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Novel PtCo alloy nanoparticles decorated 2D g-C$_3$N$_4$ nanosheets with enhanced photocatalytic activity for H$_2$ evolution under visible light irradiation

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Abstract

Novel two-dimensional (2D) graphitic carbon nitride (g-C$_3$N$_4$) photocatalysts decorated with PtCo bimetallic alloy nanoparticles (NPs) were prepared via an in-situ chemical deposition method. The physical and chemical properties of the as-prepared PtCo/g-C$_3$N$_4$ samples were characterized by X-ray diffraction (XRD), ultraviolet-visible diffuse reflection spectroscopy (DRS), transmission electron microscope (TEM), X-ray photoelectron spectroscopy (XPS) and surface photovoltage spectroscopy (SPV). The photocatalytic H$_2$ evolution experiments indicate that the PtCo alloy co-catalyst can effectively promote the separation efficiency of photo-generated charge carriers in g-C$_3$N$_4$, and consequently enhance the H$_2$ evolution activity. The 1.0 wt% PtCo/g-C$_3$N$_4$ nanosheet catalyst shows the highest catalytic activity, and corresponding H$_2$ evolution rate is 960 µmol·h$^{-1}$·g$^{-1}$, which are enhanced by 2.9 times compared with that of pristine bulk Pt/g-C$_3$N$_4$ (330 µmol·h$^{-1}$·g$^{-1}$) under visible light irradiation. The photocatalyst can keep stable and maintain catalytic activity after irradiated for 28 h. A possible photocatalytic mechanism of PtCo NPs on the enhancement of visible light performance is proposed to guide further improvement for other desirable functional materials.
Keywords: Water splitting; g-C₃N₄ nanosheets; PtCo bimetallic alloy; Photocatalysis.

1. Introduction

Over the past few decades, semiconductor photocatalysis has drawn great attention due to its environmental and energy conversion application.¹⁻⁸ Graphitic carbon nitride (g-C₃N₄) is one of the most widely studied semiconducting materials with a number of advantageous characteristics including low cost, non-toxicity and superior photocatalytic activity.⁹⁻¹¹ Since the first discovery of its photocatalytic activity under visible light, g-C₃N₄ has also been widely studied as a photocatalyst in applications such as water splitting,¹²,¹³ environmental purification¹⁴ and CO₂ reduction.¹⁵ Nevertheless, pure g-C₃N₄ suffers from weakness such as low visible light utilization efficiency, a small specific surface area and rapid recombination of photo-generated charge carriers.¹⁶⁻¹⁸ In order to solve the above problems, two approaches have been employed to enhance the visible light photocatalytic performance of g-C₃N₄: (i) exfoliation into two-dimensional structure,¹⁹⁻²¹ (ii) doping with metals or surface coupling hybridization.²²,²³

In general, bulk g-C₃N₄ photocatalysts are still exhibit relatively low photocatalytic activity because of multilayer gathered to form large objects with less surface active areas. In order to increase the surface area of g-C₃N₄, great efforts have recently been devoted to preparing g-C₃N₄ nanosheets and investigating their photocatalytic performance.²⁰,²¹ For instance, g-C₃N₄ nanosheets can be obtained by liquid exfoliation bulk g-C₃N₄ in water,²⁰ methanol solution²⁴ and concentrated sulfuric acid et al.¹⁹ Unfortunately, most of the current methods to fabricate g-C₃N₄ nanosheets are usually time consuming or low yield. Recently, a facile one step method for realizing scalable production of g-C₃N₄ nanosheets were reported.²⁵ This method offers the superiority of low cost, scalable production and high efficiency, and could increase the surface area in a controllable manner while still no inhibition the activity of per unit area, and therefore achieve enhanced photocatalytic activity. However, the g-C₃N₄ nanosheets still
suffer from the fast recombination of charge carriers in the photocatalytic process.

When metals and g-C\textsubscript{3}N\textsubscript{4} semiconductors are in contact, because of the lower Fermi levels of precious metals, metals can act as an electron capturer suppressing the recombination, thus extending the lifetime of charge carriers and significantly enhancing the activity of photocatalytic redox reactions.\textsuperscript{26, 27} Among the noble metals, Pt is considered the best candidate for photocatalystic hydrogen evolution due to its high work function. Compared to monometallic NPs, bimetallic NPs show greater potential in catalytic applications due to their unique microstructures and enhanced catalytic performance. Bimetallic catalytic systems can potentially achieve chemical transformations that can hardly be accomplished by monometallic catalysts, which can be attributed to the reason that different components of the catalysts have a particular function in the reaction mechanism.\textsuperscript{28, 29} It is observed that the activity, selectivity and resistance to poisoning of the metal catalysts can be drastically influenced by the presence of a second metal component.\textsuperscript{30} In our previous work, we found that the AuPd NPs has higher H\textsubscript{2} catalytic activity than single noble metal.\textsuperscript{31} Compared with pure Pt, Pt-based transition metal alloys exhibit higher activity in many reactions. For instance, it was reported that higher oxygen reduction reaction (ORR) activity could be achieved by alloying Pt with several transition metals such as Fe, Co and Ni.\textsuperscript{32-34}

In this study, for the first time we have developed a novel photocatalyst by loading PtCo bimetallic alloy on g-C\textsubscript{3}N\textsubscript{4} nanosheets via an ethylene glycol reduction method. The activity of g-C\textsubscript{3}N\textsubscript{4} can be significantly enhanced by adding the mono-dispersed PtCo co-catalyst NPs. The 1.0 wt% PtCo/g-C\textsubscript{3}N\textsubscript{4} shows the highest H\textsubscript{2} evolution activity of 960 \(\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}\), which is 2.9 times higher than that of bulk 1.0 wt% Pt/g-C\textsubscript{3}N\textsubscript{4}. The effects of PtCo on the visible light absorption, charge transfer process and photocatalytic activity were investigated in detail, and the catalytic mechanism for the enhanced H\textsubscript{2} evolution activity was also discussed. This work may provide more insight into synthesizing novel
Pt-based alloy co-catalysts materials with high activities for applications into solar energy conversion and utilization.

2. Experimental

2.1 synthesis of PtCo/g-C$_3$N$_4$ catalyst

All chemical were reagent grade and without used further purification. The g-C$_3$N$_4$ nanosheets bulk were prepared by heating 4g cyanamide and 10g ammonium chloride in a crucible with cover to 550°C for 4h at a heating rate of 4°C/min. A light yellow powder of g-C$_3$N$_4$ was obtained. The PtCo alloy NPs were prepared according to references with slight modification. The PtCo alloy was synthesized via the reduction of Pt and Co salts together in ethylene glycol (EG). All of the EG solution was to adjust pH=11.5 by NaOH solution. In a typical experiment, 1g/L (Pt) H$_2$PtCl$_6$ and 1g/L (Co) CoCl$_2$ EG solutions were prepared at stock solutions. The mixture was stirred for 30 min to form a homogeneous and light green solution. Then, a certain amount of g-C$_3$N$_4$ was added to the above solution followed by magnetic stirring for 30 min and ultrasonic dispersion 30 min to form a homogeneous suspension. The solution was then transferred to the 50 ml Teflon-lined stainless steel autoclave and heated at 200°C for 10 h.

For comparison, we further adjusted the molar ratio of Pt to Co in the PtCo bimetallic alloy, and prepared a series of samples, including Pt/g-C$_3$N$_4$, Pt$_3$Co/g-C$_3$N$_4$, PtCo/g-C$_3$N$_4$, PtCo$_2$/g-C$_3$N$_4$, PtCo$_6$/g-C$_3$N$_4$, Co/g-C$_3$N$_4$. The loading amounts of alloys in the g-C$_3$N$_4$ are all controlled at 1.0 wt%. In order to investigate the different loading on the catalytic activity, The photocatalytic system loading amount of the PtCo were 0.1 wt% , 0.3 wt% , 0.5wt% , 1.0 wt% , 3.0wt% and 5.0 wt%, respectively.

2.2 Characterization

The crystal structure of the sample was investigated using X-ray diffraction (XRD; Bruker D8 Advance) with CuKa radiation at a scan rate of 4min$^{-1}$. The acceleration voltage and the applied current
were 40 kV and 40 mA, respectively. The morphology of the samples was examined by high resolution transmission electron microscopy (HR-TEM, FEI Tecnai G^2 F20; accelerating voltage=200kV). UV-Vis diffuse reflection spectroscopy (DRS) was performed on a Shimadzu UV-4100 spectrophotometer using BaSO\textsubscript{4} as the reference material. The X-ray photoelectron spectroscopy (XPS) was measured in a PHI 5300 ESCA system. The beam voltage was 3.0 eV, and the energy of Ar ion beam was 1.0 keV. The binding energies were normalized to the signal for adventitious carbon at 284.8 eV.

2.3 Photocatalytic activity

The photocatalytic H\textsubscript{2} evolution experiments were performed in Perfect light Labsolar IIIAG system with a 300 ml quartz reactor. The reactor is connected to a low-temperature thermostat bath at 4\textdegree C. PLS-SXE 300C Xe arc lamp with a UV-cutoff (≥400nm) filter was used as the light source. The light intensity employed was 35mW/cm\textsuperscript{2}. In a typical photocatalytic experiment, 50 mg of photocatalyst powder was suspended in a 100 mL of aqueous solution containing 10 vol.% triethanolamine (TEOA). Before photocatalytic experiments, the reaction vessel was evacuated for 30 min to remove the dissolved oxygen and to ensure the anaerobic conditions. The products were analyzed by chromatography (Beifen 3420A, high purity Argon as a carrier gas, 99.999%) equipped with a thermal conductivity detector.

2.4. SPV measurements

The surface photovoltage (SPV) measurement was carried out on a surface photovoltage spectroscopy (PL-SPS/IPCE1000 Beijing Perfect Light Technology Co., Ltd).\textsuperscript{36} The measurement system consists of a source of monochromatic light, a lock-in amplifier (SR830, Stanford research systems, inc.) with a light chopper (SR540, Stanford research systems, inc.), and a sample chamber. The monochromatic light is provided by passing light from a 500 W Xenon lamp (CHFXQ500 W, global Xenon lamp power) though a grating mono-chromator (Omni-5007, No.09010, Zolix), which chopped
with a frequency of 24 Hz. All the measurements were operated at room temperature and under ambient pressure.

3. Results and discussion

3.1. Characterization of PtCo/g-C_3N_4 composite samples

The overall fabrication procedures of the PtCo/g-C_3N_4 photocatalysts are schematically illustrated in Fig.1. The bulk g-C_3N_4 was prepared via the reported method of our group. The metal-free bulk g-C_3N_4 powders were prepared thought the heating melamine in an alumina combustion boat to 550°C for 4h at a heating rate of 2°C/min. However, g-C_3N_4 nanosheets were obtained by heating a mixture of melamine and ammonium chloride at 550°C for 4h. With the increase of temperature, melamine was gradually polymerized, at the same time NH_4Cl was decomposed into ammonia and hydrogen chloride gases, which inhibit the aggregation of melamine and resulted in 2D g-C_3N_4 nanosheets. After PtCo bimetallic NPs loaded on the surface of g-C_3N_4 nanosheets, the PtCo/g-C_3N_4 nanosheets samples were obtained.

The X-ray diffraction patterns of the pristine and modified g-C_3N_4 are shown in Fig.2. Typically, the pure g-C_3N_4 nanosheets have two distinct peaks at 13.1° and 27.4°, which can be indexed as (1 0 0) and (0 0 2) peaks in JCPDS 87-1526. These two diffraction peaks are in good agreement with the g-C_3N_4 reported in the literature. However, no diffraction peaks corresponding to PtCo co-catalysts can be observed in Fig.2. This may be due to the small amount of PtCo NPs contents and highly dispersion in the polymeric g-C_3N_4 photocatalysts. In order to better understand the nature of the PtCo “alloy” particle, we have added a series of pure PtCox to support this conclusion. From the Fig.2b XRD inset, the pure Pt (JCPDS, No. 65-2868) XRD patterns exhibit diffraction peaks at approximately 39.7° (1 1 1) and 46.2° (2 0 0). After introducing Co element to PtCox NPs, the diffraction peaks gradually moves to the right side. This result indicates that the as-prepared NPs are homogeneous PtCo bimetallic
alloys.

The UV-vis diffuse reflectance spectra (DRS) of as-prepared PtCo/g-C₃N₄ samples were investigated and shown in Fig.3. The pure g-C₃N₄ nanosheets shows absorption from the UV through the visible range up to 470 nm, the steep of the spectrum indicates that the visible light absorption is ascribed to the band gap transition, corresponding to a band gap of 2.6 eV for pure g-C₃N₄. After inducing PtCo NPs, the PtCo/g-C₃N₄ sample show the similar absorption edge in shape and enhanced light absorption compared with pure g-C₃N₄. Fig.3a illustrates that the absorption intensities of the as-prepared samples are gradually strengthened with increasing Pt percentage in the PtCoₓ NPs in the visible light region. Fig.3b shows that the absorption intensities of the as-prepares samples are strengthened with increasing PtCo NPs contents, which agrees with the color of the prepared samples that vary from yellow to gray. The DRS results also indicate that the chemical deposited PtCo NPs could improve the visible light absorption, and hence is expected to increase photocatalytic performance.

The morphology and microstructure of the 1.0 wt% PtCo/g-C₃N₄ nanosheets photocatalyst were investigated by TEM. Fig.4 displays the TEM and HRTEM images of PtCo/g-C₃N₄ composites. As shown in Fig.4a, the g-C₃N₄ samples consist of irregular ultrathin nanosheets. The Fig.4b and c illustrates the microstructures of composite samples, the g-C₃N₄ nanosheets with PtCo NPs can be found. The PtCo NPs co-catalysts are decorated on the surface of g-C₃N₄ to nanosheets form intimate interfaces facilitating charge transfer between the semiconductors; hence it is expected to improve the separation of photogenerated charge carriers and therefore the photocatalytic activity. As shown in Fig.4d, the PtCo NPs has diameters of 3-5nm and their crystallinity can be resolved. The lattice spacings measured for the crystalline planes are 0.218 nm, corresponding to the (1 1 1) plane of PtCo alloys (JCPDS 43-1358).
X-ray photoelectron spectrum (XPS) is used to investigate the valance states and chemical environment of constituent elements on the surface of the samples. The sample for XPS is 1.0 wt% PtCo/g-C₃N₄ nanosheets. The survey XPS spectrum shows that the main elements on the surface of the product are C, N and small amount of Pt and Co. Fig.5a and b presents the high-resolution XPS spectra of C1s and N1s in the PtCo/g-C₃N₄ sample. The C1s shows two distinct peaks at 284.8 and 288.2 eV. The first peak can be ascribed to carbon species adsorbed on the surface of photocatalysts; the second binding energy peak belongs to carbon atoms in g-C₃N₄. The N1s XPS binding energy can be divided into three peaks located at 398.53, 399.13 and 400.58 eV, which represent nitrogen atoms in the C=N-C, N-(C)₃ and C-N-H functional groups in the polymeric g-C₃N₄ structures.³⁹,⁴⁰ As shown in Fig.5c, the Pt 4f/2 and Pt 4f₅/2 peaks in the spectrum of Pt locate at 71.38 and 74.73 eV, respectively, which exhibit slight upshift as compared to pure Pt NPs.⁴¹ In order to further verify the valence states of PtCoₓ alloys, the Pt, Pt₃Co, PtCo and PtCo₃ samples were examined by XPS technique. Obviously, after Pt form alloy with Co, the Pt 4f binding energy of the Pt-Co bimetallic crystals shifted to right side compared to that of pure Pt NPs. The positions of Pt 4f/2 are 71.38, 71.53, 71.68 and 71.83 eV for Pt, Pt₃Co, PtCo and PtCo₃, respectively. The Co 2p₃/2 peak is about 778.2 eV, indicating the presence of bimetallic alloy.⁴² The electronic structures of PtCo NPs are modified due to the alloying of Pt with Co.⁴³,⁴⁴

3.2 Photocatalytic H₂ evolution activity

As shown in Fig.6, pure Pt/g-C₃N₄ bulk sample shows obvious visible light photocatalytic activity with H₂ evolution rate of 330 µmol·g⁻¹·h⁻¹, which can be attributed to the moderate band gap and unique electronic of Pt/g-C₃N₄. After addition of a small amount of PtCoₓ NPs, the photocatalytic activity of PtCoₓ/g-C₃N₄ is improved. The activity of the composite samples is further enhanced with higher Co contents. The bulk 1.0 wt% PtCo/g-C₃N₄ sample shows the highest H₂ evolution rate of 689 µmol·g⁻¹·h⁻¹, which is about 2.1 folds higher than that of pure bulk Pt/g-C₃N₄. A further increase in Co
content causes a decrease in the photocatalytic H\textsubscript{2} evolution. We propose that the origin of this effect is attributed to the reason that the PtCo bimetallic alloys have an appropriate mole ratio.

Compared to Fig.6, Fig.7 has a superior photocatalytic H\textsubscript{2} evolution activity when bulk g-C\textsubscript{3}N\textsubscript{4} is replaced by g-C\textsubscript{3}N\textsubscript{4} nanosheets. After introducing Pt nanoparticles, the intimate interfaces between Pt and g-C\textsubscript{3}N\textsubscript{4} are formed. It was reported that the high activity Pt can accept electrons and serve as active sites for hydrogen production. With increase of the Co content in the PtCo bimetallic alloy, the photocatalytic hydrogen evolution on PtCo\textsubscript{x}/g-C\textsubscript{3}N\textsubscript{4} is further enhanced. The PtCo/g-C\textsubscript{3}N\textsubscript{4} nanosheets sample shows the highest H\textsubscript{2} evolution rate of 960 \text{µmol⋅g}^{-1}⋅\text{h}^{-1}, which is about 1.34 folds higher than that of pure Pt/g-C\textsubscript{3}N\textsubscript{4} nanosheets (716 \text{µmol⋅g}^{-1}⋅\text{h}^{-1}).

To further investigate the catalytic activity of 2D nanosheet and bulk structures, the photocatalytic activities of bulk and nanosheet samples were conducted and compared. Fig.8 illustrates the rate of H\textsubscript{2} evolution over different bulk and nanosheet samples. After bulk materials are replaced by nanosheets, the catalytic activities are significantly enhanced. As shown in the Fig.8, the PtCo/g-C\textsubscript{3}N\textsubscript{4} nanosheet sample shows the highest photocatalytic performance with H\textsubscript{2} evolution rate of 960 \text{µmol⋅h}^{-1}⋅\text{g}^{-1}, about 2.9 times higher than of bulk Pt/g-C\textsubscript{3}N\textsubscript{4} (330 \text{µmol⋅h}^{-1}⋅\text{g}^{-1}), which indicates that the nanosheets play an important role in enhancement of H\textsubscript{2} evolution activity in the PtCo/g-C\textsubscript{3}N\textsubscript{4} composite photocatalysts.

Fig.9 presents the H\textsubscript{2} evolution over PtCo/g-C\textsubscript{3}N\textsubscript{4} nanosheets photocatalysts with different PtCo NPs contents. After introducing 0.1wt% of PtCo NPs, the catalytic activity of H\textsubscript{2} evolution is significantly increased to 458.7 \text{µmol⋅g}^{-1}⋅\text{h}^{-1}. With continue to increase the PtCo NPs amount; the H\textsubscript{2} evolution rate over g-C\textsubscript{3}N\textsubscript{4} nanosheets is further enhanced. The 1.0 wt% sample shows the highest photocatalytic H\textsubscript{2} evolution rate of 960 \text{µmol⋅g}^{-1}⋅\text{h}^{-1}. However, a further increase of PtCo NPs contents lead to a slightly decrease of H\textsubscript{2} evolution. As a consequence, the 1.0 wt% PtCo/g-C\textsubscript{3}N\textsubscript{4} presents the best H\textsubscript{2} evolution activity in this study.
Besides activity, the stability of a photocatalyst is important for practical application. To demonstrate the stability of PtCo/g-C₃N₄ nanosheets catalyst, we performed the cycled hydrogen evolution experiment over 1.0 wt% samples under the same conductions. Fig.10 presents the H₂ evolution curve in cycling photocatalytic runs. This results show that the composite sample display no obvious decrease of H₂ production activity after irradiated for 28 h, indicating that the PtCo/g-C₃N₄ nanosheet sample has excellent stability for photocatalytic H₂ production.

3.3 Photocatalytic mechanism discussion

Based on the experimental results, we try to explain the photocatalytic mechanism of PtCoₓ/g-C₃N₄. The binary alloys show different structures and electronic density of states when compared with single metal, resulting in adjustable degeneration of physical chemical properties and surface states of PtCoₓ NPs. The “synergistic effect” of alloy elements will affect the Fermi energy level of the PtCoₓ alloys. As shown in Fig.11, the Fermi energy levels of PtCoₓ alloys are lower than that of g-C₃N₄ conduction band, which makes the photo-excited electrons transfer from CB of g-C₃N₄ to surface of PtCoₓ alloys and leads to efficient separation of electron-hole pairs. In the PtCoₓ alloys, the “synergistic effect” of Pt and Co elements makes the surface defects increase, and changes the Fermi energy level position in comparison to Pt (Fig.11). It is assumed that the transfer driving force may increase for photo-excited electrons from CB of g-C₃N₄ to the PtCo alloy after introducing Co element. Hence, introduction of Co element is more beneficial to the capturing ability of photo-excited electrons in the PtCoₓ alloys, and enhance the photocatalytic activity. However, at the same time, the Co element decreases the active sites of H₂ evolution, because H⁺ in solution is much easier to be adsorbed on the surface of Pt than that of Co. The higher Co contents in PtCoₓ alloys may inhibit the adsorption of H⁺ and decrease the activity in the PtCoₓ/g-C₃N₄ samples. Therefore, for the H₂ evolution activity, introduction of Co to form PtCoₓ alloys has two influencing aspects: (1) it improves capturing ability of photo-excited...
electrons; (2) it reduces active sites of H₂ production. Based on our results, H₂ evolution activity increases when Co is added into PtCoₓ alloys at the beginning, because the factor (1) is more effective than the factor (2). However, the activity decreases when more Co is introduced as the factor (2) is more dominant (as shown in Fig. 8). The optimum ratio of Pt to Co is determined to be 1:1. Therefore, the PtCo/g-C₃N₄ samples show the best H₂ evolution activity.

Based on the results of the visible light photocatalytic performance and the structure characterizations of PtCo/g-C₃N₄ nanosheet samples, a possible mechanism for photocatalytic H₂ evolution over PtCo/g-C₃N₄ catalyst is proposed and illustrated in Fig. 12. Under visible light irradiation (λ≥400nm), the polymeric g-C₃N₄ absorbs photons and excites electron-hole pairs. However, the photo-generated charge carriers are likely to recombine without co-catalyst. The significant enhancement of H₂ evolution can be attributed to synergistic effect between g-C₃N₄ and PtCo bimetallic NPs. After introducing PtCo NPs, the two materials closely bound together and form interfaces. The PtCo alloy NPs show higher electron capture capability and can stimulate electron transfer from g-C₃N₄ towards PtCo NPs surface due to the lower Fermi level. Moreover, the CB and VB edge potentials of polymeric g-C₃N₄ are determined at -1.13 and +1.57 eV. Therefore, in the PtCo/g-C₃N₄ system, the photo-generated electrons in the CB of the g-C₃N₄ transfer to PtCo co-catalysts via contacting interfaces, giving the conduction band electrons higher mobility and promoting the separation of electron-hole pairs. The holes in the VB of g-C₃N₄ are consumed by TEOA sacrificial regents. Therefore, the recombination process of the electron-hole pairs is effectively inhibited, resulting in obviously improvement of H₂ production for the PtCo/g-C₃N₄ nanosheet photocatalysts.

To get more in-depth understanding of the electrical properties and the charge transfer process at g-C₃N₄ and PtCo NPs interfaces, surface photovoltage spectroscopy (SPV) measurement was employed to reveal the kinetic behaviors of the photo-generated charge carriers in the PtCo/g-C₃N₄ nanosheets.
The SPV survey could be beneficial for understanding the effect of PtCo NPs. Fig. 13a illustrates the SPV spectra of g-C_3N_4 and 1.0 wt% PtCo/g-C_3N_4 nanosheets. The SPV signal ranging from 470-300 nm is observed for pure g-C_3N_4. After loading PtCo NPs on the g-C_3N_4 nanosheets, the sample shows obvious responses signal. The enhanced SPV signal intensity indicates that the introduction of PtCo NPs is beneficial to the separation of photo-generated electron-hole pairs in g-C_3N_4 nanosheets. Fig. 13b presents the corresponding phase spectroscopy of PtCo/g-C_3N_4, and the phase angles in the response region are in the range of +150 to +180 (470 nm ≥ λ ≥ 400 nm). The phenomenon means that photo-generated electrons transfer from the g-C_3N_4 to the PtCo NPs when equilibrium is reached in the PtCo/g-C_3N_4 sample. The PtCo/g-C_3N_4 promotes the electron transfer from g-C_3N_4 to PtCo, resulting in the accumulation of electrons on the PtCo NPs surface. More importantly, the SPV spectra are consistent with the results of photocatalytic H_2 evolution, which can explain the origin of enhanced separation efficiency of photo-generated electron-hole pairs in the PtCo/g-C_3N_4 composites.

4. Conclusions

In summary, PtCo NPs cocatalyst decorated ultrathin 2D g-C_3N_4 nanosheet photocatalysts is successfully prepared with solvothermal synthesis approach. The doping of PtCo NPs does not affect the morphology and crystal structure of 2D g-C_3N_4 nanosheets. The composite photocatalysts exhibited enhanced photocatalytic activity in the presence of small PtCo NPs. The optimal loading content of PtCo NPs was determined to be 1.0 wt% for g-C_3N_4 nanosheets, and the corresponding H_2 production rate was 960 µmol·h^{-1}·g^{-1}. A possible photocatalytic mechanism is proposed based on the experimental results. The surface photovoltage technique can be applied to investigate the photoelectric processes of PtCo/g-C_3N_4, leading to a better understanding of photocatalytic behavior to explore novel composite photocatalysts with advanced functions. Therefore, the PtCo NPs are a promising co-catalyst material.
which can be potentially used for photocatalytic hydrogen evolution.

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Figure Captions:

Fig.1. Schematic illustration of the formation route to PtCo/g-C$_3$N$_4$ photocatalysts (Bulk and nanosheets).

Fig.2. XRD patterns of PtCo/g-C$_3$N$_4$ nanosheet photocatalysts, as well as of the pure PtCoX (X=0, 1, 3).

Fig.3. UV-vis diffuse reflectance of PtCoX/g-C$_3$N$_4$ composite samples.

Fig.4. The HRTEM images with different magnifications for the 1.0 wt% PtCo/g-C$_3$N$_4$ nanosheet photocatalysts.

Fig.5. XPS spectra of PtCo/g-C$_3$N$_4$ sample: (a) C 1s; (b) N 1s; (C) Pt 4f (Pt/Pt$_3$Co/PtCo/PtCo$_3$); (d) Co 2p.

Fig.6. Photocatalytic H$_2$ evolution over the bulk PtCo$_x$/g-C$_3$N$_4$ composite samples with different Pt/Co percentage in the same 1wt% content.

Fig.7. Photocatalytic H$_2$ evolution over the PtCoX/g-C$_3$N$_4$ nanosheet composite samples with different Pt/Co percentage in the same 1.0 wt%.

Fig.8. The H$_2$ evolution rate over different bulk and nanosheet samples.

Fig.9. Photocatalytic H$_2$ evolution over PtCo/g-C$_3$N$_4$ nanosheet samples with different PtCo contents under visible light irradiation.

Fig.10. Cycling runs for the photocatalytic hydrogen evolution in the presence of 1.0 wt% PtCo/g-C$_3$N$_4$ nanosheet sample under visible light illumination ($\lambda \geq 400$nm).

Fig.11. The schematic illustration of photo-excited electron injection from CB of g-C$_3$N$_4$ to the PtCo NPs and Pt NPs.

Fig.12. The schematic illustration for electron charge transfer and H$_2$ evolution mechanism under visible light irradiation.

Fig.13. SPV spectra of pure g-C$_3$N$_4$ and 1wt% PtCo/g-C$_3$N$_4$: (a) Photovoltage; (b) Phase.
Fig. 1. Schematic illustration of the formation route to PtCo/g-$C_3N_4$ photocatalysts (Bulk and nanosheets).
Fig. 2. XRD patterns of PtCo/g-C$_3$N$_4$ nanosheet photocatalysts, as well as of the pure PtCo$_X$ (X=0, 1, 3)
Fig. 3. UV-vis diffuse reflectance of PtCox/g-C₃N₄ composite samples.
**Fig. 4.** The HRTEM images with different magnifications for the 1.0 wt% PtCo/g-C₃N₄ nanosheet photocatalysts.
Fig. 5. XPS spectra of PtCo/g-C$_3$N$_4$ sample: (a) C 1s; (b) N 1s; (C) Pt 4f (Pt/Pt$_3$Co/PtCo/PtCo$_3$); (d) Co 2p.
Fig. 6. Photocatalytic H$_2$ evolution over the bulk PtCo$_x$/g-C$_3$N$_4$ composite samples with different Pt/Co percentage in the same 1wt% content.
**Fig. 7.** Photocatalytic H\(_2\) evolution over the PtCo/x/g-\(\text{C}_3\text{N}_4\) nanosheet composite samples with different Pt/Co percentage in the same 1.0 wt%.
Fig. 8. The H₂ evolution rate over different bulk and nanosheet samples.
Fig. 9. Photocatalytic H$_2$ evolution over PtCo/g-$\text{C}_3\text{N}_4$ nanosheet samples with different PtCo contents under visible light irradiation.
Fig. 10. Cycling runs for the photocatalytic hydrogen evolution in the presence of 1.0 wt% PtCo/g-C₃N₄ nanosheet sample under visible light illumination ($\lambda \geq 400$ nm).
Fig. 11. The schematic illustration of photo-excited electron injection from CB of g-C$_3$N$_4$ to the PtCo NPs and Pt NPs.
Fig. 12. The schematic illustration for electron charge transfer and H$_2$ evolution mechanism under visible light irradiation.
Fig. 13. SPV spectra of pure g-C$_3$N$_4$ and 1wt% PtCo/g-C$_3$N$_4$: (a) Photovoltage; (b) Phase.
Graphical Abstract

Visible light irradiation

PtCo/g-C$_3$N$_4$ samples

Novel PtCo/g-C$_3$N$_4$ nanosheets with efficient visible light induced photocatalytic activity for H$_2$ evolution.