Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information

Boosting Oxygen Evolution Reaction Activity by Tailoring MOF-Derived Hierarchical Co-Ni Alloy Nanoparticles Encapsulated in Nitrogen-Doped Carbon Frameworks

Xiaobin Liu, Xudong Zhao, and Li-Zhen Fan*

Beijing Advanced Innovation Center for Materials Genome Engineering, Institute of Advanced Materials and Technology, University of Science and Technology Beijing, Beijing 100083, China. E-mail: fanlizhen@ustb.edu.cn (L.-Z. Fan).

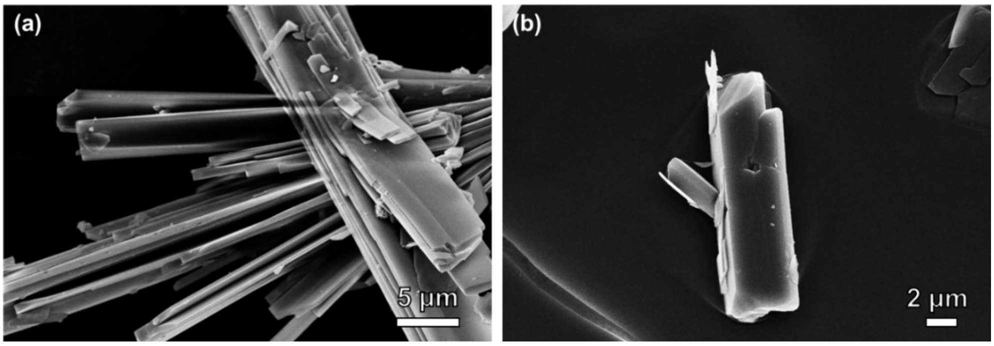

Figure S1. SEM images of the Co_2Ni-MOF precursor.

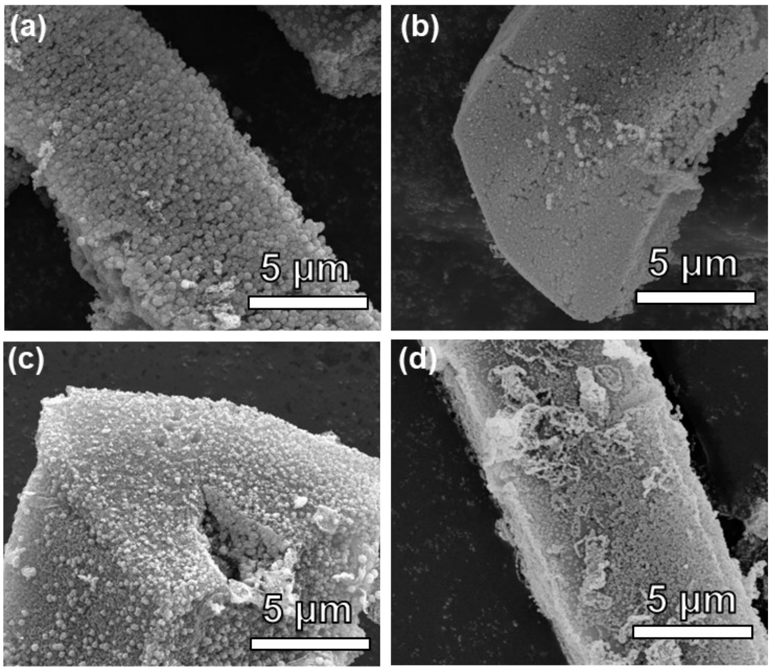

Figure S2. SEM images of (a) Co@NC, (b) $CoNi_2$@NC, (c) CoNi@NC and (d) Ni@NC.

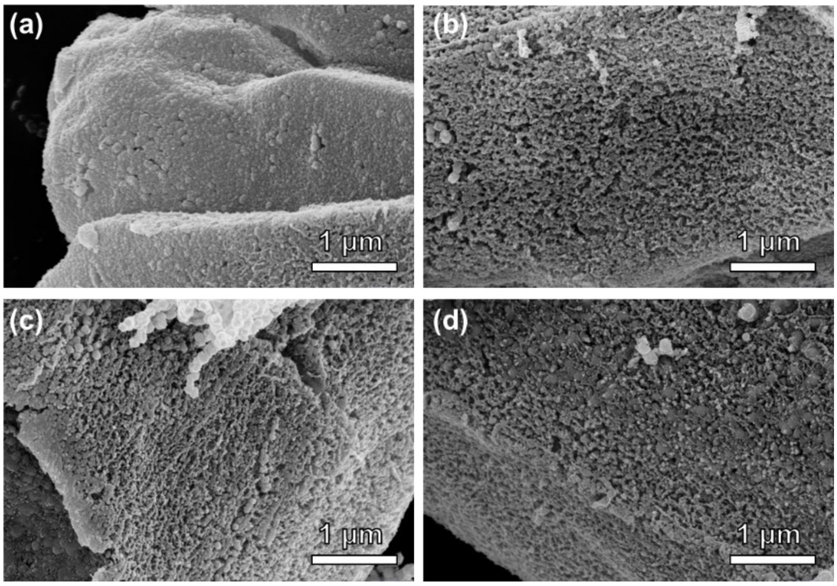

Figure S3. SEM images of (a) Co_2Ni@NC-600, (b) Co_2Ni@NC-700, (c) Co_2Ni@NC-900 and (d) Co_2Ni@NC-1000.

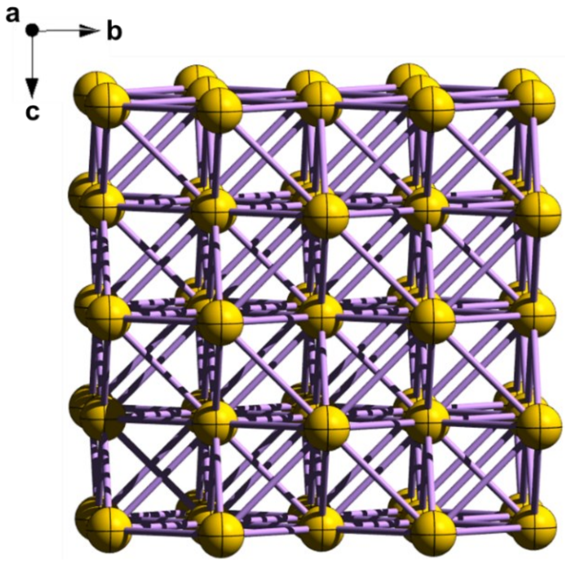

Figure S4. The face-centered cubic stack geometry configuration of cobalt and nickel metal.

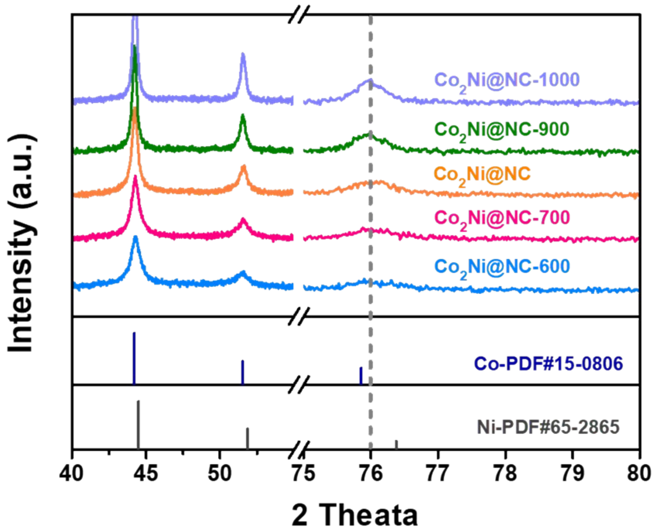

Figure S5. The XRD patterns of Co_2Ni@NC-T at different temperatures.

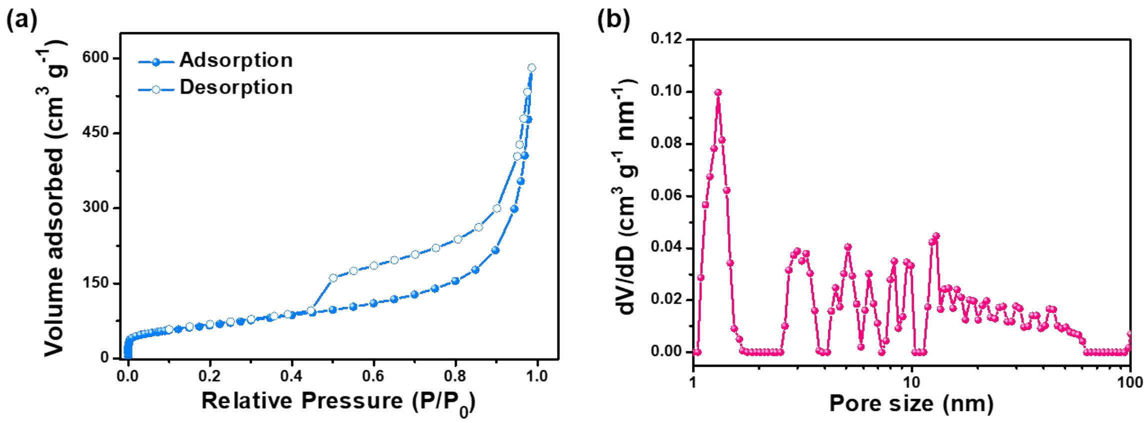

Figure S6. (a) N_2 adsorption-desorption isotherm and (b) pore size distribution curve of Co_2Ni@NC.

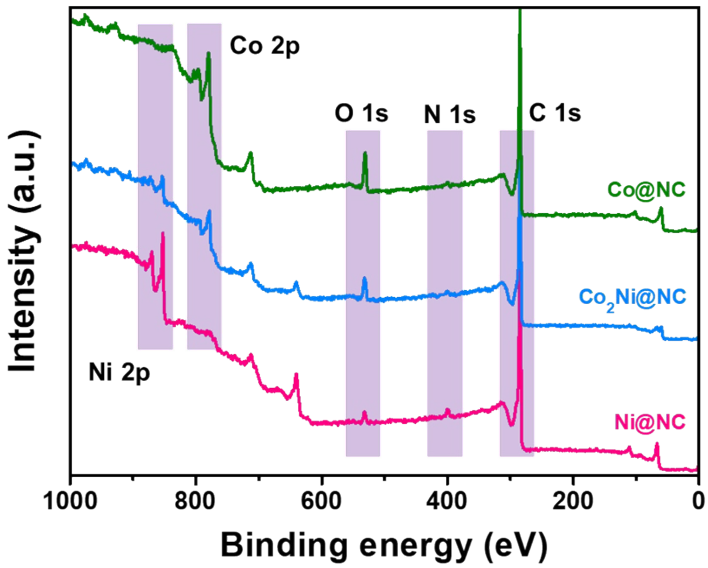

Figure S7. Survey XPS spectra of Co@NC, Co_2Ni@NC and Ni@NC.

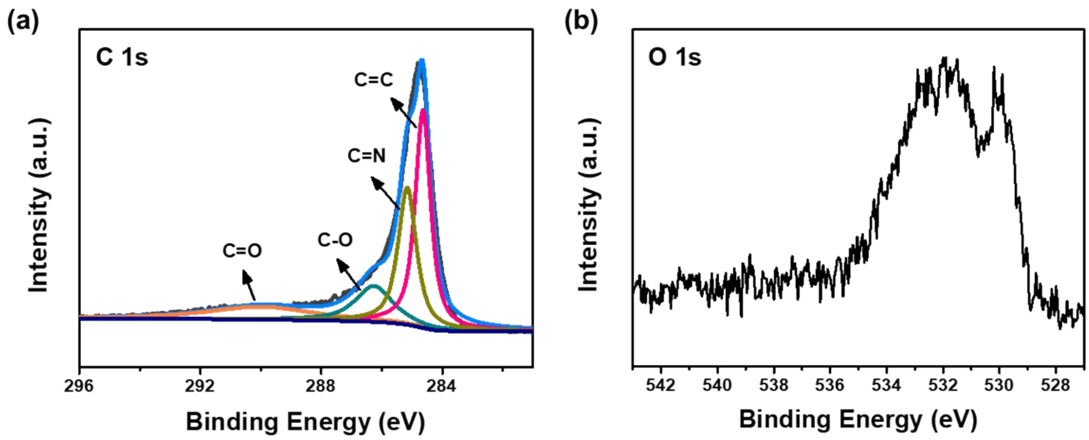

Figure S8. The high-resolution XPS spectrum of a) C 1s and b) O 1s in Co_2Ni@NC.

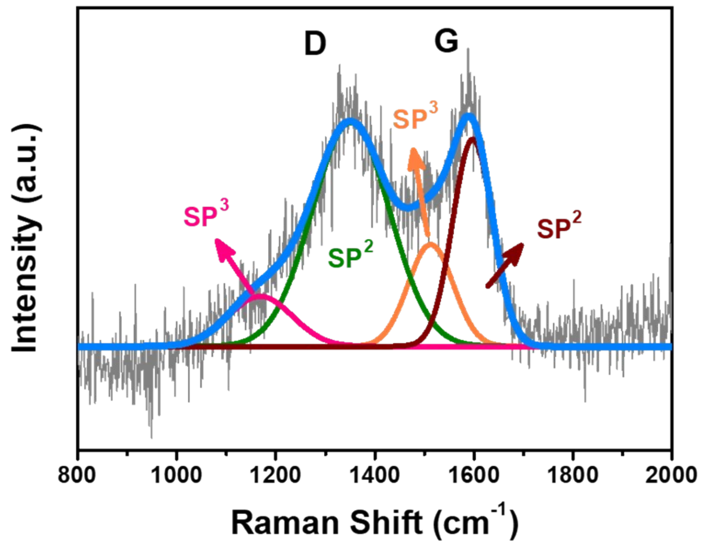

Figure S9. Raman spectrum of Co_2Ni@NC.

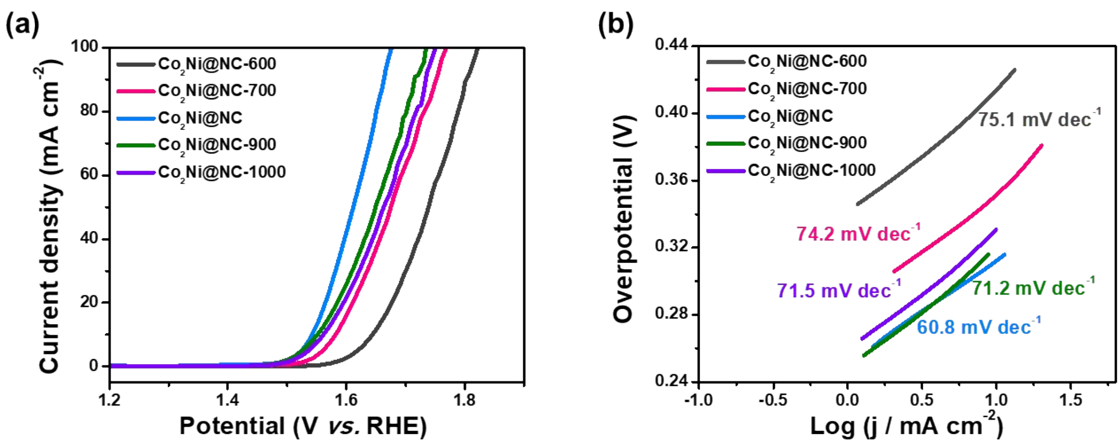

Figure S10. (a) LSV curves and the corresponding (b)Tafel slopes of Co_2Ni@NC-600, Co_2Ni@NC-700, Co_2Ni@NC, Co_2Ni@NC-900 and Co_2Ni@NC-1000.

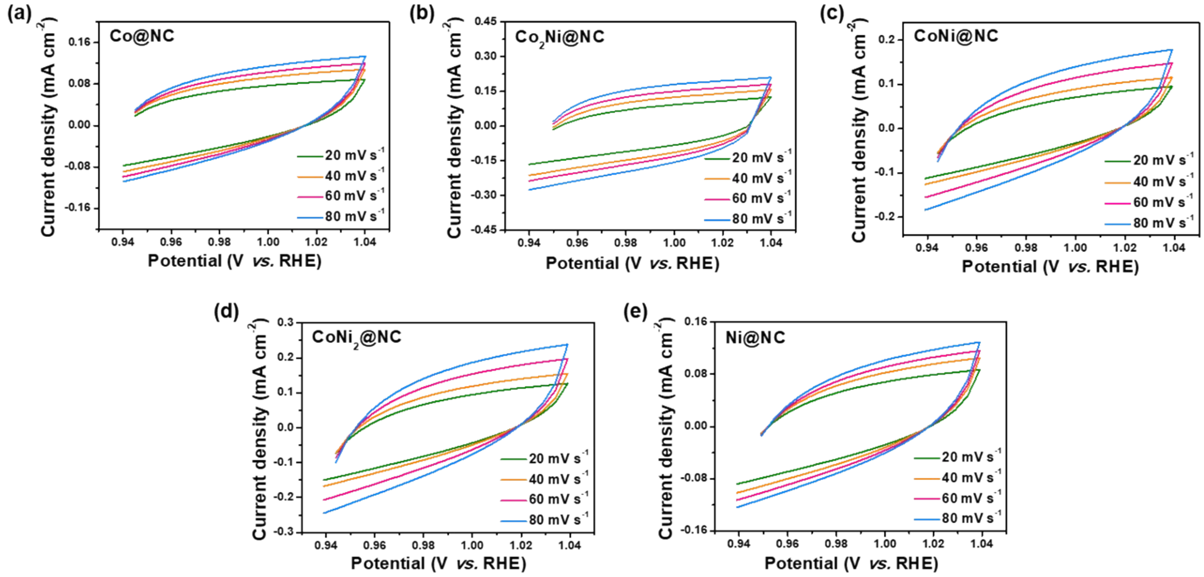

Figure S11. Cyclic voltammograms (0.94 - 1.04 V *vs.* RHE) of (a) Co@NC, (b) Co_2Ni@NC, (c) CoNi@NC, (d) $CoNi_2$@NC and (e) Ni@NC recorded in 1.0 M KOH.

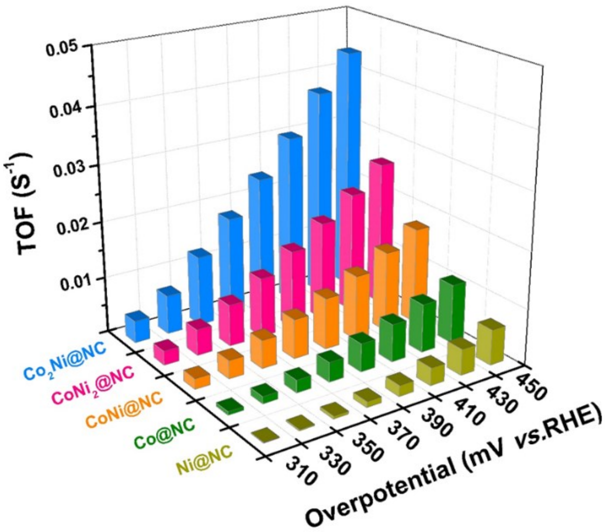

Figure S12. TOFs at different overpotentials from 310 to 450 mV by assuming that every Co or Ni atoms are catalytically active.

The TOF can be calculated with the equation as follow:

$$TOF = \frac{j \times A}{4 \times F \times n}$$

where *j* is the current density (mA cm^{-2}) at a measured overpotential in the range of 310 mV to 450 mV, *A* is the geometric area of the glassy carbon electrode, *F* is the faraday constant with value of 96485 C mol^{-1}, and *n* is the number of molecular weight of the catalyst that are deposited onto the glassy carbon electrode.

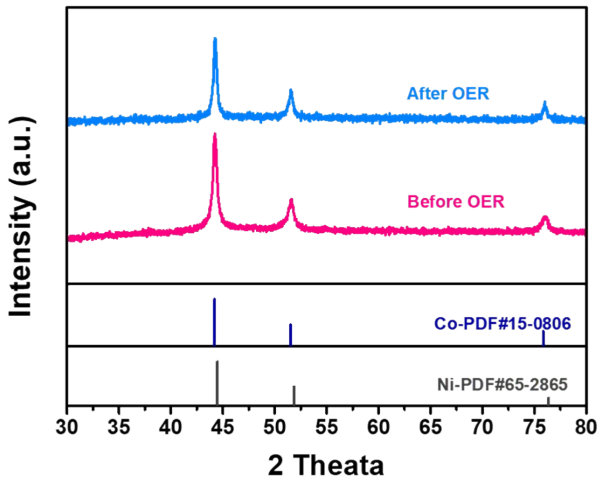

Figure S13. XRD patterns of the Co_2Ni@NC after continuous oxygen reaction evolution in alkaline electrolyte solution.

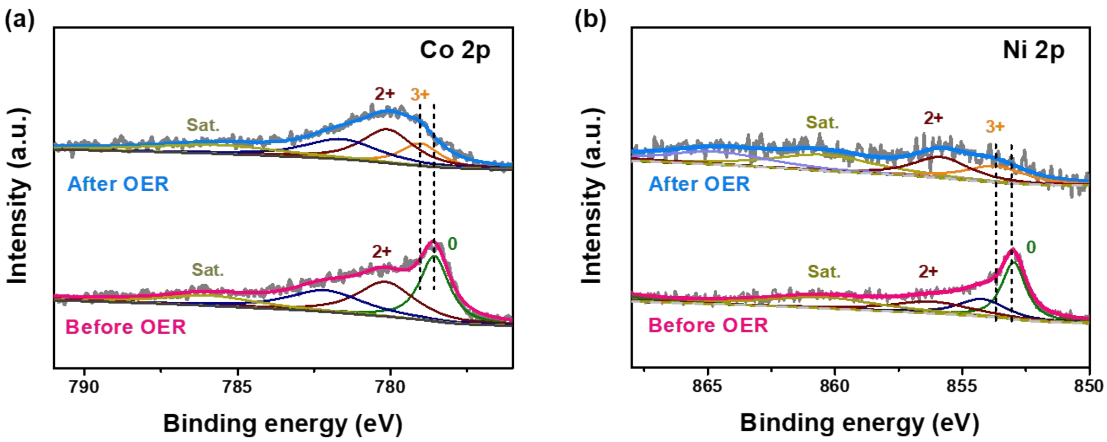

Figure S14. XPS patterns of (a) Co 2p and (b) Ni 2p in Co_2Ni@NC before and after continuous oxygen evolution reaction in alkaline electrolyte solution.

Table S1 Comparison of the OER electrocatalytic activity of Co_2Ni@NC with previously reported Co-based electrocatalysts.

Catalyst	**Electrolyte**	**η (10 mA cm^{-2})**	**Tafel slope (mV dec^{-1})**	**Ref**
Co_2Ni@NC	1 M KOH	310	60.8	This work
CoN_x	1 M KOH	315	75.7	1
$CoNiS_x$	1 M KOH	320	59	2
$Co/NiCo_2O_4$	0.1 M KOH	339	60	3
$NiO/NiCo_2O_4$	1 M KOH	340	66	4
$CoNi/CoNiO_2$	1 M KOH	341	84	5
CoNi	1 M KOH	420	107	6

1. Z. Liang, C. Zhang, H. Yuan, W. Zhang, H. Zheng and R. Cao, *Chem. Commun.,* 2018, **54**, 7519−7522.

2. Z. Yu, Y. Bai, S. Zhang, Y. Liu, N. Zhang and K Sun, *Int. J. Hydrogen Energy*, 2018, **43**, 8815−8823.

3. J. Li, S. Lu, H. Huang, D. Liu, Z. Zhuang and C Zhong, *ACS Sustainable Chem. Eng.,* 2018, **6**, 10021−10029.

4. Y. Wang, Z. Zhang, X. Liu, F. Ding, P. Zou, X. Wang, Q. Zhao and H. Rao, *ACS Sustainable Chem. Eng.,* 2018, **6**, 12511−12521.

5. H. Xu, Z.-X. Shi, Y.-X. Tong and G.-R. Li, *Adv. Mater.,* 2018, **30**, 1705442.

6. A. Jayakumar, R. P. Antony, J. Zhao and J.-M. Lee, *Electrochim. Acta,* 2018, **265**, 336−347.

The cartesian coordinates of all the optimized models:

Co(111)
1.00000000000000
4.9243001937999997 0.0000000000000000 0.0000000000000000
-2.4621500968999999 4.2645690636999998 0.0000000000000000
0.0000000000000000 0.0000000000000000 30.0000000000000000
Co
12
Selective dynamics
Direct
0.6666700500000005 0.3333400030000035 0.0003299999999982 F F
F
0.3333300170000015 0.6666700549999973 0.0673400000000015 F F
F
-0.0000003705398125 -0.0000000551219042 0.1339718564344826 T T
T
0.6666700629999980 0.8333400289999986 0.0003299999999982 F F
F
0.3333300139999977 0.1666700019999965 0.0673400000000015 F F
F
-0.0000002799796252 0.5000000665530400 0.1339718823029691 T T
T
0.1666700150000011 0.8333400289999986 0.0003299999999982 F F
F
0.8333300139999977 0.1666700019999965 0.0673400000000015 F F
F
0.4999993513037376 0.4999999687119612 0.1339718520703188 T T
T
0.1666700019999965 0.3333400030000035 0.0003299999999982 F F
F
0.8333299920000030 0.6666700549999973 0.0673400000000015 F F
F
0.4999993270247353 -0.0000002400019065 0.1339718374769871 T T
T

Co(111)-H
1.00000000000000
4.9243001937999997 0.0000000000000000 0.0000000000000000
-2.4621500968999999 4.2645690636999998 0.0000000000000000
0.0000000000000000 0.0000000000000000 30.0000000000000000
Co H
12 1
Selective dynamics

Direct
0.6666700500000005 0.3333400030000035 0.0003299999999982 F F
F
0.3333300170000015 0.6666700549999973 0.0673400000000015 F F
F
-0.0000015332425495 0.0000000278769508 0.1332994876836260 T T
T
0.6666700629999980 0.8333400289999986 0.0003299999999982 F F
F
0.3333300139999977 0.1666700019999965 0.0673400000000015 F F
F
0.0031307158081299 0.5015662839926978 0.1342328784796004 T T
T
0.1666700150000011 0.8333400289999986 0.0003299999999982 F F
F
0.8333300139999977 0.1666700019999965 0.0673400000000015 F F
F
0.4984330481127162 0.5015660057982991 0.1342331548111508 T T
T
0.1666700019999965 0.3333400030000035 0.0003299999999982 F F
F
0.8333299920000030 0.6666700549999973 0.0673400000000015 F F
F
0.4984319539673989 -0.0031333516779473 0.1342330123975682 T T
T
0.6666655290355812 0.3333309722600203 0.1662660223102070 T T
T

Co(111)-O
1.00000000000000
4.9243001937999997 0.0000000000000000 0.0000000000000000
-2.4621500968999999 4.2645690636999998 0.0000000000000000
0.0000000000000000 0.0000000000000000 30.0000000000000000
Co O
12 1
Selective dynamics
Direct
0.6666700500000005 0.3333400030000035 0.0003299999999982 F F
F
0.3333300170000015 0.6666700549999973 0.0673400000000015 F F
F
-0.0000006520794779 0.0000007391139833 0.1321002201137553 T T
T
0.6666700629999980 0.8333400289999986 0.0003299999999982 F F

F
0.3333300139999977 0.1666700019999965 0.0673400000000015 F F
F
0.0090886547868631 0.5045438851250365 0.1360183980868310 T T
T
0.1666700150000011 0.8333400289999986 0.0003299999999982 F F
F
0.8333300139999977 0.1666700019999965 0.0673400000000015 F F
F
0.4954557829599352 0.5045424145677553 0.1360189653861942 T T
T
0.1666700019999965 0.3333400030000035 0.0003299999999982 F F
F
0.8333299920000030 0.6666700549999973 0.0673400000000015 F F
F
0.4954549749989264 -0.0090892811363880 0.1360186785598667 T T
T
0.6666660216859774 0.3333252761432879 0.1739719028132380 T T
T

Co(111)-OH
1.00000000000000
4.9243001937999997 0.0000000000000000 0.0000000000000000
-2.4621500968999999 4.2645690636999998 0.0000000000000000
0.0000000000000000 0.0000000000000000 30.0000000000000000
Co O H
12 1 1
Selective dynamics
Direct
0.6666700500000005 0.3333400030000035 0.0003299999999982 F F
F
0.3333300170000015 0.6666700549999973 0.0673400000000015 F F
F
-0.0000022728212852 0.0000292359310283 0.1314711166331614 T T
T
0.6666700629999980 0.8333400289999986 0.0003299999999982 F F
F
0.3333300139999977 0.1666700019999965 0.0673400000000015 F F
F
0.0084580341682610 0.5042498200024262 0.1358654383090594 T T
T
0.1666700150000011 0.8333400289999986 0.0003299999999982 F F
F
0.8333300139999977 0.1666700019999965 0.0673400000000015 F F

F
    0.4957715591112698   0.5042551541251945   0.1358400279417204   T   T
T
    0.1666700019999965   0.3333400030000035   0.0003299999999982   F   F
F
    0.8333299920000030   0.6666700549999973   0.0673400000000015   F   F
F
    0.4958073489703548   0.9916222174513399   0.1358684949624763   T   T
T
    0.6665320962536947   0.3334646687971722   0.1816690259415031   T   T
T
    0.6660076293664297   0.3340597173751905   0.2140375537471107   T   T
T

Co(111)-OOH
    1.00000000000000
        4.9243001937999997   0.0000000000000000   0.0000000000000000
       -2.4621500968999999   4.2645690636999998   0.0000000000000000
        0.0000000000000000   0.0000000000000000   30.0000000000000000
    Co   O   H
      12   2   1
Selective dynamics
Direct
    0.6666700500000005   0.3333400030000035   0.0003299999999982   F   F
F
    0.3333300170000015   0.6666700549999973   0.0673400000000015   F   F
F
  -0.0001335700760283 -0.0000644515613440   0.1300644827858781   T   T
T
    0.6666700629999980   0.8333400289999986   0.0003299999999982   F   F
F
    0.3333300139999977   0.1666700019999965   0.0673400000000015   F   F
F
    0.9941494684583362   0.4970560138343664   0.1372077114407721   T   T
T
    0.1666700150000011   0.8333400289999986   0.0003299999999982   F   F
F
    0.8333300139999977   0.1666700019999965   0.0673400000000015   F   F
F
    0.5025412817313730   0.4971229306485292   0.1372651281086442   T   T
T
    0.1666700019999965   0.3333400030000035   0.0003299999999982   F   F
F
    0.8333299920000030   0.6666700549999973   0.0673400000000015   F   F

F
0.5025231248873665 0.0054302829158161 0.1372695237317980 T T
T
0.6665565014299120 0.3332850089292599 0.1788978070476726 T T
T
0.3327917291997627 0.6663911185646116 0.1823857551312400 T T
T
0.3298566249273242 0.6649420782401375 0.2147926215767540 T T
T

CoNi(111)
1.00000000000000
4.9243001937999997 0.0000000000000000 0.0000000000000000
-2.4621500968999999 4.2645690636999998 0.0000000000000000
0.0000000000000000 0.0000000000000000 30.0000000000000000
Co Ni
8 4
Selective dynamics
Direct
0.6666700500000005 0.3333400030000035 0.0003299999999982 F F
F
0.3333300170000015 0.6666700549999973 0.0673400000000015 F F
F
0.6666700629999980 0.8333400289999986 0.0003299999999982 F F
F
0.3333300139999977 0.1666700019999965 0.0673400000000015 F F
F
0.1666700150000011 0.8333400289999986 0.0003299999999982 F F
F
0.8333300139999977 0.1666700019999965 0.0673400000000015 F F
F
0.1666700019999965 0.3333400030000035 0.0003299999999982 F F
F
0.8333299920000030 0.6666700549999973 0.0673400000000015 F F
F
-0.0000003619079989 -0.0000001295137264 0.1346120978369993 T T
T
-0.0000003277681724 0.4999999462865708 0.1346124070159955 T T
T
0.4999996900935102 0.4999999100860196 0.1346123084198105 T T
T
0.4999996140629885 -0.0000001655750949 0.1346121826413619 T T
T

```
CoNi(111)-H
   1.00000000000000
     4.9243001937999997    0.0000000000000000    0.0000000000000000
    -2.4621500968999999    4.2645690636999998    0.0000000000000000
     0.0000000000000000    0.0000000000000000   30.0000000000000000
   Co   Ni   H
     8     4     1
Selective dynamics
Direct
  0.6666700500000005  0.3333400030000035  0.0003299999999982   F   F
F
  0.3333300170000015  0.6666700549999973  0.0673400000000015   F   F
F
  0.6666700629999980  0.8333400289999986  0.0003299999999982   F   F
F
  0.3333300139999977  0.1666700019999965  0.0673400000000015   F   F
F
  0.1666700150000011  0.8333400289999986  0.0003299999999982   F   F
F
  0.8333300139999977  0.1666700019999965  0.0673400000000015   F   F
F
  0.1666700019999965  0.3333400030000035  0.0003299999999982   F   F
F
  0.8333299920000030  0.6666700549999973  0.0673400000000015   F   F
F
  0.0000042604731429  0.0000079492156659  0.1342956235730528   T   T
T
  0.0021894711169815  0.5010975990900062  0.1352947303262866   T   T
T
  0.4988981493468221  0.5010974966890732  0.1352949756650909   T   T
T
  0.4989014642128784  0.9978129117195177  0.1352946643362380   T   T
T
  0.6666680101583616  0.3333393397440707  0.1659867416863905   T   T
T

CoNi(111)-O
   1.00000000000000
     4.9243001937999997    0.0000000000000000    0.0000000000000000
    -2.4621500968999999    4.2645690636999998    0.0000000000000000
     0.0000000000000000    0.0000000000000000   30.0000000000000000
   Co   Ni   O
     8     4     1
Selective dynamics
```

```
Direct
   0.6666700500000005    0.3333400030000035    0.0003299999999982       F       F
F
   0.3333300170000015    0.6666700549999973    0.0673400000000015       F       F
F
   0.6666700629999980    0.8333400289999986    0.0003299999999982       F       F
F
   0.3333300139999977    0.1666700019999965    0.0673400000000015       F       F
F
   0.1666700150000011    0.8333400289999986    0.0003299999999982       F       F
F
   0.8333300139999977    0.1666700019999965    0.0673400000000015       F       F
F
   0.1666700019999965    0.3333400030000035    0.0003299999999982       F       F
F
   0.8333299920000030    0.6666700549999973    0.0673400000000015       F       F
F
  -0.0000041484311401    0.0000116548819044    0.1335610098792603       T       T
T
   0.0065961994640234    0.5032830168079764    0.1367954300015742       T       T
T
   0.4966743219791426    0.5033133026756056    0.1367907124495134       T       T
T
   0.4967100670141130    0.9934022503004124    0.1367952884495853       T       T
T
   0.6666331694260142    0.3333321217287745    0.1746641003858512       T       T
T

CoNi(111)-OH
   1.00000000000000
     4.9243001937999997     0.0000000000000000     0.0000000000000000
    -2.4621500968999999     4.2645690636999998     0.0000000000000000
     0.0000000000000000     0.0000000000000000    30.0000000000000000
   Co   Ni   O    H
     8    4    1    1
Selective dynamics
Direct
   0.6666700500000005    0.3333400030000035    0.0003299999999982       F       F
F
   0.3333300170000015    0.6666700549999973    0.0673400000000015       F       F
F
   0.6666700629999980    0.8333400289999986    0.0003299999999982       F       F
F
   0.3333300139999977    0.1666700019999965    0.0673400000000015       F       F
```

F
0.1666700150000011 0.8333400289999986 0.0003299999999982 F F
F
0.8333300139999977 0.1666700019999965 0.0673400000000015 F F
F
0.1666700019999965 0.3333400030000035 0.0003299999999982 F F
F
0.8333299920000030 0.6666700549999973 0.0673400000000015 F F
F
-0.0000149447497625 0.0000189513164288 0.1326459077160841 T T
T
0.0038803124275855 0.5019885960603185 0.1351733693106736 T T
T
0.4979455403316110 0.5020520191692018 0.1351534727648177 T T
T
0.4979972632184711 0.9960918336660054 0.1351709172456407 T T
T
0.6663486178026561 0.3335323248889003 0.1813008438600054 T T
T
0.6661376744019152 0.3338664619431930 0.2136872307107690 T T
T

CoNi(111)-OOH
1.00000000000000
4.9243001937999997 0.0000000000000000 0.0000000000000000
-2.4621500968999999 4.2645690636999998 0.0000000000000000
0.0000000000000000 0.0000000000000000 30.0000000000000000
Co Ni O H
8 4 2 1
Selective dynamics
Direct
0.6666700500000005 0.3333400030000035 0.0003299999999982 F F
F
0.3333300170000015 0.6666700549999973 0.0673400000000015 F F
F
0.6666700629999980 0.8333400289999986 0.0003299999999982 F F
F
0.3333300139999977 0.1666700019999965 0.0673400000000015 F F
F
0.1666700150000011 0.8333400289999986 0.0003299999999982 F F
F
0.8333300139999977 0.1666700019999965 0.0673400000000015 F F
F
0.1666700019999965 0.3333400030000035 0.0003299999999982 F F

F

0.8333299920000030	0.6666700549999973	0.0673400000000015	F	F	F
-0.0038485068637157	-0.0018548568275637	0.1323860797531532	T	T	T
-0.0040945437069109	0.4980143385730522	0.1325064717011286	T	T	T
0.4879663383084742	0.4993657069179948	0.1407092321129029	T	T	T
0.4879223986267510	0.9886938678168486	0.1407102644125726	T	T	T
0.6973389049990412	0.3486882515447656	0.1755726661909900	T	T	T
0.4250240898497025	0.7124635520959617	0.1919244393853458	T	T	T
0.2144401734126165	0.6071831534223043	0.2050446244684276	T	T	T