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Synergistic effect of Co(II)-hole and Pt-electron cocatalysts for enhanced photocatalytic hydrogen evolution performance of P-doped g-C₃N₄

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ABSTRACT

g-C₃N₄ is a metal-free semiconductor and a potential candidate for photocatalytic H₂ production, however, the drawbacks, rapid recombination rate and limited migration efficiency of photogenerated carriers, restrict its photocatalytic activity. Herein, Co(II) as a hole cocatalyst modified P-doped g-C₃N₄ were successfully prepared to ameliorate the separation efficiency of photoinduced carriers and enhance the photocatalytic hydrogen production. The photocatalytic results demonstrated that the P-doped g-C₃N₄ (PCN) exhibited higher photocatalytic activity compared with pure g-C₃N₄, while Co(II)/PCN photocatalyst exhibited further enhancement of photocatalytic performance. The proposed possible mechanism based on various characterizations is that P-doping can modulate the electronic structure of g-C₃N₄ to boost the separation of photogenerated-e⁻ and h⁺; while the synergistic effect of both Co(II) (as hole cocatalyst) and Pt (as electron cocatalyst) can not only lead to the directional shunting of photogenerated e⁻-h⁺ pairs, but further accelerate the photogenerated electrons transfer to Pt in order to join the photocatalytic reduction process for hydrogen evolution. As a result, the transportation and separation of photoinduced carriers were accelerated to greatest extent in the Pt/Co(II)/PCN photocatalyst.

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1. Introduction

Technology requirements for a sustainable society lead to the surge of clean and renewable energy research in the 21st century. Compared with other chemical fuels, hydrogen (H₂) as a new type of clean energy exhibits the highest specific energy

of combustion [1–4]. The photocatalytic H₂ generation from water splitting based semiconductor technology is proved to be a sustainable solution to resolve the current environmental and energy issues [5–7]. Various semiconductor-based photocatalysts (such as TiO₂ [8], ZnO [9], CdS [10], and g-C₃N₄ [11] etc.) have been developed for the photocatalytic H₂-evolution appli-

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cation. Among these reported semiconductors, g-C₃N₄, as a new class of nonmetallic organic polymer semiconductor, has attracted huge interest due to inimitable layer structure, suitable energy structure (2.7 eV), simple fabrication and outstanding stability [12–14]. However, single g-C₃N₄ demonstrates low activity owing to the poor utilization of photoexcited charge carriers caused by the weak van der Waals force [15].

A great deal of approaches have been proposed to improve the photocatalytic performance of g-C₃N₄, for example, liquid exfoliation of bulk g-C₃N₄, surface modification, elemental doping, construction of heterojunction with other semiconductors or loading of co-catalysts [16–22]. Heteroatoms doping (non-metal elements such as P, S and N etc.) can tune energy bands of semiconductor at atomic level, which not only improves light absorption, but boost photogenerated-carrier separation [23–26]. For example, Guo et al. [27] employed phosphorus acid to fabricate P-doped g-C₃N₄ with hexagonal tubular morphology; Ran et al. [28] prepared P-doped g-C₃N₄ using 2-aminoethylphosphonic acid and melamine as P source and g-C₃N₄ precursor, respectively; and Bellardita and coauthors [29] synthesized P-doped g-C₃N₄ using NH₄H₂PO₄ as P source. For enhancing the photocatalytic activity, cocatalyst is considered more efficient to speed up the transportation and separation of photoinduced carriers [30,31]. Usually, the photocatalytic cocatalysts could be divided in two types. The first type of cocatalyst is called photogenerated electron-transfer (usually noble metals, Pt, Pd and Au) acting as electron sink and the second type of cocatalyst is called hole-transfer (MoO₃, MnO₂ and CoO etc.) [32,33]. Keller et al. [34] fabricated an Au/TiO₂-g-C₃N₄ nanocomposite photocatalyst which can achieve to produce hydrogen utilizing ultra low amounts of sacrificial agents under the action of the Au electron cocatalyst. Kang et al. [35] confirmed that CoO/g-C₃N₄ heterojunction exhibited higher overall water splitting performance due to the presence of CoO as a hole cocatalyst. More importantly, Xing et al. [36] have fabricated a novel MnO_x@CdS/CoP catalyst in which MnO_x act as a hole-transfer cocatalyst and CoP act as an electron-transfer cocatalyst, thus accelerating the photocatalytic activity by spatially separating the reduction surface. Yang et al. [37] reported excellent photocatalytic hydrogen evolution by spatial separation of dual cocatalysts (Au and CoP) to accelerate charge transfer in 3D ordered microporous g-C₃N₄. From previously reported results, it can be suggested that simultaneous modification of g-C₃N₄ by dual cocatalysts containing electron-transfer and hole-transfer cocatalysts may accelerate the transportation and separation of photogenerated carriers more efficiently, resulting in higher photocatalytic activity.

Herein, we employed low-temperature phosphating method to fabricate Co(II)-modified P-doped g-C₃N₄ nanosheets via simultaneous doping of P atom and coupling of Co(II) as hole cocatalyst. In the process of photocatalytic hydrogen production, Pt nanoparticles (NPs) as electron cocatalyst could be deposited on the Co(II)-modified P-doped g-C₃N₄ nanosheets. Furthermore, the synergistic effect of Pt and Co(II) cocatalysts for the enhanced photocatalytic performance of P-doped g-C₃N₄ photocatalyst is studied in detail. It has been supposed that the P-doping could optimize the band energy of g-C₃N₄ nanosheets

to increase visible-light absorption, while Pt electron-transfer cocatalyst and Co(II) hole-transfer cocatalyst could accelerate the transportation and separation of photoinduced carriers to improve the photocatalytic activity.

2. Experimental

2.1. Synthesis of the Co(II)/PCN composites

Bulk g-C₃N₄ powders were fabricated using the method of thermal polymerization of urea in accordance to previous literature [38]. The bulk g-C₃N₄ powder (100 mg) was ultrasonically dissolved in 200 mL deionized H₂O to obtain g-C₃N₄ nanosheets solution for further use. The schematic illustration for fabrication of Co(II)/PCN composites is shown in Scheme 1. Firstly, a certain amount of Co(NO₃)₂·6H₂O was added into deionized water (200 mL) containing 100 mg of g-C₃N₄ nanosheets and then the mixture solution was stirred for another 2 h to result in the adsorption equilibrium of cobalt ions. Then the mixture was collected by centrifugation and washed several times with deionized water and ethanol, followed by drying at 60 °C for 12 h. Subsequently, 50 mg of Co(II)/g-C₃N₄ nanosheets and 500 mg of NaH₂PO₂ powder were put into the closed porcelain boat, respectively. Afterwards, the samples were put in a quartz tube of the furnace, maintained at 300 °C for 2 h with a heating rate of 2 °C/min in an inert atmosphere (Ar flow). After cooling to room temperature, the obtained powders were collected, which were labeled as Co(II)/PCN-*x* (*x* = 0.5, 2.0, 4.0, 6.0, 8.0), where *x* indicates the weight percentage of Co(II) in the g-C₃N₄ nanosheets. P doped g-C₃N₄ nanosheets were fabricated by the same method except the Co(II) addition and labeled as PCN.

2.2. Characterization

The phase, morphology, composition of the as-synthesized materials were characterized by a Ultima IV diffractometer (Rigaku) with Cu K_α radiation ($\lambda = 1.5406 \text{ \AA}$), a field-emission transmission electron microscopy (Tecnai G2 F30 S-TWIN, FE-TEM), and a ray photoelectron spectroscopy (XPS) spectra (G Scientific ESCALAB Mark II spectrometer), respectively. The optical properties and the electron spin resonance experiments

Scheme 1. Schematic illustration of synthesis of Co(II)/PCN composites.

were characterized by a UV-vis diffuse reflection spectroscopy (DRS, Shimadzu UV2600) and a X-band frequency on a Bruker A300 Spectrometer, respectively. The photocurrent, EIS and Mott-Schottky plots were explored by a CHI 660E electrochemical workstation and the photoluminescence spectra was characterized on a QuantaMaster™ 40.

2.3. Photocatalytic H_2 production measurement

50 mg of samples were ultrasonically suspended in a 100 mL of glass reaction cell containing 80 mL of H_2O with 10 vol% triethanolamine and 400 μL of $H_2PtCl_6 \cdot 6H_2O$ (10 g/L, theoretically depositing 3.0 wt.% on the catalyst). Then the cell was kept under a 300 W Xe lamp with a cutoff filter ($\lambda > 420$ nm). The amount of H_2 was tested by a gas chromatograph equipped with a thermal conductivity detector (TCD) (GC-2014, Shimadzu Co., Japan). The external quantum efficiencies (EQE) of optimized Co(II)/PCN were calculated via the following equation:

$$EQE = \frac{2 \times \text{the amount of hydrogen molecules evolved in unit time}}{\text{number of incident photons in unit time}} \times 100\%$$

3. Results and discussion

The crystal structures and phase compositions of the as-prepared g- C_3N_4 nanosheets and Co(II)/PCN-2 were studied by XRD as shown in Fig. 1(a). Two characteristic peaks are existed in the XRD patterns of both g- C_3N_4 nanosheets and Co(II)/PCN-2. The (100) peak at 13.1° and (002) peak at 27.5° are assigned to the in-plane structural packing motif of tris-triazine units and the interlayer stacking of aromatic seg-

ments [39]. The XRD pattern of the Co(II)/PCN is similar to that of g- C_3N_4 nanosheets. The presence of Co(II) and confirmation of P doping are verified by XPS and TEM-EDX. The XPS survey spectra of g- C_3N_4 nanosheets and Co(II)/PCN-2 are shown in Fig. 1(b). As expected, two peaks of Co and P appear in the spectrum of Co(II)/PCN-2 except for the peaks of C and N elements in both g- C_3N_4 nanosheets and Co(II)/PCN-2. Figs. 1(c)–(f) show high-resolution XPS spectra of individual elements. The dominant peak in the high-resolution C 1s spectra located at 284.8 eV is assigned to the C–C species of g- C_3N_4 nanosheets, while the peak at 288.0 eV is originated from the sp^2 -hybridized C in N=C–N [40,41]. The spectrum of N 1s signal is deconvoluted into four peaks centered at 398.7, 399.6, 401.0, and 404.5 eV, which are attributed to the triazine rings (C=N–C) of g- C_3N_4 , N–(C)₃ groups, C–N–H and C=N conjugated structures, respectively [42]. Obviously, the binding energy of Co(II)/PCN displayed in the high-resolution C and N XPS spectra shows a significant positive shift, revealing the reduction of electron density in g- C_3N_4 due to the incorporation of dopant (P) and the Co(II) deposition. The high-resolution Co 2p XPS spectrum of Co(II)/PCN-2 exhibits two strong peak located at 780.3 and 795.7 eV, respectively, manifesting the existence of the Co(II) in the heterojunction [43]. Considering a low-temperature hydrolysis process in this study, the Co(II) cocatalyst may be in the amorphous CoOOH-like structure, similar to the reported phenomenon of the other transition metal (such as Fe elements) [44]. The high-resolution P 2p XPS spectrum exhibits a strong peak at 133.4 eV attributing to P–N coordination, revealing that P atoms may substitute the C atom

Fig. 1. XRD patterns (a), XPS survey spectra (b), C 1s (c), N 1s (d), Co 2p (e) and P 2p (f) high-resolution spectra of g- C_3N_4 nanosheets and Co(II)/PCN-2 composite.

Fig. 2. AFM images of (a) bulk g-C₃N₄ and (b) g-C₃N₄ nanosheets.

in the triazine rings of the g-C₃N₄ and thus form P–N bonds [45]. The results of the XRD and XPS confirm the successful preparation of coupling of Co(II) with P-doped g-C₃N₄.

The atomic force microscope (AFM) was employed to investigate the thickness of as-prepared samples. Fig. 2 indicates that bulk g-C₃N₄ has a thickness of 15–20 nm, while the thickness of g-C₃N₄ nanosheets ranges from 5 to 10 nm, manifesting that the bulk g-C₃N₄ can exfoliate into few-layered structures after ultrasonic exfoliation process. Such ultrathin g-C₃N₄ nanosheets were utilized to further realize P doping and heterojunction construction.

Furthermore, TEM and STEM-EDX elemental mapping were conducted to observe the morphologies of pure g-C₃N₄ nanosheets and Co(II)/PCN-2. As observed in Fig. 3(a), g-C₃N₄ nanosheets have small thin flat irregular two-dimensional shape. TEM image of Co(II)/PCN-2 (Fig. 3(b)) shows that phosphorus doping and Co(II) loading did not affect the morphology of g-C₃N₄ nanosheets. STEM-EDX elemental mappings (Fig. 3(c)) confirm the existence and uniform distributions of C, N, Co, P elements. Based on XRD, XPS, TEM and EDX analysis, it can be concluded that P atoms are doped into g-C₃N₄ nanosheets and Co(II) exists on the surface of the P-doped g-C₃N₄ nanosheets.

The visible light photocatalytic H₂ production activity over

pure g-C₃N₄ nanosheets, PCN and Co(II)/PCN were evaluated. As shown in Figs. 4(a) and (b), pure g-C₃N₄ nanosheets have relatively low hydrogen production rate (89.2 μmol·g⁻¹·h⁻¹). However, the hydrogen production of PCN (155.2 μmol·g⁻¹·h⁻¹) exhibits 1.7 folds higher than that of pristine g-C₃N₄ nanosheets. Generally, P doping into g-C₃N₄ nanosheets can introduce an impurity level which can accelerate the separation of photogenerated carriers and result in the improvement of the photocatalytic activity. Also Co(II)/PCN with different mod-

Fig. 3. (a) TEM image of g-C₃N₄ nanosheets; TEM image (b) and STEM-EDX elemental mapping (c) for Co(II)/PCN-2.

Fig. 4. Photocatalytic H₂-production activity (a) and H₂-production rate (b) of g-C₃N₄ nanosheets and Co(II)/PCN with different contents of Co(II); Recycling of the H₂ production tests (c) and external quantum efficiency (d) of Co(II)/PCN-2.

ified amounts of Co(II) shows the improved photocatalytic properties in comparison to pure g-C₃N₄ nanosheets. Upon increasing the loading amount of Co(II) from 0.5 wt% to 2 wt%, the Co(II)/PCN samples show continuously increasing photocatalytic activity. However, When the loading amount of Co(II) was further increased from 2.0 wt% to 6.0 wt%, the photocatalytic H₂ activity decrease, which can be ascribed to the shielding effect of Co(II). The Co(II)/PCN-2 sample shows the highest photocatalytic performance (774 μmol·g⁻¹·h⁻¹), exhibiting 8.6 folds higher than that of pure g-C₃N₄ nanosheets. This indicates that the optimized Co(II) loading can effectively enhance the water-reduced H₂-production activity.

The cyclic stability of the Co(II)/PCN-2 sample was also studied. The composite exhibits almost stable H₂-evolution rate with a little decline after four cycles, revealing that Co(II)/PCN-2 sample exhibits reliable stability for the photocatalytic H₂-evolution, as shown in Fig. 4(c). The external quantum efficiencies (EQE) at different wavelengths of Co(II)/PCN-2 were measured, and the EQE at λ = 402 nm is determined to be 2.76% (Fig. 4(d)).

Strong light-harvest capability, high separating efficiency of photoinduced carriers, as well as large surface reactions efficiency are important determining factors for excellent photocatalytic H₂-evolution property. The UV-vis DRS of g-C₃N₄ nanosheets and Co(II)/PCN-2 composite shown in Fig. 5(a) demonstrated that an enhancement of light absorption over g-C₃N₄ is achieved after P doping and Co(II) decoration, and thus the Co(II)/PCN-2 has the better visible light absorption ability than pure g-C₃N₄ nanosheets. Kubelk-Munk function is

employed to calculate the bandgap of g-C₃N₄, which is determined to be 2.66 eV (Fig. 5(b)). As shown in Figs. 5(c)–(d), both g-C₃N₄ nanosheets and Co(II)/PCN-2 show positive slopes at different frequencies, indicating the classic n-type nature of semiconductor whether or not modified. According to the Mott-Schottky plots shown in Fig. 5(c) and the equation of the $E_{fb} = E_{Ag/AgCl} + 0.059 \times pH + E^*_{Ag/AgCl}$ [46], the hydrogen electrode potentials (NHE) of g-C₃N₄ nanosheets and Co(II)/PCN-2 are determined as -0.67 and -0.53 V versus NHE, which are consistent with reported literatures [47]. Obviously, Co(II)/PCN-2 shows more positive flat-band potential than g-C₃N₄ nanosheets, which might be caused by the lower overpotential as well as splendid electronic conductivity of Co(II) [48,49].

The photocurrent-time curves (*i-t*) of Co(II)/PCN-2 working electrode were measured to examine the separation efficiency of photo-excited carriers. Apparently, the Co(II)/PCN-2 exhibits stronger photocurrent density than that of the g-C₃N₄ nanosheets (Fig. 6(a)), implying Co(II)/PCN-2 exhibits faster separation of photo-generated electron-holes [50,51]. Also, Co(II)/PCN-2 possesses a smaller arc than that of g-C₃N₄ nanosheets (Fig. 6(b)), which is the indication of rapid transportation rate of photogenerated electrons occurs due to P-doping and Co(II) decorated nanosheets surface [52]. The photoluminescence (PL) measurement had also been applied to study the separation of the photo-excited carriers. Fig. 6(c) shows the PL emission spectra of Co(II)/PCN-2 and g-C₃N₄ nanosheets both located at ~450 nm. The intensity of PL emission peak for Co(II)/PCN-2 is lower than that of g-C₃N₄

Fig. 5. UV-vis DRS (a) and estimated band energy spectra (b) of g-C₃N₄ nanosheets and Co(II)/PCN-2; Mott-Schottky plots of g-C₃N₄ nanosheets (c) and Co(II)/PCN-2 (d) at different frequencies in 0.5 M Na₂SO₄ solution.

Fig. 6. Transient photocurrent responses (a), Electrochemical impedance spectroscopy (EIS) Nyquist plots (b), Photoluminescence spectra (c), and Time-resolved photoluminescence (d) of pure g-C₃N₄ nanosheets and Co(II)/PCN-2.

nanosheets, indicating faster charge separation ability over the Co(II)/PCN-2 [53]. Time-resolved photoluminescence measurements were employed to explore the lifetime of photogenerated carriers. The PL intensities, corresponding pre-exponential factors and mean lifetimes of g-C₃N₄ and Co(II)/PCN-2 are shown in Fig. 6(d), a smaller lifetime (0.41 ns) is observed for the Co(II)/PCN-2 compared with the g-C₃N₄

nanosheets (1.07 ns), revealing that Co(II)/PCN-2 has the faster transportation of photogenerated electrons in case of Co(II)/PCN-2 [54]. The results of PL measurement are well consistent with the results of photocurrent and EIS measurements. The improved separation efficiency of the photo-generated carriers of Co(II)/PCN composite can enhance the photocatalytic activity.

Fig. 7. TEMPO- e^- (a) and TEMPO- h^+ (b) of pure g- C_3N_4 and Co(II)/PCN-2 sample under visible light irradiation.

The generation of the e^- and h^+ of g- C_3N_4 and Co(II)/PCN-2 were characterized by the electron spin resonance (ESR). Usually, reduced ESR signal intensity indicates faster transfer rate of electrons from semiconductor to the spin label [55,56]. As shown in Figs. 7(a) and (b), whatever for the TEMPO- e^- and TEMPO- h^+ , both of the signal intensities of the g- C_3N_4 and Co(II)/PCN-2 aqueous solution decreased within 5 min, however, more attenuation could be observed in the Co(II)/PCN-2. The above results demonstrate that, under light irradiation, Co(II)/PCN-2 composite excites more active electrons and holes compared to g- C_3N_4 nanosheets, which also means P doping and Co(II) decorated nanosheets surface could effectively improve the reactivity of the photoinduced e^- and h^+ . It is evident from the above results that Co(II)/PCN-2 sample demonstrates better separation of the photo-generated e^- and h^+ .

The XRD patterns of the Co(II)/PCN-2 sample before and after the photocatalytic reaction are shown in Fig. 8(a), There is no obvious difference between Co(II)/PCN-2 and Pt/Co(II)/PCN due to loading of a small amount of Pt on the Co(II)/PCN (only 3.0 wt% relative to Co(II)/PCN). The TEM image of the Co(II)/PCN-2 sample after the photocatalytic reaction is shown in Fig. 8(b), Some nanoparticles of diameter 5 nm were found on the Co(II)/PCN-2 sample, which were not present previously. Furthermore, interplanar spacing of 0.23 nm corresponding to (111) facets of Pt was determined in HRTEM image [57]. It is assumed that under the irradiation of the Xe lamp, the $PtCl_6^{2-}$ is reduced to Pt by the incoming the electron from the conduction band of P-doped g- C_3N_4 nanosheets and acting as electron-transfer cocatalyst to promote half-reaction

Fig. 8. XRD patterns (a) and TEM (HRTEM inset) images (b) of Co(II)/PCN-2 composite loaded with 3.0 wt% Pt.

of hydrogen production [58].

The proposed mechanism for photocatalytic hydrogen production over Co(II)/PCN in the light of the above discussion is shown in Fig. 9. The g- C_3N_4 nanosheets could be excited to generate e^- and h^+ under light irradiation. The dopant “P” in the g- C_3N_4 nanosheets could provide new channels to mediate electron migration and restrain the recombination of electrons and holes. In case of Co(II) decorated P-doped g- C_3N_4 nanosheets, Co(II) captures photogenerated hole to form Co(III), and the new-formative Co(III) will be reduced to Co(II) by oxidizing sacrificial agent (TEOA) due to the high oxidative capacity of Co(III) [59]. Herein, the Co(II) plays role of h^+ -transfer cocatalyst to capture h^+ in present photocatalytic system. Furthermore, the photogenerated- e^- will first reduce $PtCl_6^{2-}$ to Pt according photoreduction deposition. After the formation of Pt, it can act as the electron-transfer cocatalysts to take control of the photogenerated- e^- in order to provide the active sites for hydrogen production. Therefore, with the synergistic effect of Co(II) as a hole cocatalyst and Pt as electron cocatalyst, electrons and holes demonstrated the directional shunting, which could further accelerate the migration of photogenerated electrons to platinum in order to join the photocatalytic reduction process for hydrogen evolution. It can be concluded that the transportation and separation of photogenerated carriers were accelerated to the greatest extent over the

Fig. 9. Mechanism for photocatalytic hydrogen generation over Pt/Co(II)/PCN system.

Pt/Co(II)/PCN photocatalyst. The enhancement of photocatalytic performance of Co(II)/PCN-2 can be ascribed to the synergistic effects of Co(II), Pt deposition and P doping.

4. Conclusions

In summary, we employed low-temperature phosphating method to fabricate Co(II)-modified P-doped g-C₃N₄ nanosheets, which simultaneously realized the P-doping and Co(II) as hole cocatalyst co-modification, and Pt is deposited as electron cocatalyst for the photocatalytic H₂ generation. The results of XRD, XPS, TEM and STEM confirmed the successful preparation of the Co(II)/PCN samples, in which P element is doped into g-C₃N₄ nanosheets and Co(II) is decorated on the surface of P-doped g-C₃N₄ nanosheets successfully. The optimized Co(II)/PCN sample exhibited the highest photocatalytic hydrogen evolution (774 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$) by using Pt as electron transfer cocatalyst, which is ~ 8.6 fold higher than pristine g-C₃N₄ nanosheets (89.2 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$). The enhancement in photocatalytic activity is resulted from the faster separation of photogenerated e⁻ and h⁺ caused by the synergistic effect of Co(II) (hole transfer cocatalyst), Pt (electron transfer cocatalyst) and P doping (modulate the electronic structure of g-C₃N₄) of the Co(II)/PCN heterojunction. This work offers a novel insight into the designing of excellent photocatalysts consisting of both hole-transfer and electron-transfer cocatalysts for energy conversion application.

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Graphical Abstract

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Synergistic effect of Co(II)-hole and Pt-electron cocatalysts for enhanced photocatalytic hydrogen evolution performance of P-doped g-C₃N₄

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Co(II) decorated P doped g-C₃N₄ with optimized electronic structure shows excellent photocatalytic H₂-production, which is ascribed the directional shunting of electron-hole pairs via Co(II) and Pt.

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Co(II)-空穴和Pt-电子助催化剂协同作用增强P掺杂g-C₃N₄光催化产氢性能

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摘要: 石墨相氮化碳(g-C₃N₄)是一种新型的有机半导体材料, 具有独特的层状结构、合适的能带位置、简单的制备方法以及出色的稳定性等特点, 因而被广泛应用于光催化产氢领域。但是, 较高的光生载流子的复合率和受限的迁移率大大地限制了g-C₃N₄的光催化产氢性能。目前, 大量的研究证实块状g-C₃N₄的液相剥离、表面改性、元素掺杂、与其他半导体复合构筑异质结以及负载助催化剂等方法可以在一定程度上提高g-C₃N₄的光催化产氢性能。但是单一的g-C₃N₄改性方法往往并不能获得最理想的光催化产氢性能, 因此, 本文采用低温磷化法制备了二价钴(Co(II))修饰的磷(P)掺杂的g-C₃N₄纳米片(Co(II)/PCN), 同时实现了掺杂P原子和负载空穴助催化剂Co(II), 该催化剂表现出出色的光催化产氢性能。在光催化制氢过程中, 铂(Pt)纳米颗粒作为电子助催化剂成功的负载在Co(II)/PCN上。光催化实验结果表明, 最佳的Pt/Co(II)/PCN复合材料光催化产氢速率达到774 μmol·g⁻¹·h⁻¹, 比纯相的g-C₃N₄纳米片(89.2 μmol·g⁻¹·h⁻¹)提升8.6倍。同时优化的光催化剂具有良好的光催化稳定性, 并在402 nm处具有2.76%的量子产率。XRD, TEM, STEM-EDX和AFM结果证明, 成功制备了纳米片状形貌的g-C₃N₄及其复合材料, 催化剂中均匀分布着Co和P元素。通过XPS证明了P-N的存在以及Co(II)的存在, 并且Co(II)是

以一种无定型的CoOOH的形式吸附在g-C₃N₄表面。光照后的TEM证明Pt颗粒成功的负载在Co(II)/PCN表面。UV-vis DRS表明, 由于P的掺杂以及Co(II)的修饰, Co(II)/PCN相比于g-C₃N₄纳米片在可见光区域光吸收有了明显的增强。通过稳态和瞬态光致发光光谱分析, 同时结合电化学分析表征(*i-t*、EIS)以及电子顺磁共振技术分析, 证实了Co(II)/PCN高效光催化性能的原因可能是由于更高效的光生载流子分离效率。本文对Pt/Co(II)/PCN可能的光催化增强机理提出了设想。P的掺杂可以优化g-C₃N₄的电子结构, 提高其光生载流子分离效率。而以Pt作为电子助催化剂, 可以有效地捕获P掺杂的g-C₃N₄导带中的光生电子, 进而发生水还原产氢反应; 以Co(II)作为空穴助催化剂, 可以捕获价带中的光生空穴, 进而发生三乙醇胺氧化反应。通过采用不同功能的助催化剂, 实现P掺杂g-C₃N₄光生电子空穴的定向分流, 促进了P掺杂g-C₃N₄的光生载流子的分离, 从而提高催化剂的光催化产氢性能。本文可以为设计具有空穴-电子双助催化剂的光催化产氢系统提供一个新的思路。

关键词: 光催化产氢; 空穴助催化剂; 电子助催化剂; 磷掺杂氮化碳

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