Journal of Catalysis 357 (2018) 238–246

Contents lists available at ScienceDirect

Journal of Catalysis

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

Crystal-plane engineering of $NiCo_2O_4$ electrocatalysts towards efficient overall water splitting

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ARTICLE INFO

Article history:
Received 27 August 2017
Revised 7 November 2017
Accepted 10 November 2017

Keywords:
$NiCo_2O_4$
Crystal plane effect
Nanosheet array
Water splitting
Octahedron

ABSTRACT

Understanding and designing versatile electrocatalysts for the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) in alkaline electrolyte is of great interest and importance towards overall water splitting. Here we investigated the crystal-plane-dependent electrocatalytic activity of $NiCo_2O_4$ crystals by combining experimental studies and theoretical calculations for the first time. It is revealed that $NiCo_2O_4$ nanosheet exposing {1 1 0} crystal planes shows higher catalytic activity for both HER and OER than that of $NiCo_2O_4$ octahedron exposing {1 1 1} crystal planes and $NiCo_2O_4$ truncated octahedron exposing {1 1 1} and {1 0 0} crystal planes. Furthermore, we grew the nanosheet with {1 1 0} planes on nickel foam (NF), which could guarantee fast electron and ion transport, rapid release of evolved bubbles and good structural stability, leading to the improved electrochemical performance. Acting as both anode and cathode electrocatalysts with a two-electrode electrolyzer in alkaline medium, $NiCo_2O_4$ nanosheet array produced a small cell voltage of 1.59 V to drive a current density of 10 mA cm^{-2}. The research presented here is of both fundamental and instructional significance because it unveils that selectively exposing specific crystal planes is very effective to receive promising catalysts for overall water splitting.

1. Introduction

Electrochemical water splitting, which includes producing clean hydrogen via the cathodic hydrogen evolution reaction (HER) and oxygen via the anodic oxygen evolution reaction (OER), is a promising technology to generate renewable energy sources [1,2]. In this electrochemical process, efficient catalysts are always required to address the sluggish kinetic reactions [3,4]. Currently, noble-metal oxides (e.g. Ir and Ru oxides) [5] are known as superior OER catalysts and Pt-based catalysts [6–8] exhibit glorious activity towards the HER, respectively, whereas their use is restricted by the scarcity and high expense [9,10]. Moreover, a highly efficient bifunctional electrocatalyst that can simultaneously catalyze HER and OER in a same solution has always been desired because it can enhance the water-splitting efficiency and simplify the system [11,12]. Unfortunately, these noble metal catalysts cannot simultaneously display high catalytic activity for both HER and OER. Accordingly, much research has been devoted to searching cheaper and bifunctional alternatives such as abundant 3d metals and their derivatives [13–15]. Cobalt-based spinel structures, especially nickel cobaltite ($NiCo_2O_4$), have attracted impressive interest owing to their low cost, abundant resources and better electronic conductivity (two orders of magnitude higher than conventional single metallic oxides), which have been widely employed as electrocatalysts for OER in alkaline solution [16–19]. Their applications in full water splitting, however, received much less attention [20]. Therefore, it becomes considerably attractive and necessary to study the application of $NiCo_2O_4$ for overall water splitting in depth.

Numerous innovative strategies such as integrating non-noble metal-based materials with the related two-dimensional (2D) materials [21–23], downsizing the active particles or clusters to single atoms [24–27], precisely controlling the surface structure over electrocatalysts [28–31] and engineering the heterogeneous structures [32–35] have been developed to achieve more ideal electrocatalysts with increased number and reactivity of active sites. It has been shown that elaborately controlling the surface composition/structure of a catalyst would govern its catalytic performance, because the heterogeneous catalysis process often occurs on the catalyst surface [30,36]. In this regard, facet-controlled synthesis of catalysts is also proven as an effective approach to establish the relationship between surface structure and catalytic properties [37]. The surface atomic configuration

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https://doi.org/10.1016/j.jcat.2017.11.017
0021-9517/

and the number of dangling bonds of the different crystal planes can immensely affect the amount and reactivity of active sites, from which we would acquire the desired catalysts enclosed by rational specific facets. Moreover, it is found that the crystal planes exposed on the surface of a catalyst largely depend on its shape [38]. Therefore, tuning the morphology and structure of the catalysts, which could predominantly expose the specific crystal facets showing dramatically higher catalytic activity, is a potential strategy to further maximize the catalytic reactions. Since the concept of shape dependency was firstly proposed in the study of CeO_2 [39], attention on the crystal plane effect of nanocatalysts has been more devoted to methane combustion [40], CO oxidation [41–43], supercapacitors [44] and other selective oxidation [36,45]. However, investigations of the crystal plane effect on the electrocatalysts for full water splitting revealed by both experimental and theoretical researches are still limited.

Herein, we used a simple and general method to synthesize $NiCo_2O_4$ nanocrystals exposing different crystal planes, including $NiCo_2O_4$ nanosheet exposing {1 1 0} crystal planes, $NiCo_2O_4$ octahedron exposing {1 1 1} crystal planes and $NiCo_2O_4$ truncated octahedron exposing {1 1 1} and {1 0 0} crystal planes. Notably, the monocrystalline $NiCo_2O_4$ octahedron and $NiCo_2O_4$ truncated octahedron were synthesized for the first time. We systematically investigated the effect of different crystal plane exposure on the electrocatalytic activity. The results showed that $NiCo_2O_4$ nanosheet with {1 1 0} planes exhibited best catalytic activity for both HER and OER. Combined with the computational analysis, we found that {1 1 0} crystal planes have the relatively small free energy for HER and the correspondingly small overpotential for OER, respectively. As far as we know, it is the first time to research the crystal plane effect on the full water splitting of $NiCo_2O_4$. Additionally, we further grew the $NiCo_2O_4$ nanosheet exposing {1 1 0} crystal planes on nickel foam (NF) and then the nanosheet array was straightway served as electrode for the overall water splitting. In this case, the complex electrode preparation could be averted and more critically, the binder-free $NiCo_2O_4$/NF electrode would guarantee the sufficient contact with the electrolyte. In addition, good electrical conductivity could be expected for the array structure owing to the direct connection between the electroactive $NiCo_2O_4$ and the substrate [46]. When used as bifunctional catalyst for both OER and HER as well as overall water splitting, the nanosheet array electrode exhibits superior performance compared with the random $NiCo_2O_4$ nanosheet, $NiCo_2O_4$ octahedron and $NiCo_2O_4$ truncated octahedron.

2. Results and discussion

The $NiCo_2O_4$ nanosheet, octahedron and truncated octahedron were successfully prepared firstly undergoing a controllable hydrothermal process. The morphology of the uncalcined material was recognized by scanning electron microscopy (SEM). As shown in Fig. S1a and Fig. S1b, the nanosheet precursor with length of several microns and thickness less than 20 nm distributes uniformly on a large scale. The powder X-ray diffraction (XRD) (Fig. S2a) shows the nanosheet precursor is $Co(CO_3)_{0.5}(OH)\cdot 0.11H_2O$ (JCPDS No. 48-0083) and $Ni_2(OH)_2CO_3\cdot 4H_2O$ (JCPDS No. 38-0714). Notably, the XRD profiles of uncalcined octahedron and truncated octahedron are both indexed to the standard card No. 73-1702 of $NiCo_2O_4$ (Fig. S2b), indicating that $NiCo_2O_4$ octahedron and truncated octahedron can be obtained through a one-step hydrothermal process. Moreover, the SEM images reveal that the $NiCo_2O_4$ octahedron and truncated octahedron are enclosed by well-defined facets and the centroid lengths are about 600 nm (Fig. S1c–f). The morphology of $NiCo_2O_4$ is closely related to the amount of reagents NaOH, $Co(NO_3)_2\cdot 6H_2O$ and $Ni(NO_3)_2\cdot 6H_2O$. Specifically, higher amount of NaOH, $Co(NO_3)_2\cdot 6H_2O$ and $Ni(NO_3)_2\cdot 6H_2O$ tends to produce $NiCo_2O_4$ octahedron and $NiCo_2O_4$ truncated octahedron was obtained at a low amount of the reactants (experimental section in the supporting information).

After calcination, the final products were acquired and characterized by XRD, and the sharp diffraction peaks (Fig. S3) suggested well-crystallized $NiCo_2O_4$ with cubic structure (JCPDS No. 73-1702). In addition, X-ray energy dispersive spectroscopy (EDS) analysis in Fig. S4 verifies the existence of the Ni, Co and O and the atomic ratio of Ni:Co:O is close to 1:2:4. We further carried out the SEM, transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) technique to discover the morphological and structural details. As-synthesized $NiCo_2O_4$ nanosheet has thickness and edge length of ~20 nm and several microns, respectively, inheriting the morphology of the nanosheet precursor (Fig. 1a and b). The corresponding HRTEM image indicates that the dominant exposed planes of $NiCo_2O_4$ nanosheet are {1 1 0}, which are the solely planes perpendicular to both the set of (0 0 4) planes with a lattice spacing of 0.20 nm and the set of (2 2 0) planes with a orthogonal lattice spacing of 0.29 nm (Fig. 1c). From Fig. 1d and g, we can see a large amount of uniform $NiCo_2O_4$ octahedron and $NiCo_2O_4$ truncated octahedron with similar morphology to the uncalcined sample can be obtained. From the zoom-in SEM images (Fig. 1e and h), it is observed that the $NiCo_2O_4$ octahedron and truncated octahedron with the sizes of 600–700 nm exhibit sharp corner, implying the calcination process does not destroy the morphology of the samples. Moreover, the HRTEM image (Fig. 1f) of $NiCo_2O_4$ octahedron shows two sets of planes with an included angle of 60°, and their lattice spacings are 0.30 and 0.29 nm, in accordance with the standard crystal plane spacing of (2 2 0) and (2 0 2) in cubic $NiCo_2O_4$. Accordingly, the dominant exposed crystal planes of $NiCo_2O_4$ octahedron are {1 1 1}. For truncated octahedron, it exposes additional six facets compared with octahedron. Based on the structural analysis, the additional six facets can be indexed as {1 0 0}, which are the solely planes perpendicular to the set of (0 0 4) planes with interplanar spacing of 0.19 nm (Fig. 1i). Besides, the {1 1 1} crystal planes can be detected, which are normalized by (2 2 0) and (2 0 2) planes with a lattice distance of 0.29 nm and an interfacial angle of 60° (Fig. 1j). Therefore, the $NiCo_2O_4$ truncated octahedron is enclosed by eight {1 1 1} crystal planes and six {1 0 0} crystal planes. As far as we know, this is the first time to demonstrate the successful fabrication of single crystal $NiCo_2O_4$ octahedron and truncated octahedron. It is widely recognized that controlled synthesis of crystals with uniform and regular shape that can expose specific crystal planes is of great significance for their attractive applications, particularly in the field of catalysis [36,38,47]. These obtained samples have great potential to be used in fundamentally investigating the effect of crystal facets on the properties of surface reactions.

In order to gain more detailed information about the surface electronic states and chemical composition of the obtained samples, we further conducted X-ray photoelectron spectroscopy (XPS) measurement. As shown in Fig. 2, these three samples all contain Ni, Co, and O elements. The Ni $2p_{1/2}$ and Ni $2p_{3/2}$ spectra (Fig. 2a) could be fitted with two spin-orbit doublets, which is the typical feature of Ni^{2+} and Ni^{3+} [48]. Specifically, the binding energies at 855.9 and 873.5 eV are ascribed to Ni^{3+}, while those at 854.3 and 871.7 eV are indexed to Ni^{2+}. Likewise, several Co species are clearly identified by the Co $2p_{1/2}$ and Co $2p_{3/2}$. The fitting peaks at 779.4 and 794.5 eV are ascribed to Co^{3+}, while the banding energies centered at 780.9 and 795.8 eV are associated with Co^{2+} [31,48,49]. In the O 1s region, three peaks can be clearly observed, which have been labeled as O1, O2 and O3 (Fig. 2c), respectively. In detail, the O1 peak at 529.3 eV is characteristic of metal-oxygen bond, the O2 peak centered at 531.0 eV conforms