RESEARCH PAPER

In situ growth of NiO nanostructures supported on nickel foam as an efficient electrocatalyst for oxygen evolution reaction

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ABSTRACT

Recently, the concerns about depletion of fossil fuels and also the environmental pollution resulting from resources burning have driven scientists to look for clean and sustainable energy resources. Some advantages of hydrogen have made it an alternative energy resource to fossil fuels. Electrochemically splitting of water is considered as one of the main techniques to produce high-purity hydrogen. Fabrication of cost-effective electrocatalysts for oxygen evolution reaction (OER) in a water splitting process is vital for large-scale practical applications. Herein, we present an affordable and straightforward method for synthesis of NiO nanoparticles supported on Ni foam for oxygen evolution reaction (OER). A single-step annealing process was carried out at different temperatures to achieve an optimal temperature, at which an electrocatalyst with a tailored morphology and high electrocatalytic activity is obtainable. The best electrocatalytic activity was achieved by the electrode fabricated at 400 °C, delivering current density of 10 mA/cm^2 at 1.59 mV potential versus reversible hydrogen electrode (RHE) under alkaline condition. Various material characterization tests accompanied by electrochemical measurements were used to clarify the excellent electrocatalytic activity of the electrode fabricated at 400 °C.

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INTRODUCTION

The environmental pollution resulting from the burning of fossil fuels and depletion of these limited resources have prompted researchers to look for clean and sustainable energy resources [1,2]. Due to its high energy density and benignity to environment, hydrogen is considered as a promising alternative to traditional fossil fuels. However, this scenario requires a clean and durable source of hydrogen [3]. One of the main techniques employed to obtain high-purity hydrogen is electrochemically or photoelectrochemically splitting of water, which is made up of two half reactions including oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) [4-6]. The kinetically sluggish reaction at the anode as OER is one of the main challenges in electrochemical water splitting. Ir-based materials are highly efficient electrocatalysts in the OER. However, these electrocatalysts are costly and their scarcity hinders their large-scale practical applications to economically produce high-purity hydrogen by water splitting [8, 9]. Recently, considerable effort has been made on the development of cost-effective electrocatalysts for OER, which are largely

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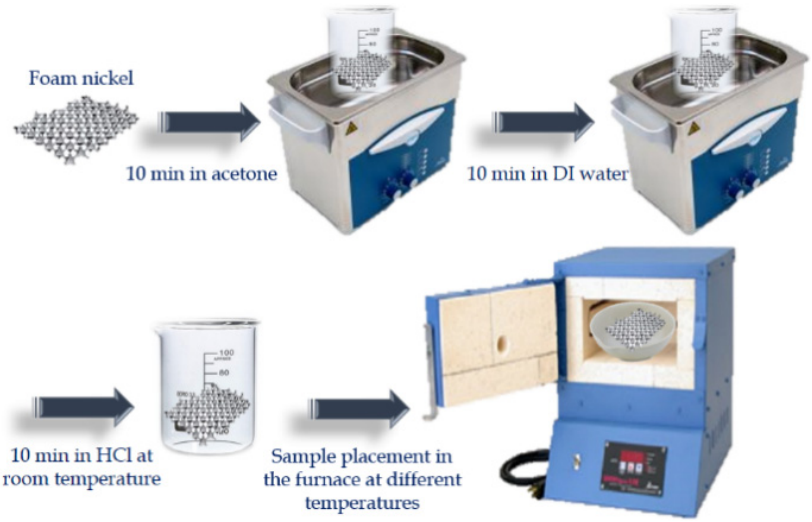

Fig. 1. Schematic illustration of the fabrication process of the NiO nanostructures on the nickel foam.

based on earth-abundant transition metal oxides for instance Ni, Fe, and Co [7,10]. However, these oxide based electrocatalysts greatly suffer from the poor electrical conductivity, which in turn contributes to slowing down the critical charge transport involved in the electrochemical process [8]. The usage of highly electrically conductive metal foams as the substrate to accommodate the catalyst layer can be an efficient remedy to overcome the aforementioned problem and subsequently to enhance the electrocatalytic activity of the oxide based electrocatalysts [8]. Some merits of nickel foam (NF), including proper flexibility, mechanical strength, and high electrical conductivity have made it a suitable candidate to be used as a conductive substrate. Furthermore, the porous structure of the NF provides it with enhanced mass transport engaged in the electrochemical process. Moreover, the growth of electrocatalysts on the surface of NF would guarantee an appropriate contact between the substrate and the electrocatalyst for an effective charge transport in OER [8, 11–14]. In this research, we develop a facile, affordable, and direct approach for synthesis of porous NiO electrocatalysts on the NF substrate for water splitting by means of thermal oxidation. In addition, the influence of a thermal annealing process on the structural, morphological, and electrochemical properties of NiO nanostructures is investigated. It is worth mentioning that in this method, no binder is needed to anchor the electrocatalyst layer on the top of the substrate, which can highly improve the adhesion between the fabricated electrocatalyst layer and the conductive substrate.

EXPERIMENTAL

Fabrication of electrodes

The commercial NF with the thickness of 1.5 mm was purchased (nano-BAZAR, Iran) and cut into pieces of 1 cm × 0.5 cm. The NF piece was first sonicated in aceton for 10 min, followed by washing with DI water in ultrasonic for 10 min. Finally, the NF was immersed in 0.1 M HCl for 10 min to remove the native surface oxide layer. Afterward, the pretreated NF was annealed in the furnace for 1 hour at different temperatures, including 400, 600, and 700 °C to investigate the effect of thermal annealing temperature on the morphology of NiO nanostructures and subsequently their electrocatalytic activity. The schematic illustration of the process used for the fabrication of the NiO nanostructures on the backbone of the NF is depicted in **Fig. 1**.

Electrochemical measurements

All electrochemical measurements were performed at room temperature with a three-electrode system by means of a potentiostat/galvanostat (SAMA 500, Electro analyzer system, Iran). Ag/AgCl electrode, Pt electrode, and the fabricated electrodes were adopted as the reference electrode, counter electrode, and working electrode, respectively. Linear sweep voltammetry (LSV) measurements were done in an equeous solution of

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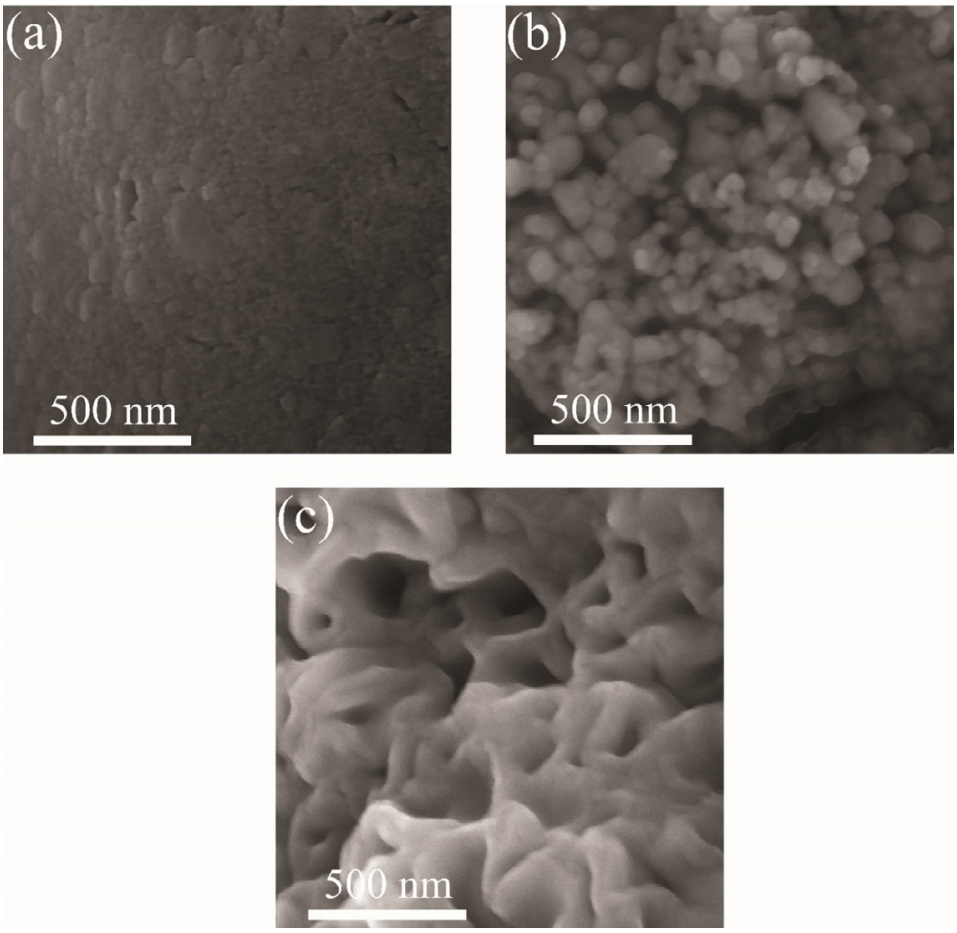

Fig. 2. FESEM images of the NiO nanostructures synthesized at a) 400 °C, b) 600 °C, and c) 700 °C.

1 M NaOH to evaluate the electrocatalytic activity of the fabricated electrodes. The stability of the NiO nanostructures was investigated by performing the chronoamperometry meaurements.

Characterization

An EQUINOX 3000 Intel X-ray diffractometer using Cu-Kα radiation was adopted to monitor the crystalline structure of the fabricated electrodes. The changes in the morphology of the NiO nanostructures as the result of changing the temperature were investigated by means of a field-emission scanning electron microscope (FESEM) (Tescan-Mira III). Raman spectra of the electrodes were taken using a Teksan (Takram P50C0R10) Raman spectrometer with a 532 nm Nd:YAG laser.

RESULTS AND DISCUSSION

Fig. 2 illustrates the FESEM images of the NiO nanostructures synthesized at the varied temperatures. According to **Fig. 2a**, the size of the NiO nanostructures synthesized at 400 °C is approximately less than 40 nm. Notably, the size of NiO nanostructures increases with the increase in annealing temperature (**Fig. 2b,c**). In fact, the increment in the size of the nanoparticles associated with increasing the temperature originates from a reduction in the free energy (ΔG) of the reaction [15–18]. The possible explanation for the growth of the NiO nanostructures is vapour-solid (VS) mechanism. The first reaction happens between Ni gas and O_2 to form NiO_X. In the second stage, O_2 (gas) is reacted with NiO_X on the nickel foam, and therefore, NiO nanostructures are easily nucleated and grown on the surface of the nickel foam [19, 20].

The LSV polarization curves of the NiO nanoparticles synthesized at different temperatures are shown in **Fig. 3**. Potentials are measured with respect to reference electrode and reported with

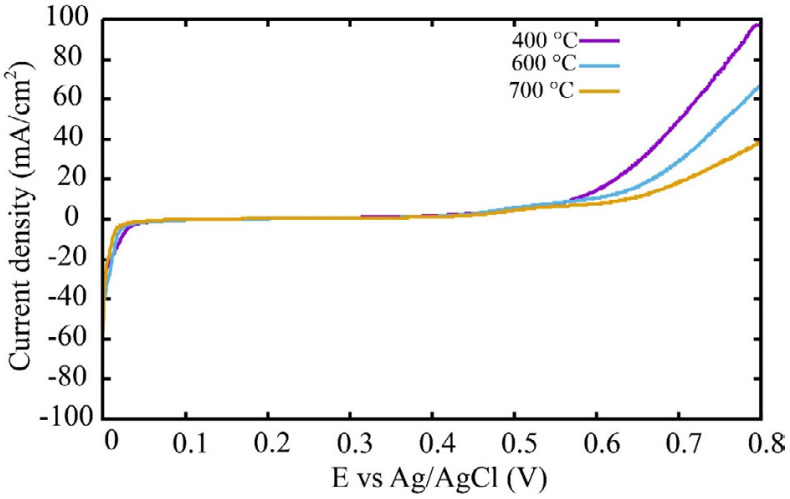

Fig. 3. LSV polarization curves of the NiO nanoparticles synthesized at the different annealing temperatures.

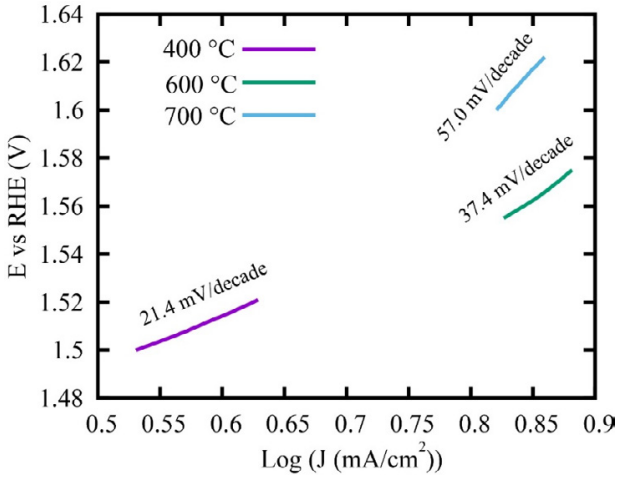

Fig. 4. The Tafel slope values of the electrodes synthesized at different temperatures.

respect to the reversible hydrogen electrode at a scan rate of 2 mV/s. The electrode fabricated at 400 °C requires 1.59 V to generate a current density of 10 mA/cm^2. Obviously, the OER onset of the electrode fabricated at 400 °C shows an improved efficiency compared to other electrodes. The reason behind this improvement is likely due to the high surface area of the small NiO nanoparticles anchored on the surface of NF.

The enhanced catalytic activity of the electrode fabricated at 400 °C is also reflected by its low Tafel slope value. The Tafel slope values of the electrodes are obtained from their polarization curves, as shown in **Fig. 4**. The electrode exposed to 400 °C has a Tafel slope value of 21.4 mV/decade, which is lower than that of 600 °C (31.4 mV/decade) and 700 °C (57.0 mV/decade). The smaller Tafel slope value of the electrode fabricated at 400 °C in comparison with other electrodes demonstrates its better reaction kinetics in OER. By taking the abovementioned reasons into account, the electrode fabricated at 400 °C was chosen as the optimal sample for further study.

The XRD pattern of the electrode fabricated at 400 °C is shown in **Fig. 5**. The strong and sharp peaks belong to crystallite facets of (111), (200), and (220) are related to the nickel foam substrate. In addition, the crystallite facets of (111), (200) and (220) testify the formation of the NiO nanoparticles on the nickel foam [4,21–23].

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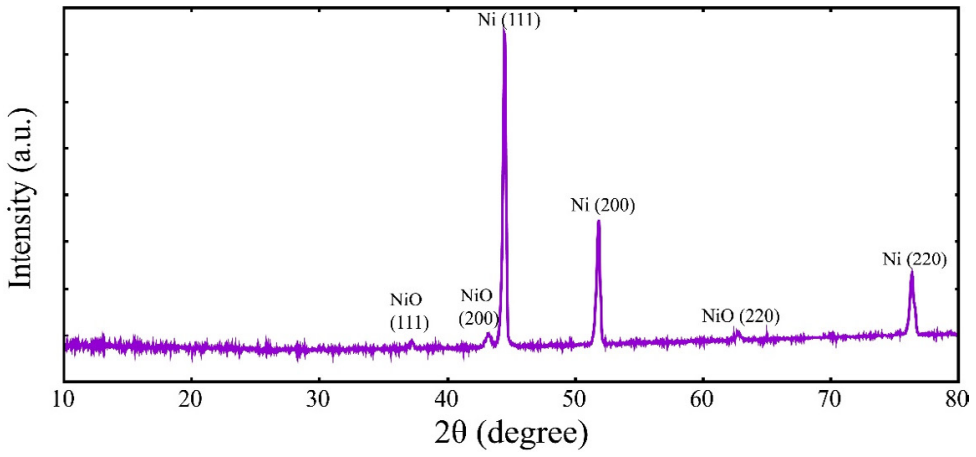

Fig. 5. The XRD pattern of the electrode fabricated at 400 °C.

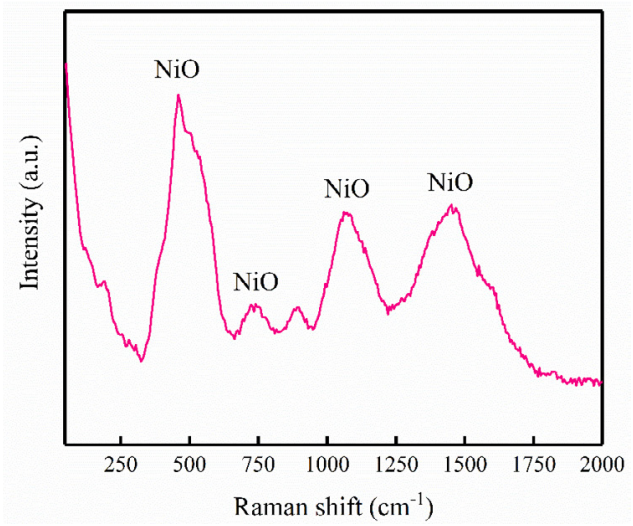

Fig. 6. The Raman spectrum of the electrode exposed to 400 °C.

The grown NiO nanoparticles on the nickel foam was also verified by taking the Raman spectrum of the electrode fabricated at 400 °C (see **Fig. 6**). The four well-defined peaks centered at about 450, 740, 1070, and 1450 cm^{-1} are respectively assigned to the first-order longitudinal optical phonon mode of the Ni-O lattice vibration, the second-order transverse, the second-order longitudinal optical phonon modes, and the two-magnon mode of the NiO [24–27].

The stability of the electrode fabricated at 400 °C was assessed for 6 hours with chronoamperometric measurements under the voltage of 0.6 V with respect to Ag/AgCl electrode (see **Fig. 7**). The current density of the electrode increased continuously with the time and exhibited long-term stability with no loss during the chronoamperometric measurements.

The stability of the electrode fabricated at 400 °C was further analyzed by conducting the LSV measurements before and after the six-hour chronoamperometric test (see **Fig. 8**). As it is clear from the LSV curves, the electrode shows an identical behavior before and after the chronoamperometric test, indicating its excellent stability.

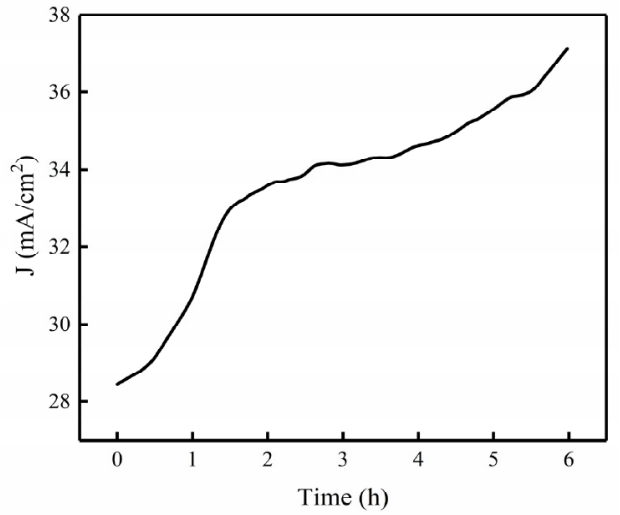

Fig. 7. Chronoamperometric curve of the electrode fabricated at 400 °C. The measurements were conducted in 1 M NaOH electrolyte and under the voltage of 0.65 V for 6 hours.

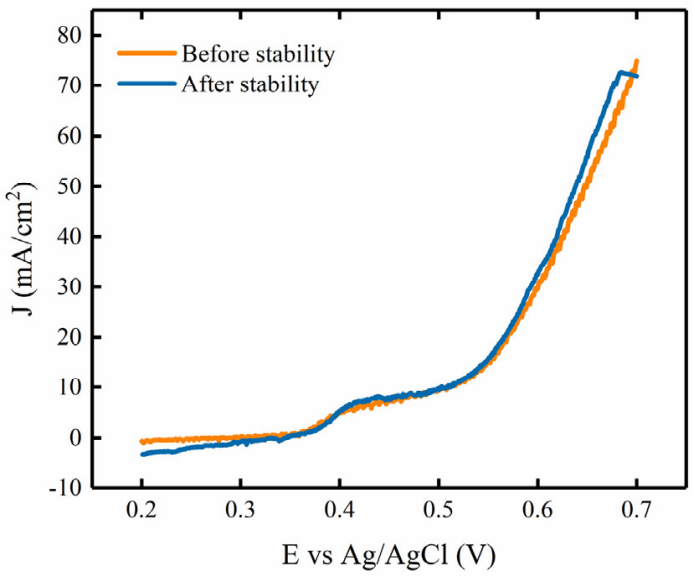

Fig. 8. The LSV curves of the NiO nanoparticles fabricated at 400 °C in 1 M NaOH electrolyte before and after the six-hour chronoamperometric test. The measurements were done at the scan rate of 2 mV/s.

CONCLUSION

In conclusion, a simple and cost-effective method has been developed to prepare NiO nanoparticles supported on NF substrate for OER. Among the fabricated electrodes at different temperatures, the one exposed to 400 °C delivered the best OER electrocatalytic activity with an overpotential of 1.59 V at a current density of 10 mA/cm^2 and a low Tafel slope of 19.27 mV/decade. The superior electrocatalytic activity of the electrode fabricated at 400 °C was attributed to the small size of NiO nanoparticles, which resulted in their high surface area. The strategy developed in this research can be applicable and useful for the synthesis of highly efficient non-noble metal electrocatalysts for water splitting applications.

CONFLICTS OF INTEREST

The authors announce that there are no conflicts of interest.

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