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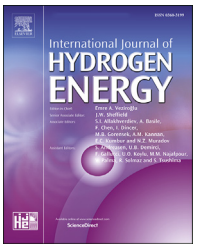

Mesoporous NiO with different morphology: Synthesis, characterization and their evaluation for oxygen evolution reaction

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ABSTRACT

Mesoporous NiO samples with different morphology were synthesized by hydrothermal method, and they were studied as electrocatalysts for oxygen evolution reaction in alkaline solution. The NiO samples were characterized by X-ray diffraction, transmission electron microscopy, N_2-adsorption, scanning electron microscopy and X-ray photoelectron spectroscopy. The critical synthesis parameters like hydrothermal reaction temperature, time and molar ratio of precursors were varied using Taguchi experimental method to investigate their effect on morphology and specific surface area of mesoporous NiO samples. The characterization data illustrated the formation of nanoplates, nanorods, and nanoparticles. All the NiO samples exhibited mesoporosity and the specific surface area values in the range of 88–156 m^2/g. One of the synthesized mesoporous NiO samples, largely constituting of nanoplates and nanorods with high porosity, exhibited a Tafel slope of 62 mV/dec and achieved a current density of 41.6 mA/cm^2 at 1.6 V (vs. RHE). It showed better electrocatalytic activity for oxygen evolution reaction than remaining samples.

Introduction

Over several decades now, researchers have focused extensively on the development of potential renewable energy systems to meet the increasing energy demand [1,2]. In this context, hydrogen gas is an energy-rich chemical which can be used in producing electricity in a fuel cell, fuel for aircrafts, power stations and semiconductor industry [3–5]. Additionally, hydrogen is a key starting material for many chemical industries such as petroleum, fertilizer etc. [6,7]. Presently, these industries mainly rely on fossil fuels for the hydrogen production, which emit pollutants such as CO, CO_2, NO_x, SO_x leading to air pollution [8]. Thus, there is a need to overcome the serious adverse effects on the environment due to current hydrogen production methods. Electrochemical water splitting is an attractive green method for hydrogen production with almost zero emissions. In electrochemical water splitting, among the two half reactions, oxygen evolution reaction (OER) at anode becomes crucial because of its high kinetic barrier and high performance catalysts are essential to improve the rate of reaction. This in turn would improve the economics of hydrogen production by electrolytic water splitting. Furthermore, OER also has various commercial applications in storage devices, etc. [4,6–8].

Many electrocatalysts have been studied for OER in alkaline medium, among them, RuO_2 and IrO_2 displayed the best activity. However, they are not economically viable for large-scale production because of their scarcity and consequently

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high cost. Hence, there is need to develop efficient, robust and low-cost electrocatalysts for OER. The earth abundant transition metal based electrocatalysts such as cobalt oxide [9–12], manganese oxide [13–15], copper oxide [16,17], Ni–Co alloy [18,19], Ni–Co sulfides [20–22], Co–Fe layered double hydroxide [23–25], Co–Cu mixed oxides [26,27], Ni–Fe mixed oxide [28] and Ni–Fe alloy [29] have been developed for OER in alkaline media. Predominantly, the search for efficient electrocatalysts revolves around transition metal oxides. Several transition metal oxides have been explored as electrocatalysts for the OER. Some of these non-precious metal oxides will be ideal as electrocatalysts due to their viability and abundance. Among the transitional metal oxides, Ni based oxides have shown good activity towards OER. Both NiO_x and $Ni(OH)_2$ nanoparticles, ultra small crystalline NiO nanoparticles, ultrathin NiO/Ni nanosheets and three dimensional NiO/Ni structures were also reported as electrocatalysts for OER in alkaline medium [30–36]. Other than oxides, various Ni based catalysts such as nickel nitrides [37,38], nickel sulfides [39], Ni–Se alloys etc. [40–42] have also been studied.

A key feature of the transition metal oxide based electrocatalysts is their tunable morphology. Different morphologies of electrocatalysts have also been explored for their activities for OER in alkaline condition [43,44]. Recently, L. Zhang et al. studied nanosheets of Co_3O_4 and observed improved OER activity compared to rod-like structures due to their high surface area and porosity [45]. Q. Z. Xu et al. reported high OER activity of Co_3O_4 nanowires which consisted of urchin-like spheres [46]. X.F. Luo et al. reported high activity for MnO_2 nanowires which was ascribed to transport of active species and electrons through the nanowire array [47]. It is evident that other than the active material, morphology of the nanostructures also plays a crucial role in their electrocatalytic activities. In turn, the morphology is influenced primarily by the reaction and synthesis conditions. A wide variety of synthesis conditions such as template synthesis, chemical vapour deposition, microwave, solvothermal, hydrothermal etc. have been used to make different nanostructures [45,48–55]. Among all of them, hydrothermal method is probably the simplest one. Therefore, it may be of interest to investigate the effect of experimental parameters such as reaction temperature, reaction time and ratio of precursors on the formation of different nanostructures and their effect on the activity for OER. Among all other experiment designs, the Taguchi method is a well-known technique to investigate the significant effect of synthesis parameters on physicochemical characteristics of synthesized materials. It is an orthogonal array based robust design. This Taguchi method is far more efficient than the conventional methods to design an experimental approach. This approach reduces the number of experiments which saves time and valuable resources [56].

Based on above discussions, this work is primarily focused on the study of synthesis factors on mesoporous NiO samples like nanoplates, nanorods, and nanoparticles using Taguchi method and evaluating their OER activity in alkaline media. As far as we know, a comprehensive study on the effect of different morphology of NiO nanostructures on OER has not been undertaken. Herein, we report the synthesis of mesoporous NiO samples by a simple surfactant free hydrothermal method at various experimental conditions. In this study, parameters like reaction temperature, reaction time and the ratio of precursors were varied for the preparation of mesoporous NiO samples. After synthesis, they were characterized by X-Ray Diffraction (XRD), Scanning Electron microscopy (SEM), Transmission Electron microscopy (TEM) and Brunauer–Emmett–Teller (BET). The electrocatalytic activities of all the catalysts were studied by recording cyclic voltammogram (CV) and linear sweep voltammogram (LSV) using a potentiostat.

Experimental

Materials

Nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$, $\geq$ 98% purity) was obtained from Loba Chemie Pvt. Ltd. Sodium hydroxide (NaOH, $\geq$ 98% purity) and potassium hydroxide (KOH, $\geq$ 98% purity) were purchased from E.Merck India Ltd. Nafion solution (5 wt %) was supplied by Sigma Aldrich and RuO_2 catalyst (for comparison) was obtained from SDFC Ltd, India.

Synthesis of mesoporous NiO samples

Mesoporous NiO samples were prepared by hydrothermal method. Taguchi experimental method L9 was used to design the experimental approach. According to this design mainly 3 synthesis parameters temperature, time of reaction and molar ratio of precursors (NaOH: $Ni(NO_3)_2$) were varied. The selected synthesis parameters, levels and synthesis conditions were presented in Tables 1 and 2. The calculated amount of nickel nitrate (3 mmol) was dissolved in 20 mL of distilled water. Then 20 mL of the sodium hydroxide solution (corresponding to 6, 24 and 48 mmol of NaOH) was slowly added to above solution under constant stirring. After 30 min, the green solution was transferred to a stainless steel autoclave of 50 mL capacity for hydrothermal treatment. The reactions were performed at three different temperatures for 1, 6, and 12 h (see Table 2 for details). After the hydrothermal treatment, the precipitate was washed with distilled water thoroughly and dried at 75 °C. Finally, the obtained solids were calcined at 400 °C for 2 h at the rate of 6 °C/minute. By varying the temperature, time and molar ratio of precursors of reaction total 9 different mesoporous NiO samples were prepared. They were named as E1, E2, E3, E4, E5, E6, E7, E8 and E9 (Table 2).

Materials characterization

XRD patterns of the samples were recorded (X'Pert Pro Diffractometer, Panalytical, Netherland) using Cu Kα

Table 1 – Factors and their levels in the experimental design.

Levels	Temperature (C°)	Time (Hrs)	Molar ratio of precursors (NaOH: $Ni(NO_3)_2$)
1	180	12	16
2	140	6	8
3	100	1	2

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