Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Nitrogen Promoted Molybdenum Dioxide Nanosheets for Electrochemical Hydrogen Generation

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[§] These authors contributed equally to this work.

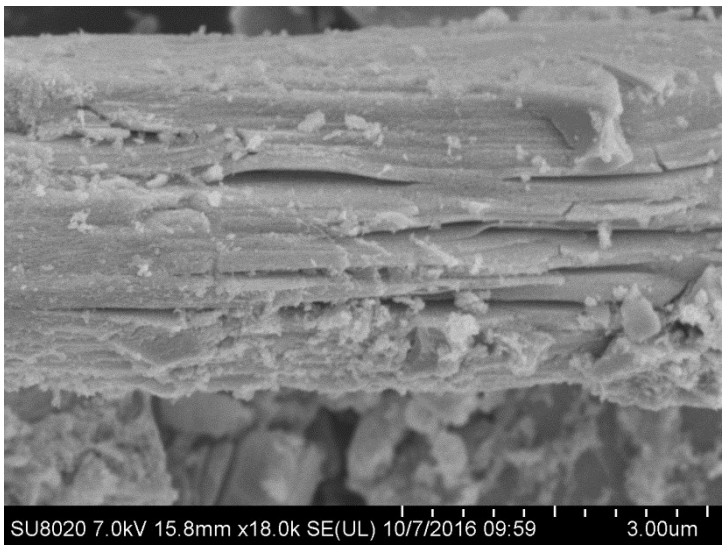

Figure S1. The SEM image of $MoO_3 \cdot nH_2O$, which works as the precursor of studied MoO_2 based samples.

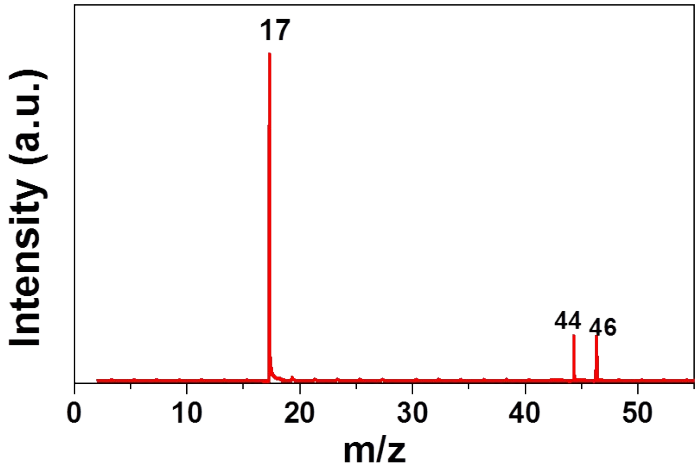

Figure S2. The TG mass spectrum (TG-MS) of the reaction gases of the reactions in **Figure 1**. The three peaks at m/s 17, 44 and 46 can be assigned to the NH_3, CO_2 and NO_2, respectively.

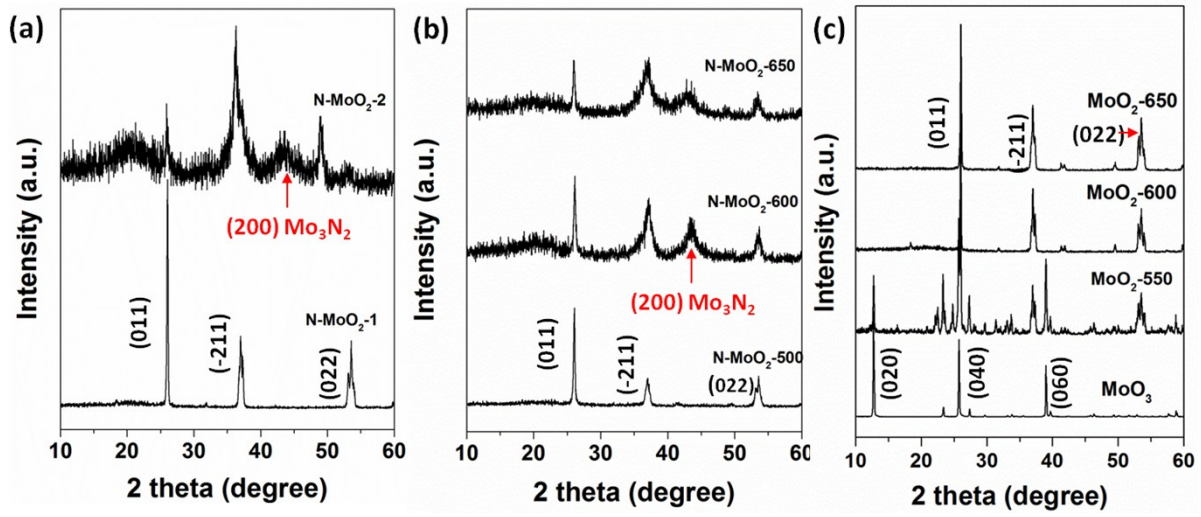

Figure S3. XRD pattern of the reference samples: (a) the $MoO_3 \cdot nH_2O$ with molar ratios to urea of 1:1 and 1:3 were treated under the temperature of 550 ℃, the obtained samples were named as N-MoO_2-1 and N-MoO_2-2, respectively. (b) The samples under the molar ratios of 1:2 of $MoO_3 \cdot nH_2O$ to urea were synthesized under the three temperature of 500, 600 and 650 ℃, and named as N-MoO_2-500, N-MoO_2-600 and N-MoO_2-650, respectively. (c) The pure $MoO_3 \cdot nH_2O$ was treated in argon atmosphere under 550, 600 and 650 ℃ with the names of MoO_2-550, MoO_2-600 and MoO_2-650, respectively.

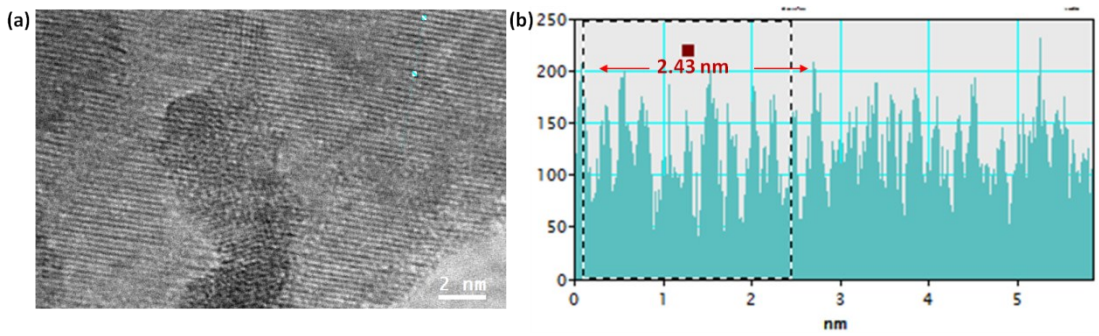

Figure S4. (a) HRTEM of N-MoO_2 sample and (b) the corresponding lattice analysis. The calculated interplanar spacing is 0.243 nm.

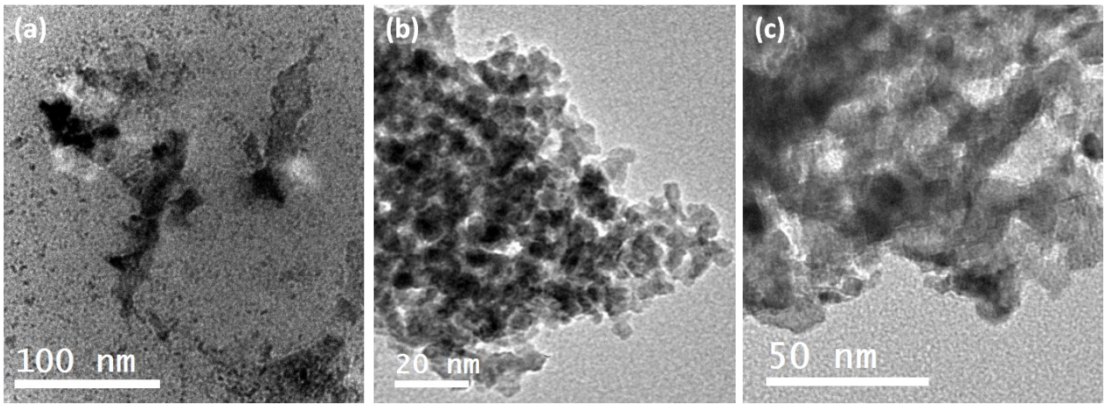

Figure S5. TEM images of reference samples of (a) N-MoO_2-500, (b) N-MoO_2-600 and (c) N-MoO_2-650, which were synthesized under the three temperature of 500, 600 and 650 ℃, respectively.

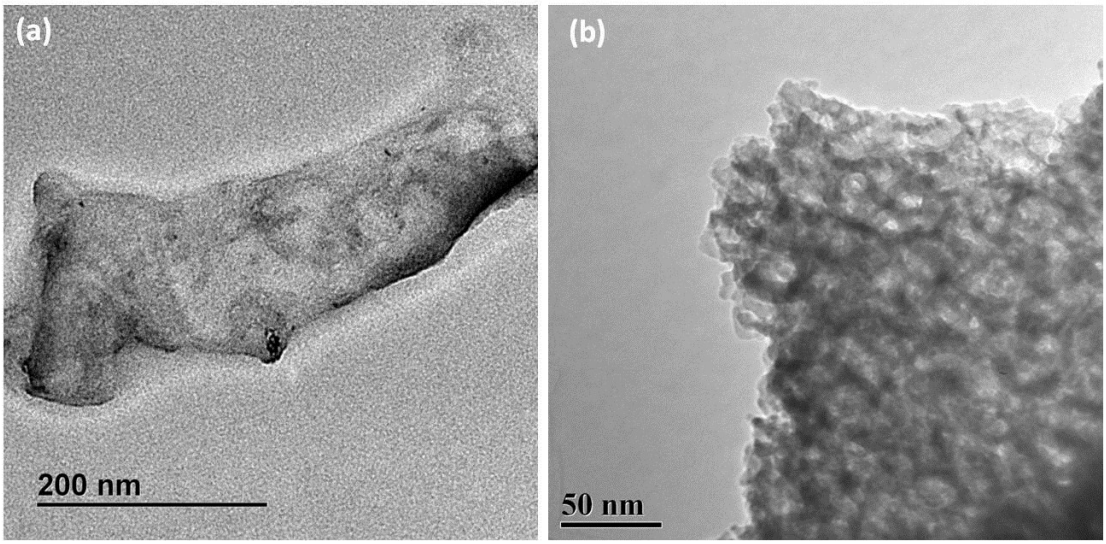

Figure S6. TEM images of reference samples of (a) N-MoO_2-1 and (b) N-MoO_2-2.

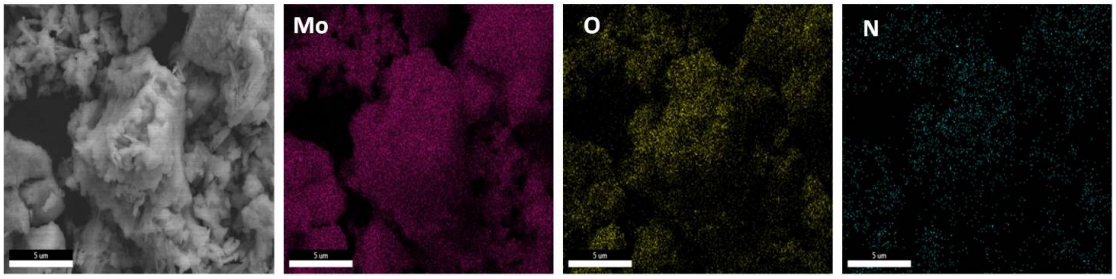

Figure S7. SEM image of N-MoO_2 sample and the corresponding element mapping.

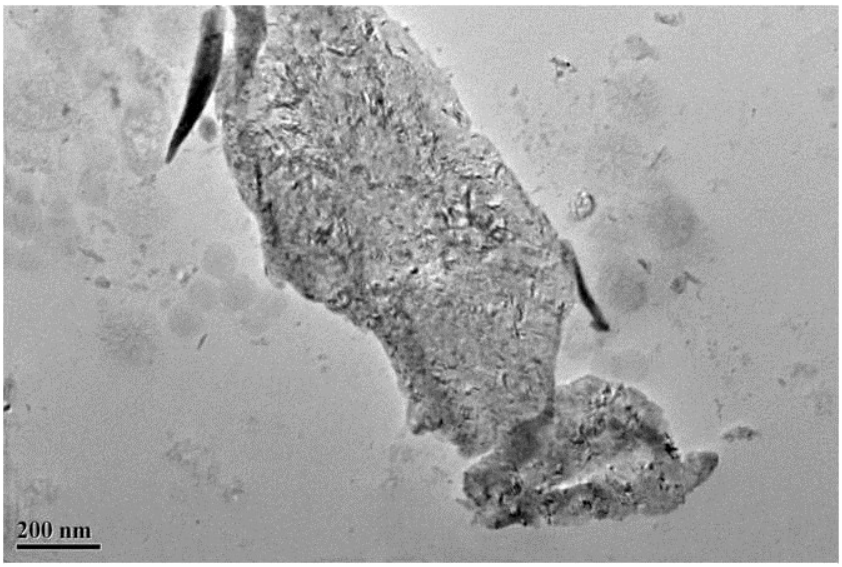

Figure S8. TEM image of reference MoO_2 sample, the sample of MoO_2-600.

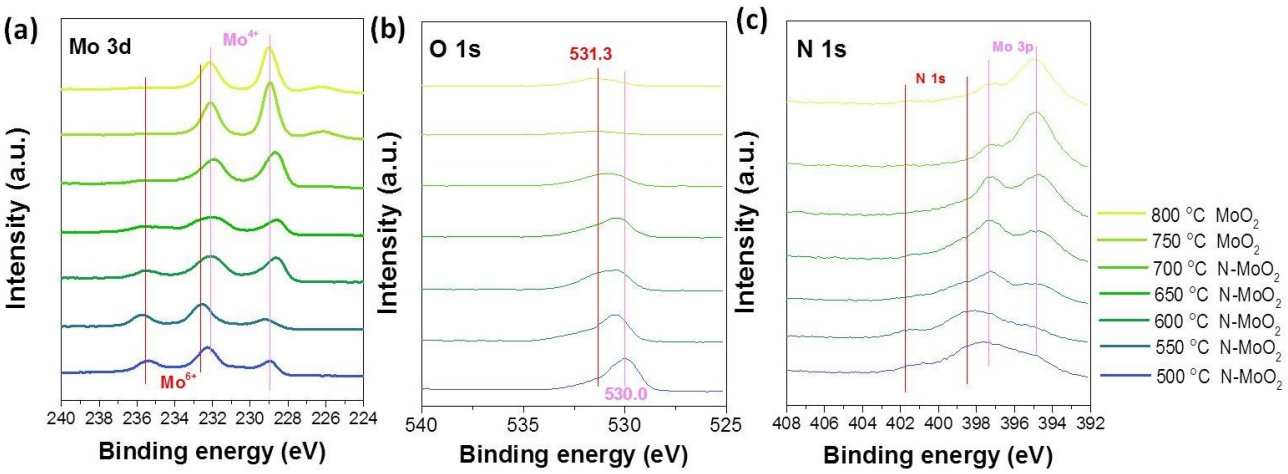

Figure S9. XPS analysis of N-MoO_2 samples synthesized under the different synthesis temperature from 500 to 800 ℃. Please note that the molar ratio of MoO_2 precursor to urea is 1:2. With the temperature increasing, the amount of N element doping into the obtained products is decreasing. Under the temperature of 700 ℃, almost no N doping with the pure MoO_2 formation (XRD results are not shown here) can be found. And at the temperature of 750 and 800 ℃, pure MoO_2 are obtained, because under these two temperature, the urea is decomposed to NH_3 and CO_2 quickly and then the gases are carried away by Ar without the chance of reacting with MoO_3. The pure MoO_2 comes from the self-transformation of MoO_3 (Figure S3).

Moreover, for the samples of 600°C, 650°C and 700°C N-MoO_2, the N content is decreasing (Figure S8c) and also the surface Mo^{6+} (Figure S8a). However, the O 1s spectra does not show the obvious shift especially the 600°C and 650°C N-MoO_2, suggesting that the N element indeed replaces the surface O element. Please note that the O 1s high binding energy shift at the high temperature of 750 and 800°C originates from the pure MoO_2 formation (strengthening the Mo-O bond). The Mo 3d XPS values are first high binding energy shift and then a slight low energy shift from 500 to 600°C N-MoO_2, clearly suggesting that the Mo-N bonds are formed during the nitridation process.

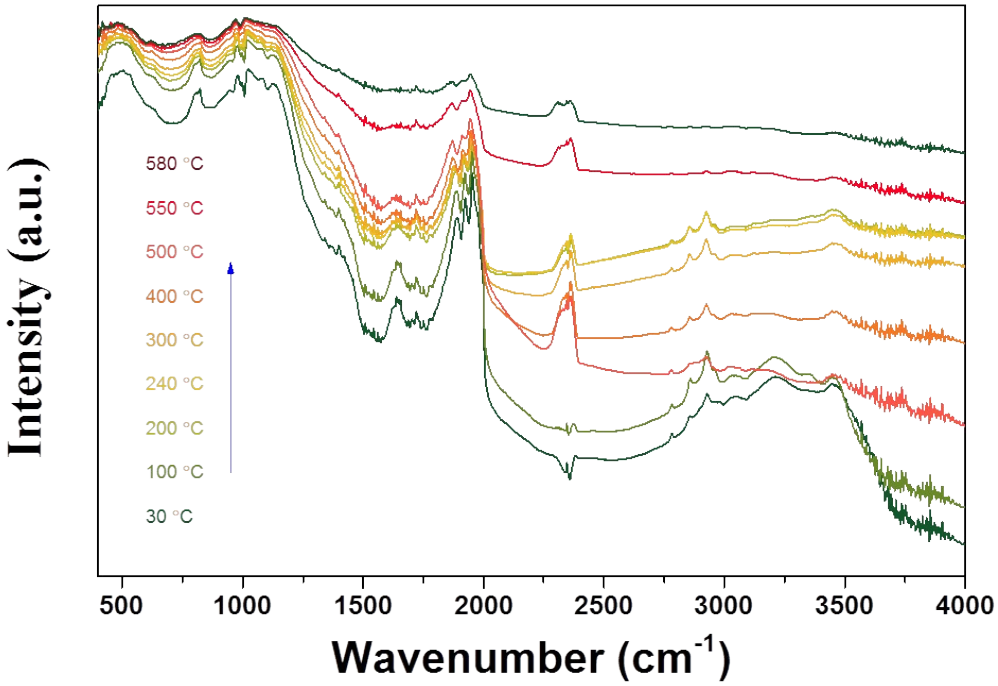

Figure S10. *In situ* FTIR studies on the thermal reaction pathway between MoO_3 and urea (molar ratio was 1:5) under different calcination temperature.

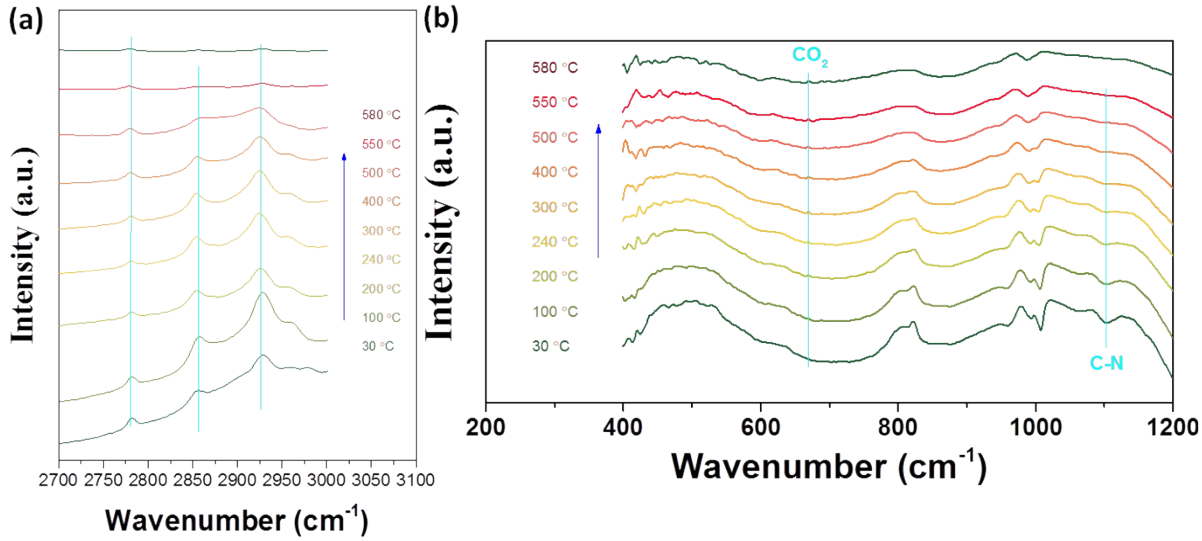

Figure S11. *In situ* FTIR studies on the thermal reaction pathway between MoO_3 and urea (molar ratio was 1:2) under different wavenumber ranges: (a) 2700-3100 cm $^{-1}$ and (b) 400-1200 cm^{-1}.

Table S1. The molar ratio of N to O element of the synthesized N-MoO_2 sample through XPS, SEM-EDX and ICP measurements.

Method	Ratio
XPS	1: 8.6
SEM-EDX	1: 9.1
ICP	1: 8.8

Table S2. Summary of literature HER performance of various Mo-based HER catalysts.

Catalyst	Electrolyte	Onset potential (mV VS. RHE)	Tafel slope (mV dec^{-1})	η (at j=10 mA cm^{-2})	Loading	Ref.
MoO_2/RGO/PI-CNT	0.5M H_2SO_4	N/A	68	110 mV	0.04 mg cm^{-2}	1
nanoflower-like MoO_2 on nickel foam	1M KOH solution	0	66	55 mV	4.5 mg cm^{-2}	2
2D $MoO_2/MoSe_2$	0.5M H_2SO_4	-63	49.1	181	N/A	3
1D MoO_2	0.5M H_2SO_4	-115	58	169	N/A	4
MoO_2/rGO	0.5M H_2SO_4	-190	49	352	0.10mg cm^{-2}	5
P-MoO_2 on Mo foil	0.5M H_2SO_4	-80	62	135	0.10 mg cm^{-2}	6
MoP@PC	0.5M H_2SO_4	-77	66	153	0.41 mg cm^{-2}	7
Mo_2C	1M H_2SO_4	-151	56	~214	1.4 mg cm^{-2}	8
MoB	1M H_2SO_4	-155	55	~212	2.5 mg cm^{-2}	9
MoO_3/MoS_2 nanowires	0.5M H_2SO_4	-150~-200	50~60	200	N/A	10
Mo_2C/carbon nanotubes	0.1M $HClO_4$	N/A	55.2	152	2 mg cm^{-2}	11
$NiMoN_x$/C	0.1M $HClO_4$	-78	35.9	N/A	N/A	12
MoP/CF	0.5M H_2SO_4	-100	56.4	200	0.36 mg cm^{-2}	13
Mo_2C/ GCSs	0.5M H_2SO_4	-120	62.6	~210	N/A	13
$MoSe_{2-x}$ nanosheets	0.5M H_2SO_4	-170	98	~280	0.285 mg cm^{-2}	14
P-MoO_{3-x}	0.5M H_2SO_4	~100	42	166	0.285 mg cm^{-2}	15
N-MoO_2 nanosheet	0.5M H_2SO_4	~0	33	96	0.10mg cm^{-2}	This work

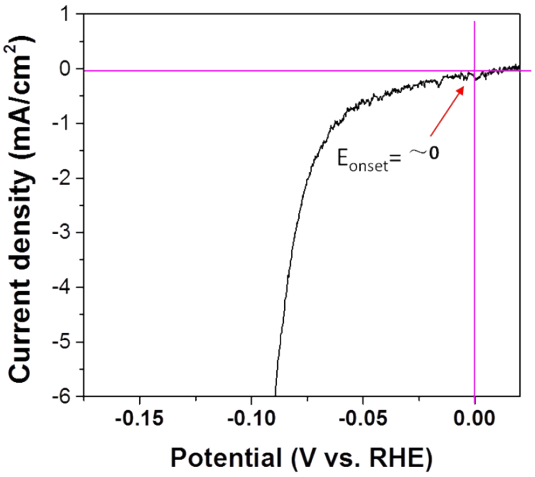

Figure S12. The determination of the onset potential of the N-MoO_2 sample. The onset potential was defined as the point, where the reduction current of the polarization curve deviates from the baseline by a value of 1.0 μA cm^{-2} (*J. Mater. Chem. A*, 2015, **3**, 11358-11366). And the value of onset potential of N-MoO_2 sample was calculated to be near 0 V.

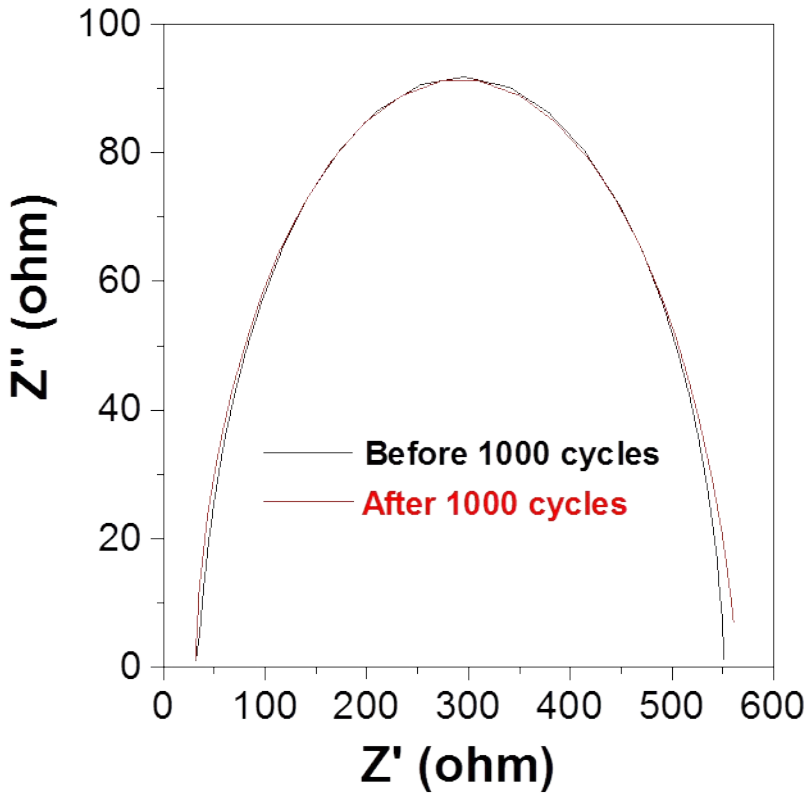

Figure S13. The EIS comparison before and after 1000 cyeles.

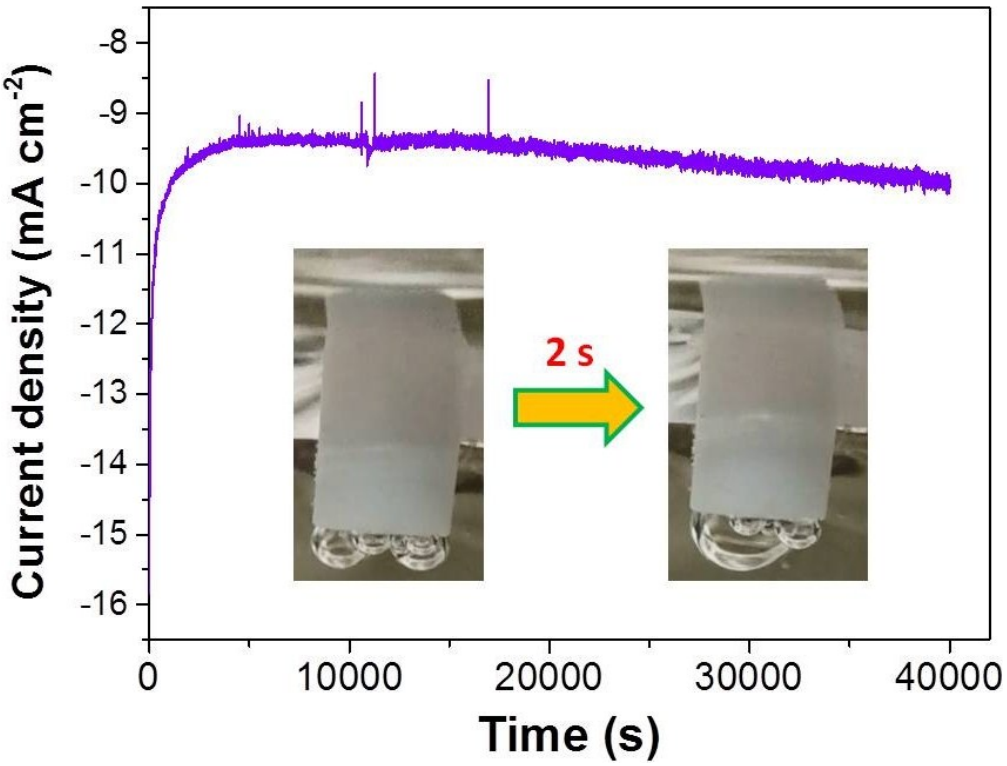

Figure S14. The stability of the N-MoO_2 sample under the condition of current density of 10 mA/cm^2 during the test of ca. 11h. The insets shows the pictures of hydrogen evolution process during 2s.

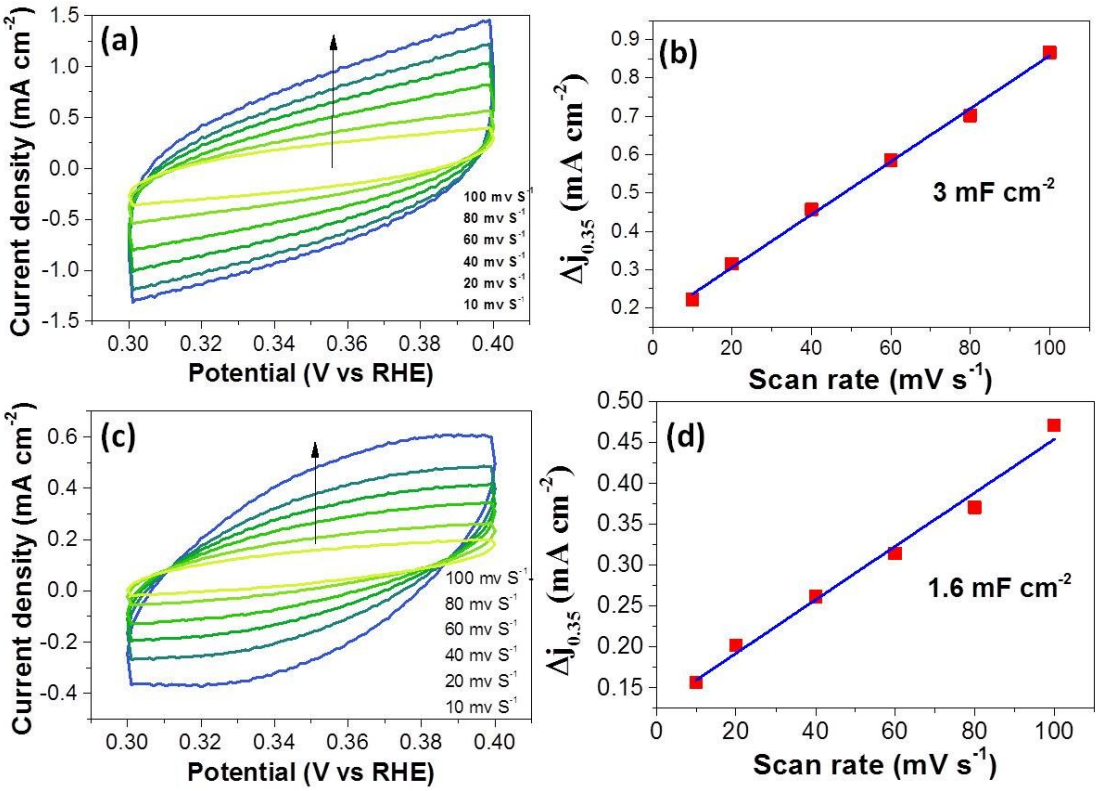

Figure S15. The cyclic voltammetry curves and the corresponding plots showing with the extraction of the double-layer capacitance (C_{dl}) values for the (a) and (b) MoO_2 and (c) and (d) N-MoO_2 samples under different scan rates in the region of 0.3-0.4 V vs. RHE. By plotting the difference in current density (J) between anodic and cathodic sweeps (ΔJ) at a fixed potential of 0.35 V against the scan rate, a linear trend is observed. And the fitting slope is twice of the double-layer capacitance (C_{dl}).

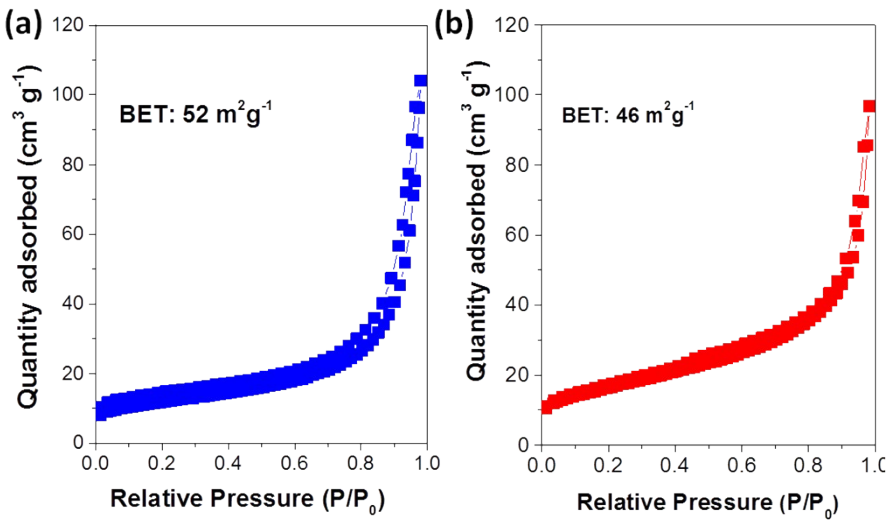

Figure S16. The surface area of studied samples based on nitrogen desorption and adsorption.

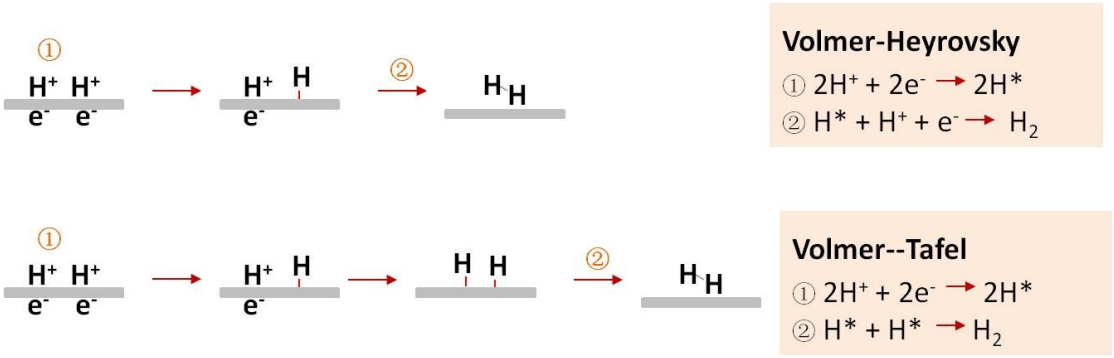

Figure S17. The reaction pathways of Volmer–Heyrovsky and Volmer–Tafel routes.

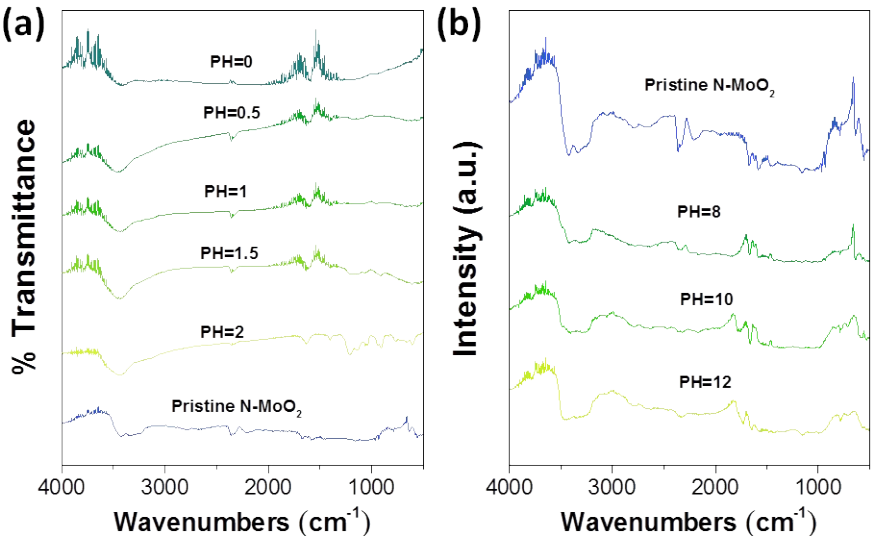

Figure S18. FTIR spectra of the N-MoO_2 sample treated by different PH solution (acid, HCl; alkaline, NaOH).

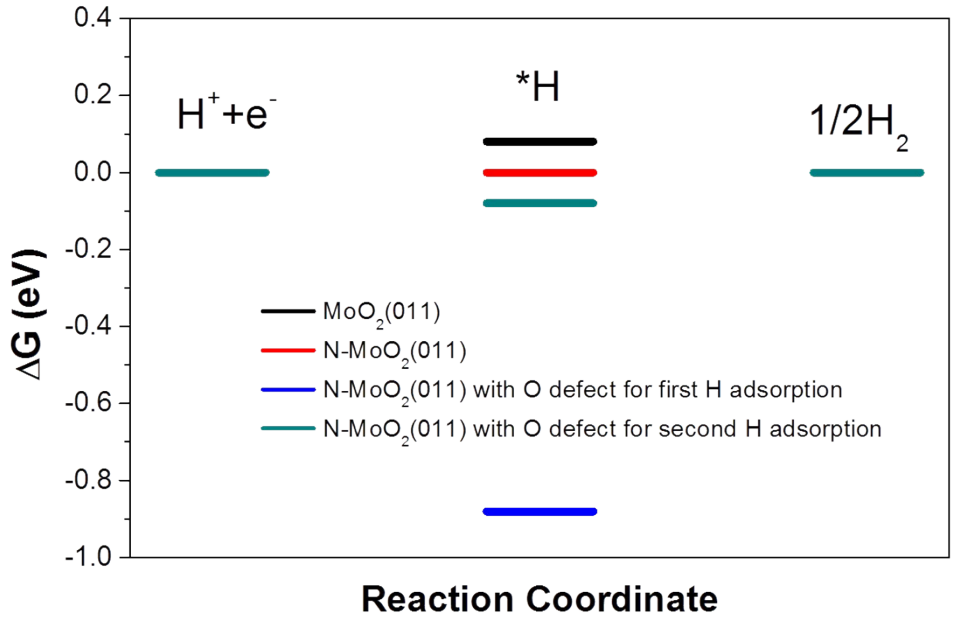

Figure S19. The corresponding DFT results of the N-MoO_2 (011) with an oxygen vacancy.

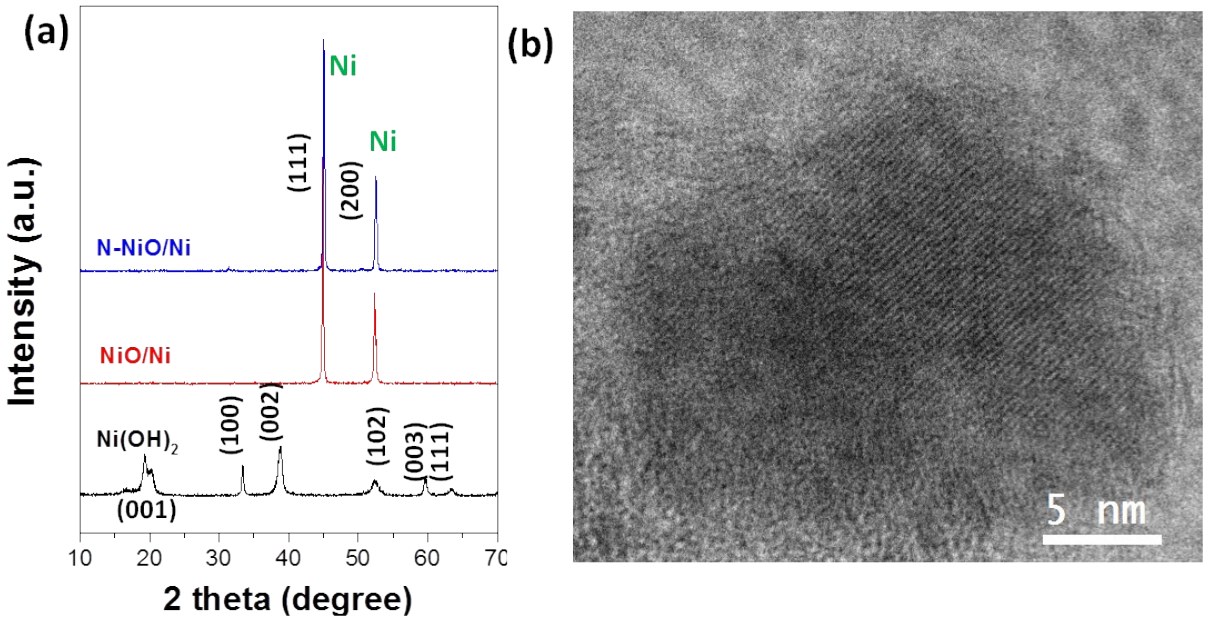

Figure S20. (a) XRD pattern of the $Ni(OH)_2$, NiO/Ni and N-NiO/Ni samples, (b) HRTEM image of N-NiO/Ni sample.

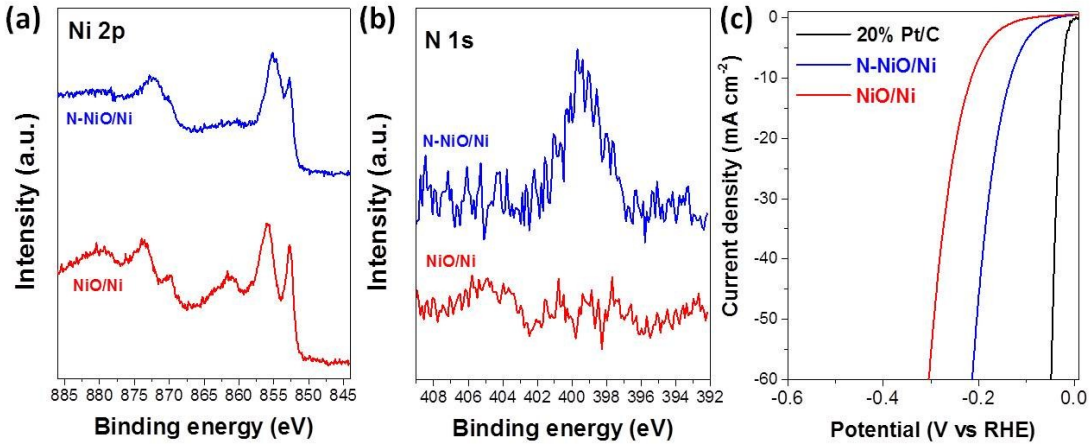

Figure S21. (a) Ni 2p and (b) N 1s XPS spectra of the NiO/Ni and N-NiO/Ni samples. (c) The corresponding HER performance of the NiO/Ni and N-NiO/Ni samples with 20% Pt/C working as the reference. The electrolyte is 0.5 M H_2SO_4.

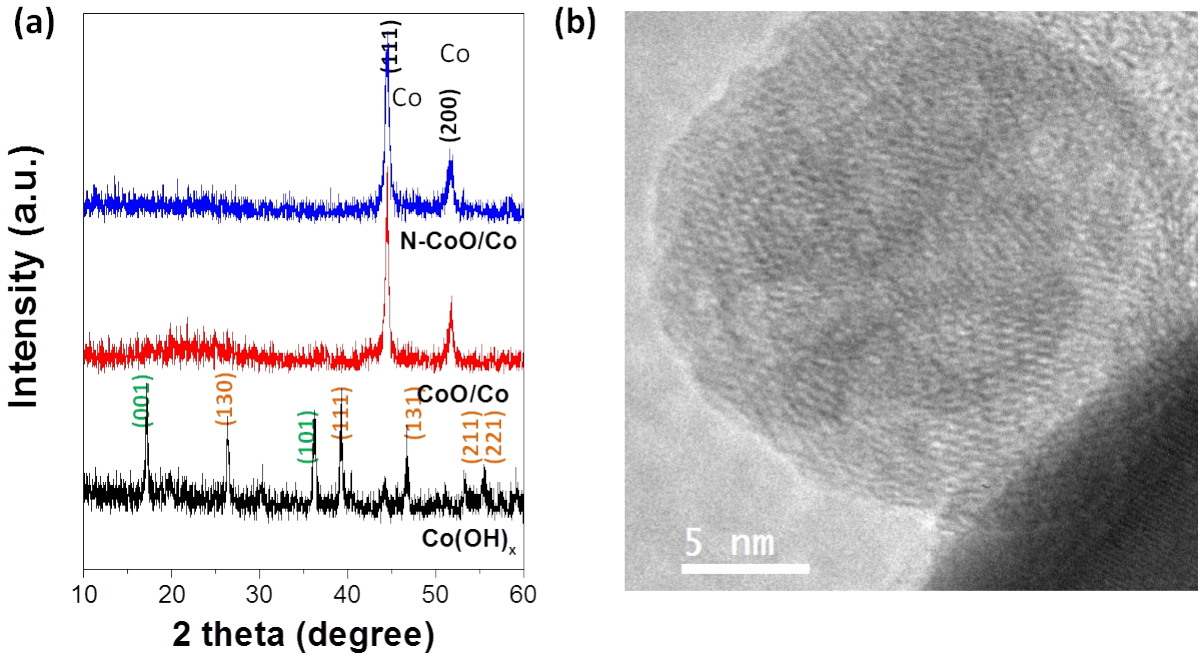

Figure S22. (a) XRD pattern of the Co(OH)x, CoO/Co and N-CoO/Co samples, (b) HRTEM image of N-CoO/Co sample. The (001) and (101) peaks belong to the $Co(OH)_2$ (PDF:45-0031); meanwhile, the peaks of (130), (111), (131), (211) and (221) are assigned to the CoOOH (PDF: 26-0480).

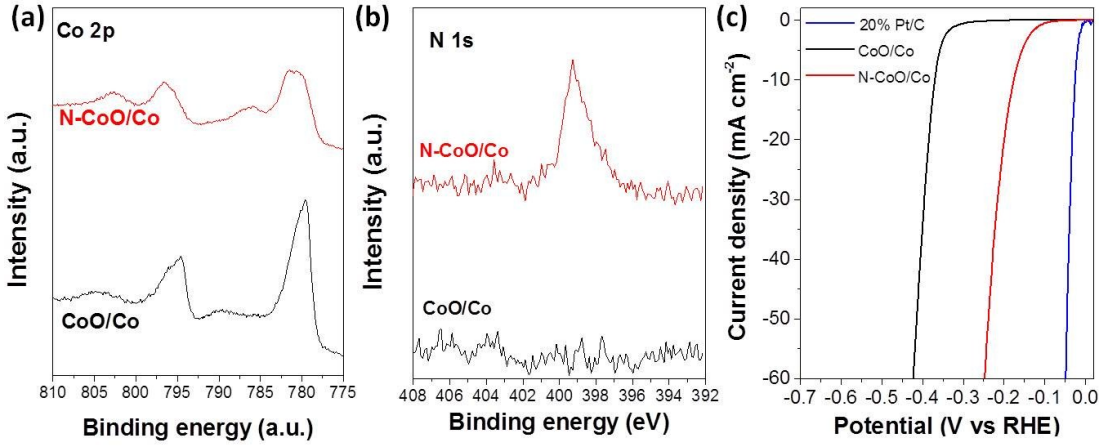

Figure S23. (a) Co 2p and (b) N 1s XPS spectra of the CoO/Co and N-CoO/Co samples. (c) The corresponding HER performance of the CoO/Co and N-CoO/Co samples with 20% Pt/C working as the reference. The electrolyte is 0.5 M H_2SO_4.

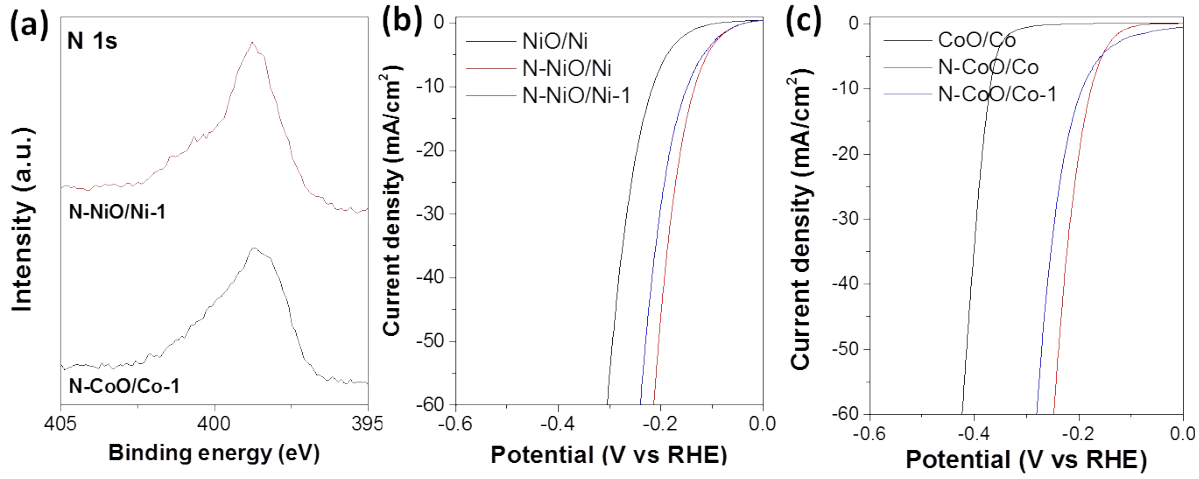

Figure S24. (a) N 1s XPS spectra, (b) and (c) HER performance of N doped oxide/metal samples.

Table S3. The detail structure information based on the DFT calculation in Figure S15.

1. MoO_2-H (011)

```
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      0.0000000000      11.4989995956       0.0000000000
      0.0000000000       0.0000000000      24.6665992737
  O   Mo    H
 64   32    1
Cartesian
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    3.822695265       8.992102598       0.833977743
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```

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5.673504626	11.384699215	2.467893315
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0.000000000 11.234752875 4.328494673
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0.157297460 7.423369873 9.494193264
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4.919607100 7.364042187 9.480589833
5.524282009 3.544489976 11.098577793

2. N-MoO2-H (011)

O N O Mo H
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9.4961996078 0.0000000000 0.0000000000
0.0000000000 11.4989995956 0.0000000000
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O N Mo H
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Cartesian
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3.822695265 8.992102598 0.833977743
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3.822695265 1.414146954 3.511537117
3.822695265 7.163646752 3.511537117
8.570889877 1.414146954 3.511537117
8.570889877 7.163646752 3.511537117

3.820379121	5.303597337	6.152092566
3.823366562	11.049038575	6.156716851
8.568723161	5.296518589	6.146381404
8.569061640	11.046970742	6.151017083
3.770517781	3.471781347	8.755028885
3.755312567	9.248427537	8.747900407
8.551521320	3.408319709	8.777813254
8.531710704	9.175739470	8.770431895
0.925404681	5.635199760	2.467893315
0.925404681	11.384699215	2.467893315
5.673504626	5.635199760	2.467893315
5.673504626	11.384699215	2.467893315
0.925309660	3.806858718	5.145452597
0.925309660	9.556358516	5.145452597
5.673504626	3.806858718	5.145452597
5.673504626	9.556358516	5.145452597
0.930793239	1.943037409	7.696831874
0.928877269	7.696852960	7.694736776
5.669037615	1.940959638	7.687656817
5.686149459	7.688934606	7.705120374
1.026770651	0.119202317	10.185180692
1.024701290	5.865681584	10.198828231
5.769593473	0.131412178	10.240057545
1.448740171	2.760564836	2.467893315
1.448740171	8.509949317	2.467893315
6.196744884	2.760564836	2.467893315
6.196744884	8.509949317	2.467893315
1.448740171	0.932108905	5.145452597
1.448740171	6.681608617	5.145452597
6.196744884	0.932108905	5.145452597
6.196744884	6.681608617	5.145452597
1.453470380	4.819458469	7.690229743
1.448929221	10.569399318	7.689883501
6.177312933	4.830722574	7.707054479
6.200791344	10.567576171	7.696216577
1.370394703	2.993597181	10.249100280
1.360332183	8.741392405	10.253962376
6.098522717	2.981435211	10.183414929
6.076609911	8.773708037	10.210671045
3.299359633	0.367738012	0.833977743
3.299359633	6.117352699	0.833977743
8.047554528	0.367738012	0.833977743
8.047554528	6.117352699	0.833977743
3.299359633	4.288896853	3.511537117
3.299359633	10.038396651	3.511537117
8.047554528	4.288896853	3.511537117
8.047554528	10.038396651	3.511537117
3.302217456	2.425550522	6.151385379
3.305446303	8.179157028	6.152339200
8.049296164	2.427280799	6.153961246
8.049932934	8.174050844	6.151490501

3.355819323	0.610981739	8.756494718
3.342795258	6.345920560	8.760185765
8.089937360	0.553107088	8.761977993
8.099271556	6.288895797	8.747178518
5.784299742	5.888696422	10.366402953
2.374049902	4.438958682	1.650935575
2.374049902	10.188343676	1.650935575
7.122149706	4.438958682	1.650935575
7.122149706	10.188343676	1.650935575
2.374049902	2.610502836	4.328494673
2.374049902	8.360002976	4.328494673
7.122149706	2.610502836	4.328494673
7.122149706	8.360002976	4.328494673
2.410962457	0.743283088	6.945735730
2.413109362	6.495694181	6.940872898
7.160730032	0.741188010	6.939279154
7.162381105	6.488446142	6.936704757
2.215660347	4.491884447	9.475976207
2.197348404	10.239277345	9.478740266
6.986313405	4.523303927	9.460681995
6.987355444	10.265320252	9.477331772
0.000000000	1.564208954	1.650935575
0.000000000	7.313593777	1.650935575
4.748099804	1.564208954	1.650935575
4.748099804	7.313593777	1.650935575
0.000000000	5.485252735	4.328494673
0.000000000	11.234752875	4.328494673
4.748099804	5.485252735	4.328494673
4.748099804	11.234752875	4.328494673
4.705124634	3.616282234	6.939541593
4.716631489	9.369965675	6.946302509
9.464116032	3.617449117	6.941361754
9.459375069	9.364915694	6.940495781
0.130590308	1.652598022	9.472208707
0.134652440	7.382754123	9.470143015
4.911686816	1.623602096	9.471153072
4.895537768	7.382264066	9.468123635
5.661454677	5.844518680	11.393607959

3. N-MoO_2-H (011) with an oxygen vacancy

O N O Mo H
1.0

9.4961996078	0.0000000000	0.0000000000
0.0000000000	11.4989995956	0.0000000000
0.0000000000	0.0000000000	24.6665992737

O N Mo H
62 1 32 2
Cartesian

3.822695265	3.242487997	0.833977743
3.822695265	8.992102598	0.833977743

8.570889877	3.242487997	0.833977743
8.570889877	8.992102598	0.833977743
3.822695265	1.414146954	3.511537117
3.822695265	7.163646752	3.511537117
8.570889877	1.414146954	3.511537117
8.570889877	7.163646752	3.511537117
3.809382248	5.305904372	6.146476602
3.823679003	11.041185333	6.154692692
8.571570230	5.296087819	6.146858498
8.566959451	11.054441534	6.155287039
3.797428805	3.436811871	8.789059885
3.782649802	9.207283348	8.767662691
8.542762764	3.392658461	8.807856953
8.509136224	9.181953935	8.763594526
0.925404681	5.635199760	2.467893315
0.925404681	11.384699215	2.467893315
5.673504626	5.635199760	2.467893315
5.673504626	11.384699215	2.467893315
0.925309660	3.806858718	5.145452597
0.925309660	9.556358516	5.145452597
5.673504626	3.806858718	5.145452597
5.673504626	9.556358516	5.145452597
0.937226241	1.941511380	7.690626709
0.921545714	7.694123037	7.697553028
5.705558203	1.973043606	7.686378440
5.699011077	7.693589115	7.711770287
1.030443397	0.104951770	10.232196151
1.001836302	5.862743986	10.231298567
5.804154507	0.203077595	10.166588723
1.448740171	2.760564836	2.467893315
1.448740171	8.509949317	2.467893315
6.196744884	2.760564836	2.467893315
6.196744884	8.509949317	2.467893315
1.448740171	0.932108905	5.145452597
1.448740171	6.681608617	5.145452597
6.196744884	0.932108905	5.145452597
6.196744884	6.681608617	5.145452597
1.454955044	4.818064721	7.697840461
1.447572335	10.561910020	7.696740719
6.156083877	4.841003823	7.687886175
6.202517131	10.575260806	7.696956109
1.378132163	2.985693563	10.218821342
1.361172578	8.731196487	10.234874200
6.090086225	8.777720332	10.261658368
3.299359633	0.367738012	0.833977743
3.299359633	6.117352699	0.833977743
8.047554528	0.367738012	0.833977743
8.047554528	6.117352699	0.833977743
3.299359633	4.288896853	3.511537117
3.299359633	10.038396651	3.511537117
8.047554528	4.288896853	3.511537117

8.047554528	10.038396651	3.511537117
3.299904142	2.415263275	6.152365296
3.307596038	8.175253025	6.155090761
8.055387646	2.429573270	6.153303312
8.054891248	8.180431175	6.143381371
3.320180025	0.565641955	8.768757287
3.342770919	6.306548114	8.773459862
8.126753409	0.565436937	8.753353542
8.101657321	6.283847187	8.739018664
5.809143953	5.840043744	10.364085849
2.374049902	4.438958682	1.650935575
2.374049902	10.188343676	1.650935575
7.122149706	4.438958682	1.650935575
7.122149706	10.188343676	1.650935575
2.374049902	2.610502836	4.328494673
2.374049902	8.360002976	4.328494673
7.122149706	2.610502836	4.328494673
7.122149706	8.360002976	4.328494673
2.410798312	0.727604191	6.931247947
2.408992999	6.497649610	6.944944739
7.169394629	0.747227101	6.946728145
7.164982522	6.498413139	6.924955303
2.224632150	4.525799103	9.484722688
2.226716510	10.240132716	9.481298490
7.020991606	4.548841356	9.387387397
6.963094797	10.266397006	9.490020712
0.000000000	1.564208954	1.650935575
0.000000000	7.313593777	1.650935575
4.748099804	1.564208954	1.650935575
4.748099804	7.313593777	1.650935575
0.000000000	5.485252735	4.328494673
0.000000000	11.234752875	4.328494673
4.748099804	5.485252735	4.328494673
4.748099804	11.234752875	4.328494673
4.698908912	3.617634173	6.927937693
4.723459643	9.361745062	6.949348854
9.469151325	3.613935446	6.944014810
9.455770668	9.370958811	6.946344411
0.178225412	1.621796083	9.479836333
0.140572940	7.390665623	9.482634207
4.834306549	1.660131014	9.426037903
4.903324472	7.374081835	9.476308482
5.706461001	5.804162694	11.392646419
6.091474666	3.059533434	10.130251645

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