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Short communication

Porous cobalt phosphide nanorod bundle arrays as hydrogen-evolving cathodes for electrochemical water splitting

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An advanced electrode composed of porous CoP nanorod bundle arrays (NBAs) on Ti plate was fabricated by using Co_3O_4 NBAs as precursors and developed as a robust self-supported hydrogen-evolving cathode for electrochemical water splitting. Such electrode exhibited remarkable activity for hydrogen evolution reaction in a wide pH range, affording a low onset overpotential, small Tafel slope, and long-term stability.

1. Introduction

Hydrogen is considered as a promising alternative to fossil fuels in the future due to its zero carbon emission. The electrochemical water splitting is an important process to produce hydrogen. However, both half-reactions of water splitting still remain technical challenges. Platinum is most effective for hydrogen evolution reaction (HER), but low reserve and high price limit its practical application. Although nickel and its alloys are potential materials for HER in alkaline media, they experience extensive deactivation during alkaline water electrolysis [1]. In addition to the carbon matrixes-based electrocatalysts [2,3], metal phosphides have also received great attention and emerged as new alternatives for HER. The intense interest is driven by their intrinsically charged natures, where metal and nonmetal components have partial positive and negative charges, respectively, analogous to those of active centers (i.e. proton acceptors and hydride acceptors) in hydrogenase, as demonstrated by both theoretical calculations [4] and experimental investigations [5]. Besides, phosphorus promotes the activity of primary metal through altering its electronic and geometric properties [6,7]. Indeed, metal phosphides including CoP [8–10], Ni_2P [5,11], FeP [12], MoP [13], Cu_3P [14] and WP_2 [15], and their composites [2,16,17] have shown remarkable HER performances.

Recently, Sun et al. have demonstrated that metal phosphides can be transformed from the corresponding metals [18], metal oxides [9, 19–21] and hydroxides [11,22,23]. Our group also found that the HER-active Ni_2P can be chemically converted from a metal-organic framework [24]. Herein, we report the direct synthesis of porous CoP nanorod bundle arrays (NBAs) on Ti plate from Co_3O_4 NBAs and utilize them as robust self-supported hydrogen-evolving cathodes for electrochemical water splitting in a wide pH range, achieving a low onset overpotential, small Tafel slope, and long-term stability.

2. Experimental

Typically, $Co(NO)_3 \cdot 6H_2O$ (4 mmol), NH_4F (16 mmol) and urea (20 mmol) were dissolved in 70 mL of distilled water and stirred for 10 min. The solution was transferred into a 100 mL autoclave, and a piece of cleaned Ti plate (3 cm × 4 cm) was immersed into the solution. The autoclave was maintained at 120 °C for 9 h. The obtained product was rinsed with distilled water, dried at 60 °C for 6 h and annealed at 350 °C for 2 h in air. To convert Co_3O_4/Ti into CoP/Ti, the Co_3O_4/Ti and NaH_2PO_2 were placed at two separate positions in a porcelain boat with NaH_2PO_2 at the upstream side of the quartz tube, and annealed at 300 °C in argon atmosphere for 2 h [17].

The morphology, microstructure and composition of samples were characterized by X-ray diffraction (XRD, Rigaku Dmax/Ultima IV), scanning electron microscopy (SEM, Hitachi S4800 and JEOL JSM-6510LV), transmission electron microscopy (TEM, FEI Tecnai G20) and X-ray photoelectron spectroscopy (XPS, Perkin-Elmer PHI 5000C).

All electrochemical measurements were performed in a typical three-electrode mode using CoP/Ti (loading: 1.96 mg cm^{-2}) as the work electrode, a Pt wire as the counter electrode and an Ag/AgCl as the reference electrode. The 0.5 M H_2SO_4 (pH 0), 1.0 M phosphate buffer (PBS, pH 7), or 1.0 M KOH (pH 14) were used as electrolytes. Before the electrochemical measurement, the electrolyte was degassed by bubbling argon for 30 min. All potentials measured were converted to the reversible hydrogen electrode (RHE) scale ($E_{RHE} = E_{Ag/AgCl} + 0.197 + 0.059pH$). The mass loading of CoP on Ti plate was calculated from the weight difference between the pristine Ti plate and CoP/Ti.

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3. Results and discussion

A general SEM image (Fig. 1a) of Co_3O_4 NBAs/Ti confirms that the Ti plate is covered by numerous nanorod arrays with high density. The magnified image (Fig. 1b) presents that the structure actually consists of bundles of smaller nanorod subunits. These nanorods have diameters of 50–110 nm (inset). SEM image (Fig. 1c) of CoP NBAs reveals that they effectively preserve the morphological profile of Co_3O_4 NBAs. Close observation (Fig. 1d) reveals the porous morphology of CoP NBAs, consisting of several nanoparticles and pores on rough surfaces. TEM image (Fig. 1e and f) of CoP NBAs further confirms their nanorod bundle structures. The bundles consist of aligned porous nanorods with about 90 nm in diameter. The magnified image (Fig. 1g) suggests that nanorods are constructed from numerous aggregated nanoparticles with sizes of 10–20 nm. HRTEM image (Fig. 1h) displays the distance between lattice fringes is 0.19 nm, corresponding to the (211) plane of CoP. EDX spectrum confirms the presence of Co, P and Ti elements in CoP NBAs/Ti (not shown). The estimated atomic ratio of Co to P is consistent with stoichiometric CoP. SEM-EDX elemental mapping images (not shown) suggest that both Co and P elements are uniformly distributed in CoP NBAs. XRD patterns (Fig. 1i) clearly reveal that Co_3O_4 NBAs change completely into CoP phase.

Before polarization curve measurements, cyclic voltammetry (CV) curves were performed to stabilize CoP NBAs in electrolytes (Fig. 2a). Fig. 2b shows the polarization curves of CoP NBAs/Ti, Co_3O_4 NBAs/Ti, commercial Pt/C and bare Ti plate in 0.5 M H_2SO_4. Pt/C presents the expected HER activity. Bare Ti plate is totally inactive for HER and Co_3O_4 NBAs/Ti shows negligible activity. In contrast, CoP NBAs/Ti delivers a small onset potential (conventional calculation from extrapolation of polarization curve [25]) of ~155 mV and achieves a sharp increase in cathodic current at more negative potentials, reflecting its excellent HER activity. Furthermore, CoP NBAs/Ti at 10 mA cm^{-2} affords an overpotential of ~203 mV, which is lower than that of Co_3O_4-derived CoP nanoparticles (~212 mV [2], ~226 mV [9], ~221 mV [19]) and CoP/graphene [16], and compares favorably to other reported metal phosphides [15,24,26]. Also, CoP NBAs exhibit a Tafel slope of 40 mV dec^{-1} (Fig. 2c), which is much smaller than that of the best reported CoP [8–10] and Co_3O_4-derived CoP catalysts [2,16], implying more favorable HER kinetics. To further explore the electrocatalytic activity, turnover frequency (TOF) is estimated by calculating the number of active sites from the CV sweep [8,27]. CoP NBAs/Ti shows a TOF of 4.36 s^{-1} at an overpotential of 250 mV, which is close to reported values for CoP nanostructures [8,27]. The durability was tested by cycling CoP NBAs/Ti continuously at a scan rate of 100 mV s^{-1} in 0.5 M H_2SO_4 (Fig. 2d). After 3000 cycles, the overpotential to attain a current density of 10 mA cm^{-2} increases by less than 10 mV. The chronoamperometric measurement on CoP NBAs/Ti further confirms its long-term stability (inset), showing cathodic current attenuation less than 10% within 10 h.

We further examined the HER activity of CoP NBAs/Ti in alkaline media (Fig. 2e). In 1.0 M KOH (pH 14), it affords an onset overpotential of ~96 mV and a Tafel slope of ~115 mV dec^{-1}. The HER current generated by CoP NBAs/Ti at 250 mV sustains about 78% after 1000 cycles. We also studied the HER activity of CoP NBAs/Ti under neutral condition (Fig. 2f). In 1.0 M PBS (pH 7), it achieves an onset overpotential of ~126 mV, a Tafel slope of ~116 mV dec^{-1} as well as a good long-term stability (~12% of current decay after 3000 cycles at 250 mV). Notably, CoP NBAs/Ti delivers lower onset overpotential in alkaline and neutral conditions but larger Tafel slope compared with those in acidic condition. This result is consistent with the Ni_2P/Ni electrode [28]. Additionally, SEM and XRD (Fig. 1i) results indicate that CoP NBAs/Ti preserves original morphology and crystalline structure after cycling test in acidic

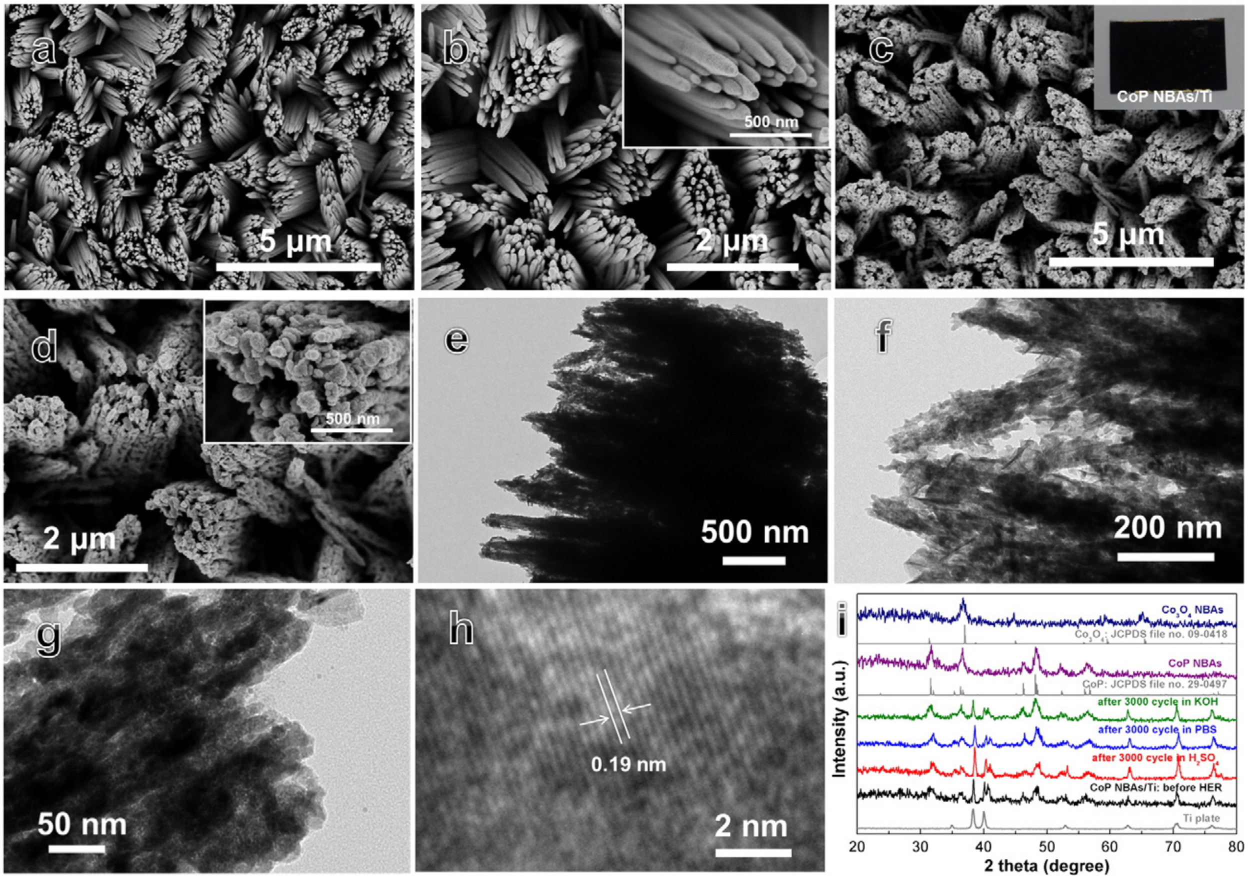

Fig. 1. SEM images of Co_3O_4 (a, b) and CoP NBAs (c, d). TEM (e–g) and HRTEM (h) images of CoP NBAs. XRD patterns (i) of Co_3O_4, and CoP NBAs before and after cycling test under different conditions.