Supporting information

Fe (Ⅲ) doped NiS_2 nanosheet: A highly efficient and low-cost hydrogen evolution catalyst

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DFT calculations

DFT calculations were performed with program package DMol in Materials Studio of Accelrys Inc. The exchange-correlation energy was treated by the Perdew-Burke-Ernzerhof (PBE) functional based on the generalized gradient approximation (GGA) [1]. In order to consider dispersion force, a semiempirical DFT-D2 method proposed by Grimme was exploited. [2] The NiS_2 (002) was cleaved from the optimized bulk Pd and PdZn alloy. The surface was modeled using a (1 × 1) surface unit cell with eight atomic layers, separated by 10 Å of vacuum. The Fe-doped NiS_2 (002) was constructed by replacing one Ni atom on surface with Fe atom. The reciprocal space was sampled with a (5 × 5 × 1) k-points grid generated automatically using the Monkhorst–Pack method. [3] Full-geometry optimization was performed for all relevant adsorbates and the uppermost three layers without symmetry restriction, while the bottom layer metal atoms were fixed at the bulk-truncated positions at the calculated lattice constants. Transition state (TS) searches were performed with the complete LST/QST method implemented in DMol. [4]

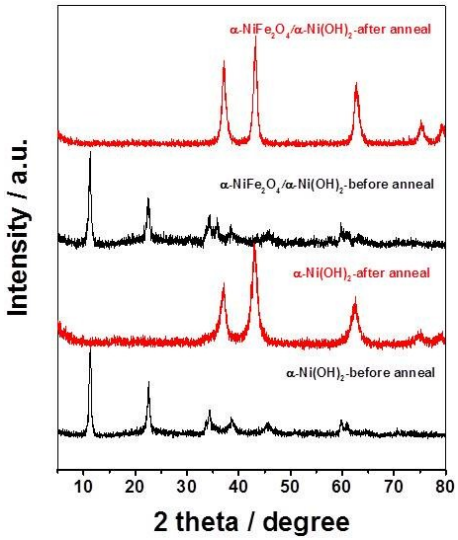

Figure S1. XRD patterns of the used precursor and the results after 400deg anneal under N_2 atmosphere without sulfur powder.

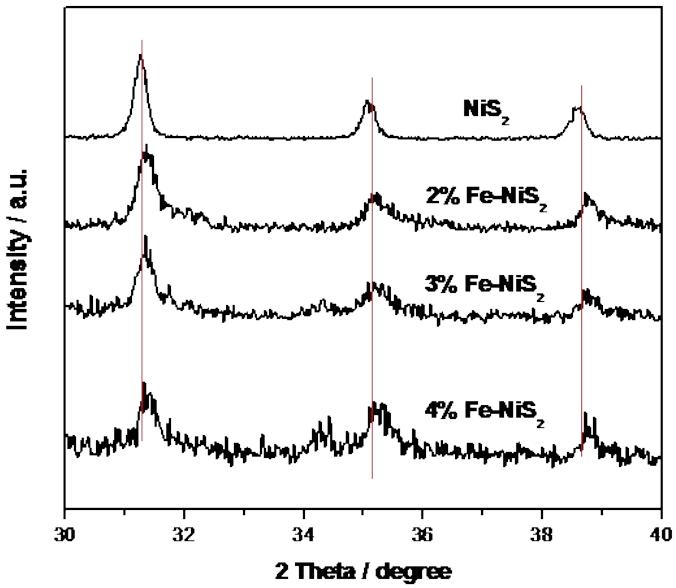

Figure S2. The magnified XRD patterns of the Fe doped and bare NiS_2 at 2 theta from 30 to 40 degree.

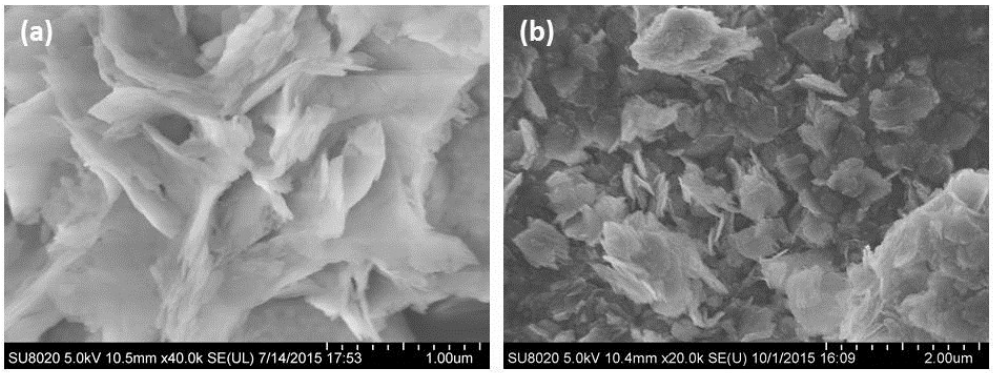

Figure S3. SEM images of the used precursor (a) $Ni(OH)_2$, (b) $NiFe_2O_4/Ni(OH)_2$.

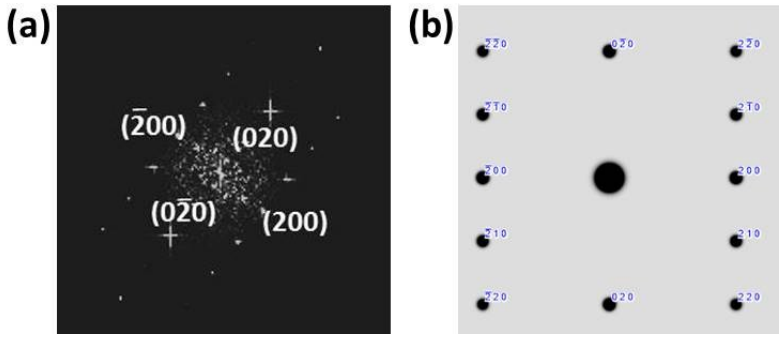

Figure S4. (a) FFT result of the HRTEM of NiS_2 in Figure 2 (g); (b) the simulated FFT result with the (020) facet.

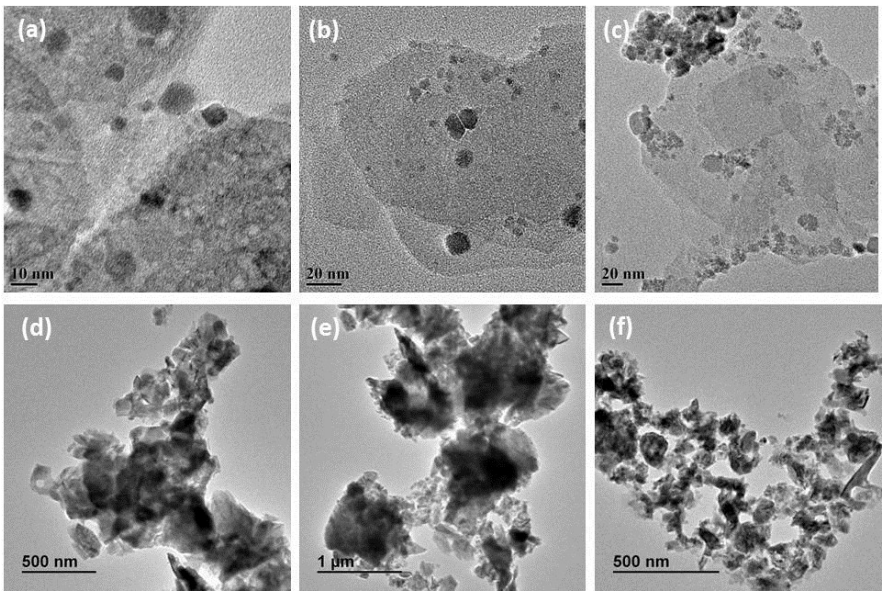

Figure S5. (a) and (d) TEM image before and after sulfurization of sample (1), which was synthesized from 4% Fe; (b) and (e) TEM image before and after sulfurization of sample (2), which was synthesized from 3% Fe; the sulfur is 50 mg; (c) and (f) TEM image before and after sulfurization of sample (2); which was synthesized from 3% Fe.

Table S1 The full width at half maximum (FWHM) **o**f Ni 2p XPS of NiS_2 and Fe-NiS_2.

Sample	Position / eV	FWHM / eV	Position / eV	FWHM / eV
NiS_2	852.9	1.7	870.4	2.3
Fe-NiS_2	852.9	2.5	870.4	2.8

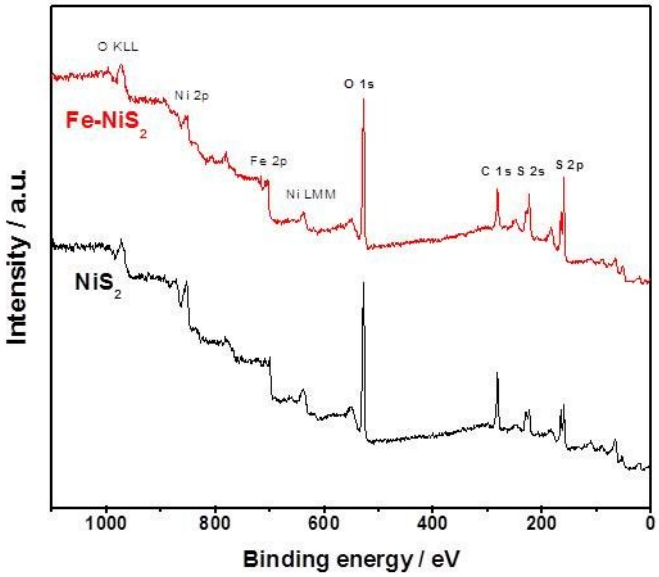

Figure S6. The wide XPS spectra of NiS_2 and Fe-NiS_2 sample.

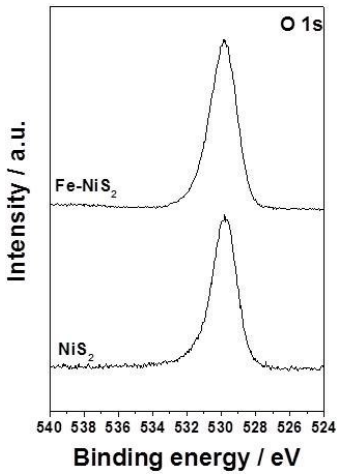

Figure S7. The O 1s XPS spectra of NiS_2 and Fe-NiS_2 sample.

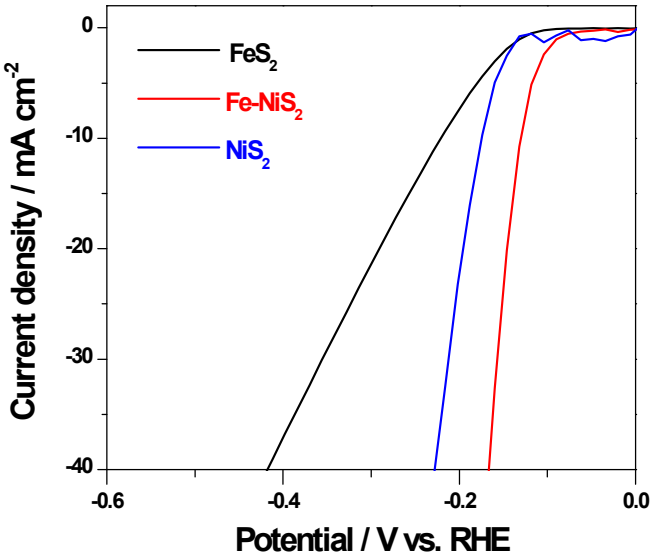

Figure S8. The HER performance of FeS_2, NiS_2 and Fe-NiS_2. 0.5 M H_2SO_4 was used as the electrolyte, the scan rate was 2mv/s.

Table S2 The relative content **o**f Fe element obtained from XPS, EDS and ICP methods. Fe/Ni (mole ratio) / %

Sample	XPS	TEM-EDS	ICP
1% Fe-NiS_2	0.98	0.99	0.99
2% Fe-NiS_2	2.02	2.02	1.99
3% Fe-NiS_2	2.98	2.99	3.02
4% Fe-NiS_2	3.97	4.02	3.99
5% Fe-NiS_2	4.97	5.00	4.98

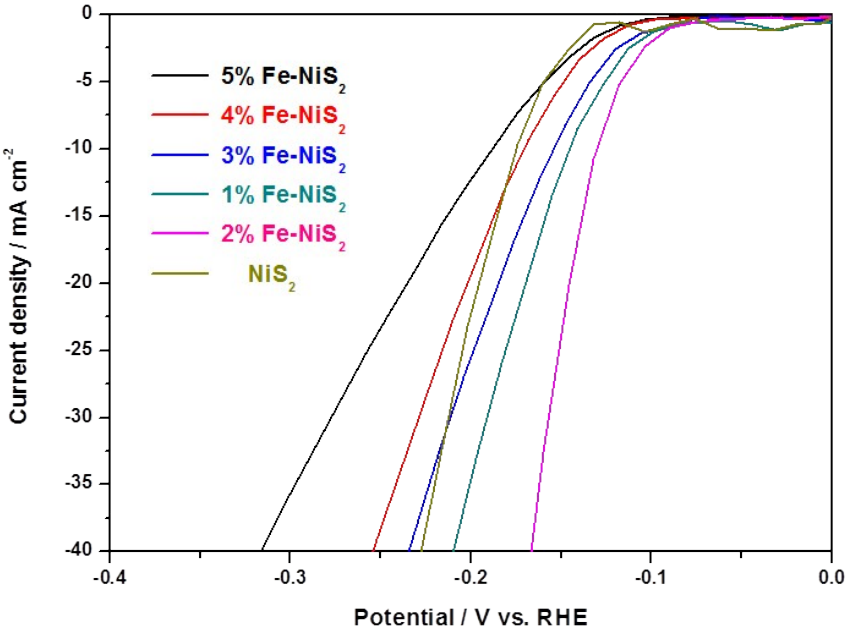

Figure S9. The polarization curves of the Fe-NiS_2 samples with the different Fe doping. 0.5 M H_2SO_4 was used as the electrolyte, the scan rate was 2mv/s.

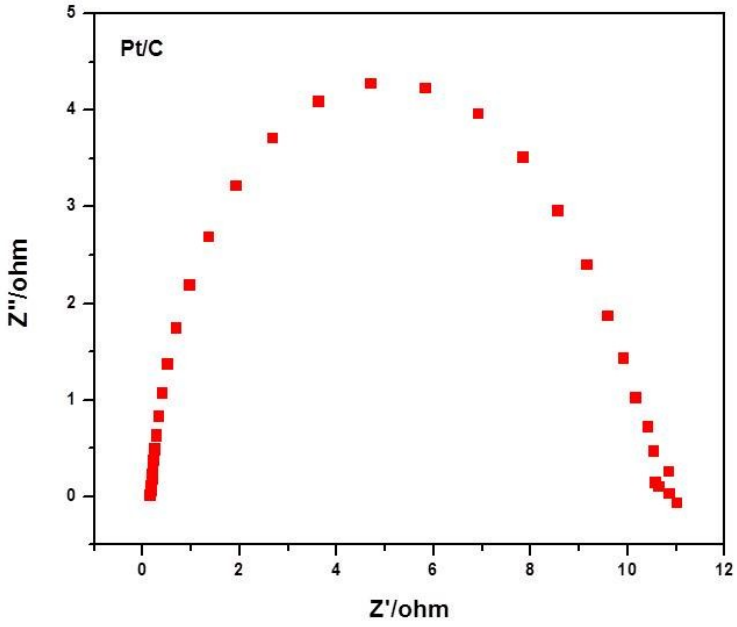

Figure S10. The electrochemical impedance spectra (EIS) of reference Pt/C electrode.

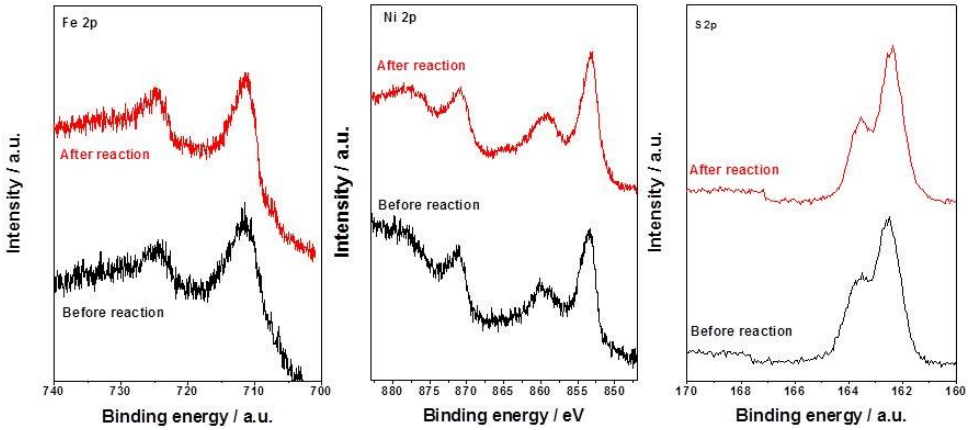

Figure S11. XPS curves of Fe 2p, Ni 2p and S 2p of the Fe-NiS_2 before and after reaction.

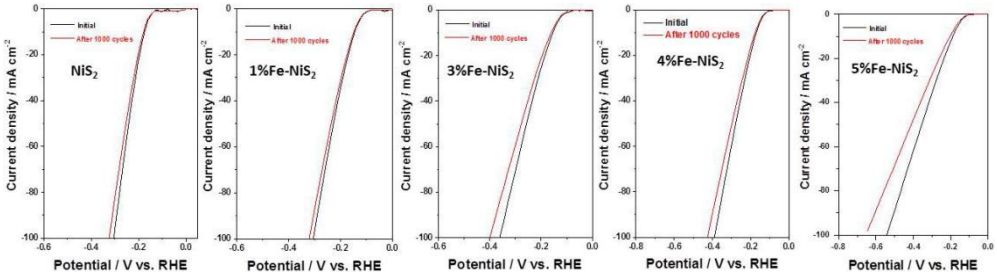

Figure S12. The stability performance of NiS_2 and other Fe doped NiS_2 samples.

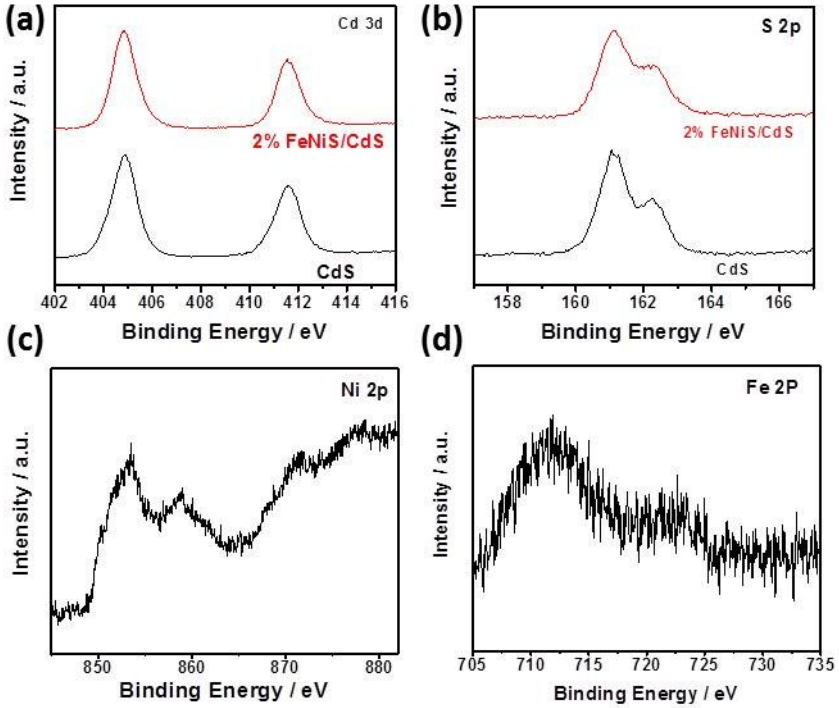

Figure S13. XPS curves of (a) Cd 3d, (b) S 2p, (c) Ni 2p and (d) Fe 2p of the FeNiS/CdS and bare CdS under study.

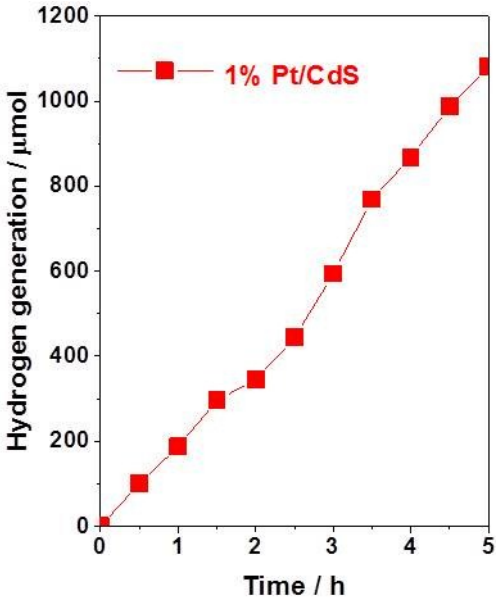

Figure S14. Photocatalytic H_2 evolution of the 1% Pt/CdS catalyst, impregnation method was carried out for the Pt loading and then through hydrogen reduction process for the Pt/CdS formation.

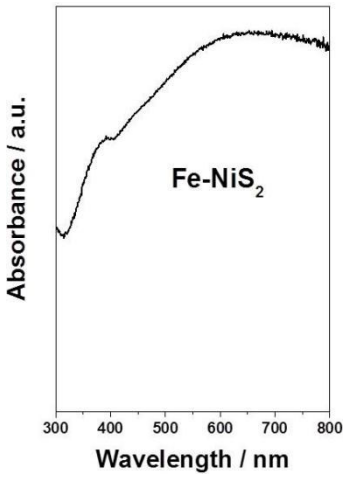

Figure S15. UV-Vis diffuse reflectance spectra of Fe-NiS_2 under study.

Reference

[1] J. P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett., 1996, 77, 3865.

[2] S. Grimme, J. Comput. Chem., 2006, 27, 1787.

[3] H. J.Monkhorst and J. D. Pack, Phys. Rev. B: Solid State, 1976, 13, 5188.

[4] T. A. Halgren and W. N. Lipscomb, Chem. Phys. Lett., 1977, 49, 225.