Bimetallic oxide coupled with B-doped graphene as highly efficient electrocatalyst for oxygen evolution reaction

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ABSTRACT Developing electrocatalysts with high performance and low cost for the oxygen evolution reaction (OER) is of great importance for fabricating renewable energy storage and conversion devices. Here, a series of boron-doped graphene (BG)-supported bimetallic oxides of Co and Ni were obtained and served as OER electrocatalysts. Surprisingly, the annealed Co-Ni-O_x/BG with a Co/Ni ratio of 1:1 exhibits high performance toward oxygen evolution in alkaline electrolyte. The overpotential is only 310 mV at the current density of 10 mA cm⁻², superior to many mono-metallic oxides reported before, and even comparable to the commercial RuO₂. The regulation of charge distribution in bimetallic oxides and the strong synergistic coupling effects together contribute to the superior electrocatalytic performance of the Co-Ni-O_x/BG toward OER. This study also offers several effective ways to design high-performance OER electrocatalysts for water splitting.

Keywords: bimetal oxide, B-doped graphene, oxygen evolution reaction, electrocatalyst, hydrogen generation

INTRODUCTION

With the ever-growing focus of attention on the global energy shortage and environmental pollution, exploring clean and renewable energy source is unprecedented during the last few decades [1,2]. Among these innovative solutions, the production and storage of hydrogen (H₂) is appealing for its high mass-specific energy density and the clean nature [3,4]. Some methods are frequently used for generating hydrogen, such as reforming fossil fuels and electrolysis of water. Considering the factors including cost, purity and the environmental implication, the most promising way to produce H₂ is water splitting

triggered by sunlight or electricity [5]. However, the anodic oxygen evolution reaction (OER) during water splitting always suffers from sluggish kinetics process with complicated multi-electron transfer steps, leading to undesired large overpotential [6]. Therefore, exploiting OER catalysts with high activity and stability is vital to increase the overall efficiency of the water splitting. Some noble metal-based compounds, such as iridium oxide (IrO₂) and ruthenium oxide (RuO₂), have been regarded as the state-of-the-art OER electrocatalysts for their low overpotentials and Tafel slopes [7–9]. Nevertheless, the scarcity, high cost and unacceptable durability of these noble metal-based electrocatalysts hinder their commercial implementation [10,11]. Thus it is highly imperative to develop earth-abundant element-based catalysts with decent activity as well as long-term stability for the oxygen evolution process [12].

Hitherto, transition metal catalysts, especially cobalt- and nickel-based electrocatalysts, have drawn tremendous attention because of their attractive features, such as availability, low cost and superior activity [13]. Over the past years, transition metal oxides/hydroxides [14–16], sulphides [17,18], phosphides [19,20], and borides [21,22] have been extensively investigated as OER electrocatalysts. Although the sulphides, phosphides and borides have shown better catalytic activity than the oxides in some cases, they suffer from lower controllability, more harsh condition, and probable contamination during the syntheses. Among these well-developed catalysts, the transition metal oxides (especially cobalt/nickel oxides) have attracted increasing attention on account of their unique 3d electronic configurations and high stability. Nevertheless, the oxides generally exhibit low OER elec-

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trocatalytic activity due to their inferior intrinsic electrical conductivity and inevitable self-aggregation. Therefore, developing a facile way to modulate the electrical conductivity and the charge distribution of the metal oxides is necessary to improve their electrocatalytic activities. Coupling the metal oxides with highly conductive carbon nanomaterials, including but not limited to carbon nanotubes and graphene, has been testified to be an effective way to facilitate the charge transport and increase the exposure of active sites [23,24]. Furthermore, incorporating a second metal into the metal oxide catalysts has been proposed as an efficient strategy to modulate the charge distribution and energy level, due to their synergistic effects [25,26]. For example, it has been reported that multi-metallic electrocatalysts such as Co-Ni-B-O nanosheets [27], CoNiP_x [28], CoMoS [29], CoMoB [30] and CoFe layered double hydroxides [31] exhibit distinctly improved catalytic activity for the OER process, compared with their mono-metallic counterparts.

Herein, we report a room-temperature chemical reduction method combined with a subsequent annealing treatment to fabricate a bimetallic oxide strongly coupled with two dimensional (2D) boron-doped graphene sheets (Co-Ni-O_x/BG). Benefiting from the highly exposed surface active sites, enhanced electron transfer capacity and strong synergetic coupling effects, the as-prepared Co-Ni-O_x/BG hybrid exhibits a high activity for OER with an overpotential of 310 mV at the current density of 10 mA cm⁻² and a Tafel slope around 54.8 mV dec⁻¹ in alkaline electrolyte, which is among the best, compared with the transition metal oxide-based OER electrocatalysts reported. Therefore, this study proposes a facile and effective way to improve the OER electrocatalytic activity of the transition metal oxides which have intrinsic lower electron transfer kinetics than their counterparts, such as phosphides, sulfides, etc. The strategies proposed in this study are not only appropriate for improving the electrocatalytic performance of metal oxides, but also valuable for designing highly-active transition metal-metalloid-based electrocatalysts.

EXPERIMENTAL SECTION

Chemicals

Co(NO₃)₂·6H₂O, NaBH₄, Ni(NO₃)₂·6H₂O, Nafion solution (5 wt.%) and RuO₂ were obtained from Sigma-Aldrich; KOH was obtained from Beijing Chemical Corporation; aqueous solution of graphene oxide (GO) (2.0 mg mL⁻¹ single layer GO, with the size in the range of 0.5–5 μm, and the thickness of 0.8–1.2 nm) was ac-

quired from XFNANO Corporation. All reagents were analytical grade and used without any further purification.

Synthesis of Co-Ni-O_x/BG and the samples in the control experiments

The Co-Ni-O_x/BG was prepared with a room temperature chemical synthesis method, followed by annealing treatment. In a typical synthesis, 0.5 mmol of cobalt (II) nitrate hexahydrate (Co(NO₃)₂·6H₂O) and 0.5 mmol of nickel (II) nitrate hexahydrate (Ni(NO₃)₂·6H₂O) were added into 100 mL of deionized water under continuous and vigorous stirring to complete dissolution. Then, 7.5 mL of GO (2.0 mg mL⁻¹) aqueous dispersion was added to the above solution and stirred for another 30 min. After full electrostatic attraction of the Co²⁺ and Ni²⁺ on the GO nanosheets, 5 mL of sodium borohydride (NaBH₄, 0.5 mol L⁻¹, prepared at 0°C and deaerated with Ar gas) solution was slowly dropped in and maintained at room-temperature for 40 min under vigorous stirring. The resulting products were gathered by centrifuging and washed with ethanol and water, successively. The as-prepared precursors were dried by lyophilization. The graphene-supported bimetal oxides with other Co:Ni ratios were also synthesized by varying the molar ratio of the metal precursors (2:1, 1:2) with the same total amount of the transition metal (1 mmol) under the same condition. Mono-metallic oxides were also prepared for comparison, in which only Co salt or Ni salt was used with a quantity of 1 mmol to prepare cobalt oxide and nickel oxide, respectively. The annealed Co-Ni-O_x/BG was synthesized by annealing the precursor powder under Ar at 400°C for 2 h. The samples were also annealed at other temperatures (300, 500, 600°C) for comparison.

The graphene sample and the unsupported Co-Ni-O_x sample in the control experiments were synthesized with the same procedure, without adding the transition metal salts and GO, respectively.

Electrochemical measurements

We investigated the electrochemical performances of the electrocatalysts on a CHI 760E electrochemical workstation. The electrocatalyst inks were obtained by dissolving 4 mg of catalyst powder in a mixed solution composed of 0.4 mL of water, 1.56 mL of isopropanol, and 40 μL of Nafion (5 wt.%) to form a 2 mg mL⁻¹ suspension under sonication. 10 μL of homogeneous ink was coated onto a glassy carbon electrode (GCE) with 3 mm diameter. The electrochemical tests were carried out in a three-electrode system in 1.0 mol L⁻¹ KOH solution (sa-

turated with O₂ before use), with the modified electrode acting as the working electrode, the saturated calomel electrode (SCE) as the reference electrode, and a carbon rod as the counter electrode. The potentials measured *versus* SCE, were referenced to the reversible hydrogen electrode (RHE) by adding a value of (0.241+0.059pH) V.

All of the potentials in the linear scan voltammograms (LSV) polarization plots were *iR*-compensated with respect to the ohmic resistance of the system, unless otherwise stated. The *iR*-correction was done based on the equation:

$$E_{\text{corr}} = E_{\text{mea}} - iR, \quad (1)$$

where E_{corr} is the *iR*-corrected potential, E_{mea} is the experimentally measured potential, and R is the cell ohmic resistance. The overpotentials in this work were obtained by subtracting the theoretical value of the water oxidation:

$$\eta = E(\text{RHE}) - 1.23. \quad (2)$$

Prior to the LSV tests, the modified working electrodes were subjected to continuous activation process by cyclic voltammetry (CV) scanning until reproducible voltammograms appeared. The electrochemical impedance spectroscopy (EIS) information was obtained by the alternating current (AC) impedance spectroscopy in 1.0 mol L⁻¹ KOH. The frequency ranged from 100 kHz to 0.1 Hz. A potential of 1.55 V was applied for the OER process and the amplitude was 5 mV. The measured impedance data were fitted with an equivalent circuit by the ZView software.

To explore the reaction mechanism and the Faradaic efficiency for the OER process, the rotating ring-disk electrode (RRDE) measurement was carried out. To explore the intermediate content of the possibly generated hydrogen peroxide, we fixed the ring potential at 1.50 V, and did the tests in the O₂-saturated KOH electrolyte. The disk and the ring polarization curves were recorded at 5 mV s⁻¹ under 1600 rpm. The Faradaic efficiency was calculated as:

$$\varepsilon = I_r / (I_d N), \quad (3)$$

in which I_d and I_r is the disk and ring current, respectively. The coefficient N is the current collection efficiency of the RRDE equipment ($N = 0.37$). The I_d was fixed at a constant current of 180 and 470 μA , respectively to generate O₂ and then reduced by sweeping across the surrounding Pt ring electrode which was set at 0.45 V for exhaustive oxygen reduction.

The accelerated stability tests were done by CV scanning between 1.20 and 1.60 V for 1000 cycles at 50 mV s⁻¹. The obtained LSV plots before and after the multi-circle CV scanning were compared. The long-term

operation stability of electrocatalysts was also evaluated by the chronopotentiometry method at a constant current density of 10 mA cm⁻².

Characterizations

The morphologies of the catalysts were first observed with the field emission scanning electron microscope (FESEM, QUANTA FEG 250, FEI), and the transmission electron microscope (TEM, JEM-1400, JEOL Ltd., Japan). High-resolution TEM (HRTEM) and the dark field (DF)-scanning transmission electron microscopy (STEM), and element mapping analysis were acquired from the FEI Talos F200s microscope equipped with energy-dispersive X-ray spectroscopy (EDS) at 200 kV. The X-ray diffraction (XRD) results were obtained by an X-ray diffractometer (D8-Advance, Bruker) with the Cu K α radiation ($\lambda = 1.5414 \text{ \AA}$). The X-ray photoelectron spectroscopy (XPS) measurements were performed on ESCALAB 250Xi instrument. The samples were also characterized by the Raman spectra (Renishaw Raman system model 1000 spectrometer with an excitation laser of 514 nm). The surface areas of different electrocatalysts were measured by the N₂ adsorption and desorption isotherms at -196°C on a SSA-6000 (Builder) instrument.

RESULTS AND DISCUSSION

The Co-Ni-O_x/BG hybrid was fabricated by a facile chemical reduction method, followed by annealing treatment in Ar atmosphere at various temperatures. To be specific, the cobalt and nickel salts with different molar ratios were mixed with GO. After the metal ions were homogeneously adsorbed on the GO sheets, the mixture was subjected to reduction by NaBH₄. Further heat treatment was also conducted to obtain the final product. The synthesis procedure and the electrocatalytic process for OER by the electrocatalyst-modified electrode are illustrated in Scheme 1.

The morphology of the as-prepared hybrid was evaluated by the FESEM, as shown in Fig. 1a. The SEM image of the 400°C-annealed Co-Ni-O_x/BG exhibits nanosheet morphology with a lateral size of several micrometers (similar to the unannealed samples in Fig. S1). High-magnification SEM images demonstrate the existence of smaller nanosheets attached on the graphene sheets (Fig. 1b, c). The XRD pattern of the 400°C-annealed Co-Ni-O_x/BG sample is shown in Fig. 1d. The diffraction peak around 21° corresponds to the diffraction of partially reduced graphene [32]. The peaks observed at 36.7°, 42.9° and 62.2° are symmetric and located between those of CoO (JCPDS card 44-1159) and NiO (JCPDS card 43-

Scheme 1 Schematic illustration of the fabrication of the Co-Ni-O_x/BG and the oxygen evolution process catalyzed by the Co-Ni-O_x/BG modified electrode.

1004) [24]. It is consistent with the micro-adjustment of the lattice parameters, implying the formation of the cobalt nickel oxide alloy. The peak of graphene is much stronger than those of the bimetal oxide, indicating the weak XRD diffraction signals of the bimetal oxides, owing to the low annealing temperature. The XRD patterns of the composite with different Co:Ni ratios are shown in

Fig. S2. The different nanosheet structures can be distinguished by the HRTEM images (Fig. 2). The EDS mapping results shown in Fig. 2d–h and Fig. S3 indicate that the Co, Ni, O, B, and C are well-distributed throughout the nanosheet matrix. The measured lattice spacing of 0.211 nm (Fig. 2c) is between those of CoO and NiO. The lattice spacing data together with the XRD information imply the formation of cobalt nickel oxide alloy.

The Raman spectra further supports the formation of bimetallic oxide and graphene hybrid structure. In Fig. 3a, the broad Raman peak at ca. 520 cm⁻¹ corresponds to the vibrations of cobalt oxide and nickel oxide [33,34]. The two main peaks at about 1351 and 1592 cm⁻¹ are the D band peak (vibrations of sp³-bonded carbon atoms of the disordered graphene) and the G band peak (in-plane vibration of sp²-bonded carbon atoms of the graphene), respectively [35].

The elemental composition and the valence state of the Co-Ni-O_x/BG hybrid were studied by XPS. The XPS survey spectrum (Fig. S4) confirms that the hybrid consists of Co, Ni, O, C, and B elements. The high-resolution core spectrum of Co 2p in Fig. 3b exhibits two main peaks

Figure 1 (a–c) SEM images of the Co-Ni-O_x/BG hybrid under different magnifications (the arrows point to the more wrinkled nanosheet structures which are different from the graphene substrate). (d) XRD pattern of the Co-Ni-O_x/BG, below which the standard peaks of CoO and NiO are shown.

Figure 2 TEM (a, b) and HRTEM (c) images of the Co-Ni-O_x/BG, ((c) is the amplified image of the blue square marked in (b)). The DF-STEM image (d) and the corresponding EDS elemental mappings of Co (e), Ni (f), O (g), and their overlap (h).

Figure 3 (a) The Raman spectrum of the Co-Ni-O_x/BG. The refined XPS spectra for the Co-Ni-O_x/BG: (b) Co 2p, (c) Ni 2p, and (d) B 1s.

located at 780.4 and 796.3 eV associated with two satellite peaks, which both belong to Co²⁺. The results are similar with the previously reported CoO XPS spectra [36,37]. Similarly, the Ni²⁺ is also clearly identified by the Ni 2p_{1/2} (873.1 eV) and Ni 2p_{3/2} (855.4 eV) peaks with two satellite peaks (Fig. 3c) [37]. The high resolution spectrum of B 1s

is overlapped by two peaks (Fig. 3d). The peak located at 190.3 eV corresponds to BC₂O groups, indicating B is doped within graphene in the epoxy form. The other peak located at 191.7 eV is ascribed to the existence of small amount of boronic acid (borate) groups (BCO₂) [38,39]. Combined with the previous characterizations, the an-

nealed product is identified as BG-supported cobalt nickel oxide. We could also propose the formation process of the Co-Ni-O_x/BG. As seen in Fig. S5, the unannealed product shows a broad peak at around 46°, indicating the formation of an amorphous bimetal borate structure [40]. During the annealing process, oxygen atoms from the borate and mildly reduced GO facilitate the formation of crystalline bimetal oxide with higher stability. Besides, some of the boron atoms are doped into the graphene skeleton, resulting in the formation of the Co-Ni-O_x/BG, confirmed by the XPS results and EDS elemental mapping.

The electrocatalytic properties were evaluated by dropping the as-prepared catalysts onto the RDE. All electrochemical measurements in this study were carried out in a three-electrode system in 1.0 mol L⁻¹ KOH electrolyte. The LSV curves were obtained after *iR* compensation (Fig. S6). Fig. S7 shows the LSV curves of the as-prepared mildly reduced GO-supported metal borate samples with different Co:Ni ratios (1:1, 2:1, 1:2, 1:0, 0:1) for OER. Note that all the bimetal borate samples exhibit much lower overpotentials than the mono-metal borate samples, indicating the favorable catalytic activity of the bimetal hybrids. These samples were then subjected to annealing treatment at 400°C in Ar atmosphere for 2 h. The overpotentials and the Tafel slopes of the annealed products obviously reduce compared with those of the unannealed samples (Fig. 4a). Besides, the mildly reduced GO-supported bimetal borate (denoted as Co-Ni-BO_x/mrGO) precursor was also annealed at several temperatures, and the results were compared in Fig. S8. Electrochemical tests manifest that both the electrocatalyst composition and the annealing temperature have significant impacts on the activity of the graphene-supported bimetal oxide catalysts.

The overpotentials and the Tafel slopes obtained from various control experiments are depicted and compared in Fig. 4e, f (the abbreviations and their representative substances in Fig. 4e, f are stated in the Supplementary information). The Co-Ni-O_x/BG shows the highest activity considering both the overpotential and Tafel slope. It is therefore selected for the detailed examination of the OER electrocatalytic performance. Fig. 4b presents the LSV polarization curves of the Co-Ni-O_x/BG, the 400°C-annealed unsupported bimetal borides (Co-Ni-O_x) and the graphene, the commercial RuO₂, and the bare GCE. The Co-Ni-O_x/BG exhibits the lowest overpotential at 10 mA cm⁻² (310 mV) compared with the bimetal oxides (400 mV) and graphene (520 mV), suggesting the coupling effect between the bimetal oxides and the graphene

can improve the OER electrocatalytic activity of the hybrid. The Tafel slopes calculated from the LSV curves are also given in Fig. 4c. The Co-Ni-O_x/BG shows the smallest Tafel slope (54.8 mV dec⁻¹), demonstrating its fast kinetics. This Tafel slope is close to the ideal value of 59.0 mV dec⁻¹ (equivalent to 2.3 RT/F), involving a one-electron transfer process prior to the rate-limiting step [41,42]. The Co-Ni-O_x/BG even outperforms the commercial RuO₂ in the aspect of overpotential and Tafel slope (330 mV and 62.7 mV dec⁻¹ for the overpotential at 10 mA cm⁻² and Tafel slope of commercial RuO₂, respectively). To the best of our knowledge, this Co-Ni-O_x/BG exhibits better activity than many of the earth-abundant transition metal-based OER catalysts (as seen in Table S1), even competitive with noble-metal-based ones [43].

The EIS measurements of the Co-Ni-O_x/BG, Co-Ni-O_x, graphene, and the commercial RuO₂ were conducted in KOH solution (Fig. 4d). The EIS curves can be fitted with an equivalent circuit composed of a series of resistance (*R_s*, mainly the solution resistance, and *R_{ct}*, the charge transfer resistance) and a constant phase element. The *R_s* value and the *R_{ct}* value are closely related to the kinetics of the electrocatalytic process. These data indicate that the Co-Ni-O_x/BG has smaller charge transfer resistance than Co-Ni-O_x, graphene, and RuO₂, indicating a faster charge transfer process in the Co-Ni-O_x/BG electrocatalysts [44]. This is in accordance with the low overpotential and small Tafel slope of the Co-Ni-O_x/BG.

In order to further ascertain the catalytic mechanism of the electrocatalysts, the RRDE method was also used to oxidize the possible hydrogen peroxide intermediates generated at the electrocatalyst surface during the water oxidation process. The Pt ring electrode was set at 1.50 V vs. RHE. Fig. 5a shows fairly low ring current (about three orders of magnitude lower than that of the disk current), demonstrating the negligible H₂O₂ generation, which corresponds to a desired four-electron transfer pathway of the Co-Ni-O_x/BG for water oxidation [40,45]. Furthermore, the Faradaic efficiency tests were also conducted to confirm this result. The ring electrode was applied with a potential of 0.45 V to reduce the *in-situ* generated O₂ in the disk electrode, giving a persistent OER (disk electrode)→ORR (ring electrode) process. Fig. 5b exhibits that the collected ring current is ca. 66.5 and 171.4 μA, with the applied disk current at 180 and 470 μA, corresponding to the calculated Faradaic efficiency of 99.7% and 98.6%, respectively.

The accelerated degradation test was carried out by comparing the LSV polarization curves before and after

Figure 4 (a) The LSV curves of the annealed BG coupled bimetal oxides with different Co:Ni ratios in 1.0 mol L⁻¹ KOH solution. (b, c) The LSV curves and the corresponding Tafel plots of the Co-Ni-O_x/BG, Co-Ni-O_x, graphene and commercial RuO₂. (d) EIS spectra of the Co-Ni-O_x/BG, Co-Ni-O_x, graphene, and commercial RuO₂ samples (inset: the corresponding equivalent circuit). (e, f) Bar graphs for easy comparison of the overpotentials of various catalysts (10 mA cm⁻²), and the Tafel slopes obtained from the OER polarization curves.

multiple CV cycling to evaluate the durability of the catalyst in the OER process. As seen in Fig. 6a, after 1000 cycles, the LSV curve of Co-Ni-O_x/BG only shifts marginally compared with the initial one. This small change in the potential demonstrates good cycling performance of the Co-Ni-O_x/BG catalysts. We also examined the morphology change of the catalyst before and after the above-mentioned durability test. The structure maintains well in the graphene-supported bimetal oxides after the test, which can be discerned from the SEM images

(Fig. S9), demonstrating that after long-term operation, the high OER activity of the catalyst can be well-maintained. The Co-Ni-O_x/BG shows a potential change of only 17 mV during 12 h constant-current (10 mA cm⁻²) measurements, further confirming its high stability in the OER process (Fig. 6b).

The electrochemical surface area (ECSA) is frequently served as an approximate presentation for the surface roughness of electrocatalyst within one order-of-magnitude accuracy [46]. We measured the double layer capa-

Figure 5 (a) The disk and ring current of Co-Ni-O_x/BG electrocatalyst on the RRDE equipment (1600 rpm) with the ring potential applied at 1.50 V in 1.0 mol L⁻¹ KOH solution. (b) Ring currents of the Co-Ni-O_x/BG on the RRDE equipment (1600 rpm) with the ring potential applied at 0.45 V at different disk currents (180 and 470 μA).

Figure 6 (a) LSV curves of the Co-Ni-O_x/BG electrocatalyst before and after 1000 CV cycles. (b) The chronopotentiometric curve (vs. RHE) at 10 mA cm⁻² for the Co-Ni-O_x/BG in 1.0 mol L⁻¹ KOH electrolyte.

citance at the solid-liquid interface to estimate the electrochemical surface areas. The double layer capacitance values of the annealed graphene-supported bimetal oxide samples with different Co:Ni ratios are close to each other (Fig. S10). The Brunauer-Emmett-Teller (BET) measurements were also carried out, as shown in Fig. S11. The results manifest that the BET surface areas of the graphene-supported bimetal oxide samples with different Co:Ni ratios have little difference (Fig. S11). This indicates that the activity advantage of the Co-Ni-O_x/BG has little relationship with the specific surface area or the ECSA. The higher activity of the Co-Ni-O_x/BG can be attributed to the appropriate Co:Ni ratio, which induces the enhancement in the charge transfer ability. The activity improvement arising upon annealing treatment primarily depends on the enhanced conductivity induced by the reduction of GO, as manifested by the EIS results shown in Fig. S12. By reasonably designing and carrying out a series of control experiments, this study offers effective ways for improving the OER performance of the

electrocatalyst. First, the elementary composition of the bimetal oxides should be modulated in order to change the microenvironment of the surface electron of the transition metal. Second, a post-annealing process is necessary to regulate the crystalline structures of the catalysts. Lastly, taking advantage of the strong coupling effect between the active electrocatalyst and the conductive support, the synergetic effects between the coupled materials may lead to distinct improvement on the electrocatalytic performance.

CONCLUSIONS

In summary, a novel Co-Ni-O_x/BG nanohybrid was fabricated *via* a facile co-reduction approach followed by an annealing process, providing a scalable and economical method for the preparation of graphene-supported bimetal oxide catalysts. The properly annealed sample with an optimal composition (Co-Ni-O_x/BG) exhibits a high electrocatalytic activity for the OER in alkaline electrolyte. High stability of the catalyst is also testified by the long-

term operation process and the accelerated degradation test. The high OER electrocatalytic performance of the Co-Ni-O_x/BG can be attributed to the unique structure of the hybrid which is favorable for the exposure of active sites, and the strong synergistic coupling effects between the bimetal oxides and graphene. This work offers several effective ways for improving the OER performance of the electrocatalyst, such as modulating the elemental ratio of the bimetal oxides, appropriate annealing treatment, and capitalizing on the strong coupling effect. This study can promote the development of non-noble metal hybrid materials for highly active OER electrocatalysts in the electrochemical water splitting process.

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硼掺杂石墨烯耦合双金属氧化物作为高效氧气析出电催化剂

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摘要 开发高效价廉的氧气析出反应电催化剂对于制备多种可再生能源转化和存储器件至关重要。本文中, 我们设计合成了一系列硼掺杂石墨烯负载的钴镍双金属氧化物, 并研究了其氧气析出电催化性能。研究结果表明适当温度下退火后的Co-Ni-O_x/BG (Co/Ni比为1:1)在碱性条件下表现出非常高的氧气析出电催化性能。在电流密度为10 mA cm⁻²时, 该电催化剂对氧气析出反应的过电位仅为310 mV, 优于绝大多数已报道的基于单金属氧化物的催化剂, 甚至可与商业RuO₂电催化剂的性能相媲美。该双金属氧化物复合材料中, 电荷分布的微调控及协同耦合效应都对该材料的电催化性能起到了促进作用。另外, 本文还提出了几种可有效提高氧化物材料氧气析出电催化活性的方法。