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Ultrafine metal phosphide nanoparticles *in situ* encapsulated in porous N,P-codoped nanofibrous carbon coated on carbon paper for effective water splitting

Jin-Tao Ren [a, b], Ge-Ge Yuan [a, b], Chen-Chen Weng [a, b], Zhong-Yong Yuan [a, b, *]

[a] *National Institute for Advanced Materials, School of Materials Science and Engineering, Nankai University, Tianjin, 300350, China*
[b] *Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Nankai University, Tianjin, 300071, China*

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ABSTRACT

The rapid growth of environment pressures and fast depletion of fossil fuels compel public to pay more attention on developing affordable and efficient catalysts for renewable energy production. Metal (Co, Fe, Ni, etc.) phosphide nanoparticles uniformly encapsulated in porous N,P-codoped nanofibrous carbon coated on carbon paper (MeP@NPC/CP) are prepared through one-pot carbonization-phosphorization strategy, which are potential for effective electrocatalytic water reduction/oxidation reactions. The well-designed self-supported structure and the abundant accessible active centers together contribute to the high electrocatalytic performance for hydrogen and oxygen evolution. Remarkably, an alkaline electrolyzer assembled from CoP@NPC/CP as cathode and anode can afford the current density of 10 mA cm^{-2} at the voltage of 1.67 V for overall water splitting in alkaline media with excellent stability. The easily prepared route with suitable structural and textural properties endows this self-supported materials with versatile function as abundant metal catalysts for realistic energy conversion and storage systems.

1. Introduction

Owing to the energy crisis and environmental problems, rising attention has been concentrated on the clean and sustainable energy carries to replace fossil fuels. Hydrogen (H_2), as a promising fuel, has a high energy density and non-pollution [1–4]. Although various strategies have been employed to produce hydrogen, electrochemical water splitting is considered as a promising approach to produce hydrogen to meet the need of future energy demand, due to environmental-friendly and no emission of greenhouse gases [5–8]. The oxygen and hydrogen evolution reactions (OER and HER) constitute the overall splitting of water, wherein the noble metals, for instance, Pt, IrO_2 and RuO_2, exhibit high catalytic performance at low overpotentials, while the unfavorable cost greatly limits the extensive actual applications [9–11]. Therefore, the active, durable and low-cost electrocatalytic catalysts are needed urgently. Recently, many effects have been concentrated on transition metal electrocatalysts, including oxides, carbides, phosphides, nitrides and chalcogenides, which have exhibited promising catalytic capacity [7,12–15]. Among them, metal phosphides with superior electronic and catalytic properties have worked as a promising functional materials applied for catalysis, supercapacitor, Li-ion battery, and so on [13,15–17]. In addition, the similar working principle on the reversible binding of the hydrogen and catalysts makes the metal phosphides to great potency of HER and hydrodesulfurization (HDS). The utilization of inorganic phosphorization reagents under pyrolysis and organic chemicals through hydrothermal treatment are widely used strategies for the preparation of transition metal phosphides with different catalytic activities, but the associated harmfulness and complexity propose urgent demand to pursue an efficient alternative. Meanwhile, the unsuitable charge carriers derived from poor electrical conductivity and the insufficient active sites caused from limited textual properties widely present restraints for metal phosphide catalysts [18–20]. Nanostructuring to fabricate interconnected architecture provides the possibility to overcome the limitations of conductivity and active centers, and thus the enhanced catalytic performance could be obtained. However, though much process has been achieved for metal phosphides,

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* Corresponding author. National Institute for Advanced Materials, School of Materials Science and Engineering, Nankai University, Tianjin, 300350, China.
E-mail address: zyyuan@nankai.edu.cn (Z.-Y. Yuan).

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there also calls for novel synthesized strategy to fabricate metal phosphides to realize efficient electrocatalysis.

Featuring adjustable composition and structures, carbonaceous materials with heteroatoms doping have been widely performed for electrocatalytic reactions, including HER and OER as well. Generally, the hybridization of conductive carbonaceous materials with nonprecious transition metal materials can efficiently enhance the electrical conductivity of the hybrid materials and relieve the aggregation of metal nanoparticles, achieving the high electrocatalytic activity and operation stability. Up to now, the carbon nanotubes, graphene, carbon nanofibers and porous carbon have been employed as supports for the conjugation of metal-carbon hybrid catalysts. Specially, the utilization of carbonaceous materials as supporting species is an effective way to improve the corrosion susceptibility of metal phosphides, ensuring their utilization in acidic media for hydrogen production. However, the majority of metal-carbon hybrid materials were prepared in the form of powder, followed by coating on current collector by using of polymeric binders [21–23]. The whole process is not only complicate and complex to electrode fabrication but also fails to render poor mass/charge transport and enhanced resistance of catalysts. Therefore, the well-designed hierarchical porous and self-supported electrocatalysts with high electrical conductivity and intimate contact between catalysts and current collectors, leading to efficient activity and robust stability as well as versatile functions under different pH atmosphere, are urgently desired [14,24,25].

Under the guide of abovementioned features together, we herein rationally design and synthesize the self-supported transition metal (Co, Ni, Fe, etc.) phosphides–containing nitrogen and phosphorus co-doped carbon nanofibers (MeP@NPC/CP) through pyrolysis of the polymer (polyaniline - organophosphonic acid) that is coated on carbon paper (CP) by electropolymerization, which is used as bifunctional self-supported catalyst, revealing promising hydrogen evolution capacity in alkaline and acidic electrolyte. This synthetic strategy provides facile access to a homogeneous distribution of metal phosphide nanoparticles as well as nitrogen and phosphides atoms within the porous carbon matrix which not only ensures the abundant active sites for the catalytic process but also represents a novel synthesized strategy to synthesize hybrid materials with integrated configuration. Indeed, the arrangement of the fabricated CoP@NPC on carbon paper further promote the superiority of fabricated catalyst for electrochemical processes. In addition, significant property of this electrochemical strategy is the ability to tailor the microstructure by the modification of organophosphonic acid, obtaining favorable architecture of catalyst towards electrochemical reaction. Specially, the thin carbon layer coated on CoP nanoparticle surface during the pyrolysis process of precursor provides the protection to resistant the corrosion in acidic media. As a result, the as-prepared CoP@NPC/CP exhibits outstanding electrocatalytic feature towards overall water splitting with the cell voltage of 1.67 V to afford 10 mA cm^{-2} of current density in 1.0 M KOH, together with exceptional durability.

2. Experimental section

2.1. Synthesis of CoP@NPC hybrid carbon electrocatalyst on carbon paper

A piece of carbon paper was used as substrate for electrodeposition. Before each experiment, carbon paper was firstly immersed into HCl solution (10%), then washed with water. The CoP@NPC precursor was electrodeposited on the carbon paper in the 50 mL aqueous solution of mixture consisting of 4 mL aniline, 15 mL 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP, 50 wt%) and 2 mmol $CoCl_2$ at a potential of 0.8 V (vs. Ag/AgCl) for 30 min on a Zahner IM6eX (Zahner, Germany) electrochemical workstation, wherein carbon paper was directly used as working electrode, Pt wire and Ag/AgCl acted as counter and reference electrodes, respectively. The obtained material was pyrolyzed at 900 °C for 3 h in N_2 flow, named as CoP@NPC/CP, which can be directly used as working electrode for electrochemical reaction. The increased mass between pristine carbon paper and CoP@NPC/CP wias the loading mass of CoP@NPC electrode, and the loading mass is 1.2 g cm^{-2}.

2.2. Preparation of Co_2P nanoparticles

For the comparison purpose, the Co_2P nanoparticles were also prepared by direct phosphorization. Typically, 500 mg of NaH_2PO_2 and 200 mg of $CoCl_2$ were placed into the upstream side and the middle of the tubular furnace, and then heated to 350 °C for 2 h in the N_2 flow. Finally, the obtained materials was Co_2P nanoparticles, and named as Co_2P NPs.

2.3. Preparation of NPC/CP porous carbon electrocatalyst on carbon paper

The fabricated process was similar with the synthesis of CoP@NPC/CP, expect the addition of $CoCl_2$ in the mixture solution. The finally obtained material was named as NPC/CP.

2.4. Preparation of NC/CP porous carbon electrocatalyst on carbon paper

The fabricated process was similar with the synthesis of CoP@NPC/CP, expect the addition of $CoCl_2$ in the mixture solution, and using HCl to replace the HEDP. The finally obtained material was named as NC/CP.

2.5. Scratched CoP@NPC hybrid carbon materials coated on carbon paper.

The as-prepared CoP@NPC and NPC were carefully scraped off from the corresponding carbon paper, ultrasonically dispersed into the mixture of water and isopropanol (1 mL, $v/v = 1:1$) with 50 μL 5 wt% Nafion under sonication to obtain homogeneous ink, followed by directly dropping the obtained ink onto pristine carbon paper. The resulting electrode was placed in air to evaporate solvent for overnight with a loading mass of 1.2 g cm^{-2}, and named as scratched CoP@NPC.

2.6. Preparation of Pt/C on pristine carbon paper

50 mg Pt/C was dispersed in the mixture solution of water and isopropanol (1 mL, $v/v = 1:1$) with 50 μL 5 wt% Nafion solution and sonicated to obtain homogeneous ink. Then, the catalyst ink was drop-coated on carbon paper and followed by drying at room temperature overnight in air to evaporate solvent, which was named as Pt/C.

2.7. Physical characterization

Scanning electron microscopy (SEM) was carried out on a Jeol JSM-7500L microscope at 5 kV. Transmission electron microscopy (TEM) was employed on a Jeol JSM-2800 F microscope at 200 kV. X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Focus diffractometer with Cu-$K\alpha$ radiation ($\lambda = 0.15418$ nm) operated at 40 kV and 40 mA. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo Scientific ESCALAB 250Xi spectrometer equipped with a monochromatic Al-$K\alpha$ X-ray source (1486.6 eV). N_2 adsorption-desorption isothermals were measured