**In Situ** Phase Transformation on Nickel-Based Selenides for Enhanced Hydrogen Evolution Reaction in Alkaline Medium

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**ABSTRACT:** Identification of the active species in electrocatalysts toward hydrogen evolution reaction (HER) is of great significance for the development of the catalytic industry; however, it is still the subject of considerable controversy. Herein, we applied operando synchrotron X-ray powder diffraction (SXRD) in the NiSe$_2$ electrocatalyst system, and an *in situ* phase transformation from cubic NiSe$_2$ to hexagonal NiSe was revealed. The NiSe phase showed an enhanced catalytic activity. Operando Raman spectroscopy verified the decomposition of NiSe$_2$ during HER. Theoretical calculations suggested that the charge transfers from the Se site to Ni site during this evolution process, leading to an increased conductivity and a shifting up of $d$-band center, which is attributed to the enhanced activity. The generated NiSe phase acts as the "real" active species. Our work unravels the underlying phase transition of the electrocatalyst on reductive conditions in alkaline medium and highlights the significance of identifying the intrinsic active sites under realistic reaction conditions.

Because of the limited source of fossil fuels and increasing environmental contamination, large-scale production of hydrogen fuel from water splitting is considered as a promising alternative strategy for green energy generation.\textsuperscript{1–3} Although platinum is recognized as the most efficient catalyst for HER, the high cost and scarcity severely impede its extensive application.\textsuperscript{4,5} In the last several decades, significant efforts have been made to develop nonprecious metal electrocatalysts, among which includes a large family of transition-metal chalcogenides\textsuperscript{6,7} and phosphides.\textsuperscript{8–10} Because of the metalloid property of sulfur, selenium, and phosphorus, these compounds show narrow band gaps or metallic conductivities which facilitate the electron transportation. Accordingly, some of them have shown superior electrocatalytic performance in alkaline water splitting and possess huge potential in commercial utilization. Nevertheless, the underlying mechanism for HER is still under considerable debate, and the understanding of the electrocatalytic process and the identification of the real active sites are still lacking, especially when compared with the rather well-explored oxygen evolution reaction (OER) process.\textsuperscript{11–13}

The transition-metal-based catalysts have been regarded stable for HER when compared with the harsh OER conditions. Very recently, it was noticed that some catalysts may experience a structural reorganization or phase evolution during the reduction process. For instance, NiS$_2$-based electrocatalysts were considered durable for alkaline HER.\textsuperscript{14,15} However, it was reported that NiS$_2$ could be reduced into metallic Ni, which acted as the real active site for hydrogen generation.\textsuperscript{16,17} Similarly, by applying comprehensive postcatalytic measurements, Co$_2$P was observed to degrade into hydroxide after a prolonged HER.\textsuperscript{18} Nevertheless, it should be noted that sample oxidation due to the ambient exposure could not be excluded. From this perspective, the conventional *ex situ* techniques are not capable of qualitatively identify the active catalysts, let alone dynamically capture the structural or compositional transformation under working conditions. In contrast, *operando* or *in situ* methods are...
emerging as indispensable tools to track the self-reorganization process and to reveal the active sites. Recently, a P-substituted CoSe2 was found to reduce into metallic cobalt which acted as the active site for HER.19 Our previous research also confirmed the morphological and compositional changes of NiSe2 after both HER and OER.20 Because of the limitation of ex situ characterization tools, employing operando instruments to track the phase evolution and identify the active sites of these electrocatalysts is urgently needed.

In this work, we developed an electrochemical cell which can measure the evolution of the SXRD pattern of the NiSe2 electrocatalyst toward HER under operando conditions. The dynamic structural and compositional transformation from cubic NiSe2 (JCPDS no. 65-3425) to hexagonal NiSe (JCPDS no. 65-2901) under a series of reductive conditions were revealed. Through this self-reorganized phase transformation process, the current density of the electrocatalyst could be increased by 27.3%. Then, operando Raman spectroscopy further confirmed the decomposition of NiSe2. Moreover, a phase evolution mechanism was proposed with the combination of ex situ measurements, such as high-resolution transmission electron microscopy (HRTEM) and X-ray photoelectron spectroscopy (XPS). Additionally, the density functional theory (DFT) studies further revealed the increase in conductivity and the rise of the d-band center, which lead to the enhancement of catalytic activity. Our work provides new insights into the chemical and physical transformation of the electrocatalyst during the electrochemical process. It may enable the development of the high-efficiency and stable electrocatalysts for hydrogen production.

The NiSe2 nanoparticles were synthesized through a thermal selenization method with carbon paper (CP) as substrates (see details in Supporting Information). As shown in Figure S1a, the NiO nanoparticles were anchored onto the carbon fiber, and the pristine carbon fiber shows a smooth cylindric surface with a diameter of ~10 μm (Figure S1b). After selenization, the morphology is well-conserved, as shown in Figure 1a. Powder X-ray diffraction (XRD, Figure S2) patterns reveal the compositional change from NiO (JCPDS no. 65–2901) to NiSe2. The narrow and sharp peaks reflect the highly crystalline nature of the NiSe2, which is further confirmed by the HRTEM results. As shown in Figure 1b, the large domain presents a typical surface of (210) phase. The lattice d-spacings of 2.7, 3.0, and 6.0 Å are also consistent with the values of (210), (200), and (010) planes, respectively. Moreover, the energy-dispersive X-ray (EDX) elemental mapping (Figure 1c) reveals the homogeneous distribution of Ni and Se throughout the particle with a Se/Ni atomic ratio of 2.17. The slight excess Se derives from the absorbed species on its surface.19,21 For better comparison, Ni(OH)2 was also prepared by an electrodeposition method (see details in the Supporting Information). As shown in Figure S3, the carbon fiber is uniformly covered by the as-prepared Ni(OH)2; the XRD pattern is also consistent with α-Ni(OH)2 (JCPDS no. 38-0715).

The electrochemical behavior of the as-prepared NiSe2 toward HER was first examined in 1 M KOH by linear sweep voltammetry (LSV). Ni(OH)2, NiO, commercial 20% Pt/C, and bare CP were also tested as reference catalysts. Before testing, the fresh NiSe2 was immersed in the electrolyte without any potential for 12 h and examined by XRD. As
shown in Figure S4, the patterns show no obvious difference, confirming the stability of NiSe2 in KOH without potential. The LSV curves were obtained at a scan rate of 5 mV s⁻¹ after the initial cyclic voltammetry (CV) for 20 cycles at a scan rate of 50 mV s⁻¹. As shown in Figure 1d, the bare CP shows negligible activity while the 20% Pt/C demonstrates a lowest overpotential of 65 mV to reach a current density (j) of −10 mA cm⁻² (η₁₀ = 65 mV). As compared to the Ni(OH)₂ and NiO with poor catalytic activities (η₁₁₀ᵣ = 411 mV, η₁₁₀ᵢ = 232 mV), the NiSe₂ exhibits much superior performance, as indicated by the largely decreased overpotential (η₁₁₀ ≈ 157 mV). To further evaluate the stability of the NiSe₂ catalyst, chronoamperometry measurement was conducted at a constant potential of −0.16 V (initial current density ≈ −10 mA cm⁻²) for 24 h. As shown in Figure 1e, the current density shows negligible degradation, indicating excellent stability of the sample. Interestingly, the current density was found to gradually increase from −9.5 to −16.7 mA cm⁻² in the first 2 h. This phenomenon is also verified by the increased activity with increasing cycling number as shown in Figure S5. These facts indicate a probable electrochemical activation process of the NiSe₂ nanoparticles during alkaline HER.²²,²³

To further investigate the performance of the catalyst after deep activation, the sample after 2 h of chronoamperometry is denoted as NiSe₂-A. As revealed in the polarization curves (Figure 1d), the NiSe₂-A achieves a current density of −93 mA cm⁻² at an overpotential of 0.2 V, which is three times higher than that of NiSe₂ at the same overpotential, indicating a much enhanced catalytic activity after full activation. Additionally, the corresponding Tafel slopes were also investigated to gain kinetic insights into the HER process (Figure S6). The NiSe₂-A catalyst achieves the lowest value of Tafel slope (76 mV dec⁻¹) as compared with that of Ni(OH)₂ (134 mV dec⁻¹), NiO (94 mV dec⁻¹), and NiSe₂ (79 mV dec⁻¹), demonstrating the rapid HER rate after activation. The faradaic efficiency (FE) of the NiSe₂-A during alkaline HER was also calculated to be 99% (Figure 1e inset). Furthermore, the turnover frequencies (TOFs) of the above-mentioned nickel-based electrocatalysts were evaluated by assuming that all nickel atoms in the materials were catalytically active (Figure S7). The TOF of NiSe₂-A is 8.6 × 10⁻² s⁻¹ at η = 210 mV, which is much greater than that of Ni(OH)₂ (1.2 × 10⁻⁴ s⁻¹), NiO (1.5 × 10⁻³ s⁻¹), and NiSe₂ (3.3 × 10⁻² s⁻¹). The higher TOF value of NiSe₂-A suggests enhanced intrinsic catalytic activity.

To gain further insight into the charge-transfer behavior at the interface of the catalyst and the electrolyte, the electrochemical impedance spectroscopy (EIS) was performed (all parameters are listed in Table S1). As shown in Figure S8, the Nyquist plot of NiSe₂-A reveals a lowest charge-transfer resistance (Rct) value of 1.97 Ω, suggesting the superior charge-transfer property after activation.

The electrocatalytic performance of the electrode is largely affected by the electrochemical surface area (ECSA). To eliminate the effect of surface coarseness, ECSA values were calculated from the corresponding double-layer capacitance (Cdl) (see details in the Supporting Information). The Cdl values were obtained from CV at different scan rates in the nonfaradaic region as shown in Figure S9. The ECSA-normalized polarization curves are shown in Figure 1f to reveal the intrinsic activity after activation. Clearly, the Cdl value is slightly increased after activation; the enhanced activity of the NiSe₂-A indicates that in addition to the higher active surface area, the intrinsic catalytic activity of the catalyst is also improved by the activation process.

In order to explore the underlying activation process of the NiSe₂ during HER in alkaline medium, an operando high-resolution SXRD characterization was conducted. Figure S10 shows the experimental set up. The synchrotron data was collected using a pixel area detector in transmission geometry. The NiSe₂ catalyst was applied at a constant potential of −0.18 V for 6 h; the i-t curve and time-resolved diffraction patterns were collected in operando as shown in Figure 2a. The current
density of the NiSe₂ is \(-16.2\) mA cm\(^{-2}\) at the beginning and gradually increased by 27.3\% in the first 2 h. Meanwhile, the characteristic peaks of the cubic NiSe₂ at 10.7° (210), 13.6° (220), and 15.9° (311) are shown but gradually decrease in intensity as the reaction progresses. Then after 2 h, the current density reaches 20.5 mA cm\(^{-2}\) and remains unchanged. At the same time, three new diffraction peaks at 10.4°, 14.0°, and 15.6° become prominent in the SXRD patterns as shown in Figure 2b−g, which are the characteristic peaks for the hexagonal NiSe phase. These can be readily identified as (011), (012), and (110) reflection, respectively. Interestingly, the increasing of the NiSe peaks comes at the expense of the NiSe₂ peaks, signifying a phase transformation from cubic NiSe₂ to hexagonal NiSe. The background-subtracted diffraction patterns as a function of reaction time are shown in Figure S11a. By refining the synchrotron data using TOPAS analytical software, we obtained the lattice parameters of the NiSe phase (Table S2). As the electrochemical reaction progresses, the NiSe unit cell contracts along the a-axis but expands along the c-axis. It suggests compressing forces on the b−c surface and drawing forces on the a−b surface, which can be ascribed to the electric stress and the interaction with the neighbor NiSe₂ nanocrystallites or domains. The chronoamperometry measurement was prolonged for 24 h; the corresponding SXRD pattern is shown in Figure S11b. Clearly, the characteristic peaks of the NiSe show no obvious change after 2 h while the characteristic peaks of the NiSe₂ keep declining until almost undetectable. This result confirms the complete decomposition of the NiSe₂. It should be noted that the phase evolution after the reaction (Figure S12a). Then, the electrolyte was filtered and a thin layer of red precipitate was collected as shown in Figure S12b−c. Raman spectra of the precipitate show peaks at 146.8 and 242.5 cm\(^{-1}\), which matches well with the elemental Se (Figure S12d). EDX spectra also confirm the existence of Se (Figure S13). When these are combined with the SXRD results, it can be concluded that the NiSe₂ nanoparticles are unstable during alkaline HER and readily disproportionate into NiSe and Se during the reaction (NiSe₂ → NiSe + Se). For comparison, the operando measurement of the NiO during HER was conducted under \(-0.23\) V (current density \(\approx -10\) mA cm\(^{-2}\)). As shown in Figure S14, the current density is decreased because of the degradation of activity, and the characteristic peaks of NiO do not show any change over time, indicating the unique phase evolution property of the NiSe₂ reaction system.

With the aim to further study the phase evolution in higher biased potentials, operando SXRD at \(-0.38\) V and \(-0.58\) V were also conducted. As shown in Figure S15, the evolution of the SXRD patterns is similar to a previous result (\(-0.18\) V) but with a faster rate. It should be noted that the characteristic peaks of the NiSe at \(-0.58\) V are broader, indicating smaller domains. This change may be due to the drastic electron transportation and environmental stress.

With the aim of revealing the surface states of the NiSe₂ electrocatalyst during reaction, operando Raman spectroscopy was employed to monitor the real-time evolution using the specially designed setup as shown in Figure S16. The bare CP shows no obvious peaks in the range of 100−800 cm\(^{-1}\) (Figure S17), whereas the as-prepared NiSe₂ shows characteristic peaks at 155, 169, 216, and 243 cm\(^{-1}\) for Tₓ (libration), E_g (libration), A_g (stretching), and T_g (stretching) modes, respectively (Figure 3a). As the pristine NiSe₂ was immersed into deionized (DI) water and KOH, the peak intensity was decreased because of the scattering. Additionally, the relative peak intensity of Tₓ (0) and A_g (I_T/A_g) increases from 0.4 to 1.0, indicating a prominent Tₓ (0) mode in liquid. Because this change has already appeared in pure DI water, we suppose it is due to the constraints by the neighboring water molecules. The sample was then characterized under different potentials. The peak intensities are further declined, which is due to the structural decomposition of NiSe₂; the Tₓ/I_A_g value increases to 1.9 when the potential is \(-0.8\) V, confirming the preference of the Tₓ (0) mode in liquid. Notably, the Tₓ (0) peak is red-shifted to 147 cm\(^{-1}\) and the A_g peak is blue-shifted to 228 cm\(^{-1}\). This result can be attributed to two reasons: (i) The charge accumulation on the cathode leads to lattice distortion. (ii) The phase evolution from NiSe₂ to NiSe leads to an unsymmetrical structure. To further evaluate the time-resolved phase transformation, a constant potential of \(-0.2\) V was applied for 5 h. As shown in Figure 3b, the declined intensity of the characteristic peaks confirms the decreasing of NiSe₂ quantity; the peak shifting is maintained during the whole process. These findings confirm the decomposition of NiSe₂, which is in accordance with the SXRD results.

To further verify the structural and compositional changes of the NiSe₂, ex situ TEM was employed to clarify the time-dependent phase evolution. The reaction time were chosen as...
0, 1, 2, and 6 h as compared to the SXRD results. As shown in Figures 4a,b, the pristine NiSe₂ nanoparticle shows a smooth surface with a regular round shape. The HRTEM image reveals a (210) reflection, and the corresponding selected area electron diffraction (SAED) pattern also shows the highly crystalline nature of the NiSe₂. After 1 h of reaction, the edge of the particle becomes coarse and thinner (Figure 4c), indicating the structural changes start from the surface. The SAED pattern demonstrates that the NiSe₂ is the major phase. The HRTEM image still shows a (210) reflection of NiSe₂, while a (102) reflection of NiSe is captured as shown in Figure 4d. This new phase is generated along with the distortion of the lattice in the NiSe₂. This heterostructure confirms the early stage of the phase transformation which is consistent with the SXRD results. After 2 h of reaction, the particle structure continues to evolve and becomes irregular (Figure 4e). The HRTEM shows multiple orientations containing both NiSe₂ and NiSe phases (Figure 4f), while the SAED indicates the NiSe phase is increased further (Figure 4e inset). Additionally, the SAED pattern exhibits blurry rings rather than the scattered dots, which are due to the multiple small domains. Finally, after 6 h of reaction, the particle is further decomposed with thinner edges (Figure 4g), the structure is dominated by the NiSe phase as shown in Figure 4h. Meanwhile, the SAED pattern displays only the NiSe phase. When the SXRD and TEM results are combined, it can be concluded that during the reaction in an alkaline medium, each crystalline NiSe₂ particle (approximately hundreds of nanometers) in the bulk gradually transforms into multiple small domains (size of approximately tens of nanometers) with a dominating NiSe phase and a diminishing NiSe₂ phase. The phase transformation can be named as a “catalytic domainsing process” as shown in Figure 4i. We speculate that, under cathodic potentials, the charge aggregation on the Se₂⁻ dimers breaks the Se−Se bonds in NiSe₂. Then one of the Se⁻ ions lost an electron and rearranged; the other Se⁻ ion gains an electron and bonds with the Ni atom with lattice distortion (cell contraction). This phase evolution randomly occurred on the particle and generated multiple phase boundaries (domain structure). While the insight of the precipitation of Se needs more study in the future, it is beyond the scope of our work. The changes of atomic ratios of Se/Ni were also examined by EDX as listed in Table S3. The value is 2.17 for the pristine NiSe₂, while after 6 h of reaction, it reduces to 0.92, which is even lower than that in pure NiSe. This result confirms the large-scale detachment of Se and also suggests the probable Se vacancies. Electron paramagnetic resonance (EPR) was conducted to verify the existence of Se vacancies. As shown in Figure 4j, the EPR signals can be found at the g value of 2.001; a stronger signal indicates a higher level of Se vacancies.25,26 As for pristine NiSe₂, the weak signal suggests negligible Se vacancy. After HER, the peak signal is increased as a function of reaction time. This trend is maintained as the reaction time prolonged, indicating the NiSe₂/NiSe hybrid is Se-vacancy-rich. It is well-accepted that vacancies and defects are beneficial for the improvement of catalytic activity.27,28

Figure 4. TEM images, HRTEM images, and the corresponding SAED patterns of (a and b) pristine NiSe₂, (c and d) after 1 h, (e and f) 2 h, and (g and h) 6 h of reaction. Yellow and red reflections represent NiSe₂ and NiSe phases, respectively. (i) Schematic illustration of the domaining process. (j) EPR spectra of the pristine NiSe₂ and after various HER reaction times.
To further investigate the oxidation state of the NiSe2 prior to and post HER, XPS characterization was employed. All the samples were etched by Ar ions for 60 s to clean the surface. As shown in Figure 5a, the pristine NiSe2 shows Ni 2p spectrum at 853.3 and 870.5 eV, representing the Ni2+ oxidation state.29 The deconvoluted Ni 2p$_{3/2}$ peaks reveal the Ni – Se bond at 853.3 eV and Ni – O bond (due to surface oxidation) at 854.5 eV. These results are consistent with previous studies.30,31 After reaction, the bonding energy of Ni – Se is red-shifted by 0.5 eV. On the basis of the previous result, the pure NiSe2 has transformed into NiSe (remains a small ratio of NiSe2) with Se vacancies. In viewing that the binding energy of Ni – Se in NiSe is lower than that in NiSe2,32 it is natural to consider the peak at 852.7 eV as a mixed state of Ni – Se in the NiSe2/NiSe hybrid. Additionally, the binding energy of Ni – O reveals continuous blue shift, representing the Ni – OH bond33,34 which is caused by the strong KOH electrolyte and Se vacancies. For the pristine Se 3d spectrum (Figure 5b), two peaks located at 54.5 and 55.5 eV are indexed to Se 3d$_{5/2}$ and Se 3d$_{3/2}$, matching well with previous reports.29,34 After reaction, the peaks are red-shifted by 0.6 eV, confirming a lower oxidation state. These results are consistent with the TEM results, confirming the phase transformation process.

To decipher the modulation essence of the phase transformation in NiSe2 for alkaline HER under atomic level, DFT calculations were further applied. A cell model of NiSe1.5 is also

Figure 5. XPS spectra of (a) Ni 2p region and (b) Se 3d region as a function of reaction time.

Figure 6. (a) DOS plots of NiSe2, NiSe1.5, and NiSe. The Fermi level and the d-band center are also highlighted. (b) Polyhedral cell structures of NiSe2, NiSe1.5, and NiSe. (c) Isosurfaces of the charge density difference at one Se atom in a unit cell. Yellow and cyan clouds indicate charge gain and loss, respectively. The isosurface is 0.005 e Bohr$^{-3}$. 

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To decipher the modulation essence of the phase transformation in NiSe2 for alkaline HER under atomic level, DFT calculations were further applied. A cell model of NiSe1.5 is also
constructed as a transition phase, where two Se atoms are taken out from the NiSe₂ unit cell. The structures and lattice parameters of NiSe₂, NiSe₁₋₀, and NiSe are given in Figure S18 and Table S4. The total density of states (DOS) were first calculated as shown in Figure 6a, and the polyhedral cell structures are given in Figure 6b. Partial density of states (PDOS) values of Ni d-band and Se p-band are also given, as they are the main factors that determine the electronic properties. Clearly, the Ni₇Se₂ shows a semiconductor property with a narrow band gap of 0.24 eV, which is consistent with previous reports. Compared with the Ni d-band, the Se p-band is much more delocalized with a broad width, confirming the strong interaction with the neighbors. In the Ni₇Se₂ structure, the Ni 3d orbital owns a fully occupied t₂g band and a half-filled e_g band, and the Se−Se bond is covalent with pairs of sp and pσ bondings. Thus, we expect the covalent bonding in the Se₂− band is interrupted because of the negative potential on the cathode. Partial charge then transfers from the Se p orbital to the Ni e_g orbital, leading to the rise of the Se p-band and crossover of the Fermi level. When the crystal further transforms into hexagonal NiSe, the Ni d-band also passes through the Fermi level with increased energy in states, which is in accordance with previous literature contributions. The d-band center and occupied electron numbers in Ni d-band and Se p-band are also calculated as shown in Table S5. The d-band center is a reasonable descriptor to predict the catalytic activity of transition metals, which is a measure of the strength between metal and adsorbate (i.e., hydrogen adsorption energy). Because the d-band is much more localized than sp-bands in transition metals, the hydrogen adsorption energy depends, to a large extent, on the electronic interaction between the hydrogen s states and the metal d states, forming bonding and antibonding states. Then a higher d-band center of the catalyst leads to less filled antibonding states, increasing the bonding energy with the hydrogen. An optimized bonding energy should be neither too strong nor too weak. Because Pt is widely accepted as a benchmark among HER catalysts, its d-band center position (−1.93 eV vs Fermi level) is usually regarded as an ideal value. Given the calculation result, the d-band center of Ni is shifted up during the phase transition, which is closer to the position of Pt. This trend matches well with the increased activity in the experiments. In addition, the trends of electron occupancy per atom also show charge accumulations on Ni site and charge depletions on Se site. This result is further confirmed by the charge density difference maps as shown in Figure 6c. It is obvious that the charge accumulates on the Se site in NiSe₂, but on the Ni site in NiSe. On the basis of these results, it can be concluded that the NiSe₂-to-NiSe phase transformation is accompanied by the charge transfer from Se sites to Ni sites, leading to an improved conductivity and shift up of d-band center. This phase evolution results in an enhanced catalytically active, and the newly generated NiSe species act as the real active site.

In summary, the NiSe₂ electrocatalyst during alkaline HER was investigated through operando SXRD and Raman spectroscopy and other ex situ approaches (SEM, HRTEM, XPS, and DFT calculations). From the synchrotron work, an in situ phase transformation from cubic NiSe₂ to hexagonal NiSe was observed during the reaction process. The transformation is supported by the findings in the detailed study of HRTEM imaging and diffraction. From the complementary X-ray spectroscopic and calculation results, the charge transfer from Se site to Ni site leads to an enhanced conductivity and shifting up of d-band center, which contributes to improving the HER performance. Our work provides evidence and information for understanding the fundamentals of electrocatalysis and offers insights into the nature of catalytic active sites. We expect this work could inspire more investigations of self-assembled reconstructions beyond the NiSe₂ system such as other transition-metal chalcogenides because these catalytic materials are promising for the efficient production of hydrogen energy in industrial applications.

### ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsenergylett.0c01385.

- Experimental details, SEM images, XRD patterns, LSV curves, SXRD setup images, SXRD patterns, Raman spectra, DFT calculations, etc. (PDF)

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### Notes

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Structure of NiSe$_2$ Nanoparticles@ Nitrogen-Doped Graphene for Substitution and Holey Engineering for Efficient Hydrogen Evolution. Both Acidic and Alkaline Media.


