Supporting Information

Highly Efficient Electrocatalytic Hydrogen Production by Nickel promoted Molybdenum Sulfide microspheres Catalysts

Xiao-Jun Lv*[a], Guang-Wei She[a], Shi-Xiong Zhou[a] and Yue-Ming Li*[b]

[a]Key Laboratory of Photochemical Conversion and Optoelectronic Materials and HKU-CAS Joint Laboratory on New Materials, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, P.R. China

[b]State Key Laboratory of Metastable Materials Science and Technology, College of Material Science and Engineering, Yanshan University, Qinhuangdao 066004, China

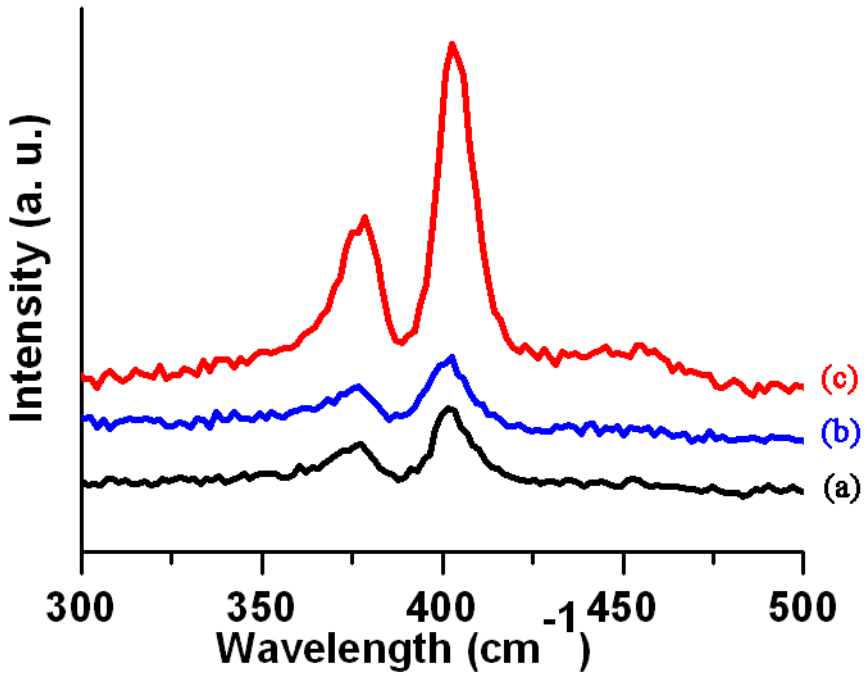

Figure S1. Raman spectrum of undoped MoS_2 (curve a), Nickel doped MoS_2 (NM1, curve b; NM2 curve c)

As shown in Figure S1, two characteristic Raman active modes for undoped and Ni doped MoS_2 (E_{2g}^1 and A_{1g}) are present in the spectrum. There is negligible change for undoped MoS_2 and Ni-doped MoS_2 in Raman spectrum. The A1g mode involves the S atoms vibration along the *c* axis, and the E_{2g}^1 is attributed to the vibration of Mo and S atoms in the basal plane. The peak values for doped MoS_2 are close to that of MoS_2 nanostructures reported.[1]

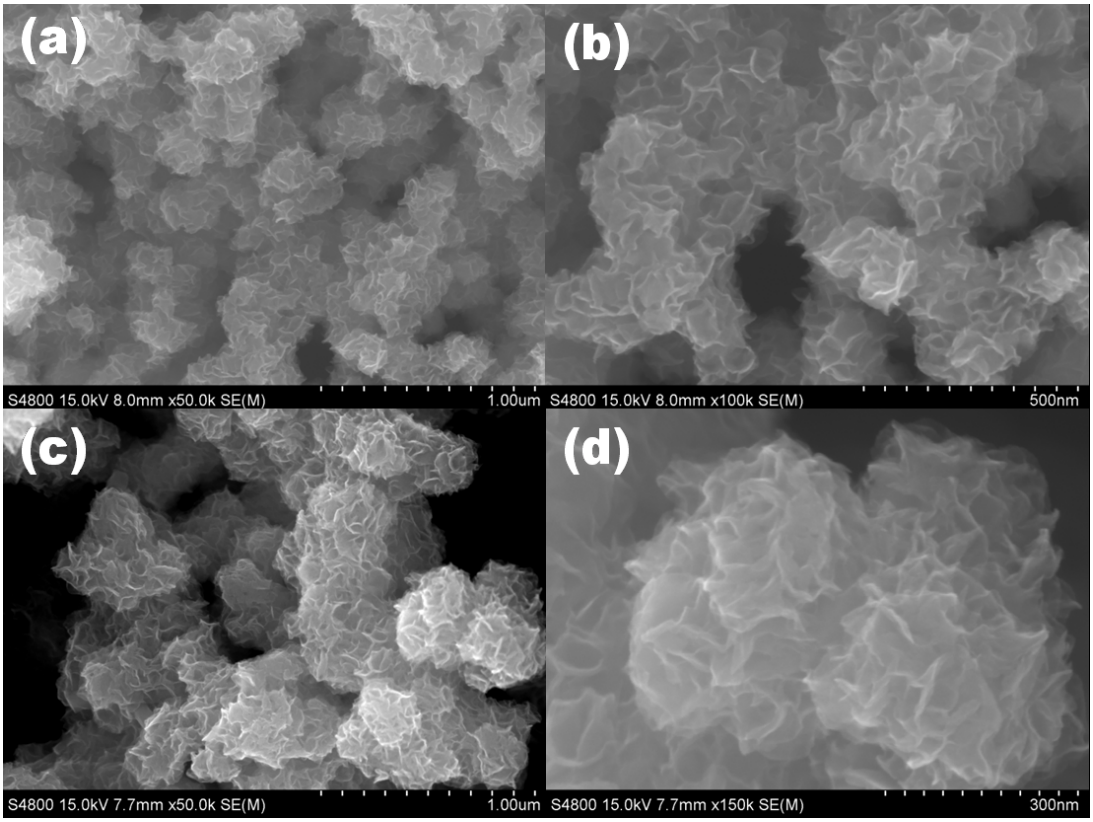

Figure S2. SEM image of NM1 (Mo: Ni = 40:1) at different magnification (a) low magnification and (b) high magnification; SEM image of NM3 (Mo: Ni = 10:1) at different magnification (c) low magnification and (d) high magnification;

Table S1. the comparison of the Ohmic resistance as measured with different content Ni promoted MoS_2 electrodes

Sample	Resistance values (Ω)
unpromoted MoS_2	25.3 ± 1.0
NM1 (Mo:Ni = 40:1)	13.1 ± 1.0
NM2 (Mo:Ni = 20:1)	10.0 ± 0.5
NM3 (Mo:Ni = 10:1)	15.6 ± 0.3

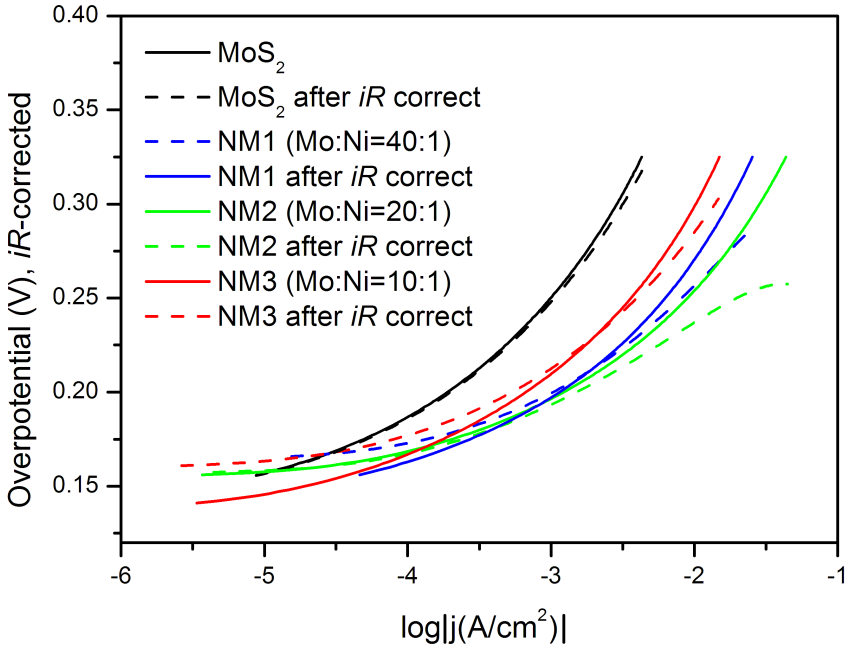

Figure S3. Tafel Plot of MoS_2 electrodes before and after *iR* correct with the different nickel doping content. NM1 (Mo: Ni = 40:1), NM2 (Mo: Ni = 20:1), NM3 (Mo: Ni = 10:1)

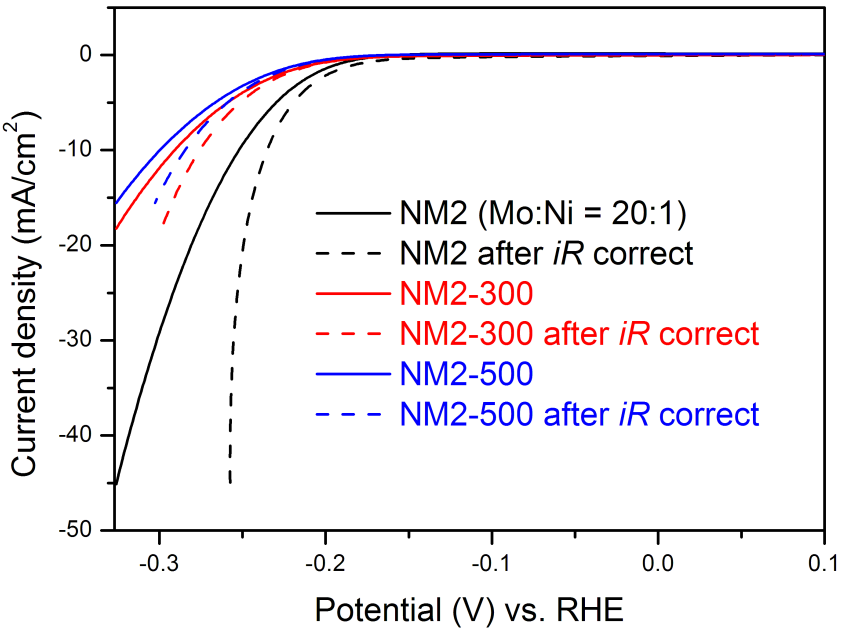

Figure S4. Polarization curves of heat-treated Ni-doped MoS_2 (NM2 (Mo: Ni = 40:1)) at varied temperatures (black line, as prepared sample, red line, heat-treated at 300 ^{o}C; blue line heat-treated at 500 ^{o}C).

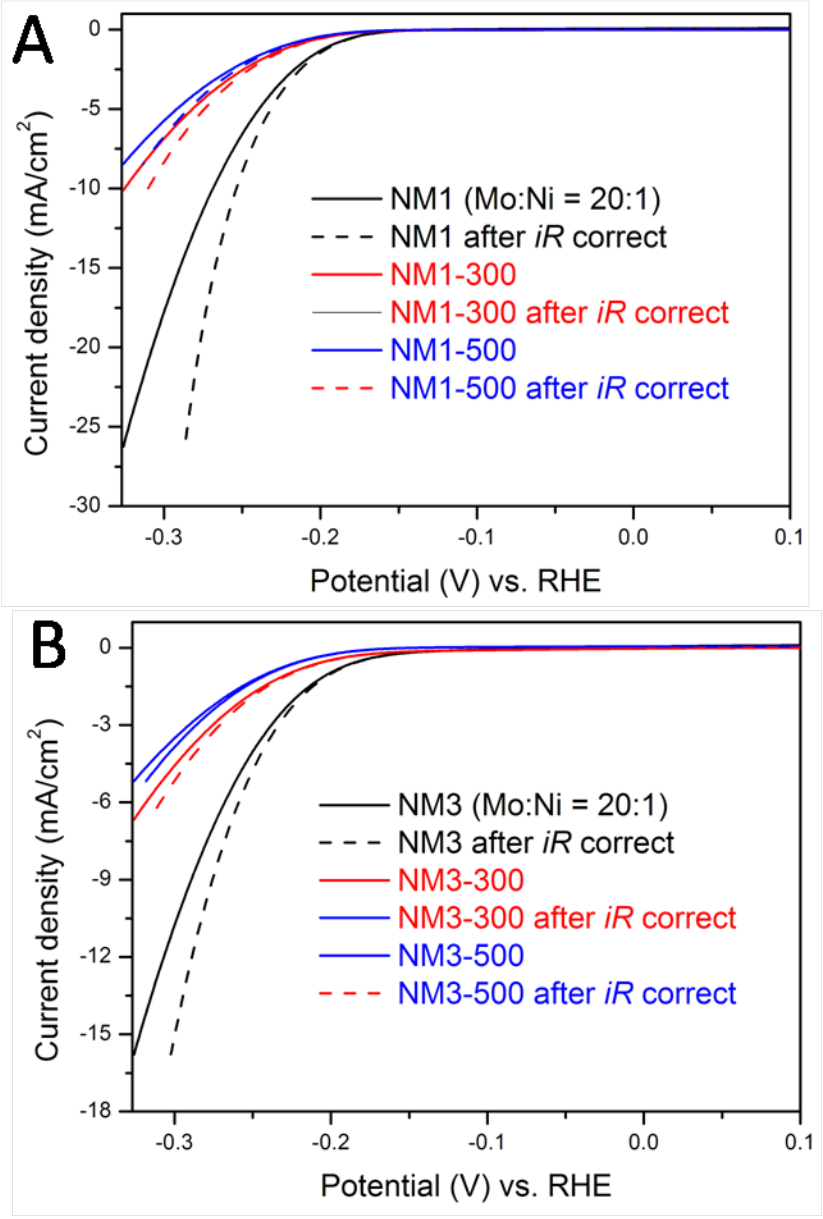

Figure S5. Comparison of polarization curves for the different electrocatalyst before and after annealed treatment with different temperature (300 ^{o}C and 500 ^{o}C): (A) the NM1 (Mo: Ni = 40:1), (B) the NM3 (Mo: Ni = 10:1).

References:

(1) (a) W. K. Hsu, Y. Q. Zhu, N. Yao, S. Firth, R. J. H. Clark, H. W. Kroto and D. R. M. Walton, *Adv. Funct. Mater.* 2001, **11**, 69; (b) J. L. Verble and T. J. Wieting, *Phys. Rev. Lett.* 1970, **25**, 362.