Supporting Information

Well-dispersed molybdenum nitrides on nitrogen-doped carbon matrix for highly efficient hydrogen evolution in alkaline media

*Zhe Lv[a], Muhammad Tahir[a, b], Xuewei Lang[a], Gang Yuan[a], Lun Pan[a], Xiangwen Zhang[a], Ji-Jun Zou[a]**

[a] *Key Laboratory for Green Chemical Technology of the Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China; Collaborative Innovative Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, China*

[b] *Department of Physics, The University of Lahore, I-Km Raiwind Road, Lahore, 53700, Pakistan.*

* E-mail: jj_zou@tju.edu.cn

ECSA and TOF

The electrochemical active surface area (ECSA) was estimated using the capacitance (C) by the following equation, where the specific capacitance for a flat surface is used as 40 μF cm^{-2} as reported.[1, 2]

$$ECSA = \frac{C}{40\ \mu F\ cm^{-2}\ per\ cm^2}$$

$$TOF = \frac{number\ of\ total\ hydrogen\ turnovers\ per\ cm^2}{number\ of\ active\ sites\ per\ cm^2}$$

$$number\ of\ total\ hydrogen\ turnovers\ per\ cm^2 = \left(j\frac{mA}{cm^2}\right)\left(\frac{1\ C\ s^{-1}}{1000\ mA}\right)\left(\frac{1\ mol\ of\ e^-}{96485.3\ C}\right)\left(\frac{1\ mol\ of\ H_2}{2\ mol\ of\ e^-}\right)\left(\frac{6.02\times10^{23}\ H_2\ molecules}{1\ mol\ of\ H_2}\right)$$

$$= 3.12\times10^{15}\frac{H_2/s}{cm^2}\times|j|$$

$$number\ of\ active\ sites\ per\ cm^2 = number\ of\ active\ sites\ per\ real\ surface\ area\times ECSA = \left(\frac{6\frac{atoms}{unit\ cell}}{72.2\frac{Å^3}{unit\ cell}}\right)^{2/3}$$

$$= 1.90\times10^{15}\frac{atoms}{cm^2}\times ECSA$$

(a). j: the current density/mA cm^{-2}

(b). The crystal data needed for the calculation of number of active sites was used as early reported.[2]

(c) The lattice parameters of Mo_2N are used in the above formula for calculation of Mo-600. Since exact cell parameters for composites are unknown and the surface sites of MoO_2, Mo_2N and Mo_2C are similar with little difference, therefore the average value of MoO_2 and Mo_2N is used for Mo-550, the average value of Mo_2N and Mo_2C is used for Mo-650 as early report.[3]

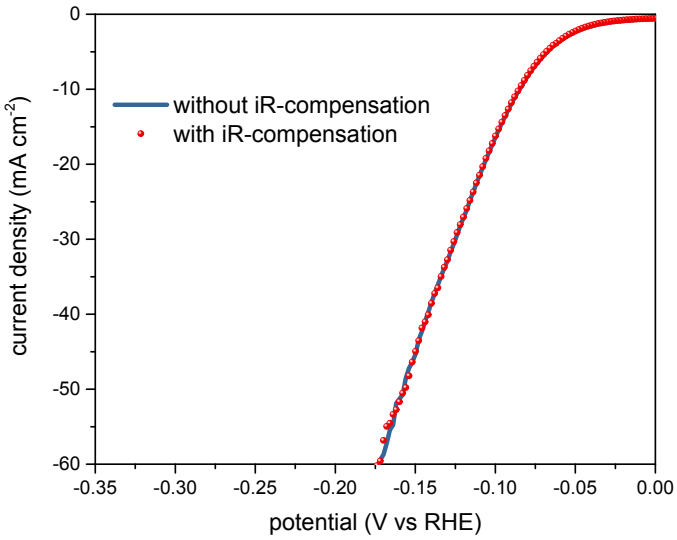


Figure S1 LSV curves of Mo-600 with and without iR compensation.

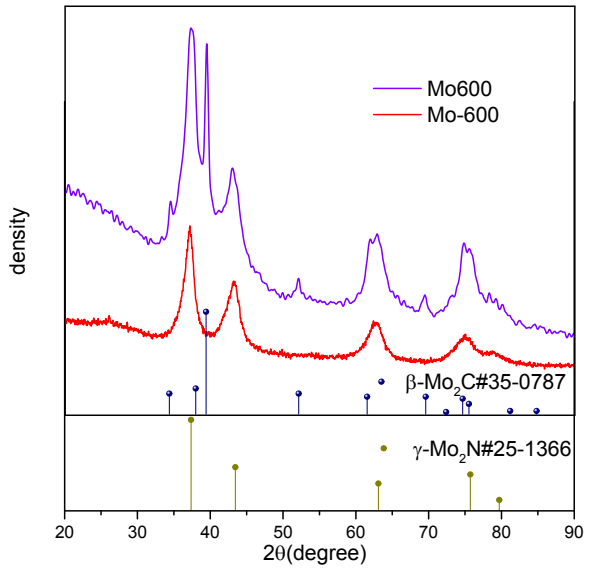


Figure S2. XRD results of Mo-600 and Mo600

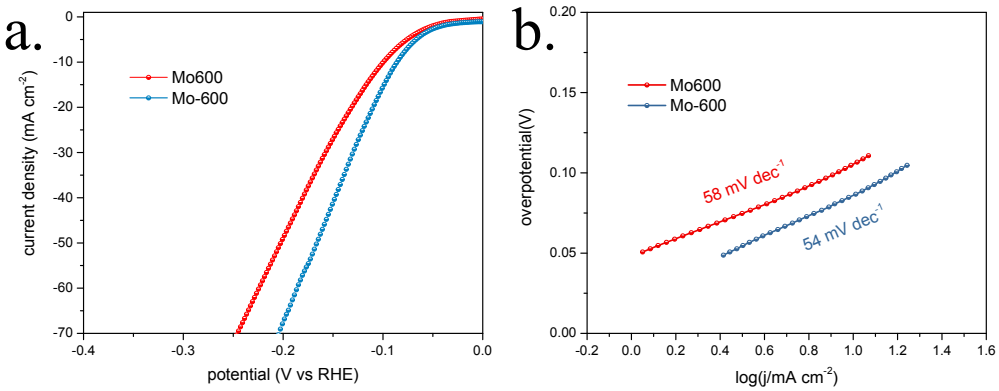


Figure S3. (a) Polarization curves of Mo-600 and Mo600 in 1 M KOH and corresponding (b) Tafel plots.

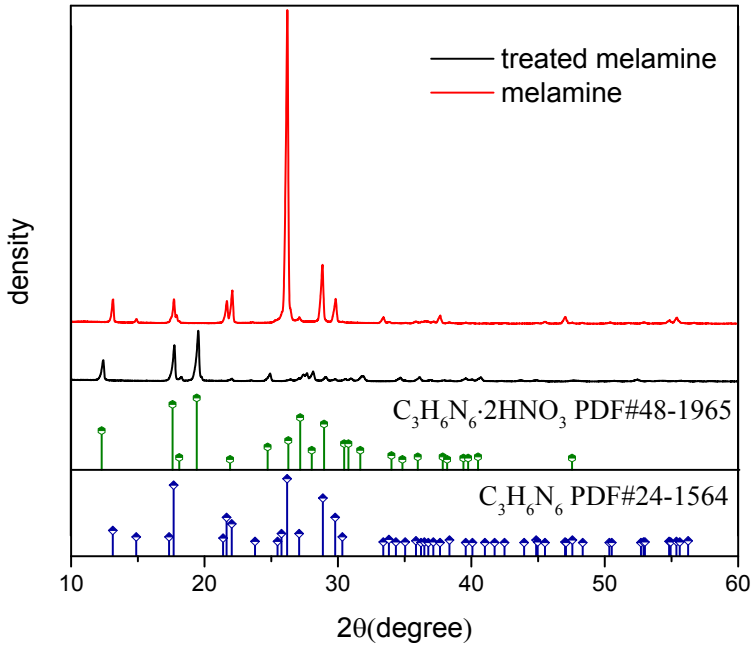


Figure S4.XRD results of pretreated melamine and pure melamine

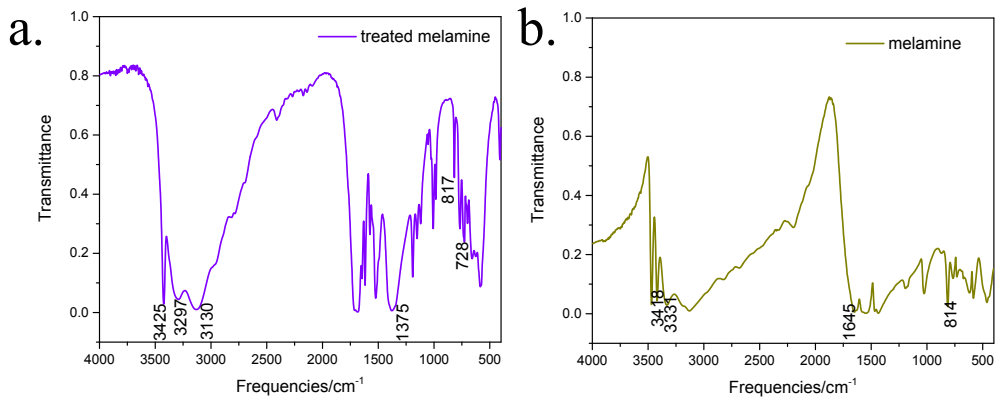
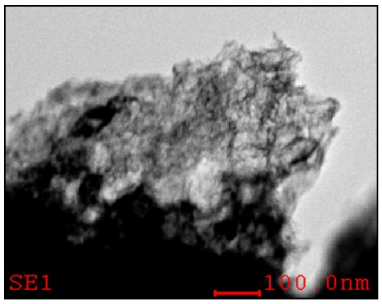
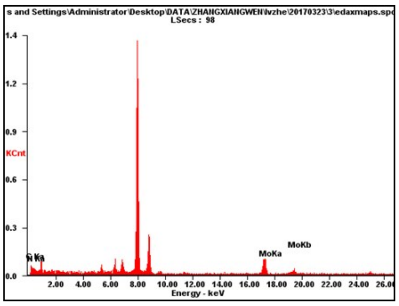


Figure S5 .FTIR results of (a) HNO_3 pretreated melamine and (b) pure melamine





Element	Wt%	At%
CK	10.48	39.28
NK	06.82	21.93
MoK	82.69	38.79
Matrix	Correction	MThin

Figure S6.TEM image of Mo-600 and corresponding EDX results

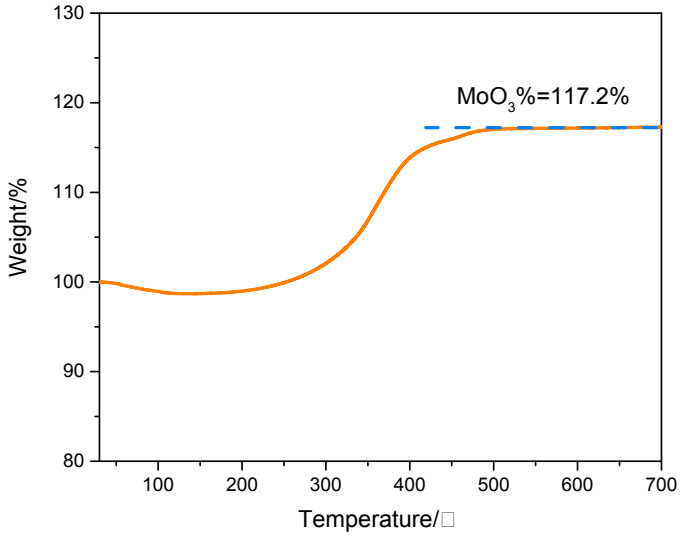


Figure S7. TGA curves of Mo-600 under air flow

As shown in the TGA curves, the weight loss below 150 ℃ is due to the loss of water. The weight begins to gain from then on is ascribed to the oxidation process of Mo_2N and the transformation to MoO_3. There is no obvious weight loss region of carbon probably because it happens during the gradual oxidation of Mo_2N, as a result it can't be extinguished. The weight remained after 500 ℃ is about 117.2 wt.% and the amount of Mo_2N can be calculated from the following equation:

$$\text{m\% } (Mo_2N) = \text{residual weight} \times \frac{M\ (Mo_2N)}{2\ M\ (MoO_3)}$$

$$= 117.2\ wt.\% \frac{206}{2 \times 144} \approx 83.8\ wt.\%$$

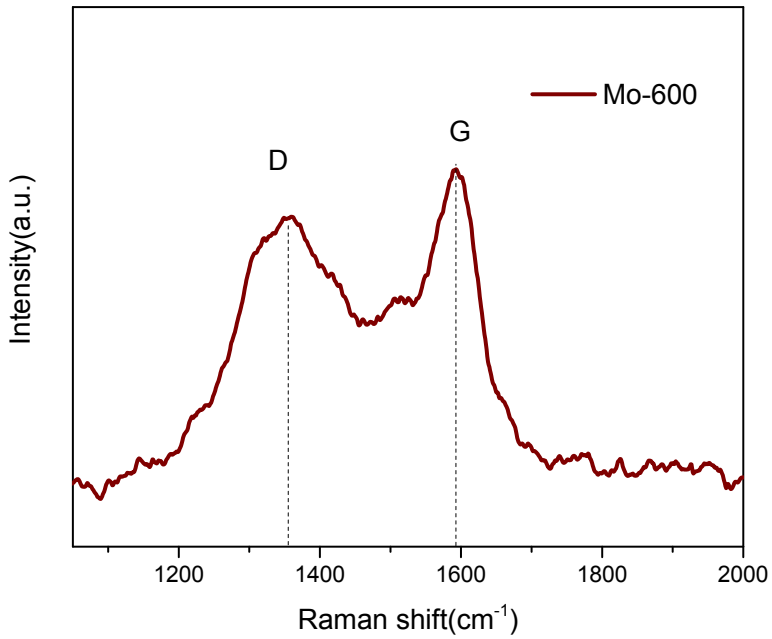


Figure S8 Raman spectra of Mo-600.

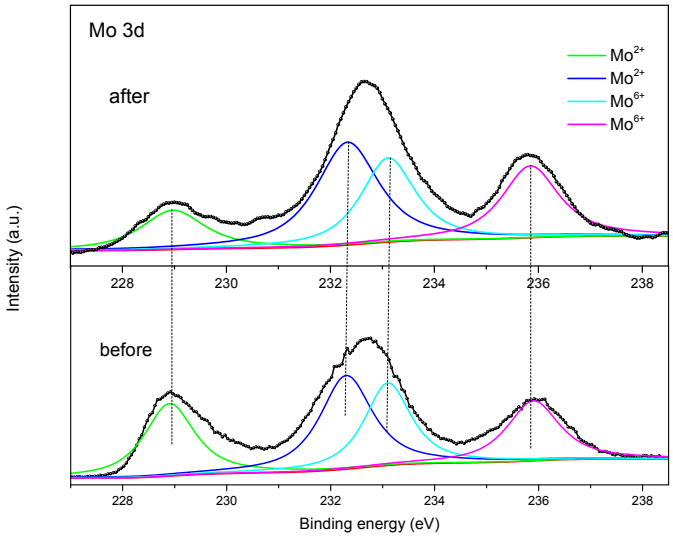


Figure S9 XPS spectra for Mo-600 before and after 1000 cycles CV measurement.

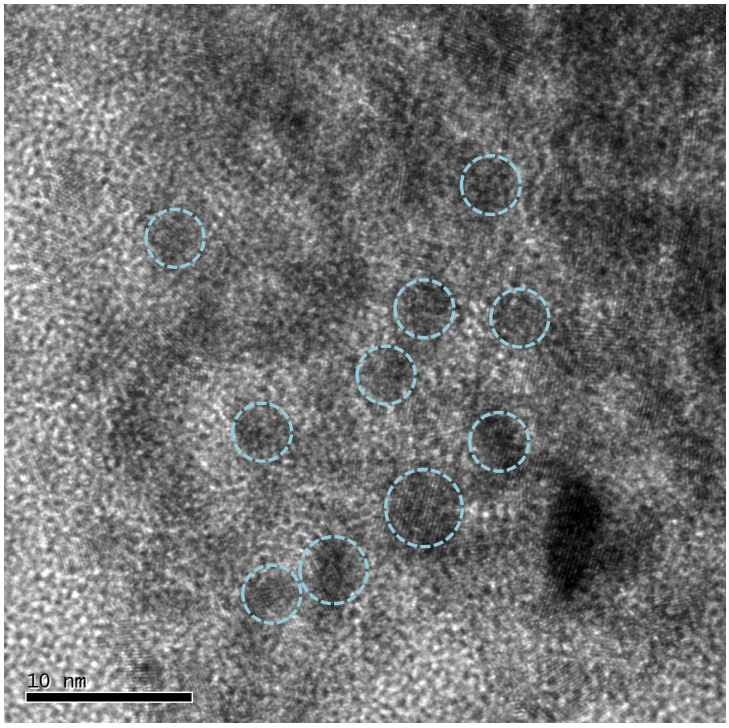


Figure S10 TEM image of Mo-600 after 1000 cycles CV measurement.

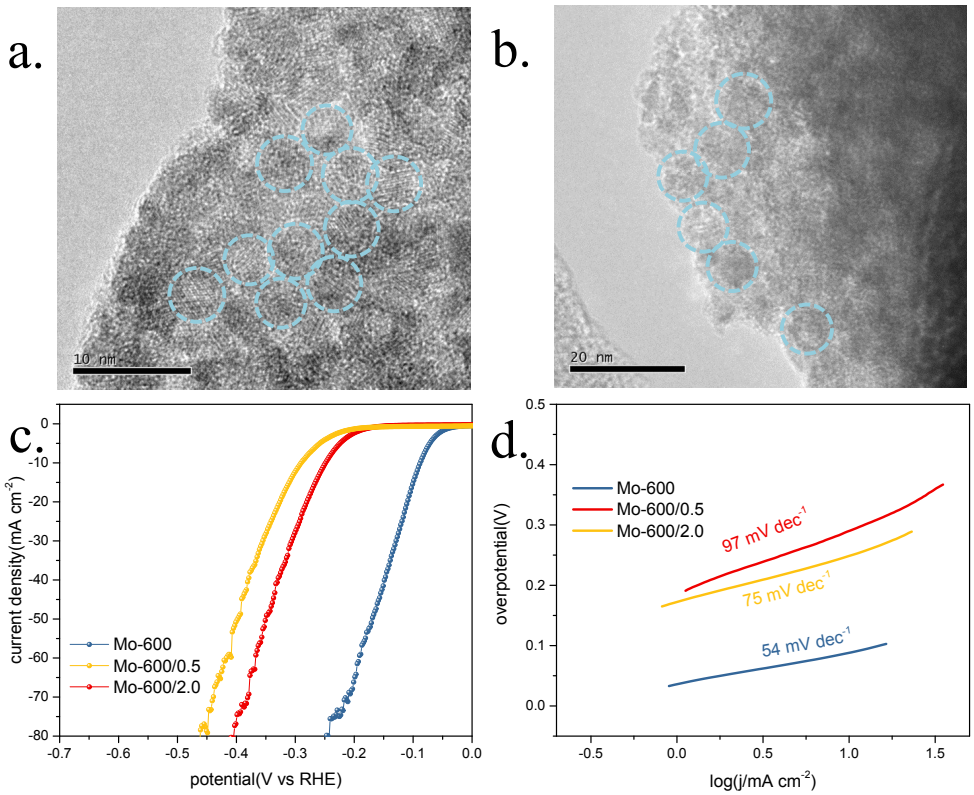


Figure S11 TEM image of (a) Mo-600/0.5 and (b) Mo-600/2.0; (c) Polarization curves and (d) Tafel slope.

Table S1. Comparable results of molybdenum-based catalysts reported in literature for HER

Material	Electrolyte	η_{onset} (mV vs RHE)	η_{10} (mV vs RHE)	Tafel slop (mV dec^{-1})	Ref
γ-Mo_2N@NC (Mo-600)	1 M KOH	26	85	54	This work
NiMoN	1 M KOH	50	109	95	[4]
Mo_2C	1 M KOH	-	290	216	[5]
MoC_x	1 M KOH	80	151	59	[6]
Mo_2C/carbon microflowers	1 M KOH	-	100	65	[7]
Mo_2C/graphene	0.1 M KOH	53	121	54	[8]
Mo_2C nanotubes	0.1 M KOH	37	112	55	[9]
MoC@NC	0.1 M KOH	36	~170[a]	51	[10]
MoP	1 M KOH	-	130	48	[11]
CoN_x/C	0.1 M KOH	-	170	75	[12]
Co-NMC/NC	0.1 M KOH	-	220	81	[13]

a. the guess value from the LSV figures.

Table S2. Summary of element information for the melamine precursors.

Material	N/%	C/%	N/C ratio	N/C theoretical value
Pure melamine	67.07	27.72	2.419553	2.00
HNO_3 treated melamine	47.97	17.39	2.758482	2.67

Table S3. Electrocatalysts with different amount of treated melamine during fabrication.

Name	MoO_3	treated melamine	η_{10} (mV)
Mo-600/0.5	100 mg	0.5 g	290
Mo-600	100 mg	1.0 g	85
Mo-600/2.0	100 mg	2.0 g	249

References

1. Y.-Y. Chen, Y. Zhang, W.-J. Jiang, X. Zhang, Z. Dai, L.-J. Wan and J.-S. Hu, *ACS Nano*, 2016, **10**, 8851-8860.
2. C. Tang, W. Wang, A. Sun, C. Qi, D. Zhang, Z. Wu and D. Wang, *ACS Catalysis*, 2015, **5**, 6956-6963.
3. X.-D. Wang, Y.-F. Xu, H.-S. Rao, W.-J. Xu, H.-Y. Chen, W.-X. Zhang, D.-B. Kuang and C.-Y. Su, *Energy & Environmental Science*, 2016, **9**, 1468-1475.
4. Y. Zhang, B. Ouyang, J. Xu, S. Chen, R. S. Rawat and H. J. Fan, *Advanced Energy Materials*, 2016, **6**, 1600221.
5. J. Wang, H. Xia, Z. Peng, C. Lv, L. Jin, Y. Zhao, Z. Huang and C. Zhang, *ChemSusChem*, 2016, **9**, 855-862.
6. H. B. Wu, B. Y. Xia, L. Yu, X.-Y. Yu and X. W. Lou, *Nature Communications*, 2015, **6**, 6512.
7. Y. Huang, Q. Gong, X. Song, K. Feng, K. Nie, F. Zhao, Y. Wang, M. Zeng, J. Zhong and Y. Li, *ACS Nano*, 2016, **10**, 11337-11343.
8. X. Fan, Y. Liu, Z. Peng, Z. Zhang, H. Zhou, X. Zhang, B. I. Yakobson, W. A. Goddard, X. Guo, R. H. Hauge and J. M. Tour, *ACS Nano*, 2017, **11**, 384-394.
9. F. X. Ma, H. B. Wu, B. Y. Xia, C. Y. Xu and X. W. D. Lou, *Angewandte Chemie International Edition*, 2015, **54**, 15395-15399.
10. Z. Cheng, J. Gao, Q. Fu, C. Li, X. Wang, Y. Xiao, Y. Zhao, Z. Zhang and L. Qu, *ACS Applied Materials & Interfaces*, 2017, **9**, 24608-24615.
11. P. Xiao, M. A. Sk, L. Thia, X. Ge, R. J. Lim, J.-Y. Wang, K. H. Lim and X.

Wang, *Energy & Environmental Science*, 2014, **7**, 2624-2629.
12. H.-W. Liang, S. Brüller, R. Dong, J. Zhang, X. Feng and K. Müllen, *Nature Communications*, 2015, **6**, 7992.
13. B. Bayatsarmadi, Y. Zheng, Y. Tang, M. Jaroniec and S.-Z. Qiao, *Small*, 2016, **12**, 3703-3711.