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Solid-Solution Hexagonal Ni_{0.5}Co_{0.5}Se Nanoflakes toward the Boosted Oxygen Evolution Reaction

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The oxygen evolution reaction (OER) with sluggish kinetics is a bottleneck for the large-scale application of water electrolysis. Herein, solid-solution hexagonal $Ni_{0.5}Co_{0.5}Se$ nanoflakes are designed and successfully synthesized via a facile hydrothermal method with much lower overpotential of 216 mV at 10 mA cm⁻² and Tafel slope of 37.08 mV dec⁻¹.

Over the past decades, energy crisis and environmental pollution have posed great challenges to humankind. To address these issues, various sustainable energy systems or techniques have been explored, such as solar cells, lithium ion batteries, supercapacitors, and fuel cells.¹ Among them, electrochemical water splitting $(2H_2O \rightarrow 2H_2+O_2)$ is a promising candidate, which can produce high-energy carrier H_2 from abundant water resources in the Earth.² However, the oxygen evolution reaction (OER) with sluggish kinetics is a bottleneck, severely limiting the water electrolysis. Although noble metal oxides IrO_2 and RuO_2 have demonstrated low overpotential for OER, the scarce reserve and high price restrict their widespread application.³ Consequently, it is imperative to develop non-noble metal electrocatalysts with high activity and durable stability for OER.

Transition metal (TM) chalcogenides have especially attracted considerable attention due to the low cost, facile structural/compositional modulation and robust stability at room temperature.⁴ Among them, TM selenides possesses unique advantages over TM oxides and sulfides:⁵ (1) good electrical conductivity, (2) abundant active sites, and (3) intrinsic corrosion stability in alkali electrolyte. Local density of

states (LDOS) of many selenides are largely across the Fermi level, which exhibit metallic property and are highly beneficial for the electron transfer. In addition, TM selenides usually have the nearly optimal e_g filling (e_g =1), which are highly potential candidates as ideal OER electrocatalysts. For example, Xie's group reported that atomically thick CoSe₂ nanosheets can effectively catalyze the OER due to the abundant intrinsic Co vacancies.⁶ NiSe nanowires anchored on nickel foam (NF) in situ synthesized by hydrothermal treatment of NF and NaHSe, exhibit high activity for OER with an overpotential of 270 mV at 20 mA cm⁻².⁷

Moreover, it is also reported that the integrated hybrid catalysts with several components or heteroatom doping could obtain remarkably improved catalytic activity toward OER.⁸ Zhou and coworkers demonstrated that the presence of FeSe can significantly affect the electrochemical oxidation process of CoSe, in spite of no electronic interaction between Co and Fe.^{8a} In contrast, Guo et al synthesized CoSe/FeSe₂ nanohybrid by one-step hydrothermal method, which presents a small overpotential of 246 mV at a current density of 10 mA cm⁻² due to the synergistic effect among different components.^{8b} Benefiting from synergistic effects of metallic nature, Yu's group synthesized NiCo2Se4 with holey nanostructures to motivate the oxygen evolution and obtained a low overpotential of 295 mV and a low Tafel slope of 53 mV dec^{-1.8c} Amorphous Fe-NiSe/NF in situ fabricated by Li's group, also shows good durability and low overpotentials of 233 and 275 mV at the current density of 10 and 100 mA cm⁻² in 1 M KOH, respectively.8e

Although great progress has been achieved, a challenge still remains. Namely, hexagonal-phase TM selenides (e.g. CoSe) have relatively low electrical conductivity, tremendously hindering electron transfer and electrocatalytic activity.⁹ Mixed-TM oxides have been reported to demonstrate an improved electrocatalytic performance via cation doping or nanostructure engineering, which could be ascribed to the modulation of electronic structure of different metal atoms and lowered energy barrier.¹⁰ Herein, we report a facile hydrothermal method to synthesize solid-solution Ni_{0.5}Co_{0.5}Se nanoflakes based on the similar atomic radius and electron

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configuration. Moreover, the mismatch of crystal lattices in the degree of Jahn-Teller distortion between the Ni-Se and Co-Se coordination octahedra introduces unavoidable crystal strain and electron polarization, which is beneficial for lowering the absorption energy. The synergistic effect between the oxidation of Co^{2+} to Co^{3+} and that of Ni²⁺ to Ni³⁺ only extracts one electron from the eg band with two electrons, making the eg filling to be one, and resulting in fast O₂ gas evolution kinetics. The as-prepared Ni_{0.5}Co_{0.5}Se shows a low overpotential of 216 mV at the current density of 10 mA cm⁻² and a small Tafel slope of 37.08 mV dec⁻¹, indicating high electrocatalytic activity and boosted oxygen reaction kinetics. The strategy provides new insights into the design of mixed metal selenides and the development of efficient non-noble metal catalysts for large-scale applications.



Fig. 1 Crystal structure of (a) CoSe, (b) NiSe, and (c) Ni_{0.5}Co_{0.5}Se, respectively. (d) LDOS of CoSe and NiSe, respectively. (e) XRD patterns of CoSe, NiSe, and Ni_{0.5}Co_{0.5}Se nanoflakes, respectively. High-resolution XPS spectra of (f) Ni 2p, and (g) Co 2p, respectively.

CoSe and NiSe have the almost same hexagonal structure, with tiny difference of lattice constants, as shown in Fig. 1a-c. Moreover, similar 3d electron orbitals endow them the similar electron configuration as revealed by the local density of states (LDOS) in Fig. 1d, which provide high possibility of solid solution without destroy the original crystal structure.¹¹ As illustrated in Fig. 1c, the relaxed crystal structure of Ni_{0.5}Co_{0.5}Se by density functional theory (DFT) calculations, shows a little expansion as marked by the c constant and Co-Se and Ni-Se bonds, which will lead to tensile strain and thus modulate the OER kinetics.¹² The crystal structures of the asprepared samples are investigated by X-ray diffraction (XRD) patterns (Fig. 1e). The as-prepared CoSe and NiSe show similar characteristic diffraction peaks indexed to the (101), (102), (110), (103) and (112) crystal planes, respectively. It can be noted that the three strongest peaks of CoSe shift obviously to

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high-angle direction compared to those of NiSe. This is caused by the little smaller crystal parameters $\partial P C \delta S \partial (a 4 b 2 3.60\% Å)$, c=5.207 Å, PDF#89-2004) than those of NiSe (a=b=3.692 Å, c=5.215 Å, PDF#02-0892). It was such high similarity in the lattice parameters and crystal structure that makes the solidsolution Ni_{0.5}Co_{0.5}Se possible.¹³ Consequently, XRD pattern of Ni_{0.5}Co_{0.5}Se shows obviously broadened peaks, indicating a chemical fusion, not just merging together. Moreover, the characteristic peaks shift to the lower angles, indicating the expanded crystal lattice (a=b=4.025 Å, c=5.675 Å).

X-ray photoelectron spectroscopy (XPS) analysis is conducted to further determine the surface composition (Fig. 1f & 1g). The survey spectrum shows that the as-prepared Ni_{0.5}Co_{0.5}Se nanoflakes are composed of Ni, Co and Se elements (Fig. S2a, ESI⁺), agreeing well with the elemental mapping. The presence of O peak is ascribed to the absorbed H_2O , O_2 or the oxidized species of TM selenides upon exposure to air.^{7,8e, 9a} The Ni 2p high-resolution spectrum (Fig. 1f) shows that two notable peaks at 874.0 and 856.6 eV, which are assigned to the Ni 2p_{1/2} and Ni 2p_{3/2} signals of Ni²⁺, accompanying two shake-up satellite peaks (marked as "Sat.").¹⁴ The Co 2p XPS spectrum in Fig. 1g can be deconvoluted into the peaks at 797.3 eV for Co $2p_{1/2}$ and 781.4 eV for Co $2p_{3/2}$, indicating the Co²⁺ state.¹⁵ For the Se 3d spectrum in Fig. S2b (ESI⁺), the peaks located at 58.9 and 54.4 eV should be attributed to Se $3d_{3/2}$ and Se $3d_{5/2}$, respectively, which proves the presence of TM-Se bonds. Therefore, XPS results further confirm the formation of solidsolution Ni_{0.5}Co_{0.5}Se.



Fig. 2 (a) SEM image, (b) enlarged SEM image, (c) elemental mapping images, (d) TEM image and (e) HRTEM image of $Ni_{0.5}Co_{0.5}Se$ nanoflakes.

The morphological and structural properties of Ni_{0.5}Co_{0.5}Se were characterized by scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM) images. As shown in Fig. 2a, SEM image reveals the overview of Ni_{0.5}Co_{0.5}Se, illustrating the lamellar shape. The enlarged SEM image (Fig. 2b) displays the thickness of Ni_{0.5}Co_{0.5}Se nanoflake is about 20 nm. The specific surface area is calculated to 39.57 m² g⁻¹ by the Brunauer-Emmet-Teller N₂ adsorption isotherms, and the pore size is mainly 3.5~5 nm by the Barrerr-Joyner-Halenda model (Fig. S1, ESI⁺). In Fig. 2c, the

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corresponding elemental mapping images obtained from Fig. 2b show the presence and homogeneous distribution of Co, Ni and Se elements. TEM image in Fig. 2d further confirms the stacked lamellar morphology of $Ni_{0.5}Co_{0.5}Se$. The selected area electron diffraction (SAED) image shows distinct polycrystalline rings corresponding to the (100), (101) and (002) facets, respectively (inset of Fig. 2d). HRTEM image of $Ni_{0.5}Co_{0.5}Se$ in Fig. 2e clearly displays the lattice fringes of (101) and (102) with the spacing of 2.69 and 2.16 Å, respectively, demonstrating good crystallinity and polycrystalline nature. The energy-dispersive spectroscopy (EDS) also confirms the atomic ratio of Ni to Co is about 1:1 (Fig. S3, ESI⁺).



Fig. 3 (a) LSV curves, (b) Tafel plots, (c) Capacitive current difference vs. scan rates, (d) Nyquist plots for NiSe, CoSe, Ni_{0.5}Co_{0.5}Se nanoflakes, and RuO₂, respectively, (e) Chronopotentionmetric curve at current density of 10 mA cm⁻² for Ni_{0.5}Co_{0.5}Se nanoflakes, insets show the HRTEM image (e1) and corresponding SAED image (e2) after activation of Ni_{0.5}Co_{0.5}Se.

The electrocatalytic properties of Ni_{0.5}Co_{0.5}Se for OER were estimated by linear sweep voltammetry (LSV) by glassy carbon electrode with different loadings (Fig. S4 ESI⁺) in a threeelectrode configuration with a 90% iR compensation in 1.0 M KOH solution. Compared to CoSe (242 mV), NiSe (259 mV) and commercial RuO₂ (288 mV), Ni_{0.5}Co_{0.5}Se nanoflakes delivers the lowest overpotential (η) of 216 mV at the current density of 10 mA cm⁻² (Fig. 3a), and is comparable to the reported results (Table S1, ESI⁺). Even at the high current density of 100 mA cm⁻², Ni_{0.5}Co_{0.5}Se nanoflakes also exhibit a much lower overpotential of 274 mV, than CoSe (317 mV), NiSe (337 mV) and RuO₂ (442 mV). The corresponding Tafel plots of the electrocatalysts are shown in Fig. 3b. In comparison with other samples in this study, the Tafel slope of Ni_{0.5}Co_{0.5}Se is 37.08 mV dec⁻¹, much lower than those of CoSe (45.77 mV dec⁻¹) and NiSe (50.84 mV dec⁻¹) and RuO_2 (65.41 mV dec⁻¹), indicating the fast reaction kinetics.¹⁶ The double-layer capacitance was

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measured by cyclic voltammetry (CV) to estimate othe electrochemical surface area (ECSA), which is an Dimportant indicator for the exposure of active sites (Fig. S5, ESI⁺). In Fig. 3c, Ni_{0.5}Co_{0.5}Se nanoflakes have the largest capacitance (48.21 mF cm⁻²), which is superior to CoSe (39.57 mF cm⁻²), NiSe (30.07 mF cm^2) and RuO_2 (20.66 mF cm^2) . This can be attributed to the increased crystal strain arising from the tiny atomic radius difference of Ni and Co, and more exposure of a mixture of edge, corner, and face-sharing NiSe₆ octahedra. Electron-transfer resistance (R_{ct}) is determined electrochemical impedance spectroscopy. The Nyquist plots (Fig. 3d) show that not only the R_{ct} of $Ni_{0.5}Co_{0.5}Se$ (15.3 Ω) is much lower than those of CoSe (20.1 Ω), NiSe (27.1 Ω) and RuO_2 (33.9 Ω), but also the Ohmic resistance (R_o , the intersection with the real axis) is much small (6.4, 7.3, 8.6, and 11.5 Ω Ni_{0.5}Co_{0.5}Se, CoSe, NiSe, and RuO₂ in order). The low R_{ct} signifies that electron transfer at the interface of catalysts and electrolyte is much fast, while the small Ro means good electrical conductivity, both of which are credited to the modulated intrinsic conductivity by Ni-Co solid solution.

To evaluate the stability of electrocatalyst, LSV curves over 2000 cycles are firstly investigated (Fig. S6, ESI⁺), the overpotential of Ni0.5Co0.5 e nanoflakes only increases by 3.2 mV at 10 mA cm⁻² and 24.2 mV at 100 mA cm⁻², respectively, suggesting good stability. Moreover, chronoamperometric (CA) curve of Ni_{0.5}Co_{0.5}Se at different current densities (Fig. S7, ESI⁺) demonstrates a steady increased potential steps with the increase of current density. A long-time durability test over 20 hours at 10 mA cm⁻² (Fig. 3e) shows the overpotential only increases by 2.9%, remaining 97.1% of the initial activity. Cyclic voltammetry (CV) curves during the initial activation (Fig. S8, ESI⁺) clearly show the anodic peaks at 1.375 V vs. RHE, which is attributed to the conversion TM²⁺ to TM³⁺, accompanying the loss of Se element (Fig. S9, ESI⁺). The current density recorded after this potential is credited to water oxidation.¹⁷ The HRTEM image and corresponding SAED image after activation reveal the conversion from Ni_{0.5}Co_{0.5}Se to Ni/CoOOH (insets of Fig. 3), which is consistent with the latest result.¹⁸ The lattice spacings of 0.259 and 0.315 nm are assigned to the (130) plane of CoOOH (PDF#26-0480) and (110) of NiOOH (PDF# 27-0956), respectively. And the ploycrystalline rings are also indexed to (130), (221) of CoOOH and (110), (210), (121) of NiOOH, respectively, clearly confirming the activation/reconstruction of the surface of Ni_{0 5}Co_{0 5}Se.

To gain insights into the underlying reason of improved activity, the electronic structures of $\text{Co}^{2+}/\text{Co}^{3+}$ and $\text{Ni}^{2+}/\text{Ni}^{3+}$ are analyzed as shown in Scheme 1. The incorporation of Ni^{2+} ($t_{2g}^{6}e_{g}^{2}$) without Jahn-Teller effect into the original CoSe lattice, where the Co^{2+} ($t_{2g}^{6}e_{g}^{1}$) with strong Jahn-Teller effect could bring out a subtle mismatch in the degree of Jahn-Teller distortion, thus changing the electron configuration.¹⁹ Upon the oxidation of Co^{2+} to Co^{3+} , the electron will be extracted from the e_{g} band, making the e_{g} band of Co^{3+} empty (right panel of Scheme 1),²⁰ while the conversion of Ni^{2+} to Ni^{3+} leave one electron in the e_{g} band after removal of one electron (left panel of Scheme 1).²¹ Such synergic effect leads to a nearly optimal e_{g} filling of unity, which will increase the overlap

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between Co/Ni 3d states and O 2p states and modulating the Co/Ni-O covalency, thus promoting the OER kinetics according to Shao-Horn's e_g theory.²²



Scheme 1 Illustration of electronic structure change of Co²⁺ and Ni²⁺ during OER process.

In summary, solid-solution hexagonal Ni_{0.5}Co_{0.5}Se nanoflakes are successfully synthesized via a hydrothermal method based on the structure similarity CoSe and NiSe. Compared with pure CoSe and NiSe nanoflakes, Ni_{0.5}Co_{0.5}Se nanoflakes show much lower overpotential of 216 mV at 10 mA cm⁻² and Tafel slope of 37.08 mV dec⁻¹ in 1 M KOH electrolyte, indicating the efficient activity and fast reaction kinetics. For Ni_{0.5}Co_{0.5}Se, a smaller Ohmic resistance (6.4 Ω) in the electrolyte and chargetransfer resistance (15.3 Ω) at the interface, but larger doublelayer capacitance, indicate the improved electrical conductivity and more active sites. Such boosted activity can be fundamentally attributed to synergistic modulation of eg band filling during the oxidation of Co²⁺ and Ni²⁺ ions. This synthetic strategy provides new insights into the design and fabrication of efficient and low-cost electrocatalysts in the future.

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Conflicts of interest

There are no conflicts to declare.

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Scheme 1 Schematic representation of the crystal structure of Ni_{0.5}Co_{0.5}Se and the LSV curves for NiSe, CoSe, Ni_{0.5}Co_{0.5}Se nanoflakes, and RuO₂, respectively.

Solid-solution hexagonal $Ni_{0.5}Co_{0.5}Se$ nanoflakes are designed and successfully synthesized in terms of intrinsic similarity in crystal structure, atomic radius and electron configuration via a facile hydrothermal method, which demonstrate remarkably improved electrocatalytic activity due to the synergistic electron ineteraction between Co ions and Ni ions.