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From water reduction to oxidation: Janus Co-Ni-P nanowires as high-efficiency and ultrastable electrocatalysts for over 3000 h water splitting

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HIGHLIGHTS

- Co-Ni-P nanowire arrays are grown on Ni foam forming an integrated electrode.
- The electrode can catalyze both H_2 and O_2 evolution showing bifunctionality.
- An electrolyzer is assembled using two symmetrical integrated electrodes.
- The electrolyzer shows high energy efficiency for overall water splitting.
- The electrolyzer can sustain 3175 h at 100 mA cm^{-2} without degradation.

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ABSTRACT

Vertically-aligned cobalt nickel phosphide nanowires (Co-Ni-P NWs) are synthesized on Ni foam by phosphorizing cobalt carbonate hydroxide precursor NWs in red phosphorous vapor at an elevated temperature. The as-fabricated self-supported integrated electrode (Ni@Co-Ni-P) exhibits outstanding electrocatalytic activity for the hydrogen evolution reaction (HER) in alkaline solution, delivering a cathodic current density of 100 mA cm^{-2} at a small overpotential of 137 mV and a Tafel slope of 65.1 mV dec^{-1}. Furthermore, the electrode shows remarkable catalytic performance towards the oxygen evolution reaction (OER), affording an anodic current density of 90.2 mA cm^{-2} at an overpotential of 350 mV, superior to many other transition metal based OER catalysts. Given the well-defined bifunctionality, an alkaline electrolyzer is assembled using two symmetrical Ni@Co-Ni-P as the cathode and anode, respectively, which demonstrates outstanding catalytic performance for sustained water splitting at varying current densities from 10 to 240 mA cm^{-2}. Significantly, the Ni@Co-Ni-P electrolyzer is able to operate for 3175 h (*ca.* 132 days) without degradation at an industry-relevant current density of 100 mA cm^{-2}, leading to exceptionally high H_2 production rate of 311 mmol h^{-1} $g^{-1}_{catalyst}$ cm^{-2} with an energy efficiency of 76% at ca. 1.9 V.

1. Introduction

Exploitation of abundant yet intermittent renewable energy sources (e.g., sunlight, wind, waves) requires efficient and robust energy storage technologies [1–4]. Electrochemical water splitting has emerged as a promising technique to convert electricity harvested from renewable sources into high-purity hydrogen (H_2) fuel. As a clean energy carrier, H_2 can be stored, transported, and consumed without producing greenhouse gases [5–7]. Therefore water splitting has been proposed to be a core clean energy technology enabling a hydrogen economy in the future [7–9].

Water splitting is composed of two half reactions: the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER) occurring at cathode and anode, respectively, both of which

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contribute to the overall efficiency of water electrolysis. The sluggish kinetics of both reactions necessitate the development of efficient electrocatalysts to reduce the overpotentials [10–13]. Currently, precious metal Pt and noble metal oxides (RuO_2 and IrO_2) are the state-of-the-art electrocatalysts for the HER and the OER, respectively. However, the scarcity, high cost and limited durability of these noble metal catalysts severely restrict their widespread implementation in mass production of H_2 through water splitting on a global scale [14]. In this context, the development of novel, cost-effective and highly efficient water splitting catalysts, particularly those based on earth-abundant elements, has recently attracted significant research interest [14–17]. For example, various transition metal sulfides, selenides, nitrides, carbides, borides and phosphides have been explored as HER electrocatalysts mostly in strong acidic electrolytes, including MoS_2 [18–20], WS_2 [21–23], MS_2 and MSe_2 (M = Fe, Co, and Ni) [24], $MoSe_2$ [25,26], MoN [27], $NiMoN_x$ [28], MoC and MoB [29], MoP [30,31], CoP [32–36], Ni_2P [37,38], Ni_5P_4 [39,40], FeP [41,42], CoPS [43], etc. On the other hand, transition metal oxides [44–46], hydroxides [47–50], phosphates [51], and perovskite oxides [52] have been recently identified as promising OER electrocatalysts in alkaline electrolytes. However, most of these catalysts are generally prepared in the form of nanopowders that are prone to agglomerate and show high series resistance. Additionally, practical utilization of these powder-like catalysts requires grafting them onto current collectors using binder additives, after which the intrinsic catalytic activity and durability could deteriorate. Therefore, tremendous efforts have recently been devoted to synthesizing nanostructured catalysts directly on current collectors (e.g., nickel foam, carbon paper) to obtain self-supported three-dimensional (3D) integrated electrodes, enabling their direct use in water electrolyzers and photoelectrochemical cells [35–37,44]. More importantly, to accomplish overall water splitting, coupling of HER and OER catalysts in the same electrolyte is highly desirable. Currently, the prevailing approaches often give rise to incompatible integration of HER and OER catalysts and thus lead to inferior overall water splitting performance [5,12]. In this respect, the emerging bifunctional Janus catalysts capable of catalyzing both the HER and the OER in the same electrolyte have become greatly attractive, because the use of such catalysts would significantly simplify the design and construction of water splitting devices and potentially lower production cost. Notwithstanding recent remarkable progress in water splitting catalysts, there are by far only few efficient bifunctional earth-abundant catalysts that are active for both the HER and the OER in the same electrolyte [1,5,12,39,47,53–55]. Moreover, in most cases the reported bifunctional-catalyst-enabled overall water splitting was only evaluated at a low current density relevant to solar water splitting (e.g., 10 mA cm^{-2}), with a limited durability test (<30 h). For industry-relevant electrochemical water splitting, electrolyzers must be able to operate at much higher current densities (e.g., $\geq$100 mA cm^{-2}) to attain a high H_2 production rate and meanwhile have excellent stability and long enough lifetime. However, fabrication of bifunctional catalysts that can sustain at high current densities without degradation for sufficiently long time remains very challenging.

In this article, we report the fabrication of self-supported 3D electrodes covered with densely-packed, vertically-aligned Co-Ni-P ternary nanowires (Ni@Co-Ni-P). We demonstrate that the Ni@Co-Ni-P electrode exhibits outstanding electrocatalytic performance towards both the HER and the OER, showing well-defined bifunctionality. Furthermore, we construct an electrolyzer using two symmetrical Ni@Co-Ni-P electrodes as cathode and anode, respectively, and test its overall water splitting performance in alkaline solution. The electrolyzer is able to work at 10 mA cm^{-2} with an energy efficiency as high as 91% for 528 h without discernible performance degradation. Significantly, even at 100 mA cm^{-2} the electrolyzer is still capable of splitting water at an efficiency of 76% for up to 3175 h (*ca.* 132 days) with no degradation, showing the best ever durability among the noble-metal-free HER or OER electrocatalysts reported to date. To the best of our knowledge, this is the first report on the alkaline electrolyzers which can constantly split water at high current densities for over 3000 h.

2. Experimental

2.1. Chemicals and materials

Red phosphorous (P $\geq$ 97.0%), cobalt (II) nitrate hexa-hydrate ($Co(NO_3)_2\cdot 6H_2O$, 98%), urea, ammonium fluoride ($NH_4F \geq 98.0\%$) and potassium hydroxide pellets (KOH $\geq$ 85%) were purchased from Sigma-Aldrich, and used as received without any further purification. Ni foam with a thickness of 0.3 mm and 110 ppi (pore per square inch) was used. Deionized (DI) water from a Millipore system (18.2 MΩ cm) was used for solution preparation.

2.2. Growth of cobalt carbonate hydroxide hydrate (CCHH) precursor nanowires on Ni foam (Ni@CCHH)

CCHH precursor nanowires (NWs) were synthesized on Ni foam by adapting a previous work for growing similar precursor NWs on carbon substrate [43]. In a typical synthesis, $Co(NO_3)_2\cdot 6H_2O$ (2 mmol), NH_4F (5 mmol) and urea (10 mmol) were dissolved in 40 mL of DI water under vigorous stirring for 30 min, resulting in a homogenous pink solution. Next, the solution was transferred to a Teflon-lined autoclave (45 mL). A piece of Ni foam (3.4 × 3.4 cm) was cleaned by ultrasonication successively in 6 M HCl, water and acetone for 10 min each time, and then dried under vacuum at 60 °C. The clean Ni foam was completely immersed in the pink solution and placed against the inner wall of the Teflon liner. The autoclave was sealed and maintained at 120 °C for 6 h. After cooling the autoclave down to room temperature, the foam was taken out and thoroughly rinsed several times with DI water and acetone, and subsequently dried under vacuum at 60 °C.

2.3. Fabrication of self-supported Ni@Co-Ni-P electrodes

The as-fabricated Ni@CCHH foam was loaded in a ceramic boat, and 3.0 g of red P powder was placed 0.5 cm away from the foam at the upstream side. Afterwards, the ceramic boat was put into a tube furnace (Carbolite). The furnace was then purged with nitrogen (N_2 99.999%), vacuumed for 30 min, heated to 500 °C at a ramping rate of 5 °C min^{-1}, and maintained at this temperature for 3 h. Finally, the furnace was naturally cooled down to room temperature. The N_2 flow (1000 sccm) and vacuum pumping were maintained throughout the whole process. The obtained Ni@Co-Ni-P foam was thoroughly washed with water and acetone, and then dried at 60 °C under vacuum and stored in a vacuum desiccator at room temperature. The loading mass of Co-Ni-P NWs on Ni foam is *ca.* 6.0 mg cm^{-2}.

2.4. Synthesis of CoP nanowire powders

CCHH precursor NWs were prepared in the absence of Ni foam under the similar hydrothermal conditions as those aforementioned. After hydrothermal reaction, the pink powders were collected, separated by centrifugation, thoroughly rinsed with DI water and acetone, and then dried under vacuum at 60 °C. To convert CCHH NWs into CoP NWs, phosphorization was carried out under the same conditions as those described above except that the