Fabrication of nanocage structured based electrocatalyst for oxygen evolution reactions

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Abstract:

The development of efficient, eco-friendly, and inexpensive electrocatalysts has become crucial and significant in water-splitting applications. Herein, we developed a nickel-cobalt nanocage (Ni/Co-NC) electrocatalyst via the solvothermal method which can boost the performances towards oxygen evolution reactions (OER) and hydrogen evolution reactions (HER). The Ni/Co-NC reveals significant performance at an onset potential of 350 mV for the OER at delivered current density of 10 mAcm^{-2}. Furthermore, the synergic effect between various Ni^{3+}/Ni^{2+} and Co^{2+} could optimize the performance resulting in a smaller Tafel slope of 70 mV dec^{-1} for Ni/Co-NC.

Keywords: Oxygen evolution reaction, Metal-organic framework, Nanocage, Electrocatalyst

Introduction:

Metal-Organic Framework (MOF) is considered a promising material for electrochemical performances, due to its extremely large surface area, variable active sites for redox reactions, and abundant micropores [1-2]. The high HER and OER performances of metal embedded carbon were obtained from the decomposition of MOF. Numerous metals or carbon composites obtained by decomposition in an inert atmosphere have extensively been used for electrocatalysis and energy storage devices [3-4]. The crystalline structure, microstructure, and electronic structure play a vital role in the electrocatalytic performance and are beneficial for oxygen evolution reactions due to the enhancement in active sites [5-6]. The nanocages structure widely known as layered double hydroxide structure is beneficial during the electrochemical processes for charge transfer. Ni-derived composites have gained significant attention owing to their low cost, abundance, and easy

accessibility in energy conversion and storage [7-8]. The excellent performances were reported for OER and HER using nickel chalcogenides, which results in different phases due to unique electron states [9]. Therefore, the fabrication of catalysts using transition metals is an efficient and effective way to improve water splitting. Herein, we report the fabrication of Ni/Co-NC composite using zeolitic imidazolate framework-67 as a precursor. The significant enhancement in the electrochemical properties depends on the unique structure (nanocage) and the synergistic effect between the two compounds. The obtained non-noble metal, bifunctional catalyst when used for both the OER and HER reveals a promising electrocatalyst for overall water splitting.

Materials and Methods:

Synthesis of Ni/Co-NC:

The Ni/Co-NC was synthesized by the similar procedure reported previously with slight modifications [10]. The solvothermal approach was used to make the Co-MOF. Firstly, Co $(Ac)_2.4H_2O$ (1.25g, 5 mmol) and 2-methylimidazole (4.11g, 50 mmol) were dissolved separately in 25 mL of DI water. Afterward, the two solutions were mixed and vigorously agitated for 4 hours, after which crystals were collected by centrifugation and dried to obtain dark purple crystals.

The former obtained product was dispersed in the solution of Ni $(NO_3)_2.6H_2O$ (25 mmol) and methanol (25 mL) to form a clear solution. The prepared solution was poured to an autoclave and kept in the oven for 12 hours. The mixture was then allowed to cool to room temperature before being washed with methanol and dried in a vacuum oven at 60°C for 12 hours.

Results and Discussion:

A three-dimensional nanocage catalyst represented as Ni/Co-NC was prepared via hydrothermal reaction as shown in Fig. 1a. As demonstrated by the HRTEM images (Fig. 1b), nanocages of Ni/Co-NC shows distinct hollow nanocages that are well dispersed. An energy-dispersive X-ray

spectroscopy (EDX) analysis was used to determine the composition of Ni/Co-NC. The Ni/Co-NC contains Co (1.62 wt.%), Ni (14.24 wt.%), O (49.46 wt.%), C (14.21 wt.%), and N (16.48 wt.%) respectively. Since nickel is incorporated, the amount of cobalt in Ni/Co-NC reduces. Fig. 1d shows the elemental mapping of Ni/Co-MOF, the concentration of cobalt increases towards the edges of the nanocages, and the other elements are homogeneously distributed. The elemental mapping of Co-MOF was displaced in supporting information (Figure S1).

XRD analysis for Co-MOF and Ni/Co-NC (Fig. 1c) was measured and the characteristic peaks of Co-MOF exactly matched with the results reported previously [11]. Three broad peaks were observed in Ni/Co-NC with their corresponding positions at 12.56˚(003), 33.54˚(012), and 59.43˚ (110) respectively.
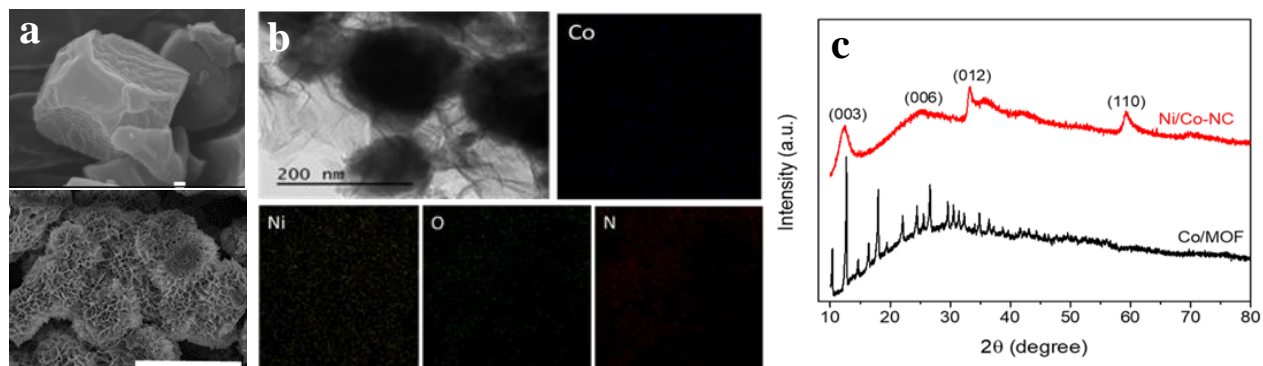

Figure 1. SEM Images of synthesized (a) Co-MOF (Scale bar: 100 nm), and Ni/Co-NC (Scale bar: 5 µm), (b) TEM images of Ni/Co-NC and elemental mapping of synthesized Ni/Co-NC, (c) XRD analysis of synthesized Co-MOF and Ni/Co-NC.

As shown in Fig. 2, an XPS analysis was carried out to explore the valence states of Ni, Co, and O. The spectrum contains characteristic bands of Ni^{2+} and Co^{2+} in tetrahedral coordination at a binding energy of 867.1 and 796.6 eV respectively. Two spin-orbit doublets were obtained in the Ni 2p spectrum as shown in Fig. 2(a). At binding energies of 856.40 and 873.90 eV, the de-convoluted doublets could be attributed to the Ni^{3+} phase [12]. The oxygen spectrum can be de-

convoluted to three corresponding metal-oxygen bonding (529.91 eV), oxygen lattice atoms (531.24 eV), and OH⁻ (532.29 eV) respectively [13]. Finally, the XPS data confirms the presence of active sites (oxygen vacancies) for oxygen evolution reaction. The presence of high oxidation states, Ni^{3+} along with low Ni^{2+} and Co^{3+} oxidation states are favorable for OER and HER performance [14]. Additionally, oxygen vacancies further support the catalyst/electrolyte interaction [15].

Fig. 3(a) shows the I-R corrected polarization curves to evaluate the OER activity of prepared samples at 10 mAcm⁻² with Hg/HgO as a reference electrode. The required overpotential for Ni/Co-LDH and NiO were 346 mV and 336 mV respectively. These catalysts exhibit a smaller overpotential for OER and their performance is comparable with reported non-precious metal catalysts, as summarized in Table S1.
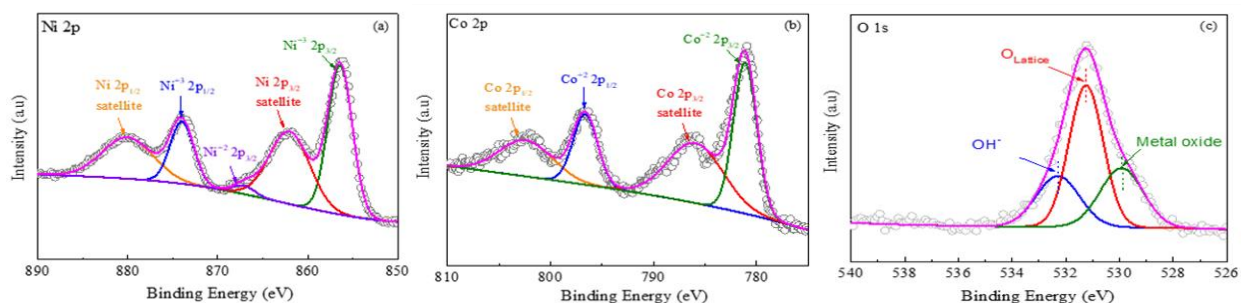

Figure 2. XPS analysis of synthesized Ni/Co-NC catalyst (a) Ni 2p scan (b) Co 2p scan and (c) O 1s scan.

Fig. 3(b) represents the impedance plot along with its fitting circuit. Impedance data explains the active surface area and its catalytic behavior. The components of our equivalent circuit include solution resistance (R_s), double layer capacitance (C_{dl}), charge transfer resistance (R_{ct}), adsorption capacitance (C_a), and adsorption resistance of intermediates (R_a). The R_s is the inert resistance of the solution (1 M KOH) and the half-cell test connection. The fitting measurements show the R_{ct}, R_a, and C_{dl} of 1.01ohm, 48-ohm, 69 mF/cm², and 3.65-ohm, 115-ohm, 38 mF/cm² for NiO and

Ni/Co-NC respectively. This prominent difference confirms that Ni/Co-NC has more active sites that support good catalytic performance.

The smaller Tafel slopes (Fig. 3c) of Ni/Co-NC and NiO were presented in Table S1 which indicates these catalysts are favorable for the OER kinetics. The variations in the Tafel slope come from different rate-determining steps that resulted in the rate of the OER. Furthermore, the rise in the Tafel slope could be due to the harsher operational conditions, which means the active sites for the OER decreases [16]. Although there is an increase in the Tafel slopes, these values are still comparable to the commercial RuO_2 (90 mVdec^{-1}) and other non-noble metal catalysts [17]. The low overpotential reported for OER is usually cobalt and nickel catalysts supported on nickel foam. Therefore, nickel-supported catalysts became intrinsically active for OER by using Ni foam as a substrate which might have contributed to their catalytic activity.
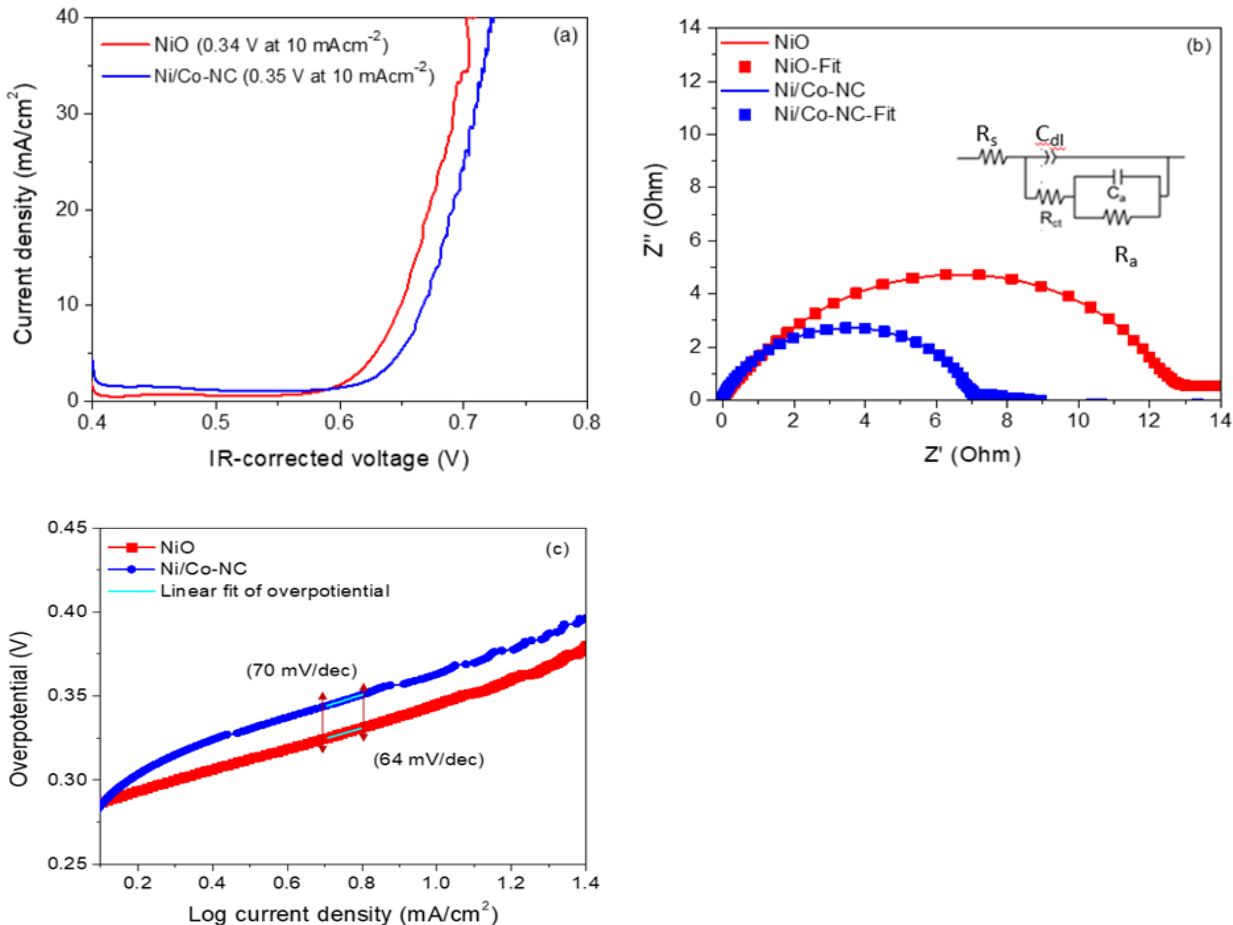
Figure 3. Electrochemical measurements of Ni/Co-NC and NiO. (a) Linear scanning polarization curve, (b) Impedance, and (c) Tafel plots for the OER.

Conclusion:

The newly scalable Ni/Co nanocage as an efficient noble metal-free catalyst towards OER and HER based on MOF has been developed. The synergic effect of cobalt-nickel, high crystalline nanocage structure, and intrinsic activity of active sites decreased their overpotential. The synergic effect of various factors, comprising: (i) the addition of Ni metal induces defect sites into the metal-organic framework derived catalysts through the partial substitution, leading to the enhancement in the conductivity and active sites; (ii) presence of carbon layer which reduces the aggregation, and the presence of both microporous and mesoporous structures reduces the diffusion. Therefore,

the promising prospects for low cost and highly efficient metal complexes, the above non-noble metal can be used as a bifunctional catalyst in alkaline electrolyzers.

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