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Article (Special Issue on Photocatalytic H₂ Production and CO₂ Reduction)Photocatalytic H₂ generation via CoP quantum-dot-modified g-C₃N₄ synthesized by electroless platingKezhen Qi ^{a,b}, Wenxiu Lv ^a, Iltaf Khan ^c, Shu-yuan Liu ^{d,e,*}^a Institute of Catalysis for Energy and Environment, College of Chemistry and Chemical Engineering, Shenyang Normal University, Shenyang 110034, Liaoning, China^b Research Institute of Photocatalysis, State Key Laboratory of Photocatalysis on Energy and Environment, College of Chemistry, Fuzhou University, Fuzhou 350116, Fujian, China^c Key Laboratory of Functional Inorganic Material Chemistry, Ministry of Education, School of Chemistry, Chemical Engineering and Materials, Heilongjiang University, Harbin 158308, Heilongjiang, China^d Department of Pharmacology, Shenyang Medical College, Shenyang 110034, Liaoning, China^e Key Laboratory for Photonic and Electronic Bandgap Materials, Ministry of Education, College of Physics and Electronic Engineering, Harbin Normal University, Harbin 150025, Heilongjiang, China

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ABSTRACT

Photocatalytic water splitting is a promising method for hydrogen production. Numerous efficient photocatalysts have been synthesized and utilized. However, photocatalysts without a noble metal as the co-catalyst have been rarely reported. Herein, a CoP co-catalyst-modified graphitic-C₃N₄ (g-C₃N₄/CoP) is investigated for photocatalytic water splitting to produce H₂. The g-C₃N₄/CoP composite is synthesized in two steps. The first step is related to thermal decomposition, and the second step involves an electroless plating technique. The photocatalytic activity for hydrogen evolution reactions of g-C₃N₄ is distinctly increased by loading the appropriate amount of CoP quantum dots (QDs). Among the as-synthesized samples, the optimized one (g-C₃N₄/CoP-4%) shows exceptional photocatalytic activity as compared with pristine g-C₃N₄, generating H₂ at a rate of 936 μmol g⁻¹ h⁻¹, even higher than that of g-C₃N₄ with 4 wt% Pt (665 μmol g⁻¹ h⁻¹). The UV-visible and optical absorption behavior confirms that g-C₃N₄ has an absorption edge at 451 nm, but after being composited with CoP, g-C₃N₄/CoP-4% has an absorption edge at 497 nm. Furthermore, photoluminescence and photocurrent measurements confirm that loading CoP QDs to pristine g-C₃N₄ not only enhances the charge separation, but also improves the transfer of photogenerated e⁻-h⁺ pairs, thus improving the photocatalytic performance of the catalyst to generate H₂. This work demonstrates a feasible strategy for the synthesis of highly efficient metal phosphide-loaded g-C₃N₄ for hydrogen generation.

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1. Introduction

In recent decades, global energy consumption has increased

rapidly. Developing renewable energy technologies has thus become a critical task. Keeping this in mind, researchers in various communities are searching for alternate energy re-

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sources. Recently, great effort has been expended to search for an inexhaustible, renewable, and clean energy resource to satisfy future energy demands and cope with environmental hazards [1–5]. Hydrogen is an ideal source that can produce clean and green energy without forming secondary pollution, and it also has a high combustion efficiency.

In the modern era, hydrogen production through water splitting utilizing semiconductor photocatalysis is a promising method that has received much attention. The ideal source for hydrogen generation is water because of its high abundance, availability, and renewability. Many photocatalysts and photoelectrodes have been employed for hydrogen generation. For example, in the recent past, various types of photocatalysts, including TiO_2 , LaFeO_3 , CdS , SrTiO_3 , and CoP , have been utilized for hydrogen generation [6–13]. However, because of various limitations, the hydrogen generation performance via such materials is inconsistent. Accordingly, photocatalytic water splitting to generate H_2 needs to be further pursued.

More recently, among many investigated photocatalysts, non-metal materials like $\text{g-C}_3\text{N}_4$ have attracted a great amount of attention because of their suitable band gap (2.7 eV) and stability. $\text{g-C}_3\text{N}_4$ is considered to be a highly efficient photocatalyst in many reactions, such as CO_2 reduction [14,15], water splitting [16,17], and organic pollutant degradation [18,19]. Most importantly, $\text{g-C}_3\text{N}_4$ fulfills the standard thermodynamic requirements of water splitting by light, i.e., $\text{g-C}_3\text{N}_4$ has a suitable band gap and appropriate position for the conduction band (CB) and valence band (VB) [20–22]. However, the photocatalytic activity of $\text{g-C}_3\text{N}_4$ is not satisfactory because of various limitations, including the low efficiency of visible light adsorption and high recombination rate of photogenerated carriers. Various approaches have been adopted to improve the performance of pristine $\text{g-C}_3\text{N}_4$. Among these strategies, forming a heterojunction between two semiconductors with wide and narrow band gaps [23–27], surface modification [28–31], metal and nonmetal doping [32], and utilization together with a co-catalyst are all well known. Many investigators have reported that some noble metals, including Au, Pt, Pd, and Ag are efficient [33–38], their high cost restricts large-scale usage, making it urgent to develop new strategies.

Transition metal-based phosphides, including FeP [39], CoP [40], NiP [41–44], and CuP [45], have been extensively used as co-catalysts in photocatalysis reactions. Moreover, surveying the relevant literature reveals that the photocatalytic reaction pathway and mechanism of Co-based phosphides are identical to what the hydrogenases do naturally. It is expected that Co-based phosphides can also be utilized as efficient catalysts for the hydrogen evolution reaction because of their unique physical and chemical properties and easy synthesis [46]. To the best of our knowledge, limited work has been performed to utilize CoP in the field of photocatalysis as a co-catalyst, i.e., forming $\text{g-C}_3\text{N}_4/\text{CoP}$ for efficient photocatalytic water splitting to produce H_2 . Thus, it is worth investigating how CoP can be loaded on $\text{g-C}_3\text{N}_4$ and applied as a co-catalyst.

In this work, $\text{g-C}_3\text{N}_4$ loaded with various amounts of CoP quantum dots (QDs) is fabricated by two steps, including pyrolysis and electroless plating. The bare $\text{g-C}_3\text{N}_4$ is prepared by a

previously reported method, i.e., thermal polymerization of urea. After this, in the second step, an electroless plating process is adopted for CoP growth in situ on the surface of $\text{g-C}_3\text{N}_4$. The optimized structure is $\text{g-C}_3\text{N}_4/\text{CoP-4\%}$, which shows higher photocatalytic activity for H_2 production than that of pristine $\text{g-C}_3\text{N}_4$ under simulated solar light radiation, even higher than that of Pt-modified $\text{g-C}_3\text{N}_4$. Finally, this work demonstrates that $\text{g-C}_3\text{N}_4/\text{CoP}$ nanocomposites demonstrate promising applications in the fields of photocatalysis and H_2 production.

2. Experimental

2.1. Preparation

Typically, $\text{g-C}_3\text{N}_4$ is synthesized via heating of urea. A total of 15 g of dry and solid urea was transferred to a crucible, after which the crucible was heated in a muffle furnace at 500 °C for 2 h, with a heating rate of 10 °C min⁻¹. After the prepared material cooled down naturally, the product was ground into powder and stored. For coating CoP on the surface of $\text{g-C}_3\text{N}_4$, an electroless plating technique was employed. A total of 1 g of $\text{g-C}_3\text{N}_4$ was placed in 40 mL of H_2O and treated ultrasonically for 5 min. Then, it was dispersed in a solution of sensitizer SnCl_2 (1 g L⁻¹) + HCl (1 mL L⁻¹) for 2 min and excited in a solution of exciter PdCl_2 (0.1 g L⁻¹) + HCl (1 mL L⁻¹) for 2 min. It was washed using distilled water before electrolysis deposition. The reaction vessel contained $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.4 mol L⁻¹), $\text{NH}_2\text{CH}_2\text{COOH}$ (1.2 mol L⁻¹), and $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ (1.6 mol L⁻¹). The pH value was kept at 11 by adding the proper amount of sodium hydroxide (NaOH). The electroless plating procedures were performed at 55 °C for 4 h. The as-prepared material was centrifuged and washed with water and alcohol three times. The as-obtained sample was dried in a vacuum oven at 75 °C for 6 h. Finally, samples with various weight percentages of coated CoP were synthesized; these are denoted $\text{g-C}_3\text{N}_4/\text{CoP-1\%}$, $\text{g-C}_3\text{N}_4/\text{CoP-2\%}$, $\text{g-C}_3\text{N}_4/\text{CoP-3\%}$, $\text{g-C}_3\text{N}_4/\text{CoP-4\%}$, and $\text{g-C}_3\text{N}_4/\text{CoP-5\%}$ for coating with 1%, 2%, 3%, 4%, and 5% by weight of CoP , respectively.

2.2. Characterization

X-ray diffraction (XRD) measurements were carried out on a Bruker D5005 X-ray diffractometer, with $\text{Cu K}\alpha$, $\lambda = 1.54056 \text{ \AA}$. Fourier transform infrared spectra (FT-IR) of the samples were recorded utilizing a Nicolet Magna 560 spectrophotometer. The elemental analysis of samples was conducted using Thermo Scientific ESCALAB 250Xi X-ray photoelectron spectroscopy (XPS). Transmission electron microscopy (TEM) was performed using an electron microscope (JEOL JEM-2100). UV-vis absorbance spectra were recorded by a Shimadzu UV-3100 spectrophotometer with BaSO_4 as a reference. The photoluminescence spectra of $\text{g-C}_3\text{N}_4$ and $\text{g-C}_3\text{N}_4/\text{CoP}$ modified materials were observed using a Varian Cary Eclipse spectrometer with an excitation wavelength of 325 nm.

2.3. Photocatalytic water splitting

The photocatalytic activity experiment for evaluation of the hydrogen reaction was carried out in a 100 mL Pyrex reactor with three openings, which were sealed by rubber plugs to avoid hydrogen leakage. This glass reactor was connected to a gas chromatographic assembly (GC-14C, Shimadzu, Japan, TCD; N_2 is used as the carrier gas). To produce hydrogen gas, a 350 W xenon lamp was used as a light source. The reactor assembly was placed at a distance of 15 cm from the xenon lamp. Typically, 10 mg of photocatalyst was placed into 70 mL water, and then 10 mL of triethanolamine (TEOA) was added. The reaction was completed under continuous magnetic stirring. N_2 gas was passed through the assembly to create and maintain an inert atmosphere and to remove any produced hydrogen gas.

2.4. Photoelectrochemical measurements

The photoelectrochemical performance was investigated using a CHI 660D electrochemical work station with the assistance of a commercial computer-controlled system. A paste was made by blending 5 mg of photocatalyst with 2 mL of isopropyl alcohol under magnetic stirring for 1 h, then adding approximately 0.15 g of macrogol-6000, 0.05 mL of acetyl acetone, and 1 mL of ethanol; after 24 h of stirring the mixture, the paste was finally produced. The mixture was coated on 1 cm × 2 cm ITO glass and bonded to an electrode, and a three-electrode system was utilized. For photoelectrochemical measurements, an estimated amount of the sample was pasted on the ITO glass surface as the working electrode, and a calomel electrode and Pt wire were used as the reference electrode and counter electrode, respectively. A 0.1 mol L⁻¹ Na₂SO₄ aqueous solution was used as the electrolyte.

3. Results and discussion

3.1. XRD

The crystallinity and structure of the as-prepared samples were investigated by XRD. Fig. 1 shows the XRD patterns of pristine g-C₃N₄ and g-C₃N₄/CoP composites loaded with various amounts of CoP. The two predominant peaks are at 13.1° and

Fig. 1. XRD patterns of pristine g-C₃N₄ and g-C₃N₄/CoP-X samples (X = 1%–5%).

27.5°, respectively, representing the g-C₃N₄ itself (JCPDS Card No 87-1526). The diffraction peaks at 27.5° correspond to the (002) typical plane with a planar distance of 0.33 nm, analogous to the interlayer stacking of the related aromatic segments. The peaks located at 13.1° are related to the (100) plane [47]. This result confirms that after loading of CoP QDs, the XRD peaks do not change, which suggests that CoP QDs do not affect the crystal lattice and structure of g-C₃N₄. Note that no distinct peaks for CoP are observed because of both, the small loading amount and the high dilution of CoP on the g-C₃N₄ surface [48].

3.2. FTIR

The FTIR technique was employed to further confirm the structure of the prepared samples. As shown in Fig. 2, the FTIR spectra of pristine g-C₃N₄ and g-C₃N₄/CoP composites are almost identical, in which the peak at 1638 cm⁻¹ is credited to the stretching vibration of C-N related groups and the intense peaks located at 1248, 1319, and 1433 cm⁻¹ are also attributed to the stretching vibrations of the C-N bonds in aromatic rings; these results are consistent with those reported in the literature [49]. The peak positioned at 804 cm⁻¹ represents a different type mode of the tri-azine group unit in g-C₃N₄ [50], and the peaks at 3255 cm⁻¹ are associated with the N-H stretching vibration [51]. The FTIR results confirm that the structure of the bare g-C₃N₄ sample is not altered after loading with CoP. The information given by the FTIR spectra is in good agreement with the XRD data.

3.3. UV-DRS

Fig. 3 shows the UV-visible reflectance spectra of pristine g-C₃N₄ and g-C₃N₄/CoP-4% samples. The pristine g-C₃N₄ sample displays a light absorption edge at 451 nm. According to the band gap equation ($E_g = 1240/\lambda$) the calculated band gap is 2.75 eV, which is similar to that 2.82 eV obtained by Ong et al. [52]. Conversely, CoP shows a light absorption peak at 1240 nm, and its band gap is 1.0 eV [53]. However, the g-C₃N₄/CoP-4% composite displays a light absorption peak at 497 nm, which indicates that the visible light absorption effi-

Fig. 2. FTIR spectra of pristine g-C₃N₄ and g-C₃N₄/CoP-X samples (X = 1%–5%).

Fig. 3. UV-Vis diffuse reflectance absorption spectra of pristine g-C₃N₄ and g-C₃N₄/CoP-4% samples.

ciency of g-C₃N₄ is enhanced. This also explains why the yellow pure g-C₃N₄ turns to dark gray after loading with CoP.

3.4. XPS

XPS analysis has been engaged to study the elemental states and chemical composition of samples. The detailed XPS profiles and chemical bonding features of the g-C₃N₄/CoP-4% sample are given in Fig. 4. The high-resolution XPS profile of carbon shows that C has XPS peaks at 284.8 eV and 288.3 eV (Fig. 4A). Actually, the XPS peak at 284.8 eV can be ascribed to *sp*² hybridized carbon atoms; however, the peak at 288.3 eV is related to N–C=N₂ related functional groups [54]. Furthermore, Fig. 4B

identifies the peaks for the N 1s electron at 398.8 eV, 400.6 eV, and 404.7 eV, which are related to a *sp*² type nature and the bonded tightly bound nitrogen C–N–C type family; similarly, the *sp*³ results arise from tertiary nitrogen N–(C)₃ and amino-related elements of (C–N–H) [47]. The XPS results given in Fig. 4C explain the Co 2*p*_{3/2} energy level and nature. It is confirmed that three peaks, at 781.7, 783.3, and 786.8 eV, are the reduced Co, oxidized Co²⁺, and satellite peak, respectively. The Co 2*p*_{1/2} shows an XPS peak at 787.5 eV along with one satellite peak at 803.2 eV [55]. As shown in Fig. 4D, two P 2*p* peaks are recorded, at 129.5 and 133.3 eV, which are credited to P^{δ-} of CoP and oxidized P species, respectively [56]. All the XPS results confirm that CoP was successfully loaded on the surface of

Fig. 4. High-resolution XPS profiles of C 1s (A), N 1s (B), Co 2*p* (C), and P 2*p* (D) of g-C₃N₄/CoP-4%.

Fig. 5. TEM (A) and HR-TEM (B) images of the g-C₃N₄/CoP-4% sample.

g-C₃N₄.

3.5. TEM

The structural and morphological features of g-C₃N₄/CoP-4% were inspected using TEM. In Fig. 5A, the TEM image illustrates the clear appearance and texture of CoP quantum dots with g-C₃N₄, i.e., the CoP QDs are uniformly dispersed as black dots on the surface of g-C₃N₄ nanosheets. The size of the CoP QDs ranges from 3 nm to 6 nm, which proves that these CoP QDs are indeed the CoP clusters on the surface of g-C₃N₄. The HR-TEM image (Fig. 5B) shows clear lattice fringes for the CoP QDs, with a lattice distance of 0.26 nm. These outcomes clearly confirm the (211) plane of CoP [57], and that the CoP quantum dots are evenly loaded on the surface of g-C₃N₄.

3.6. Photocatalytic performance

The photocatalytic performances of the pristine g-C₃N₄ and g-C₃N₄/CoP-X samples (X = 1%–5%) were evaluated with respect to H₂ generation under simulated solar light (Fig. 6). g-C₃N₄ exhibits a poor, nearly negligible efficiency. However, after loading various weights (1–5 wt%) of CoP to g-C₃N₄, the photocatalytic activity for H₂ production was greatly enhanced. The g-C₃N₄/CoP-4% sample showed the best hydrogen production, 936 $\mu\text{mol g}^{-1} \text{h}^{-1}$, which is superior to that produced by 4 wt% Pt/g-C₃N₄ (665 $\mu\text{mol g}^{-1} \text{h}^{-1}$). When loading CoP to 5 wt%, the activity decreased to 569 $\mu\text{mol g}^{-1} \text{h}^{-1}$, which can be attributed to the over-coverage of CoP on the surface of g-C₃N₄, resulting in a decrease in activity [58,59]. Indeed, CoP QDs catalyze the hydrogen evolution reaction but block the surface of g-C₃N₄ for light absorption. Thus, loading a moderate amount of CoP plays an important role in improving the photocatalytic performance of g-C₃N₄.

3.7. Photoelectrochemical property

Photoelectrochemical measurements were conducted using g-C₃N₄ and g-C₃N₄/CoP-4% samples. The results in Fig. 7A demonstrate that the photocurrent performances of as-prepared samples, as determined by the photoelectrochemical curves, can stably reproduce the photocurrent responses over 5 on-off cycles. The activation of the photocurrent signal starts by turning on the light, while the photocurrent is negligible and nearly zero after switching off the light. Noticeably, the photocurrent density for g-C₃N₄/CoP-4% (which is 0.43 $\mu\text{A cm}^{-2}$) is higher than that of pristine g-C₃N₄ (0.04 $\mu\text{A cm}^{-2}$), which is in consistent with its higher activity for hydrogen generation. Similarly, the strong photocurrent predicts a greater efficiency of charge separation and propagation for photo-generated electron (e^-) and hole (h^+) pairs in the g-C₃N₄/CoP-4% composite, which enhances the hydrogen production. Meanwhile, the results of electrochemical impedance spectroscopy (EIS), i.e., Nyquist plots, as displayed in Fig. 7B, are also displayed to further support and confirm our outcomes. EIS Nyquist plots with smaller and lower radii represent greater separation ability with respect to photogenerated e^- and h^+ [35]. Clearly, loading CoP on the surface of g-C₃N₄ causes the radius of the EIS Nyquist plot to decrease, confirming that CoP QDs reduce the recombination rate, resulting in an in-

Fig. 6. Photocatalytic activities for H₂ production of pristine g-C₃N₄ and g-C₃N₄/CoP-X (X = 1%–5%) (A) and comparative activities of g-C₃N₄/CoP-X vs g-C₃N₄/Pt (B).

Fig. 7. Photocurrent signals (A) and electrochemical impedance spectra (B) of pristine g-C₃N₄ and g-C₃N₄/CoP-4% samples.

crease in the separation efficiency of e⁻ and h⁺ pairs.

3.8. PL spectra

The photoluminescence (PL) spectra of the as-prepared samples are recorded in Fig. 8. The effectiveness of generation and separation of photogenerated charge carriers is further confirmed by the PL spectra. The pristine g-C₃N₄ sample exhibits a stronger PL signal than do g-C₃N₄/CoP-X%. It is well known that a strong PL signal is attributed to a high charge recombination rate [48]. Therefore, the g-C₃N₄/CoP-4% composite exhibits the lowest PL signal because more of CoP QDs are adsorbed on the surface of g-C₃N₄, capturing more photoexcited electrons, and finally improving the internal charge transfer, which can decrease the charge recombination process of photogenerated e⁻ and h⁺ pairs. These results increase the life time of excited electrons, resulting in increased reaction time for any sort of photolytic reaction.

3.9. Photoactivity mechanism

Based on the above findings and understanding of the charge transfer and separation process, a proposed schematic diagram for charge transfer processes and energy band levels is depicted in Scheme 1 for the g-C₃N₄/CoP-4% nanocomposite. This sketch shows the possible reaction mechanism of

Fig. 8. Photoluminescence spectra of pristine g-C₃N₄ and g-C₃N₄/CoP-4%.

g-C₃N₄/CoP-4% in photocatalytic H₂ production. Under appropriate energy, the g-C₃N₄ is excited and finally generates photoexcited electrons with higher energy, which are excited into CoP through the CB of g-C₃N₄, leaving holes in the VB of g-C₃N₄, which can react with sacrificial agents such as TEOA. CoP QDs have a large work function, so they can be used as the co-catalyst [41].

4. Conclusions

A simple method is reported for the preparation of CoP QDs by an in situ growth strategy on the surface of g-C₃N₄. CoP QDs as a co-catalyst were loaded on the surface of g-C₃N₄ by a simple pyrolysis-based method and electroless plating. The as-prepared g-C₃N₄/CoP composite shows much higher photocatalytic activity for H₂ production than that of pristine g-C₃N₄. Among the as-prepared samples, the optimized one, i.e., g-C₃N₄/CoP-4%, shows remarkable improvement with respect to hydrogen generation (936 μmol g⁻¹ h⁻¹), which is 1.6-fold higher than that when using Pt (665 μmol g⁻¹ h⁻¹) as a co-catalyst at the same loading amount. This work provides a new, feasible strategy for the preparation of a g-C₃N₄/CoP photocatalyst for hydrogen production.

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Scheme 1. Schematic diagram for the photocatalytic mechanism and photogenerated charge separation and transfer in g-C₃N₄/CoP-4%.

Graphical Abstract

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Photocatalytic H₂ generation via CoP quantum-dot-modified g-C₃N₄ synthesized by electroless plating

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The photocatalytic activity of H₂ generation over g-C₃N₄/CoP composites prepared by an electroless plating method is much higher than that over pure g-C₃N₄. The composites boosted the separation and migration of photo-generated carriers, resulting in a higher photocatalytic activity.

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化学镀法制备CoP量子点修饰g-C₃N₄用于光催化产氢

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摘要: 光催化分解水制氢被认为是解决当前能源危机和环境污染问题的重要途径之一。在众多光催化剂中, 石墨相氮化碳(g-C₃N₄)因其具有高的热稳定性、高的化学稳定性、合适的能带位置以及成本低廉等优点, 受到光催化领域研究者的广泛关注, 成为研究热点。然而, 由于g-C₃N₄的禁带宽度较大($E_g = 2.7$ eV), 导致其对可见光的响应较差, 而且光生电子-空穴对在其中易于复合, 从而导致其光催化产氢活性较低。已有研究表明, 助催化剂可以有效地促进催化剂中光生载流子的分离和传输, 从而提高光催化剂的光催化活性和氢气的产生速率。目前使用最广泛的助催化剂多为贵金属(Au, Ag, Pt和Pd等), 然而贵金属储量低、成本高, 极大地限制了其实际应用。因而, 开发适用于光催化水分解制氢的非贵金属助催化剂成为该领域的研究热点。其中, 用非贵金属助催化剂修饰g-C₃N₄制备高效光催化剂分解水制氢技术引起了人们极大的兴趣。

过渡金属磷化物(FeP, CoP, CuP, NiP等)是一种有效的光催化辅助催化剂。然而, 这些金属磷化物的合成通常使用有毒的有机磷化合物和白磷或涉高温煅烧。特别是在传统水热法制备金属磷化物过程中会释放大量的氢气, 导致容器内压力过高, 造成较大的安全问题。据报道, 在这些磷化物中, 磷化钴由于其合适的能带结构和较高的导电性, 作为光催化分解水助催化剂受到了广泛关注。然而, 截至目前, 关于磷化钴作为助催化剂用于光催化的实用技术报道很少, 特别是在温和条件下制备磷化钴修饰的g-C₃N₄复合光催化剂的研究还有待进行。

本文研究了以CoP作为助催化剂来改进g-C₃N₄(制备g-C₃N₄/CoP), 并用于光催化水裂解制氢气。复合光催化剂g-C₃N₄/CoP经由两步反应合成。第一步采用尿素热分解法制备g-C₃N₄, 第二步通过化学镀法将CoP修饰在g-C₃N₄表面。采用XRD, TEM, UV-DRS和XPS等手段表征了g-C₃N₄/CoP光催化剂的性质。结果表明, CoP以量子点(QDs)形式均匀分布在g-C₃N₄表面, 显著提高了g-C₃N₄的光催化活性。不同CoP负载量的样品中, g-C₃N₄/CoP-4%表现出优异的光催化活性, H₂生成速率为936 $\mu\text{mol g}^{-1} \text{h}^{-1}$, 甚至高于4% Pt负载的g-C₃N₄ (H₂的生成速率仅为665 $\mu\text{mol g}^{-1} \text{h}^{-1}$)。从紫外可见光谱上看, g-C₃N₄在451 nm达到吸收波长上限, 但与CoP复合后, g-C₃N₄/CoP-4%的吸收波长上限延展到497 nm。此外, 光致发光和光电流测试结果证实, 将CoP量子点负载到g-C₃N₄上不仅可以降低光生电荷-空穴对的复合, 而且可以改善光生e⁻-h⁺对的转移, 从而提高光催化剂的产氢性能。这项工作为开发高效的非贵金属助催化剂修饰g-C₃N₄的技术提供了一个可行策略, 所制材料在光催化制氢领域显示出潜在的应用前景。

关键词: 光催化; CoP; 量子点; 化学镀; 产氢; g-C₃N₄

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