Journal of Materials Chemistry A



View Article Online

View Journal | View Issue

PAPER

Check for updates

Cite this: J. Mater. Chem. A, 2019, 7, 25908

Visual observation of hydrogen bubble generation from monodisperse CoP QDs on ultrafine $g-C_3N_4$ fiber under visible light irradiation[†]

Yunxiong Zeng, 🕑 * Yingchun Xia, Wenjia Song and Shenglian Luo*

Solar-driven hydrogen evolution reaction (HER) *via* water splitting is an attractive technology to address the growing demand for clean fuels. $g-C_3N_4$ is a promising candidate among photocatalysts, but it is plagued by its puny HER activity and miserly quantum efficiency. Tremendous efforts have been made to enhance $g-C_3N_4$ performance on HER; however, it is still far below the expectations in industrial production. Herein, we report a monodisperse CoP QDs-modified ultrafine $g-C_3N_4$ fiber (CoP/CNF) *via in situ* electrostatic adsorption deposition followed by low-temperature phosphatization treatment. The CoP/CNF showed an HER activity of 2.42 mmol h⁻¹ under visible light, 34.9 times higher than that of Pt/CNF, in which hydrogen bubbles evolution was observed with an apparent quantum efficiency of 59.9% at 420 nm. This benchmark HER activity was mainly because the CoP QDs could significantly suppress photoinduced charge recombination and improve the heterointerface HER rate. This work provides a useful strategy for designing highly active catalysts for solar-to-hydrogen fuel conversion.

Received 8th September 2019 Accepted 22nd October 2019

DOI: 10.1039/c9ta09897f

rsc.li/materials-a

Introduction

Water splitting HER is of great interest because it can provide fuel energy that is free from environment pollution.^{1,2} Often, high-performance catalysts, especially Pt-based catalysts, are usually required for splitting water HER at a low energy barrier.³ The scalable consumption of Pt though is greatly hindered by its high cost and scarcity.⁴ In this case, diverse non-precious compound catalysts, such as transition-metal carbides (TMCs),⁵ phosphides (TMPs),⁶ and chalcogenides (TMDs),⁷ have been widely investigated as alternatives to Pt. However, these transition metal composites still cannot achieve HER activity matching that of Pt-group catalysts, except for TMPs.⁸

Usually, TMPs are a significant class of composites derived from the alloying of metals and phosphorus, and they have been employed in electrochemical water splitting. In recent years, a growing amount of TMPs have been exploited for HER, such as Ni₂P,⁹ FeP,^{6,10} Cu₃P,¹¹ MoP,¹² WP₂ ¹³ and CoP,^{14,15} which have shown competitive HER activity compared to Pt-based catalysts. Although breakthroughs have been made to improve the HER performance of TMPs,^{10,12,14} there are very limited investigations on TMPs applied in photocatalytic HER compared to electrochemical HER. Ni₂P QDs/CdS nanorods were reported with an around 1200 mmol h^{-1} g⁻¹ photocatalysis HER rate,¹⁶

meanwhile, the turnover number (TON) and turnover frequency (TOF) reached *ca.* 3 270 000 in 90 h and 36 400 for Ni₂P QDs, respectively. Inspired by such unprecedented progress, TMPs are considered to be a promising alternative to precious metals and noble-metal alloys for photocatalytic HER in the future.¹⁷

Photocatalysts are also equally pivotal to HER catalysis.18,19 Metal-free g-C₃N₄ is a distinctive photocatalyst due to its visible light absorption and extremely low cost.16,17,20 Compared to the typical transition-metal-based photocatalysts (TMBPs),¹⁶ g-C₃N₄ displays environmental pollution-free activity without being oxidized or suffering from toxic ions leakage.21 To exploit a costeffective solar water-splitting system, integrating TMPs with g-C₃N₄ into a hierarchical heterojunction could still be considered an ideal option.17,19 Hitherto, limited studies have focused on TMPs/g-C₃N₄ composites, yet in those the HER performance of TMPs/g-C₃N₄ was found to be fairly inferior to that of TMPs/ TMBPs.⁸ This situation is mainly caused by the following three factors. First, g-C₃N₄ generally possesses a broader band gap $(\sim 2.7 \text{ eV})$ than that of TMBPs, leading to lower light utilization.^{17,19} Second, the photoinduced charge-recombination rate of g-C₃N₄ is faster than that of TMBPs owing to the larger carrier-migration resistance.22 Third, the absence of active sites of TMPs leads to slow HER kinetics in TMPs/g-C₃N₄.²³ Thus, the fabrication of monodisperse TMPs with abundant active sites on the nanostructured g-C₃N₄ with robust photocatalysis HER activity and long-term stability is of great significance.

Herein, a CoP QDs/CNF heterogeneous nanojunction was prepared *via* an *in situ* electrostatic adsorption deposition, followed by low-temperature phosphatization treatment (Scheme 1). At first, bulk $g-C_3N_4$ was oxidized into $g-C_3N_4$ quantum dots

State Key Laboratory of Chemo/Biosensing and Chemometrics, College of Chemistry & Chemical Engineering, Hunan University, Changsha 410082, P. R. China. E-mail: yxzeng@hnu.edu.cn; sllou@hnu.edu.cn

[†] Electronic supplementary information (ESI) available. See DOI: 10.1039/c9ta09897f

Scheme 1 Preparation of CoP/CNF via an in situ electrostatic adsorption deposition followed by a low-temperature phosphorization.

by the hydrothermal method, which then self-assembled into g-C₃N₄ nanofibers (CNFs) after hydrothermal treatment. The cobalt ions were absorbed by the CNF followed by cobalt oxidation, until finally, they are converted into cobalt phosphide quantum dots by a low-temperature process. The CoP QDs were monodispersed on the CNF, enhancing the electronhole pair separation efficiency and providing abundant active sites for HER. So far, CoP/CNF has showed a HER rate of 2.42 mmol h⁻¹ in 15 vol% triethanolamine under visible light (λ \geq 420 nm), which was 34.9 times higher than that of Pt/CNF. The CoP/CNF heterojunction produced a large amount of gas bubbles in a cuvette, which was observable by the naked eye (Movie S1[†]). Meanwhile, the turnover number (TON) reached 519 with a turnover frequency (TOF) of 172.9 h^{-1} for CoP QDs, and the apparent quantum efficiency was 59.9% at 420 nm. So far, to the best of our knowledge, CoP/CNF in our study has shown one of the highest visible-light HER activities among all g-C₃N₄-based photocatalysis systems and can even rival the best visible light HER photocatalyst of the Ni₂P QDs/CdS nanorods heterogeneous nanojunction.16

Experimental section

Chemicals

All reagent grade chemicals were purchased from Sinopharm Chemical Reagent Co. Ltd and used without further purification. Ultrapure water was used in the whole experiment process (Millipore-Q Century, $18.2 \text{ M}\Omega$ cm).

Synthesis of pristine g-C₃N₄

Pristine g-C₃N₄ was prepared by the polycondensation of melamine (126.12 g mol⁻¹, 6.0 g) from room temperature to 550 °C under a N₂ (99.999%) atmosphere at a ramping rate of 5 °C min⁻¹ and kept for 4 h in a furnace, then cooled naturally to room temperature and well ground by an agate mortar to obtain pristine g-C₃N₄ powder.

Preparation of g-C₃N₄ nanofiber (CNF)

To prepare the g- C_3N_4 nanofiber, pristine g- C_3N_4 (0.92 g) was dispersed in 60 mL distilled water, vigorously stirred overnight, and then sonicated for 2 h. The bulky g- C_3N_4 particles were removed from the flask bottom to put in suspension. Finally, the g- C_3N_4 suspension was added into an 80 mL volume stainless steel vessel, and heated at 200 °C for 6 h in an oven. After hydrothermal treatment, the solution was cooled down to room temperature to obtain the product, which was named as CNF.

Co_3O_4/g - C_3N_4 nanofiber (Co_3O_4/CNF) and bare Co_3O_4 preparation

First, 50 mg g- C_3N_4 nanofiber was dispersed in a mixed solution containing 50 mL absolute ethanol and 0.6 mL concentrated aqueous ammonia. A certain amount of Co(OAc)₂ solution (60.0 μ M) was gradually dropped into the mixed solution and stirred for 20 h at 80 °C on a magnetic stirring apparatus simultaneously. Then the mixed solution was transferred to an 80 mL Teflon-lined autoclave and maintained at 150 °C for 3 h. After that, the as-prepared product was collected by centrifugation and washed with ethanol and deionized water. The obtained composites with 1.0, 3.0, 5.0, 7.0 and 10.0 wt% Co₃O₄ QDs were named as 1-Co₃O₄/CNF, 3-Co₃O₄/CNF, 5-Co₃O₄/CNF, 7-Co₃O₄/CNF, and 10-Co₃O₄/CNF, respectively. Bare Co₃O₄ without g-C₃N₄ nanofiber was prepared using the same method.

Synthesis of CoP QDs/g-C $_3N_4$ nanofiber (CoP/CNF) and bare CoP

First, 20.0 mg Co_3O_4/CNF mixture with various amounts of Co_3O_4 QDs and 100.0 mg of sodium hypophosphite (NaH₂-PO₂·H₂O, 105.99 g mol⁻¹) were mixed together and ground to a fine powder by using a mortar. Then, the mixture was calcined at 280 °C for 2 h with a heating speed of 2 °C min⁻¹. The obtained product was washed with deionized water and freeze dried overnight to obtain 1-CoP/CNF, 3-CoP/CNF, 5-CoP/CNF, 7-CoP/CNF, and 10-CoP/CNF, respectively. The same procedure was used to prepare bare CoP.

Preparation of Pt/g-C₃N₄ nanofiber (Pt/CNF)

Various mass percents of Pt were *in situ* photodeposited on the g-C₃N₄ nanofiber in 15 vol% triethanolamine (TEOA) including a suitable amount of H₂PtCl₆ under room temperature and a full arc light ($\lambda > 300$ nm) for 2 h. Before irradiation, the mixed solution was bubbled with high purity nitrogen for 45 min to remove the air, ensuring that the reaction system was in an inertial condition without oxygen reduction side reactions. Finally, the appearance of a gray-black precipitate indicated that the Pt particles were well deposited on the CNF and the precipitate was renamed as 1 wt% Pt/CNF (1-Pt/CNF), 2 wt% Pt/CNF (2-Pt/CNF), 3 wt% Pt/CNF (3-Pt/CNF), 4 wt% Pt/CNF (4-Pt/CNF) and 5 wt% Pt/CNF (5-Pt/CNF).

The morphologies and chemical composition characterization were performed using powder X-ray diffraction (XRD) with Cu-Ka radiation (Rigaku, Smartlab), UV-vis diffuse reflectance spectrophotometer (DRS) (Varian, Cary 300), Fourier transform infrared (FT-IR) spectroscopy (Nicolet 380, Thermo Fisher Scientific), transmittance electron microscopy (TEM) (JEOL, JEM-2100F), field-emission scanning electron microscopy (FE-SEM) (Hitachi, S-4800), and X-ray photoelectron spectroscopy (XPS) with Al-Ka radiation (K-Alpha 1063, Thermo Fisher Scientific). The photoluminescence (PL) spectra were recorded with a Hitachi F-7000 fluorescence spectrophotometer. The chemical element compositions were analyzed by EDS mapping images captured on a Tecnai G2 F20 S-TWIN atomic resolution analytical microscope. Time-resolved transient

photoluminescence (TRPL) spectroscopy was performed using an Hamamatsu universal streak camera C10910. Measurements for the photocurrent Nyquist plots without bias potential were carried out with a CHI 660C electrochemical analyzer (CHI Inc., USA) in 0.5 M Na₂SO₄ aqueous solution with a three-electrode configuration: FTO electrodes deposited with the samples acted as the photoanode, a platinum wire as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. A 300 W xenon arc lamp with lighting wavelength range of 320–780 nm (Perfect-light, PLS-SXE 300C, Beijing) was used as the light source.

Photocatalytic test for water-splitting hydrogen evolution reaction

The photocatalytic HER was performed at room temperature. A 300 W xenon arc lamp was equipped with a 420 nm wavelength cutoff filter and it had a light intensity of 120 mW cm⁻². The photocatalyst sample (20.0 mg) was dispersed in TEOA solution (15 vol%, 80 mL). H₂ was analyzed using gas chromatography (Shimadzu, GC2010), equipped with a 5 Å molecular sieve column (Plot-Q column, 0.32 μ m) and high purity nitrogen as the carrier gas (99.999%).

Apparent quantum yield (AQE) calculation

The AQE was measured at 420 ± 10 nm by a 300 W Xe lamp with specific band-pass filters. The average irradiation intensity was determined to be 2.39 mW cm⁻² and the irradiation area was 5.9 cm². The amount of H₂ generated in 5.0 h was 266.5 µmol.

$$AQE = \frac{\text{Number of reacted electrons}}{\text{Number of incident photons}} \times 100\%$$
$$= \frac{\text{Number of H}_2 \text{ molecules} \times 2}{\text{Number of incident photons}} \times 100\%$$

Number of H_2 molecules = 6.02 \times 10^{23} \times 266.5 \times 10^{-6} = 16.1 \times $10^{19}.$

Number of incident photons $= E\lambda/hc = (2.39 \times 10^{-3} \times 5.9 \times 3600 \times 5.0 \times 420 \times 10^{-9})/(6.626 \times 10^{-34} \times 3 \times 10^{8}) = 5.36 \times 10^{20}$.

The calculated AQE at 420 \pm 10 nm was 59.9%.

Turnover number (TON) and turnover frequency (TOF) calculations

The turnover number (TON) and turnover frequency (TOF) were calculated by the following equations:

$$TON = \frac{moles of evolved H_2}{moles of CoP QDs on photocatalyst}$$

$$TOF = \frac{TON}{reaction time}$$

The TON and TOF of CoP QDs on the 7-CoP/CNF nanofiber were measured under Xe lamp incident wavelength ($\lambda \ge 420$

nm). The average moles of evolved hydrogen in 3 h was determined at 7.26 \times 10^{-3} mol in Fig. S11c.†

The mass percentage of CoP QDs in the 7-CoP/CNF was 6.32 wt% by EDS technology (Table S1†). Herein, the moles of CoP QDs on 7-CoP/CNF was calculated by the equation:

$$20 \times 10^{-3} \times 6.32\% / (58.9 + 31.0) = 1.4 \times 10^{-5}$$
 mol.

Thus, the TON and TOF were 519 and 172.9 $h^{-1}.$

Results and discussion

Structure and component characterization

Scanning electron microscopy (SEM) was used to investigate the nanostructures and morphologies of CoP, CNF, and CoP/CNF. CNF exhibited uniform fiber-like morphology with ca. 100 nm diameter, as shown in Fig. 1a. When Co₃O₄ was loaded on the CNF with 1.0 wt% mass content, Co3O4 was well monodispersed on the CNF without aggregation occurrence, as shown in Fig. 1b, showing the 0D ultrafine quantum dot structure. With the Co₃O₄ mass content increased up to 3.0 wt%, the size also got bigger, as clearly observed by SEM in Fig. 1c. Along with further increasing the content up to 5.0, 7.0, and 10.0 wt%, Co₃O₄ grew larger but did not grow together (Fig. 1d-f). Comparatively, the bare Co₃O₄ without CNF as a host displayed a solid micro-scale structure, growing together into a bulk whole in Fig. S1.† The X-ray diffraction (XRD) pattern revealed peaks at 18.9°, 31.2°, 36.9°, 38.5°, 44.9°, 55.8°, 59.3°, 65.3°, 74.2°, and 30.5° (Fig. S2^{\dagger}), which were indexed to the (111), (220), (311), (222), (400), (422), (511), (440), (620), and (533) facets of Co₃O₄ (JCPDS 42-1467),¹⁵ respectively. Besides, the Co₃O₄ QDs on CNF possessed the same lattice structure as bare Co₃O₄ (Fig. S3a[†]), showing CNF did not affect the crystal structure of Co₃O₄. The X-ray energy dispersed spectrum (EDS) in Fig. S3b[†] exhibited C, N, Co, and O elements in 7-Co₃O₄/CNF, further confirming the existence of cobalt oxidation in the Co₃O₄/CNF hybrids.

When processing the low-temperature phosphatization treatment toward the bare Co_3O_4 under an argon atmosphere, Co_3O_4 was well converted to CoP and showed a similar microstructure with the bare Co_3O_4 in Fig. S4.[†] Phosphorus-



Fig. 1 (a) SEM images of CNF, (b) 1-Co₃O₄/CNF, (c) 3-Co₃O₄/CNF, (d) 5-Co₃O₄/CNF, (e) 7-Co₃O₄/CNF and (f) 10-Co₃O₄/CNF.



Fig. 2 SEM images of: (a) phosphide CNF, (b) 1-CoP/CNF, (c) 3-CoP/CNF, (d) 5-CoP/CNF, (e) 7-CoP/CNF and (f) 10-CoP/CNF.

containing particles were not observed on the CNF in Fig. 2a, indicating the phosphatization treatment toward CNF did not affect the CNF nanostructures. After the phosphatization on 1-, 3-, 5-, and 7-Co₃O₄/CNF, the Co₃O₄ QDs turned into CoP QDs and grew larger than Co₃O₄, but without leading to agglomeration problems, as seen from Fig. 2b–e. When 10-Co₃O₄/CNF was suffering from low-temperature phosphatization, although CoP was obtained, they were seriously stuck together on the CNF, as shown in Fig. 2f. The SEM images demonstrated that low-temperature phosphatization treatment could convert the Co₃O₄ to CoP, but an excessive amount of Co₃O₄ on the CNF could cause CoP connecting with adjacent particles, leading to a bulk whole, causing the surface area and active sites to overlap, which is not beneficial for HER.



Fig. 3 (a–c) Low-resolution TEM images of 7-CoP/CNF, (d) CoP QDs diameter size distribution, (e) XRD pattern of 7-CoP/CNF and the CoP standard card (JCPDS 29-0497), (f) energy dispersed X-ray spectrum (EDS) of 7-CoP/CNF, (g and h) high-resolution TEM images (HR-TEM) of CoP QDs in 7-CoP/CNF and (i) selected area electron diffraction (SAED) of CoP QDs in 7-CoP/CNF.

In the transmission electron microscopy (TEM) images, numerous CoP ODs were observed and monodispersed on the CNF without CoP QDs and CNF agglomeration (Fig. 3a-c). It could also be clearly observed that the size of these CoP and the integration of the 0D/1D CoP QDs/CNF nanohybrid were well preserved. The diameter size of the CoP QDs remained at 6.8 \pm 0.2 nm, as seen in Fig. 3d. X-ray diffraction (XRD) patterns of 7-CoP/CNF presented five peaks at 31.6°, 36.3°, 46.3°, 48.2°, and 57.0° in Fig. 3e, corresponding to the (011), (111), (112), (211), and (203) facets of CoP (JCPDS-29-0497),24 respectively, which showed they had the same crystal structure as that of bare CoP in Fig. S5.† In Fig. S6A,† the XRD records showed that the CoP QDs hybridized with g-C₃N₄ nanofiber without affecting the crystal structure of g-C₃N₄. In the FT-IR spectra in Fig. S6B,† the 810, 1200–1700, and 3200–3400 cm⁻¹ peaks were ascribed to the tri-s-triazine ring out-of-plane bending, and N-C=N and NH₂ stretching vibrations,25,26 respectively. The FT-IR spectrum demonstrated that bare CoP had wide peaks at 1050 cm⁻¹, but these were not found in the individual CNF. Comparatively, 7-CoP/CNF had both characteristic peaks of CNF and CoP, implying CoP was well loaded on the CNF. The energy dispersed X-ray spectrum (EDS) disclosed the coexistence of Co and P in the CNF (Fig. 3f), in a 1 : 1 ratio between Co and P and 6.32 wt% CoP in 7-CoP/CNF (Table S1[†]), which was highly consistent with the results from the atomic absorption spectroscopy (AAS) analysis in Fig. S6C and S6D.† High-resolution transmission electron microscopy (HR-TEM) was applied to determine the crystal structures of CoP QDs. As shown in Fig. 3g and h, the lattice fringes with the interplane distances of 0.306 and 0.197 nm were measured, corresponding to the (011) and (112) facets of the CoP QDs,14 respectively. The corresponding selected area electron diffraction (SAED) pattern in Fig. 3i exhibited five bright rings made up of discrete spots, which



Fig. 4 (A) Photocatalytic HER rate of CNF hybridizing with various mass amounts of CoP QDs, (B) turnover number (TON) and turnover frequency (TOF) of 7-CoP/CNF, (C) single-wavelength AQE *versus* UV-vis diffuse reflectance spectrum of 7-CoP/CNF in 15 vol% TEOA, (D) HER rate comparisons between 3-Pt/CNF and 7-CoP/CNF. Conditions (A, B, and D): 15 vol% TEOA and visible light ($\lambda \ge 420$ nm).

could be indexed to the (011), (201), (111), (211), and (301) facets of the orthorhombic CoP QDs.²⁷

Photocatalytic water-splitting hydrogen evolution

As shown in Fig. 4A, the photocatalytic HER performances of CNF hybridizing with various mass amounts of CoP ODs in 15 vol% triethanolamine (TEOA) under visible light ($\lambda \ge 420$ nm) were identified. Bare CNF showed a negligible HER activity, while 7-CoP/CNF exhibited the highest HER performance, which was determined to be 2.42 mmol h⁻¹, 201.7 times higher than that of the naked CNF. In the Pt/CNF hybrids, the optimal Pt content loaded on CNF was 3 wt% and 3-Pt/CNF had the highest HER rate of ca. 0.1 mmol h⁻¹ among Pt/CNF composites, as shown in Fig. S7.† The 7-CoP/CNF produced a large number of gas bubbles in a cuvette, observable by the naked eye (Movie S1[†]). The turnover number (TON) and turnover frequency (TOF) were 519 and 172.9 h^{-1} for CoP QDs in the 7-CoP/CNF (Fig. 4B). The apparent quantum efficiency (AQE) of 7-CoP/CNF reached as high as 59.9% at 420 nm (Fig. 4C), presenting one of the best state-of-the-art g-C₃N₄-based photocatalytic HER rates, higher than most semiconductor composites for photocatalytic HER (Table S2[†]). Unexpectedly, the photocatalytic HER activity of 7-CoP/CNF was 34.9 times higher than that of 3-Pt/CNF in Fig. 4D, indicating CoP may be a promising alternative to Pt-based catalysts in solar-tohydrogen fuel conversation.

Photoelectrochemical properties

As shown in Fig. 5A, the bare CoP exhibited full spectrum absorption in the UV-visible light range due to its intrinsic black color. CNF alone displayed a characteristic DRS spectrum and



Fig. 5 (A) UV-vis diffuse reflectance spectrophotometry (DRS) results of CoP, CNF, and 7-CoP/CNF, (B) band gap of CNF and 7-CoP/CNF, (C) steady-state photoluminescence (PL) spectra of bare CoP, CNF, and 7-CoP/CNF under room temperature (inset: PL spectrum of bare CoP and 7-CoP/CNF) and (D) time-resolved photoluminescence (TR-PL) spectrum through 375 nm light excited and collected at 480 nm under room temperature.

the absorption edge was expanded to about 470 nm. Comparatively, CNF demonstrated a red-shift of the absorption edge after hybridizing with CoP QDs. Moreover, 7-CoP/CNF had narrower band gap (2.59 eV) than that of CNF (2.79 eV) (Fig. 5B). Furthermore, the steady-state photoluminescence (PL) peak intensity of 7-CoP/CNF remarkably decreased compared to CNF. This measurement revealed that photogenerated electron-hole pairs recombination in the 7-CoP/CNF had drastically decreased compared to CNF (Fig. 5C and S8[†]), implying that the electron-hole pairs recombination rate was efficiently suppressed with the assistance of CoP QDs.4,5 Time-resolved photoluminescence (TR-PL) spectroscopy in Fig. 5D proved the photoexcited charge average emission lifetime was 6.39 ns for 7-CoP/CNF, which was much shorter than that of CNF (8.28 ns) (Table S3[†]). This result further confirmed the charge-transfer pathway from CNF to CoP QDs in a nonradiative quenching manner.²¹ Thereby, an efficient interface charge migration and separation pathway were achieved in the 7-CoP/CNF. Furthermore, the electrochemical impedance spectroscopy (EIS) results revealed that 7-CoP/CNF manifested a smaller charge-transfer resistance (1.24 k Ω) than that of CNF (1.84 k Ω) and CoP (23.9 $k\Omega$), as seen in Fig. S9a and Table S4,[†] confirming the lower charge-transfer resistance in the 7-CoP/CNF heterostructure, which permitted efficient separation of the photoinduced charges.²⁸ The identical ohmic resistance (0.16 k Ω) for CoP, CNF, and 7-CoP/CNF was a consequence of the same concentration of Na₂SO₄ electrolyte used during the experiments. Moreover, the transient visible-light photocurrent indicated that 7-CoP/CNF exhibited a higher photocurrent enhancement than that of CNF and bare CoP (Fig. S9b[†]). All these observations demonstrated that CoP QDs could enhance the separation and transportation of photoinduced charges, rendering a high efficiency of photocatalysis for the HER.



Fig. 6 (A) X-ray photoelectron survey spectra (XPS) survey of CNF and 7-CoP/CNF, (B) high-resolution N 1s XPS of CNF and 7-CoP/CNF, (C) high-resolution Co 2p XPS of 7-CoP/CNF and (D) high-resolution P 2p XPS of 7-CoP/CNF.

Paper

In Fig. 6A, the low-resolution X-ray photoelectron spectroscopy (XPS) survey spectrum displayed C, N, and O elements in the CNF, while in comparison, both Co and P were detected in the 7-CoP/CNF, showing the presence of CoP after the phosphatization of 7-Co₃O₄/CNF. In Fig. S10,† the high-resolution C 1s XPS at 284.5 and 288.0 eV are for the standard reference carbon and sp²-bonded C in N=C-N,²⁹ respectively. Three pairs of N 1s peaks at 398.5, 399.1, and 400.7 eV in Fig. 6B correspond to C=N-C, N-(C)₃, and N-H of CNF,³⁰ respectively. The slight shift of the C=N-C and N-(C)₃ peaks of 7-CoP/CNF was likely due to their lone pair of electrons, which can serve as Co metalcoordination sites. The high-resolution Co 2p XPS peak could be deconvoluted into two peaks at 789.9 and 783.0 eV, which correspond to Co $2p_{3/2}$ and Co $2p_{1/2}$,³¹ respectively (Fig. 6C). In Fig. 6D, the P 2p peak of 7-CoP/CNF, was deconvoluted to three peaks at 129.7, 130.6, and 133.6 eV, corresponding to the P $2p_{2/}$ 3, P/2p_{1/2}, and P-O species,³² respectively. The XPS proved that CoP QDs were well hybridized with CNF and displayed a solid interaction with CNF, which was beneficial to photoexcited charges direct separation and photocatalysis for the HER.

Photocatalytic hydrogen evolution mechanism

Based on the results above, a possible photocatalytic hydrogen evolution mechanism on CoP/CNF is proposed in Scheme 2. Under visible light irradiation, protons were absorbed by the g- C_3N_4 nanofiber and the electrons in the valence band of the g- C_3N_4 nanofiber were excited, and migrated to its conduction band, and were then transferred to CoP quantum dots for proton reduction hydrogen generation. The generated holes in the valence band oxidized the sacrificial agent TEOA. During the photocatalysis hydrogen evolution process, the CoP quantum dots in CoP/CNF not only helped separate the electron-hole pairs and suppress electron-hole recombination, but also acted as a cocatalyst and provided abundant sites for proton reduction hydrogen evolution.

Photocatalytic performance and nanostructure stability

The nanostructure stability of a catalyst is considered as one of the most indispensable factors when used in practical applications. After nine cycles, the HER performance of 7-CoP/CNF was highly stable and its catalytic activity remained as high as



Scheme 2 Photocatalytic hydrogen generation mechanism on CoP/ CNF under visible light.



Fig. 7 (a–c) TEM images of 7-CoP/CNF, (d) CoP QDs diameter size distribution, (e) EDS of 7-CoP/CNF and (f) HR-TEM of CoP QDs.

95.6% (Fig. S11[†]). Based on the TEM images in Fig. 7, the nanoheterojunction structure and composition of 7-CoP/CNF remained stable after long-time cyclic HER. The CNF retained the uniform nanofiber morphology and CoP kept the quantum dot shape without growing into bulky microspheres (Fig. 7a and S12a[†]). CoP QDs were clearly detected in the HR-TEM (Fig. 7bd) without obvious aggregation issues after the cycling experiments. Based on EDS analysis, the Co content kept stable after long-term cycling test compared to fresh 7-CoP/CNF (Fig. 7e and Table S5[†]). HR-TEM showed the CoP QDs special lattice fringe d = 0.233, 0.290, and 0.245 nm, corresponding to (222), (220),and (311) facets in Fig. S12b⁺ and 7f. The high-resolution XPS of 7-CoP/CNF indicated the CoP QDs were stable without obviously being oxidized before and after the cycling experiment, as seen in Fig. S13.† In summary, the nanostructure and chemical composition of 7-CoP/CNF were extremely stable after the longterm cycling test.

Conclusions

In conclusion, a visible light-driven system using CoP QDs as a HER cocatalyst to form an integrated nanostructure with g- C_3N_4 nanofiber for photocatalytic HER was exploited. The reaction components in the system consisted of catalysts made of earth-abundant elements only, which made this system quite intriguing for the conversion of solar energy to chemical fuels. CoP QDs could highly promote electron-hole pair separation and the subsequent reduction of water to generate hydrogen. The photocatalytic activity of CoP/CNF was extremely high, with impressive HER performance, which was one of the highest among g- C_3N_4 -based hybrids reported to date. Furthermore, the idea of loading transition-metal phosphides (TMPs) QDs on metal-free g- C_3N_4 nanostructures could be an efficient design that can guide and benefit future research regarding the development of photocatalytic hydrogen generation.

Conflicts of interest

The authors declare no conflict of interests.

Acknowledgements

The authors appreciate the support from the China Scholarship Council for Y. Zeng and Y. Xia, and Hunan Provincial Innovation Foundation for Postgraduate (CX2017B139 and CX2017B141). Meanwhile, thanks Dr Jinming Luo of Georgia Institute of Technology, Dr Qingmei Chen of Boston College and Mr Joey Yourg of University of Illinois at Urbana-Champaign for grammar and expression corrections. The views and ideas expressed herein are solely those of the authors and do not represent the ideas of the funding agencies in any form.

References

- 1 T. Hisatomi and K. Domen, Nat. Catal., 2019, 2, 387-399.
- 2 M. Sonnberger, Nat. Energy, 2019, 4, 265-266.
- 3 Y. Zeng, H. Li, J. Luo, J. Yuan, L. Wang, C. Liu, Y. Xia, M. Liu, S. Luo and T. Cai, *Appl. Catal.*, *B*, 2019, **249**, 275–281.
- 4 Y. Zeng, X. Liu, C. Liu, L. Wang, Y. Xia, S. Zhang, S. Luo and Y. Pei, *Appl. Catal.*, *B*, 2018, 224, 1–9.
- 5 W. Cui, N. Cheng, Q. Liu, C. Ge, A. M. Asiri and X. Sun, *ACS Catal.*, 2014, **4**, 2658–2661.
- 6 J. Tian, Q. Liu, Y. Liang, Z. Xing, A. M. Asiri and X. Sun, *ACS Appl. Mater. Interfaces*, 2014, **6**, 20579–20584.
- 7 J. Liu, Y. Liu, D. Xu, Y. Zhu, W. Peng, Y. Li, F. Zhang and X. Fan, *Appl. Catal.*, *B*, 2019, **241**, 89–94.
- 8 Z. Sun, H. Zheng, J. Li and P. Du, *Energy Environ. Sci.*, 2015, **8**, 2668–2676.
- 9 Z. Pu, Q. Liu, C. Tang, A. M. Asiri and X. Sun, *Nanoscale*, 2014, 6, 11031–11034.
- 10 P. Jiang, Q. Liu, Y. Liang, J. Tian, A. M. Asiri and X. Sun, Angew. Chem., 2014, **126**, 13069–13073.
- 11 J. Tian, Q. Liu, N. Cheng, A. M. Asiri and X. Sun, *Angew. Chem.*, 2014, **126**, 9731–9735.
- 12 Z. Xing, Q. Liu, A. M. Asiri and X. Sun, *Adv. Mater.*, 2014, **26**, 5702–5707.
- 13 Z. Xing, Q. Liu, A. M. Asiri and X. Sun, *ACS Catal.*, 2014, 5, 145–149.
- 14 Q. Liu, J. Tian, W. Cui, P. Jiang, N. Cheng, A. M. Asiri and X. Sun, Angew. Chem., Int. Ed., 2014, 53, 6710–6714.

- 15 P. Jiang, Q. Liu, C. Ge, W. Cui, Z. Pu, A. M. Asiri and X. Sun, *J. Mater. Chem. A*, 2014, **2**, 14634–14640.
- 16 Z. Sun, H. Zheng, J. Li and P. Du, *Energy Environ. Sci.*, 2015, **8**, 2668–2676.
- 17 W. Liu, L. Cao, W. Cheng, Y. Cao, X. Liu, W. Zhang, X. Mou, L. Jin, X. Zheng, W. Che, Q. Liu, T. Yao and S. Wei, *Angew. Chem.*, *Int. Ed.*, 2017, 56, 9312–9317.
- 18 A. Li, W. Zhu, C. Li, T. Wang and J. Gong, Chem. Soc. Rev., 2019, 48, 1874–1907.
- 19 S. Hua, D. Qu, L. An, W. Jiang, Y. Wen, X. Wang and Z. Sun, *Appl. Catal.*, *B*, 2019, **240**, 253–261.
- 20 C. Yang, Z. Xue, J. Qin, M. Sawangphruk, S. Rajendran, X. Zhang and R. Liu, *J. Phys. Chem. C*, 2019, **123**, 4795–4804.
- 21 Y. Zeng, C. Liu, L. Wang, S. Zhang, Y. Ding, Y. Xu, Y. Liu and S. Luo, *J. Mater. Chem. A*, 2016, 4, 19003–19010.
- 22 Y. Deng, B. Chi, X. Tian, Z. Cui, E. Liu, Q. Jia, W. Fan, G. Wang, D. Dang and M. Li, *J. Mater. Chem. A*, 2019, 7, 5020–5030.
- 23 J. Fu, Q. Xu, J. Low, C. Jiang and J. Yu, *Appl. Catal., B*, 2019, **243**, 556–565.
- 24 L. Hu, Y. Liu, G. Zeng, G. Chen, J. Wan, Y. Zeng, L. Wang,
 H. Wu, P. Xu, C. Zhang, M. Cheng and T. Hu, *Chemosphere*, 2017, 184, 1071–1079.
- 25 D. Wu, S. Hu, H. Xue, X. Hou, H. Du, G. Xu and Y. Yuan, *J. Mater. Chem. A*, 2019, 7, 20223–20228.
- 26 J. Ran, T. Pan, Y. Wu, C. Chu, P. Cui, P. Zhang, X. Ai, C.-F. Fu, Z. Yang and T. Xu, *Angew. Chem., Int. Ed.*, 2019, 58, 1–8.
- 27 P. Jiang, Q. Liu, C. Ge, W. Cui, Z. Pu, A. M. Asiri and X. Sun, J. Mater. Chem. A, 2014, 2, 14634–14640.
- 28 M. A. Hossain, D. J. Burritt and M. Fujita, *Abiotic Stress Response in Plants*, 2016, pp. 323–375.
- 29 Y.-J. Yuan, Z. Shen, S. Wua, Y. Su, L. Pei, Z. Jia, M. Ding, W. Bai, Y. Chena, Z.-T. Yu and Z. Zou, *Appl. Catal.*, *B*, 2019, 246, 120–128.
- 30 Y. Ding, Y. Tang, L. Yang, Y. Zeng, J. Yuan, T. Liu, S. Zhang,
 C. Liu and S. Luo, *J. Mater. Chem. A*, 2016, 4, 14307–14315.
- 31 T. Liu, Q. Liu, A. M. Asiri, Y. Luo and X. Sun, *Chem. Commun.*, 2015, **51**, 16683–16686.
- 32 T. Liu, P. Li, N. Yao, G. Cheng, S. Chen, W. Luo and Y. Yin, *Angew. Chem., Int. Ed.*, 2019, **58**, 4679–4684.