



# Reduced graphene oxide supporting hollow bimetallic phosphide nanoparticle hybrids for electrocatalytic oxygen evolution



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## ABSTRACT

Nanohybrids with hollow CoNiP nanoparticles decorating reduced graphene oxide (h-CoNiP/rGO) are prepared by a low-temperature phosphorization method. The h-CoNiP/rGO present favorable electrocatalytic advantages toward the oxygen evolution reaction (OER) in alkaline solution, including an onset potential of 1.44 V, a low overpotential of 280 mV at a current density of 10 mA cm<sup>-2</sup>, a small Tafel slope of 65.2 mV dec<sup>-1</sup>, and pretty good durability. The use of earth-abundant elements in a high-activity OER electrocatalyst may provide an effective way of advancing the development of full water splitting.

## 1. Introduction

Electrolytic water splitting holds great potential to afford sustainable and clean hydrogen source, which is considered as one of the most promising candidates to replace fossil fuels due to its outstanding energy density and environmental friendliness [1]. Oxygen evolution reaction (OER), as the critical half reaction of water splitting, is a thermodynamically unfavorable and kinetically sluggish process and requires a high overpotential at most electrocatalyst, greatly hindering the realization of large-scale electrochemical water splitting [2]. Therefore, exploring efficient OER catalysts has become one of the hottest research topics for water electrolysis. So far, the most widely used and most efficient OER catalysts are ruthenium (Ru) and iridium (Ir) based oxides, the high cost and source scarcity greatly prohibit the widespread use of such noble-metal catalysts [3]. Therefore, exploration of alternative low-cost catalysts allowing for large-scale application with high activity is of great significance.

Transition metal phosphides (TMPs) have attracted great attention as new earth-abundant OER catalysts owing to their metalloid characteristics of high activity, good stability, and decent electrical conductivity, which is of great benefit for improving electrocatalytic performance [4–5]. As a typical TMP, CoNiP has been reported to be appealing material in a variety of fields, such as hydrogen evolution, oxygen evolution, and supercapacitor [6–8]. Since the nanomaterials' properties are highly dependent on the size, shape and dimensionality. CoNiP nanostructures with different morphologies, including nanosheets [9], nanorods [10] and nanoparticles [11] have been developed. Among various nanoarchitectures, hollow micro-/nano-

structured materials have aroused tremendous interest for higher catalytic performance since they can provide abundant catalytic active sites and facilitate the mass and charge transport. For example, by using ZIF-67 as a sacrificial template, CoNiP nanosheets assembled on the hollow quasi-polyhedron were reported to show high activity toward hydrogen evolution reaction [6]. However, to the best of our knowledge, there is still little report on the fabrication of hollow structured CoNiP.

In this work, we report the fabrication of nanohybrids of hollow CoNiP nanoparticles decorating reduced graphene oxide (rGO) through a convenient synthetic process. The h-CoNiP/rGO shows highly efficient OER activity in terms of activity and stability. To the best of our knowledge, this is the first report developing graphene supporting hollow bi-metal phosphide nanoparticles for catalyzing OER with achieving decent catalytic properties.

## 2. Experimental

### 2.1. Catalyst preparation

#### 2.1.1. Preparation of h-CoNiP/rGO nanocomposite

Graphene oxide (GO) was synthesized according to a minor modified Hummers' method [12]. Precursors were prepared by dissolving Co(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O (124 mg), Ni(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O (124 mg), and PVP (0.32 g) in 20 mL of 1,3-propanediol (PDO). Then, GO (3 mg) was added to the above solution, followed by ultrasonication for 30 min. Afterwards, the suspension was heated at 150 °C in an oil bath for 3 h and the precipitate was collected. The resulted powder and NaH<sub>2</sub>PO<sub>2</sub>

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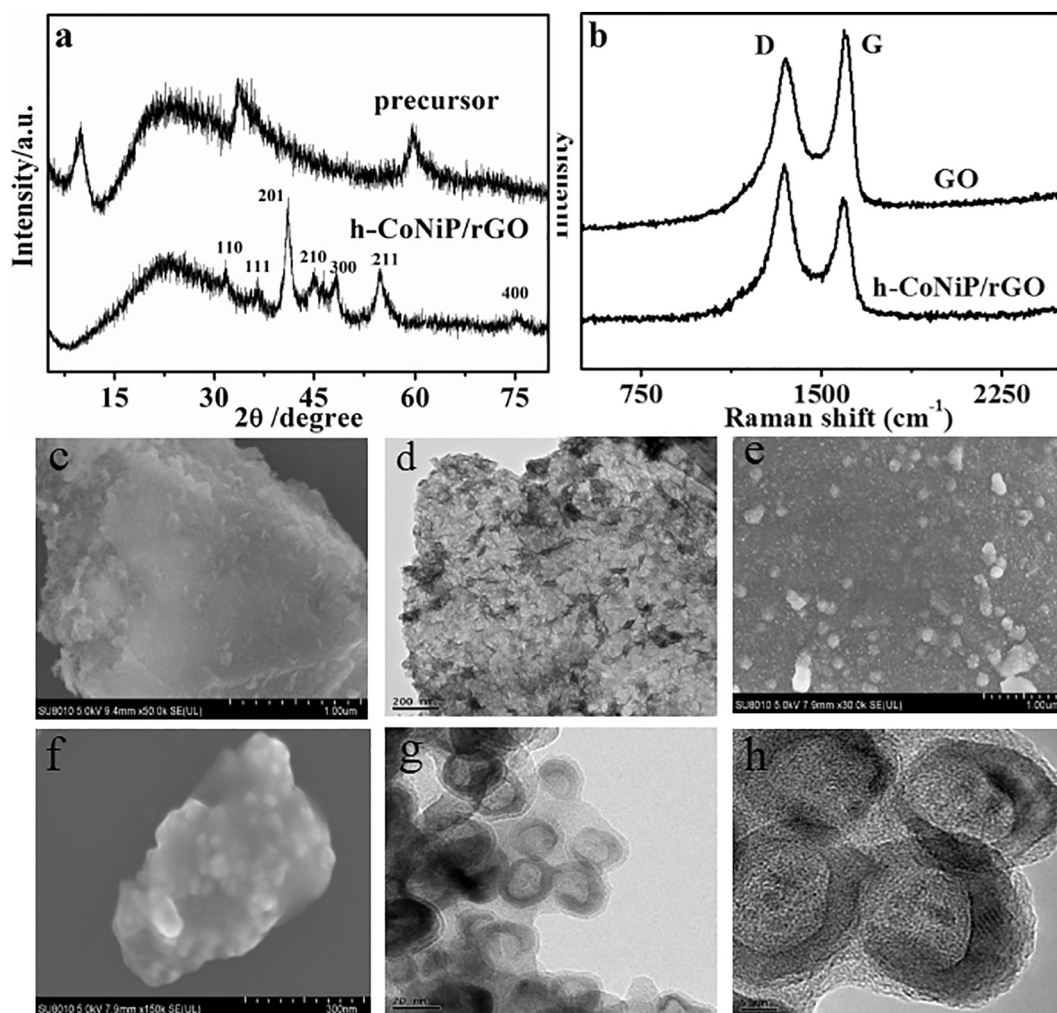


Fig. 1. (a) XRD patterns of precursor and h-CoNiP/rGO; (b) Raman spectroscopy of GO and h-CoNiP/rGO; (c) SEM and (d) TEM images of the as-prepared precursor; (e–f) SEM and (g–h) TEM of the h-CoNiP/rGO.

were placed separately in a porcelain boat, accompanying with heating in a tube furnace at 300 °C for 2 h under Ar atmosphere for finally evolving the precursor powder into the h-CoNiP/rGO. For comparison,  $\text{CoP}_x/\text{rGO}$ ,  $\text{NiP}_x/\text{rGO}$  and  $\text{CoNiP}$  were also prepared in a similar way without adding  $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  or GO, respectively.  $\text{Co}_3\text{Ni}_1\text{P}/\text{rGO}$  and  $\text{Co}_1\text{Ni}_3\text{P}/\text{rGO}$  were fabricated in the same way using different initial molar ratios of  $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  and  $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  as 1:3 and 3:1, respectively.

## 2.2. Electrochemical tests

Typically, 5 mg of catalyst was dispersed into  $\text{H}_2\text{O}$  (840  $\mu\text{L}$ ) and anhydrous ethanol (60  $\mu\text{L}$ ), then the Nafion solution (100  $\mu\text{L}$ ) was added to achieve a homogeneous ink by sonication. Next, 3  $\mu\text{L}$  of the catalyst ink was pipetted onto a glassy carbon electrode ( $d = 3 \text{ mm}$ ,  $S = 0.07 \text{ cm}^2$ ) with a loading of 0.21  $\text{mg cm}^{-2}$ . For the measurement on nickel foam (NF), the working electrode was prepared by loading 2.0 mg of sample on 1  $\text{cm}^2$  NF. All the electrochemical measurements were carried out in a three-electrode cell using a CHI660E electrochemical work station (Shanghai Chenhua Instrument Co., China). The scan rate was 5  $\text{mV s}^{-1}$  for all measurements. All potentials were referenced to reversible hydrogen electrode (RHE) by following calculations:  $E(\text{RHE}) = E(\text{Ag}/\text{AgCl}) + 0.197 \text{ V} + 0.059 \times \text{pH}$ .

## 3. Results and discussion

The as-synthesized precursor and h-CoNiP/rGO were characterized by X-ray diffraction (XRD). The precursor shows three peaks, which is characteristic for stacked metal-oxygen sheets separated by bonded alcoholate anions [13]. After calcination, the as-obtained product shows peaks at  $2\theta$  of 30.15°, 40.99°, 45.00°, 47.68°, 54.46° and 75.05°, which can be indexed to the (110), (111), (201), (210), (300), (211) and (400) planes of CoNiP (PDF#71-2336), respectively (Fig. 1a). No diffraction peak corresponding to either GO or rGO, probably due to its low amount or relatively low diffraction intensity. The presence of the rGO in the nanocomposites is confirmed by the Raman spectroscopy (Fig. 1b). The h-CoNiP/rGO shows characteristic peaks at 1346 and 1596  $\text{cm}^{-1}$ , corresponding to the D and G bands of rGO, respectively. According to the previous reports, the relative intensity ratio of D bands and G bands ( $I_D/I_G$ ) is an indication of the graphitization degree of carbonaceous materials. The calculated value of  $I_D/I_G$  at the h-CoNiP/rGO is determined to be 1.20, which is much higher than that observed over the original GO (0.91). This indicates a successful reduction of GO to rGO during the calcination process [14].

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were applied to investigate the structure and morphology of the as-prepared precursor and h-CoNiP/rGO nanocomposites, as shown in Fig. 1c–d. A large amount of thin nanosheets are uniformly anchored on the surface of flexible rGO for the precursor. It is interesting that the sheet-by-sheet structure of the h-CoNiP/rGO

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