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Facile formation of 2D $Co_2P@Co_3O_4$ microsheets through *in-situ* toptactic conversion and surface corrosion: Bifunctional electrocatalysts towards overall water splitting

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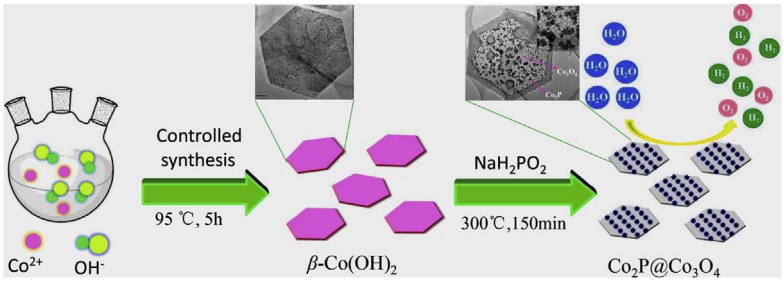
HIGHLIGHTS

- 2D $Co_2P@Co_3O_4$ microsheets was prepared through in-situ toptactic conversion.
- Bifunctional electrocatalysts present effective overall water splitting.
- Co_2P nanoparticles (5 nm) enlarges the exposure of electroactive sites and surfaces.

GRAPHICAL ABSTRACT



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ABSTRACT

Exploring efficient non-precious electrocatalysts for both the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) is crucial for many renewable energy conversion processes. In this work, we report that 2D $Co_2P@Co_3O_4$ microsheets can be prepared through an *in-situ* toptactic conversion from single-crystal β-$Co(OH)_2$ microplatelets, associated with a surface phosphatization and corrosion process. The resultant $Co_2P@Co_3O_4$ 2D hybrid materials can further serve as self-supported bifunctional catalytic electrodes to drive the overall water splitting for HER and OER simultaneously, with low overpotentials and high long-term stability. Furthermore, a water electrolyzer based on $Co_2P@Co_3O_4$ hybrid as both anode and cathode is fabricated, which achieves 10 mA cm^{-2} current at only 1.57 V during water splitting process. Therefore, this work provides a facile strategy to obtain 2D Co_2P-based micro/nanostructures, which act as low-cost and highly active electrocatalysts towards overall water splitting application.

1. Introduction

Development of advanced renewable energy can serve as cost-effective and environmentally responsible alternatives to conventional energy [1]. Hydrogen generated from water splitting process is a promising way to get clean and sustainable energy [2]. An efficient and

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abundant water electrolysis device can act as important components for sustainable hydrogen evolution [3]. The key to reduce energy supply and maximize the water splitting efficiency lies on developing earth-abundant and stable electrocatalyst to drive reactions for the simultaneous generation of hydrogen and oxygen gases in the same electrolyte [4,5]. In this content, Co-based electrocatalysts have received considerable attention from the research community because of its high-performance and earth-abundant characteristics [6–9]. For example, in past few years, Co-based phosphides (such as CoP) with different morphologies, including nanowires [10], nanosheets [11], nanoparticles [12], nanotubes [13] have been of great interest as electrocatalysts because they exhibit intriguing hydrogen evolution reaction (HER) activities in acidic conditions. Meanwhile, Co_2P with different structures and arrangement fashions have been reported as efficient electrocatalyst for HER, such as nanorods [14], nanowires [15] and 3D nanoporous structures [16]. Recently, cobalt oxides/(oxy)hydroxides have present better catalytic activities in OER [17,18]. This means that cobalt-based micro/nanostructures with diverse active species are potentially capable of accomplishing the overall splitting to produce both hydrogen and oxygen [19–21]. However, to date, how to integrate the advantages of Co-based hybrids with suitable morphologies for desirable HER and OER remains a significant challenge because of the lack of effective synthesis methods.

From a structural and morphological perspective, two-dimensional (2D) micro/nanostructures (such as nanosheets and nanoplatelets) have emerged as a fascinating class of electrocatalysts for water splitting during last one decade. For example, $NiCo_2O_4$ nanosheets [22], Ni-Fe-base layered double hydrocides [23], and rhombus-shaped Co_3O_4 nanosheets [24], have been demonstrated as highly active electrocatalysts for oxygen evolution reaction (OER). Additionally, 2D NiFeS [25] and Ni_3FeN [26] have also been synthesized through a topotactic conversion from a hydroxide precursor, which exhibited high active electrocatalysis for water splitting. Generally, the high electrocatalytical activities are related to their tunable chemical compositions, rich catalytic active sites, high electrical conductivity and easy adsorption of H_2O [27–29]. Therefore, the construction of 2D micro/nanostructures supplies an effective platform to develop excellent electrocatalysts for both HER and OER.

In this work, we report the formation of 2D $Co_2P@Co_3O_4$ nanohybrids through a topotactic conversion reaction, based on the surface corrosion of hexagonal single-crystal β-$Co(OH)_2$ platelets with NaH_2PO_2 under Ar atmosphere at 300 °C, in which the Co_2P nanoparticles are highly dispersed and immobilized onto the Co_3O_4 surface (a schematic illustration was shown in Scheme 1, see the experimental section for detailed information). The as-prepared 2D $Co_2P@Co_3O_4$ nanosheets serve as efficient catalysts for overall water-splitting with potentials of 1.57 V at 10 mA cm^{-2} in 1 M KOH. Therefore, this work not only supplies a facile way to obtain 2D Co_2P-based micro/nanostructures, but also develops new types of bifunctional electrocatalysts towards overall water-splitting application.

2. Experimental

2.1. Synthesis of β-Co(OH)$_2$

β-$Co(OH)_2$ hexagonal platelets were prepared from a solution of cobalt chloride under a hydrolysis of HMT [62]. Cobalt chloride ($CoCl_2$ $6H_2O$, 5 mM) and hexamethylenetramine (HMT, 90 mM) were dissolved in a flask of deionized water (500 mL). The solution was refluxed at 95 °C for 5 h under continuous stirring in a N_2 atmosphere. After centrifuged at 3000 rpm for 10 min and washed with deionized water for three time and ethanol one time, the pink colloid of brucite β-$Co(OH)_2$ was collected. Then the colloid was dried in an oven at 50 °C overnight.

2.2. Synthesis of $Co_2P@Co_3O_4$

For the formation of hexagonal layered $Co_2P@Co_3O_4$ hybrid, 50 mg of β-$Co(OH)_2$ was put into two separate positions in a porcelain boat with NaH_2PO_2. The mass ratio for $Co(OH)_2$ to NaH_2PO_2 is 1:40. Subsequently, the samples were heated at 300 °C for 150 min with an increasing temperature rate of 2 °C/min under a slow Ar blowing at a rate of 10 mL/min, and then naturally cooled to ambient temperature. Finally, black product was collected. The sample is named as $Co_2P@Co_3O_4$. Co_3O_4 was synthesized as the same prepared condition without NaH_2PO_2 in air.

2.3. Materials characterization

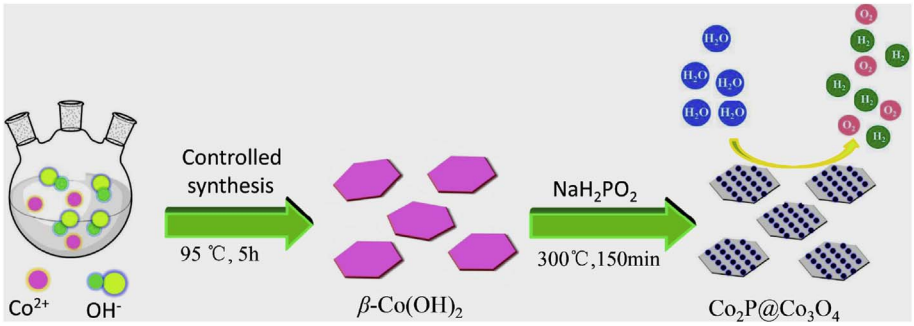
The crystal structure and phase purity of the resultant samples were analyzed by powder X-ray diffraction (PXRD) recorded on a Bruker D8 Advance X-ray diffractometer using Cu-Kα radiation. The morphology and microstructure of the samples were observed by scanning electron microscopy (JEOLS-4800) and transmission electron microscopy (JEOL JEM-2010). The surface composition was analyzed by X-ray photoelectron spectroscopy (XPS) on ESCALAB 250 electron spectrometer.

2.4. Preparation of the working electrode

4 mg of catalyst and 1 mg of acetylene black were dispersed in a mixture of 970 μL water-ethanol solution ($V_{water}/V_{ethanol}$ = 70/27) and 30 μL of Nafion solution (5% wt, Sigma). After ultrasonical dispersion of 30 min, 5 μL of catalyst ink was loaded into a glass carbon electrode with diameter of 3 mm (the loading of catalyst was 0.285 mg cm^{-2}).

2.5. Electrochemical measurements

Electrochemical tests were carried out in a standard three electrode system controlled by a CHI 660C workstation. Catalyst was loaded on the glass carbon electrode (3 mm in diameter) as the working electrode; a graphite rod was as the counter electrodes and Ag/AgCl (saturated KCl) was as reference electrode. The reference was calibrated and converted to revisable hydrogen electrode (RHE). Aqueous 1 M KOH



Scheme 1. Schematic illustration for the synthesis of $Co_2P@Co_3O_4$.