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Controllable synthesis of Co_2P nanorods as high-efficiency bifunctional electrocatalyst for overall water splitting

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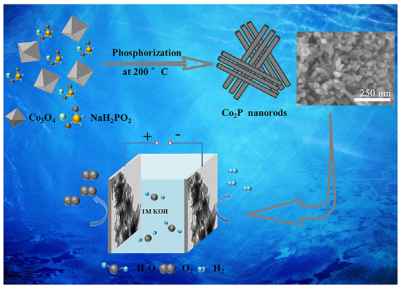
HIGHLIGHTS

- Co_2P nanorods with the diameter and length of around 200 nm and 10–20 nm.
- Firstly prepared via a substrate- and template-free facile phosphating reaction.
- With the increase in active area and the minimum in charge transfer resistance.
- Displaying superior bifunctional activity and stability for water splitting.
- Paving the way to in large scale obtain highly active and durable TMPs.

GRAPHICAL ABSTRACT



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ABSTRACT

One-dimensional transition metal phosphides with large specific surface areas and efficient conductivity have the great potential in both hydrogen and oxygen evolution reaction (HER and OER) as bifunctional catalysts, which are at the heart of water splitting. Herein, we firstly report the controllable synthesis of Co_2P nanorods through a substrate- and template-free facile phosphating reaction. Electrochemical test results reveal that the synthesized Co_2P nanorods exhibit superior bifunctional activity with overpotentials of 87 mV for HER and 310 mV for OER at 10 mA cm^{-2}, respectively, relative to Co_2P/CoP branched nanostructure, CoP nanoparticles and commercial Co_2P in alkaline media. In addition, the bifunctional Co_2P nanorods catalysts enable overall water splitting with a cell voltage of 1.65 V to achieve 10 mA cm^{-2} and stabilized potentials at different current densities testing over 24 h. Further analysis demonstrate that the remarkably bifunctional activity is contributed to high charge transfer efficiency, large contact area with electrolyte and a large number of exposed active sites provided by the rod-like nanostructure. This work should shed light on an industrialized pathway for the future design of phosphide catalysts to apply to overall water splitting even other emerging energy devices.

1. Introduction

Hydrogen energy has been considered as a promising alternative to fossil fuels to resolve current environmental problem [1–3].In many emerging hydrogen production technologies, water electrolysis is an efficient and potential way which consists of two half-reactions, i.e., HER in the cathode and OER in the anode, yet needs large voltage to drive. The practical voltage was reported at the range of 1.8–2.0 V which is much higher than theoretical value of 1.23 V [4–7]. At present, precious metals (e.g., Pt-based metals [8]) and metal oxides (e.g., Ru/

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Ir-based oxides [9,10]) have been viewed as state-of-the-art catalysts for HER and OER, respectively. However, the scarce reserves and high cost [11], as well as the limited bifunctional activity hindered their practical applications. Thus, it is of great significance to develop advanced bifunctional catalysts toward HER and OER with high efficiency and low cost.

For the past few years, much effort has been devoted to develop transition metal phosphides (TMPs), due to their high abundance, excellent electronic structure and prominent chemical stability [12–15]. Particularly, cobalt phosphides behave well in simultaneously optimizing HER [16,17] and OER [18,19] process. Among the investigation of morphology and phase for cobalt phosphides catalyst as reported in literature [20,21], the nanostructure rather than phase exerts much more impact on the catalytic performance. To further promote the catalytic property, the surface morphology and structure were extensively explored [22–24]. In particular, one-dimensional nanostructures have attracted increasing attention, owing to the large number of active sites exposed, contact area with electrolyte solution improved and electron transfer path shortened [25–27]. At present, the synthetic strategies to successfully obtain 1D nanostructure can be divided into liquid-phase reaction (e.g., wet-chemical solution [20] and hydrothermal [28] strategy) and solid-state reaction (e.g., template-assisted [29] and substrate-assisted synthesis [27]), while most of which involved a variety of drawbacks, For example, it is of great necessity to maintain harsh reaction conditions in liquid-phase reaction, and template and substrate required in solid-phase reaction lead to low yield, which is not adequate for the need of large-scale production. It is highly desirable but still remains challenging to design a controllable and mild synthetic route towards TMPs 1D nanocatalysts for overall water splitting.

In this work, we first propose a facile and productive method to controllably synthesize Co_2P nanorods without templates and substrate. Meanwhile, the contrast samples of Co_2P/CoP branched nanostructures and CoP nanoparticles were also prepared by only employing various phosphating temperatures. Electrochemical test results illustrate that the Co_2P nanorods exhibit bifunctional catalytic performances with overpotentials of 87 mV for HER and 310 mV for OER to achieve 10 mA cm^{-2} and their corresponding Tafel slopes of 60.3 and 73.2 mV dec^{-1}, respectively, which are superior to Co_2P/CoP branched nanostructure, CoP nanoparticles, commercial Co_2P and even exceeds other transition metal phosphides previously reported [23,30]. Moreover, the Co_2P nanorods enable the assembly of alkaline electrolyzer with a lower potential of 1.65 V at 10 mA cm^{-2}, a faradaic efficiency of 100%, and a longer catalytic lifetime over 24 h at large current density of 50 mA cm^{-2}. The remarkable bifunctional activity is contributed to the 1D nanostructure exposing a large number of active sites, providing a sufficient interfacial contact area with the electrolyte, and the unobstructed electronic conduction path along the interior of nanorods. This study paves the way to in large scale obtain highly active and durable phosphide electrocatalysts for practical clean energy devices.

2. Experimental

2.1. Materials

Cobalt nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$, 99.99%), anhydrous sodium nitrate ($NaNO_3$, 99.0%), ammonium hydroxide ($NH_3{\cdot}H_2O$, 25–28%), sodium hypophosphite ($NaH_2PO_2{\cdot}$ H_2O, 99.0%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Commerical cobalt phosphide (Co_2P) and carbon fiber paper was obtained from Alfa Aesar Co., Ltd. Isopropyl alcohol and cobalt oxide were purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. Deionized water (18.2 MΩ cm) used was obtained via Millipore, an ultrapure water system. Nafion perfluorinated resin solution was obtained from Sigma Aldrich Co., Ltd. Rhodium dioxide (RuO_2, 99.95%) was purchased from Aolamas Reagent Co., Ltd. Pt/C (20 wt%) catalyst was purchased from Shanghai Hesen Electric Co., Ltd. Potassium hydroxide (KOH, 95%) was obtained from Aladdin Reagent Co., Ltd. All chemicals were used as received without further purification.

2.2. Synthesis of Co_3O_4 octahedral nanoparticles

Based on our previous research [31], Co_3O_4 precursor was synthesized via hydrothermal method. 0.215 g of NaNO3 was dissolved in the mixed solution of 5 mL of $Co(NO_3)_2$, (1 M) and 10 mL of DI water. The mixture was stirred until NaNO3 was completely dissolved. Then, 10 mL of $NH_3{\cdot}H_2O$ was dropped in to form cobalt ammonium complex. After being stirred for 4 h, the mixed solution was sealed into a 100 mL Teflon-lined stainless steel autoclave and maintained at 155 °C for 12 h. By the time autoclave had cooled to room temperature, the products were washed with DI water and ethanol for several times. The Co_3O_4 octahedral nanoparticles were finally obtained by drying at 60 °C overnight. (Fig. S2)

2.3. Synthesis of Co2P nanorods

50 mg of Co_3O_4 octahedral nanoparticles and 330 mg of $NaH_2PO_2{\cdot}$ H_2O (the mole ratio of P to Co is 5:1) were added in 25 ml of DI water and the mixture was powerfully sonicated for 10 min, and then the mixture was dried through a freeze-drying process. The obtained powder was thermally treated at 200 °C for 1 h under an Ar static atmosphere. After cooling to room temperature, the Co_2P nanorods were collected by washing with DI water for three times and drying by lyophilization overnight.

Through tuning reaction temperatures (250 and 350 °C), we also obtained Co_2P/CoP branched nanostructure and CoP nanoparticles. Through tuning the mole ratio of P to Co (10 and 20), we obtained two different phase proportion samples: 49.0% Co_2P/CoP nanorods and 17.7% Co_2P/CoP nanorods.

2.4. Materials characterization

The phases of all samples were determined by powder X-ray diffraction (XRD) performed on Bruker/D8 Advance X-ray diffractometer (Cu Kα radiation). The morphologies and surface chemical valence states were characterized using transmission electron microscopy (TEM, JEOL JEM-2100F, 200 kV) and X-ray photoelectron spectroscopy (XPS, an incident radiation of Monochromatic Al KR X-rays), respectively. The special surface areas were measured by Brunauer–Emmett–Teller (BET) performed on fully automatic sorption analyzer (Micromeritics U.S.) at liquid-N_2 temperature.

2.5. Electrochemical measurements

Catalytic performances of the mentioned catalysts towards HER and OER were evaluated on IviumStat electrochemical workstation in a typical three-electrode system and a two-electrode electrolyzer was assembled for overall water splitting in 1.0 KOH at room temperature. The catalyst ink was prepared by dispersing 10 mg of catalysts powder in the mixture of 750 μl of DI water, 250 μl isopropyl alcohol and 100 μl of Nafion (wt 5%) with the assistance of sonication for 30 min. The catalyst electrodes were fabricated by drop-castting of 150 μl of catalytic ink onto 1 cm × 1 cm carbon paper with a loading of 1.36 mg cm^{-2} (Fig. S1).

In the three-electrode configuration, the catalytic electrode, carbon rod and saturated calomel electrode (SCE) were served as work electrode, counter electrode and reference electrode, respectively. Polarization curves of various samples were collected by linear sweep voltammetry (LSV) and corrected with IR compensation according to the equation $E_{\text{Corrected}} = E_{\text{Raw}} - IR_s$ ($E_{\text{Corrected}}$, E_{Raw}, I, R_s is the compensating potential, measured potential, measured current and electrolyte resistance, respectively.). All the potentials were calibrated by