Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Supplementary Materials for

Non-precious Metal Electrocatalyst for Hydrogen Oxidation Reaction in Alkaline Electrolytes

Wenchao Sheng,[1] Adam P. Bivens,[1] MyatNoeZin Myint,[1] Zhongbin Zhuang,[1] Robert V. Forest,[1] Qianrong Fang,[1] Jingguang G. Chen,[2,3,*] and Yushan Yan[1,*]

[1] Department of Chemical and Biomolecular Engineering and Center for Catalytic Science and Technology, University of Delaware, Newark, DE 19716.
[2]Department of Chemical Engineering, Columbia University, New York, NY 10027
[3]Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973, United States

[*]*Corresponding Authors:* jgchen@columbia.edu, *yanys@udel.edu*

Electrodeposition of Ni-based electrocatalysts

Samples of CoNiMo were prepared by electrodeposition of plating solution containing Co, Ni and Mo precursors onto a 5 mm diameter Au rotating disk electrode (RDE, Pine Instrument). The electrode was first polished with 0.05 μm alumina (Buehler) to a mirror finish, triply rinsed with deionized water, and leached in a 1 M H_2SO_4 (98% Fisher) solution for 2 minutes to remove residual alumina. The electrode was subsequently placed in the electroplating bath. The electrochemical measurements were recorded using EC-Lab software (Bio-Logic Scientific Instruments).

The metal precursor concentrations were adjusted to find the composition with the best electrochemical performance. CoMo was deposited using the same procedure from the plating solution containing 0.254 M $CoSO_4$, 0.049 M Na_2MoO_4, 0.216 M $Na_3C_6H_5O_7$ and no $NiSO_4$, and the resulting CoMo layer showed low but measurable HOR activity. NiMo was similarly deposited from a bath containing 0.254 M $NiSO_4$, 0.049 M Na_2MoO_4, 0.216 M $Na_3C_6H_5O_7$ and no $CoSO_4$, and the resulting NiMo layer showed markedly enhanced activity. When adjusting the ratio between Co and Ni precursors, the concentration of Na_2MoO_4 was fixed as a constant because the reduction in Mo content showed only negative results in the hydrogen evolution reaction (HER) activity suggested in previous literature, and increasing Mo content results in proportionate increases in the oxide content.[1] The concentrations of all the elements and the hydrogen oxidation reaction (HOR) currents at 0.05 V vs. reversible hydrogen electrode (RHE) on the resulting electroplated catalysts are listed in Table S1.

Table S1. Concentrations of elements in the plating solution and the HOR currents at 0.05 V on the resulting electrodeposited catalysts at room temperature.

Sample #	C_{Co} (M)	C_{Ni} (M)	C_{Co+Ni} (M)	C_{Mo} (M)	$C_{Na3C6H5O7}$ (M)	$i_{HOR,\ 0.05V}$ (mA/cm^2_{geo})
1	0	0.254	0.254	0.049	0.216	1.591
2	0.003	0.251	0.254	0.049	0.216	1.887
3	0.006	0.248	0.254	0.049	0.216	1.979
4	0.009	0.245	0.254	0.049	0.216	1.853
5	0.014	0.240	0.254	0.049	0.216	1.716
6	0.025	0.229	0.254	0.049	0.216	1.625
7	0.051	0.203	0.254	0.049	0.216	1.032

CoNiMo layer deposited from sample #3 plating solution containing 0.248 M $NiSO_4$, 0.049 M Na_2MoO_4, 0.006 M $CoSO_4$, and 0.216 M $Na_3C_6H_5O_7$ shows the best HOR performance. The following studies on the temperature-dependence of the HOR kinetics of CoNiMo were based on this composition.

Physical characterization

Scanning electron microscopy (SEM). SEM was used to illustrate the surface morphology of the electrodeposited CoNiMo catalyst. The measurements were performed on a JEOL (JSM-7400F) scanning electron microscope at an acceleration voltage of 2 kV. Energy-dispersive X-ray spectrum was collected at an acceleration voltage of 25 kV.

High-resolution transmission electron microscopy (HRTEM). HRTEM was performed on a JEOL 2010F high-resolution transmission electron microscope operated at 200 kV. The as-prepared CoNiMo catalyst was scraped off from the Au electrode and then dispersed in ethanol by sonication. The dispersion was drop cast on a lacey carbon coated copper grid (EMS) for HRTEM characterization.

Glancing incidence X-ray diffraction (GIXRD). The crystalline phase of the thin film electrode was determined by glancing incidence X-ray diffraction (GIXRD). The spectra were collected on a Rigaku D-Max B x-ray diffractometer with Cu Kα radiation (λ=0.15418 nm), operating at 40 kV and 40 mA from 10 ° to 90 ° at 1 ° incidence.

The diffraction pattern of bare Au electrode is also shown in the figure for comparison. Broad peaks at ~ 44 ° and at ~ 51 ° for the electrodeposited samples are attributed to the CoNiMo. However, the peak at ~ 44 ° is overlapped with the Au (200) peak. This peak is enlarged (Inset) and de-convoluted to have CoNiMo (111) at 43.9 ° and Au (200) at 44.4 ° diffraction peaks. The CoNiMo (111) peak is slight shifted to a lower angle comparing to the (111) peak of Ni (44.3 °), which suggests the CoNiMo maintained the Ni like fcc lattice and doped with larger Mo atoms. This result is consistent with the elemental analysis, which Ni is the majority. The broad peak at 51.2 ° has a d spacing that is $\sqrt{3}/2$ times that of the (111), so it can be signed to the (200) diffraction peak of CoNiMo. The purple line is the simulated result which matches the experimental result very well. Thus the CoNiMo have an fcc cell with a = 0.357 nm. The lattice fringe measured from the HRTEM shows a spacing of 0.20 nm (corresponding to (111) plane), which is also consistent with the XRD result.

Electrochemical characterization

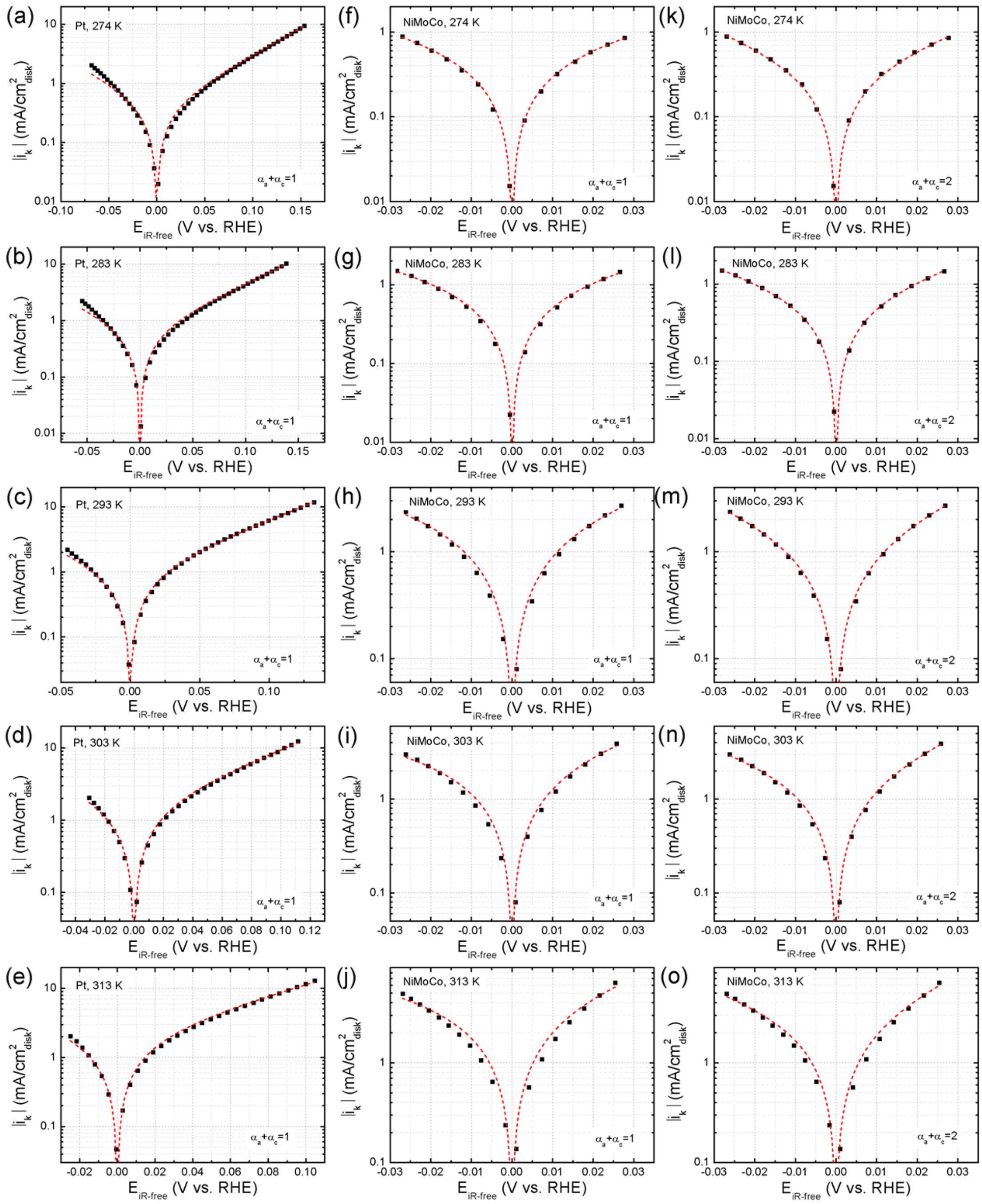

Figure S1. HOR/HER kinetic currents on Pt and CoNiMo at different temperatures and their fits to the Butler-Volmer equation.

Electrochemical surface area (ESA) measurements

The ESA of Pt disk, electroplated Ni and CoNiMo was measured in Ar-saturated 0.1 M KOH at room temperature using cyclic voltammetry method. The hydrogen underpotential deposition (H_{UPD}) region, after subtraction of the double layer capacitive current was used to estimate the Pt ESA, assuming an electrical charge density of 210 μC/cm$^2_{Pt}$ for one monolayer of hydrogen adsorption on Pt. OH desorption region on Ni and CoNiMo was used to estimate the Ni and CoNiMo ESA using a charge density of 514 μC/cm$^2_{Ni}$ for one monolayer of OH adsorption on Ni.

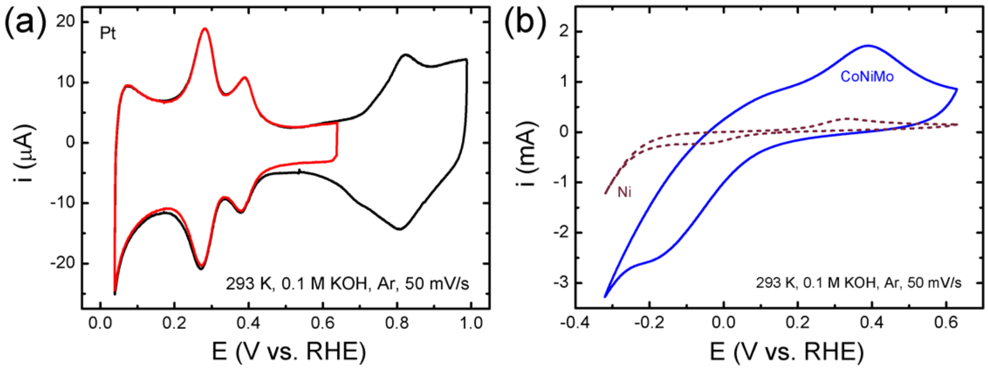

Figure S2. (a) Cyclic voltammograms of Pt; and (b): Cyclic voltammograms of Ni and CoNiMo at room temperature, collected in Ar-saturated 0.1 M KOH at sweep rate of 50 mV/s. The CVs of Pt were recorded with different upper limit potentials.

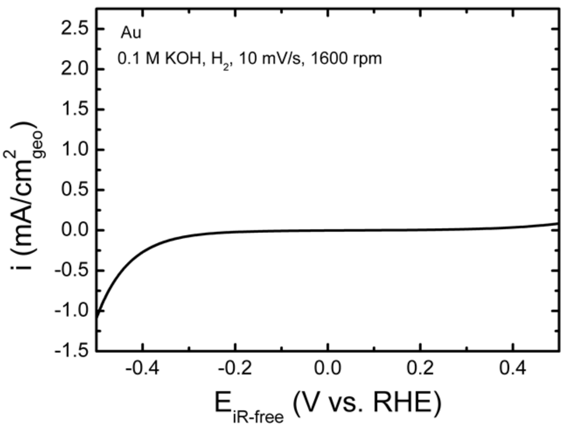

Figure S3. HOR/HER Polarization curve on Au in H_2-saturated 0.1 M KOH at 10 mV/s and 1600 rpm.

H_2-temperature programmed desorption (H_2-TPD)

The ultrahigh-vacuum (UHV) chamber used in this study is a two-level stainless steel chamber with a base pressure of 1×10−8 Torr equipped with Auger electron spectroscopy (AES) for surface characterization and a quadrupole mass spectrometer (MS) for TPD experiment. The Mo single-crystal sample is a (110) oriented disk (99.99%) that has a thickness of 1.50 mm and a diameter of 12.00 mm. The crystal was spot welded directly to two tantalum posts which served as thermal contacts and electrical connections. Hydrogen, oxygen and neon were all of research grade purity (99.99%).

The Mo(110) surface was cleaned by repeated cycles of Ne+ sputtering at 300 K and annealing at 1100 K. Following the last sputter cycle, 1 Langmuir (1 L = 1x10−6 Torr s) of O2 at 1000 K was used to remove carbon left on the surface, followed by annealing at 1100 K This cleaning procedure was repeated until negligible C or O was detected by AES. The surface was then modified by depositing 3d metals (Ni, Co) using physical vapor deposition (PVD). The evaporative PVD doser consisted of a tungsten filament with a high purity Ni or Co wire (99.9999+% from Alfa Aesar) wrapped around it, mounted within a tantalum enclosure. During deposition, the Mo(110) surface was held at 600 K. The Ni (849 eV)/Mo (190 eV) AES ratios were used to determine the Ni monolayer coverage on Mo(110). The Ni-Co-modified Mo(110) surface was prepared by depositing ~ 1 ML of Ni, followed by ~ 0.5 ML of Co on Mo(110) held at 600 K.

Ni(111) and Mo(110) exhibit higher H_2 desorption temperatures, and therefore higher hydrogen binding energies, than Pt(111) (340 K for Ni(111), 370 K for Mo(110), and 325 K for Pt(111)). Also consistent with the DFT trend, the H_2 desorption temperature is decreased to 280 K when the Mo(110) surface is modified with one monolayer of Ni. Further modification of the NiMo bimetallic surface with Co leads to a H_2 desorption temperature (300 K) between NiMo and Mo surfaces.

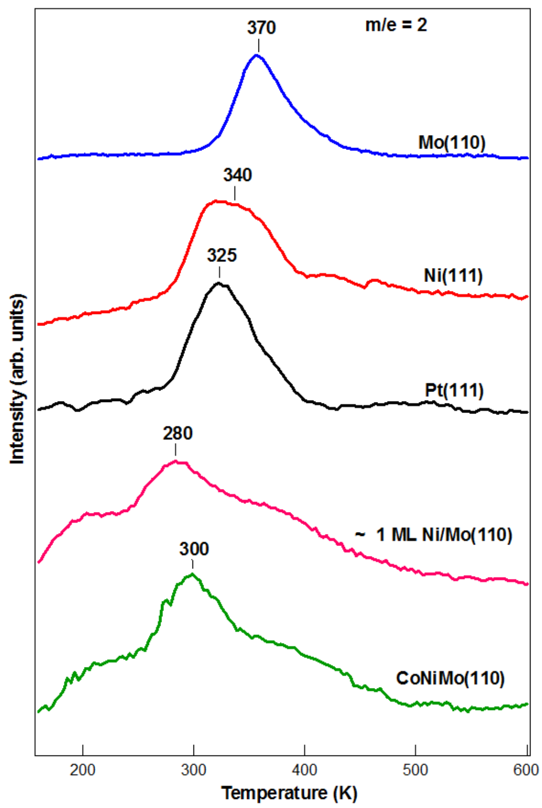

Figure S4. TPD spectra of H_2 desorption from various mono- and multi-metallic surfaces.

Coordinates in the xyz format for the optimized structure on each surface

1. Mo(110)

Mo : Mo(110) [3x3, 4 layers]

1.0

+8.2818875390 +0.0000000000 +0.0000000000

```
 +2.4643300000    +8.2818880000    +0.0000000000
 +0.0000000000    +0.0000000000 +22.5404428600
 36 1
Selective
Direct
 +0.1666700000    +0.1666700000    +0.1000100000    F F F
 +0.5000000000    +0.1666700000    +0.1000100000    F F F
 +0.8333300000    +0.1666700000    +0.1000100000    F F F
 +0.1666700000    +0.5000000000    +0.1000100000    F F F
 +0.5000000000    +0.5000000000    +0.1000100000    F F F
 +0.8333300000    +0.5000000000    +0.1000100000    F F F
 +0.1666700000    +0.8333300000    +0.1000100000    F F F
 +0.5000000000    +0.8333300000    +0.1000100000    F F F
 +0.8333300000    +0.8333300000    +0.1000100000    F F F
 +0.0000000000    +0.0000000000    +0.2000200000    F F F
 +0.3333300000    +0.0000000000    +0.2000200000    F F F
 +0.6666700000    +0.0000000000    +0.2000200000    F F F
 +0.0000000000    +0.3333300000    +0.2000200000    F F F
 +0.3333300000    +0.3333300000    +0.2000200000    F F F
 +0.6666700000    +0.3333300000    +0.2000200000    F F F
 +0.0000000000    +0.6666700000    +0.2000200000    F F F
 +0.3333300000    +0.6666700000    +0.2000200000    F F F
 +0.6666700000    +0.6666700000    +0.2000200000    F F F
 +0.1654367904    +0.1679406585    +0.2971845329    T T T
 +0.5016664092    +0.1648294731    +0.2963062209    T T T
 +0.8315684105    +0.1681861332    +0.2959284996    T T T
 +0.1678741711    +0.4987791360    +0.2971885303    T T T
 +0.5017426946    +0.4984909771    +0.2959181740    T T T
 +0.8315873960    +0.5018689032    +0.2963065461    T T T
 +0.1666799340    +0.8333813052    +0.2958767174    T T T
 +0.5010393219    +0.8313446501    +0.2965793818    T T T
 +0.8323378103    +0.8353094864    +0.2966059384    T T T
 +0.0022038511    +0.9973172762    +0.3867264425    T T T
 +0.3389296470    +0.9914787082    +0.3859777722    T T T
 +0.6657223804    +0.0009225424    +0.3868701278    T T T
 +0.0080846560    +0.3220395731    +0.3883788015    T T T
 +0.3252201632    +0.3445804063    +0.3884275283    T T T
 +0.6666546706    +0.3333886594    +0.3861607703    T T T
 -0.0055653696    +0.6751712090    +0.3859987709    T T T
 +0.3311443321    +0.6692354723    +0.3867117598    T T T
 +0.6675901355    +0.6658114520    +0.3868742528    T T T
 +0.1666305841    +0.3326601383    +0.4476781720    T T T
```

2. Ni(111)

```
Ni H : Ni(111) [3x3, 4 layers]
1.0
 +7.4763814190   +0.0000000000   +0.0000000000
 +3.7381907090   +6.4747360000   +0.0000000000
 +0.0000000000   +0.0000000000 +20.3481300000
 36 1
Selective
Direct
 +0.0000000000   +0.0000000000   +0.1000000000   F F F
 +0.3333333333   +0.0000000000   +0.1000000000   F F F
 +0.6666666667   +0.0000000000   +0.1000000000   F F F
 +0.0000000000   +0.3333333333   +0.1000000000   F F F
 +0.3333333333   +0.3333333333   +0.1000000000   F F F
 +0.6666666667   +0.3333333333   +0.1000000000   F F F
 +0.0000000000   +0.6666666667   +0.1000000000   F F F
 +0.3333333333   +0.6666666667   +0.1000000000   F F F
 +0.6666666667   +0.6666666667   +0.1000000000   F F F
 +0.1111111111   +0.1111111111   +0.2000000000   F F F
 +0.4444444444   +0.1111111111   +0.2000000000   F F F
 +0.7777777778   +0.1111111111   +0.2000000000   F F F
 +0.1111111111   +0.4444444444   +0.2000000000   F F F
 +0.4444444444   +0.4444444444   +0.2000000000   F F F
 +0.7777777778   +0.4444444444   +0.2000000000   F F F
 +0.1111111111   +0.7777777778   +0.2000000000   F F F
 +0.4444444444   +0.7777777778   +0.2000000000   F F F
 +0.7777777778   +0.7777777778   +0.2000000000   F F F
 +0.2222127278   +0.2222126660   +0.3003686866   T T T
 +0.5556745797   +0.2219867355   +0.3001131126   T T T
 +0.8889088292   +0.2222137263   +0.3003684548   T T T
 +0.2219867657   +0.5556746006   +0.3001130860   T T T
 +0.5556743427   +0.5556744465   +0.3001132432   T T T
 +0.8891104783   +0.5551148266   +0.3002585012   T T T
 +0.2222137414   +0.8889088105   +0.3003684522   T T T
 +0.5551151643   +0.8891102613   +0.3002585320   T T T
 +0.8891104230   +0.8891103507   +0.3002580055   T T T
 -0.0010268745   -0.0010271200   +0.4009370615   T T T
 +0.3353917495   -0.0010287463   +0.4009371004   T T T
 +0.6667301678   -0.0001241159   +0.3991510486   T T T
 -0.0010284739   +0.3353914007   +0.4009371688   T T T
 +0.3341580777   +0.3341580393   +0.3992599726   T T T
 +0.6650183979   +0.3341592819   +0.3992602530   T T T
 -0.0001241359   +0.6667299607   +0.3991510234   T T T
```

+0.3341592992 +0.6650183719 +0.3992603248 T T T
+0.6667309145 +0.6667305070 +0.3991516830 T T T
+0.1111121323 +0.1111110143 +0.4449796014 T T T

3. Ni_{ML}/Mo(110)

Mo Ni H : Mo(110) [3x3, 4 layers]
1.0
+8.2818875390 +0.0000000000 +0.0000000000
+2.4643300000 +8.2818880000 +0.0000000000
+0.0000000000 +0.0000000000 +22.5404428600
27 9 1
Selective
Direct
+0.1666700000 +0.1666700000 +0.1000100000 F F F
+0.5000000000 +0.1666700000 +0.1000100000 F F F
+0.8333300000 +0.1666700000 +0.1000100000 F F F
+0.1666700000 +0.5000000000 +0.1000100000 F F F
+0.5000000000 +0.5000000000 +0.1000100000 F F F
+0.8333300000 +0.5000000000 +0.1000100000 F F F
+0.1666700000 +0.8333300000 +0.1000100000 F F F
+0.5000000000 +0.8333300000 +0.1000100000 F F F
+0.8333300000 +0.8333300000 +0.1000100000 F F F
+0.0000000000 +0.0000000000 +0.2000200000 F F F
+0.3333300000 +0.0000000000 +0.2000200000 F F F
+0.6666700000 +0.0000000000 +0.2000200000 F F F
+0.0000000000 +0.3333300000 +0.2000200000 F F F
+0.3333300000 +0.3333300000 +0.2000200000 F F F
+0.6666700000 +0.3333300000 +0.2000200000 F F F
+0.0000000000 +0.6666700000 +0.2000200000 F F F
+0.3333300000 +0.6666700000 +0.2000200000 F F F
+0.6666700000 +0.6666700000 +0.2000200000 F F F
+0.1623965941 +0.1673109986 +0.2945091106 T T T
+0.4970699331 +0.1706250859 +0.2944216352 T T T
+0.8320522634 +0.1685210338 +0.2951277957 T T T
+0.1709970429 +0.4994292988 +0.2945161378 T T T
+0.5011116622 +0.4981972914 +0.2951148936 T T T
+0.8362230626 +0.4959810270 +0.2943860368 T T T
+0.1667334003 +0.8333742490 +0.2945200607 T T T
+0.4981206831 +0.8363539765 +0.2948477637 T T T
+0.8353842905 +0.8301367319 +0.2948555758 T T T
-0.0027470166 -0.0037132377 +0.3716415048 T T T

+0.3319364123   +0.0035581434   +0.3718904542   T T T
+0.6652573470   -0.0001066460   +0.3708538733   T T T
+0.0107746783   +0.3334164701   +0.3756019689   T T T
+0.3219990463   +0.3331061253   +0.3756166073   T T T
+0.6664853854   +0.3333997608   +0.3726470858   T T T
+0.0015306030   +0.6629808024   +0.3719155273   T T T
+0.3361409175   +0.6704556990   +0.3716649429   T T T
+0.6683898574   +0.6667206290   +0.3708677199   T T T
+0.1662936999   +0.3331113229   +0.4208129474   T T T

4. CoNi/Mo(110)

```
Mo Co Ni H : Mo(110) [3x3, 4 layers]
1.0
  +8.2818875390    +0.0000000000    +0.0000000000
  +2.4643300000    +8.2818880000    +0.0000000000
  +0.0000000000    +0.0000000000 +22.5404428600
  27 3 6 1
Selective
Direct
  +0.1666700000    +0.1666700000    +0.1000100000    F F F
  +0.5000000000    +0.1666700000    +0.1000100000    F F F
  +0.8333300000    +0.1666700000    +0.1000100000    F F F
  +0.1666700000    +0.5000000000    +0.1000100000    F F F
  +0.5000000000    +0.5000000000    +0.1000100000    F F F
  +0.8333300000    +0.5000000000    +0.1000100000    F F F
  +0.1666700000    +0.8333300000    +0.1000100000    F F F
  +0.5000000000    +0.8333300000    +0.1000100000    F F F
  +0.8333300000    +0.8333300000    +0.1000100000    F F F
  +0.0000000000    +0.0000000000    +0.2000200000    F F F
  +0.3333300000    +0.0000000000    +0.2000200000    F F F
  +0.6666700000    +0.0000000000    +0.2000200000    F F F
  +0.0000000000    +0.3333300000    +0.2000200000    F F F
  +0.3333300000    +0.3333300000    +0.2000200000    F F F
  +0.6666700000    +0.3333300000    +0.2000200000    F F F
  +0.0000000000    +0.6666700000    +0.2000200000    F F F
  +0.3333300000    +0.6666700000    +0.2000200000    F F F
  +0.6666700000    +0.6666700000    +0.2000200000    F F F
  +0.1672315242    +0.1602552547    +0.2937705681    T T T
  +0.4920611124    +0.1781850053    +0.2954605795    T T T
  +0.8306803437    +0.1695869398    +0.2951751327    T T T
  +0.1720993843    +0.4926012434    +0.2952653526    T T T
```

```
+0.4968583441    +0.5081757366    +0.2950117709    T T T
+0.8360125513    +0.4955208249    +0.2943994044    T T T
+0.1715765842    +0.8244574009    +0.2951446797    T T T
+0.4939375731    +0.8438827450    +0.2960419844    T T T
+0.8356345780    +0.8304997576    +0.2945434293    T T T
+0.3302583960    +0.0084629455    +0.3733106976    T T T
+0.3278932844    +0.3463099845    +0.3776703529    T T T
+0.3368350125    +0.6673159590    +0.3747076655    T T T
+0.0011196783    -0.0062797719    +0.3703955624    T T T
+0.6661707647    +0.0046292977    +0.3701343712    T T T
+0.0178483088    +0.3284944722    +0.3742176875    T T T
+0.6593030548    +0.3383104105    +0.3719059802    T T T
+0.0019526345    +0.6600614732    +0.3716908958    T T T
+0.6670314919    +0.6694489038    +0.3701030985    T T T
```

5. Pt(111)

```
Pt H :Pt(111) [3x3, 4 layers]
1.0
 +8.4956758440    +0.0000000000    +0.0000000000
 +4.2478379220    +7.3574710000    +0.0000000000
 +0.0000000000    +0.0000000000 +23.1223009300
 36 1
Selective
Direct
 +0.0000000000    +0.0000000000    +0.1000000000    F F F
 +0.3333333333    +0.0000000000    +0.1000000000    F F F
 +0.6666666667    +0.0000000000    +0.1000000000    F F F
 +0.0000000000    +0.3333333333    +0.1000000000    F F F
 +0.3333333333    +0.3333333333    +0.1000000000    F F F
 +0.6666666667    +0.3333333333    +0.1000000000    F F F
 +0.0000000000    +0.6666666667    +0.1000000000    F F F
 +0.3333333333    +0.6666666667    +0.1000000000    F F F
 +0.6666666667    +0.6666666667    +0.1000000000    F F F
 +0.1111111111    +0.1111111111    +0.2000000000    F F F
 +0.4444444444    +0.1111111111    +0.2000000000    F F F
 +0.7777777778    +0.1111111111    +0.2000000000    F F F
 +0.1111111111    +0.4444444444    +0.2000000000    F F F
 +0.4444444444    +0.4444444444    +0.2000000000    F F F
 +0.7777777778    +0.4444444444    +0.2000000000    F F F
 +0.1111111111    +0.7777777778    +0.2000000000    F F F
```

+0.4444444444	+0.7777777778	+0.2000000000	F F F
+0.7777777778	+0.7777777778	+0.2000000000	F F F
+0.2220358250	+0.2220866897	+0.2987096289	T T T
+0.5556904688	+0.2218850466	+0.2980475657	T T T
+0.8891766164	+0.2220872460	+0.2986927585	T T T
+0.2219195731	+0.5556531815	+0.2980550452	T T T
+0.5556940945	+0.5556466737	+0.2980667863	T T T
+0.8890128012	+0.5552609772	+0.2981438233	T T T
+0.2220723999	+0.8891625953	+0.2986951718	T T T
+0.5550872920	+0.8890976396	+0.2981796807	T T T
+0.8891414910	+0.8891308373	+0.2981991237	T T T
-0.0028035058	-0.0025215057	+0.3996034274	T T T
+0.3391035031	-0.0027317025	+0.3995966860	T T T
+0.6666497190	+0.0002474756	+0.3982831763	T T T
-0.0032074468	+0.3397783504	+0.3995221789	T T T
+0.3343142954	+0.3344623213	+0.3979794567	T T T
+0.6646122130	+0.3343996620	+0.3979855603	T T T
+0.0001170320	+0.6669531289	+0.3982700043	T T T
+0.3342369228	+0.6647982293	+0.3979964894	T T T
+0.6663578000	+0.6668368288	+0.3982800947	T T T
+0.1113965227	+0.1128651084	+0.4353637400	T T T

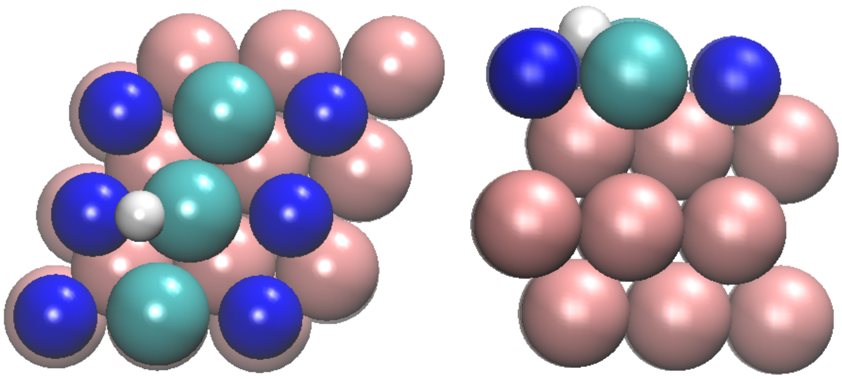

Figure S5. Top and side views of adsorption geometry of hydrogen on CoNi/Mo(110) (Mo, pink; Ni, blue; Co, cyan; H, white).

1. L. S. Sanches, S. H. Domingues, C. E. B. Marino and L. H. Mascaro, *Electrochemistry Communications*, 2004, **6**, 543-548.