



## Research paper

# Toward noble-metal-free visible-light-driven photocatalytic hydrogen evolution: Monodisperse sub-15 nm Ni<sub>2</sub>P nanoparticles anchored on porous g-C<sub>3</sub>N<sub>4</sub> nanosheets to engineer 0D-2D heterojunction interfaces



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## ABSTRACT

Exploring robust and low-cost noble-metal-free co-catalysts to substitute precious noble-metal is of great importance in both fundamental research and practical applications. Herein, we employ a novel solution-phase method to synthesize highly monodisperse zero-dimensional (0D) nickel phosphide (Ni<sub>2</sub>P) nanoparticles, which were then anchored on two-dimensional (2D) porous g-C<sub>3</sub>N<sub>4</sub> nanosheets via a facile self-assembly route to develop the intimate 0D-2D heterojunction interface. The outstanding feature of the material is that the resultant hybrid nanocomposite exemplified efficient noble-metal-free photocatalytic H<sub>2</sub> production under visible light. Under optimal conditions, the Ni<sub>2</sub>P embedding was found to be 3.5 wt%, giving a remarkable H<sub>2</sub> production rate of 474.7 μmol g<sup>-1</sup> h<sup>-1</sup> and an apparent quantum yield (AQY) of 3.2% at 435 nm, surpassing most of the reported noble-metal-free co-catalysts-modified g-C<sub>3</sub>N<sub>4</sub> photocatalysts. The superior photoactivity of the hybrid nanostructure is attributed to the profound role of Ni<sub>2</sub>P as an excellent reduction co-catalyst to hamper the recombination of charge carriers from g-C<sub>3</sub>N<sub>4</sub> and also provide good electrical conductivity, which could be substantiated by photoelectrochemical (PEC) experiments, photoluminescence (PL) spectra, and electron paramagnetic resonance (EPR) spectroscopic studies. Benefitting from the intriguing properties of Ni<sub>2</sub>P and g-C<sub>3</sub>N<sub>4</sub>, this work presents a new platform to uncover the immense potential of noble-metal-free nanomaterials as the next generation photocatalysts in multifunctional application prospects not only in the water splitting reaction, but also in other energy-related fields such as CO<sub>2</sub> reduction and solar cells. It is also anticipated that the solution-phase hybridization technique could be extended to synergistically integrate g-C<sub>3</sub>N<sub>4</sub> with a myriad of nanocrystals for multitudinous chemical reactions.

## 1. Introduction

As a low-cost renewable carbon-free energy source, solar light can be harvested and converted into highly energetic sustainable fuels in chemical bonds such as hydrogen (H<sub>2</sub>) without any carbon footprint with the aid of appropriate catalysts. At present, photocatalytic production of H<sub>2</sub>, which is one of the Holy Grails of chemistry, has been widely reported as an attractive and sustainable approach for effective utilization of clean and inexhaustible solar energy, by itself, will simultaneously circumvent the global energy and environmental problems caused by the rampant consumption of fossil fuels [1,2].

Recently, as a metal-free polymeric-like semiconductor photocatalyst, graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) has enthralled enormous attention in the realm of energy production due to its suitable band gap positions for photocatalytic water splitting, high chemical- and photo-stability [3–9]. However, the high recombination rate of photo-excited carriers significantly limits the photocatalytic H<sub>2</sub> evolution activity of the single-component g-C<sub>3</sub>N<sub>4</sub> photocatalyst [10–14]. Hitherto, unremitting efforts have been devoted to designing and engineering co-catalysts-modified g-C<sub>3</sub>N<sub>4</sub> as an auspicious and fascinating solution to ameliorate its photoactivity towards H<sub>2</sub> evolution [15,16]. The co-catalysts play an indispensable role in extracting photo-generated charge carriers,

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hosting reaction active sites, and reducing the reaction energy barriers for photocatalytic  $H_2$  generation [15,17]. Undeniably, noble metals such as Pt are commonly utilized as efficient co-catalysts for improving photocatalytic  $H_2$  evolution of  $g-C_3N_4$  based on the previous studies [18–23]. However, the scarcity and extremely high-cost of noble metals widely impede their practical use in the hydrogen production at a large scale. Therefore, daunting challenges still exist in constructing  $g-C_3N_4$  hybrid systems, which comprise relatively less expensive and earth-abundant co-catalysts for remarkable photocatalytic water splitting.

In the last several years, noble-metal-free co-catalysts such as  $MoS_2$  [24,25],  $WS_2$  [26],  $NiS$ , [27,28],  $Ni(OH)_2$  [29], and  $Ni$  nanoparticles [17,30,31] decorated onto  $g-C_3N_4$  have underpinned a renaissance of surging interest stemming from their extraordinary  $H_2$  evolution photoactivity. In contrast with the aforementioned co-catalysts, transition metal phosphides (e.g.,  $Ni_2P$ ,  $Co_2P$ ,  $FeP$ , etc.) as co-catalysts modified  $g-C_3N_4$  systems are relatively seldom reported in the literature and thus worthy of extensive research. As a proof of concept, transition metal phosphides have been employed as highly active non-noble-metal electrocatalysts in electrochemical hydrogen generation [32,33], and also as efficient co-catalysts for photocatalytic and photoelectrochemical  $H_2$  generation, which ensued from their approximate zero-valent metallic properties and long-term stability [34]. For example,  $Ni_2P$  [35,36],  $MoP$  [37], and  $Co_2P$  [38] can all act as efficient co-catalysts integrated  $CdS$  nanorods and highly improve the performance for photogeneration of hydrogen in water. Additionally,  $CoP$ ,  $Ni_2P$  and  $Cu_3P$  that were produced by thermal reduction of hypophosphite and supported on hexagonal  $CdS$  has also been used as efficient heterojunction nanocomposites for hydrogen evolution under solar irradiation [39]. To the best of our knowledge, only a few reports have demonstrated the use of transition metal phosphides as co-catalysts incorporated with  $g-C_3N_4$  for the photocatalytic hydrogen evolution reaction since 2016, namely  $CoP$  [40–42],  $Ni_{12}P_5$  [43], and  $Ni_2P$  nanoparticles [44–47]. Nevertheless, the preparation and hybridization of metal phosphides with the aim of attaining simultaneously pure phase, well-crystallized, and monodisperse nanosized particles remain an onerous task to be achieved in the  $g-C_3N_4$  nanohybrid systems. Notably, it has become a stumbling block and a burgeoning challenge to develop a facile and convenient strategy to couple metal phosphides with  $g-C_3N_4$  nanosheets for the intimate connection and tight heterojunction for boosted photocatalytic performance.

Thus far, the gas-solid reaction strategy with both  $NaH_2PO_2$  and  $NH_4H_2PO_4$  as P sources is widely utilized, but the decomposition of hypophosphites releasing  $PH_3$  necessitates high temperature and multiple steps to achieve metal phosphides [34]. Furthermore, conventional mechanical blending or suspension solvent stirring method for the loading of co-catalysts on  $g-C_3N_4$  would cause the irregularly-

distributed load or particle shedding during the catalytic reaction, which leads to markedly reduced photocatalytic performance. At this juncture, the synthesis of pure phase and monodisperse metal phosphides remains a scientifically arduous task as a result of their various multifarious phases and uncontrolled morphology. Considering the rapidly-blossoming progress in the solution-phase synthesis of metal phosphides, it is envisioned that an efficient strategy in anchoring  $g-C_3N_4$  with metal phosphides through a solution-phase method is of utmost significance for the formation of well-contacted heterojunction nanostructures between  $g-C_3N_4$  and metal phosphides. Therefore, the preparation of metal phosphide nanoparticles with pure phase, well-crystallized and narrow particle size distribution via a solution-phase method should be further examined. Compared to the conventional gas-solid reaction strategy which requires multiple steps, high temperature and the release of highly toxic gas ( $PH_3$ ) for the development of  $g-C_3N_4$ /metal phosphide, the hybridization technique of 0D monodisperse metal phosphide nanoparticles and 2D  $g-C_3N_4$  nanosheets through a solution-phase self-assembly approach at room temperature warrants a special level of merits for further scrutiny.

In view of the above-mentioned Achilles' heels, we present a facile solution-phase self-assembly route to incorporate two-dimensional (2D) porous  $g-C_3N_4$  nanosheets and zero-dimensional (0D) nanocrystalline  $Ni_2P$  co-catalysts, in which the monodisperse  $Ni_2P$  nanoparticles are pure phase, well-crystallized and endow narrow particle size distribution of 10.3 nm in average synthesized by the phosphorization of intermediate monodisperse  $Ni$ . The as-prepared  $Ni_2P$  nanoparticles were then tightly anchored on the porous  $g-C_3N_4$  nanosheets through continuous ultrasonication in the mixture of DMF/hexane solution. Interestingly, the as-obtained  $g-C_3N_4/Ni_2P$  heterojunction nanocomposites exhibit conspicuously enhanced hydrogen evolution under visible light radiation even in the absence of noble metals. To this end, it is expected that our study will eminently contribute to a new research paradigm for the rational development of cost-effective, high-efficient, and environmental friendly hybrid heterojunction nanocomposites for sustainable solar energy production.

## 2. Results and discussion

Herein, we present a novel two-step synthetic route to synthesize  $Ni_2P$  in the oleylamine (OAm) system, and also to introduce a new optimization technique incorporating  $Ni_2P$  nanoparticles into porous  $g-C_3N_4$  nanosheets. Fig. 1a illustrates an optimized synthetic strategy for fabrication of  $Ni_2P$  nanoparticles, which includes the preparation of intermediate monodisperse  $Ni$  nanoparticles, and the formation and growth of  $Ni_2P$  by using tri-*n*-octylphosphine (TOP) as a phosphorus source heated at a higher temperature. More specifically, firstly,

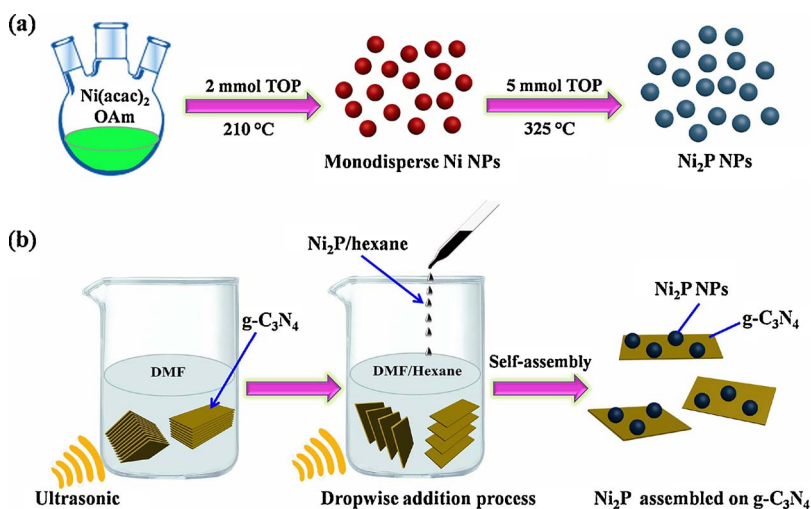


Fig. 1. (a) Schematic synthesis of  $Ni_2P$  nanoparticles. (b) Schematic of 0D  $Ni_2P$  nanoparticles assembled on the 2D  $g-C_3N_4$  nanosheets.

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