



Short communication

# The influence of $\text{Co}_3\text{V}_2\text{O}_8$ morphology on the oxygen evolution reaction activity and stability



Suyeon Hyun, Vignesh Ahilan, Hasuck Kim, Sangaraju Shanmugam\*

Department of Energy Systems Engineering, Daegu Gyeongbuk Institute of Science and Technology (DGIST), Daegu 42988, Republic of Korea

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## ABSTRACT

The effect of  $\text{Co}_3\text{V}_2\text{O}_8$  morphology on the electrocatalytic oxygen evolution reaction (OER) activity was evaluated using one- and zero-dimensional nanostructures. The microscopic analyses reveal the existence of thin coating of nitrogen-doped amorphous carbon on the surface of  $\text{Co}_3\text{V}_2\text{O}_8$  nanostructures. The 1D- $\text{Co}_3\text{V}_2\text{O}_8$  electrocatalyst delivers  $10 \text{ mA cm}^{-2}$  at overpotential of 0.350 V versus reversible hydrogen electrode for OER in 0.1 M KOH, whereas 0D- $\text{Co}_3\text{V}_2\text{O}_8$  catalyst showed 0.397 V, benefited from the morphological characteristics of 1D. Moreover, the 1D- $\text{Co}_3\text{V}_2\text{O}_8$  catalyst exhibits much lower OER overpotential than that of commercial noble metal oxide catalysts,  $\text{RuO}_2$  (0.41 V) and Pt/C (0.79 V).

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## 1. Introduction

Growing energy demands provide opportunities for the development of new technologies and efficient materials for electrochemical energy conversion and storage devices [1]. Water splitting technology to produce pure hydrogen gas has been investigated for many years to store a large scale of electrochemical energy. In the water splitting reaction, a high overpotential at the anode due to the sluggish four electron transfer oxygen evolution kinetics has to be addressed to produce pure hydrogen in a facile way [2]. Thus, in order to accelerate the reaction rate and lower the anode overpotential, an efficient oxygen evolution reaction (OER) catalyst is essential. So far, the noble metal catalysts such as  $\text{RuO}_2$ ,  $\text{IrO}_2$ , and Pt/C have shown to be promising candidates as OER catalysts. Despite their good catalytic activity, high cost and scarcity limit their commercial applications. Thus, a material with high-performance, inexpensive and eco-friendly design is required.

Recently, transition metal oxides such as cobalt, nickel, and perovskites have been reported as highly active and robust catalysts for OER in alkaline medium. Among them, cobalt-based oxides exhibit an outstanding OER performance [3–6]. In addition to looking for new cost-effective materials with stable structure and also tuning, the morphology of the existing material to improve their catalytic activity has been practicing and taken into consideration. Based on this aspect, we have synthesized a highly active and stable noble metal-free OER electrocatalyst based on earth abundant metals,  $\text{Co}_3\text{V}_2\text{O}_8$  with one-dimensional morphology consisting of nanotubes and nanorods

(denoted to 1D- $\text{Co}_3\text{V}_2\text{O}_8$ ). To understand the effect of  $\text{Co}_3\text{V}_2\text{O}_8$  morphology on the OER activity, we have also synthesized  $\text{Co}_3\text{V}_2\text{O}_8$  nanoparticles (0D- $\text{Co}_3\text{V}_2\text{O}_8$ ) and evaluated their performance.

## 2. Experimental section

$\text{Co}_3\text{V}_2\text{O}_8$  nanostructures (1D and 0D) were synthesized by the electrospinning method. One gram of PAN (polyacrylonitrile,  $M_w = 150,000 \text{ g mol}^{-1}$ ) was used as a carbon precursor, and cobalt acetylacetonate ( $\text{C}_{10}\text{H}_{14}\text{CoO}_4$ ) and vanadyl acetylacetonate ( $\text{VO}(\text{C}_5\text{H}_7\text{O}_2)_2$ ) were used as metal precursors. The weight of metal precursor in the precursor solution was varied to 0.5 and 0.25 g and resulted in 1D and 0D- $\text{Co}_3\text{V}_2\text{O}_8$  nanostructures, respectively. By tuning the weight ratio of PAN to the metal precursor, the viscosity of electrospinning solution was different, leading to the products with different morphologies [7]. During the electrospinning process, a voltage of 12 kV was applied between the needle tip and an aluminum foil collector with a distance of 10 cm and a flow rate of  $1 \text{ mL h}^{-1}$ . As-spun fiber mat was stabilized in air at 250 °C for 1 h, followed by crystallization process at 500 °C for 3 h under air atmosphere with a heating rate of  $3 \text{ °C min}^{-1}$ . The  $\text{Co}_3\text{V}_2\text{O}_8$  nanoparticles without carbon coating was prepared using as-spun fibers preheated in air at 250 °C for 1 h, and subsequently the temperature was increased to 600 °C for 2 h, which resulted in  $\text{Co}_3\text{V}_2\text{O}_8$  nanoparticles with the carbon coating.

## 2.1. Electrochemical measurements

The OER activity of  $\text{Co}_3\text{V}_2\text{O}_8$  catalysts was assessed using an RDE system with a three-electrode system in which a glassy carbon electrode,

\* Corresponding author. Tel.: +82 53 785 6413; fax: +82 53 785 6402.  
E-mail address: [sangarajus@dgist.ac.kr](mailto:sangarajus@dgist.ac.kr) (S. Shanmugam).

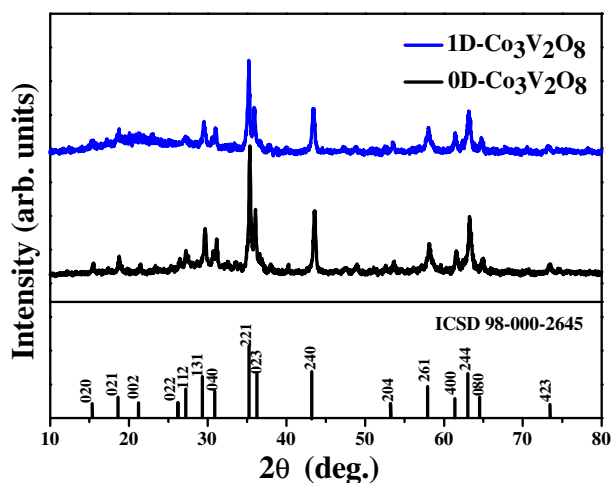


Fig. 1. XRD patterns of  $\text{Co}_3\text{V}_2\text{O}_8$  nanostructures.

saturated calomel electrode (SCE), and Pt wire as the working, reference, and counter electrodes, respectively. All potentials reported in this work were converted to the reversible hydrogen electrode (RHE) scale using the equation  $E(\text{RHE}) = E(\text{SCE}) + 0.991 \text{ V}$ . The potentials reported in this work were  $iR$  corrected and the electrolyte ohmic

resistance ( $iR$ ) was  $\sim 65 \Omega$  in 0.1 M KOH measured with high-frequency AC impedance. To make a catalyst ink, 1.5 mg of catalyst was dispersed in 30  $\mu\text{L}$  DI water and 160  $\mu\text{L}$  IPA (Isopropyl alcohol), and then 10  $\mu\text{L}$  of Nafion (5 wt%) was added to the mixture. By sonicating for 30 min, a homogenous ink was formed. After that, 2  $\mu\text{L}$  of the catalyst ink was drop casted onto the surface of polished glassy carbon electrode and a catalyst loading of  $0.21 \text{ mg cm}^{-2}$  is obtained. Then, the OER polarization curves were recorded by linear sweep voltammetry (LSV) at a scan rate of  $5 \text{ mV s}^{-1}$  at 1600 rpm. Chronoamperometric stability tests were carried out using an overpotential of 1.59 V vs. RHE.

### 3. Results and discussion

The X-ray diffraction (XRD) patterns of 1D and 0D- $\text{Co}_3\text{V}_2\text{O}_8$  nanostructures are shown in Fig. 1. The XRD patterns of both  $\text{Co}_3\text{V}_2\text{O}_8$  samples match well with  $\text{Co}_3\text{V}_2\text{O}_8$  (ICSD PDF no. 98-000-2645). These data are based on an orthorhombic crystal structure with  $Cmca$  space group, which has the lattice parameters of  $a = 6.0300 \text{ \AA}$ ,  $b = 11.4860 \text{ \AA}$ , and  $c = 8.3120 \text{ \AA}$ . The BET surface area of 1D- $\text{Co}_3\text{V}_2\text{O}_8$  is  $21.9 \text{ m}^2 \text{ g}^{-1}$ , whereas 0D- $\text{Co}_3\text{V}_2\text{O}_8$  is  $10.3 \text{ m}^2 \text{ g}^{-1}$  with mesoporous nature. The morphology and microstructure of the materials were characterized using a field emission scanning electron microscope (FE-SEM) and a field emission transmission electron microscope (FE-TEM). FE-SEM images, as shown in Fig. 2a, d, clearly show the formation of 1D and 0D- $\text{Co}_3\text{V}_2\text{O}_8$  with porous nanostructures due to the partial removal

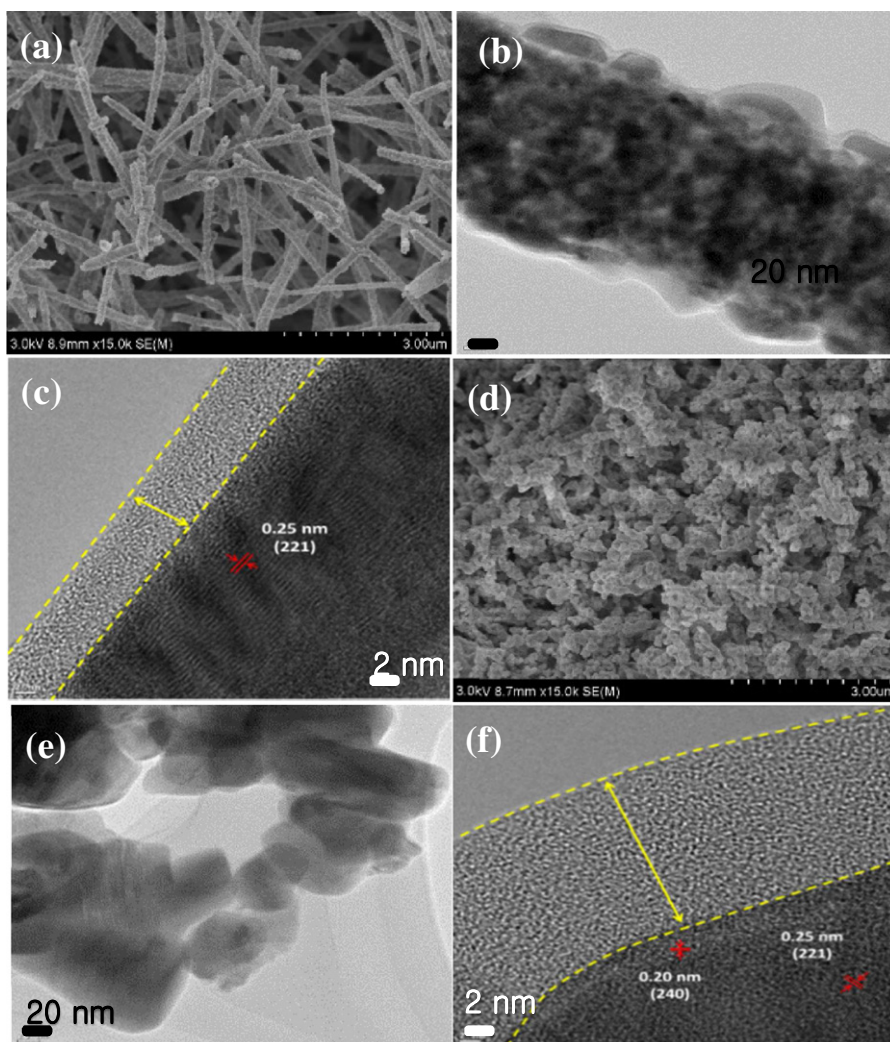


Fig. 2. (a) FE-SEM and (b, c) FE-TEM images of 1D- $\text{Co}_3\text{V}_2\text{O}_8$ , (d) FE-SEM, and (e, f) FE-TEM images of 0D- $\text{Co}_3\text{V}_2\text{O}_8$ . Carbon coating in (c, f) are outlined with dotted lines.

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