{Al K}\alpha$ radiation source. The binding energy was calibrated with referenced to the C 1s peak at 284.8 eV. Electrochemical analysis was carried out on a CHI660C electrochemical workstation (Chenhua Instrument, Shanghai, China) with a three-electrode electrochemical cell. This includes a working electrode, a platinum counter electrode and an Ag/AgCl reference electrode. The electrolyte consists of an aqueous solution of 0.5 mol/L Na_2SO_4 . The light source is a 420-nm LED with a power of 3 W. The working electrode was prepared by coating samples slurry onto a F-doped SnO_2 -coated glass (FTO glass). The coating area is $2 \times 1.2 \text{ cm}^2$.

2.3. Photocatalytic H_2 evolution reactions

The light source in the photocatalytic reaction is a 350 W xenon arc lamp (Changzhou Siyu, China) with an AM1.5 filter. In detail, 50 mg photocatalyst was dispersed by continuous sonication and stirred in the aqueous solution of 80 mL 25 vol% CH_3OH in a 100 mL three-necked Pyrex flask. The flask was sealed by silicone rubber septum. The system was kept at 25 °C and 1 atm pressure, and was then purged with N_2 for 30 min to ensure an anaerobic condition. During irradiation, 0.4 mL gas was extracted from the reactor every hour and was analyzed by a GC-14C gas chromatograph (Shimadzu, Japan, TCD).

3. Results and discussion

3.1. Molecular structure

The XRD patterns of CN and NP-CN (shown in Fig. 1(a)) exhibit two characteristic diffraction peaks at 13.1° and 27.6° , which correspond to the (100) and (002) crystalline feature of layered carbon nitride, respectively. The former peak can be attributed to the in-plane periodically repeated tri-s-triazine heterocycles in the CN frameworks, and the latter peak corresponds to the interlayer stacking [46,47]. Besides, the pattern of NP-CN shows a broad peak ranging from 20° to 30° . This is because the surface of CN is covered by the ultra-small clusters of Ni-P alloy after chemical plating process, which induces the amorphous-like peak in the XRD pattern. The contents of Ni, P,

Fig. 1. XRD patterns (a) and FTIR spectra (b) of CN and NP-CN.

and Pd determined by ICP-AES were 1.85, 0.66 and 0.86 wt% in NP-CN.

The chemical structure of the samples was further investigated by the FTIR spectra shown in Fig. 1(b). The sharp peak at 806 cm^{-1} belongs to the typical bending vibration of tri-*s*-triazine heterocycles. The clear peak at 883 cm^{-1} originates from the deformation mode of N-H [48–50]. Those intensive absorption peaks in the range of 1200–1650 cm^{-1} correspond to the different vibration modes of the C–N bond involved in the tri-*s*-triazine heterocycles [49,50]. Besides, the broad absorption band from 3000 to 3500 cm^{-1} originates from the various vibration modes of the N–H bond of the uncondensed amine groups and adsorbed H_2O molecules [50,51]. Note that CN and NP-CN show almost identical FTIR spectra, indicating that the tri-*s*-triazine-based molecular structure of polymeric carbon nitride was not broken during the chemical plating process.

3.2. Morphology and microstructure

The electron microscopic observation shows that the CN sample (Fig. 2(a) and (b)) was composed of a large number of sheet-like structure, which is the representative structural feature of polymeric carbon nitride. After chemical plating, the nanosheets aggregated (Fig. 2(c)). Moreover, uniformly distributed dots with dark color could be clearly seen on the surface of CN (Fig. 2(d)), suggesting the successful deposition of

Fig. 2. FESEM and TEM images of CN (a,b) and NP-CN (c,d).

Fig. 3. FESEM image (a), elemental mapping images of C (b), N (c), Ni (d), P (e) and Pd (f) of NP-CN.

Ni–P alloy with good dispersion. The ultra-small size ($< 3 \text{ nm}$) of Ni–P alloy could also provide effective active sites when serving as co-catalysts. The good dispersion of Ni–P in the sample was further confirmed by elemental mapping analysis (Fig. 3), which reveals the homogenous distribution of C, N, Ni, P and Pd in the NP-CN sample.

The BET surface areas and pore volumes of the CN and NP-CN were obtained by N_2 adsorption–desorption isotherms, as shown in Fig. 4 and listed in Table 1. The type IV isotherms

Fig. 4. Nitrogen adsorption-desorption isotherms and pore size distribution curves (inset) of CN and NP-CN.

Table 1

Physical properties of CN and NP-CN.

Sample	Color	A_{BET} (m^2/g)	V_{pore} (cm^3/g)	d_{pore} (nm)
CN	yellow	78	0.30	19
NP-CN	black	42	0.21	20

with H3 hysteresis loops could be clearly observed for both samples. This implies that the pore structure of the two samples are mesoporous and the pores are slit-shaped, which is in agreement with the typical microstructure of aggregates of flake-like particles belonging to the polymeric carbon nitride. The pore size distributions (inset of Fig. 4) for both CN and NP-CN range in the entire mesoporous range and a part of macroporous range. Note that NP-CN shows smaller BET surface area and pore volume than CN. The reason could be that the pores of CN are partially filled by the ultra-small Ni-P clusters, revealing the excellent anchoring effect of CN frameworks and the strong interaction between Ni-P cocatalyst and CN substrate.

3.3. Optical property

The photo-absorption characteristic of CN and NP-CN are shown in Fig. 5. The absorption edge of CN is at about 448 nm. The NP-CN shows similar light absorption edge of CN, indicating that the chemical plating process did not affect its pristine

Fig. 5. UV-vis DRS of CN and NP-CN.

electronic structure. The introduction of Ni-P with residual Pd further enhances the photo-absorption in the whole range, which is caused by the charge transfer and the formation of active heterojunctions between CN substrate and the cocatalysts, bringing relaxation strength. This causes the weak background absorption of Ni-P and Pd.

Fig. 6. High-resolution XPS spectra of C 1s (a), N 1s (b) for CN and NP-CN, Ni 2p (c) and P 2p (d) for NP-CN.

Fig. 7. (a) Photocatalytic hydrogen production activities of CN, CN1, NP-CN and Pt-CNs. (b) Cycling test of photocatalytic hydrogen production over NP-CN.

3.4. XPS analysis

The XPS analyses of CN and NP-CN were used to obtain more detailed information about the chemical environment and elemental states near/on the surface and the interfacial interaction between Ni-P and carbon nitride. The C 1s spectrum of CN in Fig. 6(a) displays two peaks at 284.8 and 287.9 eV. These two peaks are attributed to the surface adventitious carbon from testing apparatus and the sp²-hybridized carbon in N=C-N bonding, respectively [52,53]. For N 1s spectra (Fig. 6(b)) of CN, four fitted characteristic peaks are obtained at 398.3, 399.4, 400.6 and 404.5 eV. These are related to the nitrogen in C=N-C bonding, N-(C)₃ groups, N-H_x bonding, and π-excitations, respectively [54–56]. As compared to the peaks of CN, the peaks assigned to the structural C 1s (N=C-N) and N 1s (C=N-C, N-H_x and π-excitations) of NP-CN all have a positive shift, indicating the electron transfer from carbon nitride to the surface anchored Ni-P clusters and thus a strong interfacial interaction. Meanwhile, Ni 2p spectrum in Fig. 6(c) presents two peaks appearing at 856.0 (Ni 2p_{3/2}) and 873.5 eV (Ni 2p_{1/2}), which are positively shifted with reference to metallic Ni [57,58]. This indicates that Ni is partially positive in Ni-P alloy. The two satellite peaks were located at 860.9 and 878.4 eV. Moreover, the two peaks at 129.3 and 130.2 eV in the P 2p XPS spectrum (Fig. 6(d)) reveal the existence of elemental P (in a partially negative state) in NP-CN, while the other two peaks at

132.9 and 133.8 eV are attributed to the adsorbed oxidation products HPO₃²⁻ or unreacted H₂PO₂⁻ [57,59].

3.5. Photocatalytic proton reduction activity

Hydrogen generation from photocatalytic proton reduction was examined for the as-prepared photocatalysts under solar simulated irradiation. From Fig. 7(a), one can see that pristine CN shows no noticeable hydrogen production. This implies the severe recombination of photoexcited charge carriers within CN frameworks and suggests that the incorporation of cocatalyst in the photocatalytic system is of vital importance. Obviously, the H₂-evolution rate over NP-CN is as high as 1506 μmol h⁻¹ g⁻¹, which is comparable to the value of the optimized 1 wt% Pt-modified carbon nitride (Pt-CN, prepared by the popular photo-deposition method). The sensitized and activated sample without Ni-P modification (CN1) also shows a H₂ yield of 237 μmol h⁻¹ g⁻¹, revealing the cocatalytic behavior of residual Pd. Note that NP-CN exhibits much better (6.4 times) performance than CN1. Moreover, the photocatalytic activity of NP-CN remains stable in a 9-h cycling test (Fig. 7(b)). These results reveal that Ni-P alloy could serve as a potential alternative to noble metal cocatalysts in the reaction of photocatalytic proton reduction.

3.6. Essence of photocatalytic performance enhancement

Fig. 8. PL (a), TRPL (b), and EIS (c) spectra of CN and NP-CN.

Table 2

The fitted emission decay lifetime of CN and NP-CN.

Sample	τ_1 (ns) (rel. %)	τ_2 (ns) (rel. %)	τ_m (ns)
CN	4.44 (80.02)	21.76 (19.98)	13.97
NP-CN	2.66 (80.03)	12.72 (19.97)	8.13

As afore-discussed, the specific surface area was reduced after chemical plating process, hence we attribute photocatalytic performance enhancement mainly to the improvement of charge transfer dynamics rather than microstructure. We applied a series of technology including PL, TRPL and electrochemical impedance spectroscopy (EIS) to elucidate such properties. From Fig. 8(a), one can see that the PL spectra of CN and NP-CN show similar peaks, however, the peak intensity of NP-CN is much weaker than that of CN. This is a strong evidence that the recombination of photoexcited electrons and holes has been largely reduced in NP-CN. A deep insight of this point was investigated by TRPL spectra in Fig. 8(b). The two decay curves can be fitted with the double-exponential decay mode, and the fitted results are listed in Table 2. Obviously, the mean fluorescence lifetimes (τ_m) of NP-CN (8.13 ns) is dramatically shortened as compared to that of CN (13.97 ns), indicating that NP-CN has much slower electron-hole recombination than CN because of an effective electron transfer process from the conduction band (CB) of carbon nitride to the surface of Ni-P cocatalysts. The more efficient electron transfer in NP-CN was further confirmed by the EIS spectra in Fig. 8(c). The arc radius of NP-CN is smaller than that of CN, namely, a smaller impedance for the transfer of electrons in NP-CN. Hence, the most important effect of Ni-P alloy clusters here as cocatalysts in the prepared photocatalytic system is that, it greatly boosts the charge separation and transfer due to the strong interfacial interaction. The photoexcited electrons of polymeric carbon nitride can be captured by Ni-P alloy and accumulate on its surface, and subsequently react with the adsorbed protons. At the same time, the photoexcited holes left behind in the valence band of carbon nitride are depleted by CH_3OH . Recent studies have indicated that both metal phosphide and graphitic carbon nitride materials possess special dipole rotations. Such property could affect the microwave absorption over these materi-

als [60,61], and may also affect the photo-absorption and charge transfer ability and thus the photocatalytic activity.

4. Conclusions

In summary, Ni-P alloy clusters are effectively anchored on the surface of polymeric carbon nitride photocatalyst through a chemical plating method. The Ni-P alloy clusters could act as stable and efficient cocatalysts, for the improvement of the photocatalytic proton reduction into hydrogen over carbon nitride photocatalyst, due to the effective role of Ni-P alloy clusters in promoting the charge separation and transfer. The resultant H_2 -evolution rate could be as high as $1506 \mu\text{mol h}^{-1} \text{g}^{-1}$, which is comparable to that of the benchmark of Pt-modified carbon nitride. Hence, the Ni-P alloy clusters could be regarded as a low-cost alternative to noble metal cocatalyst in the reaction of photocatalytic proton reduction.

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Graphical Abstract

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Ni-P alloy clusters function as efficient and stable cocatalysts for photocatalytic H_2 generation over carbon nitride photocatalyst, which is comparable to that of the benchmark of Pt-modified carbon nitride.

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可用于高效光催化制氢的Ni-P团簇改性氮化碳材料

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摘要: 在过去的几十年里, 化石能源的过度消耗导致了全球能源短缺和环境污染, 这严重制约着人类社会的发展。因此, 寻找一种清洁的可再生的能源成为了人们亟待解决的问题。太阳能是地球上最丰富的能源, 通过半导体光催化技术把太阳能转化为清洁的氢能是解决能源危机和缓解环境污染最有效的方法之一。石墨相氮化碳(CN)具有合适的能带结构、良好的稳定性、无毒性, 且合成方法简单、成本低廉, 因而被视为是一种非常有潜力的半导体光催化剂。然而, 由于CN在光催化反应过程中光生电子与空穴极易发生复合, 严重影响了电子从体相到外表面的转移过程以及随后的光催化质子还原反应, 使得CN光催化制氢效率不高。通过负载助催化剂可以有效地促进光生电子和空穴的分离。但是现有的高效助催化剂一般为

贵金属, 如Pt, Pd和Au等, 成本较高, 不利于实际应用. 因此, 寻找高效、稳定且廉价的助催化剂成为光催化领域的挑战之一. 本文通过化学镀的方法将Ni-P合金团簇锚定在CN表面, 并通过X射线衍射(XRD)、傅里叶变换红外光谱(FTIR)、场发射扫描电子显微镜(FESEM)、透射电子显微镜(TEM)、紫外-可见漫反射光谱(UV-vis DRS)、X射线光电子能谱(XPS)、稳态荧光光谱(PL)、时间分辨荧光光谱(TRPL)、光电化学测试和光催化制氢测试等方法研究了负载Ni-P助催化剂对CN晶体结构、化学组成、微观形貌、吸光能力、电荷转移以及光催化性能的影响.

XRD, FTIR, FESEM和TEM的结果显示, Ni-P均匀紧密地与CN结合在一起. UV-vis DRS测试表明, 负载Ni-P提高了材料体系的光吸收能力. XPS结果表明, 在复合光催化剂中电子从CN转移到了Ni-P助催化剂上, 表明光催化剂和助催化剂之间强的界面相互作用. PL, TRPL和光电化学测试结果表明, 与普通CN相比, 负载了Ni-P的CN有更小的荧光强度、更短的荧光寿命和更小的电荷转移电阻. 这说明负载Ni-P助催化剂提高了CN的电荷转移效率, 抑制了光生电子和空穴的复合. 因此在光催化制氢反应中, 复合光催化剂的氢气产率可高达 $1506 \mu\text{mol h}^{-1} \text{g}^{-1}$, 可以与负载贵金属Pt助催化剂的CN相媲美, 并且在9 h的循环试验中, 产氢性能没有明显下降. 综上所述, Ni-P合金团簇在光催化质子还原反应中有望作为贵金属助催化剂的高效、稳定且廉价的替代品.

关键词: 光催化; 制氢; 助催化剂; Ni-P合金; 电荷转移

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