Supporting Information

Electronic structures modulation of NiS_2 by transition metal doping for accelerating hydrogen evolution reaction

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ΔG_{H*} calculations.

In order to reveal the Gibbs free energy (ΔG_{H*}), which equals to the energy of hydrogen adsorption on the catalyst surface, a surface was cleaved from the crystal and a vacuum space of 15 Å was introduced to avoid interaction between adjacent surfaces. The total hydrogen evolution reaction can be written as $H^+ + e^- \rightarrow 1/2H_2$. The ΔG_{H*} is calculated as $\Delta G_{H*} = \Delta E_H + \Delta E_{ZPE} - T\Delta S_H$, where ΔE_H is the hydrogen chemisorption energy per atom ($\Delta E_H = E_{(surf + H)} - E_{(surf)} - 1/2E_{H2}$). $E_{(surf + H)}$ and $E_{(surf)}$ are the total energy of the surface model with and without H adsorption, respectively. E_{H2} is the energy of a single H_2 molecule isolated in a vacuum. ΔE_{ZPE} is the difference between the zero-point energy of the adsorbed hydrogen and that of the gas phase hydrogen, which can be obtained from vibrational frequency calculation as implemented in VASP. $T\Delta S_H \cong -1/2S_0$, where S_0 is the entropy of H_2 in the gas phase at standard conditions.[1] $T\Delta S_H$ is estimated to be 0.2 eV to consider the entropy change at room temperature. In this work, ΔG_{H*} of the Ni and dopants sites on (001), (110) and (111) surfaces were calculated. For transition metal doped NiS_2, we used one dopant atom to replace one Ni atom at the surface when calculating the H absorption free energy.

Turnover frequency calculations.

In order to know turnover frequency (TOF), we need to calculate electrochemical active surface firstly. Electrochemical capacitance measurements were used to determine the active surface area of each catalyst. We have obtained the electrochemical capacitance value by the cyclic voltammograms for pure $NiSe_2$ and Fe doped $NiSe_2$ catalysts. The specific capacitance can be converted into an electrochemical active surface area (ECSA) using the specific capacitance value for a flat standard with 0.071 cm^2 of real surface area. The specific capacitance for a flat surface is generally found to be in the range of 20-60 $\mu F/cm^2$.[2, 3] In the following calculations of TOF, we assume 40 $\mu F/cm^2$.

The electrochemical active surface area can be calculated.

$$A_{ESCA}^{Fe} = \frac{Electrochemical\ capacitance\ of\ Fe}{40\ \mu F\ cm^{-2}\ per\ cm_{ESCA}^{2}}$$

We calculate the per-site turnover frequency (TOF) via the following formula:

$$\mathrm{TOF} = \frac{\#\text{total hydrogen turn over } /cm^2 geometric\ area}{\#\text{surface sites } /cm^2\ geometric\ area}$$

The total number of hydrogen turn overs was calculated from the current density according to:

$$\#H_2 = \left(j\frac{mA}{cm^2}\right)\left(\frac{1\ C\ s^{-1}}{1000\ mA}\right)\left(\frac{1\ mol\ e^-}{96485.3\ C}\right)\left(\frac{1\ mol\ H_2}{2\ mol\ e^-}\right)\left(\frac{6.022\times 10^{23}\ H_2\ molecules}{1\ mol\ H_2}\right)$$

$$= 3.12\times 10^{15}\frac{H_2/s}{cm^2}\ per\ \frac{mA}{cm^2}$$

Since the exact hydrogen binding sites are not known, we conservatively estimate the number of active sites as the total number of surface sites (including both the transition metal and Ni atoms as possible active sites) from the roughness factor together with the unit cell of the Fe doped NiS_2.

surface sites per real surface area (here calculated for NiS_2):

$$\#surface\ sites = \left(\frac{4 \frac{atoms}{unit} cell}{\frac{170.89\ \text{Å}^3}{unit} cell} \right)^{\frac{2}{3}} = 7.1827 \times 10^{14}\ atoms\ cm^{-2}$$

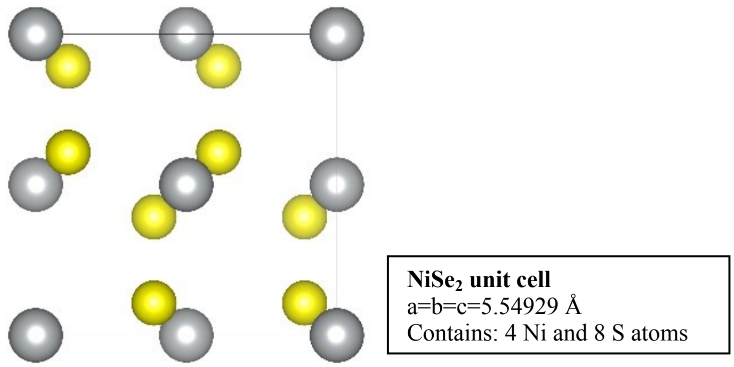

Figure S1. NiS_2 unit cell. Ni: gray and S atoms: yellow.

Finally, the plot of current density can be converted into a TOF plot according to:

$$\mathrm{TOF} = \frac{(3.12 \times 10^{15} \frac{H_2/s}{cm^2} per \frac{mA}{cm^2}) \times |j|}{\#surface\ sites \times A_{ESCA}^{Fe}}$$

Where j is current density obtained from the polarization curve, A_{ESCA}^{Fe} has been calculated above.

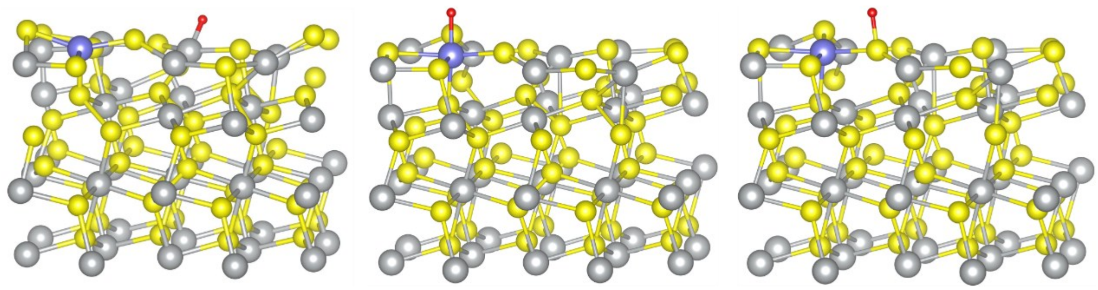

Figure S1. The optimized structures of Fe-doped NiS_2 (100) surface with H adsorbed on the Fe, Ni, and S sites. The gray, yellow, violet and red balls represent Ni, S, Fe and H atoms, respectively.

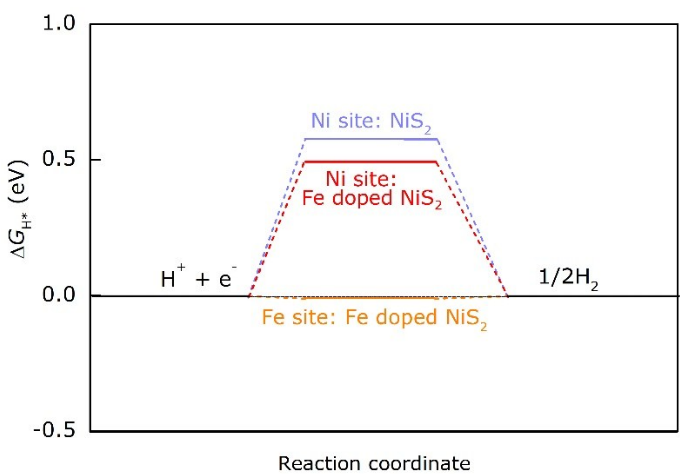

Figure S2. The diagram of ΔG_{H*} at Fe and Ni sites on the (110) surface of NiS_2 and Fe-doped NiS_2.

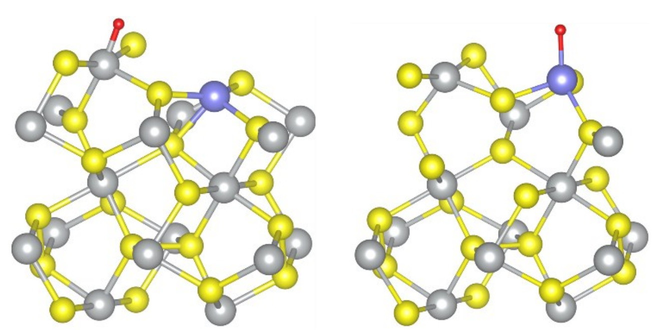

Figure S3. The optimized structures of Fe-doped NiS_2 (110) surface with H adsorbed on the Fe and Ni sites. The gray, yellow, violet and red balls represent Ni, S, Fe and H atoms, respectively.

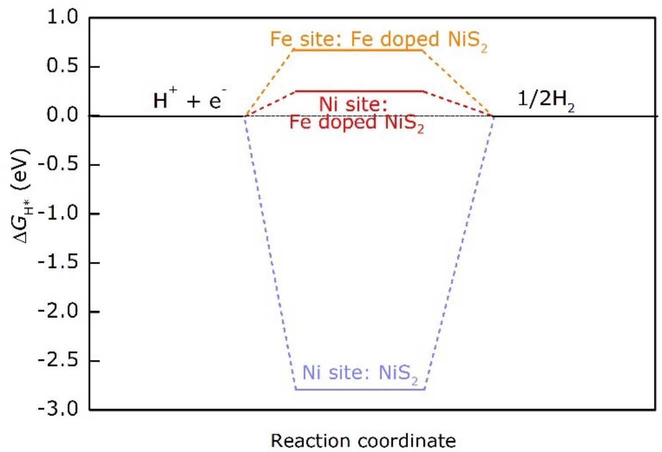

Figure S4. The diagram of ΔG_{H*} at Fe and Ni sites on the (111) surface of NiS_2 and Fe-doped NiS_2.

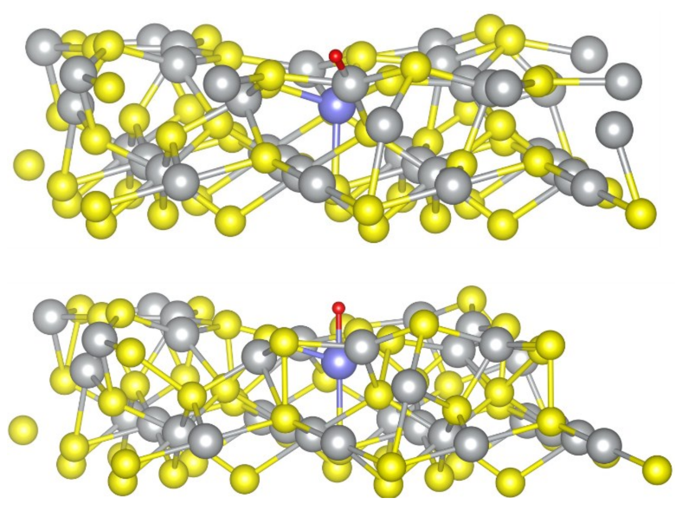

Figure S5. The optimized structures of Fe-doped NiS_2 (111) surface with H adsorbed on the Fe and Ni sites. The gray, yellow, violet and red balls represent Ni, S, Fe and H atoms, respectively.

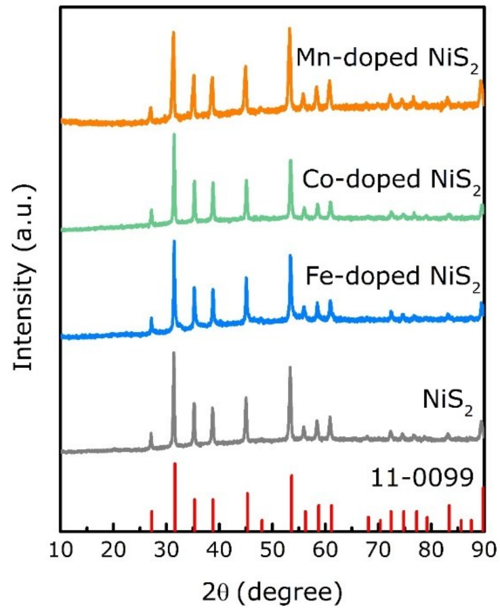

Figure S6. XRD patterns of bare NiS_2 and NiS_2 doped with Fe, Co, and Mn.

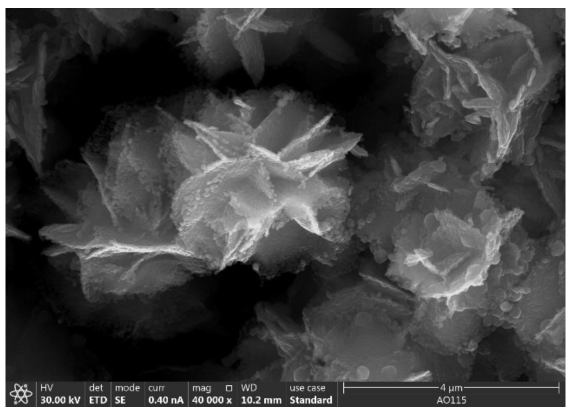

Figure S7. SEM image of Co-doped NiS_2.

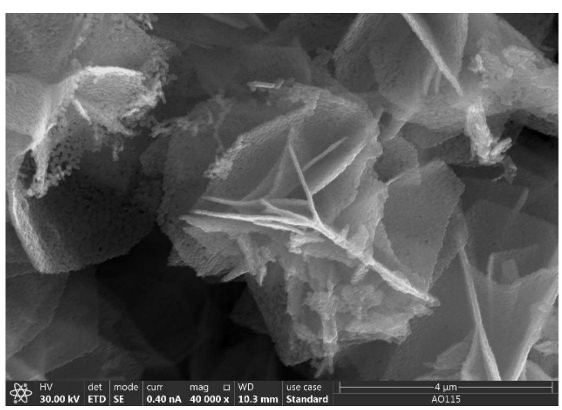

Figure S8. SEM image of Mn-doped NiS_2.

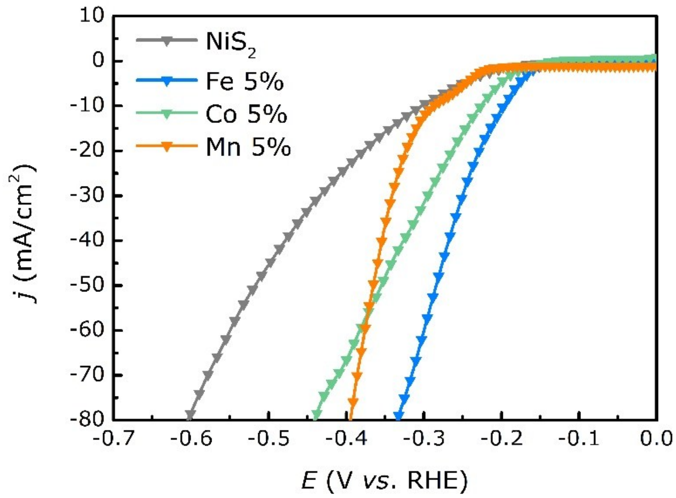

Figure S9. Linear sweep voltammetry curves of bare NiS_2 and NiS_2 doped with Fe, Co, and Mn.

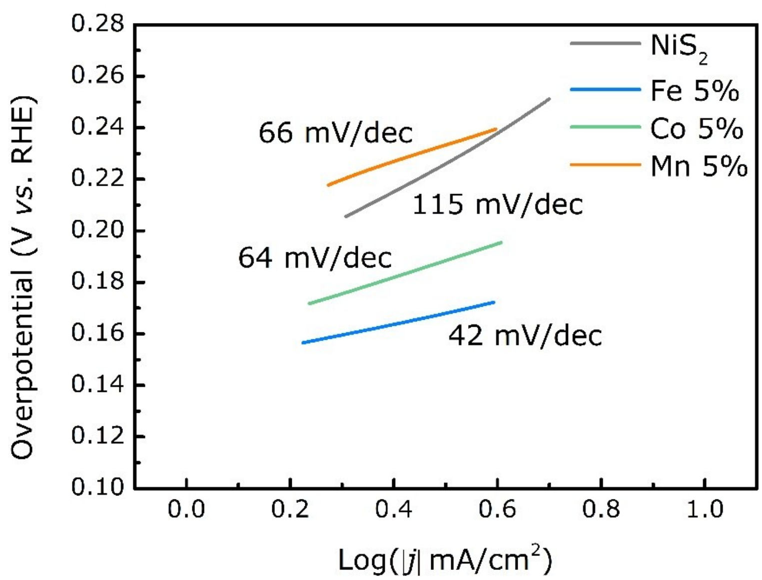

Figure S10. Tafel plots of bare NiS_2 and NiS_2 doped with Fe, Co, and Mn.

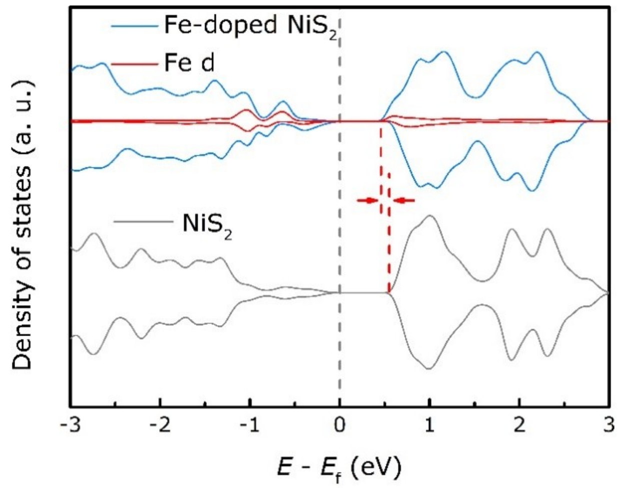

Figure S11. PDOS of Fe-doped NiS_2.

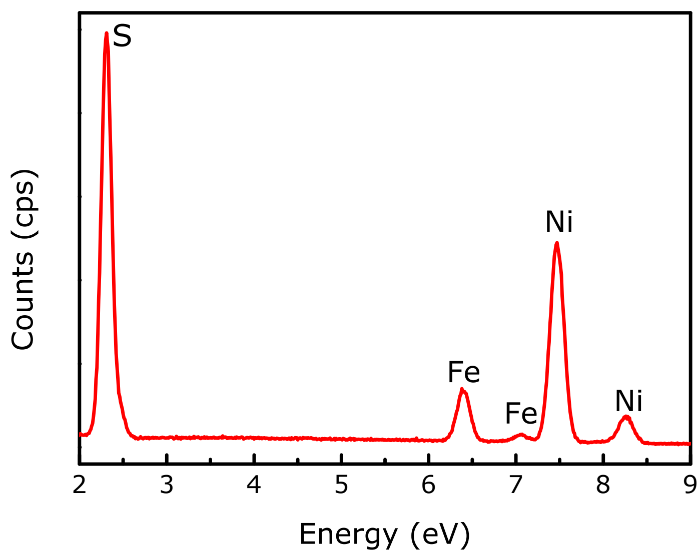

Figure S12. EDS spectrum of Fe-doped NiS_2.

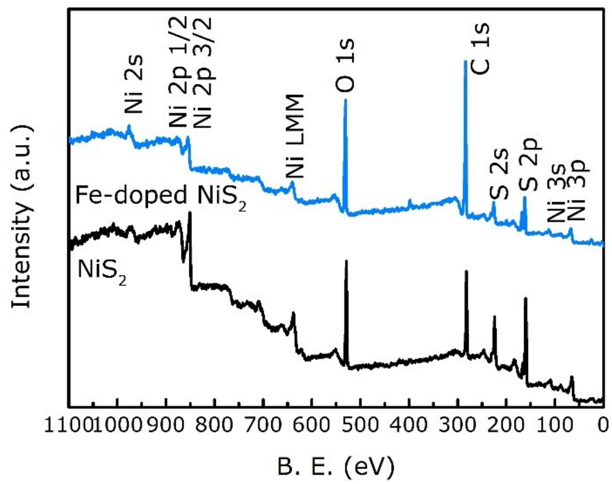

Figure S13. XPS survey spectrum of Fe-doped NiS_2 and NiS_2.

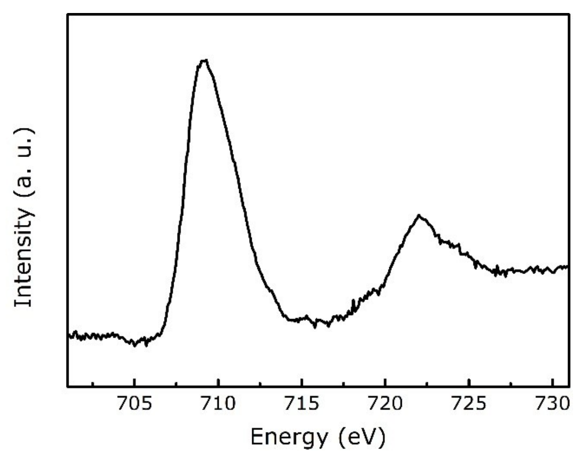

Figure S14. XAS curve of Fe L-edge of Fe-doped NiS_2.

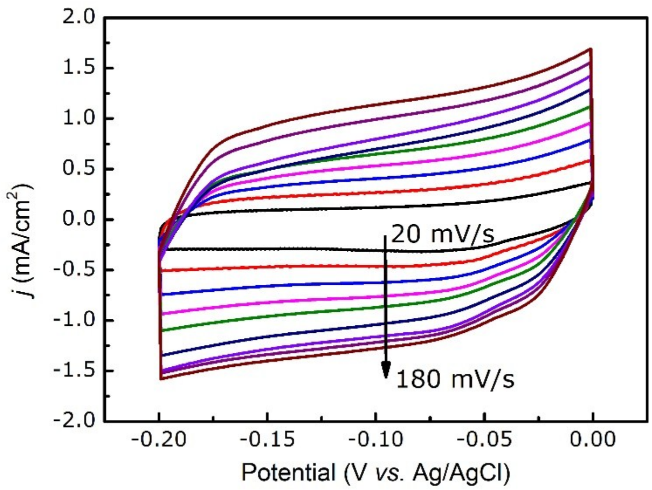

Figure S15. CV curves of NiS_2.

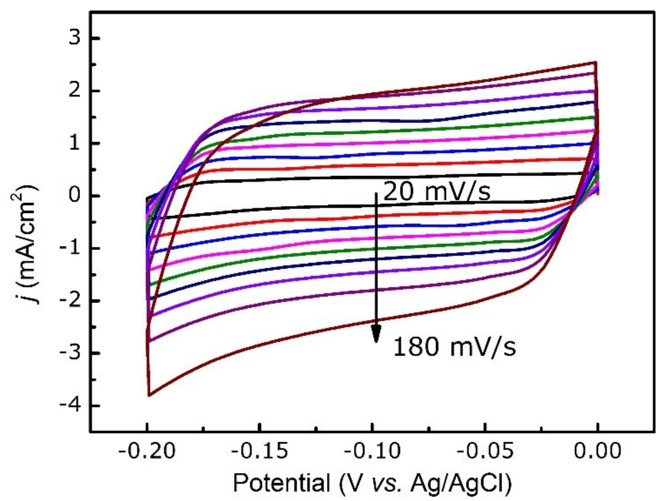

Figure S16. CV curves of Fe-doped NiS_2.

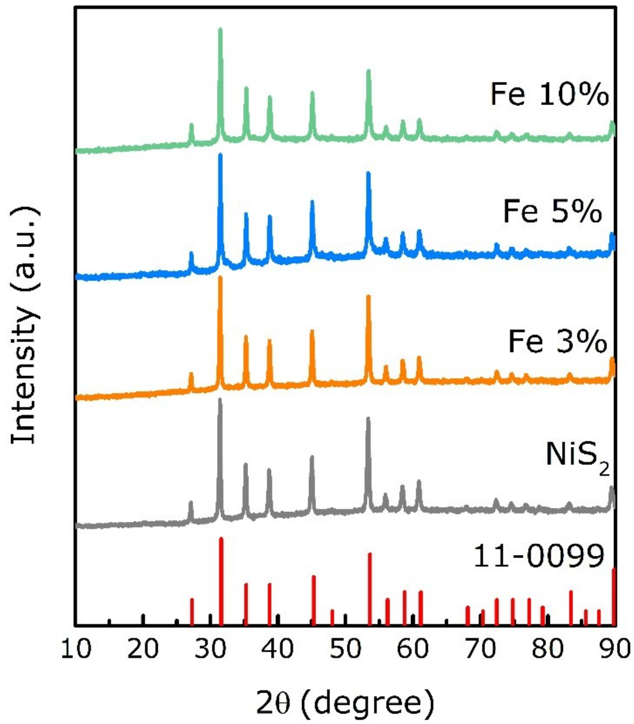

Figure S17. XRD patterns of NiS_2 doped with Fe at different doping amounts.

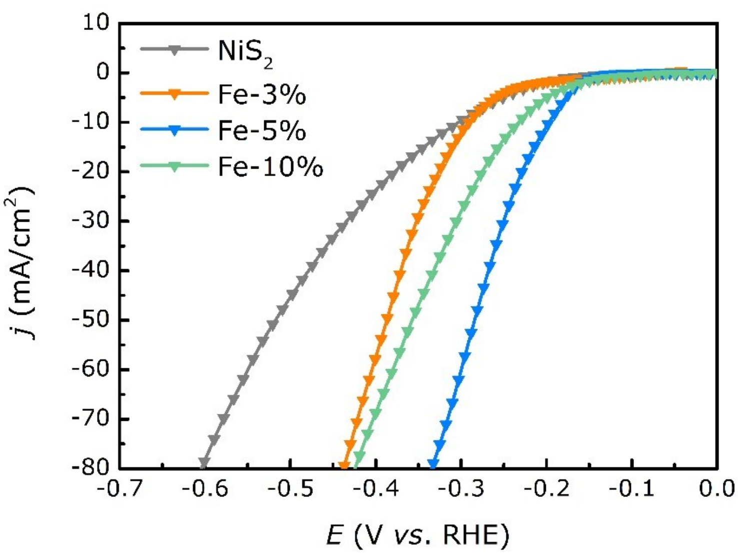

Figure S18. Linear sweep voltammetry curves of NiS_2 doped with Fe at different doping amounts.

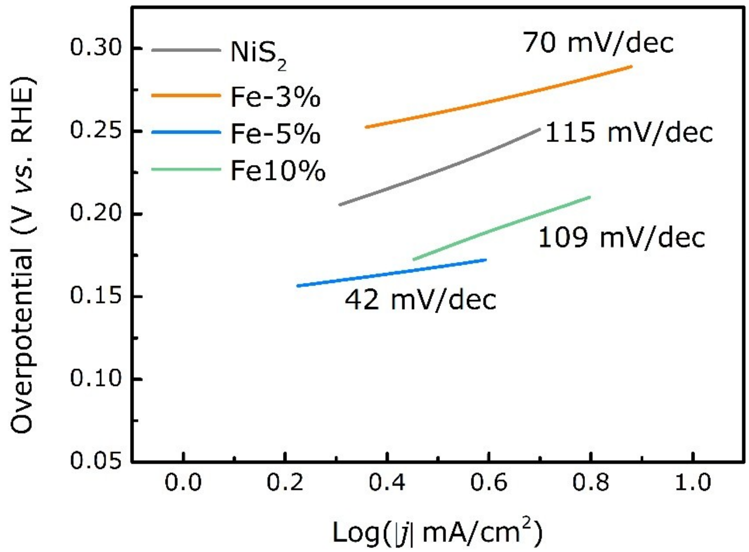

Figure S19. Tafel plots of NiS_2 doped with Fe at different doping amounts.

References

1. J. K. Nørskov, T. Bligaard, A. Logadottir, J. R. Kitchin, J. G. Chen, S. Pandelov and U. Stimming, *J. Electrochem. Soc.*, 2005, **152**, J23.
2. B. E. Conway and B. V. Tilak, *Electrochim. Acta*, 2002, **47**, 3571-3594.
3. J. D. Benck, Z. Chen, L. Y. Kuritzky, A. J. Forman and T. F. Jaramillo, *ACS Catal.*, 2012, **2**, 1916-1923.