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# $Ni_5P_4$-$NiP_2$ nanosheet matrix enhances electron-transfer kinetics for hydrogen recovery in microbial electrolysis cells

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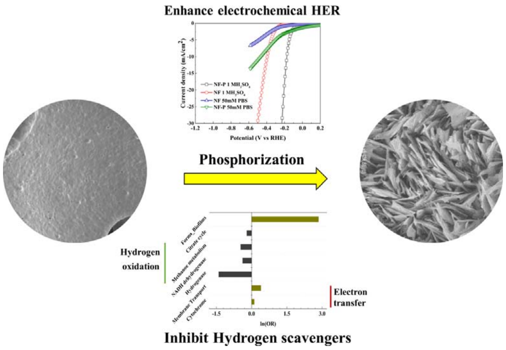
## HIGHLIGHTS

- One-step synthesis of the $Ni_5P_4$-$NiP_2$ owns highly catalytic performance.
- Enhanced electron transfer was achieved by expanding active sites.
- NF-P as cathode showed a high hydrogen recovery in neutral condition.
- 3D NF-P cathode stimulated the functional genes over-presentation.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

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## ABSTRACT

Due to the crucial role of the cathodic catalyst in the electron-transfer rate and hydrogen recovery in bioelectrochemical systems, coupling nickel and earth-abundant transition metal phosphides with high catalysis efficiency and low cost could provide a promising alternative to Pt/C catalysts. Herein, we fabricated a three-dimensional (3D) biphasic $Ni_5P_4$-$NiP_2$ nanosheet matrix to act as a cathodic tunnel for electron transfer for hydrogen coupled with a microbially catalyzed bioanode. Benefiting from the "ensemble effect" of P, the Tafel slope obtained from voltammetry reflected the improved catalytic performance (83.9 mV/dec vs. 113.6 mV/dec) and contributed to a higher hydrogen production rate of $9.78 \pm 0.38\,mL\,d^{-1}\,cm^{-2}$ that was 1.5 times faster than that of NF, which was even faster than that reported for commercial Pt/C. The impedance resistance obtained using electrochemical impedance spectroscopy (EIS) showed that the NF-P simultaneously exhibited $< 10\%$ electron loss, corresponding to a 2.5-fold improvement over the $\sim 25\%$ electron loss of NF. The long-term durability of the new material was verified through long-term operation with high performance in practice. It is proved that a good catalytic property of cathode was well maintained, even with microorganism attachment on NF-P cathode.

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## 1. Introduction

MECs are a promising technology for hydrogen conversion from biomass or bio-waste that exhibit the advantage of a lower energy input than that of steam reforming or water electrolysis [1]. Extracellular electron-transporting bacteria on the anode can oxidize organic matter to narrow the potential gap between the anode and cathode for the HER, leading to lower essential requirements for external voltage than water electrolysis (0.114 V vs. 1.2 V in theory) [2]. Importantly, in contrast with the anode, which is dependent on microbial-driven reactions, cathode materials are the key to the successful development of MECs as the tunnel for electron transfer from organic matter to hydrogen. To date, the Pt/C catalysts exhibit the unique performance for the HER, but the scarcity and high cost of Pt restrict its application in such bioelectrochemical technologies [3–6].

Developing commercially feasible and earth-abundant catalysts to replace precious metal catalysts is not only important for the field of energy generation (electricity, hydrogen) [7–11], but also for microbial electrolysis cells (MECs). For this purpose, many efforts have been devoted to fabricating inexpensive metal or carbon materials, such as stainless steel mesh [12,13], nickel foam modified with graphene [14], graphene doped with $MoS_2$ [15] and carbon/iron-based nanorods [16]. Among these materials, nickel foam (NF) has attracted increasing attentions because of its unique three-dimensional (3D) structure and advantages as a cost-effective cathodic catalyst for electron recovery. However, its sluggish catalytic activity and sensitivity to corrosion have always hindered the use of this material in bioreactor applications. Transition metal phosphides, such as CoP, MoP, FeP, and WP [17–20], are emerging catalysts for the hydrogen evolution reaction (HER), with Ni-P being developed as a novel earth-abundant catalyst since 2013. Density functional theory calculations previously indicated that $Ni_2P$ surpassed the activity of Pt for the HER due to the ensemble effect [21]. Subsequent studies demonstrated that hydrogen recovery and quantitative faradaic yield afforded stability only in acidic media [22]. However, phosphorus-rich catalysts such as $Ni_5P_4$ and $NiP_2$ can exhibit outstanding efficiency in a wide range of pH conditions when used as hydrogen evolution electrocatalysts [23,24], implying their improved ability to catalyze the HER with various proton sources ($H_3{}^+O$ or $H_2O$). This characteristic is very important for bio-hydrogen production systems because most microbes require pH-neutral conditions for optimal growth. The combination of $Ni_5P_4$ and $NiP_2$ can meet the MEC cost and catalytic performance requirements, on the one side, the transient metals could decrease the cost compared with the precious metals, on the other side, its outstanding performance of catalyzing hydrogen evolution that reported in previous studies could promisingly match the electron production rate from anode. Therefore, a composite of $Ni_5P_4$ and $NiP_2$ could be an alternative to noble-metal catalysts in a biosystem that focuses on hydrogen recovery from biomass.

In the conventional electrode preparation process, conductive binders are always used to immobilize nanostructured catalysts on the conductive substrate, which covers some active sites [19,20,25–27]. It has been shown that the conventional method cannot be used fabricate 3D structures such as NF. Instead, the transition metal oxide/hydroxide must be grown on the substrate and then subsequently converted. Multiple steps are required for electrodeposition and electroless plating, which are too moderate to directly deposit nickel phosphide [28–30]. Additionally, multiple steps are undesirable for practical commercial applications. Therefore, a straightforward synthesis method should be developed using phosphorous vapor to phosphide NF, which not only maintains the original 3D structure without conductive binders but also advances the commercial potential of MEC applications [31].

Herein, we developed a one-step phosphorization of NF using phosphorous vapor, and we successfully obtained an undamaged 3D structure and exposed the active sites on the peeled phosphide nanosheet matrix on the surface. The exposing facets were shown to favor the HER with an outstanding catalytic performance and good electron-transfer process kinetics. The practical performance in terms of hydrogen yield and hydrogen production rate was evaluated and compared with that for NF as the cathode material.

## 2. Experimental section

### 2.1. One-step synthesis of nickel phosphide

Nickel phosphide with NF was synthesized *in situ* in one step to obtain a 3D structure. The materials (NF vs. red phosphorous) were placed in the “U”-shaped glassy boat at a weight ratio of 0.58:1.67. The red phosphorous was stacked in the head section, and several square NF sheets (1 cm × 2 cm) were stacked together at the distance of 2 cm from the phosphorus. The boat filled with nickel and phosphorous was settled into the middle of the tube furnace to heat it under flowing gas. As the carrier gas, pure nitrogen steadily flowed over the boat at the 800 sccm/min. The temperature was programmed to rise up to 500 °C within 30 min by heating gradually. The samples were kept at 500 °C for 4 h and were naturally cooled down to the room temperature. (N.B.: since white phosphorous is extremely sensitive to oxygen, while the high temperature can transfer red phosphorous into white phosphorous, the entire process should be conducted under strictly sealed conditions without leaking oxygen.) The obtained catalyst is denoted by NF-P.

### 2.2. MEC construction and operation

A glassy cylinder was constructed and sealed with a top cap. The anode was made of carbon fiber, which was shaped like a brush with a diameter of 25 mm, with PANEX 33 160 K fibers (ZOLTEK), and all anode brushes were soaked in acetone for 24 h and subsequently heated in a muffle furnace at 450 °C for 30 min [32]. The cathode was the NF-P composite. To preserve the original 3D structure, a small skeleton was employed to fix the NF-P, as shown in Fig. S1. The emission gas was collected in a gas bag (0.2 L capacity, Dalian Delin Co. Ltd) that was connected to the top of the reactor. The Ag/AgCl reference electrode was used to determine the anode and cathode potentials. The working electrolyte was 50 mM phosphate-buffered solution (PBS) containing $Na_2HPO_4 \cdot 12H_2O$ (11.55 g/L), $NaH_2PO_4 \cdot 2H_2O$ (2.77 g/L), $NH_4Cl$ (0.31 g/L), and KCl (0.13 g/L). The acetate concentration was 1.5 g/L. All reactors were operated in the batch mode. The external voltage was 0.8 V and was supplied from the switching power supplier. The external ohmic resistance (10 Ω) was set in a closed circuit to obtain the working current.

*Measurements and calculation:* The current was automatically monitored by a Keithley instrument (2700, US). The gas composition (hydrogen) was detected by gas chromatography (GC) (EWAI, 4000A). All calculations associated with the MEC performance were based on a previous study [33]. The coulomb efficiency (CE) of the anode was the ratio of the total coulombic recovery from the current to the theoretical coulombs of acetate ($CE = It/Q_{acetate}$). The electron recovery at the cathode was determined by the total coulombs in hydrogen compared to the total coulombs in the current, according to:

$$\text{CER} = \frac{\frac{V_{hydrogen}}{V_m}F}{It},$$

where t F is the Faraday constant (96,485 C/mol), and $V_m$ represents the gas constant (22.4 L/mol).

The energy efficiency was evaluated with the following equation:

$$\text{Energy efficiency} = \frac{W_{hydrogen}}{W_U} = \frac{n \cdot \Delta H_{hydrogen}}{U_{external} \cdot I \cdot t},$$

considering the input electricity and the heat energy in the hydrogen (−237.1 kJ/mol). The hydrogen yield represents the conversion from acetate to hydrogen, where the theoretical ratio is 4 mol hydrogen/mole acetate.