Electronic Supplementary Information (ESI)

Atomically-Thin Molybdenum Nitride Nanosheets with Exposed Active Surface Sites for Efficient Hydrogen Evolution

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1. Morphology of the bulk MoN material.

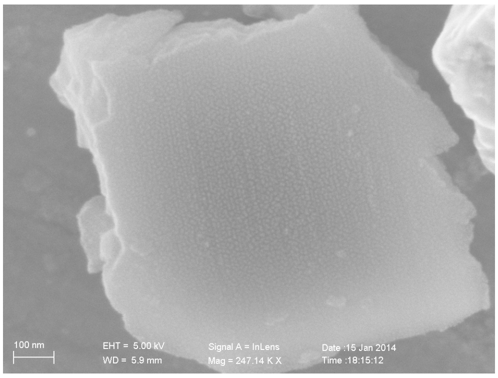

Figure S1. FE-SEM image of the bulk MoN material.

2. Calculation of the exchange current densities.

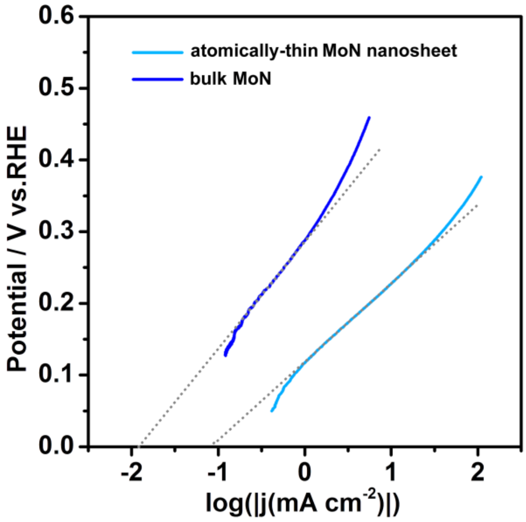

Figure S2. Calculated exchange current densities of the atomically-thin MoN nanosheets and the bulk materials by applying extrapolation method to the Tafel plots.

3. Capacitance measurements and the comparison of the electrochemical parameters.

The estimation of the effective active surface area of the samples was carried out according to literature.[1] Cyclic voltammetry (CV) were performed at various scan rates (20, 40, 60 mV s^{-1}, etc.) in 0.1V – 0.2 V vs. RHE region. The double-layer capacitance (C_{dl}) of various samples can be determined from the cyclic voltammograms, which is expected to be linearly proportional to the effective surface area. CV measurements were taking in the region of 0.1V – 0.2 V vs. RHE, which could be mostly considered as the double-layer capacitive behavior. The double-layer capacitance is estimated by plotting the Δj (j_a-j_c) at 0.15 V vs. RHE against the scan rate, where the slope is twice C_{dl} (Figure S3). The calculated values of double-layer capacitance are listed in Table S1, where C_{dl} were calculated to be 1.56 mF cm^{-2} and 0.53 mF cm^{-2} for the atomically-thin MoN nanosheets and bulk MoN, respectively. Since the C_{dl} is proportional to the surface area of the materials, the ratio of the C_{dl} can be regarded as the ratio of the electrochemical surface area.

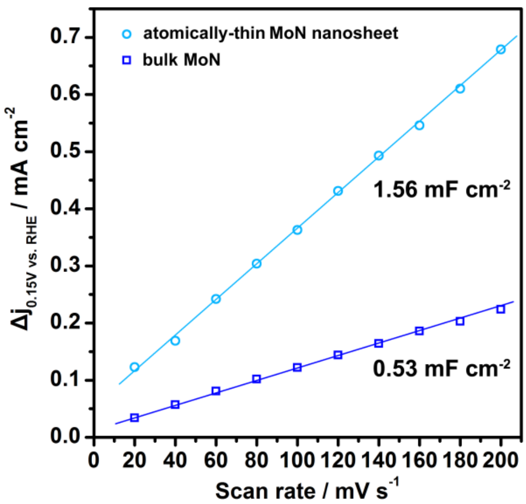

Figure S3. The differences in current density variation ($\Delta j = j_a - j_c$) at an overpotential of 0.15 V plotted against scan rate fitted to a linear regression enables the estimation of C_{dl}.

Materials	Bulk MoN	Atomically-thin MoN nanosheets
Exchange current density (j_0) / A cm^{-2}	1.219×10^{-5}	8.375×10^{-5}
Enhancement relative to bulk	1	6.87
Double-layer capacitance (C_{dl}) / mF cm^{-2}	0.53	1.56
Surface area relative to bulk	1	2.94
Number of active sites per surface area relative to bulk	1	2.34

Table S1. Electrochemical analysis of the atomically-thin MoN nanosheets and bulk MoN based on the exchange current density and the double-layer capacitance.

The total relative activity is proportional to the total relative number of active sites, which can be further decoupled as contributions from the relative surface area and the relative density of active sites per surface area[2]:

$$j \propto (\text{Surface Area}) \times \left(\frac{\text{Active Sites}}{\text{Surface Area}} \right)$$

Therefore, through the comparison between the exchange current density and the double-layer capacitance for both nanosheets and the bulk material, the number of active sites per surface area relative to bulk can be identified as shown in Table S1. Thus, the possibility that the HER activity is enhanced by the enlargement of surface area is excluded, and the activity enhancement can be identified as the result of the high exposure of apical Mo atoms on the surface of the nanosheets.

References

(1) Lukowski, M. A.; Daniel, A. S.; Meng, F.; Forticaux, A.; Li, L.; Jin, S. *J. Am. Chem. Soc.* **2013**, *135*, 10274.

(2) Kibsgaard, J.; Chen, Z.; Reinecke, B. N.; Jaramillo, T. F. *Nat. Mater.* **2012**, *11*, 963.