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Strong Electronic Interaction in Dual-cation Incorporated NiSe₂ Nanosheets with Lattice Distortion for Highly Efficient Overall Water Splitting

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<p>Please submit a plain text version of your cover letter here.</p> <p>If you are submitting a revision of your manuscript, please do not overwrite your original cover letter. There is an opportunity for you to provide your responses to the reviewers later; please do not add them here.</p>	<p>Dear Editor,</p> <p>We would like to resubmit our manuscript (adma.201800368) entitled "Strong Electronic Interaction in Dual-cation Incorporated NiSe₂ Nanosheets with Lattice Distortion for Highly Efficient Overall Water Splitting" for consideration in Advanced Materials.</p> <p>*** Justification of the novelty and significance****</p> <p>There isn't any work before us reporting dual metal incorporating and the effect of lattice distortion – this is more than just doping. Our novelty has two:</p> <p>(a) New material system. Our dual cation doping is a new strategy to promote catalyst activity of NiSe₂ nanosheets, which is a recent popular pyrite type TMD catalyst. Conventional single cation doping has rarely shown any lattice distortions. Herein, we demonstrate the positive effect of lattice distortion in significant enhancement of the catalytic activity.</p> <p>(b) New mechanism. We provide large amount of data about optimizing the doping ratios and verifying the enhancement mechanism: HRTEM reveals clear atomic lattice distortion in the co-doped NiSe₂ nanosheets, which increases active sites exposure as evidenced by EDLC measurements. XPS peak shift indicates a much stronger electronic interaction in the co-doped electrocatalyst than mono-cation doped sample, and pure NiSe₂. DFT results verify the optimal the adsorption energy of reaction intermediates on the surface of Co, Fe co-doped NiSe₂.</p> <p>**** Justification of resubmission****</p> <p>We appreciate referees' comments, most of which are insightful. Referee #2's comments are mostly constructive and addressable. But Referee #3's comments are very subjective and not scientifically specific. Especially for the comments of no novelty or no big improvement, we strongly disagree.</p> <p>First, there are already so much data to present all necessary details (6 figures in main text, 29 Supporting Figures) including comprehensive characterization, systematic electrochemistry, and DFT – So we don't think this "lacks systematic study". Second, we emphasize the novelty again above, that both the material system (dual metal doping) and mechanism (lattice distortions) in catalyst enhancement are new.</p> <p>We have carefully addressed all comments and have added substantial new data into SI (Three tables and 6 more figures). We look forward to hearing from you and receiving comments from the reviewers.</p> <p>Yours sincerely,</p> <p>Prof. Hong Jin Fan</p>

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Abstract:	Exploring highly efficient and low-cost electrocatalysts for electrochemical water splitting is of great significance for the conversion of intermediate energy. Herein, we report the synthesis of dual-cation (Fe, Co) incorporated NiSe ₂ nanosheets (Fe,Co-NiSe ₂) and systematical investigation of the electrocatalytic performance for water splitting as a function of the composition. We demonstrate that the dual-cation incorporation can significantly distort the lattice and induce stronger electronic interaction, leading to increased active site exposure and optimized adsorption energy of reaction intermediates compared to single cation doped or pure NiSe ₂ . As a result, the obtained Fe _{0.09} Co _{0.13} -NiSe ₂ porous nanosheet electrode shows an excellent catalytic activity with a low overpotential of 251 mV for OER and 92 mV for HER (both at 10 mA cm ⁻² in 1 M KOH). When used as bi-functional electrodes for overall water splitting, the current density of 10 mA cm ⁻² is achieved at a low cell voltage of 1.52 V. Our work highlights the importance of dual cation doping in enhancing the electrocatalyst performance of transition metal dichalcogenides.

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**Strong Electronic Interaction in Dual-cation Incorporated NiSe₂ Nanosheets
with Lattice Distortion for Highly Efficient Overall Water Splitting**

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Abstract

Exploring highly efficient and low-cost electrocatalysts for electrochemical water splitting is of great significance for the conversion of intermediate energy. Herein, we report the synthesis of dual-cation (Fe, Co) incorporated NiSe₂ nanosheets (Fe,Co-NiSe₂) and systematical investigation of the electrocatalytic performance for water splitting as a function of the composition. We demonstrate that the dual-cation incorporation can significantly distort the lattice and induce stronger electronic interaction, leading to increased active site exposure and optimized adsorption energy of reaction intermediates compared to single cation doped or pure NiSe₂. As a result, the obtained Fe_{0.09}Co_{0.13}-NiSe₂ porous nanosheet electrode shows an excellent catalytic activity with a low overpotential of 251 mV for OER and 92 mV for HER (both at 10 mA cm⁻² in 1 M KOH). When used as bi-functional electrodes for overall water splitting, the current density of 10 mA cm⁻² is achieved at a low cell voltage of 1.52 V. Our work highlights the importance of dual cation doping in enhancing the electrocatalyst performance of transition metal dichalcogenides.

Electrocatalytic water splitting, involving hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), has been recognized as one of the most promising ways for the storage and conversion of intermediate energy.^[1, 2] The current research focuses on exploration of efficient electrocatalysts that can overcome the sluggish kinetics and accelerate the evolution rates of H₂ and O₂ at low overpotentials.^[3-7] While the state-of-the-art electrocatalysts are noble metal and their oxides, such as Pt and Ir/Ru based materials,^[8-10] it is imperative to develop low-cost catalyst materials that can have compatible efficiency and stability with relatively low overpotentials. However, most of recently developed HER and OER catalysts work in either acidic or alkaline medium. When a single water splitting device uses different catalyst materials as the cathode and anode, the incompatibility of two electrodes may result in inferior efficiency.^[11, 12] In this content, the development of bifunctional catalysts which are highly active for both HER and OER in the same medium is highly desirable for overall water splitting.

Accordingly, great efforts have been paid to developing bifunctional electrocatalysts based on transition metal nanomaterials and their derivatives, including metal oxides or hydroxides,^[13, 14] metal chalcogenides,^[15-17] metal nitrides^[18, 19] and metal phosphides.^[20, 21] Among these noble metal-free materials, transition metal selenides with a suitable *d*-electron configuration are regarded as the promising candidate.^[22, 23] For example, DFT calculations show that the Se atoms at the edge sites of transition metal selenides are HER active sites.^[24] In order to boost the catalytic activity of transition metal selenides, it is necessary to introduce defects by, such as, adding metal dopings and creating lattice vacancies to maximize the number of exposed edge sites. Indeed, incorporation of heterogeneous metal atoms can induce atomic distortions due to strain and result in additional exposed active sites^[24]. Furthermore, it has been shown that the heterogeneous metal atoms doping could optimize the hydrogen adsorption kinetic energy and improve the HER catalytic activity in comparison to monometallic ones^[25-28]. Although mono-cation doping has been proven effective in enhancing the electrocatalytic activity, the enhancement is still very limited probably due to an insufficient modulation of the electronic structure. Moreover, the electronic interaction between each element in mono-cation doped electrocatalysts has been always ignored.^[29-31] In this case, it is expected that simultaneous incorporation of two foreign cations may be more effective in regulating the lattice structure and electronic interaction, thus leading to further improvement in catalytic performance. So far there has been rare reports on dual-cation doped transition metal selenides for overall water electrolysis.

Herein, we show that Co, Fe co-doping in NiSe₂ can trigger more efficient overall electrochemical water splitting due to a stronger electronic interaction between the cations and

significant lattice distortion. The lattice distortions increase the active sites exposure. XPS data indicates stronger electronic interaction between the cations, which is beneficial to optimizing the adsorption energy of reaction intermediates. As a result, the co-doped NiSe₂ (with an optimal composition of Fe_{0.09}Co_{0.13}-NiSe₂) nanosheet array electrode displays excellent catalytic activity for both OER (overpotential of 251 mV at 10 mA cm⁻²) and HER (92 mV at 10 mA cm⁻²). When the same material is employed as both the cathode and anode for overall water splitting reactions, a low cell voltage of 1.52 V is required to reach a current density of 10 mA cm⁻². We hypothesize that such dual-cation doping strategy can be also extended to other transition metal compounds, when appropriate cations and concentration are selected in order to induce significant lattice strain and strong electronic interactions.

Sample characterization. The Co, Fe co-doped NiSe₂ nanosheets were synthesized by topotactical transformation from Co, Fe co-doped Ni(OH)₂ nanosheets using a vapor selenization technique (**Figure S1**). The scanning electron microscopy (SEM) images (**Figure S2**) showed that the Co, Fe co-doped Ni(OH)₂ precursor nanosheets, with a thickness of ≈ 25 nm and smooth surface, densely grew on the carbon fiber cloth with a similar morphology to the pure Ni(OH)₂ sheets (**Figure S3**). After selenization, the original smooth sheets become rugged and porous for both the co-doped NiSe₂ (**Figure 1a, b**) and pure NiSe₂ sheet arrays (**Figure S3**). The surfaces are composed of dense-packed small particles. The porosity of the Fe_{0.09}Co_{0.13}-NiSe₂ nanosheets sample was characterized by N₂ sorption analysis (**Figure S4**), from which the BET specific surface area of Fe_{0.09}Co_{0.13}-NiSe₂ nanosheets was determined to be 328 m²/g and the average pore diameter was 7.15 nm. X-ray diffraction (XRD) patterns demonstrate that the precursor co-doped oxide sheets are in a hexagonal crystal phase (**Figure S5**), and the as-selenized products are cubic pyrite-phase NiSe₂ (**Figure 1c**). **Note that the Fe, Co atoms incorporation does not change the crystal structure of NiSe₂. However, as shown in the inset of Figure 1c, the diffraction peaks of Fe_{0.09}Co_{0.13}-NiSe₂/CFC shifts slightly to a lower angle compared to that of pure NiSe₂/CFC. This shift suggests increased lattice parameters in the co-doped NiSe₂ due to the larger atomic sizes of Fe and Co than that of Ni atom.** The energy-dispersive X-ray spectroscopy (EDX) revealed all the elements of Fe, Co, Ni and Se (**Figure S6**. The Cu and C come from the TEM grid substrate). The inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis showed that the atomic ratio of Co and Fe to Ni is 0.13: 0.09:1. The porous nanosheet after selenization can also be seen from the TEM image (**Figure 1d**). The corresponding HRTEM image in **Figure 1e, f** show well-resolved lattice fringes with interplanar distances of 2.7 Å corresponding to the (210) planes of NiSe₂. Interestingly, the local wavy lattice structure can be observed in some parts of the HRTEM

image of $\text{Fe}_{0.09}\text{Co}_{0.13}\text{-NiSe}_2$ (marked in Figure 1e and f). The distorted atomic arrangement was induced by the extraneous Fe, Co atoms incorporated into the NiSe_2 lattice, which is similar with previous literature^[24]. The atomic distortion may provide additional active sites for HER in the NiSe_2 atomic layers (more evidence is to be provided below). Moreover, the corresponding EDX mapping reveals that the Fe, Ni, Co, and Se elements are uniformly distributed in the entire nanosheet (see Figure 1g-k). For comparison, the morphology, crystal structure, and composition of the Co_xFe_y doped NiSe_2 sheet arrays/CFC precursors with different x, y values were also investigated (data presented in **Figures S7 – S10**). It is shown that all these samples had the similar morphology and crystal structure.

X-ray photoelectron spectroscopy (XPS) measurement was carried out to investigate the surface chemical composition of the $\text{Fe}_{0.09}\text{Co}_{0.13}\text{-NiSe}_2$ nanosheets. First, the XPS survey spectrum confirms the presence of Fe, Co, Ni, and Se in the sample (**Figure S11**). The ratio of the integral peak area of Co, Fe, and Ni is 0.129: 0.088:1 (**Figure S12**), which is consistent with the EDX and ICP-AES results. XPS fine structures further confirm the valences of Ni^{2+} , Co^{2+} and Fe^{3+} (see **Figure S13** for details). The important information we would like to obtain from XPS data is the change in electronic structure after selenization. We note that the mono-cation doped materials, e.g. $\text{Fe}_{0.2}\text{-NiSe}_2$ and $\text{Co}_{0.2}\text{-NiSe}_2$, showed a slight shift compared with that of pure NiSe_2 (**Figure 2**). In general, the XPS peak shift of the doped sample reflects a change in electronic configuration and possible electron transfer between cations, indicating the existence of electronic interaction between each element after cation doping^[25, 28]. Noticeably, compared with the mono-cation doped catalysts, the binding energy of $\text{Fe}_{0.09}\text{Co}_{0.13}\text{-NiSe}_2$ sample are more negatively shifted. This implies more significant electron transfer and stronger electron interaction in the co-doped sample. As we know, with the increase of atomic number, the electronegativity of the element changes periodically. The order of the electronegativity of Fe, Co, Ni is: $\text{Fe} < \text{Co} < \text{Ni}$. The larger the electronegativity of the metal element, the more active the metal element is, and the stronger the ability to attract electrons. That is consistent with the fact that the XPS peak for Ni in $\text{Fe}_{0.09}\text{Co}_{0.13}\text{-NiSe}_2$ shifts to lower binding energies. The strong electronic interaction in the dual-cation doped sample may play important role in modulating the electronic environments of the metal centers, leading to the optimal adsorption energy of reaction intermediates.

OER and HER performance. The electrocatalytic performance of the Co_xFe_y co-doped NiSe_2 /CFC with different x, y values were studied systematically by steady-state linear sweep voltammetry (LSV) in N_2 -saturated 1.0 M KOH. Obviously, the stoichiometry of the Co_xFe_y co-doped NiSe_2 had a great impact on the catalytic performance, and the $\text{Fe}_{0.09}\text{Co}_{0.13}\text{-NiSe}_2$ /CFC

was determined to be the most optimized composition among all control samples investigated herein (**Figure S14**). The bare CFC, pure NiSe₂, Fe_{0.2}-NiSe₂ and Co_{0.2}-NiSe₂ were also evaluated to highlight the superiority of the Fe_{0.09}Co_{0.13}-NiSe₂/CFC. The performance enhancement after Fe, Co dual-cation incorporation is clearly shown from the LSV (**Figure 3a**). Obviously, the specific current density of Fe_{0.09}Co_{0.13}-NiSe₂/CFC is indeed higher than that of mono-cation doped catalysts and pure NiSe₂ nanosheets under a certain applied voltage. And our Fe_{0.09}Co_{0.13}-NiSe₂ porous nanosheet electrode can be even better than the commercial RuO₂. The comparison of overpotentials at various current densities in **Figure S15** shows clearly that the dual-cation doping has a stronger effect than simple cation doping. Impressively, at a higher current density of 200 mA cm⁻², the Fe_{0.09}Co_{0.13}-NiSe₂ has a greatly decreased overpotential of about 92 mV with respect to pure NiSe₂. We note that our Fe_{0.09}Co_{0.13}-NiSe₂ catalyst is superior to other Ni, Fe, and Co based OER catalysts (**Table S1**). Tafel slope, as a key kinetic parameter, is usually used to investigate the rate determining step of an electrochemical process.^[32] Generally, the mechanism of OER in alkaline solution involves a four-electron transfer process.^[33, 34] The Fe_{0.09}Co_{0.13}-NiSe₂/CFC shows the smallest Tafel slope of 63 mV/dec among all the electrodes (**Figure 3b**). It is close to a featured Tafel slope of 60 mV/dec, indicating a changed rate-determining step. The lowered Tafel slope should be a result of the dual cation incorporation, which introduces a more favorable electronic structure and increased additional active sites for OH⁻ adsorption^[35]. Electrochemical impedance spectroscopy tests were conducted to further investigate the electrode kinetics during the OER process. The Nyquist plots (**Figure 3c**) unravel that the charge-transfer resistance of the Fe_{0.09}Co_{0.13}-NiSe₂ nanosheets is significantly decreased in comparison with the mono-cation doped catalysts and pure NiSe₂ nanosheets. This may account for the highest evolution kinetics as indicated by the smallest Tafel slope.

Next, we characterize the HER performance of the samples in the same electrolyte (1.0 M KOH). For this, steady-state LSV curves after iR compensation were recorded and depicted in **Figure 3d**. The Fe_{0.09}Co_{0.13}-NiSe₂ catalyst has an overpotential of 92 mV, close to the value from the Pt/C but much smaller than the other control samples. Noticeably, the Fe_{0.09}Co_{0.13}-NiSe₂ only needs a small overpotential of 255 mV to achieve a high current density of 200 mA cm⁻², which is much lower than that of Fe_{0.2}-NiSe₂ (328 mV), pure NiSe₂ (305 mV) and Co_{0.2}-NiSe₂ (428 mV). Detailed comparison is presented in **Figure S15c**. The HER performance of Fe_{0.09}Co_{0.13}-NiSe₂ is also superior to other Ni, Fe, and Co based HER catalysts, as seen from the comparison in **Table S2**. Furthermore, the Tafel slope is fitted to be 89 mV dec⁻¹ for the Fe_{0.09}Co_{0.13}-NiSe₂ electrode, which is smallest compared to other control samples (**Figure 3e**).

Small Tafel slope values are favorable for practical applications because it corresponds to high gas evolution rates at given overpotentials. Again, similar as the OER process, the electrochemical impedance spectroscopy test revealed that the $\text{Fe}_{0.09}\text{Co}_{0.13}\text{-NiSe}_2$ electrode has the lowest impedance for charge transfer (**Figure 3f**), which is accordance to the highest kinetics induced by the Fe, Co co-doping.

The durability of a catalytic electrode is another important parameter to consider for practical applications. The long-term stabilities of the $\text{Fe}_{0.09}\text{Co}_{0.13}\text{-NiSe}_2$ electrode for OER and HER were examined by 3000-cycle continuous chronoamperometry scans in 1.0 M KOH (**Figure S16**). The polarization curve after 3000 cycles showed negligible difference compared to the initial ones after the OER and HER tests. Moreover, we also evaluated the durability through the chronopotentiometric method up to 50 h, during which a nearly constant voltage is maintained at a set current density of 10 mA cm^{-2} . The results suggest good stability of the $\text{Fe}_{0.09}\text{Co}_{0.13}\text{-NiSe}_2$ electrode for both OER and HER in the same basic media. The SEM and XRD analyses confirm that the morphology, structure and bulk composition of the $\text{Fe}_{0.09}\text{Co}_{0.13}\text{-NiSe}_2$ remained unchanged after the OER and HER tests (**Figure S17**). In addition, the HRTEM images provide strong evidence that the lattice distortion still exists in the $\text{Fe}_{0.09}\text{Co}_{0.13}\text{-NiSe}_2$ after the catalysis processes (**Figure 4a and b**). As for the sample after OER, a thin layer of nickel (cobalt, iron) oxide/hydroxide is observed on the surface (**Figure 4b**). EDX elemental mapping analysis reveals homogenous distribution of Co, Fe, Ni, Se, and O throughout the whole electrode (**Figure 4c-h**). The presence of O also suggests surface oxidation during the OER process, which also confirmed by Raman, XPS and ICP measurements (see data in **Figure S18-20**). Hence, we may conclude that $\text{Ni}(\text{Co, Fe})\text{O}_x\text{H}_y/\text{Fe}_{0.09}\text{Co}_{0.13}\text{-NiSe}_2$ heterostructure is the actual catalyst for OER. Similar OER induced oxidation has been observed in many other Ni-based electrocatalysts.^[36-39]

To confirm the increased exposure of active sites of the dual-cation doped samples, we conducted electrochemical double-layer capacitance measurements (Data are presented in **Figure S21 – 22**). For HER, the $\text{Fe}_{0.09}\text{Co}_{0.13}\text{-NiSe}_2$ (6.23 mF cm^{-2}) electrode has about 1.20, 1.50 and 5.80 times C_{dl} than $\text{Fe}_{0.2}\text{-NiSe}_2$, $\text{Co}_{0.2}\text{-NiSe}_2$, and pure NiSe_2 , respectively (**Figure S21**). As for OER, the $\text{Ni}(\text{Co, Fe})\text{O}_x\text{H}_y/\text{Fe}_{0.09}\text{Co}_{0.13}\text{-NiSe}_2$ show a 1.27, 1.78 and 3.02 times C_{dl} than the corresponding control samples (**Figure S22**). Based on the C_{dl} measurement, we verify that the lattice distortion in the structure of Co, Fe co-doped NiSe_2 porous nanosheets indeed have induced more active sites exposure. However, the electrocatalytic activity enhancement is not totally dependent on the increased active sites. For example, at potential of -0.20 V vs RHE , the HER current density of $\text{Fe}_{0.09}\text{Co}_{0.13}\text{-NiSe}_2$ is 90 mA cm^{-2} , which is approximately 1.8, 1.5,

and 7.63 fold higher than that of $\text{Fe}_{0.2}\text{-NiSe}_2$, $\text{Co}_{0.2}\text{-NiSe}_2$, and pure NiSe_2 , respectively. The “discrepancy” implies that other factors have played constructive role in boosting the electrocatalyst processes. One of most likely reasons is a stronger electronic interaction in the $\text{Fe}_{0.09}\text{Co}_{0.13}\text{-NiSe}_2$ (as indicated by XPS) which has modulated the adsorption energies for HER intermediates and thus optimized the catalytic reaction path.

To investigate the effect of metal cation incorporation on the adsorption energies for HER intermediates on the surface of NiSe_2 , the free energy of hydrogen adsorption (ΔG_{H^*}) was calculated using density functional theory (DFT). Herein, we use the (001) surface of NiSe_2 as example as the (001) is the most common surface for pyrite.^[40] **Figure 5a and b** depict the top and side view of monolayer NiSe_2 (001) surface with H adsorption. The ΔG_{H^*} value was calculated to be 0.947 eV on pristine NiSe_2 , which was reduced to 0.359 eV and -0.822 eV on Co-doped NiSe_2 and Fe-doped NiSe_2 . As for the dual cation incorporated NiSe_2 , the ΔG_{H^*} value of Co, Fe co-doped NiSe_2 was significantly lowered to -0.012 eV. As well known, the value of ΔG_{H^*} of a good HER catalysts should be close to 0.^[41] This reduced adsorption energy for HER intermediates implies the strongest electronic interaction in the $\text{Fe}_{0.09}\text{Co}_{0.13}$ -doped NiSe_2 compared to un-doped or single cation doped samples, which is consistent to the highest catalytic performance.

Based on the above results, we attribute the outstanding bifunctional electrocatalytic activity of our Co, Fe co-doped NiSe_2 nanosheets/CFC electrode to the following reasons: (1) the nanosheet morphology provides a high active surface area, while the dual-cation incorporation has further increased active sites exposure due to the lattice distortions on the surface; (2) the stronger electronic interaction associated with optimal adsorption energy of reaction intermediates enhances the intrinsic electrocatalyst activity compared to the un-doped NiSe_2 ; (3) the 3D nanosheets array structure not only facilitate the penetration of electrolyte and electron transfer process, but also the release of evolved gas bubble, which leads to fast kinetics. As a result, these effects render the Co, Fe co-doped NiSe_2 nanosheets/CFC electrode superior electrocatalytic performance for both HER and OER in the same medium.

Overall water splitting. Bifunctional electrocatalysts with earth-abundant materials for overall water splitting has attracted tremendous interests. Inspired by the outstanding OER and HER activities of our $\text{Fe}_{0.09}\text{Co}_{0.13}\text{-NiSe}_2$ nanosheets/CFC electrode, we then assembled a full electrolyzer using the $\text{Fe}_{0.09}\text{Co}_{0.13}\text{-NiSe}_2$ as both the anode and cathode in 1 M KOH (**Figure 6a**). A cell voltage of only 1.52 V is needed to reach a current density of 10 mA cm^{-2} , and this situation can last up to 3000 cycles with only minor degradation (**Figure 6b**). This indicates the superiority of our $\text{Fe}_{0.09}\text{Co}_{0.13}\text{-NiSe}_2$ nanosheets/CFC to many other reported bifunctional

electrocatalysts (see detailed comparison in **Table S3**). We also used galvanostatic testing method to assess the durability for overall water splitting. To do this, electrolysis at five different current densities (10, 20, 50, 20 and 10 mA/cm²) was conducted sequentially for up to 30 h (**Figure 6c**). The corresponding potential at each current density remains stable. The Faradic efficiency for both the HER and OER processes was assessed by comparing the theoretical amount of evolved gas with the experimental value as quantified by the water drainage method. As shown in **Figure 6d**, the cathode/anode shows stable hydrogen/oxygen evolution rates that match well theoretical values, implying nearly 100% Faradic efficiency of the Fe_{0.09}Co_{0.13}-NiSe₂-based electrolyzer. Finally, the water electrolysis can be powered by a 1.5-V commercial battery and obvious evolution of both O₂ and H₂ is observed by naked eyes (see **Figure S23** and video in supporting information). All in all, it is very encouraging that our carefully designed noble-metal-free electrocatalyst can trigger overall water splitting with excellent efficiency and stability.

In summary, we have demonstrated a dual cation doping strategy to enhance the electrocatalyst performance of transition-metal dichalcogenide nanosheets, and the realization of overall water splitting in same alkaline medium. Exemplified by NiSe₂ nanosheets, dual cation (Fe, Co) incorporation has significantly lowered the overpotentials for both OER and HER with high stability within measurement period (50 h). As evidenced by HRTEM, XPS capacitive measurements and DFT, we propose that this enhancement is correlated with the lattice distortion and strong electronic interaction between the metal cations. Furthermore, we demonstrate the true bi-functionality of our Fe, Co co-doped NiSe₂; a full cell using the co-doped NiSe₂ as both the anode and cathode for overall water splitting only need a cell voltage of 1.52 V to approach 10 mA cm⁻². Our work provides new insights for designing high-efficiency and lost-cost bifunctional electrocatalysts for overall water splitting.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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References

- [1] Y. M. Shi, B. Zhang, *Chem. Soc. Rev.* **2016**, *45*, 1529.
- [2] L. Han, S. J. Dong, E. K. Wang, *Adv. Mater.* **2016**, *28*, 9266.
- [3] A. Gupta, W. D. Chemelewski, C. B. Mullins, J. B. Goodenough, *Adv. Mater.* **2015**, *27*, 6063.
- [4] H. G. S. Casalongue, M. L. Ng, S. Kaya, D. Friebe, H. Ogasawara, A. Nilsson, *Angew. Chem. Int. Ed.* **2014**, *53*, 7169.
- [5] Y. Jiao, Y. Zheng, M. Jaroniec, S. Z. Qiao, *Chem. Soc. Rev.* **2015**, *44*, 2060.
- [6] M. Ledendecker, S. K. Calderon, C. Papp, H. P. Steinruck, M. Antonietti, M. Shalom, *Angew. Chem. Int. Ed.* **2015**, *54*, 12361.
- [7] K. Xu, H. Ding, H. F. Lv, S. Tao, P. Z. Chen, X. J. Wu, W. S. Chu, C. Z. Wu, Y. Xie, *ACS Catal.* **2017**, *7*, 310.
- [8] Y. Y. L. F. Hui, G. D. Ruan, J. M. Tour, *Adv. Mater.* **2017**, *27*, 3175.
- [9] K. Xu, H. Cheng, L. Q. Liu, H. F. Lv, X. J. Wu, C. Z. Wu, Y. Xie, *Nano Lett.* **2017**, *17*, 578.
- [10] L. Yu, B. Y. Xia, X. Wang, X. W. Lou, *Adv. Mater.* **2016**, *28*, 92.
- [11] C. Xia, H. F. Liang, J. J. Zhu, U. Schwingenschlogl, H. N. Alshareef, *Adv. Energy Mater.*, **2017**, *7*, 1602089.
- [12] X. B. Zhang, J. Wang, H. X. Zhong, Z. L. Wang, F. L. Meng, *ACS Nano* **2016**, *10*, 2342.
- [13] B. Hua, M. Li, Y. F. Sun, Y. Q. Zhang, N. Yan, J. Chen, T. Thundat, J. Li, J. L. Luo, *Nano Energy* **2017**, *32*, 247.
- [14] H. S. Ahn, A. J. Bard, *J. Am. Chem. Soc.*, **2016**, *138*, 313..
- [15] C. Xia, Q. Jiang, C. Zhao, M. N. Hedhili, H. N. Alshareef, *Adv. Mater.* **2016**, *28*, 77.
- [16] J. Q. Yan, H. Wu, P. Li, H. Chen, R. B. Jiang, S. Z. Liu, *J. Mater. Chem. A*, **2017**, *5*, 10173.
- [17] Y. Q. Yang, K. Zhang, H. L. Lin, X. Li, H. C. Chan, L. C. Yang, Q. S. Gao, *ACS Catal.* **2017**, *7*, 2357.
- [18] Y. Q. Zhang, B. Ouyang, J. Xu, G. C. Jia, S. Chen, R. S. Rawat, H. J. Fan, *Angew. Chem. Int. Ed.* **2016**, *55*, 8670.
- [19] J. Yin, Y. X. Li, F. Lv, Q. H. Fan, Y. Q. Zhao, Q. L. Zhang, W. Wang, F. Y. P. X. Xi, S. J. Guo, *ACS Nano*, **2017**, *11*, 2275.
- [20] L. Jiao, Y. X. Zhou, H. L. Jiang, *Chem. Sci.* **2016**, *7*, 1690.
- [21] H. W. Huang, C. Yu, C. T. Zhao, X. T. Han, J. Yang, Z. B. Liu, S. F. Li, M. D. Zhang, J. S. Qiu, *Nano Energy* **2017**, *34*, 472.

- [22] C. Panda, P. W. Menezes, C. Walter, S. L. Yao, M. E. Miehl, V. Gutkin, K. Meyer, M. Driess, *Angew. Chem. Int. Ed.* **2017**, *56*, 10506.
- [23] F. M. Wang, Y. C. Li, T. A. Shifa, K. L. Liu, F. Wang, Z. X. Wang, P. Xu, Q. S. Wang, J. He, *Angew. Chem. Int. Ed.* **2016**, *55*, 6919.
- [24] Y. W. Liu, X. M. Hua, C. Xiao, T. F. Zhou, P. C. Huang, Z. P. Guo, B. C. Pan, Y. Xie, *J. Am. Chem. Soc.* **2016**, *138*, 5087.
- [25] J. J. Duan, S. Chen, A. Vasileff, S. Z. Qiao, *ACS Nano* **2016**, *10*, 8738.
- [26] C. Tang, R. Zhang, W. B. Lu, L. B. He, X. Jiang, A. M. Asiri, X. P. Sun, *Adv. Mater.*, **2017**, *29*, 1602441.
- [27] X. Xu, F. Song, X. L. Hu, *Nature Comm.* **2016**, *7*, 12324.
- [28] T. T. Liu, A. M. Asiri, X. P. Sun, *Nanoscale* **2016**, *8*, 3911.
- [29] Y. J. Li, H. C. Zhang, M. Jiang, Q. Zhang, P. L. He, X. M. Sun, *Adv. Funct. Mater.* **2017**, *27*, 1702513.
- [30] Z. G. Ye, T. Li, G. Ma, Y. H. Dong, X. L. Zhou, *Adv. Funct. Mater.* **2017**, 1704083.
- [31] H. S. Fan, H. Yu, Y. F. Zhang, Y. Zheng, Y. B. Luo, Z. F. Dai, B. Li, Y. Zong, Q. Y. Yan, *Angew. Chem. Int. Ed.* **2017**, *56*, 12566.
- [32] R. S. Conell, D. A. Corrigan, B. R. Powell, *Sol. Energy Mater. Sol. Cells.* **1992**, *25*, 301.
- [33] J. O. Bockris, T. Otagawa, *J. Phys. Chem.* **1983**, *87*, 2960.
- [34] H. Y. Su, Y. Gorlin, I. C. Man, F. Calle-Vallejo, J. K. Nørskov, T. F. Jaramillo, *Phys. Chem. Chem. Phys.* **2012**, *14*, 14010.
- [35] Y. Surendranath, D. G. Nocera, *In Progress in Inorganic Chemistry*, John Wiley & Sons, Inc.: Hoboken, NJ, **2011**, 505.
- [36] C. Tang, N. Y. Cheng, Z. H. Pu, W. Xing, X. P. Sun, *Angew. Chem. Int. Ed.* **2015**, *54*, 9351.
- [37] K. Xu, H. Ding, K. C. Jia, X. L. Lu, P. Z. Chen, T. P. Zhou, H. Cheng, S. Liu, C. Z. Wu, Y. Xie, *Angew. Chem. Int. Ed.* **2016**, *55*, 1710.
- [38] K. Xu, H. Ding, H. F. Lv, P. Z. Chen, X. L. Lu, H. Cheng, T. P. Zhou, S. Liu, C. Z. Wu, Y. Xie, *Adv. Mater.* **2016**, *28*, 3326.
- [39] B. M. Hunter, H. B. Gray, A. M. Muller, *Chem. Rev.* **2016**, *116*, 14120.
- [40] A. Hung, J. Muscat, I. Yarovsky, S. P. Russo, *Surf. Sci.*, **2002**, *513*, 511.
- [41] R. Parsons, *Trans. Faraday Soc.* **1958**, *54*, 1053.

Figure 1. Morphology and composition of the dual cation doped NiSe_2 nanosheets. (a, b) SEM images, (c) XRD pattern (d) TEM images, and (e, f) high-resolution TEM image of the $\text{Fe}_{0.09}\text{Co}_{0.13}\text{-NiSe}_2$ nanosheets. The circles indicate the lattice distortion. (g-k) STEM images and the corresponding elemental mapping of Ni, Fe, Co, and Se.

Figure 2. XPS spectra for Fe_{0.09}Co_{0.13}-NiSe₂ nanosheets, pure NiSe₂ nanosheets, Fe_{0.2}-NiSe₂ nanosheets and Co_{0.2}-NiSe₂ nanosheets. Evident shift of the binding energy for both (a) Ni 2p region and (b) Se 2p region are observed. High-resolution spectra of Ni, Co, Fe, and Se regions are presented in Figure S13, *Supplementary Information*.

Figure 3. Electrochemical performance for OER and HER. The four samples are: $\text{Fe}_{0.09}\text{Co}_{0.13}\text{-NiSe}_2$ nanosheet arrays, $\text{Fe}_{0.2}\text{-NiSe}_2$ nanosheet arrays, $\text{Co}_{0.2}\text{-NiSe}_2$ nanosheet arrays, and pure NiSe_2 nanosheet arrays. All the nanosheets are grown on CFC. (a, d) Polarization curves. (b, e) Tafel plots. (c, f) Nyquist plot of electrochemical impedance spectra (EIS). More electrochemistry data are presented in Figure S14-16, *Supplementary Information*.

Figure 4. Characterization after electrochemistry test. HRTEM images of the $\text{Fe}_{0.09}\text{Co}_{0.13}\text{-NiSe}_2$ sample after HER (a) and OER (b) electrolysis in 1.0 M KOH. STEM image (c) and element mapping (d-h) after OER electrolysis in 1.0 M KOH.

Fig 5. DFT Calculations. Top (a) and side (b) view of monolayer NiSe₂ (001) surface. The white ball represents H atom. The red and green rings are the doping sites with Co and Fe, respectively. (c) Calculated free energies of H adsorption on different slabs. **Note: the chemical composition for the DFT calculation are Co_{0.1}-NiSe₂, Ni_{0.1}-NiSe₂ and Fe_{0.1}Co_{0.1}-NiSe₂.**

Figure 6. Bi-functionality in overall water splitting. (a) Schematic illustration of full water splitting using the $\text{Fe}_{0.09}\text{Co}_{0.13}\text{-NiSe}_2$ nanosheets/CFC catalyst for both electrodes. (b) Polarization curves before and after 3000 CV cycles. The inset is photograph of the two-electrode electrolyzer using $\text{Fe}_{0.09}\text{Co}_{0.13}\text{-NiSe}_2$ nanosheets/CFC as both anode and cathode. (c) Long-term stability test carried out at different current densities. (d) Generated and theoretical volumes of H_2 and O_2 as a function of time.

Dual cation incorporation makes NiSe₂ nanosheet more effective catalyst. Introducing both Fe and Co atoms with an optimal ratio into porous NiSe₂ nanosheets cause evident lattice distortion and strong electronic interaction, leading to more efficient bi-functionality in overall electrochemical water splitting.

Keyword: Dual-cation metal doping, Lattice distortion, Strong electronic interaction, Bi-functional electrocatalyst, Water splitting

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Title: Strong Electronic Interaction in Dual-cation Incorporated NiSe₂ Nanosheets with Lattice Distortion for Highly Efficient Overall Water Splitting

Supporting Information

Strong Electronic Interaction in Dual-cation Incorporated NiSe₂ Nanosheets with Lattice Distortion for Highly Efficient Overall Water Splitting

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Experimental Section

Reagents: Carbon fiber cloth (CFC), iron (III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), KOH, urea, ammonium fluoride (NH_4F) were purchased from Aldrich or Sinopharm group and used without further purification. Millipore water (resistivity: $\sim 18 \text{ M}\Omega \cdot \text{cm}$) was used in all experiments.

Synthesis of the Co_xFe_y doped $\text{Ni}(\text{OH})_2/\text{CFC}$ nanosheet arrays: The precursors of the Co_xFe_y doped $\text{Ni}(\text{OH})_2$ nanosheet arrays/CFC were prepared as follows. Firstly, the CFC ($1 \times 4 \text{ cm}$) was cleaned for 15 min successively to remove impurity of surface in acetone, DI water and ethanol with ultrasonication, and then dried in electric vacuum drying oven. After drying, the weight of each treated CFC was recorded. Then, 0.2 mmol $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 0.2 mmol $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 2.0 mmol $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 10 mmol urea and 4 mmol of NH_4F were dissolved in 40 mL deionized water. After continuously stirring for 30 min, the solution was then transferred to a 50 mL Teflon lined stainless steel autoclave with a piece of CFC. The autoclave was sealed and heated up to 120°C for 6 h in an oven. After the reaction, the obtained Co_xFe_y doped $\text{Ni}(\text{OH})_2$ sheet arrays/CFC was immersed in DI water and ethanol several times, and then dried at 60°C for further use. For comparison, $\text{Ni}(\text{OH})_2$ sheet arrays/CFC, Fe doped $\text{Ni}(\text{OH})_2$ sheet arrays/CFC, Co doped $\text{Ni}(\text{OH})_2$ sheet arrays/CFC and another Co_xFe_y doped $\text{Ni}(\text{OH})_2$ sheet arrays/CFC with different x, y value catalysts were also synthesized, under otherwise identical conditions, except for using different amount of metal salts for hydrothermal preparation.

Synthesis of the Co, Fe dual doped NiSe_2 nanosheet arrays/CFC: To obtain Co, Fe dual doped NiSe_2 sheet arrays/CFC, the as-prepared Co_xFe_y doped $\text{Ni}(\text{OH})_2$ sheet arrays/CFC with different x, y value was placed in a crucible containing 0.15 g selenium powder. The crucible was moved to the middle of a horizontally placed quartz tube inside a tube furnace. After that, the furnace was heated 450°C at a ramping rate of $20^\circ\text{C min}^{-1}$ and kept for 60 min, and then naturally cooled to ambient temperature under Ar. Pure NiSe_2 sheet arrays/CFC, Fe doped NiSe_2 sheet arrays/CFC, and Co doped NiSe_2 sheet arrays/CFC were prepared under the same condition, respectively.

Electrochemical Measurements: The electrocatalytic activity was evaluated in a three-electrode configuration with a CHI 760E electrochemistry workstation (CH Instruments, Inc., Shanghai) at ambient temperature, where the Co, Fe dual doped NiSe_2 sheet arrays/CFC (typically $1 \text{ cm} \times$

2 cm) were directly used as the working electrode (WE), an Ag/AgCl electrode and platinum wire were used as the reference electrode (RE) and counter electrode (CE), respectively. All the potentials were converted to values with the reference to a reversible hydrogen electrode (RHE). Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), chronopotentiometric measurements were conducted, and linear sweep voltammetry (LSV) was performed at a scan rate of 2 mV/s. All potentials and voltages were IR corrected no otherwise specified.

Characterizations: X-ray diffraction (XRD) was recorded on a Philips X'pert Pro X-ray diffractometer with Cu K α radiation ($\lambda=0.15419$ nm). The morphologies and structures of the products were characterized with FESEM (Sirion 200, 10 kV) and TEM (JEOL, JEM-2010 200 kV). X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250 photoelectron spectrometer. ICP-MS was performed on Thermo Scientific iCAP6300 series instrument.

DFT calculations: Density functional theory (DFT) calculations were carried out by using the Vienna Ab-initio Simulation Package (VASP)^[1,2], with an exchange-correlation functional described by the Perdew-Burke-Ernzerhof generalized gradient approximation (PBE-GGA) method^[3], and interaction between core electrons and valence electrons described using the frozen-core projector-augmented wave (PAW) method^[4,5]. Wave functions were expanded in a plane wave basis with a high energy cut-off of 400 eV. The convergence criterion was set to 10⁻⁵ eV between two ionic steps for the self-consistency process, and 0.02 eV/Å was adopted for the total energy calculations. To avoid interactions between adjacent images, a vacuum region of 15 Å was added along the normal direction to the monolayer. Adsorption energy was calculated by the equation as follow:

$$E_{ad} = E_{ads/slab} - E_{slab} - E_{ads}$$

where $E_{ads/slab}$, E_{slab} , and E_{ads} are the total energies for the adsorbate on the slab, for the slab without the adsorbate, and for the adsorbate all alone, respectively.

Figure S1. The photographic images of (a) bare CFC, (b) Fe, Co doped Ni(OH)₂ sheet array/CFC, (c) Fe, Co doped NiSe₂ sheet array/CFC, (d) schematic illustration of the synthesis procedure for the Co, Fe co-doped NiSe₂ nanosheets on carbon fiber cloth (CFC).

Figure S2. (a) Low-magnification and (b) high-magnification SEM images of Fe, Co doped $\text{Ni}(\text{OH})_2$ sheet arrays on CFC.

Figure S3. SEM images (a, c), XRD pattern (e) of the pure $\text{Ni}(\text{OH})_2$ sheet array precursor; SEM images (b, d), XRD pattern (f) of the pure NiSe_2 sheet array. # represents the diffraction peaks from CFC.

Figure S4. N₂ adsorption desorption isotherm curves of Fe_{0.09}Co_{0.13}-NiSe₂ nanosheets. The inset shows the pore size distribution curve determined from BJH method.

Figure S5. XRD patterns of (a) Fe, Co doped $\text{Ni}(\text{OH})_2$ sheet array on CFC. # represent the diffraction peaks from CFC.

Figure S6. EDX spectrum for the as-synthesized $\text{Fe}_{0.09}\text{Co}_{0.13}\text{-NiSe}_2$ sheets array/CFC.

Figure S7. (a) Low-magnification and (b) high-magnification SEM images, (c) XRD pattern, and (d) EDX pattern of $\text{Fe}_{0.16}\text{Co}_{0.06}\text{-NiSe}_2$ sheet array/CFC.

Figure S8. (a) Low-magnification and (b) high-magnification SEM images, (c) XRD pattern, and (d) EDX pattern of $\text{Fe}_{0.04}\text{Co}_{0.17}\text{-NiSe}_2$ sheet array/CFC.

Figure S9. (a) Low-magnification and (b) high-magnification SEM images, (c) XRD pattern, and (d) EDX pattern of $\text{Fe}_{0.2}\text{-NiSe}_2$ sheet array/CFC.

Figure S10. (a) Low-magnification and (b) high-magnification SEM images, (c) XRD pattern, and (d) EDX pattern of $\text{Co}_{0.2}\text{-NiSe}_2$ sheet array/CFC.

Figure S11. XPS survey spectrum for the as grown $\text{Fe}_{0.09}\text{Co}_{0.13}\text{-NiSe}_2$ nanosheets.

Figure S12. The histogram of the integral area of the XPS pattern of different elements.

Figure S13. The high-resolution XPS spectra of (a) Ni 2p, (b) Co 2p, (c) Fe 2p and (d) Se 3d regions of the $\text{Fe}_{0.09}\text{Co}_{0.13}\text{-NiSe}_2$ sample.

Notes for Fig S13. In Figure S13a, the two peaks located at 855.9 and 873.6 eV in high-resolution Ni 2p can be assigned to Ni $2p_{3/2}$ and $2p_{1/2}$, respectively, corresponding to Ni^{2+} .^[6] The peaks at 861.4 eV and 880.4 eV can be assigned to Ni satellite peaks. In Figure S13b, the signals of Co $2p_{3/2}$ and Co $2p_{1/2}$ were observed at 781.5 and 797.4 eV, which are characteristic of Co^{2+} .^[7] Meanwhile, two distinct satellite peaks located at 786.4 eV and 803.2 eV can be assigned to Co satellite. Similarly with Co element, the peak at binding energies of 712.4 and 724.1 eV in Figure S13c should be assigned to Fe $2p_{3/2}$ and Fe $2p_{1/2}$, respectively, indicating the presence of Fe^{3+} .^[8] The peaks of Se $3d_{5/2}$ and Se $3d_{3/2}$ are located at 54.5 eV and 55.6 eV, respectively (Fig. S13d). The peak near 59.3 eV represents the oxidation state of Se species.^[9]

Figure S14. Polarization plots (a, b) for HER and (c, d) for OER measured with the Co_xFe_y doped NiSe₂ sheet array/CFC with different x, y value samples in 1.0 M KOH electrolyte at 2 mV s⁻¹.

Figure S15. (a) OER overpotential required for $J = 10$ mA cm⁻². (b) OER overpotential required for $J = 200$ mA cm⁻². (c) HER overpotential required for $J = 200$ mA cm⁻².

Figure S16. Stability of the $\text{Fe}_{0.09}\text{Co}_{0.13}\text{-NiSe}_2$ nanosheets/CFC electrode. (a, b) Polarization curves before and after 3000 CV cycles at a scan rate of 2 mV s^{-1} , respectively. (c, d) The corresponding chronopotentiometric curve at 10 mA cm^{-2} .

Figure S17. (a, c) Low-magnification and (b, d) high-magnification SEM images of Fe_{0.09}Co_{0.13}-NiSe₂ nanosheets/CFC after the stability electrocatalysis test for OER and HER in the alkaline solution. XRD pattern of Fe_{0.09}Co_{0.13}-NiSe₂ nanosheets/CFC after the OER (e) and HER (f) test in the alkaline solution.

Figure S18. Raman spectra of $\text{Fe}_{0.09}\text{Co}_{0.13}\text{-NiSe}_2$ nanosheets before and after OER stability test. The two peaks located at about 199.5 and 241.9 cm^{-1} correspond to the A_g and T_g modes of NiSe_2 , respectively. The Raman peaks centered at 541.3 cm^{-1} and 710 cm^{-1} become more obvious after the catalyst test. They are due to the first-order transverse optical (TO) and 2TO phonon modes of NiO , respectively.^[10-11] This NiO should be due to a thin layer of nickel (cobalt, iron) oxide/hydroxide formed on the surface of NiSe_2 , in consistent to our HRTEM measurement.

Figure S19. XPS spectra of Ni 2p (a), Se 3d (b) in $\text{Fe}_{0.09}\text{Co}_{0.13}\text{-NiSe}_2$ nanosheets before and after OER stability test.

Notes for Fig S19. As shown in **Figure S19a**, the two peaks located at 855.6 and 873.6 eV can be ascribed to $\text{Ni } 2p_{3/2}$ and $\text{Ni } 2p_{1/2}$ in NiSe_2 , respectively. The peaks at 861.4 eV and 880.4 eV can be assigned to Ni satellite peaks. Notably, XPS spectra after the OER stability test show the appearance of Ni^{3+} (857.3 eV and 876.2 eV) peaks that originated from the oxidation surfaces in the form of surface oxide layer, which were commonly observed in metal chalcogenides during the OER catalytic process^[12], indicating the existence of surface oxidation on the $\text{Fe}_{0.09}\text{Co}_{0.13}\text{-NiSe}_2$ nanosheets after OER stability test. Similarly, the relative intensity of Se in surface oxides to Se in NiSe_2 also becomes stronger, corroborating the formation of $\text{Ni}(\text{Co}, \text{Fe})\text{O}_x\text{H}_y$ on the catalyst surface after prolonged OER test (**Figure S19b**).

(a)	Element	Atomic percentage (At %)	(b)	Element	Atomic percentage (At %)
	Ni	20.82		Ni	14.69
	Co	2.73		Co	1.94
	Fe	1.84		Fe	1.35
	Se	50.79		Se	33.56
	O	23.82		O	48.46

Figure S20. ICP data of $\text{Fe}_{0.09}\text{Co}_{0.13}\text{-NiSe}_2$ nanosheets (a) before and (b) after OER stability test.

The inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis was used to check the possible change in chemical composition. After the OER stability test, the content of O increased obviously, while the Se content decreases. The increased O content also indicates the formation of $\text{Ni}(\text{Co}, \text{Fe})\text{O}_x\text{H}_y$ on the catalyst surface.

Figure S21. Electrochemical double-layer capacitance measurements at different scan rates for HER. Cyclic voltammograms of (a) Fe_{0.09}Co_{0.13}-NiSe₂ nanosheets/CFC, (b) pure NiSe₂ nanosheets/CFC, (c) Fe_{0.2}-NiSe₂ nanosheets/CFC and (d) Co_{0.2}-NiSe₂ nanosheets/CFC. (e) Capacitive currents with various scan rates for HER. The current density differences ($j_a - j_c$) at the open circuit potential plotted against the scan rate. The linear slope is equivalent to twice of the C_{dl} .

Figure S22 Electrochemical double-layer capacitance measurements at different scan rates for OER. Cyclic voltammograms of (a) $\text{Fe}_{0.09}\text{Co}_{0.13}\text{-NiSe}_2$ nanosheets/CFC, (b) pure NiSe_2 nanosheets/CFC, (c) $\text{Fe}_{0.2}\text{-NiSe}_2$ nanosheets/CFC and (d) $\text{Co}_{0.2}\text{-NiSe}_2$ nanosheets/CFC. (e) Capacitive currents with various scan rates for OER. The current density differences ($j_a - j_c$) at the open circuit potential plotted against the scan rate. The linear slope is equivalent to twice of the C_{dl} .

Figure S23. Overall water splitting cell made of the $\text{Fe}_{0.09}\text{Co}_{0.13}\text{-NiSe}_2$ nanosheets/CFC catalyst driven by a 1.5 AA battery in 1.0 M KOH electrolyte.

Figure S24. LSV curves of $\text{Fe}_{0.09}\text{Co}_{0.13}\text{-NiSe}_2$ porous nanosheet electrode with Pt and graphite bar as counter electrode, respectively. Note that in the process of stability test, we did not use Pt as counter electrode.

Note for Fig S24. It is known that, using Pt as counter electrode may cause contamination on the working electrode. However, it should be noted that Pt dissolution and re-deposition should be much less significant in alkaline media as compared with that in an acidic medium, because the reduction potential of Pt in alkaline media is below 0 V vs Ag/AgCl.^[13] In addition, in the process of stability test (**Figure 6b**), we did not use Pt as counter electrode, therefore, it did not cause severe Pt contamination on the working electrode during the stability measurements. In addition, we had conducted electrochemistry measurements using a graphite bar as counter electrode for comparison. As shown in **Figure S24**, the LSV curve recorded with carbon counter electrode and Pt counter electrode showed a negligible difference. Therefore, in our case, it had a negligible influence on the catalytic performance with Pt counter electrode.

Catalysts	Exchange Current Density (j_0)
Pure NiSe ₂ NSs	0.21 mA cm ⁻²
Fe _{0.2} -NiSe ₂ NSs	0.59 mA cm ⁻²
Co _{0.2} -NiSe ₂ NSs	1.01 mA cm ⁻²
Fe _{0.09} Co _{0.13} -NiSe ₂ NSs	1.21 mA cm ⁻²

Figure S25. The exchange current densities of the catalysts in case of HER. We had calculated the exchange current densities of the catalysts in case of HER by extrapolation of the Tafel plots.

Figure S26. (a) HER and (b) OER polarization curves normalized by the electrochemical double-layer capacitance. The normalized current density of the $\text{Fe}_{0.09}\text{Co}_{0.13}\text{-NiSe}_2$ nanosheets is still obviously larger than those of other test catalysts. It thus implies that the $\text{Fe}_{0.09}\text{Co}_{0.13}\text{-NiSe}_2$ nanosheets possess a higher intrinsic electrocatalytic activity than mono-cation doping and pure NiSe_2 nanosheets.

Figure S27. XPS spectra for $\text{Fe}_{0.09}\text{Co}_{0.13}\text{-NiSe}_2$ nanosheets, $\text{Fe}_{0.2}\text{-NiSe}_2$ nanosheets and $\text{Co}_{0.2}\text{-NiSe}_2$ nanosheets. Evident changes in binding energy for both (a) Co 2p region and (b) Fe 2p region are observed. One can see that, compared with the mono-cation doping catalysts, the binding energy of Fe, Co in $\text{Fe}_{0.09}\text{Co}_{0.13}\text{-NiSe}_2$ are more positively shifted, implying more significant electron transfer and stronger electron interaction with Fe, Co doping.

Figure S28. I-V curves of four prepared electrodes. In the electrical conductivity pattern, non-surprisingly $\text{Fe}_{0.09}\text{Co}_{0.13}\text{-NiSe}_2/\text{CFC}$ electrode shows the smallest value of electric resistance. The enhanced electrical conductivity of $\text{Fe}_{0.09}\text{Co}_{0.13}\text{-NiSe}_2/\text{CFC}$ electrode also suggests the existence of strong electronic interaction after dual-cation incorporation.

Table S1. Comparisons of OER performance for various Fe, Ni, Co-based electrocatalysts in alkaline condition.

Catalyst	Water electrolysis test	Overpotential (10mA cm ⁻²)	Electrolyte	Reference
Co, Fe dual doped NiSe ₂ mesoporous nanosheets/CFC	OER	251	1M KOH	This work
FeSe ₂ nanoplates	OER	330	1M KOH	Nano Energy. 2017, 31, 90.
NiSe ₂ nanowire/NiO _x NPs	OER	295	1M KOH	Small. 2017, 13, 1701478.
Orthorhombic CoSe ₂	OER	270	1M KOH	Angew. Chem. Int. Ed. 2015, 54, 12004.
Ni-Fe mixed diselenide nanocages	OER	240	1M KOH	Adv. Mater. 2017, 29, 1703870.
1.0%Ag-CoSe ₂ nanobelts	OER	320	1M KOH	Angew. Chem. Int. Ed. 2017, 56, 328.
Fe doped CoOOH nanosheets	OER	266	1M KOH	Angew. Chem. Int. Ed. 2018, 57, 2672.
Plasma modified Co-PBA	OER	274	1M KOH	Adv. Energy Mater. Doi:10.1002/aenm.201800085
CeO ₂ /NiO	OER	382	1M KOH	Adv. Funct. Mater. 2018, 28, 1706056.
Porous CoO nanoplates	OER	306	1M KOH	Nano Energy. 2018, 43, 110.
Disordered Ni ₂ Fe ₁ nanofoams	OER	190	1M KOH	Nano Energy. 2018, 44, 319.
Ni ₃ FeN/N doped G	OER	250	1M KOH	Adv. Funct. Mater. Doi: 10.1002/adfm.201706018
Ni-Co-P Nanocages	OER	300	1M KOH	Adv. Funct. Mater. Doi: 10.1002/adfm.201706008
Amorphous CoS ₂ Porous Nanocubes	OER	290	1M KOH	Angew. Chem. Int. Ed. 2017, 56, 4858.
Ultrathin Co ₃ O ₄ Nanomeshes	OER	307	1M KOH	ACS Catal 2018, 8, 1913.
Single-Atom Au/NiFe LDH	OER	210	1M KOH	J. Am. Chem. Soc. Doi: 10.1021/jacs.8b00752
CoP@N doped C nanotubes	OER	310	1M KOH	J. Am. Chem. Soc. 2018, 140, 2610.

Table S2. Comparison of the HER electrocatalytic activity in alkaline solution of Fe_{0.09}Co_{0.13}-NiSe₂ nanosheets/CFC electrocatalysts and the related electrocatalysts recently reported.

Catalyst	Water electrolysis test	Overpotential (10mA cm ⁻²)	Electrolyte	Reference
Co, Fe dual doped NiSe ₂ mesoporous nanosheets/CFC	HER	92	1M KOH	This work
Phase-Pure CoSe ₂	HER	117	1M KOH	ACS Energy Lett. 2016, 1, 607.
Selenium-Enriched Nickel Selenide	HER	117	1M KOH	Angew. Chem. Int. Ed. 2016, 55, 6919.
c-CoSe ₂ /CC	HER	190	1M KOH	Adv. Mater. 2016, 28, 7527.
CoSe ₂ -CNT	HER	174	1M KOH	Small 2017, 13, 1700068.
NiSe ₂ /Ni Foam	HER	143	1M KOH	Nano Energy. 2016, 20, 29.
Ni ₃ FeN/r-GO Aerogel	HER	94	1M KOH	ACS Nano. 2018, 12, 245.
NiCu@G	HER	74	1M KOH	Adv. Energy Mater. 2018, 8, 1701759.
ultrathin two-tiered NiSe nanosheets	HER	177	1M KOH	Adv. Energy Mater. Doi:10.1002/aenm.201702704
Ni _{0.9} Fe _{0.1} PS ₃	HER	72	1M KOH	ACS Catal 2017, 7, 8549
Pyrite NiS ₂	HER	110	1M KOH	ACS Nano. 2017, 11, 11574.
Al ₇ Cu ₄ Ni@Cu ₄ Ni	HER	125	1M KOH	Adv. Funct. Mater. Doi:10.1002/adfm.201706127

Table S3. Comparison of potential to achieve 10 mA cm^{-2} for overall water splitting of the as-prepared $\text{Fe}_{0.09}\text{Co}_{0.13}\text{-NiSe}_2$ nanosheets/CFC and some other reported bifunctional electrocatalysts in 1.0 M KOH aqueous solution.

Catalyst	Water electrolysis (V)	Electrolyte	Reference
Co, Fe dual doped NiSe_2 mesoporous nanosheets/CFC	1.52	1M KOH	This work
CoSe_2/CF	1.63	1M KOH	Nano Res. 2016, 9, 2234.
NiSe_2 nanowire/ NiO_x NPs	1.547	1M KOH	Small. 2017, 13, 1701478.
Nonlayered Nickel Selenides	1.69	1M KOH	Adv. Energy Mater. 2018, 1702704.
$\text{CoNiSe}_2/\text{NF}$	1.591	1M KOH	Nano Res. 2018, 11, 1331.
microporous nickel phosphite	1.60	1M KOH	Energy Environ. Sci., Doi: 10.1039/C7EE03619A
Se-(NiCo)S/OH	1.60	1M KOH	Adv. Mater. Doi: 10.1002/adma.201705538
$\text{Ni}_3\text{FeN/r-GO}$ Aerogel	1.60	1M KOH	ACS Nano 2018, 12, 245.
Colloidal Cobalt Phosphide	1.56	1M KOH	Adv. Mater. 2018, 30, 1705796.
Mesoporous Ni-Fe-O Nanowire	1.64	1M KOH	Adv. Energy Mater. 2018, 8, 1701347.
$\text{Co}_5\text{Mo}_{1.0}\text{O NSs@NF}$	1.68	1M KOH	Nano Energy 2018, 45, 448.
Ni@NC-800/Ni foam	1.60	1M KOH	Adv. Mater. 2017, 29, 1605957.
Exfoliated Ni-Fe Hydroxide Nanosheet	1.50	1M KOH	Adv. Mater. 2017, 29, 1700017.
$\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2$	1.53	1M KOH	Nano Energy 2017, 35, 161.
Co/CoP	1.45	1M KOH	Adv. Energy Mater. 2017, 7, 1602355.

References:

- [1] Kresse, G.; Hafner, J. *Physical Review B (Condensed Matter)*, **1993**, 47, 558.
- [2] Kresse, G.; Furthmüller, J. *Computational Materials Science*, **1996**, 6, 15.
- [3] Perdew, J. P.; Burke, K.; Ernzerhof, M. *Physical Review Letters*, **1996**, 77, 3865.
- [4] Blochl, P. E. *Physical Review B (Condensed Matter)*, **1994**, 50, 17953.
- [5] Kresse, G.; Joubert, D. *Physical Review B (Condensed Matter)*, **1999**, 59, 1758.
- [6] D. E. López, Y. Niu, J. L. Yin, K. Cooke, N. V. Rees, R. E. Palmer, *ACS Catal.* **2017**, 6, 6008.
- [7] X. Y. Yu, Y. Feng, Y. Jeon, B. Y. Guan, X. W. Lou, U. Paik, *Adv. Mater.*, **2016**, 28, 9006.
- [8] D. Li, H. Baydoun, B. Kulikowski, S. L. Brock, *Chem. Mater.* **2017**, 27, 3048.
- [9] Y. R. Zheng, M. R. Gao, Z. Y. Yu, Q. Gao, H. L. Gao, S. H. Yu, *Chem. Sci.* **2015**, 6, 4594.
- [10] Zhou, H. Q.; Wang, Y. W.; He, R.; Yu, F.; Sun, J. Y.; Wang, F.; Lan, Y. C.; Ren, Z. F.; Chen, S. *Nano Energy*, **2016**, 20, 29.
- [11] Zhao, B.; Song, J. S.; Liu P.; Xu, W. W.; Fang, T.; Jiao, Z.; Zhang H. J.; Jiang, Y.; *J. Mater. Chem.*, **2011**, 21, 18792.
- [12] Wu, H.; Lu, X.; Zheng, G. F.; Ho, G. W.; *Adv. Energy Mater.* **2018**, 1702704.
- [13] Chen, R.; Yang, C. J.; Cai, W. Z.; Wang, H. Y.; Miao, J. W.; Zhang, L. P.; Chen, S. L.; Liu, B.; *ACS Energy Lett.*, 2017, 2, 1070.

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