# Electronic Supplementary Information

## Controlled Synthesis of Mo-doped $Ni_3S_2$ Nano-rod: an Efficient and Stable Electro-catalyst for Water Splitting

Zheng Cui[1], Yuancai Ge[1], Hang Chu[1], Robert Baines[2], Pei Dong[2], Jianhua Tang[1], Yang Yang[1], Pulickel M. Ajayan[2], Mingxin Ye[1*], Jianfeng Shen[1*]

[1] Institute of Special Materials and Technology, Fudan University, Shanghai, 200433, P. R. China

[2] Department of Materials Science and NanoEngineering, Rice University, 6100 Main Street, Houston, TX 77005, USA

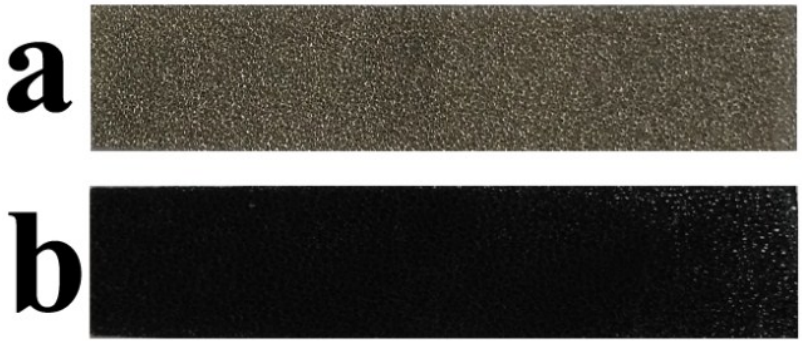


**Figure S1.** Digital images of electrode surface of 200-SMN/NF (a) before and (b) after hydrothermal process.

Figure S1 shows digital images of the Ni foam surface before and after Mo-doped $Ni_3S_2$ growth through the one-step hydrothermal method. The original color of the Ni foam electrode is brown (Figure S1a); once the Mo-doped $Ni_3S_2$ nano-rod arrays grow on the Ni foam electrode, the foam surface becomes completely black (Figure S1b). This change in color indicates the complete and uniform formation of Mo-doped $Ni_3S_2$ on the Ni foam.

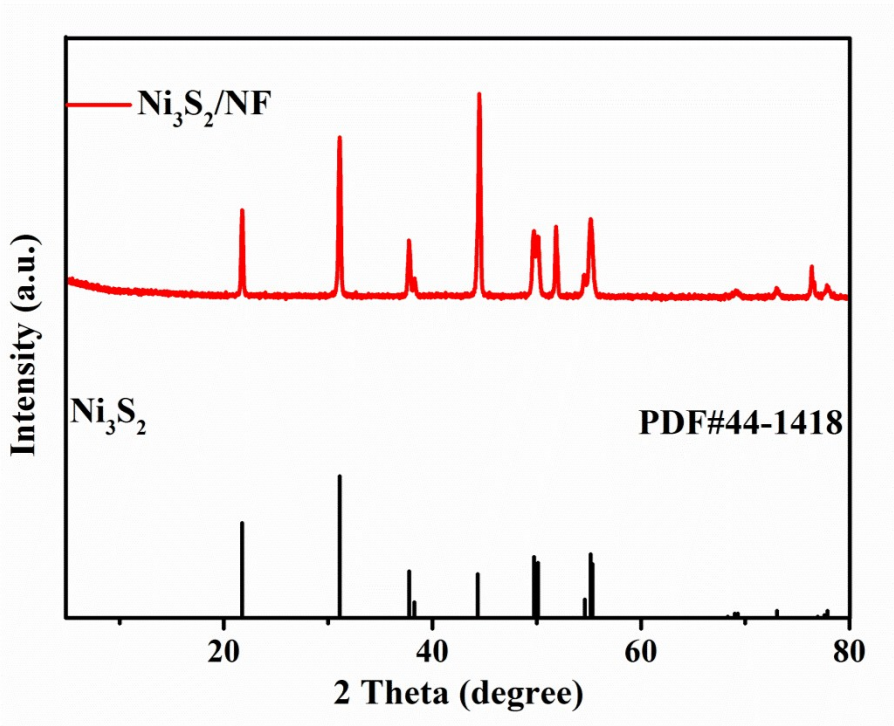


**Figure S2.** XRD patterns of $Ni_3S_2$/NF

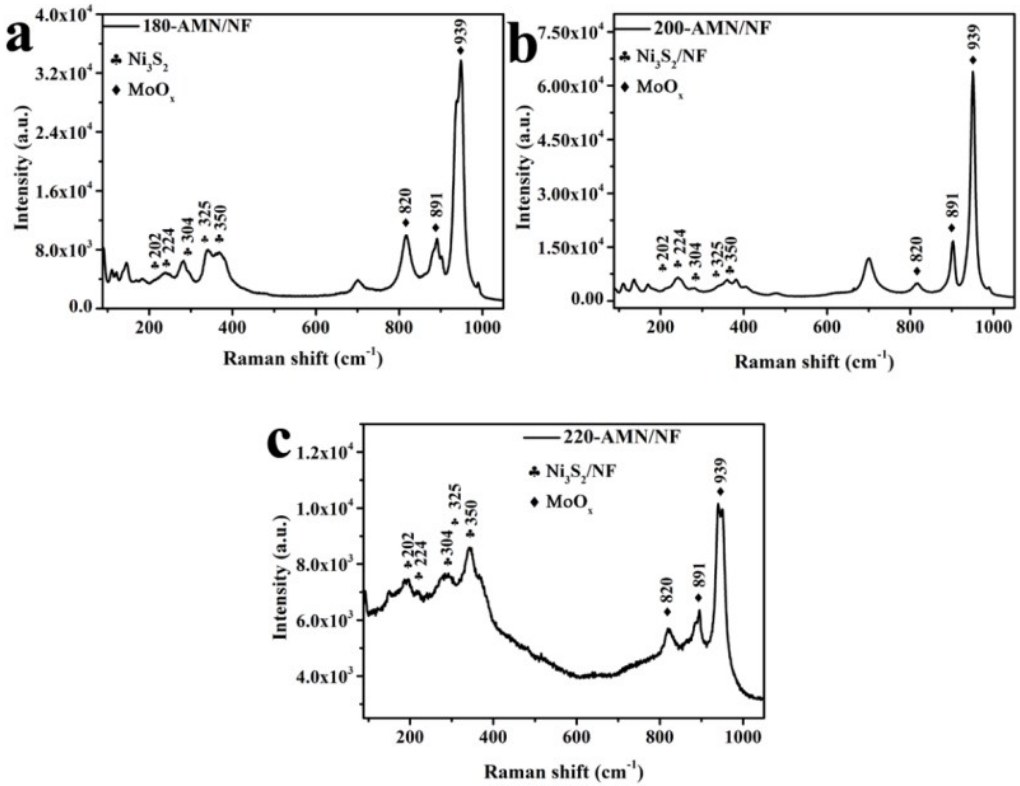


**Figure S3.** Raman spectrum of 180-AMN/NF, 200-AMN/NF, 220-AMN/NF

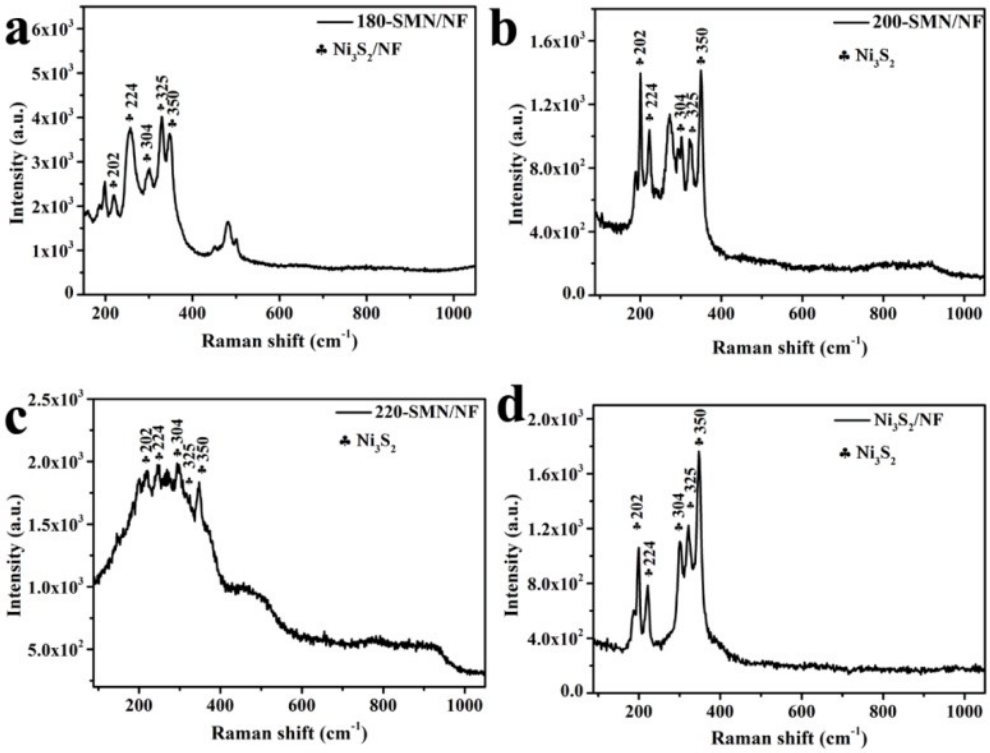


**Figure S4.** Raman spectrum of 180-SMN/NF (a), 200-SMN/NF (b), 220-SMN/NF (c), $Ni_3S_2$/NF (d)

In **Figure S3**, besides the Raman resonance bands related to $Ni_3S_2$, three Raman resonance bands at 820, 891 and 939 $cm^{-1}$, ascribed to the $MoO_x$ structure are evident. However, in **Figure S4,** the three Raman resonance bands at 820, 891 and 939 $cm^{-1}$ are not visible. These results, together with the HER and OER results, indicate that Mo-doped $Ni_3S_2$ using sodium molybdate as Mo source presents superior HER and OER activities to the Mo-doped $Ni_3S_2$ using ammonium molybdate as Mo source, because ammonium molybdate lead to the formation of $MoO_x$.[1]

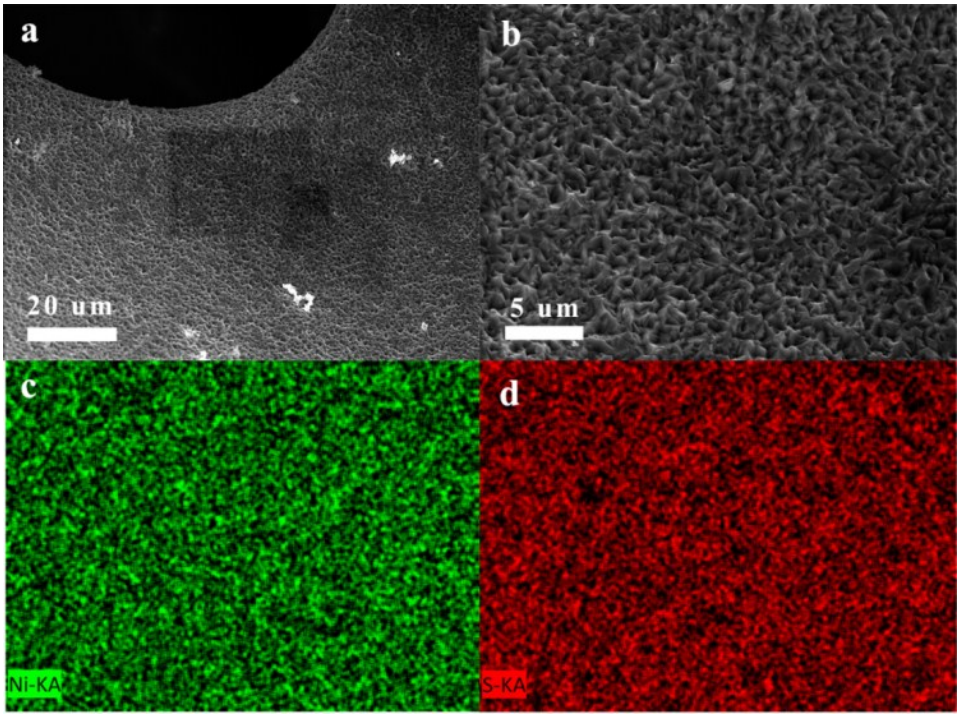


**Figure S5.** SEM images and EDX-mapping of $Ni_3S_2$/NF

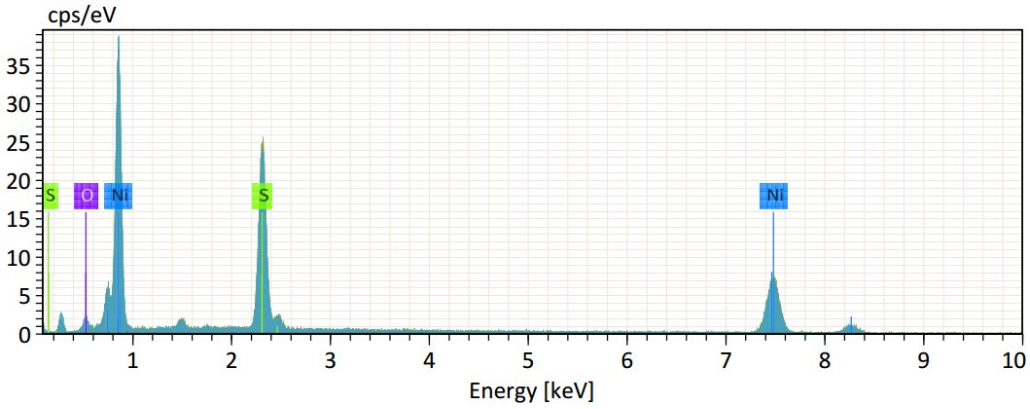


**Figure S6.** EDX spectrum of $Ni_3S_2$/NF

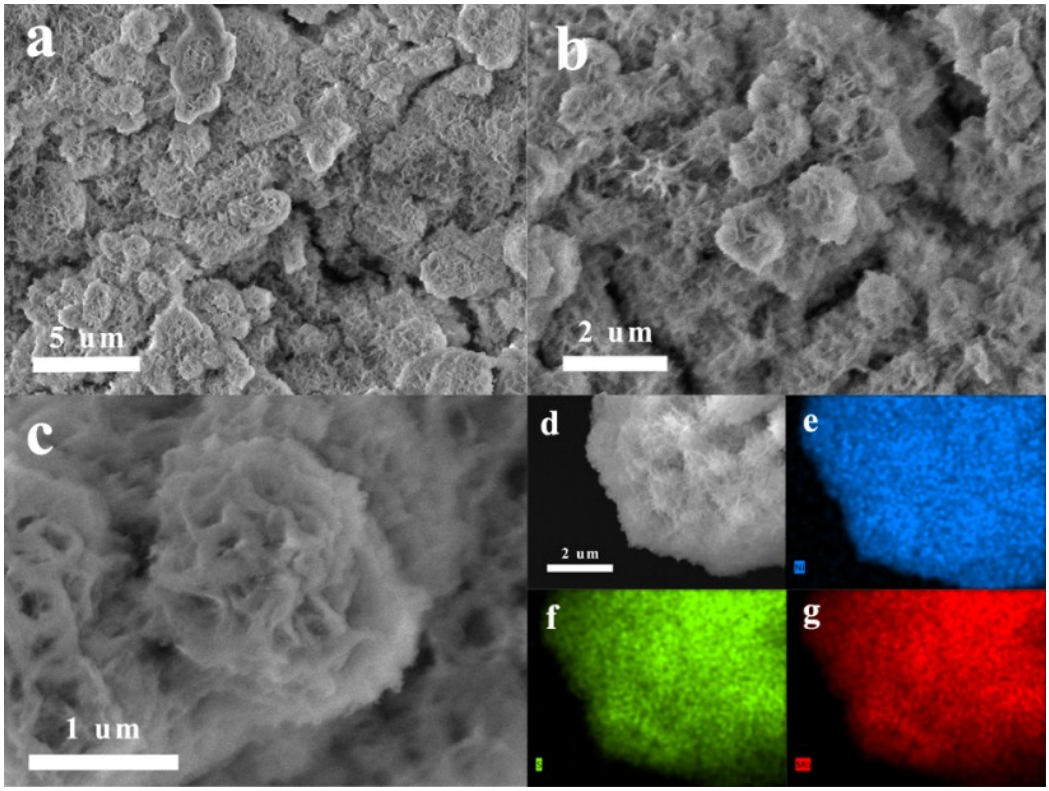


**Figure S7.** SEM images and EDX-mapping of 180-AMN/NF

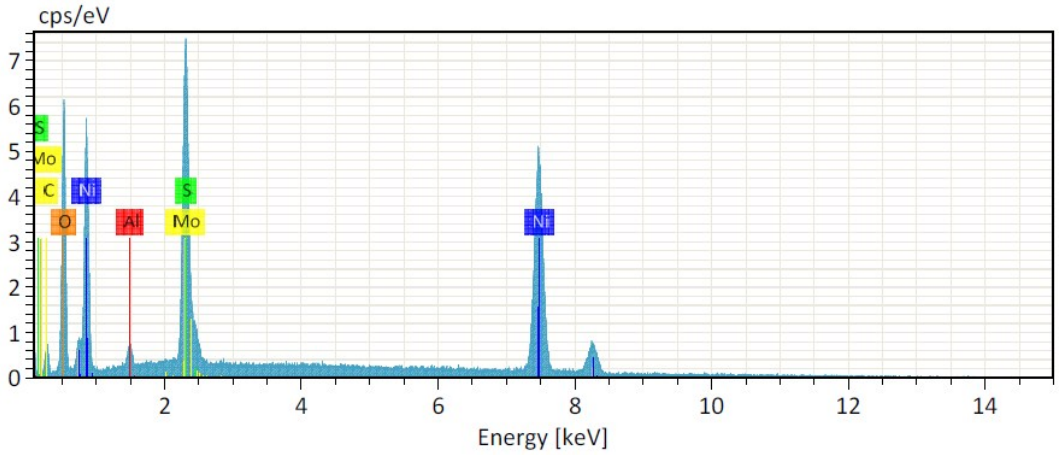


**Figure S8.** EDX spectrum of 180-AMN/NF

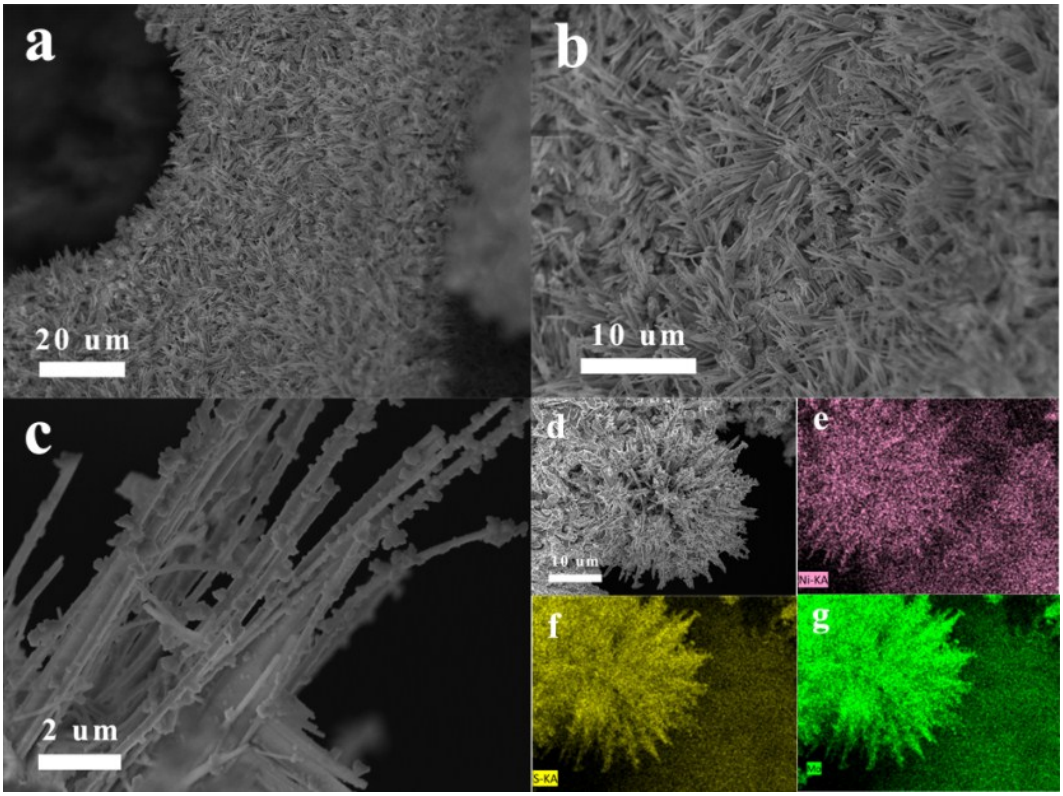


**Figure S9.** SEM images and EDX-mapping of 200-AMN/NF.

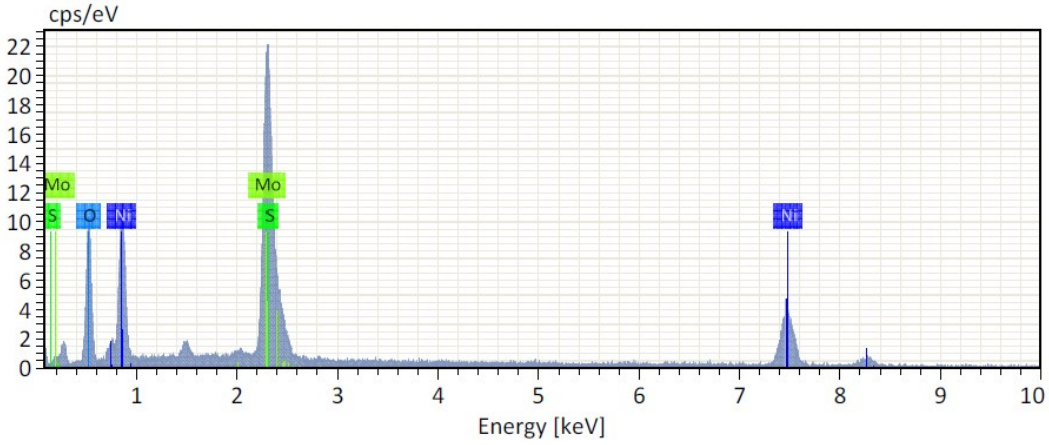


**Figure S10.** EDX spectrum of 200-AMN/NF

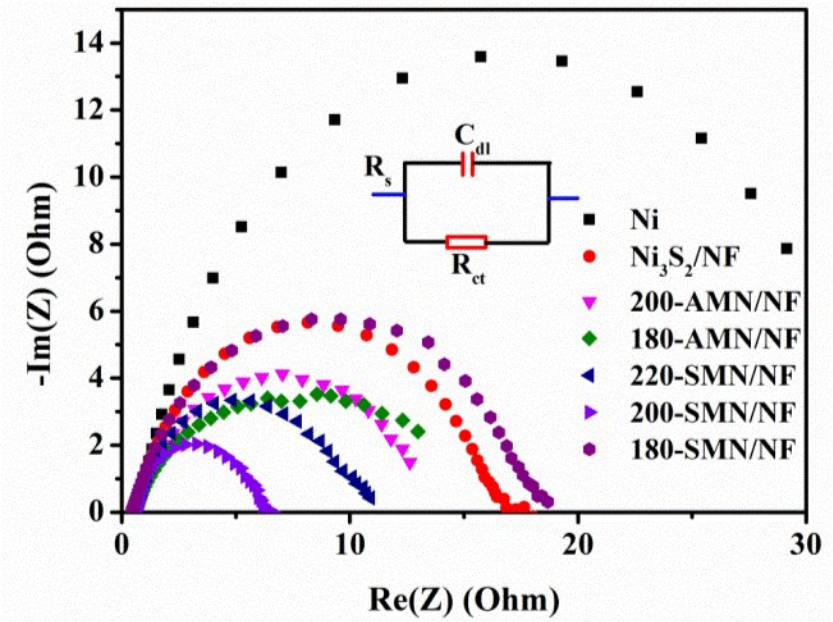


**Figure S11.** Nyquist plots of, 180-SMN/NF, 200-SMN/NF, 220-SMN/NF, 180-AMN/NF, 220-AMN/NF, $Ni_3S_2$/NF, and bare Ni foam electrodes recorded at an applied potential of -1.2 V with a frequency range of 10 kHz to 10 mHz in 1 m KOH

**References:**

[1]. Wu, Y., et al., Overall Water Splitting Catalyzed Efficiently by an Ultrathin Nanosheet-Built, Hollow $Ni_3S_2$-Based Electrocatalyst. Advanced Functional Materials, 2016. 26(27) 4839-4847.