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Promotion of electrochemical oxygen evolution reaction by chemical coupling of cobalt to molybdenum carbide

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ABSTRACT

Herein, we report a novel strategy to promote electrochemical oxygen evolution reaction (OER) on cobalt (Co) surface by coupling Co to molybdenum carbide (Mo₂C). Chemically coupled Co and Mo₂C nanoparticles were synthesized through a simple heat treatment of the mixture containing Co and Mo precursors and graphitic carbon nitride (g-C₃N₄). Transmission electron microscopy (TEM) images obviously showed that Co and Mo₂C nanoparticles were coupled at Co/Mo₂C interfaces. X-ray photoelectron spectroscopy (XPS) and density functional theory (DFT) calculation results revealed that electrons were transferred from Co to Mo₂C nanoparticles across the interfaces. The electron transfer makes the Co surface more electrophilic by *d*-band center of Co upshift, leading to an increase in OH[−] affinity. As a result, the Co nanoparticles coupled with Mo₂C have OER-favorable Co-oxo and Co-hydroxo configuration within their oxidized surfaces, and hence, can accelerate the overall OER than bare Co nanoparticles. This work demonstrates that the Co nanoparticles chemically coupled to Mo₂C exhibited excellent OER activity and stability in an alkaline electrolyte and suggests a promising way to design an active OER catalyst.

1. Introduction

Electrolyzing water into hydrogen and oxygen is an environmentally friendly method to store renewable energy in the form of hydrogen gas. The overall reaction of water electrolysis is divided into two half reactions: hydrogen evolution reaction (HER) at the cathode and oxygen evolution reaction (OER) at the anode. The efficiency of water electrolysis is primarily limited by a high anode overpotential due to sluggish kinetics of OER [1,2]. To facilitate the OER kinetics, RuO₂ and IrO₂ have been typically used as catalysts [3–6]. Although the scarcity and high cost of these noble-metal-based catalysts are impeding practical applications of water electrolysis, there is few viable alternatives with adequate stability under high anodic potentials in acidic electrolytes [7]. However, alkaline electrolytes allow a wider variety of OER catalyst materials including earth-abundant substances [8]. Therefore, it has been a major challenge to develop non-noble OER catalysts with high catalytic performances for alkaline water electrolysis [9].

A series of catalysts based on metallic cobalt (Co) or Co-oxides have been of interest owing to their low OER overpotentials in alkaline electrolytes [10]. Since OER occurs at high electrode potentials (E_0 O₂/

OH[−] = 1.23 V_{RHE}), surface of the Co-based catalysts is oxidized by OH[−] in alkaline electrolytes prior to occurrence of OER [11]. Among the oxidized phases of Co and Co-oxides, Co-(oxy)hydroxide (CoOOH) is known to be thermodynamically stable under general alkaline OER conditions [12,13]. According to the previous studies, the layered structure of CoOOH with edge-sharing of [CoO₆] subunits drives fast OER kinetics [14–21] and the Co cations coordinated by O (oxo) and OH (hydroxo) species (denoted as ‘CoOOH configuration’) serve as active sites to initiate and proceed OER [22]. However, in general, instead of the thermodynamically stable and highly OER-active CoOOH, kinetically-accessible hydrous oxide layers (CoO_a(OH)_b(OH₂)_c) are formed *in-situ* on the surface of Co and Co-oxides during OER [22]. In the hydrous oxide layers, Co cations have a variety of oxo and hydroxo configurations different from the CoOOH configuration. Thus, to enhance OER activity of Co-based catalysts, it is required to form CoOOH-like configuration in their surface hydrous oxide layers [23–25]. However, since the surface layers develop *in-situ*, it is a challenge to control the Co-oxo and Co-hydroxo configurations in the surface hydrous oxide layers toward the CoOOH configuration.

Recently, Co chalcogenides incorporated with a non-metal element, such as a selenide (CoSe₂) [26,27], phosphide (CoP) [28–30], nitride

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