**Abstract:** One of the challenges to realize large-scale water splitting is the lack of active and low-cost electrocatalysts for its two half reactions: H₂ and O₂ evolution reactions (HER and OER). Herein, we report that cobalt-phosphorous-derived films (Co-P) can act as bifunctional catalysts for overall water splitting. The as-prepared Co-P films exhibited remarkable catalytic performance for both HER and OER in alkaline media, with a current density of 10 mA cm⁻² at overpotentials of −94 mV for HER and 345 mV for OER and Tafel slopes of 42 and 47 mV/dec, respectively. They can be employed as catalysts on both anode and cathode for overall water splitting with 100% Faradaic efficiency, rivaling the integrated performance of Pt and IrO₂. The major composition of the as-prepared and post-HER films are metallic cobalt and cobalt phosphide, which partially evolved to cobalt oxide during OER.

Conversion of renewable energy resources through water splitting to H₂ and O₂ has attracted increasing attention. The sluggish kinetics of H₂ and O₂ evolution reactions (HER and OER, respectively) necessitate the development of competent catalysts. Owing to thermodynamic convenience and potential application in water-oxidation membrane or alkaline electrolyzers, most effort in this field has been devoted to developing HER catalysts for strongly acid conditions and OER catalysts for strongly basic conditions. Transition-metal sulfides, selenides, phosphides, carbides, borides, and even non-metal materials have shown catalytic performance for HER in strong acidic electrolytes, such as MoS₂,[5] M-MoSₓ,[8] CoNi-WS₂,[9] MS₅, and MSe₂ (M = Fe, Co, Ni, et al.[10]) FeSₓ,[11] CoS,[12] NiSₓ,[13] MoC and MoB,[14] MoP,[15] WP and WP₂,[16] CoP and Co₃P,[17] Ni₃P,[18] FeP,[19] and CuP.[20] On the other hand, many OER catalysts based on the oxides/hydroxides of cobalt,[21] nickel,[22] manganese,[23] iron,[24] and copper[25] have also been reported with OER catalytic activities under basic conditions. However, to accomplish overall water splitting, the coupling of HER and OER catalysts in the same electrolyte is desirable. The current prevailing approaches often result in incompatible integration of the two catalysts and lead to inferior overall performance. It remains a grand challenge to develop bifunctional electrocatalysts active for both HER and OER.

Herein, we report that a facile potentiodynamic electrodeposition using common cobalt and phosphorous reagents is able to prepare cobalt-phosphorous-derived (Co-P) films on copper foil (Figure S1 in the Supporting Information). The as-prepared Co-P films can be directly utilized as electrocatalysts for both HER and OER in strong alkaline electrolyte, which can achieve a current density of 10 mA cm⁻² with overpotentials of −94 mV for HER and 345 mV for OER with very small Tafel slopes, 42 and 47 mV/dec, respectively. When the Co-P films were deposited on the anode and cathode for overall water splitting, the superior activity and stability of the catalytic films can even compete the integrated Pt and IrO₂ catalyst couple.

Scanning electron microscopy (SEM) images of the as-prepared Co-P film showed nearly complete coverage of the rough film on copper foil (Figure 1a and Figure S2). No crystalline particles or aggregates were observed. Elemental mapping analysis indicated Co and P were distributed evenly over the entire film (Figure S3). The cross section SEM image revealed the thickness of the film in 1–3 μm (Figure 1a inset and Figure S4). The X-ray photoelectron spectroscopy (XPS) survey of the as-prepared film (Figure S5) showed all the anticipated elements. The Co 2p XPS spectrum (Figure 1b) displayed two peaks at 778.3 and 793.4 eV, corresponding to the Co 2p₁/₂ and Co 2p₃/₂ binding energies, respectively.[26] These values are extremely close to those of metallic cobalt.[22] The P 2p XPS spectrum (Figure 1c) exhibits a dominant peak at 129.5 eV, which can be attributed to the phosphide signal.[27] A broad feature at approximately 133.6 eV is assigned to phosphate.[28] In addition, elemental analysis of the as-prepared Co-P film gave the amount of Co and P as 2.52 and 0.19 mg cm⁻², respectively, with a molar ratio of 6.98 (Table S1).

We first evaluated the HER activity of the Co-P film in strong alkaline solution (Figure 2). It is evident that the blank copper foil did not show any HER catalytic activity below −0.3 V versus RHE (reversible hydrogen electrode). In contrast, a rapid cathodic current rise was observed for Co-P beyond −50 mV versus RHE (Figure 2a inset). Further scanning towards negative potential produced a dramatic increase in current density along with vigorous evolution of...
H₂ bubbles from the electrode surface. The Co-P film required an overpotential (η) of only −94 mV to reach a current density of 10 mA cm⁻². Such a low overpotential requirement compares favorably to other reported HER catalysts at pH 14 (Table S2). Remarkably, the Co-P film was able to produce a catalytic current density of 1000 mA cm⁻² within an overpotential of −227 mV. The linear fitting of its Tafel plot (Figure 2b) gave a Tafel slope of 42 mV/dec, which is among the smallest Tafel slopes of reported HER catalysts in alkaline media (Table S2). Although Pt-C exhibited a very small catalytic onset potential, its Tafel slope (108 mV/dec) was significantly larger than that of the Co-P film. Therefore, beyond −167 mV versus RHE, the catalytic current density of Co-P surpassed that of Pt-C. Additionally, the Co-P film also exhibited superior long-term stability. A 24 h controlled potential electrolysis at η = −107 mV showed a nearly linear charge accumulation and steady current over the entire course of electrolysis (Figure 2c). The blank copper foil generated negligible charge build-up under the same condition.

To probe the morphology and composition of the Co-P film after HER electrocatalysis, the SEM and XPS results of a post-HER Co-P film were collected. As shown in Figure 2d, the film still maintained a uniform coverage on the copper foil and no apparent clusters or aggregates were observed (Figure S6). Elemental mapping analysis confirmed the even distribution of Co and P in the post-HER film (Figure S7). Its Co 2p XPS spectrum showed two peaks at 793.2 and 778.2 eV (Figure 3a), corresponding to Co 2p₃/2 and Co 2p₁/2 states, respectively. The similarity of the Co 2p peaks of the post-HER Co-P film compared to those of the as-prepared one (Figure 1b) implied the major composition of the film preserved as metallic cobalt during HER. Furthermore, a peak at 129.3 eV was observed from the P 2p XPS spectrum of the post-HER sample (Figure 3b), while the phosphate peak at 133.6 eV originally observed for the as-prepared Co-P film (Figure 1c) was absent. Its absence is likely due to the dissolution of cobalt phosphate under cathodic condition. As shown in Figure S9, the as-prepared and post-HER Co-P films exhibited similar capacitance, implying their similar electrical active surface area. Elemental analysis of the post-HER film gave Co and P amounts of 2.48 and 0.12 mg cm⁻² with a Co/P ratio of 10.5 (Table S1).

We next assessed the catalytic activity of the Co-P film for OER in the same electrolyte (Figure 4). As expected, a blank copper did not show appreciable anodic current before 1.7 V versus RHE. The OER catalytic current density of the Co-P film increased dramatically beyond 1.53 V versus RHE (Figure 4a inset). It could reach current densities of 10, 100, and 500 mA cm⁻² at η = 345, 413, and 463 mV, respectively, lower than those of IrO₂ and many other reported OER catalysts (Table S3). Linear fitting of its Tafel plot resulted in a Tafel slope of 47 mV/dec. As one of the state-of-the-art OER catalysts,
IrO₂ was able to catalyze OER at a lower onset of approximately 1.50 V versus RHE, however its performance was quickly exceeded by that of the Co-P film beyond 1.58 V versus RHE. In fact, the Tafel slope of the Co-P film was 47 mV/dec, slightly inferior to that of IrO₂/Co-P couple, which has a Tafel slope of 69 mV/dec. Therefore, when the applied potential was larger than 1.67 V, Co-P/Co-P couple was able to surpass IrO₂/Pt-C in catalyzing overall water splitting. In addition, the Co-P/Co-P couple maintained excellent stability as manifested by the steady current change and nearly linear charge accumulation for a 24 h electrolysis (Figure 5c). In fact, the integrated activity of IrO₂/Pt-C was slightly inferior to that of the Co-P/Co-P couple under the same conditions. The Tafel slope of IrO₂/Pt-C is 91 mV/dec, larger than that of Co-P/Co-P (69 mV/dec). Therefore, the applied potential was higher than 1.67 V, Co-P/Co-P was able to surpass IrO₂/Pt-C in catalyzing overall water splitting. In conclusion, we have reported electrodeposited Co-P films as bifunctional catalysts for overall water splitting. The catalytic activity of the Co-P films can rival the state-of-the-art catalysts, requiring η = 94 mV for HER and η = 345 mV for OER to reach 10 mA cm⁻² with Tafel
slopes of 45 and 47 mV/dec, respectively. It can be directly utilized as catalysts for both anode and cathode with superior efficiency, strong robustness, and 100% Faradaic yield. The understanding of real-time composition and structural evolution of the films during electrolysis requires in situ spectroscopic study, which is under current investigation.

Keywords: electrocatalysts - nonprecious metal catalysts - overall water splitting - potentiodynamic deposition

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