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Novel CoP Hollow Prisms as Bifunctional Electrocatalysts for Hydrogen Evolution Reaction in Acid media and Overall Water-splitting in Basic media

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ABSTRACT

Cobalt phosphide (CoP) with hollow prisms nanostructure has been successfully synthesized via a facile two-step micro-assisted method. Firstly, uniform $Co_3(CH_3COO)_5(OH)$ cubes are prepared by microwave method. Then as-prepared $Co_3(CH_3COO)_5(OH)$ cubes as precursors have been conducted by phosphorization at low temperature. Novel CoP hollow prisms with 1 μm length, 500 nm width and 500 nm height have been synthesized. The obtained CoP hollow prisms can be used as both an efficient electrocatalyst for HER in acid media (0.5 M H_2SO_4 solution) and a remarkable bifunctional electrocatalyst for overall water-splitting in alkaline media (1.0 M KOH solution) which might be attributed to their high surface area, porosity and good distribution. The OER mechanisms of CoP in alkaline solution have been investigated through XPS and SEM Mapping, which demonstrate that the amorphous oxygen-containing nanostructure on the surface of CoP may be the real catalytic active species. In addition, phosphidation of uniform cobalt salt hydrates precursor with specific structure at low temperature is a newfangled and effective strategy to synthesis bifunctional electrocatalyst CoP.

1. Introduction

Hydrogen has been considered as the most promising alternative to petroleum fuel in the future due to its high efficiency and natural abundance [1–6]. What's more, the key problem is how to yield hydrogen massively and cheaply [7–11]. Splitting water consist of two half reactions: the hydrogen evolution reaction (HER: $2H^+ + 2e^- \rightarrow H_2$) and the oxygen evolution reaction (OER: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$) [12]. This is the optimal method to produce hydrogen and oxygen except of some technical challenges, such as, finding the stable, efficient and cheap catalyst for the overall water-splitting [13–16]. Platinum-group with nearly zero overpotential and high cathodic current in acidic media are the efficient electrocatalysts for HER, and Ir-based compounds have the highest activity for OER, but their application in the industry is limited due to their high price and low reserve [17–21]. Xie and his co-works found that defect-Rich MoS_2 ultrathin nanosheets which introduced additional active edge sites own low overpotential 120 mV and excellent durability in acidic media [22]. Dai et al. developed a highly active and stable catalyst containing Co doped earth abundant iron pyrite FeS_2 nanosheets hybridized with carbon nanotubes for HER in acidic solutions [23]. Lou's group has synthesized $Co_3O_4/NiCo_2O_4$ double-shelled nanocages using zeolitic imidazolate framework-67 (ZIF-67) as precursor, and the obtained $Co_3O_4/NiCo_2O_4$ electrocatalyze OER in 1.0 M KOH [24].

Ideal electrocatalyst for overall water-splitting is the one which could efficiently catalyze HER and OER in the same media and exhibit efficiently stability in the whole reaction. Bifunctional electrocatalyst means that it could simultaneously generating H_2 and O_2 in the same media, meanwhile, it shows long-term stability during the overall water-splitting process. In recently, the design of an efficient, stable and cheap electrocatalyst for both HER and OER in the same media has attracted lots of attention. As reported, a large numbers of nonprecious-metal materials have been proved to improve the electrocatalytic activity for HER and OER, such as transition metal phosphides (TMPs) [25–28].

TMPs are considered as the most promising electrocatalysts for water-splitting because of its metalloid characteristics and good electrical conductivity [29]. Sun's group have successfully prepared nickel–phosphorous (Ni–P) films via electrodeposition

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which show good electrocatalytic performance as efficient bifunctional electrocatalysts for overall water splitting [30]. Ledendecker and his co-works found that the in-situ growed Ni_5P_4 on Ni foil was a bifunctional catalyst for the overall water splitting reaction [31]. Hou et al. synthesized the ultrafine CoP nanoparticles supported on carbon nanotubes which could electrocatalyst both HER and OER with low overpotential and high current density [32]. You et al. fabricated nanopolyhedrons composed of CoP_x (a mixture of CoP and Co_2P) nanoparticles embedded in N-doped carbon matrices via a two-step method [33]. Yang's group reported the one-pot synthesis of monodisperse ternary NiCoP nanostructure as efficient bifunctional

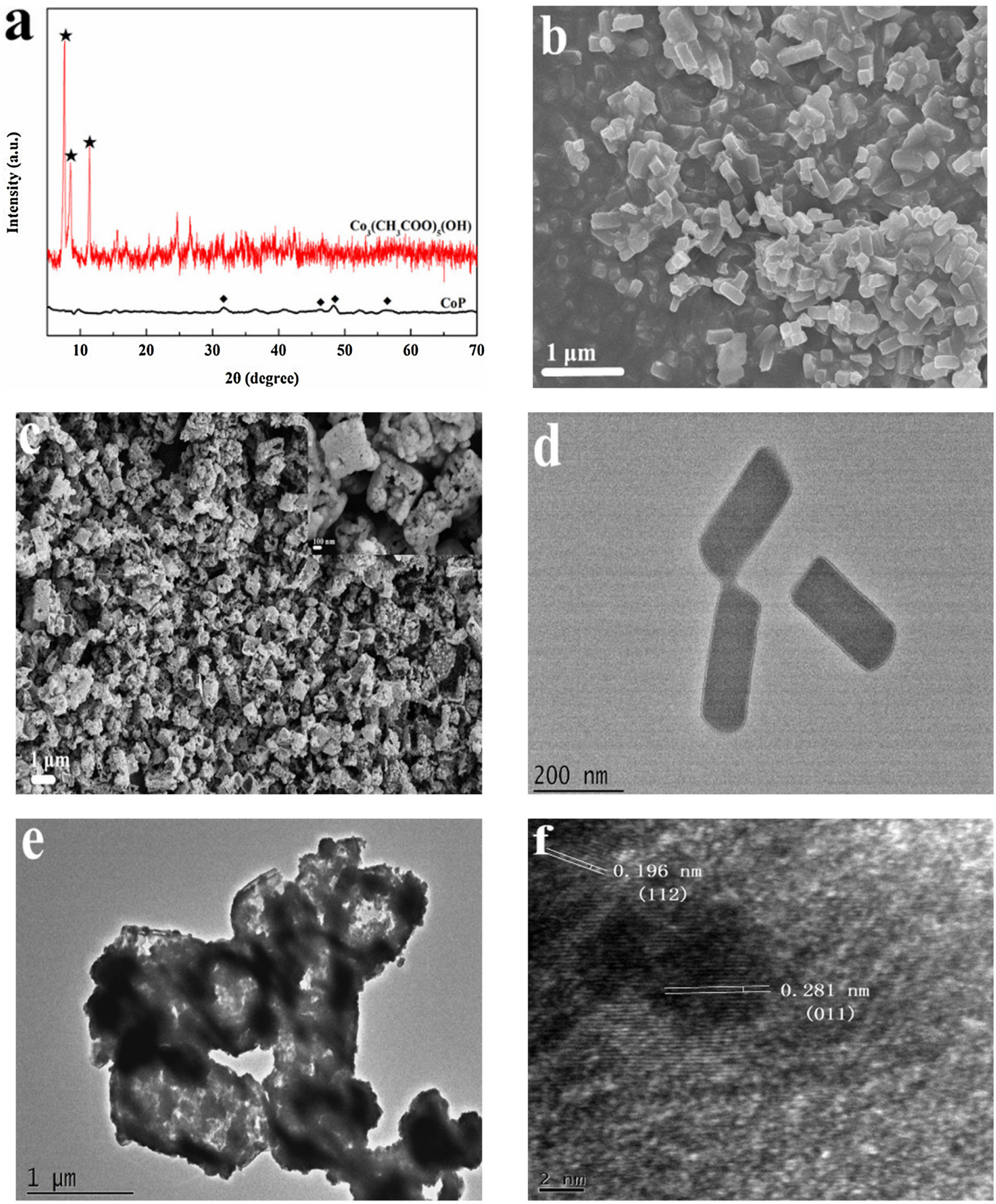

Fig. 1. (a) XRD patterns of $Co_3(CH_3COO)_5(OH)$ (red curve) and CoP hollow prisms (black curve). SEM image of (b) $Co_3(CH_3COO)_5(OH)$; (c) CoP. TEM image of (d) $Co_3(CH_3COO)_5(OH)$; (e) CoP. (f) HRTEM image of CoP.