Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting information for

Intermediate bands of MoS_2 enabled by Co doping for enhanced hydrogen evolution

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1. Theoretical calculation details

Theoretical calculations have been performed within the framework of density functional theory (DFT) as implemented by the Vienna an initio Simulation Package (VASP)[S1, S2]. The exchange-correlation energy was treated in the generalized-gradient approximation (GGA) using Perdew-Burke-Ernzerhof (PBE)-D2 method[S3] that includes vdW interactions. The $Co_{0.03}Mo_{0.97}S_2$ model was approximate constructed on the 3×3×2 supercell with 1 Co substituted in $Mo_{36}S_{72}$. The cutoff energy of plane wave was chosen at 400 eV. For the structure optimizations, 6×6×4 Monkhorst-Pack (MP) grids were used. The changes in total energies between two successive iteration steps were less than 10^{-5} eV, and all the Hellmann-Feynman force acting on each atoms was lower than 0.01 eV /Å.

References

[S1] P. E. Bl$\ddot{o}$chl, Phys. Rev. B 1994, 50, 17953.

[S2] G. Kresse, and J. Furthm$\ddot{u}$ller, Phys. Rev. B 1996, 54, 11169.

[S3] M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias, J. D. Joannopoulos, Rev. Mod. Phys. 1992, 64, 1045−1097.

2. Supplementary Figures

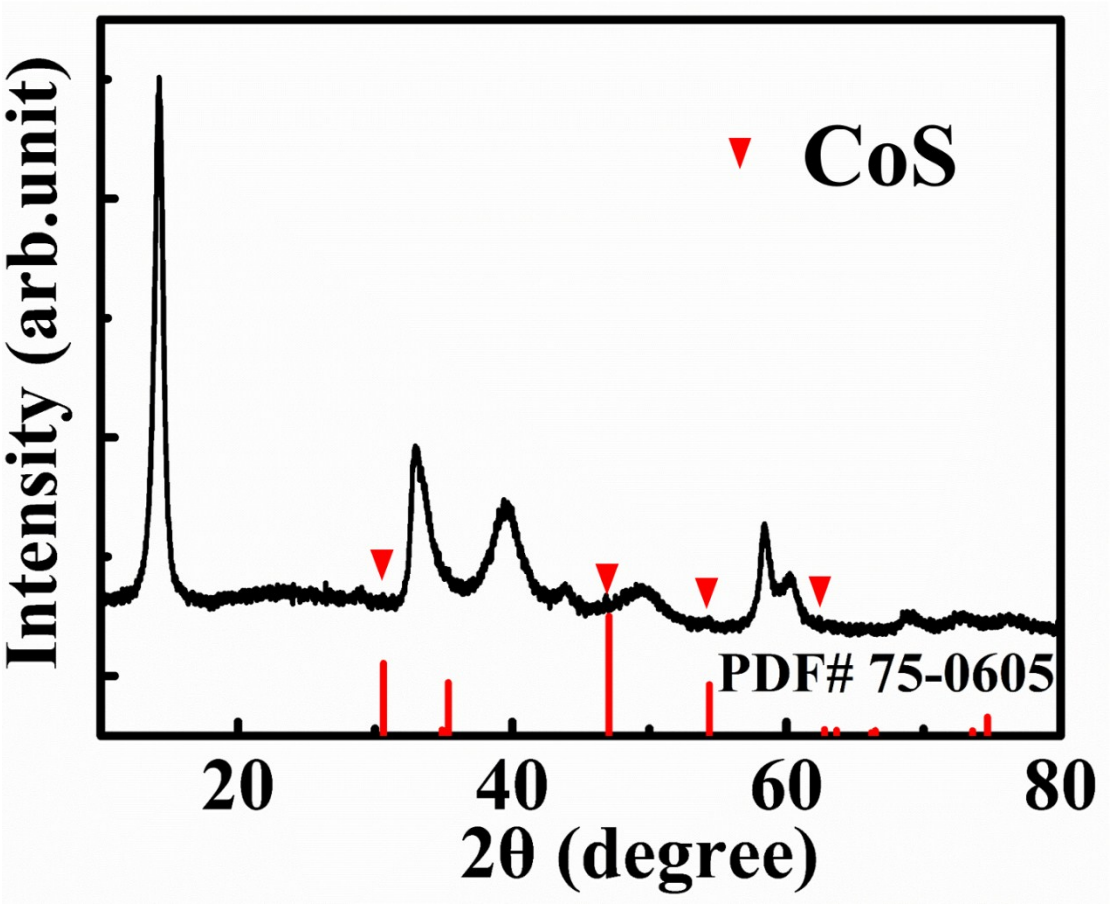

Figure S1. Powder XRD pattern of $Co_xMo_{1-x}S_2$ of **Route Ⅱ**.

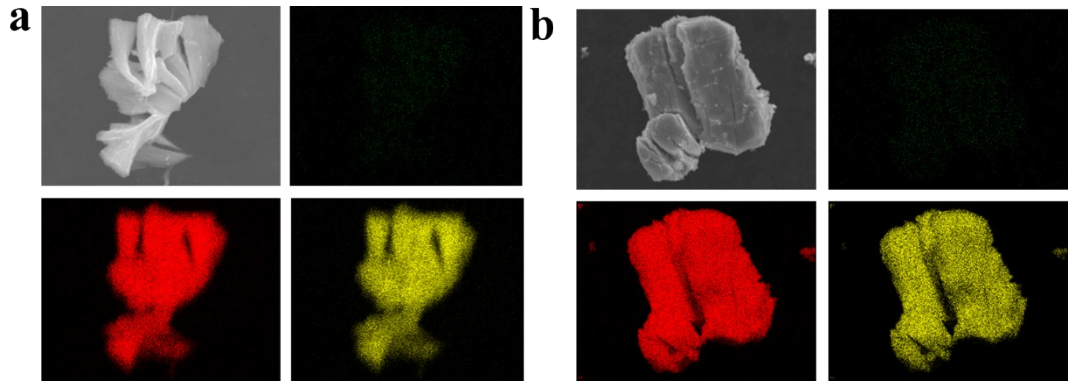

Figure S2. EDX analysis of Fe/Ni doped MoS_2 through **Route Ⅰ. a,** Fe doped MoS_2; **b,** Ni doped MoS_2.

Spectrum 28		
Element	Weight%	Atomic%
S	57.49	71.31
Co	42.51	28.69
Mo	0	0
Spectrum 30		
Element	Weight%	Atomic%
S	39.89	66.51
Co	0	0
Mo	60.11	33.49

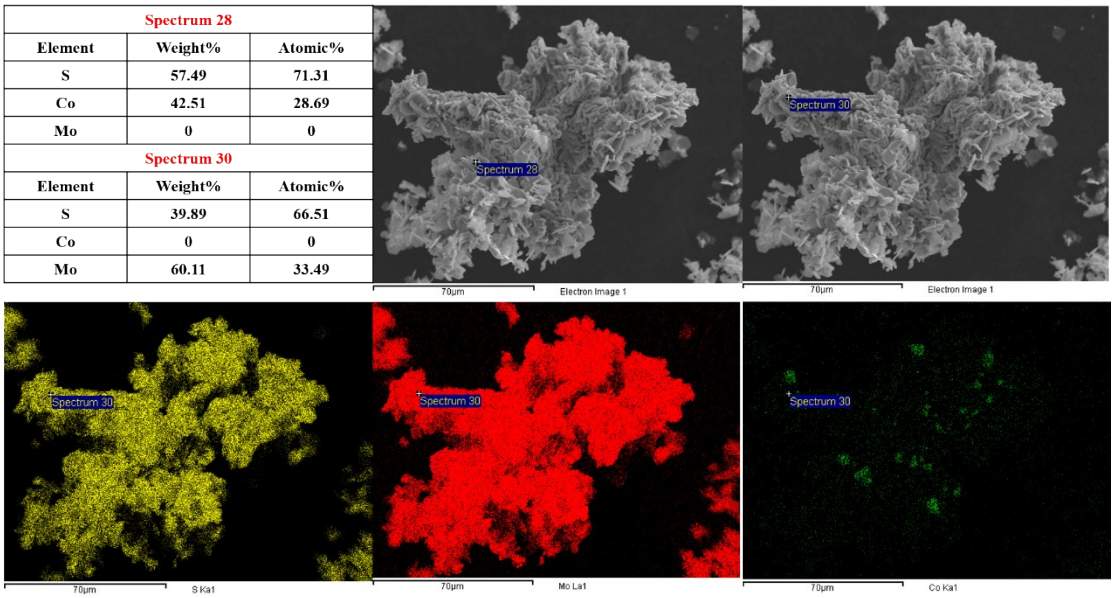

Figure S3. EDX analysis of $Co_xMo_{1-x}S_2$ through **Route Ⅱ**.

Table S1

	overpotential	Tafel slope	Reference
Co doped MoS_2 nanofilm	300 mV at 3.5 mA·cm^{-2}	110	1
Co doped amorphous MoS_3 film	200 mV at 20 mA·cm^{-2}	43	2
Co doped MoS_2 nanosheets	200 mV at 60 mA·cm^{-2}	38	3
Co-MoS_3 hollow structure	171 mV at 10 mA·cm^{-2}	57	4
Ni–Co–MoS_2 Nanoboxes	155 mV at 10 mA·cm^{-2}	51	5
$CoMoS_x$ clusters	240 mV at 6 mA·cm^{-2}	-	6
This work	357 mV at 10 mA·cm^{-2}	120	

Reference

1. H. T. Wang, C. Tsai, D. S. Kong, K. R. Chan, F. Abild-Pedersen, J. Norskov, Y. Cui, *Nano. Res.* **2015**, *8*, 566-575

2. D. Merki, H. Vrubel, L. Rovelli, S. Fierro, X. L. Hu, *Chem. Sci.* **2012**, *3*, 2515-2525

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4. Yu, L., Xia, B. Y., Wang, X., Lou, X. W., *Adv. Mater.* **2016**, *28*, 92-97

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