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Full Length Article

# Synthesis of rod-type Co<sub>2.4</sub>Mn<sub>0.6</sub>O<sub>4</sub> via oxalate precipitation for water splitting catalysts



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#### ABSTRACT

Development of a cost-effective oxygen evolution reaction (OER) catalyst for hydrogen production from water has attracted the attention of scientists due to its potential to solve current environmental and energy issues, such as  $\rm CO_2$  emissions and depletion of fossil fuels. In this paper, we report a facile synthesis to develop cobalt-manganese-oxide ( $\rm Mn_xCo_{3-x}O_4$ , CMO) nanorods via an oxalate precipitation method followed by annealing at different temperatures. Importantly, morphology and surface area of the CMO nanorods, which are directly related to the OER activity, can be precisely controlled by changing annealing temperatures. The CMO nanorods engineered by oxalate precipitation and subsequent heat treatment show promising OER catalytic performance, such as a small overpotential of 365 mV for generating a current density of 10 mA cm $^{-2}$ , a low Tafel slope of 50.6 mV dec $^{-1}$ , and excellent long-term stability in alkaline media. Electrochemical properties combined with materials characterization provide insightful information on the OER mechanism of the CMO nanorods.

## 1. Introduction

Hydrogen energy is a promising solution to the urgent problems associated with future energy and environment crises [1,2]. Hydrogen can be produced in a carbon-free way using electrolyzers via water splitting [3]. In a water-splitting electrolyzer, electrocatalysts for the oxygen  $(O_2)$  evolution reaction (OER), which is an anodic catalytic reaction, play a crucial role in reducing the overpotential and, thus, enhancing the overall electrolysis efficiency [4]. Generally, a proposed possible mechanism for oxygen evolution reaction under alkaline condition has been popularly reported as follows [5]:

$$M + OH^- \to MOH \tag{1}$$

$$MOH + OH^- \rightarrow MO + H_2O_{(l)}$$
 2)

$$2MO \rightarrow 2M + O_{2(g)} \tag{3}$$

$$MO + OH^- \rightarrow MOOH + e^- \tag{4}$$

MOOH + 
$$OH^- \to M + O_{2(g)} + H_2 O_{(l)}$$
 (5)

The OER is a thermodynamically sluggish reaction because multiple electrons and protons are involved in the anodic reaction [6,7]. Extensive research has focused on developing highly efficient OER electrocatalysts to lower the activation energy and accelerate the reaction kinetics [3,8].

Besides the high catalytic activity, long-term stability under alkaline conditions is a critical requirement for practical use of OER electrocatalysts in electrolyzers [9]. Highly active OER electrocatalysts, such as transition metal-based hydroxide [10], sulfides [11], nitrides [12,13] and phosphides [14], often exhibit poor long-term stability in alkaline solution under OER conditions. The poor long-term stability has been attributed to partial oxidation of electrocatalysts, which occurs spontaneously from a thermodynamic perspective under the OER conditions [15,16]. To eliminate the detrimental effects of partial oxidation of electrocatalysts on OER performance, oxide-based OER electrocatalysts are of particular interest as they are robust and highly efficient electrocatalysts [15–23].

Among numerous oxide-based OER catalysts, ruthenium oxide (RuO<sub>2</sub>) is regarded as the most active OER catalyst. However, its

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