

Full paper

Hollow Mo-doped CoP nanoarrays for efficient overall water splitting

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ABSTRACT

Earth-abundant, efficient and durable electrocatalysts for water splitting are vitally important for a sustainable energy system. Here we report the rational design of hollow Mo-doped CoP (Mo-CoP) nanoarrays, which simultaneously combine electronic structure modification through doping with a high density of reaction sites through nanostructuring. With this strategy the Mo-CoP arrays give significantly improved hydrogen evolution reaction (HER) performance, and also, when *in situ* transformed into Mo-doped CoOOH (Mo-CoOOH) arrays, excellent activity towards the oxygen evolution reaction (OER) is obtained. The origin of the improvement is determined by atomic-resolution imaging combined with density functional theory (DFT). An electrolyzer using Mo-CoP and Mo-CoOOH can be powered by a single AA battery (~1.5 V), and maintains a stable water-splitting current for 20 h, superior to most reported electrocatalysts in alkaline media, offering great promise for practical applications.

1. Introduction

Electrolytic water splitting, an attractive strategy to achieve clean and sustainable H₂ fuel, has received increasing worldwide concern with the ongoing energy crisis and climate change [1,2]. To achieve high performance electrolytic water splitting, which is composed of two half-reactions of HER and OER, cost-effective catalysts with low overpotential, high activity, and long-term stability are urgently required [3]. Although Pt and Ru/Ir-based materials are considered the state-of-the-art electrocatalysts for HER and OER respectively, they suffer from scarcity and high cost making them unsuitable for large-scale applications [4,5].

Considerable research efforts have been carried out to develop earth-abundant alternatives for efficient electrolytic water splitting. To increase the intrinsic activity of certain promising materials, an effective way is to develop alloyed and/or doped materials with modified electronic structures [6–9]. For example, doping Ru into Co cores has been found to be an efficient means to enhance the carbon-hydrogen bonding for better HER properties [10]. Introducing metal element into metal phosphide has also been reported as a promising way to improve the water-splitting catalytic performance [11–24]. Similarly, the hydrogen adsorption free energy of CoS₂ can be tuned for improved HER performance by substituting the S with P [25]. Another efficient way to achieve high-performance catalysts is to enhance activity through

nano/microstructure design. For example, building porous and/or hollow structured materials can achieve a large surface area with numerous reaction sites, and the open framework is also beneficial for better reaction kinetics and stability [26–28]. However, many such materials are in powder forms, thus a post-coating process with unwanted polymeric binders is involved, which can block the active sites and is easily peeled off during long-time gas evolution [29,30]. To address this concern, direct growth of catalytic materials in the form of well-aligned nanoarrays on current collectors has been regarded as another promising approach to achieve high performance catalysts; the open space within the nanoarrays can facilitate the electrolyte penetration, and the direct electrical and mechanical connection between the active materials and the current collectors can ensure efficient electron transfer paths with improved long-term stability [31–35]. Although some enhanced properties have been reported, the fabrication processes of such nanostructured electrodes have been complex and performance is generally unsatisfactory for practical applications.

In this work we combine these three effective strategies, to create high-performance catalysts with facile fabrication. Hollow Mo-CoP nanoarrays on carbon cloth (CC) are derived from a metal-organic framework (MOF) precursor, and directly utilized as a highly active and durable electrocatalyst for hydrogen evolution. The Mo-CoP arrays can also be *in situ* transformed into Mo-CoOOH with enhanced OER properties. Hence, we have both modified its electronic structure through

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Mo-doping, and achieved an effective hollow and porous structure. Our Mo-CoP arrays (i) lower the energy barrier through Mo-doping, (ii) provide a high density of reaction sites, (iii) achieve short ionic diffusion length, (iv) promote electrolyte penetration and facilitate the release of evolved gas bubbles, and (v) ensure high electrical conductivity avoiding the use of binder additives.

2. Experimental section

2.1. Material synthesis

2.1.1. Preparation of cobalt-based MOF nanowall arrays (Co-MOF) on carbon cloth (CC)

An aqueous solution contains 2-methylimidazole ($C_4H_6N_2$, 40 mL, 0.4 M) was quickly poured into the aqueous solution of $Co(NO_3)_2 \cdot 6H_2O$ (40 mL, 50 mM), after which a piece of acid-treated CC substrate ($2 \times 5 \times 0.036 \text{ cm}^3$, the upper side and back side protected with by polytetrafluoroethylene tape for electric contact), was immersed into the mixture solution. After reaction for 4 h, the sample was taken out, cleaned with deionized water and dried overnight.

2.1.2. Preparation of Mo-Co layered double hydroxide (Mo-Co LDH) arrays on CC

A piece of Co-MOF/CC was immersed into an ethanol/water solution (1:4 in volume, 100 mL) containing Na_2MoO_4 (0.2 g). After reaction at 85°C for 15 min, the purple colour of the Co-MOF disappeared, then the sample was taken out, washed with ethanol and water repeatedly, and dried at 60°C .

2.1.3. Preparation of hollow Mo-CoP arrays on CC

A piece of Mo-Co LDH/CC and NaH_2PO_2 powder (with 20 times the mass of Mo-Co LDH) were placed at two separate positions in a ceramic boat, with NaH_2PO_2 at the upstream side of a tube furnace. Then the Mo-Co LDH on CC was annealed at 350°C for 2 h with a heating rate of 2°C min^{-1} under nitrogen atmosphere with a flow rate of 300 sccm. The mass loading of Mo-CoP is $\sim 2.5 \text{ mg cm}^{-2}$.

2.1.4. Preparation of hollow CoP arrays on CC

A piece of Co-MOF/CC was immersed into a water/ethanol solution (1:4 in volume, 100 mL) at 85°C . After the purple colour of the Co-MOF disappeared ($\sim 10 \text{ min}$), the sample was taken out, washed with ethanol and water repeatedly, and dried at 60°C . Then the as-prepared sample and NaH_2PO_2 powder (with 20 times in mass) were put at two separate positions in a ceramic boat with NaH_2PO_2 at the upstream side of the tube furnace. After annealing the sample at 350°C for 2 h with a heating rate of 2°C min^{-1} under nitrogen atmosphere with a flow rate of 300 sccm, hollow CoP arrays on CC were obtained. The mass loading of CoP is $\sim 2.0 \text{ mg cm}^{-2}$.

2.1.5. Preparation of hollow Co_3O_4 arrays on CC

A piece of Co-MOF/CC was immersed into a water/ethanol solution (1:4 in volume, 100 mL) at 85°C . After the purple colour of the Co-MOF disappeared ($\sim 10 \text{ min}$), the sample was taken out, washed with ethanol and water repeatedly, and dried at 60°C . Then the as-prepared sample was annealed in air at 350°C for 2 h with a heating rate of 2°C min^{-1} . The mass loading of Co_3O_4 is $\sim 1.8 \text{ mg cm}^{-2}$.

2.1.6. Preparation of Ir/C/CC and Pt/C/CC

Commercial Pt/C (20 wt%, Alfa Aesar) or Ir/C (20 wt%, Premetek

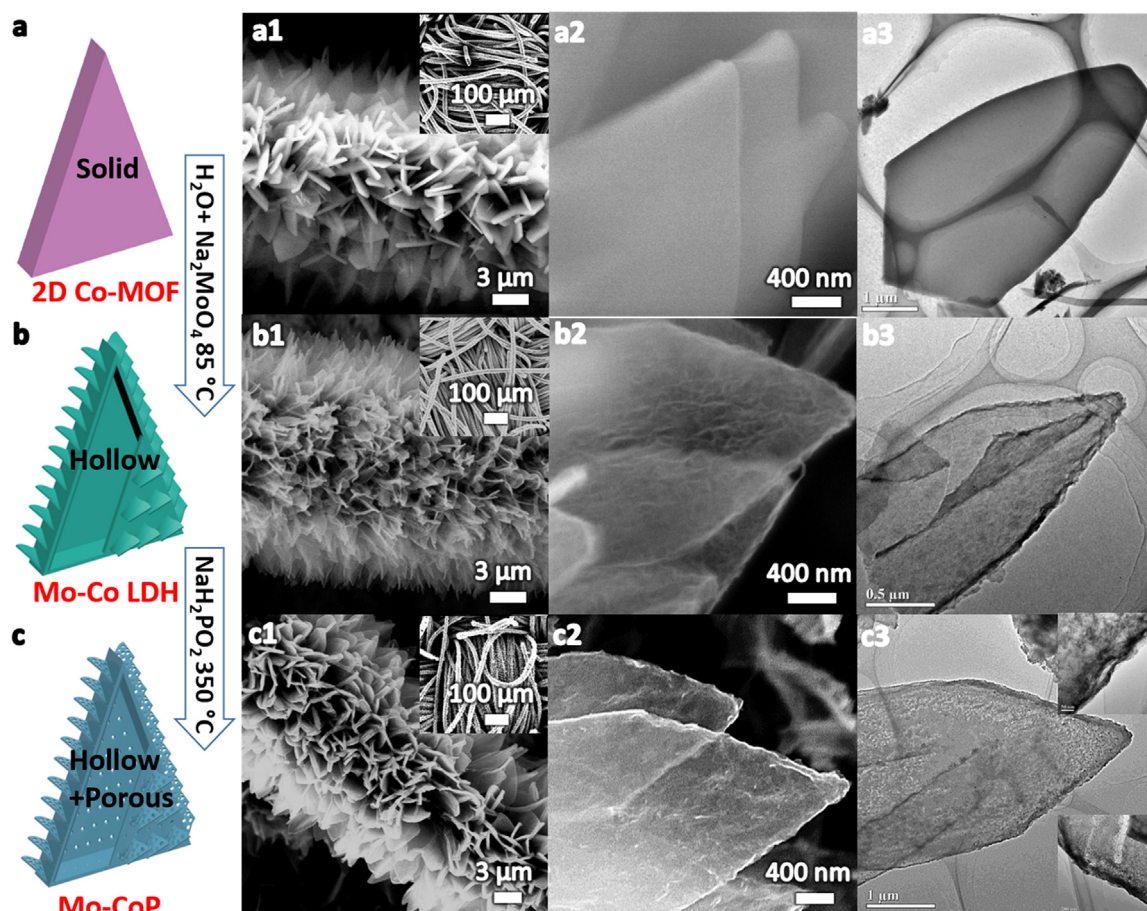


Fig. 1. Schematic fabrication process and the resulting microstructures for hollow Mo-CoP nanoarrays. (a) 2D Co-MOF arrays, (b) Mo-Co LDH, (c) Mo-CoP nanoarrays.

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