Facile synthesis of thin NiFe-layered double hydroxides nanosheets efficient for oxygen evolution

Kai Yan a,⁎, Todd Lafleur b, Jiajue Chai a, Cody Jarvis b

a School of Engineering, Brown University, Providence 02912, USA
b Department of Chemistry, Lakehead University, Thunder Bay P7B5E1, Canada

Abstract

Ultrathin NiFe-layered double hydroxide (LDH) nanosheets are facilely and cost-effectively fabricated. The as-prepared NiFe-LDH nanosheets are highly active and stable electrocatalysts for water oxidation in alkaline environment, exhibiting a much higher oxygen evolution activity and lower overpotential with the enhanced stability, much superior to the previously reported LDH-derived catalysts. This work provides a facile methodology for the fabrication of thin nanosheets, which are promising in the renewable energy conversion.

Keywords:
Layered double hydroxides
Nanosheets
Oxygen evolution reaction
Activity
Stability

1. Introduction

Electrochemical water splitting offers one of the most attractive approaches in the realization of efficient energy conversion and storage [1–3]. In oxygen evolution reaction (OER), the overall efficiency of the complicated OER is severely influenced by the energy loss and large overpotential. To date, OER catalysts based on precious metal oxides RuO2 or IrO2 are most effective, but the high price and scarcity make them impractical to use on a large scale. Besides, it has been reported that the RuO2 and IrO2 catalysts display poor stability in alkaline solution [4]. Toward this end, it is crucial to develop highly active and cost-effective OER catalysts based on earth-abundant metals. Phosphate and Ni-borate catalysts have been reported to display good performance for OER in neutral and weakly basic medium [5,6], where it required ~400 mV overpotential to reach 10 mA cm−2. Perovskite Ba0.5Sr0.5Co0.8Fe0.2O3 catalyst is also efficient for OER in alkaline medium, which are even more active than IrO2 and RuO2 [7,8]. Recently, the low-cost NiFe-derived layered material, spinel and oxides were reported to display promising performances of OER in alkaline solutions [9,10]. It has been proposed that layered metal hydroxides are the active centers [11,12].

The skeleton of layered double hydroxides (LDHs) was composed of a regular assembly of interlayer anions and positively charged metal-hydroxide layers in which the main layers are formed by MO6 octahedra that share edges [13,14]. Due to this unique structural property, LDHs exhibit promising nature as high-performance OER catalysts. However, LDHs still suffers from poor electronic conductivity and electron transport. To reduce these drawbacks, the conductivity and activity of LDHs has been further enhanced by coupling to a carbon nanotube, graphene-like network or by exfoliation [14–18]. Among them, exfoliation method appears more attractive due to the relatively easy synthesis and good performances observed in OER. The resulted LDHs by exfoliation methods often display thin nanosheets with better conductivity and large space between the layers. However, the synthesis still requires multiple steps of LDH precursor synthesis, anion-exchange, exfoliation in high boiling point solvents (e.g., formamide or N-methylpyrrolidone) and final removal of these high boiling points solvent. The removal of high boiling point solvents often associates with the utilization of excessive ester and low yield of LDHs. Besides, the resulted LDHs plates often tend to stack and lack good control over the hierarchical nanostructures.

Herein, we have developed a facile, and cost-effective route to synthesize ultrathin NiFe-LDH nanosheets in the mixed solvent of ethanol and isopropanol. The obtained nanosheets are highly active and stable catalysts for OER in alkaline conditions, where they exhibit the enhanced oxygen evolution activity in comparison with other LDH-derived electrocatalytic materials reported to date. The fabricated thin nanosheets display more active sites and improve the electronic
conductivity. This work presents a novel strategy to design low-cost and high-performances OER electrocatalysts that are attractive for the application in transformation of renewable energy sources.

2. Experimental

2.1. LDH nanosheet synthesis

Thin LDH nanosheets were synthesized in two steps of co-precipitation and delamination. In the first step, LDH precursor was synthesized by a classic co-precipitation method at room temperature as our previous report [19]. The second step of delamination was performed, where 100 mg LDHs were dispersed into the 200 mL mixed solvent of ethanol and isopropanol with the volume ratio of 1 at 60 °C under the stirring condition of 1000 rpm for 12 h. The resulting suspension was centrifugated at 5000 rpm for 5 min and dried at 80 °C under vacuum condition.

2.2. Characterizations

The powder X-ray diffraction (XRD) patterns for qualitative phase analysis were collected on a Phillips PW 1050-3710 transmission diffractometer with Cu Kα radiation (λ = 1.5406 Å). The data were collected in the range of 8–65° with a step width of 0.05/2θ. Scanning electron microscopy (SEM) analysis was performed on FEI Helios–FIB operating at an acceleration voltage of 10 kV. TEM analysis was investigated on Philips CM 20 instrument at 120 kV. HR-TEM was performed on JEOL-2010 at 200 kV to investigate their structural features. Nitrogen adsorption–desorption was measured using a Micromeritics ASAP 2020 sorption analyzer at 77 K, and the samples were activated under a vacuum of 0.01 mbar at 25 K.