

Novel Graphitic Carbon Nitride/Co-B-P Nanocomposites with Significantly Enhance Visible-Light Photocatalytic Hydrogen Production from Water Splitting

ABSTRACT

As a promising metal-free photocatalyst for hydrogen (H₂) production through water splitting under visible-light irradiation, graphitic carbon nitride (g-C₃N₄) photocatalysts decorated with CoBP was prepared via simple ultrasonification. This paper highlights the structures of the photocatalysts, their stability, rate of hydrogen evolution and the mechanism of charge transfer within the photocatalysts. The prepared C₃N₄/CoBP nanocomposite photocatalysts were characterized by using X-ray diffraction, X-ray photoelectron spectroscopy, transmission electron microscopy, scanning electron microscopy and UV–visible (UV–vis) diffuse reflectance spectroscopy. After detailed analysis, the C₃N₄/CoBP nanocomposite photocatalysts showed excellent photocatalytic performance, which was due to the formation of the heterostructured hybrids of g-C₃N₄ and CoBP. The effects of C₃N₄/CoBP nano hybrids on H₂ evolution were evaluated. The effects improved with increasing load of CoBP until the optimal level (5 wt% CoBP with visible-light irradiation at $\lambda \geq 420$ nm). The maximum and remarkable photocatalytic H₂ evolution rate of 51.68 $\mu\text{mol h}^{-1}$ was achieved, which was 3.8 times that obtained from pure g-C₃N₄. Moreover, the C₃N₄/CoBP heterostructured nano hybrids demonstrated extremely high photostability and recyclability for H₂ evolution after visible light illumination. The composite hybrid accelerated the separation and transfer of photogenerated charge carriers and subsequently suppressed charge recombination. Conclusively, this study offered an opportunity for the design and synthesis of highly stable and efficient C₃N₄/CoBP nanocomposite photocatalysts for energy conversion and utilisation.

Keywords: Heterostructured photocatalyst, C₃N₄/CoBP nanocomposite, water splitting, hydrogen evolution, charge separation efficiency.

1. INTRODUCTION

“Hydrogen (H₂) is considered as a clean, renewable, environmental friendly and attractive alternative energy source compared with fossil fuels”[1,2]. “After Fujishima and Honda reported photoelectrochemical water splitting over a TiO₂ electrode in 1972, photocatalytic H₂ production via water splitting under solar irradiation has become the most fascinating and promising strategies for solving the energy crisis and environmental pollution”[3–6]. In the past few years, extensive effort has been devoted to designing and developing various semiconductor-based photocatalysts for H₂ production via water splitting. It includes but not limited to oxides[7], sulphides[8], nitrides[2] and conjugated polymer[9,10]. “However, most of these materials are limited for practical requirements because of low efficiency, poor chemical stability and high costs”[4,5,9]. Therefore, to improve the efficiency of photocatalytic H₂ production through water splitting, considerable attention has been paid to developing potential semiconductor photocatalysts with high efficiency, chemical stability and response to visible-light irradiation.

“Recently, graphitic carbon nitride (g-C₃N₄), has emerged as a typical metal-free organic semiconductor photocatalyst for visible light photocatalytic H₂ production via water splitting. Since 2009[11], g-C₃N₄ photocatalyst associated with the

unique properties of g-C₃N₄, such as appropriate band gap (~2.7 eV), excellent in physical and chemical stability, abundance and non-toxicity, have been extensively studied"[12,13]. "However, the photocatalytic performance of the H₂ evolution of pristine g-C₃N₄ seems to be limited because of its poor light absorption and the fast recombination rate of photo induced charge carriers"[5]. To overcome these problems, researchers have developed different strategies that improve the photocatalytic efficiency of pure g-C₃N₄, such as doping with metal or non-metal elements[13,14], controlling morphology[1,15] and constructing heterojunctions with other semiconductors[5,7,12].

"Constructing heterojunctions between g-C₃N₄ photocatalysts and other materials has been identified as the most effective and feasible route for the improvement of charge migration and separation in g-C₃N₄"[5,7,12]. Therefore, g-C₃N₄ can be merged with a suitable material to form a g-C₃N₄-based heterostructure photocatalyst for H₂ production. Various cobalt-based compounds, such as CoO[16], Co₃N[17] and Co(OH)₂[18] are widely used as effective catalysts for constructing g-C₃N₄-based composite photocatalysts and show outstanding performance in photocatalytic H₂ evolution reactions. Ternary cobalt-based catalyst (CoBP) has been found to intensify significant attention in the electrocatalysis studies of H₂ production enhanced by its synergistic effect of elements P and B[19–21]. For example, Hongming Sun *et al.*[19] synthesized CoBP nanosheets supported on a Ni foam; the nanosheets were showed remarkably enhanced electrocatalytic activity in H₂ evolution. Chunduri *et al.*[20] synthesized an amorphous CoBP bifunctional electrocatalyst to enhance alkaline water splitting in electrocatalytic H₂ production reaction. Thus, a more efficient g-C₃N₄-composite can be designed according to CoBP catalyst to enhance the photocatalytic performance of H₂ production. However, the synthesis of C₃N₄/CoBP nanocomposite photocatalyst for photocatalytic H₂ production through water splitting under visible-light irradiation has not been reported.

The present study is the first to report a novel C₃N₄/CoBP nanocomposite photocatalyst by decorating an amorphous CoBP on the surface of a g-C₃N₄ photocatalyst via a simple ultrasonic process. The obtained C₃N₄/CoBP nanocomposite photocatalyst showed higher photocatalytic activity and stability for H₂ evolution under visible-light irradiation than pure g-C₃N₄. The maximum H₂ evolution rate was obtained after 5 wt% amorphous CoBP was loaded on the surface of g-C₃N₄ and reached a rate of 51.68 μmol h⁻¹, which was 3.8 times that of pure g-C₃N₄. The heterojunction formed between the planar aromatic structure g-C₃N₄ and CoBP molecule accelerated interfacial charge migration and separation. Consequently, the C₃N₄/CoBP nanocomposite photocatalyst exhibited significantly high photocatalytic activity for H₂ production. Therefore, merging CoBP with g-C₃N₄ is a promising method for developing efficient and low-cost photocatalysts for H₂ production through water splitting. This work can provide novel insights into the planning, design and development of efficient photocatalysts with high activity for solar energy applications.

2. MATERIAL AND METHODS

2.1 Chemicals.

Urea (≥ 99 %), cobalt (II) chloride hexahydrate (CoCl₂·6H₂O), ammonium chloride (NH₄Cl), ammonia solution, sodium hypophosphite monohydrate (NaH₂PO₂·H₂O), sodium hydroxide (NaOH), anhydrous sodium sulfate (Na₂SO₄), triethanolamine (TEOA, ≥ 78 %), methanol (≥ 99%), lactic acid (≥ 85%) and ascorbic acid (≥ 99%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Sodium borohydride (NaBH₄) and Chloroplatinic acid hexahydrate (H₂PtCl₆·6H₂O, ≥ 37 % Pt basis) were bought from Aldrich. All chemicals were of analytical grade and used as received from the manufactures without any purification. Double distilled water was produced from a SZ-93A auto-double distillation apparatus (Ya Rong Corp., Shanghai, China).

2.2 Preparation of the photocatalyst.

2.2.1 Preparation of g-C₃N₄

Firstly, 10.0 g of urea was added into covered alumina crucible and calcined at 550 °C for 4 h in a muffle furnace under air atmosphere, at the heating rate of 5 °C min⁻¹. After 4 h, the sample was left to cool naturally to room temperature, yellow powder (g-C₃N₄) was collected for further use.

2.2.2 Preparation of Amorphous CoBP

CoBP was prepared by a modified electroless deposition method[19]. In a typical synthesis, solution A containing a 50 mL of aqueous solution of CoCl₂·6H₂O (3.5 mmol), NH₄Cl (25 mmol) and some amount of NH₃·H₂O (for adjusting pH to 9), was deaerated and flushed with argon. Meanwhile, a solution B containing a 50 mL of aqueous solution of NaBH₄ (35 mmol), NaH₂PO₂·H₂O (500 mmol) and NaOH (3.8 mmol) which was also deaerated and flushed with argon. Then, solution B was added drop wise to solution A under ultrasonification in an ice bath (ultrasonification was applied throughout the reaction process). Vigorous frothing occurred and a dark product was formed. After the completion of the reaction, the sample was centrifuged and washed thoroughly with distilled water and dried at 50 °C under vacuum, and the corresponding sample was labelled Co-B-P.

2.2.3 Preparation of g-C₃N₄/CoBP composite photocatalyst

The C₃N₄/CoBP composite photocatalyst was obtained by mixing an appropriate amount of g-C₃N₄ and CoBP in solution and then was placed in ultrasonic bath for 3 h, followed by drying for the removal of solvent.

2.3 Characterization.

"The crystal phase of the samples were characterized by powder X-ray diffraction (XRD) measurements using X-ray diffractometer (MXPAHF, Japan) with Cu K α irradiation ($\lambda = 1.541 \text{ \AA}$) at operating voltage of 40 kV and a current of 200 mA. Morphology of the photocatalysts was confirmed by Transmission electron microscopy (TEM) on JEOL-2010, Japan) at accelerating voltage of 200 kV. The XPS was recorded to study the elemental composition and binding energies of the sample and operated by ESCALAB 250 high-performance electron spectrometer which was set to monochromated Al K α radiation as the excitation source. The UV-vis diffuse reflectance spectra of the photocatalysts were recorded by a Shimadzu spectrophotometer (Model 2501 PC). The steady-state photoluminescence (PL) spectra were conducted on a fluorescence spectrophotometer (JY Fluorolog-3-Tau) with the excitation wavelength at 325 nm. The time-resolved photoluminescence (TRPL) was measured on a Laser Strobe Time-Resolved Spectrofluorometer (Photon Technology International (Canada) Inc.) with a USHIO xenon lamp source, a GL-302 high-resolution dye laser (lifetimes 100 ps to 50 ms, excited by a Nitrogen laser) and a 914 photomultiplier detection system" [5].

2.4 Photoelectrochemical measurements

"Photoelectrochemical tests were carried out at CHI 760E electrochemical workstation (Chenhua Instrument Company, Shanghai, China) based on a standard three-electrode system, composed of Ag/AgCl as the reference electrode, Pt wire as the counter electrode and indium-tin oxide (ITO) glass as the working electrode. Na₂SO₄ (0.5 M) was used as the electrolyte solution. A 300 W Xe lamp was used as a solar light source ($\lambda \geq 420 \text{ nm}$). For the preparation of working electrodes, 2 mg of either g-C₃N₄ or C₃N₄/5 wt% CoBP samples was dispersed in 1 mL ethanol and 10 μ L Nafion solution by ultrasonification process. The resulting dispersion was spin-coated onto a piece of ITO glass with a fixed area of ca. 1 cm² and annealed at 300 °C for 2 h to remove the organic species completely. The amperometric photocurrents were measured for each switch on/off event with a bias voltage of 0.5 V under visible light irradiation. The electrochemical impedance spectroscopy (EIS) was recorded under visible light and a bias of -1 V and the frequency range was from 10 mHz to 100 kHz in parallel to an alternating current signal amplitude of 5 mV" [6].

2.5 Photocatalytic hydrogen production test.

"The photocatalytic hydrogen evolution from water splitting was carried out in an outer Pyrex top-irradiation reaction vessel (500 mL) connected to a glass closed gas circulation system. In a typical experiment, 10 mL of triethanolamine (TEOA) was used as a sacrificial agent in an aqueous solution of 100 mL. 50 mg of g-C₃N₄ powder and CoBP with different amounts were dispersed in water and then kept in an ultrasonic bath for half an hour. Then, 1 wt% Pt, as a co-catalyst to boost H₂ generation was loaded onto the surface of the catalyst by in situ photodeposition method using H₂PtCl₆·6H₂O. In order to make sure anaerobic conditions in the reaction system, the solution was evacuated 1 h to remove air completely before irradiation by a 300 W xenon lamp (Perfect Light, PLS-SXE300C, Beijing). The xenon lamp is equipped with a cut-off filter ($\lambda \geq 420 \text{ nm}$) to remove ultraviolet light. Besides, the Pyrex reactor with a double layer was continuously stirred, and a flow of cooling ethylene glycol was used during the photocatalytic reaction to maintain the temperature of the reaction solution at 10 °C. The amount of hydrogen evolution from photocatalytic splitting water was measured using on-line gas chromatography (GC1120, Shanghai Sunny Hengping Limited, HTCD, nitrogen as carrier gas). After the reaction, the photocatalysts were separated from the reaction solution for further characterization. The catalysts are denoted as C₃N₄/x CoBP, where x (x = 4, 5, 6 %) refers to the weight content of CoBP in C₃N₄/CoBP samples" [7].

The apparent quantum yield (AQY) was measured under different monochromatic light irradiation by using C₃N₄/5 wt% CoBP photocatalyst (irradiated by a 300 W Xe lamp using the bandpass filter of $\lambda \pm 5 \text{ nm}$ for 420, 450, 500, 550, 600 nm), and was calculated according to the equation given below:

$$\begin{aligned} \text{AQY (\%)} &= \frac{\text{Number of reacted electrons}}{\text{Number of incident photons}} \times 100\% \\ &= \frac{\text{Number of evolved H}_2 \text{ molecules} \times 2}{\text{Number of incident photons}} \times 100\% \end{aligned}$$

3. RESULTS AND DISCUSSION

Graphitic carbon nitride (g-C₃N₄) was prepared from urea and calcined at 550 °C for 4 h, CoBP molecule was synthesised by an electroless deposition method (Fig. S1) and g-C₃N₄/CoBP nanocomposite photocatalysts were obtained by mixing g-C₃N₄ and CoBP in a solution and then dried. The X-ray diffraction (XRD) patterns of the samples prepared are displayed in Fig. 1a. Pure g-C₃N₄ exhibited two main diffraction peaks with different intensities. The low-angle diffraction peak at 13.0° index was attributed to the (100) plane, and the high-angle diffraction peak at 27.7° was attributed to the (002)

lattice plane. These arrangements reflected an in-plane structural packing motif of a tri-s-triazine unit and the interlayer stacking peak of conjugated aromatic systems observed for g-C₃N₄, respectively[6,22]. The XRD patterns of composite C₃N₄/CoBP with 5 wt% CoBP displayed similar diffraction peaks observed on the original g-C₃N₄. Remarkably, no other impurity phase was observed. The well-crystal structure of g-C₃N₄ was not affected by CoBP loading. In addition, no intense diffraction peaks were observed in the XRD pattern of pure CoBP confirming noncrystallinity, and only a single broad peak was detected (at approximately 45°; Fig. 1b), indicating the amorphous structure of CoBP[19,23,24]. In addition, EDS measurement of CoBP molecule was performed and the spectrum (Fig. S2) confirmed the existence of only Co, B, and P in the molecule.

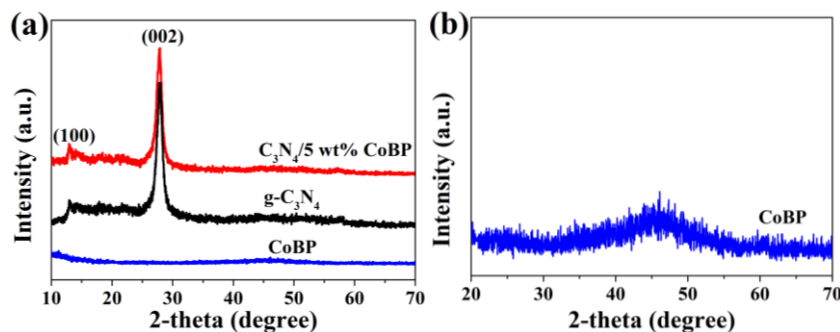


Fig.1. (a)XRD patterns of CoBP molecule, g-C₃N₄ and C₃N₄/5 wt% CoBP photocatalysts. (b) XRD patterns of amorphous CoBP.

The prepared CoBP molecule displayed a nanosphere morphology (Fig. 2a). However, after 5 wt% CoBP was loaded, the morphology of the composite photocatalyst C₃N₄/CoBP remained unchanged in contrast to the morphology of g-C₃N₄. This result demonstrated that CoBP did not affect the morphology of the g-C₃N₄ photocatalyst (Fig. 2b and c). The high-resolution TEM and selected area electron diffraction (SAED) images of CoBP were used in verifying the amorphous nature of CoBP. The HR-TEM image did not indicate the presence of any crystalline phase or lattice plane (Fig. 2d). This result was confirmed by the occurrence of diffused rings in the SAED image (inset of Fig. 2d)[19–21].

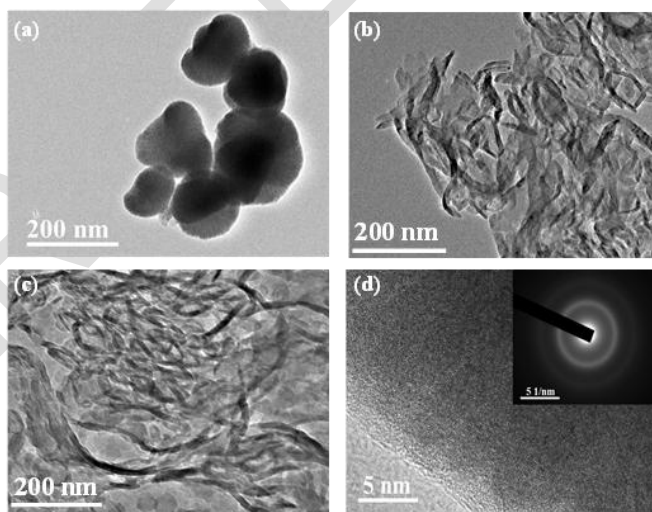


Fig.2. TEM images of (a) CoBP sample, (b) Pure g-C₃N₄, (c) g-C₃N₄/5 wt% CoBP photocatalysts. (d) HR-TEM image and SAED pattern (inset) of CoBP sample.

To investigate the chemical states of the prepared CoBP catalyst, an X-ray photoelectron spectroscopy (XPS) test was carried out (Fig. S3). The XPS spectrum of the Co 2p (Fig. S3a) displayed two major peaks. “A strong peak was detected at a binding energy 780.7 eV for Co 2p_{3/2}, and a minor peak at 796.5 eV for Co 2p_{1/2}. In addition, two satellite peaks were detected in the Co 2p spectra at binding energy of 786.5 and 802.96 eV, confirming the presence of elemental Co and the oxidised state of Co in the catalyst”[19–21,25]. The peaks of boron 1s were detected in the high-resolution XPS spectrum at 188.0 and 190.33 eV, which were attributed to boron in elemental and oxidised states, respectively (Fig. S3b). The binding energy of elemental boron shifted positively by 0.8 eV compared with the reported binding energy of pure boron (187.2 eV)[19,25].“With respect to P 2p high-resolution XPS spectrum (Fig. S3c),

phosphorous showed two distinct peaks at 129.5 and 132.83 eV, which might be assigned to the presence of P⁰ and oxidised phosphorous species, respectively”[19–21,25].

In general, the photocatalytic activity of H₂ production through water splitting depended on the optical absorption efficiency of catalysts and can be employed to determine the band gap of semiconductor photocatalyst. The UV–visible (UV–vis) diffuse reflectance spectra of CoBP, g-C₃N₄ and C₃N₄/5 wt% CoBP composite photocatalyst were collected to show their optical properties. As shown in Fig. 3a, bare g-C₃N₄ absorbed visible light with absorption edge of approximately 450 nm (band gap of ~2.7 eV) because of the excitation of electrons from the valence band to the conduction band[5]. After 5 wt% CoBP was loaded, the composite C₃N₄/CoBP showed an absorption edge nearly similar to that of pure g-C₃N₄, confirming that no structural change occurred in g-C₃N₄. Additionally, the absorption intensity of g-C₃N₄ slightly increased after the loading of 5 wt% CoBP, showing that CoBP was successfully introduced to the surface of g-C₃N₄. Based on the UV-vis spectra, the optical band gap value of CoBP was calculated from the Kubelka–Munk method (Fig. 3b) and determined to be approximately 1.59 eV.

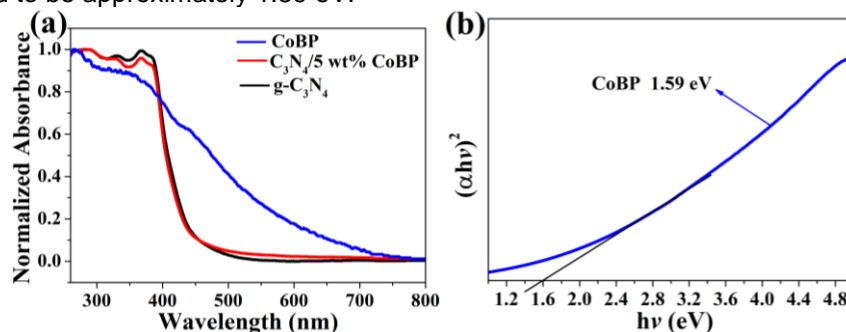


Fig. 3. (a) The diffuse reflectance UV-vis absorption spectra of solid CoBP molecule, g-C₃N₄ and C₃N₄/5 wt% CoBP photocatalysts. (b) Band gap evaluation from the plots of $(\alpha h\nu)^{1/2}$ vs the energy of the absorbed light of the NPBlm molecule.

“To explore the migration, the transfer and separation of the photogenerated electron–hole pairs over g-C₃N₄ and C₃N₄/5 wt% CoBP samples, the steady-state photoluminescence (PL) and time-resolved photoluminescence (TRPL) spectra were recorded. As displayed in Fig. 4a, the PL emission peak of pure g-C₃N₄ centered at approximately 450 nm under an excitation wavelength of 325 nm at room temperature, resulting from the electron–hole recombination in g-C₃N₄[6,26].“The C₃N₄/5 wt% CoBP composite displayed an emission peak similar to that of pure g-C₃N₄, but the peak intensity significantly declined because of the effective suppression of photogenerated charge carriers. Thus, photocatalytic activity for H₂ production was boosted. The charge transfer efficiency within the composite was measured, and the results are shown in Fig. 4b. The average lifetimes of the photogenerated charge carriers for g-C₃N₄ and C₃N₄/5 wt% CoBP samples were 2.54 ± 0.21 and 3.11 ± 0.26 ns, respectively. Long lifetimes are ascribed to the rapid transfer and separation of photogenerated charge carriers and subsequent inhibition of recombination”[6,22]. This result confirmed that loading a suitable amount of CoBP induces charge transfer and thereby significantly increase H₂ production rate.

“Moreover, photoelectrochemical tests over g-C₃N₄ and C₃N₄/5 wt% CoBP samples were performed under visible-light irradiation ($\lambda \geq 420$ nm) to investigate the effect of CoBP on the generation and migration of photogenerated charge carriers. As shown in Fig. 4c, under several on–off visible-light irradiation cycles of a photocurrent response, both electrodes generated rapid and constant photocurrent responses. Compared with the pure g-C₃N₄ photocatalyst, C₃N₄/5 wt% CoBP composite photocatalyst showed stable and higher photocurrent density (nearly twofold that of pure g-C₃N₄). The high photocurrent responses of C₃N₄/5 wt% CoBP hybrid indicated efficient charge migration and separation between g-C₃N₄ and CoBP interfaces”[5,17].“This observation is a good indicator of the inhibited recombination of photogenerated electron and holes. This effect was in a good agreement with the results of PL spectra. In addition, the electrochemical impedance spectroscopy (EIS) test of g-C₃N₄ and C₃N₄/5 wt% CoBP was performed at an alternating current voltage of 0.5 V to study charge transfer resistance. As displayed in Fig. 4d, the C₃N₄/5 wt% CoBP sample exhibited a smaller arc radius than pure g-C₃N₄, implying efficient charge migration and separation, both of which are beneficial for the photocatalytic performance of H₂ production”[17,27]. The obtained Nyquist plots data were fitted with the Randles circuit (Fig. 4d inset, where R_s and R_{ct} represent solution resistance and charge transfer resistance between the electrolyte and electrode, respectively). The EIS-fitted parameters are displayed in Table S1 in Supporting Information. The results of photoelectrochemical tests showed that charge migration and separation indeed occurred at the interface between g-C₃N₄ and CoBP.

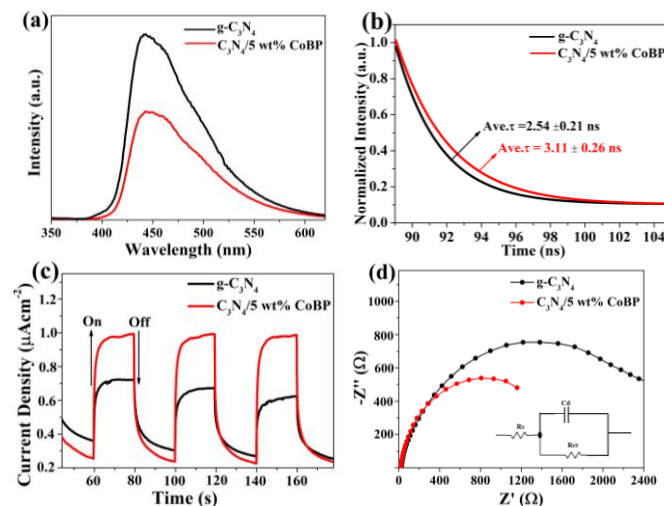


Fig. 4. (a) Steady-state photoluminescence spectra. (b) Time-resolved fluorescence decay traces for g-C₃N₄ and C₃N₄/5 wt% CoBP photocatalyst (excitation at 325 nm, emission at 450 nm). (c) Transient photocurrent response. (d) EIS Nyquist plots for g-C₃N₄ and C₃N₄/5 wt% CoBP under visible light irradiation ($\lambda \geq 420$ nm, [Na₂SO₄] = 0.5 M). The inset correspond to the fitting using the equivalent circuit.

To compare the photocatalytic activity of H₂ evolution over different prepared photocatalysts, a series of comparative experiments were performed. Firstly, the H₂ evolution rate was measured by using different sacrificial agents under visible-light irradiation ($\lambda \geq 420$ nm). As shown in Fig. S4, the C₃N₄/5 wt% CoBP composite photocatalyst exhibited a high H₂ evolution rate when triethanolamine (TEOA) was used as the sacrificial agent in the photocatalytic reaction. TEOA is suitable at high H₂ level because of its high redox potential and the created basic environment[28]. Thus TEOA was considered the best sacrificial agent.

Furthermore, the H₂ evolution rate over different samples were measured under visible-light irradiation (Fig. 5). The sample of g-C₃N₄ with 1 wt% Pt cocatalyst (Fig. 5b) displayed high photocatalytic activity (13.47 $\mu\text{mol h}^{-1}$) compared with pure g-C₃N₄ (Fig. 5a) due to the fast recombination rate of photogenerated electron-hole pairs. The visible photocatalytic H₂ evolution rate of g-C₃N₄ significantly increased up to 51.68 $\mu\text{mol h}^{-1}$ when 5 wt% CoBP was added (Fig. 5c). This value was 3.8 times that of pure g-C₃N₄. To confirm the role of CoBP in the photocatalytic system, the H₂ evolution rate of C₃N₄/5 wt% CoBP without deposition of Pt cocatalyst was 5.31 $\mu\text{mol h}^{-1}$ (Fig. 5d). A controlled experiment was then performed for a pure CoBP sample. The results demonstrated that no hydrogen evolution occurred when only pure CoBP was used as the photocatalyst. These results showed that enhanced photocatalytic activity can be attributed to the formation of heterojunction in the C₃N₄/CoBP composite photocatalyst. The heterojunction facilitated charge transfer and separation, which in turn improved photocatalytic activity during H₂ evolution.

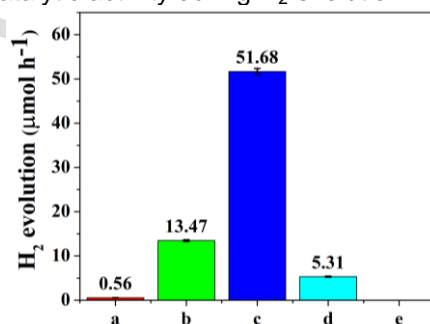


Fig. 5. Comparison of H₂ evolution rates over different samples; (a) g-C₃N₄ without the Pt cocatalyst, (b) g-C₃N₄ with 1% Pt, (c) C₃N₄/5 wt% CoBP with 1% Pt cocatalyst, (d) C₃N₄/5 wt% CoBP without the Pt cocatalyst, (e) CoBP alone without Pt cocatalyst. Reaction conditions: 50 mg of photocatalyst, $\lambda \geq 420$ nm, 100 mL of solvent, H₂O/TEOA = 9:1 (vol/vol), light source, xenon lamp (300 W) with a cutoff filter; temperature, 10 °C.

Moreover, the photocatalytic H₂ evolution rates of g-C₃N₄ at different amounts of CoBP (4, 5 and 6 wt%) were further investigated under visible-light irradiation ($\lambda \geq 420$ nm). TEOA was used as the sacrificial reagent (Fig. 6a). The introduction of CoBP greatly improved photocatalytic H₂ evolution rate. Pure g-C₃N₄ exhibited the extremely low photocatalytic activity of H₂ evolution rate (13.47 $\mu\text{mol h}^{-1}$). When 4 wt% CoBP was introduced, the H₂ evolution rate increased up to 36.37 $\mu\text{mol h}^{-1}$. Remarkably, when 5 wt% CoBP was loaded, the H₂ evolution rate further increased and reached a maximum value of 51.68 $\mu\text{mol h}^{-1}$, which was 3.8 that of bare g-C₃N₄. This value was higher than the maximum

values of other g-C₃N₄-based heterostructure photocatalysts (Table S2)[6,16,29,30]. As CoBP loading further increased to 6 wt%, the H₂ evolution rate decreased to 39.77 μmol h⁻¹. The possible reasons were as follows: (i) the black color of CoBP led to a significant increase in opacity and shielding effect that prevented incident light from reaching the surface of the g-C₃N₄ photocatalyst and (ii) an excessive amount of CoBP blocked active sites on the surface of g-C₃N₄ and impeded contact between the reactive sites and reactants[6,13]. Thus, loading a suitable amount of CoBP onto g-C₃N₄ is a suitable method for increasing photocatalytic activity in the H₂ evolution of C₃N₄/CoBP composite photocatalysts.

To test the reciprocal effects of Pt loading amount, we measured the activity of C₃N₄/5 wt% CoBP catalysts with varied wt% Pt loading content (Fig. S5). The surface area of a catalyst plays a vital role in the enhancement of photocatalytic activity of a catalyst. Catalysts with large specific surface areas have numerous active sites that improve light absorption[31]. Nitrogen sorption isotherms were measured to determine the specific surface areas of the prepared catalysts. As shown in Fig. S6, the BET specific surface areas (S_{BET}) of pure g-C₃N₄ and C₃N₄/5 wt% CoBP composite were 89 and 114 m²g⁻¹, respectively. The composite photocatalyst showed higher S_{BET} than pure g-C₃N₄ because of the insertion of CoBP, and the addition of CoBP increased the surface area of the composite catalyst. This effect enhanced the performance of C₃N₄/5 wt% CoBP for H₂ production.

Furthermore, to confirm that the photocatalytic activity of H₂ evolution is dependent on light absorption of a catalyst, the apparent quantum yield (AQY) of H₂ evolution of C₃N₄/5 wt% CoBP was measured under the same reaction conditions but different levels of monochromatic light irradiation (λ ± 5 nm for 420, 450, 500, 550 and 600 nm). The AQYs varied inversely with the UV-vis absorption spectrum of C₃N₄/5 wt% CoBP composite photocatalyst (Fig. 6b). Notably, the harvested visible photons dominated the driving force for the photocatalytic H₂ evolution reactions.[6] Interestingly, our C₃N₄/CoBP composite photocatalyst exhibited AQY of approximately 5.42% at 420 nm, which was higher than the AQYs other g-C₃N₄-based heterostructure photocatalysts (Table S2)[6,29,30].

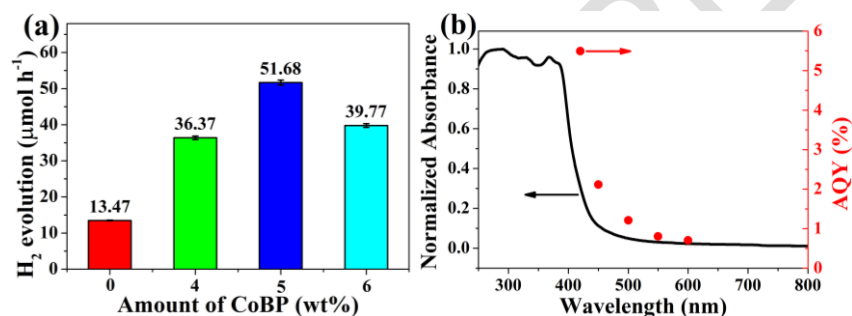


Fig. 6. (a) Comparison of the photocatalytic activity of C₃N₄/CoBP catalysts with different weight of CoBP, 1 wt% Pt as cocatalyst. (b) Wavelength-dependent apparent quantum yield (AQY) relationship for the photocatalytic hydrogen evolution.

Apart from the photocatalytic performance of H₂ evolution, an ideal photocatalyst must have photocatalytic stability and can be recycled for large-scale practical applications. To investigate photocatalytic stability, the C₃N₄/5 wt% CoBP composite photocatalyst was subjected to a recycling test involving five consecutive cycles of photocatalytic activity of H₂ evolution under the same experimental conditions (Fig. 7). No obvious loss of H₂ evolution activity was observed in the C₃N₄/5 wt% CoBP sample after 20 h of illumination, and the amount of H₂ evolved was nearly the same as that of the first cycle, implying that the composite photocatalyst exhibited good stability for photocatalytic H₂ production under prolonged visible-light irradiation. The XRD patterns of the C₃N₄/5 wt% CoBP composite photocatalyst before and after the recycling tests are shown in Fig. S7. No obvious change was observed in the C₃N₄/5 wt% CoBP composite before and after recycling. Overall, the findings of this study indicated the stability of the C₃N₄/5 wt% CoBP composite photocatalyst during the photocatalytic H₂ evolution. Therefore, the composite can be reused in photocatalytic reactions.

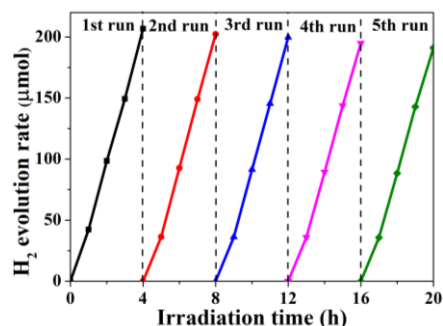


Fig.7. The reusability tests of $C_3N_4/5$ wt% CoBP with 1 % Pt cocatalyst for photocatalytic hydrogen production. Reaction conditions: 50 mg of photocatalyst, solvent [100 mL, $H_2O/TEOA = 9:1$ (vol/vol)] and a 300 W Xenon lamp as light source equipped with a cut-off filter ($\lambda \geq 420$ nm), at 10 °C, and H_2 produced was evacuated after every 4 h.

The results demonstrated that CoBP plays a crucial role in the separation and migration of electron–hole pairs in $C_3N_4/CoBP$ hybrid photocatalysts. This role benefits from the formation of a heterojunction between amorphous CoBP molecule and $g-C_3N_4$ nanosheet photocatalyst. The CB and VB energy levels of $g-C_3N_4$ are -1.12 and $+1.57$ eV (vs. NHE), respectively[32–34]. The CB and VB of CoBP were estimated using valence band X-ray photoelectron spectroscopy (VB-XPS) and UV–vis diffuse reflection spectra. As displayed in Fig. S8, the VB edge position of CoBP was 0.89 eV, and the CB was -0.7 eV. These findings suggested a possible mechanism for visible-light-induced H_2 production activity in the $C_3N_4/CoBP$ composite (Fig. 8). The CB edge position of $g-C_3N_4$ was more negative than that of CoBP, and thus CoBP acted as an outstanding electron sink. These electrons were then transported to Pt nanoparticle to prolong the lifetime of charge carriers (Fig. 8). The remaining holes in the VB of $g-C_3N_4$ and CoBP were consumed by the sacrificial electron donor (TEOA; Fig. 8). Overall, CoBP served as a charge-separation centre that restrained the recombination of photogenerated electrons and holes in $g-C_3N_4$ and significantly improved the photocatalytic activity for H_2 production.

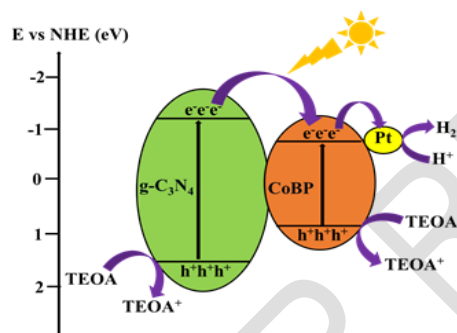


Fig. 8. Proposed mechanism of electron–hole transport process and photocatalytic activity of $C_3N_4/CoBP$ heterostructure photocatalyst under visible-light irradiation.

4. CONCLUSION

A novel type of $C_3N_4/CoBP$ composite photocatalyst was successfully fabricated by decorating CoBP on the surface of $g-C_3N_4$ through ultrasonication. The formation of a heterojunction between $g-C_3N_4$ and CoBP facilitated the migration and separation of photogenerated charge carriers in the system. Therefore, the $C_3N_4/CoBP$ hybrid photocatalyst exhibited a higher level of photocatalytic activity for H_2 evolution than pure $g-C_3N_4$ under visible-light irradiation ($\lambda \geq 420$ nm). Excellent charge transfer and separation led to a dramatic improvement in H_2 evolution rate, which reached up to $51.60 \mu\text{mol h}^{-1}$ under 5 wt% CoBP. This rate was 3.8 times that of bare $g-C_3N_4$ ($13.47 \mu\text{mol h}^{-1}$) and corresponded to an AQY of 5.42 % at 420 nm. Notably, the $C_3N_4/CoBP$ composite photocatalyst displayed excellent photocatalytic stability and reusability for H_2 evolution after 20 h of irradiation. The CoBP is a promising material that combines with the low-cost $g-C_3N_4$ to form a $C_3N_4/CoBP$ hybrid for practical use in photocatalytic H_2 production. In conclusion, this work offers a simple method for designing and developing not only highly efficient but also stable heterostructured photocatalysts for solar-to-chemical energy conversion.

REFERENCES

- [1] Ling GZS, Oh VBY, Haw CY, Tan LL, Ong WJ. $g-C_3N_4$ Photocatalysts: Utilizing Electron–Hole Pairs for Boosted Redox Capability in Water Splitting. *Energy Material Advances* 2023;4:1–27. <https://doi.org/10.34133/energymatadv.0038>.
- [2] Ding Q, Zou X, Ke J, Dong Y, Cui Y, Lu G, et al. S-scheme 3D/2D $NiCo_2O_4@g-C_3N_4$ hybridized system for boosting hydrogen production from water splitting. *Renewable Energy* 2023;203:677–85. <https://doi.org/10.1016/j.renene.2022.12.115>.
- [3] Fujishima A and Honda K. Electrochemical Photolysis of water at a Semiconductor electrode. *Nature* 1972; 238:37-38.
- [4] Tahir W, Cheang TY, Li JH, Ling C, Lu XJ, Ullah I, et al. Interfacial $Ti \equiv N$ bonding of a $g-C_3N_4/TiH_{1.92}$ type-II heterojunction photocatalyst significantly enhanced photocatalytic hydrogen evolution from water splitting. *Catalysis Science and Technology* 2022;12:2023–9.

- <https://doi.org/10.1039/d1cy02039k>.
- [5] Kombo M, Chong HB, Ma LB, Sahar S, Fang XX, Zhao T, et al. Graphitic Carbon Nitride Decorated with Nickel(II)-(3-Pyridyl) Benzimidazole Complexes and Pt Nanoparticles as a Cocatalyst for Photocatalytic Hydrogen Production from Water Splitting. *ACS Applied Nano Materials* 2020;3:10659–67. <https://doi.org/10.1021/acsnm.0c01872>.
- [6] Kombo M, Ma LB, Liu YN, Fang XX, Ullah N, Odda AH, et al. Graphitic carbon nitride/CoTPP type-II heterostructures with significantly enhanced photocatalytic hydrogen evolution. *Catalysis Science and Technology* 2019;9:2196–202. <https://doi.org/10.1039/c9cy00140a>.
- [7] Wang R, Ye C, Wang H, Jiang F. Z-Scheme LaCoO₃/g-C₃N₄ for Efficient Full-Spectrum Light-Simulated Solar Photocatalytic Hydrogen Generation. *ACS Omega* 2020;5:30373–82. <https://doi.org/10.1021/acsomega.0c03318>.
- [8] Jiang L, Wang K, Wu X, Zhang G, Yin S. Amorphous Bimetallic Cobalt Nickel Sulfide Cocatalysts for Significantly Boosting Photocatalytic Hydrogen Evolution Performance of Graphitic Carbon Nitride : Efficient Interfacial Charge Transfer. *ACS Applied Materials & Interfaces* 2019;11:26898–908. <https://doi.org/10.1021/acsomega.9b07311>.
- [9] Bai Y, Li C, Liu L, Yamaguchi Y, Bahri M, Yang H, et al. Photocatalytic Overall Water Splitting Under Visible Light Enabled by a Particulate Conjugated Polymer Loaded with Palladium and Iridium ** *Angewandte* 2022. <https://doi.org/10.1002/ange.202201299>.
- [10] Novoa-cid M, Melillo A, Alvaro M, Baldovi HG. Photocatalytic Water Splitting Promoted by 2D and 3D Porphyrin Covalent Organic Polymers Synthesized by Suzuki-Miyaura Carbon-Carbon Coupling 2022.
- [11] Wang X, Maeda K, Thomas A, Takanabe K, Xin G, Carlsson JM, et al. A metal-free polymeric photocatalyst for hydrogen production from water under visible light. *Nature Materials* 2009;8:76–80. <https://doi.org/10.1038/nmat2317>.
- [12] Tahir W, Ullah S, Ullah I, Li JH, Ling C, Lu XJ, et al. Metallic WN plasmonic fabricated g-C₃N₄ significantly steered photocatalytic hydrogen evolution under visible and near-infrared light. *Catalysis Science and Technology* 2022;12:7369–78. <https://doi.org/10.1039/d2cy01499h>.
- [13] Fang XX, Ma LB, Liang K, Zhao SJ, Jiang YF, Ling C, et al. The doping of phosphorus atoms into graphitic carbon nitride for highly enhanced photocatalytic hydrogen evolution. *Journal of Materials Chemistry A* 2019;7:11506–12. <https://doi.org/10.1039/c9ta01646e>.
- [14] Prasad C, Tang H, Liu Q, Bahadur I, Karlapudi S, Jiang Y. A latest overview on photocatalytic application of g-C₃N₄ based nanostructured materials for hydrogen production. *International Journal of Hydrogen Energy* 2020;45:337–79. <https://doi.org/10.1016/j.ijhydene.2019.07.070>.
- [15] Wudil YS, Ahmad UF, Gondal MA, Al-Osta MA, Almohammed A, Sa'id RS, et al. Tuning of graphitic carbon nitride (g-C₃N₄) for photocatalysis: A critical review. *Arabian Journal of Chemistry* 2023;16:104542. <https://doi.org/10.1016/j.arabjc.2023.104542>.
- [16] Mao Z, Chen J, Yang Y, Wang D, Bie L, Fahlman BD. Novel g-C₃N₄/CoO Nanocomposites with Significantly Enhanced Visible-Light Photocatalytic Activity for H₂ Evolution. *ACS Applied Materials and Interfaces* 2017;9:12427–35. <https://doi.org/10.1021/acsomega.7b00370>.
- [17] Jin Z, Wei T, Lixue Li, Li F, Tao R, Xu L. Loading Co₃N nanoparticles as efficient cocatalysts over Zn_{0.5}Cd_{0.5}S for enhanced H₂ evolution under visible light. *Dalton Transactions* 2019;48:2676–82. <https://doi.org/10.1039/c8dt05087b>.
- [18] Li Z, Wu Y, Lu G. Highly efficient hydrogen evolution over Co(OH)₂ nanoparticles modified g-C₃N₄ co-sensitized by Eosin Y and Rose Bengal under Visible Light Irradiation. *Applied Catalysis B: Environmental* 2016;188:56–64. <https://doi.org/10.1016/j.apcatb.2016.01.057>.
- [19] Sun H, Xu X, Yan Z, Chen X, Jiao L, Cheng F, et al. Superhydrophilic amorphous Co-B-P nanosheet electrocatalysts with Pt-like activity and durability for the hydrogen evolution reaction. *Journal of Materials Chemistry A* 2018;6:22062–9. <https://doi.org/10.1039/C8TA02999G>.
- [20] Chunduri A, Gupta S, Bapat O, Bhide A, Fernandes R, Patel MK, et al. A unique amorphous cobalt-phosphide-boride bifunctional electrocatalyst for enhanced alkaline water-splitting. *Applied Catalysis B: Environmental* 2019;259:118051. <https://doi.org/10.1016/j.apcatb.2019.118051>.
- [21] Kim J, Kim H, Kim SK, Ahn SH. Electrodeposited amorphous Co-P-B ternary catalyst for hydrogen evolution reaction. *Journal of Materials Chemistry A* 2018;6:6282–8. <https://doi.org/10.1039/c7ta11033b>.
- [22] Liu YN, Zhou X, Shen CC, Zhao ZW, Jiang YF, Ma LB, et al. Hydrogen-bonding-assisted charge transfer:

- Significantly enhanced photocatalytic H₂ evolution over g-C₃N₄ anchored with ferrocene-based hole relay. *Catalysis Science and Technology* 2018;8:2853–9. <https://doi.org/10.1039/c8cy00488a>.
- [23] Wang W, Liu P, Wu K, Tan S, Li W, Yang Y. Preparation of hydrophobic reduced graphene oxide supported Ni-B-P-O and Co-B-P-O catalysts and their high hydrodeoxygenation activities. *Green Chemistry* 2016;18:984–8. <https://doi.org/10.1039/c5gc02073e>.
- [24] Men Y, Su J, Du X, Liang L, Cheng G, Luo W. CoBP nanoparticles supported on three-dimensional nitrogen-doped graphene hydrogel and their superior catalysis for hydrogen generation from hydrolysis of ammonia borane. *Journal of Alloys and Compounds* 2018;735:1271–6. <https://doi.org/10.1016/j.jallcom.2017.11.137>.
- [25] Jia X, Sang Z, Sun L, Xu F, Pan H, Zhang C, et al. Graphene-Modified Co-B-P Catalysts for Hydrogen Generation from Sodium Borohydride Hydrolysis. *Nanomaterials* 2022;12:1–14. <https://doi.org/10.3390/nano12162732>.
- [26] Ma LB, Liu YN, Liang K, Fang XX, Sahar S, Kombo M, et al. Hantzsch ester as hole relay significantly enhanced photocatalytic hydrogen production. *Catalysis Science and Technology* 2018;8:6123–8. <https://doi.org/10.1039/c8cy01922c>.
- [27] Zhu X, Yu S, Gong X, Xue C. In Situ Decoration of Zn_xCd_{1-x}S with FeP for Efficient Photocatalytic Generation of Hydrogen under Irradiation with Visible Light. *ChemPlusChem* 2018;83:825–30. <https://doi.org/10.1002/cplu.201800316>.
- [28] Wang DH, Pan JN, Li HH, Liu JJ, Wang YB, Kang LT, et al. A pure organic heterostructure of μ -oxo dimeric iron(III) porphyrin and graphitic-C₃N₄ for solar H₂ production from water. *Journal of Materials Chemistry A* 2015;4:290–6. <https://doi.org/10.1039/c5ta07278f>.
- [29] Ye R, Fang H, Zheng YZ, Li N, Wang Y, Tao X. Fabrication of CoTiO₃/g-C₃N₄ Hybrid Photocatalysts with Enhanced H₂ Evolution: Z-Scheme Photocatalytic Mechanism Insight. *ACS Applied Materials and Interfaces* 2016;8:13879–89. <https://doi.org/10.1021/acsami.6b01850>.
- [30] Chen J, Zhao D, Diao Z, Wang M, Shen S. Ferrites boosting photocatalytic hydrogen evolution over graphitic carbon nitride: a case study of (Co, Ni)Fe₂O₄ modification. *Science Bulletin* 2016;61:292–301. <https://doi.org/10.1007/s11434-016-0995-0>.
- [31] Wang W, Liu S, Nie L, Cheng B, Yu J. Enhanced photocatalytic H₂ production activity of TiO₂ using Ni(NO₃)₂ as an additive. *Physical Chemistry Chemical Physics* 2013;15:12033–9. <https://doi.org/10.1039/c2cp43628k>.
- [32] Obregón S, Colón G. Improved H₂ production of Pt-TiO₂/g-C₃N₄-MnO_x composites by an efficient handling of photogenerated charge pairs. *Applied Catalysis B: Environmental* 2014;144:775–82. <https://doi.org/10.1016/j.apcatb.2013.07.034>.
- [33] Fu J, Chang B, Tian Y, Xi F, Dong X. Novel C₃N₄-CdS composite photocatalysts with organic-inorganic heterojunctions: In situ synthesis, exceptional activity, high stability and photocatalytic mechanism. *Journal of Materials Chemistry A* 2013;1:3083–90. <https://doi.org/10.1039/c2ta00672c>.
- [34] Huang L, Xu H, Li Y, Li H, Cheng X, Xia J, et al. Visible-light-induced WO₃/g-C₃N₄ composites with enhanced photocatalytic activity. *Dalton Transactions* 2013;42:8606–16. <https://doi.org/10.1039/c3dt00115f>.

SUPPORTING INFORMATION

Fig. S1. Schematic illustration of the formation of amorphous CoBP sample.

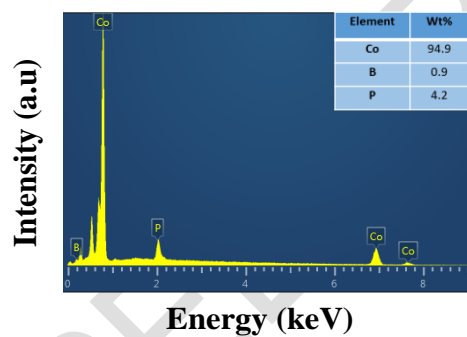


Fig. S2. High resolution XPS spectra of (a) Co 2p region. (b) P 2p region. (c) B 1s region for CoBP sample.

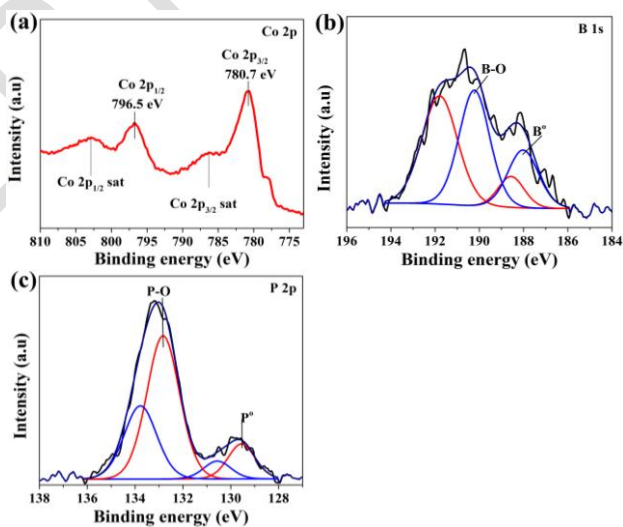


Fig. S3. High resolution XPS spectra of (a) Co 2p region. (b) P 2p region. (c) B 1s region for CoBP sample.

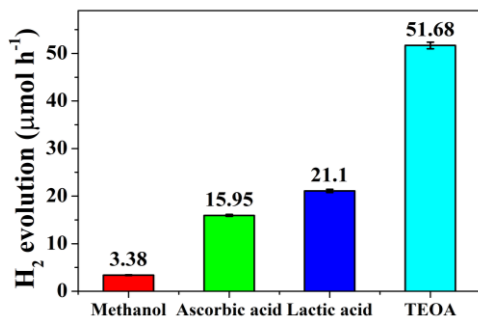


Fig. S4. Comparison of photocatalytic hydrogen evolution rates on C₃N₄/5 wt% CoBP composite photocatalyst in the presence of different sacrificial reagents under visible light ($\lambda \geq 420$ nm). Reaction conditions: Catalyst, 50 mg; 100 mL of solution containing sacrificial reagents; light source, xenon lamp (300 W) with a cutoff filter; temperature, 10 °C.

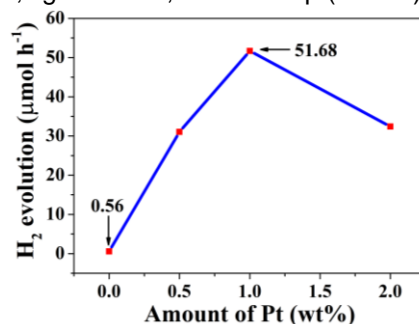


Fig. S5. Effect of the Pt loading amounts on photocatalytic hydrogen evolution of C₃N₄/5 wt% CoBP under visible light irradiation ($\lambda \geq 420$ nm).

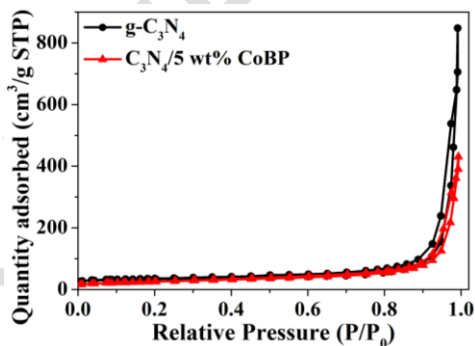


Fig. S6. Nitrogen adsorption-desorption isotherms of pure g-C₃N₄ and C₃N₄/5 wt% CoBP composite photocatalysts.

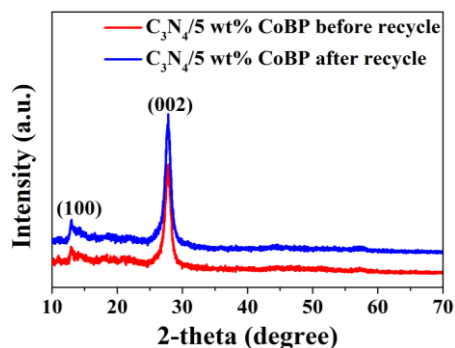


Fig. S7. XRD spectra of C₃N₄/5 wt% CoBP composite photocatalysts before and after recycle.

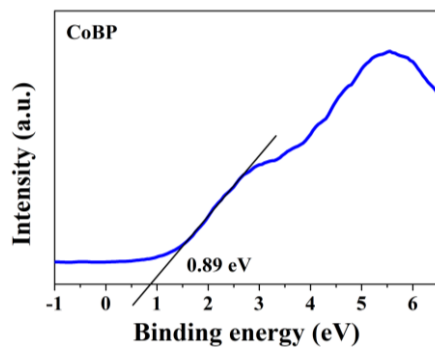


Fig. S8. Valence band XPS spectra of CoBP sample.

Table S1. Fitting parameters of EIS results

Samples	R_s	R_{ct}
$g\text{-C}_3\text{N}_4$ photocatalysts	25.67	686.1
$\text{C}_3\text{N}_4/5 \text{ wt\% CoBP}$ composite photocatalysts	19.58	652.1

Table S2. Comparison of the hydrogen production activity and AQY value of various $g\text{-C}_3\text{N}_4$ -based heterostructure photocatalysts reported previously.

Photocatalysts	Pt [wt%]	Light source	HER $\mu\text{molh}^{-1}\text{g}^{-1}$	AQY [%]	Refs.
$g\text{-C}_3\text{N}_4/\text{CoTPP}$	1	300 W Xe lamp ($\lambda \geq 420 \text{ nm}$)	938.6	4.2 ($\lambda = 420 \text{ nm}$)	[6]
$\text{CoTiO}_3/g\text{-C}_3\text{N}_4$	3	300 W Xe lamp (under simulated solar light irradiation)	858	3.23 ($\lambda = 420 \text{ nm}$)	[29]
$g\text{-C}_3\text{N}_4/\text{CoFe}_2\text{O}_4$	1	300 W Xe lamp ($\lambda > 420 \text{ nm}$)	186.1	3.35 ($\lambda = 420 \text{ nm}$)	[30]
$g\text{-C}_3\text{N}_4/\text{CoO}$	3	300 W Xe lamp ($\lambda \geq 400 \text{ nm}$)	651.3	NA	[16]
$\text{C}_3\text{N}_4/\text{CoBP}$	1	300 W Xe lamp ($\lambda \geq 420 \text{ nm}$)	1033.6	5.42 ($\lambda = 420 \text{ nm}$)	Our work