A highly stable non-noble metal Ni$_2$P co-catalyst for increased H$_2$ generation by g-C$_3$N$_4$ under visible light irradiation†

Ping Ye, Xinling Liu, James Iocozzia, Yupeng Yuan, Lina Gu, Gengsheng Xu and Zhiqun Lin

Nickel phosphide (Ni$_2$P) was grown on a graphitic carbon nitride (g-C$_3$N$_4$) surface by annealing a mixture of g-C$_3$N$_4$, NiCl$_2$, and NaH$_2$PO$_2$ at 400 °C for 2 h in an Ar atmosphere. During the annealing, Ni$_2$P particles formed intimate interfaces with g-C$_3$N$_4$. As a result, charge transfer from photo-excited g-C$_3$N$_4$ to Ni$_2$P was improved as demonstrated by the improved photocatalytic H$_2$ generation (40.5 μmol h$^{-1}$ g$^{-1}$) compared to a physical mixture of Ni$_2$P and g-C$_3$N$_4$ (trace H$_2$ generation). Under optimal and identical experimental conditions, the H$_2$ production rate on Ni$_2$P-loaded g-C$_3$N$_4$ (2 wt%) is 82.5 μmol h$^{-1}$ g$^{-1}$, which is higher than that of Pt-loaded g-C$_3$N$_4$ (0.5 wt%) (72 μmol h$^{-1}$ g$^{-1}$). Impressively, Ni$_2$P shows a highly stable H$_2$ production activity despite being a non-noble metal co-catalyst. No activity loss occurs over repeated use and 24 h long-term H$_2$ generation trials. In contrast, a pronounced reduction in H$_2$ generation was observed for Pt-loaded g-C$_3$N$_4$ (0.5 wt%) over the same 24 h trial period. Among their many advantages, including non-toxicity, low cost and natural abundance, Ni$_2$P/g-C$_3$N$_4$ composites are a promising alternative for realizing efficient, long-lasting photocatalytic H$_2$ production.

Introduction

Molecular hydrogen (H$_2$) is regarded as a renewable and environmentally friendly chemical fuel to replace fossil fuels due to its high energy density and water-only by-product. Of the available techniques, H$_2$ production from water splitting by solar irradiation of a photocatalyst is an ideal route. In recent years, hundreds of semiconductors have been investigated for photocatalytic H$_2$ production via exposure to ultraviolet and/or visible light irradiation.1–9 Researchers recognize that suitable co-catalyst coupling with photocatalysts is essential for realizing active photocatalytic H$_2$ production. A desirable co-catalyst has two functions: serves as an electron sink to draw electrons from the photo-excited semiconductor and a catalyst to lower the H$_2$ generation overpotential.10–11 Despite their exceptional activity, the natural scarcity of noble metals limits their utility as co-catalysts. For economically viable H$_2$ generation, co-catalysts made from earth-abundant materials are needed. Several non-noble metal-based materials, such as MoS$_2$, NiS$_2$, and Ni(OH)$_2$ have been shown to be efficient co-catalysts for active H$_2$ generation when deposited onto the surface of photocatalysts.12–15 Recently, transition metal phosphides (MPs), including Ni$_2$P, FeP, CoP, MoP, and Cu$_3$P have been investigated as H$_2$ evolution co-catalysts.16–22 Though the H$_2$ generation mechanism for these metal phosphide co-catalysts is not yet fully understood, coupling these co-catalysts with various photocatalysts to achieve efficient H$_2$ generation remains a worthwhile venture as mechanistic questions are worked out in parallel.

In recent years, g-C$_3$N$_4$ has received much attention due to its stability and efficiency in photocatalytic H$_2$ evolution under visible light exposure.23–24 Noble metal Pt is a typical co-catalyst employed to promote H$_2$ generation on g-C$_3$N$_4$. However, Pt is not only costly but also suffers from the back reaction with H$_2$ and O$_2$ to produce H$_2$O during longer H$_2$ production trials.25 Most recently, Xu et al. has prepared g-C$_3$N$_4$ materials through a urea polymerization method and subsequently loaded Ni$_2$P onto the g-C$_3$N$_4$ catalyst via a two-step procedure. Ni(OH)$_2$ was grown in situ on g-C$_3$N$_4$ by using a hydrothermal method and then phosphidated into Ni$_2$P to obtain the final Ni$_2$P/g-C$_3$N$_4$ hybrid.26 This work validates the role of Ni$_2$P in boosting H$_2$ generation and serving as a replacement for expensive Pt. It is well known that photocatalytic H$_2$ generation is dependent on the synthesis strategy of the co-catalyst and photocatalyst. In addition, the choice of precursors controls the physiochemical properties of g-C$_3$N$_4$. It is for these reasons that it is essential to investigate the many potential synthesis and processing strategies available for producing, ostensibly, the same final product. As is well known, g-C$_3$N$_4$ derived from melamine offers...
exceptional stability for \( \text{H}_2 \) generation, making melamine to be the most suitable precursor for verifying the stability of the non-noble metal co-catalyst. From a technological view point, the formation of \( \text{Ni}_2\text{P} \) and g-C\(_3\)N\(_4\) composites via a facile one-step procedure is highly desirable. Herein, we loaded \( \text{Ni}_2\text{P} \) onto g-C\(_3\)N\(_4\) through facile annealing of a mixture of \( \text{NiCl}_2 \), NaH\(_2\)PO\(_2\) and g-C\(_3\)N\(_4\) in an Ar atmosphere wherein the g-C\(_3\)N\(_4\) was prepared by melamine condensation. We find that g-C\(_3\)N\(_4\)/Ni\(_2\)P composites can be facilely formed in a one-step procedure, which avoids the tedious manipulation of hydrothermal synthesis in Xu’s work. The as-obtained g-C\(_3\)N\(_4\)/Ni\(_2\)P composites offer highly stable \( \text{H}_2 \) generation. To the best of our knowledge, this work is the first report on a facile one step preparation technique for g-C\(_3\)N\(_4\) and Ni\(_2\)P hybrids with highly stable \( \text{H}_2 \) generation. Moreover, the present work clearly shows the potential of metal phosphides to serve as co-catalysts for improved \( \text{H}_2 \) generation.

**Experimental**

**Synthesis of \( \text{Ni}_2\text{P}/\text{g-C}_3\text{N}_4 \) hybrids**

All reagents were used as received. g-C\(_3\)N\(_4\) was prepared by direct polycondensation of melamine in air at 520 °C for 2 hours at a heating rate of 2.3 °C min \(^{-1}\). The Ni\(_2\)P co-catalyst was grown on g-C\(_3\)N\(_4\) through a single-step thermal annealing process. Samples with different loading amounts of Ni\(_2\)P (1 wt\%, 2 wt\%, 4 wt\%, and 8 wt\%) were labelled g-C\(_3\)N\(_4\)/Ni\(_2\)P (1 wt\%), g-C\(_3\)N\(_4\)/Ni\(_2\)P (2 wt\%), g-C\(_3\)N\(_4\)/Ni\(_2\)P (4 wt\%), and g-C\(_3\)N\(_4\)/Ni\(_2\)P (8 wt\%), respectively. In a typical preparation of 2 wt\% Ni\(_2\)P-loaded g-C\(_3\)N\(_4\), g-C\(_3\)N\(_4\) (800 mg), NiCl\(_2\)·6H\(_2\)O (50 mg), and NaH\(_2\)PO\(_2\)·H\(_2\)O (84 mg) were mixed \( \text{via} \) a mortar and pestle. The mixture was then heated at 400 °C for 2 hours in an Ar atmosphere at a heating rate of 2 °C min \(^{-1}\) in a tube furnace. A 300 W xenon lamp. A cut-off filter (\( \lambda \) ≥ 420 nm) was equipped to provide only visible light. The gaseous product was analyzed by gas chromatography (GC-1690, Kexiao, China) with a TCD detector. The photocatalytic \( \text{H}_2 \) generation on Pt/g-C\(_3\)N\(_4\) and a physical mixture of Ni\(_2\)P and g-C\(_3\)N\(_4\) was also tested for comparison. Pt (0.5 wt\%) was \( \text{in situ} \) deposited on g-C\(_3\)N\(_4\) by injecting small amounts of H\(_2\)PtCl\(_6\) solution (212 µL, 1 g L \(^{-1}\)) into the reactor. Ni\(_2\)P (2 mg) and g-C\(_3\)N\(_4\) (98 mg) powders were dispersed in TEOA solution for testing the \( \text{H}_2 \) generation from the physically mixed Ni\(_2\)P and g-C\(_3\)N\(_4\) system.

**Results and discussion**

**Sample characterization**

The XRD patterns of g-C\(_3\)N\(_4\)/Ni\(_2\)P are illustrated in Fig. 1. g-C\(_3\)N\(_4\)/Ni\(_2\)P (2 wt\%), g-C\(_3\)N\(_4\)/Ni\(_2\)P (4 wt\%), and g-C\(_3\)N\(_4\)/Ni\(_2\)P (8 wt\%) preparations were used as representative samples for this work. All peaks can be indexed to g-C\(_3\)N\(_4\) and Ni\(_2\)P with no evidence of side product formation occurring during the thermal annealing process for Ni\(_2\)P. The characteristic peaks at 13° and 27.4° are evidence of the periodic in-plane tri-s-triazine motif stacking and interlayer aromatic packing. The peaks at 20.77°, 44.59°, 47.45°, and 54.16° correspond to Ni\(_2\)P. These peaks become more intense at higher Ni\(_2\)P loading contents. The FT-IR analysis (Fig. S1) further supports the fact that the original g-C\(_3\)N\(_4\) backbones are retained after Ni\(_2\)P hybridization. Although no new vibrational peaks belonging to P- and Ni-

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**Photocatalytic measurements**

Photocatalytic \( \text{H}_2 \) generation was measured in an 80 mL closed Pyrex reactor with a quartz window under visible light irradiation. The photo-catalyst (20 mg) was dispersed in 20 mL of triethanolamine (TEOA) aqueous solution. The reactor was then bubbled with Ar for 30 min to remove air. Photocatalytic \( \text{H}_2 \) evolution was then initiated by irradiating the suspension using a 300 W xenon lamp. A cut-off filter (\( \lambda \) ≥ 420 nm) was equipped to provide only visible light. The gaseous product was analyzed by gas chromatography (GC-1690, Kexiao, China) with a TCD detector. The photocatalytic \( \text{H}_2 \) generation on Pt/g-C\(_3\)N\(_4\) and a physical mixture of Ni\(_2\)P and g-C\(_3\)N\(_4\) was also tested for comparison. Pt (0.5 wt\%) was \( \text{in situ} \) deposited on g-C\(_3\)N\(_4\) by injecting small amounts of H\(_2\)PtCl\(_6\) solution (212 µL, 1 g L \(^{-1}\)) into the reactor. Ni\(_2\)P (2 mg) and g-C\(_3\)N\(_4\) (98 mg) powders were dispersed in TEOA solution for testing the \( \text{H}_2 \) generation from the physically mixed Ni\(_2\)P and g-C\(_3\)N\(_4\) system.
related groups in g-C3N4/Ni2P hybrids were detected in FT-IR spectra, the shift of the Ni 2p (Fig. S2†), P 2p (Fig. S3†), C 1s (Fig. S4†) and N 1s (Fig. S5†) binding energies in g-C3N4/Ni2P (8 wt%) hybrids compared to pure Ni3P and g-C3N4 or physical mixtures of Ni3P and g-C3N4 demonstrates that the annealing process for Ni3P hybridization likely initiates new chemical bonding between Ni3P and g-C3N4.

The UV-vis spectra (Fig. 2) of g-C3N4/Ni3P hybrids show the typical absorption edge of g-C3N4 at 460 nm. The absorption edge of g-C3N4/Ni3P hybrids becomes more intense in the visible light region with increasing Ni3P loading onto g-C3N4. This supports the increased Ni3P content in g-C3N4/Ni3P samples. This phenomenon is further verified by the Ni3P absorption spectrum. In comparison, the physical mixture of g-C3N4 and Ni3P (2 wt%) offers inferior light absorption behaviour when compared to g-C3N4/Ni3P (2 wt%) and partially for pure g-C3N4 (Fig. S6†). This further supports the presence and importance of chemical bonding between g-C3N4 and Ni3P.

The SEM image (Fig. 3a) does not show the presence of Ni3P particles in the g-C3N4/Ni3P (2 wt%) hybrid due to the low Ni3P loading content. However, the presence of Ni3P is clearly demonstrated by energy dispersive X-ray spectroscopy (EDS) as shown in Fig. 3b. A higher Ni3P content leads to a heavier coverage of the g-C3N4 surfaces (Fig. S7†). Ni3P loading was further supported by TEM as shown in Fig. 3c. Ni3P nanoparticles roughly 20 nm in diameter were intimately attached to the g-C3N4 surfaces. It should be noted that the g-C3N4/Ni3P (2 wt%) sample was ultrasonicated for 40 minutes prior to TEM observation, which supports the strong adhesion of Ni3P onto g-C3N4. High resolution TEM shows a lattice fringe of 0.507 nm, indexed to the (100) planes Ni3P (Fig. 3d). Elemental mapping further supports the uniform distribution of Ni3P (see Fig. S8†). The Ni3P particles grew into large particles and are aggregated at higher degrees of loading, as shown in the g-C3N4/Ni3P (8 wt%) sample (Fig. S9†).

In order to verify the effect of Ni3P loading on H2 evolution, g-C3N4/Ni3P samples were measured for visible-light-driven (λ > 420 nm) photocatalytic H2 generation from water reduction. TEOA (10 vol%) was used as a sacrificial reagent.† Control experiments show no H2 evolution without g-C3N4/Ni3P catalysts or light irradiation. The photocatalytic H2 generation rate was controlled by the TEOA concentration (Fig. 4a). The highest H2 generation rate of 82.5 μmol h⁻¹ g⁻¹ was achieved when using a g-C3N4/Ni3P (2 wt%) sample from 10 vol% TEOA solution. All experiments were carried out under these conditions.

Fig. 4b illustrates the average H2 generation rate of g-C3N4/Ni3P samples over the first three hours. Pure g-C3N4 samples showed very poor H2 generation properties (only trace amounts of H2 were detected). Similarly, Ni3P alone also has no H2 generation properties under visible light irradiation. For g-C3N4/Pt (0.5 wt%) and g-C3N4/Ni3P (2 wt%), the H2 generation rates are 72 and 63.5 μmol h⁻¹ g⁻¹, respectively (Fig. 4b, only the value for the g-C3N4/Ni3P (0.5 wt%) sample is incorporated for conciseness). However, for g-C3N4/Ni3P (2 wt%), the H2 evolution rate was enhanced to 82.5 μmol h⁻¹ g⁻¹, which is superior to that of g-C3N4/Pt (0.5 wt%) despite being more naturally abundant and less expensive. It is also essential to emphasize the importance of the in situ formation of the Ni3P particles for the improved performance. In a simple physical mixture of Ni3P (2 wt%) and g-C3N4, only trace H2 generation was observed under identical experimental conditions (not shown in Fig. 4b). This underscores the importance of thermal annealing which enables the formation of intimate Ni3P/g-C3N4 interfaces for effective charge transfer from excited g-C3N4 to Ni3P, which is
Mechanism of enhanced photocatalytic activity

The enhanced photocatalytic H₂ generation is likely a result of the effective interfacial charge transfer from photo-excited g-C₃N₄ to the Ni₂P co-catalyst. It has been reported that the photo-generated electrons can efficiently transfer from the conduction band (CB) of CdS to Ni₂P.²⁹ Since the CB edge of g-C₃N₄ (−1.2 V vs. NHE) is more negative than that of CdS (−0.5 V vs. NHE), the photo-excited electrons on g-C₃N₄ could thus transfer to Ni₂P through the g-C₃N₄/Ni₂P interfaces created by annealing (Fig. 5). The electrons accumulating on the Ni₂P particles can then reduce H⁺ into hydrogen while the holes on g-C₃N₄ can oxidize the sacrificial electron donor TEOA. The effective separation of the photo-generated electrons and holes in g-C₃N₄ further improves photocatalytic H₂ generation.

Interfacial charge transfer is evident from the decreased photoluminescence (PL) intensity in g-C₃N₄/Ni₂P (2 wt%) (Fig. 6a) as compared to pure g-C₃N₄. Pure g-C₃N₄ emits a strong PL peak at 472 nm. Ni₂P integration can significantly quench this peak (Fig. S13†). In addition, the PL peak shifts from 472 nm for pure g-C₃N₄ to 467 nm for g-C₃N₄/Ni₂P (2 wt%). This peak shift is caused by Ni₂P addition, as evidenced by the PL peak of the g-C₃N₄ and Ni₂P (2 wt%) mixture (Fig. S13†). As expected, Pt loading can also reduce the PL of g-C₃N₄, but the peak position remains unchanged with respect to pure g-C₃N₄ (Fig. S13†). This strong chemical interaction between g-C₃N₄ and Ni₂P affects the Stokes shift of g-C₃N₄ leading to the blue shift in the PL peak. This interaction is currently being evaluated by density functional theory (DFT) calculations. The PL spectra clearly originate from the intimate contact between Ni₂P and g-C₃N₄ which facilitates the photo-induced electron transfer from g-C₃N₄ to Ni₂P.

The ultimate cause for enhanced H₂ generation rates. Higher Ni₂P loading on g-C₃N₄ leads to larger interfacial areas, more effective separation of photo-generated electrons and holes and enhanced photocatalytic activity. When the Ni₂P loading content is further increased to 4 wt%, a reduction in hydrogen generation performance is observed. This result is explained by an emergent shading effect in which overloading by Ni₂P can reduce light absorption of the g-C₃N₄ photocatalyst. In addition, the coverage of the active sites by the Ni₂P co-catalyst also hinders H₂ generation.²⁸

The photo-stability of a co-catalyst is also essential for practical use. Therefore, we examined the stability of Ni₂P as a co-catalyst for photocatalytic H₂ generation with g-C₃N₄/Ni₂P (2 wt%) used as a representative sample. Impressively, g-C₃N₄/Ni₂P (2 wt%) shows highly stable photocatalytic H₂ generation with no decrease in the H₂ generation rate observed over the duration of the experiments (Fig. 4c and d). The cyclic H₂ generation experiments also show consistent and repeatable H₂ generation rates (see Fig. 4c) over four cycles (Fig. 4d). XRD analysis confirmed the unchanged phases of g-C₃N₄/Ni₂P (2 wt%) before and after the 24 h long-term photocatalytic H₂ generation experiments (Fig. S10†). Moreover, no aggregation or morphology changes in Ni₂P occurred during 24 h long-term H₂ generation experiments. This further supports the stability of Ni₂P as a non-noble metal co-catalyst useful in enhancing H₂ generation (Fig. S11†). In comparison, g-C₃N₄/Pt (0.5 wt%) shows a pronounced decrease in the H₂ generation rate throughout the long-term testing (Fig. 4d). TEM shows no aggregation of Pt in g-C₃N₄/Pt (0.5 wt%) after 24 hour H₂ generation experiments (Fig. S12†). This suggests that the Pt co-catalyst present in the system is deactivated during H₂ generation over long-term experiments. These results highlight the excellent stability of Ni₂P as a non-noble metal co-catalyst for enhanced H₂ generation.

**Fig. 4** (a) Photocatalytic H₂ evolution from solutions containing various amounts of TEOA on g-C₃N₄/Ni₂P (2 wt%) under visible light irradiation. (b) Effect of the Ni₂P loading content on photocatalytic H₂ generation from g-C₃N₄. In addition, g-C₃N₄/Pt (0.5 wt%) was also included for reference. The x-axis shows the loading amount of Ni₂P and Pt. (c) Cycling runs for photocatalytic H₂ generation on g-C₃N₄/Ni₂P (2 wt%) under visible light irradiation. (d) Long-term (24 h) H₂ generation on g-C₃N₄/Ni₂P (2 wt%) and g-C₃N₄/Pt (0.5 wt%) under visible light irradiation with a noticeable rate reduction for the latter.

**Fig. 5** Schematic illustration of the (left) energy position of g-C₃N₄ vs. the normal hydrogen electrode (NHE) and (right) charge transfer from photo-excited g-C₃N₄ to Ni₂P particles for H₂ evolution.
The interfacial charge transfer can be further understood by the decreased PL lifetime (Fig. 6b). The average lifetime of pure g-C3N4 and g-C3N4/Ni2P (2 wt%) are 5.43 and 3.95 ns, respectively. The decreased PL lifetime shows the rapid charge transfer in Ni2P-loaded g-C3N4, which reduces the recombination of electron–hole pairs in g-C3N4. This work shows the great potential of noble-metal free Ni2P for improving photocatalytic H2 generation of g-C3N4 and provides new insights into developing low cost and highly efficient transition-metal phosphides as co-catalysts for enhanced photocatalytic water-splitting.

Conclusions

In summary, g-C3N4/Ni2P hybrids can be facilely prepared via a single-step annealing process. Ni2P nanoparticles can serve as an active and highly stable non-noble metal co-catalyst for improving H2 generation on g-C3N4. The enhanced performance was mainly attributed to efficient charge transfer from photo-excited g-C3N4 to Ni2P, which suppressed the recombination of electron–hole pairs in g-C3N4. This work shows the great potential of noble-metal free Ni2P for improving photocatalytic H2 generation and provides new insights into developing low cost and highly efficient transition-metal phosphides as co-catalysts for enhanced photocatalytic water-splitting.

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Notes and references