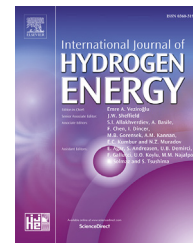




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Controlled crystal growth orientation and surface charge effects in self-assembled nickel oxide nanoflakes and their activity for the oxygen evolution reaction

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ARTICLE INFO

Article history:

Received 27 July 2017

Received in revised form

20 September 2017

Accepted 21 September 2017

Available online 18 October 2017

Keywords:

Nickel oxide

Electrocatalyst

Crystalline growth direction

Oxygen evolution reaction

Surface charge

ABSTRACT

Although sustainable hydrogen production from solar energy is a promising route for the future, the cost of the necessary photovoltaic and photoelectrochemical devices as well as a lack of detailed understanding and control of catalyst interfaces in nanomaterials with high catalytic activity are the largest impediments to commercial implementation. Here, we report how a higher catalytic efficiency can be achieved by utilizing an earth-abundant Nickel oxide (NiO) catalyst via an improved control of the crystalline growth orientation and self-assembly. The relationship between the surface charge and the morphology of the nano-catalysts is investigated using a hydrothermal method where the pH is utilized to control both the crystal growth direction and crystallization of Ni(OH)₂ and eventually in NiO, where the self-assembly properties of nanoflakes (NFs) into hierarchical flower-like nickel oxide NFs depend on balancing of forces during synthesis. The surface charge of the NiO at different pH values was measured with electrophoretic dynamic light scattering (EDLS) and is known to be closely related to that of Ni(OH)₂ and is here utilized to control the relative change in the surface charge in the precursor solution. By preparing NiO NFs under variation of the pH conditions of the precursor Ni(OH)₂ system, the surface energies of exposed lattice planes of the growing nanostructures can be altered and an enhanced crystal growth orientation in a different direction can be controlled. Specifically, the [111] and [220] growth orientation in cubic NiO can be favored or suppressed with respect to the [200] direction.

Benefiting from the large surface area provided by the mesoporous NiO NFs, the catalyst electrode exhibits high activity toward the oxygen evolution reactions in alkaline electrolyte. The NiO nanostructure synthesized at pH 10 displays oxygen evolution reaction (OER) overpotential of 0.29 V and 0.35 V versus the reversible hydrogen electrode (RHE) at 1 mA cm⁻² and 10 mA cm⁻² current density, respectively. This is compared to commercial NiO with more than 0.15 V additional overpotential and the same or lower overpotential compared to RuO₂ and IrO₂ at alkaline conditions. The results show that the OER catalytic activity can be drastically increased by a detailed control of the crystal growth orientation and the self-assembly behavior where the active surface charge around the point of zero

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<https://doi.org/10.1016/j.ijhydene.2017.09.117>

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charge during synthesis of the metal hydroxides/oxides is introduced as an important design principle for producing efficient electrocatalysts.

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Introduction

With the increasing global energy demand and continuous depletion of fossil fuel-reserves, the effective exploitation of free and renewable carbon-neutral energy sources, such as sunlight, is one of the greatest scientific challenges [1–8]. The electrochemical water splitting reaction offers a promising process in view of the energy conversion from solar light to storable hydrogen fuels [9–15]. In practice, one of the key problems is to provide not only more efficient but also cost-effective electrocatalysts for the oxygen evolution reaction (OER, $4\text{OH}^- \rightarrow 2\text{H}_2\text{O} + 4\text{e}^- + \text{O}_2$ in alkaline media) [16]. For this reason, substantial efforts have been devoted to developing both low overpotential and low-cost electrocatalysts for OER [17–19]. To date, the optimal OER anode catalysts are RuO_2 [20,21] and IrO_2 [20,21] due to the lowest overpotential at a current density of 10 mA cm^{-2} , however, Ru and Ir are considered as the rarest elements on earth, which limits their use on a large industrial scale [22–25]. Therefore, to meet the economical and practical demand, it is necessary to find earth-abundant OER catalysts, especially based on non-noble materials.

Recently, the p-type wide band gap semiconductor, nickel (II) oxide (NiO) has attracted increasing attention because of its potential applications in a variety of fields, such as supercapacitors [26,27], electrode materials for lithium ion batteries [28–30], catalysts [16,31], gas sensors [32] etc. As we all know, the structure and morphology of materials are closely related to their properties [33,34] and considerable investigations have been reported to synthesize different kinds of NiO nanostructures. Shen and co-workers found a practical and efficient strategy to synthesize hierarchically (meso- and macro-) porous NiO nano/micro spherical superstructures via refluxing an alkaline solution, which provided a good electrochemical capacitance [35]. Qiu et al. developed a novel approach to synthesize porous NiO nanofibers by impregnating electrospun polyacrylonitrile (PAN) fiber templates with corresponding nitrate aqueous and ammonia solution [36]. Wang and co-workers reported a simple nickel salt-urea- H_2O ternary system to synthesize self-assembled urchin or flower-like hierarchical microspheres selectively with the assistance of urea, which exhibited a promising electrochemical performance in anodic lithium storage for the lithium-ion battery [37]. Wet chemical method has also been proposed as a facile and cost-effective route to fabricate controlled NiO nano/microstructures. A popular synthetic method is based on the calcination of the insoluble precipitates (e.g. $\text{Ni}(\text{OH})_2$) in the presence of appropriate alkaline solution (e.g. NaOH, $(\text{NH}_2)_2\text{CO}$ or $\text{NH}_3 \cdot \text{H}_2\text{O}$) [38,39] where synthesis of NiO nanoflakes has been achieved from calcination of $\text{Ni}(\text{OH})_2$ and previously investigated for ultrafast lithium storage and nickel-zinc batteries [40,41].

In this work, we quantify how a pH environment around the isoelectric point (IEP) can be used to control the crystal growth direction in $\text{Ni}(\text{OH})_2$ used in sub-sequent calcination to produce NiO nanoflakes with controlled crystal growth direction in between the [111] and [220] direction with respect to the [200] direction and improved electrocatalytic properties. We also show how the alteration of surface charge affects the formation of different morphologies of self-assembled $\text{Ni}(\text{OH})_2$ and, after calcination, likewise controls of the resulting NiO micro/nanostructures. With the approach, uniform NiO hierarchical nanostructures consisting of thin nanoflakes were successfully synthesized without any template or seed and used as anode electrocatalysts for the oxygen evolution reaction. The prepared NiO catalysts exhibit promising properties in 1 M NaOH with a very low overpotential at 10 mA cm^{-2} , especially in the case of the as-formed NiO nanostructure at pH 10. *In-situ* electrochemical impedance spectroscopy during catalysis was utilized to quantify the charge transfer resistance at the NiO surfaces for the different nano-catalysts.

Experimental section

Materials

All chemicals used in our study were analytical grade without further purification. Nickel (II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\geq 97\%$) was purchased from Sigma-Aldrich; 2-propanol, (Reagent, ACS, $(\text{CH}_3)_2\text{CHOH}$) was purchased from VWR chemicals; and ammonia solution ($\text{NH}_3 \cdot \text{H}_2\text{O}$, 25%) from Merck was also used. Nickel (II) oxide powder (99.998%) was purchased from Alfa Caesar.

Preparation of materials

NiO nanoflakes with flower-like microstructures were prepared by the hydrothermal method [42]. In a typical experiment to prepare the NiO nanoflakes, 0.03 M $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dispersed in 50 mL of 2-propanol and deionized water (1:1, v/v) solution under sonication for 30 min. Next, an appropriate amount of ammonia solution ($\text{NH}_3 \cdot \text{H}_2\text{O}$, 25%), which controls the pH value of the precursor suspension, was slowly added to this suspension which was stirred for 1 h. The mixed suspension was transferred into a 100 mL Teflon-lined stainless steel autoclave for hydrothermal reaction at 180°C for 8 h, and then naturally cooled to room temperature. The precursor precipitate was collected after centrifuging, washing with deionized water and ethanol, and then dried at 80°C in air for 12 h. Finally, the precursor was heated to 350°C with a ramp of 5°C min^{-1} , where they were annealed for 3 h under an argon atmosphere to obtain the NiO nanoflakes (NFs).

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