In-situ tracking of phase conversion reaction induced metal/metal oxides for efficient oxygen evolution

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ABSTRACT Due to the unique interface and electronic structure, metal/metal oxide composite electrocatalysts have been designed and exploited for electrocatalytic oxygen evolution reaction (OER) in alkaline solution. However, how to fabricate metal/metal oxides with abundant interfaces and well-dispersed metal phases is a challenge, and the synergistic effect between metal and metal oxides on boosting the electrocatalytic activities is still ambiguous. Herein, by controlling the lithium-induced conversion reaction of metal oxides, metal/metal oxide composites with plentiful interfaces and excellent electrical interconnection are fabricated, which can enhance the active sites, and accelerate the mass transfer during the electrocatalytic reaction. As a result, the electrocatalytic oxygen evolution activities of the as-fabricated metal/metal oxide composite catalysts including NiCo/NiCo₂O₄, NiMn/NiMn₂O₄ and CoMn/CoMn₂O₄ are greatly improved. The catalytic mechanism is also explored using the *in-situ* X-ray and Raman spectroscopic tracking to uncover the real active centers and the synergistic effect between the metal and metal oxides during water oxidation. Density functional theory plus U (DFT + U) calculation confirms the metal in the composite can optimize the catalytic reaction path and reduce the reaction barrier, thus boosting the electrocatalytic kinetics.

Keywords: *in-situ* tracking, electrochemical conversion reaction, metal/metal oxide interfaces, electrocatalytic mechanism, oxygen evolution

INTRODUCTION

Electrochemical water splitting is widely considered to be a critical way for the clean and renewable energy pro-

duction, storage and usage such as sustainable hydrogen production, rechargeable metal-air batteries and fuel cells [1–4]. However, owing to the multistep four-electron redox process ($4\text{OH}^- \rightarrow 2\text{H}_2\text{O} + 4\text{e}^- + \text{O}_2$), oxygen evolution reaction (OER) often requires a relatively high overpotential, which leads to the sluggish kinetics and obvious energy loss [5–7]. Though the state-of-the-art precious-metal-based catalysts including IrO₂ and RuO₂ show impressive OER activities, the scarcity and high cost hinder their scale-up deployment [8–10]. Therefore, it is of great significance to develop earth-abundant transition metals (especially Fe, Co, and Ni) and their derivatives as highly efficient electrocatalysts for oxygen evolution [11–22]. Among the non-noble metal-based electrocatalysts, transition metal oxides (TMOs) and layered double-hydroxides (LDHs) have been well designed with satisfying OER activities [23–27]. However, their activity and stability require to be further improved, and in-depth research into the catalytic mechanism of non-noble metal-based electrocatalysts is still lacking.

Rational design of the electrocatalysts can not only increase the active sites, improve the intrinsic activity, but also accelerate the transfer rate of the charge and products, thus obviously boosting electrocatalytic properties. To optimize the activities of the transition-metal-based electrocatalysts, strategies such as heteroatom tailoring, interface engineering, and electronic structure modification have been proposed [28–32]. Metal/metal oxide composites, thanks to the unique two-phase interface and metal-phase-induced desirable electrical conductivity, have been designed and exploited as electrocatalysts re-

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cently [33,34]. For instance, NiCo/Fe₃O₄ heteroparticles with metal-organic frameworks demonstrated remarkable OER activity because NiCo can stabilize the active oxygen species adsorbed on Fe₃O₄ surface [35]. Experimental and theoretical results showed that MoNi₄/MoO_x@Ni composite electrocatalyst can effectively reduce the energy barrier of the Volmer step and expedite the hydrogen evolution reaction (HER) kinetics in alkaline solution due to the synergistic effect between Ni and Mo atoms as well as the improved electron transport [36,37]. However, studies on the OER activities of the metal/metal oxides are seldom and the catalytic mechanism as well as the synergistic effect between the metal and metal oxides on improving the electrocatalytic activities are still indistinct. On the other hand, the interface/boundary in the catalysts plays a key role in the electrocatalytic activities. At the interfaces of metal/metal oxides, metal cations possess positive charge and more unfilled d-orbits, which can facilitate OH⁻ adsorption due to the strong electrostatic interactions. Meanwhile, a nearby metal site would preferentially adsorb H atom thus boosting the water electrolysis [38]. As a consequence, the methods to fabricate metal/metal oxides with abundant interfaces and well-dispersed metal phases are urgently to be developed towards water oxidation.

In-situ electrochemical tuning by lithium insertion/extraction or the conversion reaction is a novel strategy to engineer the electrocatalytic activities of battery electrode materials, such as LiCoO₂, LiMPO₄ (M = Fe, Mn, Co, Ni), MoS₂, and Pd₃P₂S₈ [39–44]. For instance, through lithium-induced conversion reaction, ultra-small TMO nanoparticles (2–5 nm) can be obtained with excellent contact and more active sites, which exhibited high activity and stability for water electrolysis [45]. Distinguished from these studies, we demonstrate that metal oxides with phase conversion mechanism including NiCo₂O₄, NiMn₂O₄ and CoMn₂O₄ can be *in-situ* transformed into NiCo/NiCo₂O₄, NiMn/NiMn₂O₄ and CoMn/CoMn₂O₄ composites using the lithium-induced conversion reaction, which breaks the metal–oxygen bonds and forms metal–metal bonds [46]. The *in-situ* phase-conversion-induced metal/metal oxides possess plentiful interfaces and excellent electrical interconnection between the metal and metal oxides as well as many catalytically active sites, which are different from traditional chemical syntheses. As a result, the as-optimized NiCo/NiCo₂O₄ composite shows a relatively low overpotential of 264 mV at 10 mA cm⁻² as well as reduced Tafel slope of 64 mV dec⁻¹ towards water oxidation. Electrocatalytic OER activities of NiMn/NiMn₂O₄ and CoMn/CoMn₂O₄

are also greatly improved compared with NiMn₂O₄ and CoMn₂O₄, respectively. Real active centers and evolution of the active species were explored using the *in-situ* X-ray and Raman spectroscopic tracking. The synergistic effect between the metal and metal oxides was also analyzed by density functional theory plus U (DFT + U) calculation. This work not only presents a deeper understanding of the intrinsic mechanism of the metal/metal oxides towards oxygen evolution but also provides a new method to better design earth-abundant composite OER electrocatalysts with high efficiency and stability.

EXPERIMENTAL SECTION

Materials

Typically, nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O, 99%), cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O, 99%) and manganese nitrate hexahydrate (Mn(NO₃)₂·6H₂O, 99%) were purchased from Aladdin Ltd. (Shanghai, China). Urea (CO(NH₂)₂, 99%) and ammonium fluoride (NH₄F, 99%) were obtained from Alfa-Aesar, and carbon fiber cloth (CFC) was obtained from Cetech Co. Ltd. All the reagents were used directly without further purification.

Synthesis of NiCo₂O₄ nanowire arrays on carbon fiber cloth

Before the fabrication, CFC and Ni foam (NF) were activated with dilute hydrochloric acid by ultrasonic wave for 30 min, and then cleaned in deionized (DI) water and ethanol for 30 min, respectively. In a typical process, 1 mmol Ni(NO₃)₂·6H₂O, 2 mmol Co(NO₃)₂·6H₂O, 2 mmol NH₄F, and 5 mmol urea were dissolved in 35 mL of distilled water with constant intense stirring to form a homogeneous pink solution. After a piece of cleaned CFC (2 cm × 3 cm) was put, the solution was then transferred into a Teflon-lined stainless autoclave. The autoclave was sealed and kept at 120°C for 6 h. After hydrothermal growth, the CFC covered with NiCo-precursor was carefully rinsed several times with DI water and sonicated to remove the unstable attached materials. After drying at 60°C overnight, they were calcined at 400°C for 2 h to obtain the well crystallized NiCo₂O₄ nanowires on CFC. After calcination, the mass loading of the NiCo₂O₄ nanowires on CFC was calculated to be about 1.2 mg cm⁻². NiMn₂O₄ and CoMn₂O₄ samples grown on NFs were obtained by using the similar method. During the hydrothermal process, 150 and 200°C were used for the syntheses of NiMn₂O₄ and CoMn₂O₄ samples, respectively.

In-situ electrochemical tuning

The electrochemical tuning process was operated in an electrolytic cell. The as-synthesized NiCo_2O_4 , NiMn_2O_4 and CoMn_2O_4 were used directly as the working electrode, lithium metal foil was used for both the counter and the reference electrode, and 1 mol L^{-1} LiPF_6 in ethylene carbonate and diethyl carbonate (EC-DEC, $v/v = 1:1$) was utilized as the electrolyte. The tuning process was performed in the potential window between 0.5 and 3 V *versus* Li^+/Li . Typically, the cycles began with discharge, and the cutoff voltage of the last discharging was 0.5 V. Subsequently, the product was taken out and rinsed with acetone, ethanol and DI water successively.

Materials characterization

The as-obtained catalysts were characterized by X-ray diffraction (XRD, D8 Advance, Bruker) pattern with a Cu target ($K\alpha$, $\lambda = 0.15406 \text{ nm}$). Scanning electron microscopy (SEM) images of the catalysts were obtained with a JEOL JSM 6700F electron microscope. The morphologies and structures were explored using transmission electron microscope (TEM) and high-resolution TEM (HRTEM, Philips Tecnai F20). Chemical compositions of the prepared catalysts were examined using X-ray photoelectron spectrometer (XPS, Escalab 250Xi, Thermo Fisher). The binding energy was calibrated to the C 1s peak of 284.8 eV. *In-situ* Raman spectra of the electrodes were recorded by using a confocal Raman microscope (HR Evolution, Horiba Jobin Yvon). X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) data were collected on beamline 14 W at Shanghai Synchrotron Radiation Facility (SSRF).

Electrochemical characterizations

The OER performance was evaluated on WaveDriver 20 bipotentiostat (Pine Instrument Company, USA), using a three-electrode system. CFC substrates coated with NiCo_2O_4 or other compositions were directly used as the working electrode. A graphite rod was used as the counter electrode, and an Ag/AgCl electrode was used as the reference electrode. 1.0 mol L^{-1} KOH solution was used as the electrolyte. Linear sweep voltammetry (LSV) was recorded at a scan rate of 1 mV s^{-1} . All potentials reported were calibrated to reversible hydrogen electrode (RHE) through the equation $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.197 \text{ V} + 0.0591 \times \text{pH}$. Electrochemical impedance spectroscopy (EIS) for the NiCo-based catalysts was measured at the voltage to reach 10 mA cm^{-2} . EIS for NiMn- and CoMn-based catalysts were measured at the voltage to reach 100 mA cm^{-2} . The mass loading of the NiCo_2O_4 , the

products after the first and third discharge (denoted as the 1st and 3rd $\text{NiCo}/\text{NiCo}_2\text{O}_4$) on CFC were weighed to be about 1.2 mg cm^{-2} . In order to accurately calculate the catalyst loading, we used inductively coupled plasma mass spectrometry (ICP-MS) to measure the mass of the metal active material on the 1 cm^2 electrode, and the results are shown in Table S1. All the polarization curves were obtained with ohmic potential drop (iR) correction. The turnover frequency (TOF) values were calculated according to the following equation: $\text{TOF} = J \times A / 4 \times F \times m$, where J is the current density, A is the area of the effective CFC (1 cm^2), F is the Faraday constant (a value of $96,485 \text{ C mol}^{-1}$), m is the number of moles of the active materials that deposited onto the carbon fiber paper.

In situ Raman spectroscopy

The *in-situ* Raman spectra were obtained by a confocal Raman microscope (HR Evolution, Horiba Jobin Yvon). A custom-made poly(tetra fluoroethylene) (PTFE) electrochemical cell assembled with a graphite rod counter electrode, Ag/AgCl electrode as the reference electrode and 1.0 mol L^{-1} KOH electrolyte was used for Raman experiments. And $\text{NiCo}_2\text{O}_4/\text{CFC}$ was used as the working electrode directly. Amperometric *i-t* curves (CHI 660E, Shanghai Chenhua instrument Co. Ltd) under various potentials were carried out to deduce the OER. Spectra were acquired under laser excitation with wavelength of 633 nm.

RESULTS AND DISCUSSION

NiCo_2O_4 nanowire arrays on CFC were firstly prepared to explore the geometry and OER activity evolutions upon the lithium-induced conversion reaction. The *in-situ* electrochemical tuning process is illustrated in Fig. 1a, in which the as-synthesized NiCo_2O_4 nanowire array is used as the anode and a lithium plate serves as the counter electrode. Upon the electrochemical lithiation, high-valence nickel and cobalt species are reduced and NiCo can be obtained when discharged to 1.0 V *vs.* Li^+/Li due to the conversion reaction mechanism of the spinel NiCo_2O_4 electrode [46,47]. As well known, the full transformation of metal oxides into metal requires a relatively slow ion-diffusion rate and a necessary activation process during the first several charge-discharge cycles. In our operation, to obtain the $\text{NiCo}/\text{NiCo}_2\text{O}_4$ hybrid product, a relatively high current density of 1000 mA cm^{-2} was adopted. By regulating the charge-discharge cycles, the contents of NiCo and NiCo_2O_4 can also be controlled to optimize their electrocatalytic activities. Upon the lithiation, NiCo nanocrystallines are *in-situ* generated on

Figure 1 (a) Schematic of the *in-situ* electrochemical tuning process. (b) Galvanostatic cycling profiles of NiCo₂O₄ at 1000 mA cm⁻². (c) SEM, (d) TEM, and (e) HRTEM images of NiCo₂O₄. (f) SEM, (g) TEM, and (h) HRTEM images of the 3rd NiCo/NiCo₂O₄.

NiCo₂O₄ matrix combined with plentiful interfaces and excellent electrical interconnection, which would highly accelerate the charge transfer and increase the catalytic active sites. Fig. 1b shows the galvanostatic cycling profiles of the NiCo₂O₄ electrode. To ensure the hybrid product of NiCo/NiCo₂O₄ composite, a cutoff potential of 0.5 V vs. Li⁺/Li that below the conversion reaction was selected for the discharge. Furthermore, to maintain the micro-structure of the nanowire arrays and explore the effect of NiCo/NiCo₂O₄ ratio on the electrocatalytic activities, the 1st and 3rd NiCo/NiCo₂O₄ were studied.

XRD result of the as-synthesized product (Fig. S1) indexes well with the standard pattern of PDF card. 20-0781, indicating pristine spinel NiCo₂O₄ phase was obtained. After the lithium-induced conversion reaction, some new characteristic peaks of Ni and Co appeared, and the diffraction peaks can be indexed well with the standard patterns of Ni (JCPDS No. 04-0850) and Co (JCPDS No. 15-0806), demonstrating the successful synthesis of NiCo/NiCo₂O₄. Fig. S2 and Fig. 1c show the

scanning electron microscopy (SEM) images of the as-prepared NiCo₂O₄ electrode, where NiCo₂O₄ nanowire arrays are uniformly distributed on the CFC. Instead of the conventional single-crystalline nanowire, as displayed in the TEM image (Fig. 1d), the NiCo₂O₄ nanowires are assembled by a number of nanoparticles, forming a mesoporous structure with highly exposed active sites for electrocatalysis. Two sets of lattice fringes with spacing of 0.29 and 0.24 nm can be observed in the HRTEM image shown in Fig. 1e, which correspond well to d-spacing of the (220) and (311) planes in spinel NiCo₂O₄, respectively, further confirming the as-well synthesized NiCo₂O₄ nanowires.

After the electrochemical tuning, binary transition NiCo/NiCo₂O₄ composite with engineered micro-structure was obtained. SEM images clearly reveal that the NiCo/NiCo₂O₄ hybrid product after three discharge/charge cycles still maintains the nanowire architecture (Fig. 1f and Fig. S3). Obviously, lithiation-induced volume expansion of the NiCo₂O₄ nanowires can be found

from the TEM image (Fig. 1g). In addition, due to the electrochemical conversion reaction, more nano interfaces are expected to be generated between the newly formed NiCo and the NiCo_2O_4 matrix, which has been evidenced as the additional active sites for OER [48]. Furthermore, because of the irreversible decomposition of NiCo_2O_4 ($\text{NiCo}_2\text{O}_4 + 8\text{Li}^+ + 8\text{e}^- \rightarrow \text{Ni} + 2\text{Co} + 4\text{Li}_2\text{O}$) and oxide reorganization during the cycling process, the NiCo/ NiCo_2O_4 nanowires have a more disordered structure with rough and loose surface. As a result, the 3rd NiCo/ NiCo_2O_4 sample shows smaller chaotic grains (Fig. 1h), well consistent with the previous report [45]. Apart from the lattice fringe of NiCo_2O_4 matrix, the lattice distance of 0.2 nm (red circle area) corresponds well with the d-spacing of the (111) crystallographic planes of cubic NiCo, strongly confirming the generation of NiCo after the phase conversion reaction. These observations indicate that, by taking use of the lithium-induced electrochemical conversion reaction, binary transition metal/metal oxide composites can be achieved with smaller grain size, more grain boundaries/interfaces, and excellent electrical interconnection, which are beneficial to the electrocatalytic activity toward oxygen evolution.

XPS was used to analyze the element composition and surface chemical state of the as-prepared composite catalysts. The NiCo/ NiCo_2O_4 samples still consist of Ni, Co and O without introducing other new elements (Fig. S4) since it is just the conversion reaction that happens during the electrochemical tuning process. Fig. 2a shows

the high-resolution Ni 2p spectra of NiCo_2O_4 , the 1st and 3rd NiCo/ NiCo_2O_4 . They consist of two prominent Ni 2p_{3/2} and Ni 2p_{1/2} peaks with each satellite peak. As for the pristine NiCo_2O_4 , the Ni 2p_{3/2} portion can be divided into two peaks located at 854.2 and 855.8 eV, indicating the presence of Ni^{2+} and Ni^{3+} species. Similarly, the peaks centered at 871.6 and 873.2 eV are assigned to the Ni^{2+} 2p_{1/2} and Ni^{3+} 2p_{1/2}, respectively [49]. Different from the pristine NiCo_2O_4 , the signal of Ni^{3+} species clearly weakens after the first discharge, demonstrating the reduction of the high-valence Ni species during the lithiation. In addition, the binding energy are upshifted, revealing the engineered electronic structure. The content of low-valence Ni species increases with the charge/discharge cycles. As evidenced from the Ni 2p XPS spectrum of the 3rd NiCo/ NiCo_2O_4 , additional two peaks centered at 852.5 and 869 eV associated with the zerovalent Ni obviously appear [40]. Besides, the binding energy of Ni^{2+} species in the 1st and 3rd discharged products shifts to a higher value of 855.7 eV, demonstrating the formation of $\text{Ni}(\text{OH})_2$ on the surface of NiCo/ NiCo_2O_4 [50]. The *in-situ* generated Ni^0 in NiCo/ NiCo_2O_4 is easily oxidized to $\text{Ni}(\text{OH})_2$ upon exposing to air, which also contributes to the Ni^{2+} species on the surface detected from XPS with larger binding energy than that in the pure NiCo_2O_4 [51]. The existence of these Ni^{2+} species is conducive to attracting hydrated ions onto the catalyst surface, thus promoting the decomposition of water molecules and accelerating the oxygen evolution.

Figure 2 High-resolution XPS spectra of (a) Ni 2p and (b) Co 2p in NiCo_2O_4 , the 1st and 3rd NiCo/ NiCo_2O_4 .

Fig. 2b shows the Co 2p XPS spectra of the products. Both Co^{2+} and Co^{3+} species can be found in the as-prepared pristine NiCo_2O_4 nanowires. The content of Co^{3+} species decreases for the 1st $\text{NiCo/NiCo}_2\text{O}_4$ composite, revealing high-valence Co species is reduced during the first discharge. For the 3rd $\text{NiCo/NiCo}_2\text{O}_4$ composite, two peaks associated with zerovalent Co can be observed with binding energy of 777.5 and 792.8 eV. It is worth to note that the peaks for Co^{2+} 2p and Co^{3+} 2p shift to higher binding energy, demonstrating the engineered electronic structure of the NiCo_2O_4 after the *in-situ* electrochemical tuning operation, which keeps well with the Ni 2p XPS analysis. Fig. S5 shows the O 1s spectra of the samples. Obviously, the peaks shift to higher binding energy upon the charge/discharge cycles, further confirming the tai-

lored electronic structure. The peak at 531.8 eV for the 3rd $\text{NiCo/NiCo}_2\text{O}_4$ is associated with lattice oxygen, and the other two peaks located at 533.8 and 535.3 eV correspond to adsorbed oxygen [52]. Based on these results, we can conclude that $\text{NiCo/NiCo}_2\text{O}_4$ hybrid product can be obtained exploiting the lithium-induced electrochemical conversion reaction of NiCo_2O_4 .

To evaluate the electrochemical OER catalytic activities, the $\text{NiCo/NiCo}_2\text{O}_4$ nanowires were tested in a standard three-electrode system. Fig. 3a shows the polarization curves of the NiCo_2O_4 , the 1st and 3rd $\text{NiCo/NiCo}_2\text{O}_4$ in 1.0 mol L^{-1} KOH solution at a scan rate of 1 mV s^{-1} . As can be seen, the 1st and 3rd $\text{NiCo/NiCo}_2\text{O}_4$ present much higher currents than pure NiCo_2O_4 at a constant potential, indicating the improved electrocatalytic OER activ-

Figure 3 Electrocatalytic OER performance of NiCo_2O_4 , the 1st and 3rd $\text{NiCo/NiCo}_2\text{O}_4$. (a) LSV polarization curves with iR correction. (b) Overpotential required for 10 mA cm^{-2} . (c) Tafel plots, (d) TOF at different overpotentials, and (e) chronopotentiometric curves obtained at 10 mA cm^{-2} .

ities. Oxidation peak appears during the polarization for the NiCo/NiCo₂O₄ catalysts, which can be ascribed to oxidation of the lower-valence Ni species including Ni⁰ and Ni²⁺ which are more easily oxidized in the electrocatalytic process. Importantly, the 3rd NiCo/NiCo₂O₄ exhibits much better OER performance than the 1st NiCo/NiCo₂O₄, owing to the increased charge transfer capacity and active sites resulting from the metal/metal oxides interface along with the galvanostatic cycles. As revealed in Fig. 3b, the 3rd NiCo/NiCo₂O₄ catalyst requires a very low overpotential of 264 mV to reach a current density of 10 mA cm⁻², which is much lower than that of the 1st NiCo/NiCo₂O₄ (288 mV) and NiCo₂O₄ (390 mV).

Tafel slopes were also calculated from the polarization curves to further clarify the enhanced electrocatalytic kinetics. As displayed in Fig. 3c, the 3rd NiCo/NiCo₂O₄ presents the lowest Tafel slope of 64 mV dec⁻¹ among these catalysts, indicating the increased OER kinetics due to the improved mass transfer rate associated with the generated NiCo and the NiCo/NiCo₂O₄ interface, which can be further confirmed by the decreased charge-transfer resistances of the NiCo/NiCo₂O₄ samples (Fig. S6). The quantification of each active site was considered by calculating the TOF values, to gain further insight into the improved OER activities of the NiCo/NiCo₂O₄ composite catalysts. As expected, the smaller nanoparticles and rich nano-interfaces produced after the conversion reaction possess more boundaries and dislocations, which can act as the active sites to enhance the catalytic efficiency [53]. These changes can be reflected in the TOF values by an order of magnitude increase. As demonstrated in Fig. 3d, the 3rd NiCo/NiCo₂O₄ shows a TOF value of 0.021 s⁻¹ at an overpotential of 350 mV, which is more than 8-fold higher than that of the NiCo₂O₄ catalyst (0.00265 s⁻¹), revealing the higher intrinsic activity of the NiCo/NiCo₂O₄ composite catalyst. The long-term electrolysis stability of the catalysts was further evaluated by testing the potential stability to keep a constant current density of 10 mA cm⁻². Moreover, the double-layer capacitance (*C_{dl}*) was evaluated to compare the electrochemical surface areas (ECSAs) of the catalysts. The 2*C_{dl}* value of the 3rd NiCo/NiCo₂O₄ was calculated to be 119.8 mF cm⁻² (Fig. S7), which is two times larger than that of the pure NiCo₂O₄, demonstrating the increased ECSA induced by the conversion reaction, which provides more exposed active sites for the promotion of OER activity. Impressively, the 1st and 3rd NiCo/NiCo₂O₄ show a stable overpotential after 60,000 s without obvious degradation, confirming their remarkable OER catalytic activity and

stability. XRD in Fig. S1b and TEM images in Fig. S8 of the 3rd NiCo/NiCo₂O₄ after OER tests show that the catalyst is very robust without any phase and structural damage. The Ni⁰ and Co⁰ characteristic peaks in XPS spectra of the 3rd NiCo/NiCo₂O₄ after the OER reaction (Fig. S9) are slightly weakened, which can be attributed to the oxidation of some zero-valent Ni and Co during the OER process.

Operando techniques were performed to identify the actual electrocatalytic active centers of the NiCo/NiCo₂O₄ composite catalyst. *In-situ* X-ray absorption spectroscopy (XAS) studies were first conducted to directly monitor the electronic and geometric structure evolution of electrocatalysts during the electrocatalytic OER process. Fig. 4a, b show the XANES spectra at the Ni K-edge and Co K-edge under the altered potentials. When the NiCo/NiCo₂O₄ composite was soaked into the 1 mol L⁻¹ KOH solution at open circuit, no obvious structural change was observed from the Ni K-edge spectrum as compared with the sample in air. Then the absorption edge continuously moves to higher energy with increasing applied potential, illustrating the oxidation of Ni²⁺ ions to higher oxidation state, namely NiOOH phase which contains a mixture of Ni³⁺ and Ni⁴⁺ species [52–54]. The gradual decreasing intensity of the white-line peak in the Ni K-edge spectrum proved that the geometric structure of the catalyst has been evolved from crystal into a distorted structure upon oxidation [53,55]. More importantly, the potential-dependent process is reversible, as the applied potential is back to 0 V, the Ni K-edge spectrum returns to its initial low energy state. This evidences that nickel ions in the NiCo/NiCo₂O₄ catalyst are able to be readily oxidized to high valence, thus exhibiting more reactivity and should be the electrocatalytic active centers for oxygen evolution. Surprisingly, the features of Co K-edge absorption spectra are not obviously affected by the increasing potential from 0 to 0.45 V vs. Ag/AgCl, revealing Co maintains as the mixture of Co²⁺/Co³⁺ during oxygen evolution [56]. The feeble change of the peak intensity after soaking into the solution may be attributed to the formation of hydrates. Consequently, the XAS data reveal the fact that the nickel ions in NiCo/NiCo₂O₄ composite are the realistic active species.

To further explore the active phase and key intermediates during the OER process, *in-situ* Raman spectra were recorded from 0 to 0.7 V vs. Ag/AgCl. Fig. 4c, d compare the *operando* Raman spectroscopy of the pure NiCo₂O₄ and the 3rd NiCo/NiCo₂O₄ composite during OER. The local structure for these catalysts under potentials between 0 and 0.1 V vs. Ag/AgCl can be ascribed

Figure 4 *In-situ* XANES spectra of (a) Ni K-edge and (b) Co K-edge of the 3rd NiCo/NiCo₂O₄ in 1 mol L⁻¹ KOH. *In situ* Raman spectra of (c) NiCo₂O₄ and (d) the 3rd NiCo/NiCo₂O₄, and the corresponding normalized intensity maps of (e) NiCo₂O₄ and (f) the 3rd NiCo/NiCo₂O₄ under different applied potentials vs. Ag/AgCl (without iR correction).

to the local spinel structure of NiCo₂O₄ with characteristic phonon modes at 455, 526, and 657 cm⁻¹ [56,57]. As the potential is swept anodically to 0.2 V vs. Ag/AgCl, significant structural transformation is observed. The primary three peaks disappeared and new peaks at 471 and 557 cm⁻¹ emerged for the pure NiCo₂O₄ catalyst. The pair of new peaks are attributed to the E_g bending vibration and the A_{1g} stretching vibration of Ni–O in NiOOH [58], demonstrating the Ni species in the catalyst have been transformed into oxyhydroxides under water oxidation potential. The 3rd NiCo/NiCo₂O₄ composite shows similar structural evolution with increasing anodic polarization from 0.2 to 0.7 V vs. Ag/AgCl but with higher intensity under the same potential. As a consequence, *in-situ* Raman characterization confirms the transformation from low-valence Ni species to high-valence NiOOH, which plays a key role in the OER process. Moreover, the relative intensities of the Raman double bands associated with the generated NiOOH on the NiCo/NiCo₂O₄ are further clearly confirmed to be much stronger compared with those of the pure NiCo₂O₄ sample (Fig. 4e, f). This result allows for the conclusion that the *in-situ* electrochemical-conversion-induced NiCo combined with the formed Ni(OH)₂ on the surface of the composite benefit the electrocatalytic activities of

NiCo₂O₄ catalyst for OER.

DFT + U calculation was performed to well investigate the NiCo/NiCo₂O₄ interface effect on the electrocatalytic OER activity. We considered Ni sites on the NiCo (111), NiCo₂O₄ (100) planes and their interface due to their similar d-spacing of about 0.2 nm (Figs S10–S12). As demonstrated by the free energy diagrams (Fig. S13), the potential limiting step is to form OOH for the NiCo (111) surface. While on the NiCo₂O₄ (100) plane, the step with the release of O₂ shows the largest reaction barrier (Fig. S14), and the calculated overpotential is much lower than that of the NiCo (111) surface. Interestingly, the determining step on the NiCo (111)/NiCo₂O₄ (100) interface becomes the production of OOH species again (1.56 eV), and the calculated overpotential is reduced to 330 mV (Fig. S15), which results in the accelerated OER kinetics with lowered Tafel slope and decreased charge transfer resistance of the NiCo/NiCo₂O₄ composite catalyst [35]. These experimental and theoretical analyses further confirm the NiCo in the composite can optimize the catalytic reaction path and reduce the reaction barrier, thus expediting the electrocatalytic kinetics.

Lithium-induced phase conversion reaction can also be used to convert other metal oxides into metal/metal oxide composite electrocatalysts. Fig. S16 displays the micro-

Figure 5 LSV polarization curves of (a) NiMn_2O_4 and (b) CoMn_2O_4 composites. Nyquist plots of (c) NiMn_2O_4 and (d) CoMn_2O_4 composites.

structures of the as-prepared NiMn_2O_4 and CoMn_2O_4 on NF. After discharge, valence states of the metal cations are reduced and a certain amount of metallic Ni, Mn, and Co can be detected (Figs S17, S18), indicating $\text{NiMn}/\text{NiMn}_2\text{O}_4$ and $\text{CoMn}/\text{CoMn}_2\text{O}_4$ composites are successfully obtained, respectively, after the electrochemical conversion reaction. Compared with the metal oxides, the as-fabricated metal/metal oxide composites exhibit improved OER activities. As shown in Fig. 5a, b, to deliver a current density of 100 mA cm^{-2} , NiMn_2O_4 and CoMn_2O_4 require overpotentials of 500 and 477 mV, respectively, which are reduced to 384 and 345 mV after the third discharge. The increased OER activities of the metal/metal oxide composites can be attributed to the accelerated charge transfer (Fig. 5c, d) induced by the *in-situ* formed metal phase and the metal/metal oxide interface. These results further indicate that, using the lithium-induced chemical conversion reaction, metal/metal oxide composites can be *in-situ* fabricated with abundant metal/metal oxide interfaces and excellent electrical interconnection between the well-dispersed metal nanocrystallines and metal oxide matrix. At the interfaces, metal cations possess positive charge and more unfilled d-orbits, which can facilitate OH^- adsorption due to the strong electrostatic interactions. Meanwhile, a nearby metal site would preferentially adsorb H atom,

thus boosting the water electrolysis.

CONCLUSION

In summary, we demonstrated that metal/metal oxide composite electrocatalysts including $\text{NiCo}/\text{NiCo}_2\text{O}_4$, $\text{NiMn}/\text{NiMn}_2\text{O}_4$ and $\text{CoMn}/\text{CoMn}_2\text{O}_4$ with abundant interfaces, excellent electrical interconnection as well as more catalytically active sites can be *in-situ* fabricated through the lithium-induced conversion reaction, which greatly increase the electrocatalytic OER activities of the metal oxides. For instance, the 3rd $\text{NiCo}/\text{NiCo}_2\text{O}_4$ exhibited superior water oxidation properties by attaining an overpotential of 264 mV at 10 mA cm^{-2} with a low Tafel slope of 64 mV dec^{-1} and excellent long-term stability in alkaline solutions. We further detected that Ni sites in the $\text{NiCo}/\text{NiCo}_2\text{O}_4$ composite are the real active centers for OER by *in-situ* X-ray and Raman spectroscopic tracking. The improved OER activities could be attributed to the synergistic effect of the increased electrochemically active sites and the enhanced charge transfer.

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Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Calculation methods and supporting data are available in the online version of the paper.

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原位相转化反应制备的金属/金属氧化物用于析氧反应

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摘要 金属/金属氧化物复合材料凭借其独特的界面和电子结构已被广泛设计合成, 并应用于碱性溶液中电催化析氧反应的电催化剂。然而, 如何设计并获得丰富的金属/金属氧化物界面和均匀分散的金属相仍是一个挑战。此外, 金属和金属氧化物在增强电催化活性方面的协同机理依然不清晰。本文以金属氧化物为基体, 通过锂诱导的转化反应, 制备了具有丰富界面和优异电接触的金属/金属氧化物复合物, 增加了催化活性位点, 并加速了电催化反应过程中的传质。利用该方法制备出的NiCo/NiCo₂O₄, NiMn/NiMn₂O₄和CoMn/CoMn₂O₄催化剂的析氧性能有显著提升。通过原位X射线吸收光谱和原位拉曼光谱技术, 本文探索了复合催化剂的催化机理, 揭示了析氧反应中的催化活性中心以及金属与金属氧化物之间的协同作用机理。密度泛函理论 + U (DFT + U) 计算证实了金属/金属氧化物材料中的金属组分可以优化催化反应路径并降低反应势垒, 从而加速电催化动力学。