

Visible-light-driven photocatalytic H₂O₂ production on g-C₃N₄ loaded with CoP as a noble metal free cocatalyst

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Abstract: In this work, a composite catalyst combining CoP with g-C₃N₄ has been explored for the photocatalytic production of H₂O₂ under visible light irradiation. The composite catalyst was successfully fabricated by growth of CoP nanoparticles on the surface of g-C₃N₄. The CoP nanoparticles were well dispersed on the surface of g-C₃N₄ and could interact with g-C₃N₄ to make charge separation and electron transfer improved. The results of catalytic experiments showed that the composite catalyst had a superior catalytic activity as compared with pure CoP or g-C₃N₄ under visible light irradiation. The optimal catalyst with 1.76 wt% CoP loading amount exhibited the best photocatalytic efficiency with a H₂O₂ production of 140 uM in 2 h, which is about 4.6 and 23.3 times that of pure g-C₃N₄ and pure CoP, respectively. The possible mechanism on the visible-light-driven photocatalytic production of H2O2 was proposed. And the composite catalyst exhibited stable performance without obvious loss of catalytic activity after seven successive runs, showing a good application prospect for sustainable H_2O_2 production.

Introduction

Hydrogen peroxide (H₂O₂) as an eco-friendly oxidant is always widely applied in wastewater treatment, pulp bleaching, and disinfection.^[1] Besides, the increased usage of it in selective oxidation has attracted a lot of attention in the past few years.^[2] But until now, the commercial production of H₂O₂ is always by the anthraquinone method, which involves in organic solvents, high energy input and undesirable byproducts, and is considered as not environmentally friendly.^[3] As alternative, direct synthesis of H₂O₂ with H₂ and O₂ over metal (Pd or Pd/Au alloy) based catalysts has been studied extensively.^[4] However, not only high cost of noble metals but also potential explosion nature of the mixture gases is needed to be extremely cared. To this end, the photocatalytic synthesis of H₂O₂ as a sustainable and environmentally friendly alternative pathway compared to conventional anthraquinone method and electrochemical methods has attracted extensive attentions. The artificial photocatalytic synthesis of H2O2 just employs semiconductors,

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Department of Electronics and Tianjin Key Laboratory of Photo-Electronic Thin Film Device and Technology, Nankai University, Tianjin, 300071, P. R. China oxygen as well as electron and proton donors such as alcohols to transfer inexhaustible solar energy to H_2O_2 via a two-electron pathway as shown in the equations 1 and $2^{[5]}$ or a one-electron pathway as shown in the equations 1 and 3-6;^[6]

$R-CH_2OH + 2h^+ \rightarrow R-CHO + 2H^+$	(1)
$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	(2)
$O_2 + e^- \rightarrow O_2^-$	(3)
$\cdot O_2^- + H^+ \rightarrow HO_2$	(4)
·HO ₂ +e ⁻ →HO ₂ ⁻	(5)
$HO_2^- + H^+ \rightarrow H_2O_2$	(6)

Over the past few years, a lot of studies have been reported for the facile photocatalytic production of H₂O₂, utilizing semiconductors such as TiO₂ and q-C₃N₄.^[4b, 7] However, a couple of major challenges still limit its wide application. For example, the wide bandgap of the catalyst results in minor utilization of the visible light. And the limited transfer rate of electrons to the catalyst's surface is also a challenging problem which needs to be solved. Because the electrons transfer from the conduct band (CB) of catalyst to molecular oxygen has been recognized as the rate determining step in the process of production of H₂O₂. If oxygen cannot be reduced at a high rate, the electrons will accumulate in the catalyst and increase the recombination of photogenerated electron-hole pairs, resulting in low activity for producing H₂O₂. To address these problems, a lot of studies have tried to decorate noble metal as cocatalyst with semiconductors to separate charge carriers. For example, Elena Selli et al.[8] deposited gold nanoparticles on TiO₂ to efficiently separate charges and promote the production of H₂O₂. Shiraishi et al.^[9] prepared a bimetallic Au/Ag-loaded TiO₂ photocatalyst that facilitated the charge separation of the photogenerated carriers. Certainly, with the aid of noble metal, the host catalyst exhibited exceptional activity to form H2O2. However, the high cost and scarcity of the noble metals surely has restricted their widespread applications. Therefore, it is urgently to develop other economic and efficient cocatalysts for the semiconductorbased photocatalytic production of H₂O₂.

In recent years, various earth-abundant metal based cocatalyst have been reported, such as MoS_2 ,^[10] NiS,^[11] Ni,^[12] Cu(OH)₂.^[13] Besides, the transition metal phosphides have attracted much more attention, due to their fine qualities such as metalloid characteristics, good stability, and high electrical conductivity.^[14] Especially, Ni₂P,^[15] CoP,^[16] FeP,^[17] MoP^[18] and Cu₃P^[19] as cocatalyst have achieved outstanding charge separation and electron transport capability. Among these transition metal phosphide cocatalyst, CoP has performed more stable than others and has been widely used as cocatalyst in photocatalytic production of H₂ or applied as electrocatalyst. ^[20]

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Nevertheless, no research has been conducted on the utilization of it for the production of H_2O_2 .

Herein, according to the previous studies, the g-C₃N₄ is excellent metal-free material used in photocatalyst,^[21] including photocatalyst for production of H₂O₂.^[22] Considering of those advantages, we choose g-C₃N₄ as host structure and CoP as co-catalyst to form the composite. The composite catalyst was well characterized and firstly applied in the photocatalytic production of H₂O₂. In the catalyst, CoP nanoparticles act as a noble metal free cocatalyst for g-C₃N₄. The catalyst performed well and the best evolution of the H₂O₂ is 140 μ M in 2 h(The sample donated as 50Co/CN), which is much higher than the pure g-C₃N₄ and CoP. The mechanism for the enhanced catalytic activity was discussed and the stability of the catalyst was also investigated.

Results and Discussion

Morphology and structure



Figure 1. The TEM images of g-C_3N_4(a), CoP(b) and 50Co/CN(c); HRTEM of 50Co/CN(d).

The TEM and HRTEM were used to characterize the morphology of the samples. As shown in Figure.1a, the prepared pure g- C_3N_4 is thin nanosheets with smooth surface. Figure. 1b shows the morphology of pure bulk CoP. The CoP decorated g- C_3N_4 (50Co/CN) is shown in Figure.1c, from which we can see that small CoP nanoparticles are well dispersed on g- C_3N_4 sheet. Furthermore, the HRTEM image (Figure. 1d) taken from 50Co/CN displays the (211) diffraction plane of CoP with lattice spacing of 0.26 nm, ^[23] confirming the nanoparticles are CoP. It's worth mentioned that the CoP nanoparticles on g- C_3N_4 with the size of about 17 nm is much smaller than the pure CoP. This is probably because the pure CoP nanoparticles were



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tending to aggregate to be larger ones under the high temperature during the preparation process. While in the composite sample, some cobalt ions were confined by $g-C_3N_4$ that can greatly prevent the CoP sintering.



Figure 2. (a) XRD patterns of g-C₃N₄ and 50Co/CN.

The crystal structure of the pure g-C₃N₄ and the composite sample 50Co/CN were characterized by XRD. As we can see from the results (Figure. 2), for pure g-C₃N₄, the characteristic peaks of g-C₃N₄ located at 13.1° and 27.4° can be observed which can be attributed to the (100) peak of in-planar structure and the (002) peak with the interlayer d-spacing(indexed in JCPDS 87-1526).^[24] The pattern of the 50Co/CN is similar to that of pure g-C₃N₄ which means the structure of g-C₃N₄ is maintained after the modification. There is no characteristic peak of CoP appearing in 50Co/CN, possibly due to the low loading amount of CoP, which was demonstrated to be only 1.76 wt% by the inductively coupled plasma atomic emission spectrometry (ICP-AES).



Figure 3. High-resolution XPS spectra of C 1s (a), N 1s (b), Co 2p (c) and P 2p (d) of the 50Co/CN sample.

XPS measurement was further carried out to characterize the chemical status of the elements in 50Co/CN. Figure. 3 shows the high resolution spectra of C 1s, N 1s, Co 2p and P 2p.The peak of C 1s located at 284.6 eV and 288.2 eV are ascribed to C-NH₂ and N-C=N species.^[25] For N 1s the peak located at 398.4 eV, 399.1 eV, 400.6 eV and 404.95 eV are assigned to the species of C-N=C, N-(C)₃, C=N-H and π excitations, respectively.^[25] Both C 1s and N 1s spectrum

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demonstrate the characteristic structure of g-C₃N₄. As for the structure of CoP, the Co 2p spectrum (Figure 3c) is fitted with two spin-orbit doublets at 778.1 and 793.2 eV assigned to the binding energies (BEs) of Co 2p3/2 and Co 2p1/2, and the second at 781.6 and 797.8 eV are assigned to oxidized Co resulting from superficial oxidation of CoP, with two shakeup satellites(786.1eV and 803.1eV).^[16c] while in the XPS spectra of P, two peaks at 129.2 eV and 133.7 eV are belong to P 2p3/2 and P 2p1/2,^[26] the former is assigned to phosphide species and the later belongs to P-N coordination.^[27] In short, all of these manifest the composite of CoP and g-C₃N₄ was successfully formed.

The photocatalytic performance for H₂O₂ generation

The photocatalytic activities for H₂O₂ generation with different catalysts were evaluated in the ethanol/O2 system under visible light irradiation. As we can see from Figure. 4a, pure g-C₃N₄ exhibited photocatalytic activity for generation of H₂O₂, but the production is low, which is probably due to the low absorption of visible light and quick recombination of photogenerated electrons-hole pairs. Besides, the pure CoP showed lower activity. However, after the g-C₃N₄ was decorated with CoP, the activities of the catalysts were enhanced remarkably. The composite samples all work as effective photocatalysts for H₂O₂ generation with higher activity than that of pure g-C₃N₄ and pure CoP. The photocatalytic activity was increased with increasing CoP loading amount, which indicated that introducing a suitable amount of CoP can effectively improve the photocatalytic activity of H₂O₂ generation. Further increasing the amount of CoP, the photocatalytic activity was decreased, which may be due to the light shielding effect of CoP to g-C₃N₄ with excessive CoP. Because 50Co/CN exhibited the highest photocatalytic activity, it was considered to have the optimum loading amount of CoP, which is approximately 1.76 wt% as measured by the ICP-AES.



Figure 4. (a) Photocatalytic production of H_2O_2 over different catalysts (photocatalytic reaction conditions: 20 mg catalyst, 18 ml H_2O , 2 ml ethanol, 300 W Xe lamp with 420 cutoff filter; (b) photocatalytic production of H_2O_2 with 50Co(OH)₂/CN and 50Co/CN; (c) Comparison of the photocatalytic production of H_2O_2 under Ar, and O_2 -saturated conditions for g-C₃N₄ and 50Co/CN; (d) The production of H_2O_2 in the bare water and mixtures of water and ethanol for g-C₃N₄ and 50Co/CN.

Experiments were also carried out to demonstrate the function of phosphate in improving the catalyst's performance for producing H₂O₂. The sample without phosphorization (donated 50Co(OH)₂/CN) was prepared and tested for the as photocatalytic production of H_2O_2 . The result is shown in Figure. 4b, from which it can be obviously seen that the sample without phosphorization had much lower activity than the sample with phosphorization, proving that the phosphorization process for the sample to form CoP is essential for the photocatalytic activity enhancement of g-C₃N₄. Besides, oxygen as a key reactant as shown in the equations (2-3) mentioned above, its concentration greatly influences the production of H₂O₂. Therefore, the photocatalytic activities of g-C₃N₄ and 50Co/CN were compared under oxygen and argon atmosphere. As Figure 4c shows, under argon atmosphere, the productions of H_2O_2 were low. While under the O2-saturated conditions, the productions of H₂O₂ were greatly enhanced for both bare g-C₃N₄ and 50Co/CN, demonstrating that O_2 is necessary for the reaction. Furthermore, in the process of H₂O₂ evolution, ethanol as the hole scavenger also greatly influences the rate for producing H₂O₂. In order to investigate its influence, photocatalytic experiments without ethanol under O2 atmosphere were also carried out over g-C₃N₄ and 50Co/CN. The results are shown in Figure. 4d. It can be found that, when the H₂O₂ evolution was performed in water without ethanol, pure g-C₃N₄ and 50Co/CN could generate about 10 uM and 80 uM H₂O₂ in 2 h respectively. While in the present of ethanol, the H₂O₂ production was increased significantly. The H₂O₂ production of pure g-C₃N₄ and 50Co/CN turned to be about 20 uM and 140 uM in 2 h, proving that the ethanol played important role for the production of H_2O_2 .

In order to evaluate the stability of the composite catalyst, we did the recycling test of the H_2O_2 evolution over 50Co/CN under visible light irradiation. After recycle for 7 runs, the photocatalytic activity for synthesis of H_2O_2 was almost not decreased, as shown in Figure. 5. These results indicate that the composite catalyst is a stable and efficient catalyst for generating H_2O_2 .



Figure 5. Stability of 50Co/CN catalyst under the same conditions.

Mechanism

Normally, high photocatalytic activity for production of H_2O_2 over semiconductors depends on their excellent absorption of light, efficient separation of charges and then rapid transfer of electrons to the surface for reducing O_2 . Figure 6a shows the

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UV-vis spectra of $g-C_3N_4$ and the composite of CoP and $g-C_3N_4$ (50Co/CN). After loading CoP, the UV-vis light absorption increased over the entire wavelength range. At the same time, separation of photogenerated electron-hole pairs of the catalysts was explored by photoluminescence (PL) measurement. Figure. 6b shows characteristic PL peak of $g-C_3N_4$ at about 460 nm. The peak position doesn't change for 50Co/CN but the peak intensity exhibits significant decrease compared to g-C₃N₄, indicating the fast recombination of charges has been greatly depressed. [28]As a complement, electrochemical impedance spectroscopy (EIS) Nyquist plots were applied to investigate the transfer rate of photogenerated electrons over 50Co/CN and g-C₃N₄ (Figure. 6c). The result is that a smaller arcs has been observed for 50Co/CN as compared with g-C₃N₄, which suggests more efficient separation of charges and more quick transfer of electrons to the surface of catalyst for 50Co/CN than pure g-C₃N₄.^[29]

To further prove the idea of the CoP as a cocatalyst for g- C_3N_4 in the composite catalyst, the positive slopes of Mott-Schottky plots for CoP at 2.0, 1.5, and 1.0 kHZ frequencies respectively were examined (Figure 6d). The intersections determined by the flat-band potential of different frequencies are -0.55 eV vs standard hydrogen electrode (SHE) for CoP, which is more positive than the conduction band position of g-C₃N₄ (about -1.3 eV) .[30] Therefore, the photogenerated electrons from the conduction band of g-C₃N₄ can be quickly transferred to CoP, promoting the seperation of the electron-hole pairs. Meanwhile, the flat-band potential of CoP is more negative than the potential for H_2O_2 evolution (-0.33 eV for one-electron pathway or 0.68 eV for two-electron pathway),[31, 5] indicating the CoP nanoparticles loaded can act as active sites for the photocatalytic H₂O₂ evolution and thus the electrons transferred from $g-C_3N_4$ can participate in the process of H_2O_2 generation. At the same time, the photogenerated holes in the valence band of g-C₃N₄ were quenched by ethanol to produce H⁺. Collectively, the loading of CoP nanoparticles on g-C₃N₄ resulted in greatly enhanced photocatalytic production of H₂O₂.



Figure 6. (a) UV-vis absorption spectra of $g-C_3N_4$ and 50Co/CN; (b) PL emission spectra of $g-C_3N_4$ and 50Co/CN; (c) Electrochemical impedance spectroscopy of $g-C_3N_4$ and 50Co/CN; (d) Mott-Schottky plots of CoP at frequencies 2.0, 1.5, and 1.0 kHZ.

As H₂O₂ might be generated through either a one-step twoelectron direct reduction (O₂ \rightarrow H₂O₂) route or a sequential twostep one-electron indirect reduction (O₂ \rightarrow •O₂⁻ \rightarrow H₂O₂), as shown in equations 1-6, to clarify the mechanisms of photocatalytic H₂O₂ production on the composite catalyst, active species trapping experiments were further carried out. As shown in Figure.7, with the addition of the •O₂⁻ scavenger p-benzoquinone (BQ, 1 mM), the H₂O₂ generation on 50CO/CN was greatly depressed. This result demonstrates that the production of H₂O₂ catalyzed by 50CO/CN went through a two-step one-electron pathway.



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Figure 7.The evolution of H_2O_2 over 50Co/CN with and without 1 mM BQ .

Conclusions

In summary, we adopted an in-situ growth method to prepare CoP/g-C₃N₄ composite and firstly applied it in photocatalytic production of H₂O₂. Under visible light irradiation, an H₂O₂ evolution amount over 50Co/CN is 140 uM in 2 h, which is much higher than either pure g-C₃N₄ or CoP. In addition, the composite catalyst exhibited a high stability in recycling experiments. A mechanism was proposed that in the composite catalyst, CoP worked as a guest catalyst via accelerated the separation and transfer of photogenerated charges of g-C₃N₄ to improve the photocatalytic activity towards forming H₂O₂. What's more, our work provides a new insight that using noble metal free transition metal phosphides loading on the surface of semiconductor as a cocatalyst for the evolution of H₂O₂.

Experimental Section

Chemicals

Cobalt nitrate hexahydrate (Co $(NO_3)_2 \cdot 6H_2O$), sodium hypophosphite (NaH_2PO_2) , methylenetetramine (HMT), melamine, ammonium chloride (NH_4CI) , potassium iodide (KI), and ammonium molybdate tetrahydrate $(H_{24}Mo_7N_6O_{24} \cdot 4H_2O)$ and ethanol (CH₃CH₂OH) were all got from Aladdin Industrial Corporation. All chemicals were used as received without further purification. Through the experiments deionized water was used.

Preparation of g-C₃N₄ nanosheets

The g-C₃N₄ nanosheets were prepared by homogeneously mixing equal amounts of melamine and ammonium chloride in an agate mortar. Then the mixture was transferred to a porcelain boat and calcined in air with a ramp rate of 5°C/min until 300°C, and then heated up to 520°C with a ramp rate of 2°C/min, maintained at 520°C for 4 h. After cooling to room temperature, the resulting light yellow powder were collected and ground to the final specimen.

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Synthesis of Co (OH) 2/g-C3N4

The Co (OH) $_2$ /g-C₃N₄ were prepared by the following procedures: Firstly, 0.2 g of the preparedg-C₃N₄ nanosheets was dispersed in 50 mL of deionized water. After ultrasonic for 2 h, 10 mL of precursor solution with dissolving different amount of Co (NO₃)₂·6H₂O (30, 50, and 70 mg) and equal amount of HMT were added into the solution under magnetic stirring. After stirring for 10 min, the solution was heated to 90°C with violent stirring in an oil bath for 6 h. After cooling down to the room temperature, the sediment was collected through centrifugation, and the final precipitate was collected through washing and centrifugation with use of deionized water and ethanol for several times. Finally, the samples were dried in vacuum oven at 60°C overnight.

Synthesis of CoP/g-C₃N₄

For a typical synthesis, Co (OH) $_2$ and NaH_2PO_2 (the molar ratio of Co to P is 1:10) were put at two separated positions in a porcelain boat and placed in a furnace. Subsequently, under N_2 flow the samples were heated to 300°C with the ramp rate of 1°C/min and maintained for 2 h. Finally, the powders were collected by washing several times with ethanol and dried overnight for further use. According to the different amount of Co (NO₃)_2•6H_2O (30, 50, and 70 mg) were used, the corresponding final products were donated as 30Co/CN, 50Co/CN, and 70Co/CN respectively

Characterizations

The X-ray diffraction was carried out at room temperature to character the microstructure of the g-C_3N_4, CoP and CoP/g-C_3N_4, which were calculated on a Rigaku D/MAX 2550 VB/PC apparatus applying Cu K $\!\alpha$ radiation ($\lambda {=} 1.5406$ Å) and a graphite monochromator at 40 kV and 30 mA. Transmission electron microscopy (TEM, JEM1400) and high resolution transmission electron microscopy (HRTEM, JEM2100) was employed to get the morphologies of the samples. The UV-vis absorption was got from a Scan UV-vis spectrophotometer (Varian, Cary 500) furnished with an integrating sphere assembly, using BaSO4 as the reflectance sample. The photoluminescence spectra (PL) were carried out by a Hitachi F-4600 fluorescence spectrophotometer at room temperature and excited by an incident light of 360 nm. The X-ray photoelectron spectroscopy (XPS) data were acquired on a PerkinElmer PHI 500°C ESCA system with AI Ka radiation at 250 W. Inductively coupled plasma atomic emission spectrometry (ICP-AES, Varian 710ES) was utilized to detect the percent of Co and P in the sample. Mott-Schottky plots and the electrochemical impedance spectroscopy (EIS) were all recorded on an electrochemical workstation. A standard threeelectrode system consisting of a working electrode that was prepared through a clean fluoride-tin oxide (FTO) deposited with a sample film, a Pt wire as the counter electrode and a saturated calomel electrode as the reference electrode in dark. For Mott-Schottky plots, the aqueous solution of 0.5 M Na₂SO₄ purged with nitrogen gas was used as the electrolyte. The EIS measurements were performed in a 25 mmol/L $K_3Fe(CN)_6$ and $K_4Fe(CN)_3$ and 0.1 mol/L KCI mixture aqueous solution.

Photocatalytic experiments for H₂O₂ generation

For evolution of H₂O₂, 0.02 g of catalyst were dispersed in 18 ml deionized water and 2 ml absolute ethanol by ultrasonic. After purge O₂ for 15 min, the suspension was irradiated by a 300 W Xe lamp with 420 cutoff filter. Besides, in the whole process, the reactor was kept at room temperature and under O₂ atmosphere. After 2 h of reaction, about 1 ml solution was collected by a syringe and filtered by 0.45 μ m PTFE filter. The concentration of H₂O₂ were test by ultraviolet spectrophotometry. In details, 500 μ l of supernatant liquid was mixed with 2 ml of 0.1 M Kl and 50 μ l of 0.01 M H₂₄Mo₇N₆O₂₄·4H₂O. After 10 min of reaction, the absorbance of the solution was tested by an UV-vis spectrometer at 352 nm.

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FULL PAPER

CoP decorated $g-C_3N_4$ composite catalyst has been developed for highly efficient and stable photocatalytic production of H_2O_2 under visible light irradiation. In the catalyst, CoP nanoparticles act as a noble metal free cocatalyst for $g-C_3N_4$, which enhanced the visible light absorption and promote the separation of photogenerated charge carriers.

* H_2O_2 production · photocatalysis



Photocatalytic Production of H₂O₂

Yulan Peng, Lingzhi Wang, Yongdi Liu, Juying Lei, Jinlong Zhang

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CoP as Noble Metal Free Cocatalyst over g-C₃N₄ for Photocatalytic Production of H₂O₂ under Visible Light Irradiation