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Atoms Arrangement in Metal Doped NiS₂ for Boosting Hydrogen Evolution Reaction in Alkaline Media

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Dedication ((optional))

Abstract: Currently, achieving the highly selective water-splitting in alkaline media with spontaneous efficient electronic activity is pivotal for clean and sustainable hydrogen energy. However, compared with the excellent performances of common state-of-the-art catalysts in acidic media, the considerable reduction of catalytic performance in alkaline media is suffered from the sluggish water dissociation. Owing to the large exposed surface and unique atomic arrangements, 2D transition metal sulfides (TMS) are emerging as the promising catalysts in hydrogen evolution reaction (HER). Herein, we report a novel modulation strategy by introducing transition metals to NiS₂ nanosheets (NSs) to flexibly optimize the electronic configurations and Ni contents, which exhibit excellent HER performance with an ultra-low overpotential of 80 mV at *j* = 10 mA cm⁻² and long-term stability of 90 h in alkaline media. The TOFs of 0.55 and 4.1 s⁻¹ at an overpotential of 100 and 200 mV also confirm their remarkable performance. DFT calculations reveal that the surface dopants abnormally sensitize surface Ni-3d bands in the long-range order towards higher electron-transfer activity, acting as the electron-depletion center. Meanwhile, the pinned high lying surface S-sites possess substantially high selectivity for splitting the adsorbing H₂O that guarantee the high HER performance within alkaline conditions. This work opens opportunities for enhancing water splitting by atom arrangements assisted electronic modulation via the facile doping strategy.

Introduction

Water splitting plays an important role in the sustainable development of H₂ energy.^[1-6] In general, the industrial water splitting devices are operated in strong alkaline media to obtain H₂ and O₂.^[7] Due to the high dissociation energy cost of water, it is still challenging to generate H* through the hydrogen evolution reaction (HER) in alkaline media, which becomes a rate-determining step for water splitting in alkaline media.^[8-10] Therefore, it is crucial to design the highly active catalysts with optimal adsorption and dissociation energies of water to enhance the efficiency of HER in alkaline media. Traditionally, Pt-based nanomaterials are the most superior catalysts for HER but its high cost and low abundance severely impedes its large-scale applications.^[11-16] Thus, designing cost-effective and highly efficient HER electrocatalysts becomes the pivotal task for future research. Transition metal sulfides (TMS) with high electrical transport and ideal atomic arrangement have been considered as promising noble-metal-free electrocatalysts for HER.^[17-22] Previous studies have demonstrated excellent HER performance of several TMS, such as MoS₂,^[17] Ni₂S₃,^[19] CoS₂,^[20] etc. Recent studies indicated that ultrathin MoS₂ nanosheets with abundant edge active sites showed superior HER activity.^[23] However, these reported TMS-based catalysts are utilized only in acid media. The development of the novel TMS catalysts with good HER activity and stability in alkaline media remains a challenge that requires more in-depth studies.

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Various strategies have been designed to enhance the HER performance of the TMS-based nanocatalysts. Ultrathin 2Dnanostructures with abundant edge sites as promising catalysts have been extensively used in various reactions epically for HER.^[23] The hetero-structured TMS nanocrystals with rich interfaces show enhanced coupling, electrical transport, and improved HER performance.[24-26] Moreover, the TMS with high index crystal facets shows a high density of atomic steps, ledges, kinks that enhanced HER performance.[19,27] It is noted that the density of states (DOS) and adsorption energies of TMS materials can be tuned by non-metallic element doping, which optimizes the electronic structures of the materials towards HER.^[28] Although the various methods have been designed to prepare excellent TMS electrocatalysts, the challenge of achieving highly electroactivity in alkaline media still yet to be overcome.

Herein, the different metal doped NiS₂ NSs catalysts are prepared and their superior HER performances in alkaline media are confirmed by both electrochemical tests. Combining theoretical and experimental approaches, a long-ranged electronic sensitization is supplied by the surface dopants. The Ni-3d bands center has been elevated towards much higher electron-transfer capability near E_F without any impact between the surface S anion sites show pinned 3p bands that are

intra-site oxidations for inter p-d orbital electronic migrations. Meanwhile, the surface S-anion-sites show pinned 3p-bands that are

highly effective for coupling the $O-2p\pi$ orbital to reach a lowered barrier of H₂O splitting. This is the essential key to achieve the highest H₂O splitting performance with least H-over-binding effect on the surface cation-sites. From the atomic rearrangement perspective, the obtained Co-NiS₂ NSs show optimal eg¹ electron configuration and the increased content of Ni³⁺ species, which exhibit activity and stability for HER in alkaline media. In the strong alkaline electrolytes (i.e, 1.0 M KOH), the Co-NiS₂ NSs catalyst shows an overpotential of only 80 mV at a current density of 10 mA cm⁻². The thiocyanate ion poisoning experiments identify that after Co doping the enhanced content of eg¹ and Ni³⁺ responsible for the outstanding HER performance of the Co-NiS₂ NSs catalysts. Most importantly, the Co-NiS₂ NSs catalysts exhibit unprecedented TOFs (TOFs per Co atom of 0.55 and 4.1 s⁻¹ at an overpotential of 100 and 200 mV, respectively) in alkaline media, which are superior to recently reported HER catalysts with breakthrough performance.^[29-31] The in-depth understanding of atomic rearrangement in doping strategy offers a guideline for the fabrication of multifunctional catalysts.

Results and Discussion

The mechanism of HER performance boosting was reasoned from the surface electronic modifications based on highly efficient doping with different metals such as Co, Fe and Cu. The surface active bonding and anti-bonding orbitals near the Fermi level (E_F) have been illustrated to address the effective modifications by the doping metal Co (Figure 1a), Fe (Figure 1b), and Cu (Figure 1c), respectively. The electronic tuning trend of surface Ni-sites has been well indicated by the projected partial density of states (PDOSs). For the Co, Fe, to Cu doping cases (Figure 1d-f), the d-band centers of surface Ni-sites have been uniformly elevated towards the E_F starting from E_V-2.0 eV (bulk Ni-sites, E_V = 0 for E_F). The surface Ni-sites nearby the dopants (Co, Fe, and Cu) have been overall sensitized and playing as electron-depleting centers close to E_F for efficient on-site electron-transfer. The dominant peak positions of Ni-3d bands are staying at Ev-1.4 eV for Co-doping (Figure 1d), Ev-1.2 eV for Fe-doping (Figure 1e), and Ev-1.0 eV for Cu-doping (Figure 1f), respectively. Additionally, the electronic contrast of S-sites between surface and bulk from different doping cases has been also demonstrated. The surface S-3p bands exhibit a similar character with the dominant peak position staying at E_V -3.8 eV, which is evidently different from the bulk S-3p band. This indicates the rather effective surface Ni-3d band tuning trend without obviously impacting on the S-sites (Figure 1g). The surface S-bonding induced 3d-band features are different. Overall, the 3d-t_{2g} component of surface Co-site stays higher than the ones in Fe and Cu cases, indicating a smaller eg-t2g splitting gap for higher efficiency of electrontransfer across E_F (Figure 1h). Further comparison of 3d-band dominant positions and 3d-3p gaps evidently demonstrates that surface dopants overall elevate the electronic activities of surface Ni-sites without intra-site Ni-S oxidation and less migration of 3d-electrons towards S-sites (Figure 1i).

In accordance with these findings, experiments are designed to homogeneously incorporate different metals into NiS₂ to modulate the arrangements of the local atoms (Scheme S1 in the supporting information). First, the M-Ni-LDH (M: Fe, Co, Cu) nanosheets were built via electrochemical deposition,^[32] and then M-NiS₂ NSs are obtained through the calcination of the corresponding LDH under sulfur steam at 300 °C for 2h.^[26] Under controlled synthesis method, the Co-NiS₂, Fe-NiS₂ and Cu-NiS₂ NSs display the same X-ray diffraction (XRD) pattern of cubic NiS₂ with a space group of *Pa3* (JCPDS No. 11–99, a = b = c = 5.670 Å) (Figure S1), which are attributed to the similar ionic radius and low content of M in the LDH (Table S1).

Then, the transmission electron microscopy (TEM) is applied to characterize the morphology of the synthesized nanosheets. As shown in Figure 2a, the Co-NiS₂ exhibits a uniform nanosheetstructure, and the inset in Figure 1a also displays its colloidal properties. Likely, the Fe-NiS₂ and Cu-NiS₂ also have the ultrathin nanosheets morphology (Figure S2). Additionally, the elemental mapping of the selected sheets shows the uniform distribution of doped metals, Ni and S on the NS region (Figure S3). The ICP-AES also give clear detailed content of each metal NSs (Table S1). Through the above analysis, the different dopants successfully incorporated into NiS₂ without imposing any change on the morphology and structure. Further, the High-resolution transmission electron microscopy (HRTEM) and high-angle annular dark field aberration-corrected scanning TEM (HAADF-STEM) have been used to confirm the fine structure of Co-NiS₂ NSs. As shown in Figure 2b, the HRTEM image of Co-NiS₂ NSs displays the lattice space of 2.83 Å that matches with the (100) plane of NiS₂. This further indicates the homogenous doping. However, the corresponding FFT image (the inset in Figure 2b) of Co-NiS₂ NSs cannot match with the standard atomic arrangement of (100) face for NiS₂ (Figure S4). The reason for this difference should be attributed to successful doped Co into the NiS₂ lattice and cause the atom rearrangement to form this diverse atom structure. Therefore, the HAADF-STEM was used to evidence the fine structure of Co-NiS₂ NSs. As shown in Figure 2c, the atom arrangement of Co-NiS₂ NSs conformed to (NiCo)₃S₂ structure, which matched with the [101] orientation of Ni₃S₂.

The corresponding FFT image (Figure 1d) also shows the same structure with the insert FFT in HRTEM. Furthermore, theoretical STEM images were simulated to confirm the successful doping by using QSTEM software. The crystal structure of Co-NiS₂ NSs was built (Figure 2e) and simulation strategy was performed to study the difference in scattering strength caused by different atoms. As shown in Figure 2f, the surface intensity of Co-NiS₂ along [101] zone axes shows a similar height, which indicates that on [101] zone axes the length of atom columns should be same. It is well-known that the scattering strength of each atom column originating from

the effective *Z* or the number of atoms. Colorful spots in Figure 2g represent different atomic columns, in which dark and slight red spots suggest the different scattering strength for Ni or Co atoms. For the larger atomic number of Ni, the scattering strengths of Ni or Ni mixed Co should be stronger than that of the pure Co columns, indicating the successful doping ofCo in NiS₂ on [101] zone axes. However, both the surface intensity and scattering strength on [100] zone axes show the same height (Figure 2h) and colorful spots (Figure 2i), suggesting the same atoms in the domain.

The electronic and coordination structures of NiS₂ after doping were further investigated by using various spectroscopy methods. From X-ray absorption near-edge structure (XANES) spectra of Ni L-edge for those NSs (Figure 3a), two typical L₂ and L₃ peaks at approximately 856 and 874 eV are observed. Compared with Fe-NiS₂ and NiS₂ NSs, a positive shift about 0.9 eV are noted in Cu-NiS₂ and Co-NiS₂ NSs, supporting the electron transfer from Ni to Cu or Co with decreased electron density around the Ni atoms in Cu-NiS₂ and Co-NiS₂ NSs.^[33] Similar results are also be found in X-ray photoelectron spectra (XPS). After Co doping, in Ni 2p spectra (Figure S5a), the peaks at 858.4 eV associated with Ni³⁺ state appeared and displayed the highest content when compared with other NSs (Figure S5b).^[34] In addition, the evident change of Ni 2p peaks are discovered in Co-NiS₂ NSs (Figure S6). The Co 2p spectra (Figure S7) also shows an obvious peak at 782.7 eV for Co²⁺ and a positive shift after sulfur steam treatment, which confirms the acceptance of electron from Ni and enhanced coupling between Co and Ni in Co-NiS₂ NSs.

The EXAFS spectrum of S K-edge for Co-NiS₂ NSs exhibits a distinct positive shift about 0.2 eV compared with other NSs (Figure 3b). The S 2p XPS spectra of those NSs also show a similar bonding but a slightly negative shift for Co-NiS₂ NSs (Figure S8). Meanwhile, the extended X-ray absorption fine structure spectroscopy (EXAFS) spectra (Figure 2c) of those NSs were also tested to confirm the change of the coordination structure.^[25,35] The Ni-S bonding is examined as 1.60 Å with a slight differencebut only Co-NiS₂ NSs shows a peak at 2.80 Å relating to Ni-Ni or Ni-Co bond. The different peaks at 2.80 Å further confirm the enhanced coupling between Co and Ni in Co-NiS₂ NSs. Also, the EXAFS wavelet transform (WT) analysis was performed to further prove the atomic dispersion due to its capability of discriminating the backscattering atoms by providing both radial distance resolution and K-space resolution.^[35] In line with the FTs, the WT images of Co-NiS₂, Fe-NiS₂, Cu-NiS₂ and NiS₂ reveal the similar intensity maximum at approximately 4.8 Å⁻¹ (Figure 3d), which is assigned to the Ni–S contributions from the metal sulfide structures. Moreover, an intensity maximum at a higher K-space of 8.8 Å⁻¹ occurs in Co-NiS₂, which is arisen from the Co-Ni path. Meanwhile, a positive shift of the intensity maximum to 8.3 Å⁻¹ in Ni foil is dominated by the Ni-Ni contribution. The coordination configuration in Co-NiS₂ NSs has two backscattering paths: Ni-S and Co-Ni while other NSs only have one backscattering paths of Ni-S. The fitting of the spectrum (Figure S9, Table S2) indicated the main structure Ni-S in the synthesized NSs. The coordination numbers of Co-Ni path was 2.35 in Co-NiS₂ structure. Figure 2e displays the structure and electron change after formed the Co-NiS₂ structure. In the initial structure of NiCoLDH, the Ni²⁺ and Co³⁺ show an electron configuration of $t_{2g}^{6}e_{g}^{2}$ and $t_{2g}^{6}e_{g}^{0}$, respectively. However, the electron transferred during the formation of Co-NiS₂ structure changed the state, in which Ni³⁺ and Co²⁺ exbinit the same electron configuration of $t_{2g}^{6}e_{g}^{1}$. The prepared Co-NiS₂ NSs with optimal e_{g}^{1} electron configuration and enhanced content of Ni³⁺ significantly promote the high HER performance in alkaline media according to the relationship between electrocatalytic activity and d electron configuration in transition metal catalysts.

The electrocatalytic performances of the prepared NSs are evaluated by the linear scan voltammogram (LSV) in N₂-saturated 1.0 M KOH solution at room temperature.^[22,36,37] Figure 4a shows the HER performance of those NSs. As expected, the Co-NiS₂ NSs displays the best HER performance with the onset potential of 30 mV (vs. RHE) and overpotential of 80 mV at the current density of 10 mA cm⁻² much better than those of Cu-NiS₂ (60 mV and 143 mV), Fe-NiS₂ (90 mV and 192 mV) and NiS₂ NSs (100 mV and 172 mV). More importantly, the Co-NiS₂ NSs shows the rapidest current increase in all catalysts. For example, at 250 mV, the Co-NiS₂ NSs exhibits the current density of 235 mA cm⁻², which is much superior than this of Cu-NiS₂ (80 mA cm⁻²), Fe-NiS₂ (27 mA cm⁻²) and NiS₂ NSs (20 mA cm⁻²). Additionally, the Tafel plots (log *j*~ η) were further measured to confirm the HER rate of those catalysts (Figure 4b). The Co-NiS₂ NSs shows the smallest Tafel slope of 43 mV dec⁻¹ than those of Cu-NiS₂ (80 mV dec⁻¹), Fe-NiS₂ (156 mV dec⁻¹) and NiS₂ NSs (135 mV dec⁻¹), demonstrating the fastest HER kinetics on Co-NiS₂ NSs.

Then, the HER performances of those catalysts are compared with the recently reported TMS based catalysts (Figure S10) to further confirm the excellent HER performance of Co-NiS₂ NSs.^[37] In order to compare the initial catalytic performance, the mass activity was measured (Figure 4c and SI). As seen, Co-NiS₂ NSs diplays the highest intrinsic mass activity in those NSs catalysts. In particular, Co-NiS₂ NSs only needs an overpotential of 185.8 mV to get the current of 100 A g⁻¹, which much lower than those of Cu-NiS₂ (256.6 mV), Fe-NiS₂ (376.2 mV) and NiS₂ NSs (364.2 mV). The stability as another important factor for the electrocatalytic reaction is also measured. As shown in Figure 4d, the Co-NiS₂ NSs shows excellent stability for HER at various current densities (10, 20, 50 and 100 mA cm⁻²) for 90 h in alkaline media without any change in morphology and electronic structure that supported by the characterizations of SEM (Figure S11) and XANES (Figure S12). It is well known that the turnover frequencies (TOF), responding to the intrinsic per-site activity of a catalyst, is the best figure of merit for comparing activities among different catalysts.^[29-31] Herein, the TOF per metal site are calculated based on the hypothesis that all the metal atoms in the catalysts formed active site and all of them were accessible to the

electrolyte (SI). Accordingly, the TOF values per metal site of those NSs were calculated. In particular, the TOFs of Co-NiS₂ NSs are 0.55 H₂ per s and 4.1 H₂ per s at overpotentials of 100 and 200 mV, respectively. TOF plots against the applied overpotential are summarized in Figure 4f. The Co-NiS₂ NSs gives a higher TOF at a much lower overpotential than other NSs catalysts. Then, the TOF of Co-NiS₂ NSs was further confirmed with some superior HER catalysts, such as CoN_x -C,^[30b] [Mo₂S₃]² [HOPG,^[30e] MoO₃-MoS₂ NWs,^[31a] Ni-Mo,^[31b] NiP₂,^[29d] Co₁/PCN,^[31c] R-MoS₂@NF,^[31d] and Co-Ni₃N.^[31e] In particular, for the purpose of direct illustration, the boosted HER performance of Co-NiS₂ NSs, the overpotential, mass activity, stability and TOF values of several state-of-the-art non-precious metals HER catalysts are summarized in Table S3. Apparently, the catalytic performance of Co-NiS₂ NSs with optimal e_g^1 electron configuration and enhanced content of Ni³⁺ shows high activity and stability for HER in alkaline media.

In general, the SCN⁻ shows a good coordination ability with metal-sites, especially noble metals. After constructing the coordination bonding with the electrocatalyst metals, the actual electrocatalytic activity are much reduced. Therefore, the introduction of SCN⁻ ions in the alkaline environment is applied to confirm the the catalytic performance of Co-NiS₂ NSs. As shown in Figure 5a, the HER performance of Co-NiS₂ NSs in 1.0 M KOH with 10 mM SCN⁻ shows a serious reduction about 90 % from 235 to 20 mA cm⁻² at the overpotential of 250 mV. However, the other NSs catalysts show a weaker drop for HER performance in SCN⁻ atmosphere (Figure S13). For the strong coordination of SCN⁻ with Ni³⁺, the Co-NiS₂ NSs shows the lowest HER performance in SCN⁻ solution. DFT calculations are applied to demonstrate the catalytic activity after doping from the the electronic properties of intermediates and the overall energetic pathway.^[38] The PDOSs benchmark analysis has been also carried out. The Co-NiS₂ NSs surface shows highly selective to activating the free H₂O molecule and oxidizing the adsorbing H₂O through a strong coupling with the O-2pπ electrons. The adsorbed OH specie denotes a metallic feature and efficient electron transfer for easily de-attaching from the surface (Figure 5b). Then, the energetic pathway of Co-NiS₂ NSs for HER in alkaline media is presented. The transition-state-barrier of H₂O-splitting behavior illustrates the Co-NiS₂ system minimizes the barrier to 0.80 eV from 1.38 eV (pristine surface), as well as more energetic favorable (Figure 5c). The overall pathway consistently indicates the pristine NiS₂ possesses a barrier of 0.21 eV while the Co-NiS₂ NSs for HER in alkaline media.

Conclusion

In summary, we have successfully prepared three transition metal doped ultrathin TMS nanosheet, in which Co-NiS₂ NSs achieves the prominent HER performance in the alkaline media due to the optimized electron configuration and rich Ni³⁺ content. The prepared Co-NiS₂ NSs shows an overpotential of 80 mV at j = 10 mA cm⁻² and long-term stability of 90 h in alkaline HER electrocatalysis. More importantly, the Co-NiS₂ NSs catalysts exhibit spectacular TOFs of 0.55 and 4.1 s⁻¹ at an overpotential of 100 and 200 mV, which is substantially higher than those of previously reported noble-metal free HER catalysts. Furthermore, DFT calculations reveal that the surface Co dopants induce long-ranged sensitization on upshifting Ni-3d bands high lying near the E_F, paving a nearly barrier-free electron-transfer for HER within the alkaline condition. Meanwhile, the pinned surface S-3p bands guarantee a high selectivity of p-p coupling for H₂O splitting with lowest transition barrier. Therefore, this work has presented a promising TMS based electrocatalyst for alkaline HER based on the novel modulation of atomic rearrangement in doping strategy, which supplies critical references in guiding the developments of future multifunctional catalysts.

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Keywords: HER • DFT • metal doped • atomic rearrangement • electron configuration

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Figure 1. The real spatial contour plots for bonding and anti-bonding orbitals near E_F for a) Co-NiS₂ NSs, b) Fe-NiS₂ NSs, and c) Cu-NiS₂ NSs; d) PDOSs of site-dependent of Ni-3d and Co-3d bands on the NiS₂ surface; e) PDOSs of site-dependent of Ni-3d and Fe-3d bands on the NiS₂ surface; g) PDOSs of 3d-bands of Co, Fe, and Cu dopants; h) PDOSs of site-dependent of S-3p bands on the Co-, Fe-, and Cu-doped NiS₂ surface; i) The nearby Ni-3d dominant peak (left vertical axis) modified by Fe, Co, and Cu dopants. The 3d-3p gaps (right vertical axis) between Ni and S sites are shown.



Figure 2. a) TEM images of Cu-NiS₂ NSs, the insert in (a) displays its colloidal properties; b) HRTEM images of Co-NiS₂ NSs. The insert in (b) shows the atomic arrangement of Co-NiS₂ NSs on (100) face; c) HAADF-STEM image of Co-NiS₂ NSs. The insets show the corresponding crystal structure of Co-NiS₂ NSs unit cells taken along the [101] orientation; d) the corresponding FFT patterns for the HAADF-STEM image of Co-NiS₂ NSs; e) Crystal structure of Co-NiS₂ NSs depicting Ni/Co cations as blue spheres and S in orange; Surface intensity and atomic columns simulated by using QSTEM software along f, g) [101] and h, i) [100] zone axes.



Figure 3. a) XANES spectra at Ni L-edge, b) EXAFS spectra in R-space at S K-edge and c) EXAFS spectra in R-space at Ni K-edge of Fe-NiS₂ NSs, Cu-NiS₂ NSs, Co-NiS₂ and NiS₂ NSs; d) Wavelet transforms for the k^3 -weighted Ni K-edge EXAFS signals of Fe-NiS₂ NSs, Cu-NiS₂ NSs, Co-NiS₂, NiS₂ and Ni foil; e) The summarized eg electron change for NiS₂ and Co-NiS₂ NSs.



Figure 4. a) IR-corrected LSV curves and b) the Tafel plots of Fe-Ni-S, Cu-Ni-S, Co-Ni-S and NiS2 NSs for HER in 1.0 M KOH; c) Calculated mass activity of Fe-NiS2 NSs, Cu-NiS2 NSs, Co-NiS2 and NiS2 NSs for HER in 1.0 M KOH; d) Chronoamperometric response of the Co-NiS2 NSs at different current densities for HER; e) TOF plots of Fe-NiS2 NSs, Cu-NiS2 NSs, Co-NiS2 and NiS2 NSs for HER in 1.0 M KOH; f) Compared TOF data with previously reported catalysts.



Figure 5. a) LSV HER curves of the Co-NiS₂ NSs with or without 10 mM KSCN in 1.0 M KOH; b) The PDOSs of O-species (free H₂O, adsorbed H₂O, free OH, adsorbed OH, H, and H₂); c) Comparison of transition state barrier for H₂O-splitting; d) Energetic pathway of HER under alkaline conditions.

RESEARCH ARTICLE

For atoms rearrangement, the prepared Co-NiS₂ NSs with optimal e_{q}^{1} electron configuration and enhanced Ni³⁺ content exhibit excellent activity and stability for HER in alkaline media. DFT results further reveal that the Co-NiS₂ NSs surface abnormally sensitize Ni-3d bands in the long-range order towards higher electron-transfer activity acting as electron-depletion center.



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Page No. – Page No.

Atoms Arrangement in Metal Doped NiS₂ for Boosting Hydrogen Evolution Reaction in Alkaline Media