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Article

In situ growth of minimal Ir-incorporated $\text{Co}_x\text{Ni}_{1-x}\text{O}$ nanowire arrays on Ni foam with improved electrocatalytic activity for overall water splitting

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ABSTRACT

Exploration of cost-effective electrocatalysts for boosting the overall water-splitting efficiency is vitally important for obtaining renewable fuels such as hydrogen. Here, earth-abundant $\text{Co}_x\text{Ni}_{1-x}\text{O}$ nanowire arrays were used as a structural framework to dilute Ir incorporation for fabricating electrocatalysts for water splitting. Minimal Ir-incorporated $\text{Co}_x\text{Ni}_{1-x}\text{O}$ nanowire arrays were synthesized through the facile hydrothermal method with subsequent calcination by using Ni foam (NF) as both the substrate and source of Ni. The electrocatalytic water-splitting performance was found to crucially depend on the Ir content of the parent $\text{Co}_x\text{Ni}_{1-x}\text{O}$ nanowire arrays. As a result, for a minimal Ir content, as low as 0.57 wt%, the obtained Ir- $\text{Co}_x\text{Ni}_{1-x}\text{O}$ /NF electrodes exhibited optimal catalytic activity in terms of a low overpotential of 260 mV for the oxygen evolution reaction and 53 mV for the hydrogen evolution reaction at 10 mA cm^{-2} in 1 mol L^{-1} KOH. When used as bifunctional electrodes in water splitting, the current density of 10 mA cm^{-2} was obtained at a low cell voltage of 1.55 V. Density functional theory calculations revealed that the Ir-doped $\text{Co}_x\text{Ni}_{1-x}\text{O}$ arrays exhibited enhanced electrical conductivity and low Gibbs free energy, which contributed to the improved electrocatalytic activity. The present study presents a new strategy for the development of transition metal oxide electrocatalysts with low levels of Ir incorporation for efficient water splitting.

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1. Introduction

The depletion of fossil fuels and the associated serious environmental problems are the motivations for the intense research on new energy sources, including hydrogen [1–3]. As one of the most promising alternatives to fossil fuels, hydrogen exhibits a high energy density and is environmentally friendly [4–6]. Electrocatalytic water splitting, involving the hydrogen

($2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$) and oxygen ($2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$) evolution reactions, is one of the most appealing approaches for extracting molecular hydrogen from water [7,8]. In these two electrochemical reactions, the ideal free energy change, ΔG_0 , for the conversion of one H_2O molecule into H_2 and $1/2 \text{ O}_2$ under standard temperature and pressure is $237.2 \text{ kJ mol}^{-1}$, according to the Nernst equation, which corresponds to a reversible electrochemical cell voltage of 1.23 V [9]. However, to overcome

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the kinetic limitations of the actual electrochemical reaction, an overpotential is required to drive water splitting in an electrolyzer. Electrocatalysts can be used to promote the kinetics of the water electrolysis reaction and lower the required overpotential. For example, Ru and Ir oxides, such as RuO_2 and IrO_2 , are well-known traditional oxygen evolution reaction (OER) catalysts, and Pt is considered as the state-of-the-art electrocatalyst for the hydrogen evolution reaction (HER) [10–12]. However, the high costs and limited abundances of these noble-metal-based materials seriously restrict their wide application in the industry. It is therefore desirable and urgent to design new efficient electrocatalysts based on materials with abundant resources. To date, a variety of alternative materials, including 3d transition metal (hydro)oxides (TMOs) [13], sulfides [14], and nanocomposites [15], have been reported for the overall water splitting that exhibit good electrocatalytic activities.

In the past decade, diverse nanostructures of Fe, Co, and Ni oxides, such as Co_3O_4 nanosheets, NiO nanosheets, and FeCo_2O_4 , have been reported to be good electrocatalyst choices for both the HER and OER owing to the advantages of low toxicity, low cost, rich redox properties, and easy production [16–18]. However, their catalytic performances in terms of the overpotentials required for hydrogen and/or oxygen evolution and the long-term stabilities still need to be improved for these materials to compete with the noble metal electrocatalysts. The morphologies, chemical compositions, and electronic properties of TMO nanostructures should be elaborately tuned to obtain more efficient catalysts that display the desired catalytic performances. Recently, some studies have focused on non-noble-metal composites with minimal noble metal contents for achieving a high electrocatalytic activity. For example, Dong and coworkers [19] synthesized Ag-doped NiCoO mesoporous nanorods as a catalyst for the OER that reveal a high current density (140 mA cm^{-2}) at a low overpotential (370 mV). In addition, Zhu et al. [20] reported that Au/Ni//Fe LDH hybrid OER catalysts can display an ultrahigh current density of 500 mA cm^{-2} at an overpotential of only 270 mV in alkaline medium. These reports suggested that the incorporation of Au, Ag, and other noble metals can modulate the TMO electronic structures and produce synergetic chemical coupling effects between the TMO catalysts and the dopant atoms, thus improving their catalytic performances. In addition, *in situ* growth of TMO nanowire arrays on unique 3D open metal substrates such as Ni and Cu foams results in a high adhesive strength of each of the active units participating in the HER and/or OER process [21,22].

Here, $\text{Co}_x\text{Ni}_{1-x}\text{O}$ nanowire arrays with different Ir contents were fabricated on Ni foam through a combination of hydrothermal synthesis and subsequent calcination treatment. During the synthesis, the earth-abundant and freestanding $\text{Co}_x\text{Ni}_{1-x}\text{O}$ nanowire arrays were used as structural frameworks for diluting the incorporation of Ir (0.2 wt%–0.68 wt%). A Ni foam with a huge supporting area and a high electrical conductivity served as both a 3D substrate and Ni source for *in situ* growth of $\text{Co}_x\text{Ni}_{1-x}\text{O}$ nanowire arrays on the foam. When used as bifunctional electrocatalysts in the overall water splitting,

the performance of the Ir- $\text{Co}_x\text{Ni}_{1-x}\text{O}$ /NF electrodes was found to depend strongly on the Ir content of $\text{Co}_x\text{Ni}_{1-x}\text{O}$. The optimized Ir- $\text{Co}_x\text{Ni}_{1-x}\text{O}$ nanowire array electrocatalysts with an Ir content of only 0.57 wt% (denoted as Ir(0.57 wt%)- $\text{Co}_x\text{Ni}_{1-x}\text{O}$) displayed the highest OER and HER activities, with low overpotentials of ~ 260 and ~ 53 mV, respectively, and a current density of 10 mA cm^{-2} in an alkaline solution. Density functional theory (DFT) calculations were performed to determine why these Ir-incorporated $\text{Co}_x\text{Ni}_{1-x}\text{O}$ nanowire arrays exhibited enhanced electrocatalytic activities. The present work revealed the importance of precisely tuning TMOs through noble metal doping to obtain low-cost high-performance electrocatalysts.

2. Experimental

2.1. Chemicals

Cobalt(II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, AR, $\geq 99\%$), ammonium fluoride (NH_4F , AR, $\geq 96\%$), and urea ($\text{CO}(\text{NH}_2)_2$, AR, $\geq 99\%$) were purchased from Chemical Supply Co., Ltd. (Kent, UK). Ir chloride hydrate ($\text{IrCl}_3 \cdot x\text{H}_2\text{O}$, powder, Ir > 52%) was obtained from Shanghai Macklin Reagent Co., Ltd. (Shanghai, China). These chemicals were used as-received without further purification. All the experiments used ultrapure deionized water ($18.2 \text{ M}\Omega \cdot \text{cm}$).

2.2. Preparation of Ir-incorporated $\text{Co}_x\text{Ni}_{1-x}\text{O}$ nanowire arrays on Ni foam

Ir- $\text{Co}_x\text{Ni}_{1-x}\text{O}$ nanowire arrays were synthesized on Ni foam by hydrothermal method, which was followed by a calcination treatment. Before the synthesis, the Ni foam ($1 \text{ cm} \times 3 \text{ cm} \times 0.1 \text{ cm}$) was pretreated with acetone and concentrated HCl (3 mol L^{-1}) for 10 min each and washed thoroughly with deionized water to obtain clean surfaces. In a typical synthesis, 0.262 g $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 30 mL distilled water and stirred for 5 min to ensure homogeneity. Then, 0.1 g NH_4F and 0.162 g urea were added with stirring. Subsequently, a diluted aqueous IrCl_3 solution (0.002 mol L^{-1}) was slowly injected by using a pipetting gun. To obtain Ir- $\text{Co}_x\text{Ni}_{1-x}\text{O}$ with different Ir contents, the IrCl_3 solution was added in volumes of 500, 1000, and 1500 μL . Subsequently, the mixed solution and a piece of the cleaned Ni foam were transferred to a 50 mL Teflon-lined stainless steel autoclave, which was sealed and maintained at 120°C for 18 h. After cooling to room temperature, the Ni foam was removed, rinsed with deionized water, and dried at 60°C overnight. Finally, the resulting products were calcined in Ar atmosphere at 400°C for 2 h. $\text{Co}_x\text{Ni}_{1-x}\text{O}$ control samples, which contained no Ir, were also prepared by the same procedure in the absence of IrCl_3 solution.

2.3. Sample characterization

The synthesized products were first characterized by scanning electron microscopy (SEM; FEI Co., Hillsboro, OR, USA). Powder X-ray diffraction (XRD) analyses were conducted with a Rigaku Dmax 2500 X-ray diffractometer equipped (Rigaku

Corp, Tokyo, Japan) with Cu $K\alpha$ radiation ($\lambda = 1.541874 \text{ \AA}$). Transmission electron microscopy, high-resolution transmission electron microscopy (TEM and HR-TEM, respectively), and energy dispersive X-ray elemental mapping analyses (EDX) were performed on an FEI F20 (FEI Corp.) at 200 kV. The Ir contents of the samples were determined by inductively coupled plasma-mass spectrometry (ICP-MS). X-ray photoelectron spectroscopy (XPS) was performed on a PHI-5000 X-ray photoelectron spectrometer (Physical Electronics, Inc., Chanhassen, MN, USA) using Al $K\alpha$ X-rays as the excitation source.

2.4. Electrochemical measurements

All electrochemical measurements were performed using the standard three-electrode system that was connected to a CHI760E electrochemical workstation (CHI Instruments, Inc., Austin, TX, USA), with 1 mol L⁻¹ KOH (pH 13.7) serving as the electrolyte. Graphite rods were used as the counter electrode and 3 mol L⁻¹ KCl saturated Ag/AgCl (Tianjin Aida, China) was employed as the reference electrode. The samples on Ni foam were directly used as the working electrodes. Before the tests, the electrolyte was bubbled with high-purity N₂ (99.999%) for 30 min and the bubbling was maintained throughout the experiment. Linear sweep voltammetry (LSV) polarization curves were recorded at a scan rate of 2 mV s⁻¹ with 85% iR drop compensation. All the measured potentials (vs. Ag/AgCl) were converted to the reversible hydrogen electrode (RHE) scale, in accordance with the literature [23]. The Tafel plots were fitted using the Tafel equation ($\eta = b \log(j) + a$), in which η is the overpotential, j the current density, and b the Tafel slope. Electrochemical impedance spectroscopy (EIS) measurements were also carried out in the frequency range 0.01 Hz to 100 kHz with an applied potential at -10 and 10 mA cm⁻² for the HER and OER, respectively. Chronopotentiometric measurements were used to evaluate the long-term stabilities of the electrode materials. The overall water splitting process was carried out by using the Ir-Co_xNi_{1-x}O/NF electrode as both the anode and cathode in a two-electrode configuration to examine the resulting LSV polarization curve at 1 mV s⁻¹. The control Co_xNi_{1-x}O/NF electrodes (without any Ir incorporation) were also tested for the purpose of comparison.

2.5. Theoretical calculations

DFT+U calculations were carried out by employing the Vienna *ab initio* simulation package [24]. Generalized gradient approximation with Perdew-Burke-Ernzerh functional [25] was used to calculate the exchange-correlation energy. The cutoff energy for plane-wave expansion was set at 400 eV and the Brillouin zone sampled using 5 × 5 × 3 gamma-centered Monkhorst-Pack grids. For structural optimization, the crystal structures were fully relaxed until the residual force was <0.01 eV Å⁻¹. The electronic properties of the materials were studied by considering a Co_xNi_{1-x}O crystal structure with one Ir atom substituting one Co atom to examine the effects of Ir doping. In order to better describe the 3d electrons of the Co and Ni atoms, the effective U values of 3.7 and 6.45 eV were used, re-

spectively. For calculation of the Gibbs free energy [26,27], the (001) surface of Ir-Co_xNi_{1-x}O was used as an example, as it is a common surface of crystalline CoO, in which the Co atoms in the plane were selectively substituted with Ni and Ir atoms to form an alloy surface. The adsorption energies on different sites on the (001) plane were calculated using $\Delta G_{X^*} = E_{X^*} + E_{ZPE} - TS_{X^*}$ [28,29], where X* represents the adsorbed intermediates formed in the HER and OER, such as *H, *O, *OH, and *OOH, and E_{X*}, E_{ZPE}, and TS denote the binding energy, zero-point energy, and entropic contributions, respectively.

3. Results and discussion

The crystal structures of the as-obtained products were first characterized by XRD, which revealed peaks at 36.48°, 42.38°, and 61.48° for all the samples; this corresponded to the rock salt structure of cubic CoO (space group *P63/mmc*, $a = b = c = 3.25 \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 120^\circ$; Fig. 1). Notably, the incorporation of Ir did not alter the crystal structure and all the specimens still exhibited the cubic structure. A slight shift to higher angles was observed for the diffraction peaks of the Co_xNi_{1-x}O sample, in comparison with those of stoichiometric CoO (PDF no. 78-0431), which was attributed to the lattice contraction caused by partial Co ion substitution with the smaller Ni ions [30,31]. The three strong peaks at 44.5°, 51.8°, and 76.4° in the XRD patterns originated from the Ni substrate (PDF no. 87-0712). The morphology and microstructure of the Ir-Co_xNi_{1-x}O nanowire arrays on Ni foam were examined by SEM and TEM. The SEM images of the Ir-Co_xNi_{1-x}O products recorded at low and high magnifications showed needle-like, high-density, and vertically aligned nanowire arrays that uniformly covered the entire Ni foam surface (Figs. 2a and 2b). The average nanowire length was estimated to be ~5 μm. No obvious morphological differences were observed between the Ir-Co_xNi_{1-x}O products upon altering the amount of IrCl₃ solution added during the synthesis (Figs. S1a–S1d). The typical TEM images of Ir-Co_xNi_{1-x}O products clearly revealed highly porous nanowires ~100 nm in diameter (Figs. 2c and 2d). The pores observed in the wires are believed to be generated by the release of H₂O and other gaseous molecules during the calcination process, an effect that is commonly seen in TMO nanostructures obtained from hydroxide precursors [32]. The

Fig. 1. XRD patterns of Ir-Co_xNi_{1-x}O nanowire arrays with different Ir doping levels on Ni foams.

Fig. 2. (a and b) SEM images of Ir-Co_xNi_{1-x}O nanowire arrays on Ni foam under low and high magnifications; (c and d) TEM and (e) HR-TEM images of the Ir-Co_xNi_{1-x}O nanowires; (f-j) Elemental maps of the Ir-Co_xNi_{1-x}O nanocomposites.

HR-TEM images indicated that the grains in the nanowires were well-crystallized (Fig. 2e). The resolved lattice spacing of 0.246 nm corresponded to the (111) crystal plane distance in the cubic phase Co_xNi_{1-x}O [19]. Elemental mapping of Ir-Co_xNi_{1-x}O revealed a homogeneous distribution of Co, Ni, and O in the composite and quite uniform Ir doping throughout the nanowires (Figs. 2f–2j). The atomic ratio of Co/Ni in the products was close to 0.71/0.29. The real Ir concentrations in the prepared Ir-Co_xNi_{1-x}O composites were determined by ICP-MS analysis, and found to be 0.2 wt%, 0.57 wt%, and 0.68 wt%, respectively (Table S1).

The surface chemical states of the products were further investigated by XPS. The full XPS spectra collected from the

Ir-Co_xNi_{1-x}O products revealed the presence of Co, Ni, O, and Ir in the composites, which suggested successful synthesis of the Ir-Co_xNi_{1-x}O samples (Fig. S2). The high-resolution Co 2p and Ni 2p XPS spectra of the Co_xNi_{1-x}O products with or without Ir doping showed that both were composed of four deconvoluted peaks (Figs. 3a and 3b). The Co 2p core-level spectra exhibited two peaks at 780.52 and 796.16 eV, along with satellite peaks at 786.39 and 802.68 eV, which were assigned to the Co 2p_{3/2} and Co 2p_{1/2} orbitals, respectively. The spin-orbit split between the two main Co 2p peaks was ~16 eV, which implied that Co existed in the Co²⁺ state [33,34]. Similarly, the two peaks with the binding energies of 855.09 (Ni 2p_{3/2}) and 872.88 eV (Ni 2p_{1/2}) that were observed in the high-resolution Ni 2p spectrum originated from Ni²⁺ [35–37]. In addition, the indiscernible doublet peak feature in the Ir 4f XPS profile suggested low Ir contents of the Co_xNi_{1-x}O products, which is in accordance with the ICP results (Fig. 3c). Notably, the broad peak at 67.70 eV on the high-energy side of Ir 4f corresponds to the Ni 3s orbital [38]. The XPS spectrum of the O 1s region was fitted with two O peaks (Fig. 3d). The peak at 529.50 eV was ascribed to lattice O, and the peak at 531.10 eV to the surface hydroxyl groups [39,40]. Further, the XPS spectra of the Ir-containing materials showed slight negative shifts in the peaks of the Co and Ni species, in comparison to those of bare Co_xNi_{1-x}O (control), which suggested that the electronic structure of Co_xNi_{1-x}O had been modified by Ir doping [41–43]. Notably, the XPS peak shifts of the doped samples implied changes in the electronic configurations and possibly stronger electronic interactions in Ir-Co_xNi_{1-x}O, which might have played an important role in improving the electrocatalytic activity [44–46].

The OER catalytic activities of the obtained Ir-Co_xNi_{1-x}O/NF electrodes were first evaluated in 1 mol L^{−1} KOH solution by using the typical three-electrode system. The superiority of the

Fig. 3. (a) Co 2p and (b) Ni 2p XPS spectra of Ir-Co_xNi_{1-x}O and Co_xNi_{1-x}O on Ni foam; (c) Ir 4f spectra of Ir-Co_xNi_{1-x}O; (d) O 1s spectra of Ir-Co_xNi_{1-x}O and Co_xNi_{1-x}O.

minimal effect of Ir doping was verified by examining the weight proportion of Ir in the $\text{Co}_x\text{Ni}_{1-x}\text{O}$ nanowires, which was found to be controlled at less than ~ 1 wt%; at the same time, the bare $\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{NF}$ electrocatalysts were tested for comparison. The LSV curves of all the $\text{Ir}-\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{NF}$ electrodes exhibited sharper onset potentials at ~ 1.48 V versus RHE and displayed significantly enhanced anodic currents, compared with that of bare $\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{NF}$ (Fig. 4a). More interestingly, when tuning the minimal Ir content of the $\text{Co}_x\text{Ni}_{1-x}\text{O}$ nanowire arrays, $\text{Ir}(0.57 \text{ wt\%})-\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{NF}$ revealed the lowest overpotential of ~ 260 mV at 10 mA cm^{-2} current density, which exceeded those of $\text{Ir}(0.68 \text{ wt\%})-\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{NF}$ and $\text{Ir}(0.2 \text{ wt\%})-\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{NF}$ (~ 270 and 280 mV, respectively). In contrast, the bare $\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{NF}$ control electrodes displayed the highest overpotential of ~ 305 mV at 10 mA cm^{-2} current density. The Ir mass-related OER activities of $\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{NF}$ were also determined from the related Tafel slopes. The $0.57 \text{ wt\%}$ Ir-doped $\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{NF}$ exhibited the smallest Tafel slope of 48 mV dec^{-1} , which indicated a more rapid OER on $\text{Ir}(0.57 \text{ wt\%})-\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{NF}$ electrode than on the others (Fig. 4b) [47]. The EIS results revealed that $\text{Ir}(0.57 \text{ wt\%})-\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{NF}$ exhibited a much smaller charge-transfer resistance (R_{ct}) of 0.59Ω than $\text{Ir}(0.2 \text{ wt\%})-\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{NF}$, $\text{Ir}(0.68 \text{ wt\%})-\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{NF}$, and bare $\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{NF}$ (0.97 , 0.66 , and 1.33Ω , respectively) (Fig. 4c). This allowed identification of the highest OER rate, which corresponded to the smallest Tafel slope [48]. The durability of an electrocatalyst is another important parameter that must be considered for practical applications. Long-term chronopotentiometric measurements showed that the $\text{Ir}(0.57 \text{ wt\%})-\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{NF}$ electrodes were inherently stable in alkaline media during the OER process (Figs. 4d and S3). The double-layer capacitances (C_{dl}) were measured to determine the

electrochemical active surface areas of the different samples. As shown in Fig. S4, the C_{dl} of $\text{Ir}(0.57 \text{ wt\%})-\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{NF}$ electrode was estimated to be $\sim 80 \text{ mF cm}^{-2}$, which is much larger than those of the $\text{Ir}(0.68 \text{ wt\%})-\text{Co}_x\text{Ni}_{1-x}\text{O}$ and $\text{Ir}(0.2 \text{ wt\%})-\text{Co}_x\text{Ni}_{1-x}\text{O}$ samples. The results revealed that $\text{Ir}(0.57 \text{ wt\%})-\text{Co}_x\text{Ni}_{1-x}\text{O}$ nanowire arrays on Ni foam can provide a larger catalytically active surface area and a higher interfacial contact area with the electrolyte, which suggest a higher electrocatalytic activity of the $\text{Ir}(0.57 \text{ wt\%})-\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{NF}$ electrode.

The HER performances of the different catalysts were characterized in the same electrolyte (Fig. 5a). Similar to the results for the OER, the $\text{Ir}-\text{Co}_x\text{Ni}_{1-x}\text{O}$ electrodes with $0.57 \text{ wt\%}$ Ir exhibited the best HER activity, with an overpotential of only ~ 53 mV at a current density of 10 mA cm^{-2} , which was lower than those of the $\text{Ir}(0.68 \text{ wt\%})-\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{NF}$, $\text{Ir}(0.2 \text{ wt\%})-\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{NF}$, and bare $\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{NF}$ electrodes (83 , 127 , and 148 mV, respectively). Furthermore, as with the case of the OER, the Tafel slope was used to explore the kinetics of the HER process [49]. Again, the $\text{Ir}(0.57 \text{ wt\%})-\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{NF}$ electrodes exhibited the smallest Tafel slope of 70 mV dec^{-1} among the four catalysts, which corresponded to the fastest HER (Fig. 5b). Similarly, EIS measurements were used to further investigate the HER kinetics at the electrode surfaces. The semicircle observed in the high-frequency range of the Nyquist plot indicated that the $\text{Ir}(0.57 \text{ wt\%})-\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{NF}$ electrodes displayed a much lower charge transfer resistance than the other samples, which suggested higher charge and mass transfer efficiencies after the doping of an appropriate amount of Ir in the $\text{Co}_x\text{Ni}_{1-x}\text{O}$ nanowire frameworks (Fig. 5c). The superior robustness of the $\text{Ir}(0.57 \text{ wt\%})-\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{NF}$ electrodes for the HER was confirmed from the chronopotentiometric curves (Fig. 5d). After 50 h of continuous operation at a constant current density of 10

Fig. 4. Results of OER performance characterizations. (a) iR-corrected LSV curves, (b) Tafel plots, (c) Nyquist plots of bare $\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{NF}$, $\text{Ir}(0.2 \text{ wt\%})-\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{NF}$, $\text{Ir}(0.57 \text{ wt\%})-\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{NF}$, and $\text{Ir}(0.68 \text{ wt\%})-\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{NF}$ electrodes, and (d) chronopotentiometric measurements of $\text{Ir}(0.57 \text{ wt\%})-\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{NF}$ electrode at the current density of 10 mA cm^{-2} .

Fig. 5. Results of HER performance characterizations. (a) iR-corrected LSV curves, (b) Tafel plots, and (c) Nyquist plots of $\text{Co}_x\text{Ni}_{1-x}\text{O}$, Ir(0.2 wt%)- $\text{Co}_x\text{Ni}_{1-x}\text{O}$, Ir(0.57 wt%)- $\text{Co}_x\text{Ni}_{1-x}\text{O}$, and Ir(0.68 wt%)- $\text{Co}_x\text{Ni}_{1-x}\text{O}$ electrodes, and (d) chronopotentiometric measurements of Ir(0.57 wt%)- $\text{Co}_x\text{Ni}_{1-x}\text{O}$ electrodes at 10 mA cm^{-2} .

mA cm^{-2} , the potential of Ir- $\text{Co}_x\text{Ni}_{1-x}\text{O}/\text{NF}$ remained at almost its initial value, which indicated superior durability of the Ir- $\text{Co}_x\text{Ni}_{1-x}\text{O}$ electrocatalyst.

DFT+U calculations were performed to evaluate the effects of Ir doping of $\text{Co}_x\text{Ni}_{1-x}\text{O}$ catalysts on the HER and OER. $\text{Co}_x\text{Ni}_{1-x}\text{O}$ displays the same cubic structure as rock salt CoO (Figs. 6a and S5). Figs. 6b–d show the calculated PDOS and TDOS distributions of CoO, $\text{Co}_x\text{Ni}_{1-x}\text{O}$, and Ir- $\text{Co}_x\text{Ni}_{1-x}\text{O}$, respec-

tively. Pure CoO displays a considerably large bandgap of 1.3 eV, which is similar to the results reported by Qiao et al. [50]. Compared to that of pure CoO, the bandgap of $\text{Co}_x\text{Ni}_{1-x}\text{O}$ is slightly decreased to $\sim 0.84 \text{ eV}$. Both CoO and $\text{Co}_x\text{Ni}_{1-x}\text{O}$ exhibit semiconductor characteristics with low electrical conductivities. However, after doping $\text{Co}_x\text{Ni}_{1-x}\text{O}$ with Ir, Ir- $\text{Co}_x\text{Ni}_{1-x}\text{O}$ already exhibits a half-metal-like conductivity, as evidenced by the impurity states that are found near the Fermi energy level, which confirm that the electrical conductivity of $\text{Co}_x\text{Ni}_{1-x}\text{O}$ is significantly enhanced by Ir doping. The enhanced conductivity of $\text{Co}_x\text{Ni}_{1-x}\text{O}$ achieved through Ir doping can directly result in increased turnover frequency and hydrogen generation current [50], which play significant roles in continuous hydrogen production. To further understand the changes in the hydrogen evolution ability of $\text{Co}_x\text{Ni}_{1-x}\text{O}$ doped with Ir, we systematically calculated the Gibbs free energies (ΔG_{H^*}) of H adsorption on pure CoO, $\text{Co}_x\text{Ni}_{1-x}\text{O}$, and Ir- $\text{Co}_x\text{Ni}_{1-x}\text{O}$ surfaces. After fully optimizing the adsorption positions of H on the surfaces of the three catalysts, we found that, for the pure CoO structure, the total energy of the H atoms adsorbed on the O atoms is lower than that of the H adsorbed on the Co atoms, whereas, for the CoNiO and Ir-CoNiO structures, the total energy of the H atoms adsorbed on the Co atoms is lower than that of the H atoms adsorbed on the other atoms (Table. S2). The H adsorption energies are shown in Fig. 7; the ΔG_{H^*} of H^* on Ir- $\text{Co}_x\text{Ni}_{1-x}\text{O}$ (0.523 eV) was much less than those of H^* on CoO and $\text{Co}_x\text{Ni}_{1-x}\text{O}$ (0.882 and 0.823 eV, respectively). Clearly, these results allowed us to conclude that the Ir incorporation optimized the free energy of H adsorption on $\text{Co}_x\text{Ni}_{1-x}\text{O}$ for the HER.

Since the OER activities of electrocatalysts have proved to be closely related to the changes in the Gibbs free energies [51],

Fig. 6. (a) Atomic structure model of Ir- $\text{Co}_x\text{Ni}_{1-x}\text{O}$. Calculated partial and total electronic density of states (PDOS and TDOS) of (b) CoO, (c) $\text{Co}_x\text{Ni}_{1-x}\text{O}$, and (d) Ir- $\text{Co}_x\text{Ni}_{1-x}\text{O}$. Color notes: the light blue and red spheres denote the Co and O atoms, respectively, of CoO, the dark blue spheres denote Ni atoms, and the yellow sphere denotes Ir atom. The Fermi level is located at 0 eV.

Fig. 7. (a) The three optimized atomic structures for H^* adsorption on three catalysts, and (b) the corresponding Gibbs free energies for the HER over different catalysts.

we also calculated the catalytic activities of pure CoO, $Co_xNi_{1-x}O$, and $Co_xNi_{1-x}O$ doped with Ir atoms for the OER. Based on the calculated results, shown in Fig. 8 and Table S3, the free energy $\Delta G > 0$ of each step indicates that the transfer step of every pair of protons and electrons in the OER is endothermic. In pure CoO, the Gibbs free energy is $\Delta G_2 = 2.12$ eV, and the corresponding overpotential is calculated to be $\eta_{OER} = 0.89$ eV. For $Co_xNi_{1-x}O$ catalysts, the free energy of the second step is almost unchanged, and the overpotential is only reduced by 0.02 eV, which suggests that the substitution of Ni atoms in the CoO crystal has not greatly improved the catalytic activity of CoO. For $Co_xNi_{1-x}O$ doped with Ir atoms, the potential-limiting step is dramatically decreased in free energy to $\Delta G_2 = 1.77$ eV, and the overpotential is reduced to $\eta_{OER} = 0.54$ eV, which indicates that the Ir doping can greatly improve the oxygen evolution performances of the $Co_xNi_{1-x}O$ electrocatalysts.

Considering the outstanding OER and HER activities of these Ir- $Co_xNi_{1-x}O$ catalysts, a two-electrode system using Ir(0.57 wt%)- $Co_xNi_{1-x}O/NF$ as both the cathode and anode was constructed for water electrolysis. The polarization curves of Ir(0.57 wt%)- $Co_xNi_{1-x}O/NF||Ir(0.57 \text{ wt\%})-Co_xNi_{1-x}O/NF$ electrolyzer and its $Co_xNi_{1-x}O/NF||Co_xNi_{1-x}O/NF$ counterpart in 1.0 mol L^{-1} KOH showed that a cell voltage of only 1.55 V, without iR-correction in the Ir(0.57 wt%)- $Co_xNi_{1-x}O/NF$ -based electrolyzer, was needed to achieve a current density of 10 $mA\ cm^{-2}$;

Fig. 8. Standard free energy diagrams for the OER, calculated for pure CoO, CoNiO, and Ir-CoNiO. In addition, the illustrative structure on each step in the figure represents the intermediate product of the CoNiO structure doped with Ir atoms during the process of oxygen evolution.

thus, this electrolyzer outperformed the bare $Co_xNi_{1-x}O$ -based-electrolyzer (1.64 V, Fig. 9a). It was notable that bubbles due to hydrogen and oxygen evolutions at the cathode and anode, respectively [52–54], were clearly observed (Fig. 9a, inset). The superior OER and HER activities, as well as the higher water splitting activities, of the Ir(0.57 wt%)- $Co_xNi_{1-x}O$ catalyst are comparable and even better than those of many previously reported TMO electrocatalysts (Tables S4–S6). The durability of the fabricated Ir(0.57 wt%)- $Co_xNi_{1-x}O/NF||Ir(0.57 \text{ wt\%})-Co_xNi_{1-x}O/NF$ electrolyzer was further evaluated through long-term galvanostatic tests (Figs. 9b and S6). Impressively, an almost constant cell voltage of ~ 1.55 V was well maintained for over 50 h at the set current density of 10 $mA\ cm^{-2}$. Overall, the designed Ir- $Co_xNi_{1-x}O$ electrocatalyst exhibited efficient water splitting with good stability.

4. Conclusions

Minimal Ir-incorporated $Co_xNi_{1-x}O$ nanowire arrays on Ni foam were successfully prepared through a facile hydrothermal-annealing combined method. When used as electrocatalysts, Ir- $Co_xNi_{1-x}O/NF$ significantly lowered the overpotentials

Fig. 9. (a) Polarization curves of Ir(0.57 wt%)- $Co_xNi_{1-x}O/NF||Ir(0.57 \text{ wt\%})-Co_xNi_{1-x}O/NF$ and $Co_xNi_{1-x}O/NF||Co_xNi_{1-x}O/NF$ electrolyzers; (b) Long-term galvanostatic measurements of the Ir(0.57 wt%)- $Co_xNi_{1-x}O/NF||Ir(0.57 \text{ wt\%})-Co_xNi_{1-x}O/NF$ electrolyzer at the constant current density of 10 $mA\ cm^{-2}$.

for both the OER and HER. Among all the samples, Ir(0.57 wt%)-Co_xNi_{1-x}O/NF exhibited the highest catalytic activity in terms of low overpotentials of 260 and 53 mV for the OER and HER, respectively, at a current density of 10 mA cm⁻². Through XPS measurements, EIS analysis, and DFT calculations, this enhancement was proposed to result from the reduced charge-transfer resistance and modified electronic structure of the Co_xNi_{1-x}O catalysts after proper Ir doping. In addition, a water-splitting electrolyzer using Ir(0.57 wt%)-Co_xNi_{1-x}O/NF as both the anode and cathode afforded a cell voltage of only 1.55 V to obtain 10 mA cm⁻²; it also exhibited superior capacity retention. This study provided a rational means of using TMO nanostructures as base materials for adding small amounts of noble metals to obtain high-performance electrocatalysts.

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Graphical Abstract

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In situ growth of minimal Ir-incorporated Co_xNi_{1-x}O nanowire arrays on Ni foam with improved electrocatalytic activity for overall water splitting

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Minimal Ir-incorporated Co_xNi_{1-x}O nanowire arrays with enhanced overall water-splitting performance were synthesized through the facile hydrothermal method with subsequent calcination by using Ni foam as both the substrate and source of Ni.

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微量铱掺杂 $\text{Co}_x\text{Ni}_{1-x}\text{O}$ 纳米线阵列的制备及其电催化性能

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摘要: 电催化剂可以降低水分解反应的活化能与相应的过电势, 提高电解水的制氢效率。Pt、Ru等贵金属颗粒是最常见的高催化活性材料, 但其高昂成本严重限制了它们在工业上的广泛应用。因此, 开发以非贵金属为基础的高活性材料是实现大规模工业制氢的有效手段。本文以 $\text{Co}_x\text{Ni}_{1-x}\text{O}$ 纳米线阵列作为结构骨架对其进行微量的铱(Ir)掺杂, 同时将Ir的掺杂量控制在1%以下, 并系统地研究了Ir- $\text{Co}_x\text{Ni}_{1-x}\text{O}$ 材料的析氢反应(HER)、析氧反应(OER)和全解水性能。实验发现, 微量Ir掺杂可以有效提升 $\text{Co}_x\text{Ni}_{1-x}\text{O}$ 纳米材料的电化学性能。当Ir在样品的含量仅为0.57 wt%时, Ir掺杂的 $\text{Co}_x\text{Ni}_{1-x}\text{O}$ 样品具有最优的HER和OER性能。特别地, 在1 mol L⁻¹ KOH电解液中电流密度达到10 mA cm⁻²时的HER过电势仅为260 mV, OER过电势仅为53 mV。将Ir (0.57 wt%)- $\text{Co}_x\text{Ni}_{1-x}\text{O}$ /NF样品作为双功能催化剂用于全解水的阳极和阴极时产生10 mA cm⁻²电流密度需要施加的电压仅为1.55 V。采用第一性原理(DFT)对Ir元素掺杂在调控 $\text{Co}_x\text{Ni}_{1-x}\text{O}$ 的电子结构和HER以及OER反应中被吸附物吉布斯自由能的改变等方面进行了量化计算。结果表明, Ir掺杂后 $\text{Co}_x\text{Ni}_{1-x}\text{O}$ 总的态密度向导带移动, 带隙内电子的相互作用增强, 相应的禁带宽度变小, 表现为半金属的导电类型, 说明Ir掺杂提高了 $\text{Co}_x\text{Ni}_{1-x}\text{O}$ 材料的导电性。相应的吉布斯自由能计算结果表明, Ir掺杂后材料表面对氢原子吸附的活性加强, ΔG_{H^*} 由原来的0.823 eV变为0.523 eV, 更加接近理想催化剂的值。同样地, 计算表明 $\text{Co}_x\text{Ni}_{1-x}\text{O}$ 在参与OER反应时对中间体吸附的吉布斯自由能在Ir掺杂后也得到降低。

关键词: $\text{Co}_x\text{Ni}_{1-x}\text{O}$ 纳米线; 铱掺杂; 电催化剂; 水分解; 过电势

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