

# Photocatalytic H<sub>2</sub> generation via CoP quantum-dot-modified g-C<sub>3</sub>N<sub>4</sub> synthesized by electroless plating

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# ABSTRACT

Photocatalytic water splitting is a promising method for hydrogen production. Numerous efficient photocatalysts have been synthesized and utilized. However, photocatalysts without a noble metal as the co-catalyst have been rarely reported. Herein, a CoP co-catalyst-modified graphitic-C<sub>3</sub>N<sub>4</sub> (g-C<sub>3</sub>N<sub>4</sub>/CoP) is investigated for photocatalytic water splitting to produce H<sub>2</sub>. The g-C<sub>3</sub>N<sub>4</sub>/CoP composite is synthesized in two steps. The first step is related to thermal decomposition, and the second step involves an electroless plating technique. The photocatalytic activity for hydrogen evolution reactions of g-C<sub>3</sub>N<sub>4</sub> is distinctly increased by loading the appropriate amount of CoP quantum dots (QDs). Among the as-synthesized samples, the optimized one (g-C<sub>3</sub>N<sub>4</sub>/CoP-4%) shows exceptional photocatalytic activity as compared with pristine g- $C_3N_4$ , generating H<sub>2</sub> at a rate of 936  $\mu$  mol g<sup>-1</sup>h<sup>-1</sup>, even higher than that of g- $C_3N_4$  with 4 wt% Pt (665  $\mu$ mol g<sup>-1</sup>h<sup>-1</sup>). The UV-visible and optical absorption behavior confirms that  $g-C_3N_4$  has an absorption edge at 451 nm, but after being composited with CoP, g-C<sub>3</sub>N<sub>4</sub>/CoP-4% has an absorption edge at 497 nm. Furthermore, photoluminescence and photocurrent measurements confirm that loading CoP QDs to pristine g-C<sub>3</sub>N<sub>4</sub> not only enhances the charge separation, but also improves the transfer of photogenerated e-h+ pairs, thus improving the photocatalytic performance of the catalyst to generate H2. This work demonstrates a feasible strategy for the synthesis of highly efficient metal phosphide-loaded g-C<sub>3</sub>N<sub>4</sub> for hydrogen generation.

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# 1. Introduction

In recent decades, global energy consumption has increased

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

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

In the modern era, hydrogen production through water splitting utilizing semiconductor photocatalysis is a promising method that has received much attention. The ideal source for hydrogen generation is water because of its high abundance, availability, and renewability. Many photocatalysts and photoelectrodes have been employed for hydrogen generation. For example, in the recent past, various types of photocatalysts, including TiO<sub>2</sub>, LaFeO<sub>3</sub>, CdS, SrTiO<sub>3</sub>, and CoP, have been utilized for hydrogen generation [6–13]. However, because of various limitations, the hydrogen generation performance via such materials is inconsistent. Accordingly, photocatalytic water splitting to generate H<sub>2</sub> needs to be further pursued.

More recently, among many investigated photocatalysts, non-metal materials like g-C<sub>3</sub>N<sub>4</sub> have attracted a great amount of attention because of their suitable band gap (2.7 eV) and stability. g-C<sub>3</sub>N<sub>4</sub> is considered to be a highly efficient photocatalyst in many reactions, such as CO2 reduction [14,15], water splitting [16,17], and organic pollutant degradation [18,19]. Most importantly, g-C<sub>3</sub>N<sub>4</sub> fulfills the standard thermodynamic requirements of water splitting by light, i.e., g-C<sub>3</sub>N<sub>4</sub> has a suitable band gap and appropriate position for the conduction band (CB) and valence band (VB) [20-22]. However, the photocatalytic activity of g-C<sub>3</sub>N<sub>4</sub> is not satisfactory because of various limitations, including the low efficiency of visible light adsorption and high recombination rate of photogenerated carriers. Various approaches have been adopted to improve the performance of pristine g-C<sub>3</sub>N<sub>4</sub>. Among these strategies, forming a heterojunction between two semiconductors with wide and narrow band gaps [23-27], surface modification [28-31], metal and nonmetal doping [32], and utilization together with a co-catalyst are all well known. Many investigators have reported that some noble metals, including Au, Pt, Pd, and Ag are efficient [33-38], their high cost restricts large-scale usage, making it urgent to develop new strategies.

Transition metal-based phosphides, including FeP [39], CoP [40], NiP [41–44], and CuP [45], have been extensively used as co-catalysts in photocatalysis reactions. Moreover, surveying the relevant literature reveals that the photocatalytic reaction pathway and mechanism of Co-based phosphides are identical to what the hydrogenases do naturally. It is expected that Co-based phosphides can also be utilized as efficient catalysts for the hydrogen evaluation reaction because of their unique physical and chemical properties and easy synthesis [46]. To the best of our knowledge, limited work has been performed to utilize CoP in the field of photocatalysis as a co-catalyst, i.e., forming  $g-C_3N_4/CoP$  for efficient photocatalytic water splitting to produce H<sub>2</sub>. Thus, it is worth investigating how CoP can be loaded on  $g-C_3N_4$  and applied as a co-catalyst.

In this work,  $g-C_3N_4$  loaded with various amounts of CoP quantum dots (QDs) is fabricated by two steps, including pyrolysis and electroless plating. The bare  $g-C_3N_4$  is prepared by a

previously reported method, i.e., thermal polymerization of urea. After this, in the second step, an electroless plating process is adopted for CoP growth in situ on the surface of g-C<sub>3</sub>N<sub>4</sub>. The optimized structure is g-C<sub>3</sub>N<sub>4</sub>/CoP-4%, which shows higher photocatalytic activity for H<sub>2</sub> production than that of pristine g-C<sub>3</sub>N<sub>4</sub> under simulated solar light radiation, even higher than that of Pt-modified g-C<sub>3</sub>N<sub>4</sub>. Finally, this work demonstrates that g-C<sub>3</sub>N<sub>4</sub>/CoP nanocomposites demonstrate promising applications in the fields of photocatalysis and H<sub>2</sub> production.

## 2. Experimental

## 2.1. Preparation

Typically, g-C<sub>3</sub>N<sub>4</sub> is synthesized via heating of urea. A total of 15 g of dry and solid urea was transferred to a crucible, after which the crucible was heated in a muffle furnace at 500 °C for 2 h, with a heating rate of 10 °C min<sup>-1</sup>. After the prepared material cooled down naturally, the product was ground into powder and stored. For coating CoP on the surface of g-C<sub>3</sub>N<sub>4</sub>, an electroless plating technique was employed. A total of 1 g of g-C<sub>3</sub>N<sub>4</sub> was placed in 40 mL of H<sub>2</sub>O and treated ultrasonically for 5 min. Then, it was dispersed in a solution of sensitizer SnCl<sub>2</sub> (1 g L<sup>-1</sup>) +HCl (1 mL L<sup>-1</sup>) for 2 min and excited in a solution of exciter PdCl<sub>2</sub> (0.1 g L<sup>-1</sup>) + HCl (1 mL L<sup>-1</sup>) for 2 min. It was washed using distilled water before electrolysis deposition. The reaction vessel contained Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.4 mol L<sup>-1</sup>), NH<sub>2</sub>CH<sub>2</sub>COOH (1.2 mol L<sup>-1</sup>), and NaH<sub>2</sub>PO<sub>2</sub>·H<sub>2</sub>O (1.6 mol L<sup>-1</sup>). The pH value was kept at 11 by adding the proper amount of sodium hydroxide (NaOH). The electroless plating procedures were performed at 55 °C for 4 h. The as-prepared material was centrifuged and washed with water and alcohol three times. The as-obtained sample was dried in a vacuum oven at 75 °C for 6 h. Finally, samples with various weight percentages of coated CoP were synthesized; these are denoted g-C<sub>3</sub>N<sub>4</sub>/CoP-1%, g-C<sub>3</sub>N<sub>4</sub>/CoP-2%, g-C<sub>3</sub>N<sub>4</sub>/CoP-3%,  $g-C_3N_4/CoP-4\%$ , and  $g-C_3N_4/CoP-5\%$  for coating with 1%, 2%, 3%, 4%, and 5% by weight of CoP, respectively.

#### 2.2. Characterization

X-ray diffraction (XRD) measurements were carried out on a Bruker D5005 X-ray diffractometer, with Cu K<sub>a</sub>,  $\lambda = 1.54056$  Å. Fourier transform infrared spectra (FT-IR) of the samples were recorded utilizing a Nicolet Magna 560 spectrophotometer. The elemental analysis of samples was conducted using Thermo Scientific ESCALAB 250Xi X-ray photoelectron spectroscopy (XPS). Transmission electron microscopy (TEM) was performed using an electron microscope (JEOL JEM-2100). UV-vis absorbance spectra were recorded by a Shimadzu UV-3100 spectrophotometer with BaSO<sub>4</sub> as a reference. The photoluminescence spectra of g-C<sub>3</sub>N<sub>4</sub> and g-C<sub>3</sub>N<sub>4</sub>/CoP modified materials were observed using a Varian Cary Eclipse spectrometer with an excitation wavelength of 325 nm.

## 2.3. Photocatalytic water splitting

The photocatalytic activity experiment for evaluation of the hydrogen reaction was carried out in a 100 mL Pyrex reactor with three openings, which were sealed by rubber plugs to avoid hydrogen leakage. This glass reactor was connected to a gas chromatographic assembly (GC-14C, Shimadzu, Japan, TCD; N<sub>2</sub> is used as the carrier gas). To produce hydrogen gas, a 350 W xenon lamp was used as a light source. The reactor assembly was placed at a distance of 15 cm from the xenon lamp. Typically, 10 mg of photocatalyst was placed into 70 mL water, and then 10 mL of triethanolamine (TEOA) was added. The reaction was completed under continuous magnetic stirring. N<sub>2</sub> gas was passed through the assembly to create and maintain an inert atmosphere and to remove any produced hydrogen gas.

## 2.4. Photoelectrochemical measurements

The photoelectrochemical performance was investigated using a CHI 660D electrochemical work station with the assistance of a commercial computer-controlled system. A paste was made by blending 5 mg of photocatalyst with 2 mL of isopropyl alcohol under magnetic stirring for 1 h, then adding approximately 0.15 g of macrogol-6000, 0.05 mL of acetyl acetone, and 1 mL of ethanol; after 24 h of stirring the mixture, the paste was finally produced. The mixture was coated on 1 cm × 2 cm ITO glass and bonded to an electrode, and a three-electrode system was utilized. For photoelectrochemical measurements, an estimated amount of the sample was pasted on the ITO glass surface as the working electrode, and a calomel electrode and Pt wire were used as the reference electrode and counter electrode, respectively. A 0.1 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub> aqueous solution was used as the electrolyte.

## 3. Results and discussion

# 3.1. XRD

The crystallinity and structure of the as-prepared samples were investigated by XRD. Fig. 1 shows the XRD patterns of pristine  $g-C_3N_4$  and  $g-C_3N_4/CoP$  composites loaded with various amounts of CoP. The two predominant peaks are at 13.1° and



**Fig. 1.** XRD patterns of pristine  $g-C_3N_4$  and  $g-C_3N_4/CoP-X$  samples (X = 1%-5%).

27.5°, respectively, representing the g-C<sub>3</sub>N<sub>4</sub> itself (JCPDS Card No 87-1526). The diffraction peaks at 27.5° correspond to the (002) typical plane with a planar distance of 0.33 nm, analogous to the interlayer stacking of the related aromatic segments. The peaks located at 13.1° are related to the (100) plane [47]. This result confirms that after loading of CoP QDs, the XRD peaks do not change, which suggests that CoP QDs do not affect the crystal lattice and structure of g-C<sub>3</sub>N<sub>4</sub>. Note that no distinct peaks for CoP are observed because of both, the small loading amount and the high dilution of CoP on the g-C<sub>3</sub>N<sub>4</sub> surface [48].

### 3.2. FTIR

The FTIR technique was employed to further confirm the structure of the prepared samples. As shown in Fig. 2, the FTIR spectra of pristine g-C<sub>3</sub>N<sub>4</sub> and g-C<sub>3</sub>N<sub>4</sub>/CoP composites are almost identical, in which the peak at 1638 cm<sup>-1</sup> is credited to the stretching vibration of C-N related groups and the intense peaks located at 1248, 1319, and 1433 cm<sup>-1</sup> are also attributed to the stretching vibrations of the C–N bonds in aromatic rings; these results are consistent with those reported in the literature [49]. The peak positioned at 804 cm<sup>-1</sup> represents a different type mode of the tri-azine group unit in g-C<sub>3</sub>N<sub>4</sub> [50], and the peaks at 3255 cm<sup>-1</sup> are associated with the N-H stretching vibration [51]. The FTIR results confirm that the structure of the bare g-C<sub>3</sub>N<sub>4</sub> sample is not altered after loading with CoP. The information given by the FTIR spectra is in good agreement with the XRD data.

# 3.3. UV-DRS

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



**Fig. 2.** FTIR spectra of pristine  $g-C_3N_4$  and  $g-C_3N_4/CoP-X$  samples (X = 1%-5%).



Fig. 3. UV-Vis diffuse reflectance absorption spectra of pristine g-C<sub>3</sub>N<sub>4</sub> and g-C<sub>3</sub>N<sub>4</sub>/CoP-4% samples.

ciency of  $g-C_3N_4$  is enhanced. This also explains why the yellow pure  $g-C_3N_4$  turns to dark gray after loading with CoP.

# 3.4. XPS

XPS analysis has been engaged to study the elemental states and chemical composition of samples. The detailed XPS profiles and chemical bonding features of the g-C<sub>3</sub>N<sub>4</sub>/CoP-4% sample are given in Fig. 4. The high-resolution XPS profile of carbon shows that C has XPS peaks at 284.8 eV and 288.3 eV (Fig. 4A). Actually, the XPS peak at 284.8 eV can be ascribed to *sp*<sup>2</sup> hybridized carbon atoms; however, the peak at 288.3 eV is related to N-C=N<sub>2</sub> related functional groups [54]. Furthermore, Fig. 4B identifies the peaks for the N 1*s* electron at 398.8 eV, 400.6 eV, and 404.7 eV, which are related to a *sp*<sup>2</sup> type nature and the bonded tightly bound nitrogen C–N–C type family; similarly, the sp<sup>3</sup> results arise from tertiary nitrogen N–(C)<sub>3</sub> and amino-related elements of (C–N–H) [47]. The XPS results given in Fig. 4C explain the Co 2*p*<sub>3/2</sub> energy level and nature. It is confirmed that three peaks, at 781.7, 783.3, and 786.8 eV, are the reduced Co, oxidized Co<sup>2+</sup>, and satellite peak, respectively. The Co 2*p*<sub>1/2</sub> shows an XPS peak at 787.5 eV along with one satellite peak at 803.2 eV [55]. As shown in Fig. 4D, two P 2*p* peaks are recorded, at 129.5 and 133.3 eV, which are credited to P<sup>δ–</sup> of CoP and oxidized P species, respectively [56]. All the XPS results confirm that CoP was successfully loaded on the surface of



Fig. 4. High-resolution XPS profiles of C 1s (A), N 1s (B), Co 2p (C), and P 2p (D) of g-C<sub>3</sub>N<sub>4</sub>/CoP-4%.





## g-C<sub>3</sub>N<sub>4</sub>.

#### 3.5. TEM

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

#### 3.6. Photocatalytic performance

The photocatalytic performances of the pristine g-C<sub>3</sub>N<sub>4</sub> and g-C<sub>3</sub>N<sub>4</sub>/CoP-X samples (X = 1%-5%) were evaluated with respect to H<sub>2</sub> generation under simulated solar light (Fig. 6). g-C<sub>3</sub>N<sub>4</sub> exhibits a poor, nearly negligible efficiency. However, after loading various weights (1-5 wt%) of CoP to g-C<sub>3</sub>N<sub>4</sub>, the photocatalytic activity for H<sub>2</sub> production was greatly enhanced. The g-C<sub>3</sub>N<sub>4</sub>/CoP-4% sample showed the best hydrogen production, 936 µmol g<sup>-1</sup> h<sup>-1</sup>, which is superior to that produced by 4 wt% Pt/g-C<sub>3</sub>N<sub>4</sub> (665  $\mu$ mol g<sup>-1</sup> h<sup>-1</sup>). When loading CoP to 5 wt%, the activity decreased to 569 µmol g-1 h-1, which can be attributed to the over-coverage of CoP on the surface of g-C<sub>3</sub>N<sub>4</sub>, resulting in a decrease in activity [58,59]. Indeed, CoP QDs catalyze the hydrogen evaluation reaction but block the surface of g-C<sub>3</sub>N<sub>4</sub> for light absorption. Thus, loading a moderate amount of CoP plays an important role in improving the photocatalytic performance of g-C<sub>3</sub>N<sub>4</sub>.

#### 3.7. Photoelectrochemical property

Photoelectrochemical measurements were conducted using g-C<sub>3</sub>N<sub>4</sub> and g-C<sub>3</sub>N<sub>4</sub>/CoP-4% samples. The results in Fig. 7A demonstrate that the photocurrent performances of as-prepared samples, as determined by the photoelectrochemical curves, can stably reproduce the photocurrent responses over 5 on-off cycles. The activation of the photocurrent signal starts by turning on the light, while the photocurrent is negligible and nearly zero after switching off the light. Noticeably, the photocurrent density for g-C<sub>3</sub>N<sub>4</sub>/CoP-4% (which is 0.43 µA cm<sup>-2</sup>) is higher than that of pristine  $g-C_3N_4$  (0.04  $\mu$ A cm<sup>-2</sup>), which is in consistent with its higher activity for hydrogen generation. Similarly, the strong photocurrent predicts a greater efficiency of charge separation and propagation for photogenerated electron (e-) and hole (h+) pairs in the g-C<sub>3</sub>N<sub>4</sub>/CoP-4% composite, which enhances the hydrogen production. Meanwhile, the results of electrochemical impedance spectroscopy (EIS), i.e., Nyquist plots, as displayed in Fig. 7B, are also displayed to further support and confirm our outcomes. EIS Nyquist plots with smaller and lower radii represent greater separation ability with respect to photogenerated eand h<sup>+</sup> [35]. Clearly, loading CoP on the surface of g-C<sub>3</sub>N<sub>4</sub> causes the radius of the EIS Nyquist plot to decrease, confirming that CoP QDs reduce the recombination rate, resulting in an in-



**Fig. 6.** Photocatalytic activities for  $H_2$  production of pristine g-C<sub>3</sub>N<sub>4</sub> and g-C<sub>3</sub>N<sub>4</sub>/CoP-X (X = 1%-5%) (A) and comparative activities of g-C<sub>3</sub>N<sub>4</sub>/CoP-X vs g-C<sub>3</sub>N<sub>4</sub>/Pt (B).



Fig. 7. Photocurrent signals (A) and electrochemical impedance spectra (B) of pristine g-C<sub>3</sub>N<sub>4</sub> and g-C<sub>3</sub>N<sub>4</sub>/CoP-4% samples.

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

#### 3.8. PL spectra

The photoluminescence (PL) spectra of the as-prepared samples are recorded in Fig. 8. The effectiveness of generation and separation of photogenerated charge carriers is further confirmed by the PL spectra. The pristine g-C<sub>3</sub>N<sub>4</sub> sample exhibits a stronger PL signal than do g-C<sub>3</sub>N<sub>4</sub>/CoP-X%. It is well known that a strong PL signal is attributed to a high charge recombination rate [48]. Therefore, the g-C<sub>3</sub>N<sub>4</sub>/CoP-4% composite exhibits the lowest PL signal because more of CoP QDs are adsorbed on the surface of g-C<sub>3</sub>N<sub>4</sub>, capturing more photoexcited electrons, and finally improving the internal charge transfer, which can decrease the charge recombination process of photogenerated  $e^-$  and  $h^+$  pairs. These results increase the life time of excited electrons, resulting in increased reaction time for any sort of photolytic reaction.

#### 3.9. Photoactivity mechanism

Based on the above findings and understanding of the charge transfer and separation process, a proposed schematic diagram for charge transfer processes and energy band levels is depicted in Scheme 1 for the  $g-C_3N_4/CoP-4\%$  nanocomposite. This sketch shows the possible reaction mechanism of



Fig. 8. Photoluminescence spectra of pristine  $g-C_3N_4$  and  $g-C_3N_4/CoP-4\%$ .

g-C<sub>3</sub>N<sub>4</sub>/CoP-4% in photocatalytic H<sub>2</sub> production. Under appropriate energy, the g-C<sub>3</sub>N<sub>4</sub> is excited and finally generates photoexcited electrons with higher energy, which are excited into CoP through the CB of g-C<sub>3</sub>N<sub>4</sub>, leaving holes in the VB of g-C<sub>3</sub>N<sub>4</sub>, which can react with sacrificial agents such as TEOA. CoP QDs have a large work function, so they can be used as the co-catalyst [41].

# 4. Conclusions

A simple method is reported for the preparation of CoP QDs by an in situ growth strategy on the surface of g-C<sub>3</sub>N<sub>4</sub>. CoP QDs as a co-catalyst were loaded on the surface of g-C<sub>3</sub>N<sub>4</sub> by a simple pyrolysis-based method and electroless plating. The as-prepared g-C<sub>3</sub>N<sub>4</sub>/CoP composite shows much higher photocatalytic activity for H<sub>2</sub> production than that of pristine g-C<sub>3</sub>N<sub>4</sub>. Among the as-prepared samples, the optimized one, i.e., g-C<sub>3</sub>N<sub>4</sub>/CoP-4%, shows remarkable improvement with respect to hydrogen generation (936 µmol g<sup>-1</sup> h<sup>-1</sup>), which is 1.6-fold higher than that when using Pt (665 µmol g<sup>-1</sup> h<sup>-1</sup>) as a co-catalyst at the same loading amount. This work provides a new, feasible strategy for the preparation of a g-C<sub>3</sub>N<sub>4</sub>/CoP photocatalyst for hydrogen production.

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**Scheme 1.** Schematic diagram for the photocatalytic mechanism and photogenerated charge separation and transfer in g-C<sub>3</sub>N<sub>4</sub>/CoP-4%.

## **Graphical Abstract**

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Photocatalytic H<sub>2</sub> generation via CoP quantum-dot-modified g-C<sub>3</sub>N<sub>4</sub> synthesized by electroless plating

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The photocatalytic activity of H<sub>2</sub> generation over g-C<sub>3</sub>N<sub>4</sub>/CoP composites prepared by an electroless plating method is much higher than that over pure g-C<sub>3</sub>N<sub>4</sub>. The composites boosted the separation and migration of photogenerated carriers, resulting in a higher photocatalytic activity.

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