Applied Catalysis B: Environmental 227 (2018) 340–348

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

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

MinJoong Kim[a], Sunghyun Kim[b], DongHoon Song[a], SeKwon Oh[a], Kee Joo Chang[b], EunAe Cho[a,*]

[a] Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology (KAIST), 291 Daehak-ro, Yuseong-gu, Daejeon, 34141, Republic of Korea
[b] Department of Physics, Korea Advanced Institute of Science and Technology (KAIST), 291 Daehak-ro, Yuseong-gu, Daejeon, 34141, Republic of Korea

ARTICLE INFO

Keywords:
Cobalt
Molybdenum carbide
Oxygen evolution reaction
Electrocatalyst
Chemical coupling

ABSTRACT

Herein, we report a novel strategy to promote electrochemical oxygen evolution reaction (OER) on cobalt (Co) surface by coupling Co to molybdenum carbide (Mo_2C). Chemically coupled Co and Mo_2C nanoparticles were synthesized through a simple heat treatment of the mixture containing Co and Mo precursors and graphitic carbon nitride ($g\text{-}C_3N_4$). Transmission electron microscopy (TEM) images obviously showed that Co and Mo_2C nanoparticles were coupled at Co/Mo_2C interfaces. X-ray photoelectron spectroscopy (XPS) and density functional theory (DFT) calculation results revealed that electrons were transferred from Co to Mo_2C 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 Mo_2C 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 Mo_2C 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, RuO_2 and IrO_2 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_o $O_2/OH^- = 1.23\,V_{RHE}$), 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 $[CoO_6]$ 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 ($CoO_a(OH)_b(OH_2)_c$) 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-hydoxo configurations in the surface hydrous oxide layers toward the CoOOH configuration.

Recently, Co chalcogenides incorporated with a non-metal element, such as a selenide ($CoSe_2$) [26,27], phosphide (CoP) [28–30], nitride

---

* Corresponding author.
E-mail address: eacho@kaist.ac.kr (E. Cho).

https://doi.org/10.1016/j.apcatb.2018.01.051
Received 16 October 2017; Received in revised form 19 January 2018; Accepted 22 January 2018
0926-3373/

(Co_4N) [31] and boride (Co_2B) [32], have been reported to have OER activities comparable with RuO_2 and IrO_2. Due to the differences in the physical and chemical properties, those non-metal elements change the electronic structure of Co [28,32]. The changes in the electronic structure of Co surface facilitates the formation of hydrous oxide layers containing Co-oxo and Co-hydroxo species with Co^{3+}-OH and Co^{4+}-O [28]. As a result, Co-chalcogenides form an effective core-shell like structure composed of OER-active surface layer and electrically-conductive chalcogenide core. As a similar approach to modulate the electronic structure of surface Co, Mn_3O_4-supported $CoSe_2$ [33], Co-oxides@Au core-shell structures [34] and Co-oxides with nitrogen-doped carbon [35–38] have been proposed. In those studies, interatomic interactions between the Co-selenide or Co-oxides and other materials also enhanced OER activity of the Co-selenide or Co-oxides by modulating the electronic structure of the surface Co [34,39]. Those results demonstrate that interatomic coupling of Co to other elements or compounds can be an effective way to change surface electronic structure of Co and thereby improve OER activity.

Herein, we report a novel strategy to develop efficient OER catalysts. Our key idea was to form OER-active hydrous oxide layers on the surface of metallic Co nanoparticles by modulating electronic structure of Co. In the metallic Co-based core and hydrous oxide shell structure, metallic Co would be more favorable for OER rather than the previously reported chalcogenide or oxide-based Co compounds owing to the higher electrical conductivity. To modulate electronic structure of Co, Co nanoparticles were chemically coupled to molybdenum carbide (Mo_2C) nanoparticles. Transition metal carbides have affected electrocatalytic property of an admetal by changing electronic structure of the admetal surface [40]. Among various transition metal carbides, Mo_2C was employed in this study since Co-Mo coupling exhibited beneficial effects on oxygen electrocatalysis of Co [41,42]. Although Mo_2C is known to be unstable under the high OER overpotential [43], it was expected that Mo_2C could affect formation of the surface hydrous oxide layers prior to the occurrence of OER. The chemically coupled Co and Mo_2C nanoparticles were synthesized through a simple heat treatment of a Co and Mo precursor mixture with the addition of graphitic carbon nitride (g-C_3N_4) as a carbon source. Co nanoparticles coupled with Mo_2C nanoparticles were effectively oxidized to form the surface hydrous oxide layers with excellent OER activity. The effects of chemical coupling of Co to Mo_2C on the surface property and OER kinetics of Co were investigated through extensive characterization methods in combination with density functional theory (DFT) calculations.

2. Experimental

2.1. Material synthesis

Graphitic carbon nitride (g-C_3N_4) was used as a carbon source for the carburizing reaction of Mo into Mo_2C. To prepare g-C_3N_4, dicyandiamide ($C_2H_4N_4$) was heat treated at 550 °C for 4 h under an Ar gas atmosphere. After the heat treatment, white-colored dicyandiamide was successfully transformed to yellow-colored g-C_3N_4 (Fig. A.1).

Chemically coupled Co and Mo_2C nanoparticles were synthesized from a heat treatment of the precursor mixture containing cobalt(II) acetate tetrahydrate ($(CH_3COO)_2Co{\cdot}4H_2O$), ammonium molybdate ($(NH_4)_2MoO_4$) and the synthesized g-$C_3N_4$ at 800 °C for 1 h under an Ar gas atmosphere. Co nanoparticles were synthesized using the same heat treatment conditions with the precursor mixture containing $(CH_3COO)_2Co{\cdot}4H_2O$ and g-C_3N_4 without $(NH_4)_2MoO_4$. Mo_2C nanoparticles were synthesized from a heat treatment of $(NH_4)_2MoO_4$ at 800 °C for 1 h under H_2/CH_4 (80/20 vol.%) gas. Heating rate was 5 °C min^{-1} for all the samples.

2.2. Physical characterization

The morphologies of the prepared samples were examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Phase analysis was performed using X-ray diffraction (XRD). The chemical states of the prepared samples were analyzed using X-ray photoelectron spectroscopy (XPS). XPS results were calibrated by using 284.8 eV of C—C bond as a reference. The composition of each metallic element (Co, Mo) and non-metallic element (C, N) was measured by using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and elemental analysis (EA), respectively. For ammonia-temperature programmed desorption (NH_3-TPD) analysis, all samples were preheated at 300 °C for 1 h under vacuum to clean the surface, and then, NH_3 was chemisorbed at 100 °C for 1 h. The chemisorbed NH_3 was desorbed by increasing the temperature to 900 °C, and a thermal conductivity detector (TCD) detected the desorbed NH_3. The Brunauer-Emmett-Teller (BET) surface area was measured after pretreatment at 200 °C for 1 h under vacuum.

2.3. Electrochemical analysis

All the electrochemical measurements were conducted in a standard three-compartment electrochemical cell using a glassy carbon electrode (GCE) in the form of a rotating disc electrode (RDE), Pt mesh and mercury/mercury oxide (Hg/HgO) electrode filled with 0.1 M sodium hydroxide (NaOH) solution, as the working, counter and reference electrodes, respectively. Deionized (DI) water was purified to remove iron (Fe) impurities that Fe content in the DI water was about 0.035 ppb. All potentials were measured at 20 °C in a 0.1 M potassium hydroxide (KOH) solution and referenced against the reversible hydrogen electrode (RHE). The potential difference between the Hg/HgO electrode and the RHE was obtained from a cyclic voltammetry (CV) curve measured in the hydrogen-saturated 0.1 M KOH solution using a Pt disc as the working electrode. The sweep rate was 0.1 mV s^{-1}. A catalyst ink slurry was prepared by mixing the catalysts with 2 mL of DI water and 100 μL of 5 wt.% Nafion solution as a binding material. After mixing and ultrasonication, a drop of the ink slurry was loaded onto the GCE substrate. The dried electrode was then transferred to the electrochemical cell. Catalyst loading on the GCE was 0.24 mg cm^{-2} for all samples. The RDE rotation rate was 1600 rpm, and the sweep rate was 5 mV s^{-1} during the OER measurements. For an accelerated stress test (AST), 2000 potential cycles were conducted from 1.3 to 1.7 V_{RHE} in an Ar-purged 0.1 M KOH solution at a scan rate of 0.1 V s^{-1}. Potential of zero charge (PZC) was examined in 2 mM sodium fluoride (NaF) solution with a 100 mHz frequency and a 10 mV potential amplitude after three OER cycles in 0.1 M KOH solution.

2.4. Computational calculations

We performed first-principles calculations within the framework of density functional theory (DFT) that employed the generalized gradient approximation of Perdew, Burke, and Ernzerhof (PBE) [44] for the exchange-correlation potential and the projected augmented wave (PAW) pseudopotentials [45], as implemented in the VASP code [46]. In addition, the effective on-site Coulomb repulsion $U = 3.5$ eV on the Co-3d orbitals was included. We adopted a (111)-oriented Co on a Mo_2C (110) substrate to reduce the strain on the Co. The wave functions were expanded in plane waves up to an energy cutoff of 400 eV, and a Monkhorst-Pack mesh [47] of 9 × 6 × 1 was used for Brillouin zone integration

3. Results and discussion

3.1. Material synthesis and characterization

Chemically coupled Co and Mo_2C nanoparticles were synthesized through a simple heat treatment of the precursor mixture containing cobalt and molybdenum precursors, and g-C_3N_4 (made from dicyandiamide, Fig. A.1). g-C_3N_4 was used as a carbon source for the