Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information

Group-VIII Transition Metal Boride as promising Hydrogen Evolution Reaction Catalysts

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Contents

1. The GM structures of Pd_xB

For $Pd_{11}B$, Pd_8B and Pd_5B, the GMs are all fcc structures. The B position is at the interstitial O_h sites, which was uniformly distributed in the lattice. In the GM of Pd_3B (Z=4, #62, Pnma), the B position is in the interstitial site of Pd_6 trigonal prism. The SLM of Pd_3B is an hcp-fcc mixed structure. For Pd_2B, the GM structure (Z=2, #58, Pnnm) is a hcp structure with B occupying half of the interstitial O_h sites. For the GMs of Pd_xB (with x>3), due to the high density of B atoms, the B-B bonds start to appear in the lattice. Because the formation energy for these phases is generally above the convex hull, the GM with separated phase structures were identified from the SSW search. For example, the GM of $Pd_{1.4}B$ (i.e. $Pd_{14}B_{10}$ in simulation, #12, C2/m) can be seen as a combination of a Pd-enriched phase (hcp Pd_2B) and a boron-enriched phase (1/2 B atoms). Two different types of B position, B-Pd_6 octahedron and B_3 triangles, can be found in the lattice of $Pd_{1.4}B$. In the GM of PdB (#15, C2/c) and $Pd_{0.5}B$(#166, R-3m), the B position are all in the interconnected B_3 triangles. The GM of $Pd_{0.5}B$ has a segregated layered structure with alternated Pd and B region.

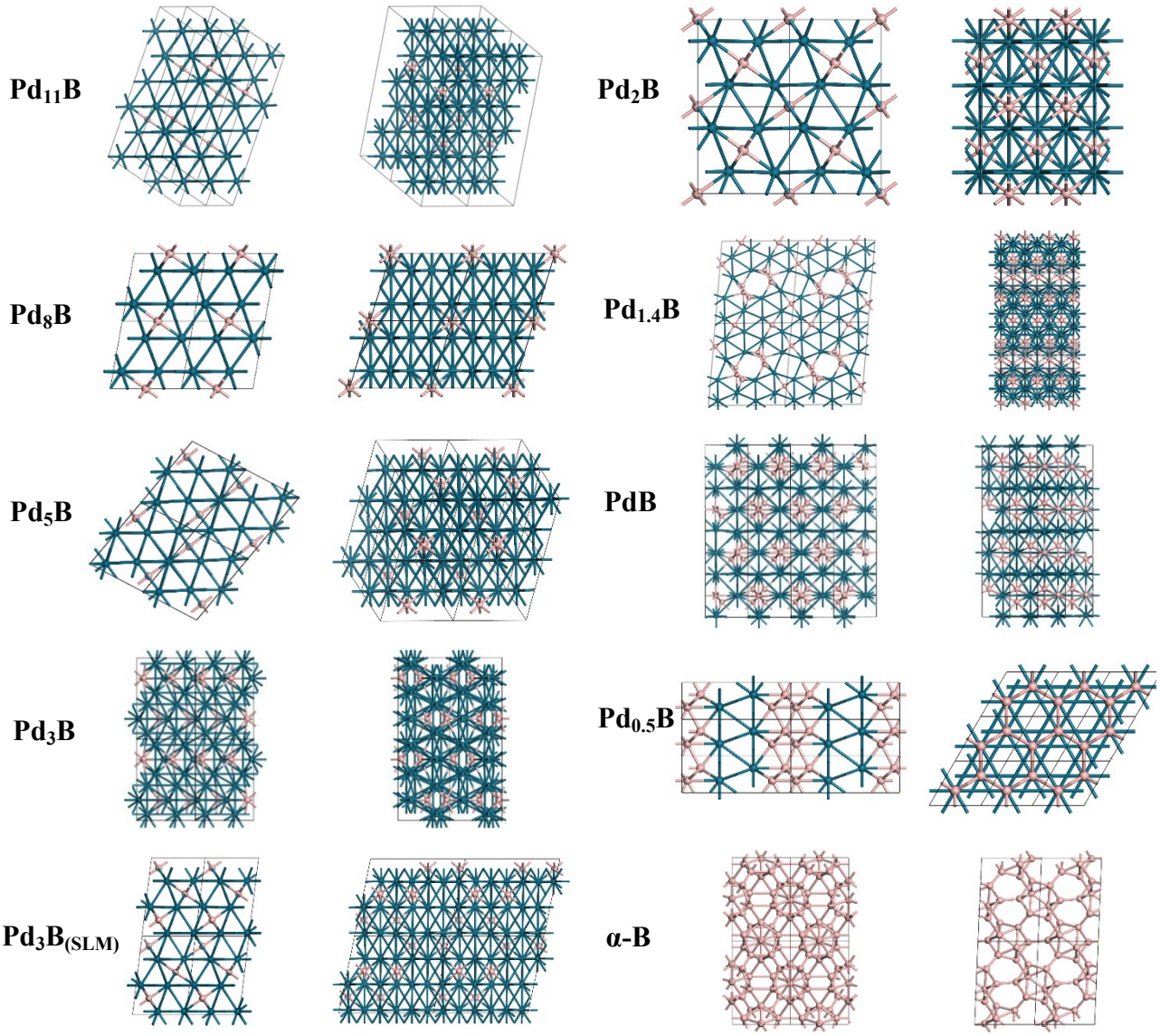

Fig S1. The GM structures for different Pd_xB compositions and boron (α-B). The dark cyan ball represents Pd; the pink ball represents B atom.

The coordinates of the GM structures of Pd_xB are listed below in .arc file format.

$Pd_{11}B$:

```
!BIOSYM archive 2
PBC=ON

!DATE
PBC       4.9205       4.9201      15.0036      89.5220      96.6930      99.4498
B          0.933992952  4.025189483 12.639767721 CORE  1 B    B     0.0000   1
B          0.984586167  2.293667804  7.137655958 CORE  2 B    B     0.0000   2
Pd         0.146373418  3.862215732  8.212258821 CORE  3 Pd Pd     0.0000   3
Pd         0.094552105  4.710659703 10.862840151 CORE  4 Pd Pd     0.0000   4
Pd         1.819708677  0.723478879  6.072625819 CORE  5 Pd Pd     0.0000   5
Pd        -0.708144620  1.160079469  7.508078736 CORE  6 Pd Pd     0.0000   6
Pd         2.636849753  2.560621975  4.082880543 CORE  7 Pd Pd     0.0000   7
Pd         0.908607837  0.739668366 13.702968721 CORE  8 Pd Pd     0.0000   8
Pd        -1.486348071  0.306633276 12.267697977 CORE  9 Pd Pd     0.0000   9
Pd         1.040788922  3.905869941  0.790640600 CORE 10 Pd Pd     0.0000  10
Pd         1.822956293  1.611675393  8.913256176 CORE 11 Pd Pd     0.0000  11
Pd         2.615014537  4.265866168  9.549021072 CORE 12 Pd Pd     0.0000  12
Pd         4.262576408  0.349448870  4.749296886 CORE 13 Pd Pd     0.0000  13
Pd         0.140361848  2.991266830  5.374400084 CORE 14 Pd Pd     0.0000  14
Pd         0.220198932  1.268131945  0.124406331 CORE 15 Pd Pd     0.0000  15
Pd         1.782984962  3.319835083 14.399501539 CORE 16 Pd Pd     0.0000  16
Pd         3.488800518  4.344252698  2.123784965 CORE 17 Pd Pd     0.0000  17
Pd         0.192499087  2.118536282  2.750521782 CORE 18 Pd Pd     0.0000  18
Pd         2.676400602  3.436925402  6.790837561 CORE 19 Pd Pd     0.0000  19
Pd         2.661042180  1.693735427  1.457961236 CORE 20 Pd Pd     0.0000  20
Pd        -0.697857431  2.057316147 10.225752684 CORE 21 Pd Pd     0.0000  21
Pd         1.771487409  2.458567874 11.562585419 CORE 22 Pd Pd     0.0000  22
Pd         1.019128355  4.770801598  3.416605949 CORE 23 Pd Pd     0.0000  23
Pd        -0.756450345  2.880801359 12.984353529 CORE 24 Pd Pd     0.0000  24
end
end
```

Pd_8B:

```
!BIOSYM archive 2
PBC=ON

!DATE
PBC       4.9195       9.9344       5.7170   106.7083      89.9678      80.4675
B          2.874529934  3.007177195  3.533230278 CORE  1 B    B     0.0000   1
B          3.696942132  8.744582653  0.798891340 CORE  2 B    B     0.0000   2
Pd         3.714969849  3.722698015  5.290354441 CORE  3 Pd Pd     0.0000   3
Pd         2.890969352 -0.342796489  2.556890545 CORE  4 Pd Pd     0.0000   4
Pd         1.195633090  4.171045737  3.876609699 CORE  5 Pd Pd     0.0000   5
Pd         0.371719264  0.105670472  1.143036571 CORE  6 Pd Pd     0.0000   6
Pd         2.035196734  2.296631937  1.775421260 CORE  7 Pd Pd     0.0000   7
Pd         2.859941588  6.362389135  4.509820613 CORE  8 Pd Pd     0.0000   8
Pd         4.554624477  1.848293640  3.189822670 CORE  9 Pd Pd     0.0000   9
Pd         5.376221096  7.581220935  0.455632552 CORE 10 Pd Pd     0.0000  10
Pd         5.343802992  6.792056590  3.187446130 CORE 11 Pd Pd     0.0000  11
Pd         4.519040279  2.726113121  0.452851437 CORE 12 Pd Pd     0.0000  12
```

```
Pd          2.840048492      7.171504681      1.862842117 CORE    13 Pd Pd     0.0000     13
Pd          2.018906367      1.438899836      4.596114581 CORE    14 Pd Pd     0.0000     14
Pd          3.731869047      4.580512850      2.469355255 CORE    15 Pd Pd     0.0000     15
Pd          2.910834665     -1.151871411      5.204451778 CORE    16 Pd Pd     0.0000     16
Pd          1.227927521      4.959748272      1.144694640 CORE    17 Pd Pd     0.0000     17
Pd          0.407452868     -0.772056204      3.879229236 CORE    18 Pd Pd     0.0000     18
end
end
```

Pd_5B:

```
!BIOSYM archive 2
PBC=ON

!DATE
PBC       7.1171       5.7462       9.1633    108.2170      74.2645      91.1719
B           6.660542083      3.086216014      0.485342915 CORE     1 B    B     0.0000      1
B           4.403672078     -1.192227739      4.662297019 CORE     2 B    B     0.0000      2
B           2.086501063      1.555475984      1.369338681 CORE     3 B    B     0.0000      3
B           6.828386104      3.019973626      5.551832455 CORE     4 B    B     0.0000      4
Pd          3.157471148      3.050377206      5.546373785 CORE     5 Pd Pd     0.0000      5
Pd          5.532503105      1.584835454      1.367590306 CORE     6 Pd Pd     0.0000      6
Pd          8.074213663     -1.223173772      4.667314085 CORE     7 Pd Pd     0.0000      7
Pd          3.214358649      3.056544277      0.487372540 CORE     8 Pd Pd     0.0000      8
Pd          3.304700058     -1.219899082      8.016459366 CORE     9 Pd Pd     0.0000      9
Pd          5.561678819      3.059330169      3.837490111 CORE    10 Pd Pd     0.0000     10
Pd          8.007092255      1.581412287      4.670710488 CORE    11 Pd Pd     0.0000     11
Pd          3.264638942      0.115991963      0.492046484 CORE    12 Pd Pd     0.0000     12
Pd          7.983057093      0.211216550      7.151632910 CORE    13 Pd Pd     0.0000     13
Pd          3.123476592      4.491191576      2.969916577 CORE    14 Pd Pd     0.0000     14
Pd          3.277937305      1.697505386      8.002900545 CORE    15 Pd Pd     0.0000     15
Pd          5.652748623      0.232014002      3.822602714 CORE    16 Pd Pd     0.0000     16
Pd          5.578803029      1.594650247      6.392021980 CORE    17 Pd Pd     0.0000     17
Pd          5.670327431     -1.231567970      6.375232213 CORE    18 Pd Pd     0.0000     18
Pd          3.225302229      0.246827728      5.540251015 CORE    19 Pd Pd     0.0000     19
Pd          5.482028825      4.525555473      1.362675446 CORE    20 Pd Pd     0.0000     20
Pd          3.248744821      1.616530311      3.061579245 CORE    21 Pd Pd     0.0000     21
Pd          7.991017799      3.081524183      7.243268126 CORE    22 Pd Pd     0.0000     22
Pd          0.810128879      3.046788317      2.197992653 CORE    23 Pd Pd     0.0000     23
Pd          0.837078468      0.130595097      2.209611764 CORE    24 Pd Pd     0.0000     24
end
end
```

Pd_3B:

```
!BIOSYM archive 2
PBC=ON

!DATE
PBC       5.5313       7.7300       4.8898     89.9574      90.0095      90.0053
B           2.150016589      1.932802566      2.116112523 CORE     1 B    B     0.0000      1
```

```
B          0.614274466     5.799960581     4.562607747 CORE     2 B    B     0.0000     2
B          3.379803276     5.800848813     2.773727798 CORE     3 B    B     0.0000     3
B          4.915385007     1.933688296     0.327184736 CORE     4 B    B     0.0000     4
Pd         0.991535631     0.559761922     0.856426177 CORE     5 Pd Pd     0.0000     5
Pd         1.772993860     7.175075444     3.302632502 CORE     6 Pd Pd     0.0000     6
Pd         4.538368913     4.426253758     4.032913393 CORE     7 Pd Pd     0.0000     7
Pd         3.757284310     3.306453597     1.588166526 CORE     8 Pd Pd     0.0000     8
Pd         4.538235574     7.173893414     4.033358304 CORE     9 Pd Pd     0.0000     9
Pd         3.756737838     0.558558076     1.587163743 CORE    10 Pd Pd     0.0000    10
Pd         0.991388339     3.307474187     0.856894512 CORE    11 Pd Pd     0.0000    11
Pd         1.772464239     4.427151282     3.301637852 CORE    12 Pd Pd     0.0000    12
Pd         0.219651403     1.933299845     3.223728312 CORE    13 Pd Pd     0.0000    13
Pd         2.544309676     5.796935950     0.779893522 CORE    14 Pd Pd     0.0000    14
Pd         5.310113839     5.800413399     1.666082011 CORE    15 Pd Pd     0.0000    15
Pd         2.985420729     1.936700524     4.109902495 CORE    16 Pd Pd     0.0000    16
end
end
```

Pd_3B(SLM):

```
!BIOSYM archive 2
PBC=ON

!DATE
PBC       8.9706       7.5278       4.9878      96.7976      90.0019     101.6028
B          8.093892709     1.094677792     3.606681126 CORE     1 B    B     0.0000     1
B          6.562001921     3.837679569     1.453391729 CORE     2 B    B     0.0000     2
B          2.020626375     5.904784253     4.190445216 CORE     3 B    B     0.0000     3
B          4.978588681     1.060760422     3.620838500 CORE     4 B    B     0.0000     4
B         -0.992131722     5.913869122     4.194429554 CORE     5 B    B     0.0000     5
B          3.421550566     3.790886672     1.421708620 CORE     6 B    B     0.0000     6
Pd         6.529701063    -0.025853519     2.669445738 CORE     7 Pd Pd     0.0000     7
Pd         8.007050179     0.270319163     0.218221209 CORE     8 Pd Pd     0.0000     8
Pd         4.986823424     5.109070346     0.799801125 CORE     9 Pd Pd     0.0000     9
Pd         0.512286551     4.761858864     3.271272911 CORE    10 Pd Pd     0.0000    10
Pd         2.032453016     0.300692303     0.184190871 CORE    11 Pd Pd     0.0000    11
Pd        -0.906742372     5.118577518     0.812907275 CORE    12 Pd Pd     0.0000    12
Pd         5.006669782     2.480757986     2.008480529 CORE    13 Pd Pd     0.0000    13
Pd         8.091375311     2.497875829     2.017965343 CORE    14 Pd Pd     0.0000    14
Pd         3.496982236    -0.035525014     2.629032804 CORE    15 Pd Pd     0.0000    15
Pd         0.568284933    -0.051837740     2.620755086 CORE    16 Pd Pd     0.0000    16
Pd         3.543477757     4.796366709     3.285747235 CORE    17 Pd Pd     0.0000    17
Pd         5.041290666     0.239022958     0.209961446 CORE    18 Pd Pd     0.0000    18
Pd         1.990637577     2.451894308     2.063426694 CORE    19 Pd Pd     0.0000    19
Pd         6.529360253     2.237500309     4.490033065 CORE    20 Pd Pd     0.0000    20
Pd         1.944227384     5.116385837     0.822465916 CORE    21 Pd Pd     0.0000    21
Pd         6.430159682     4.835307538     3.290217871 CORE    22 Pd Pd     0.0000    22
Pd         3.440929796     2.196573303     4.496957199 CORE    23 Pd Pd     0.0000    23
Pd         0.571482327     2.207007816     4.538356903 CORE    24 Pd Pd     0.0000    24
end
end
```

Pd_2B:

```
!BIOSYM archive 2
PBC=ON

!DATE
PBC      14.3238       3.0439       7.1286      89.9642      95.0379      89.9605
B          12.403005500       0.259682603       1.480428902 CORE       1 B    B      0.0000       1
B          12.091195931       1.786640299       5.030037967 CORE       2 B    B      0.0000       2
B           5.240703571       0.249863267       1.479033702 CORE       3 B    B      0.0000       3
B           1.660886526       1.768991013       1.480883265 CORE       4 B    B      0.0000       4
B           8.822908282       1.783321386       1.478405773 CORE       5 B    B      0.0000       5
B           8.510006961       0.264800883       5.027376116 CORE       6 B    B      0.0000       6
B           1.347223264       0.248353604       5.032182812 CORE       7 B    B      0.0000       7
B           4.930088224       1.773559681       5.029274731 CORE       8 B    B      0.0000       8
Pd          3.813016491       1.772277691       1.142326615 CORE       9 Pd Pd      0.0000       9
Pd         11.870656118       0.264922637       3.582252375 CORE      10 Pd Pd      0.0000      10
Pd          1.878129974       0.246223319       2.928769099 CORE      11 Pd Pd      0.0000      11
Pd          8.604909936       0.262564839       0.030082313 CORE      12 Pd Pd      0.0000      12
Pd          9.938950706       1.785804764       5.366583338 CORE      13 Pd Pd      0.0000      13
Pd          4.708425699       0.253135187       3.581709765 CORE      14 Pd Pd      0.0000      14
Pd          9.041707507       0.259925610       2.925724231 CORE      15 Pd Pd      0.0000      15
Pd         13.832383706       1.778025624       1.818304141 CORE      16 Pd Pd      0.0000      16
Pd         10.975753858       1.784202425       1.141374827 CORE      17 Pd Pd      0.0000      17
Pd          7.082742994       1.786155235       4.690735288 CORE      18 Pd Pd      0.0000      18
Pd          5.147622170       0.250384563       6.477082948 CORE      19 Pd Pd      0.0000      19
Pd          2.777044778       1.768364973       5.368376356 CORE      20 Pd Pd      0.0000      20
Pd         12.309284795       0.263331647       6.478411160 CORE      21 Pd Pd      0.0000      21
Pd          1.439692403       0.247930947       0.032848988 CORE      22 Pd Pd      0.0000      22
Pd          6.670619056       1.772092560       1.815639614 CORE      23 Pd Pd      0.0000      23
Pd         -0.080353011       1.774327884       4.693690900 CORE      24 Pd Pd      0.0000      24
end
end
```

$Pd_{1.4}B$:

```
!BIOSYM archive 2
PBC=ON

!DATE
PBC       2.9800       9.5867      11.2666      94.6897     113.2039      90.2090
B           0.279814791       4.823254933       5.628275283 CORE       1 B    B      0.0000       1
B          -1.202151145       8.406646029       5.231621905 CORE       2 B    B      0.0000       2
B           0.283227842       4.746569093       0.256920768 CORE       3 B    B      0.0000       3
B           0.253116540       9.420414394       0.290146511 CORE       4 B    B      0.0000       4
B          -1.203914893       7.618749167       3.709486661 CORE       5 B    B      0.0000       5
B          -1.208661684       4.948289701       6.501694010 CORE       6 B    B      0.0000       6
B          -2.648090445       1.353496434       7.955079964 CORE       7 B    B      0.0000       7
B          -1.219972731       2.289691374       2.904803242 CORE       8 B    B      0.0000       8
B           0.286361389       8.281243771       4.358439823 CORE       9 B    B      0.0000       9
B          -2.698350957       5.610829299       7.150561237 CORE      10 B    B      0.0000      10
Pd         -1.207608210       7.275646968       7.182436083 CORE      11 Pd Pd      0.0000      11
Pd         -1.215435041       3.620643891       4.580312294 CORE      12 Pd Pd      0.0000      12
Pd          0.275480768       8.265358695       2.107175831 CORE      13 Pd Pd      0.0000      13
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Pd      -1.158912441    2.538096715    7.128244491 CORE   14 Pd Pd    0.0000   14
Pd      -1.161268243    0.126754017    8.829732819 CORE   15 Pd Pd    0.0000   15
Pd       1.771429726    5.922269044    1.093798607 CORE   16 Pd Pd    0.0000   16
Pd       0.273362010    3.515980663    2.029847984 CORE   17 Pd Pd    0.0000   17
Pd      -2.694049606    7.307514571    9.765844495 CORE   18 Pd Pd    0.0000   18
Pd       1.776886277    1.093674824    1.098328945 CORE   19 Pd Pd    0.0000   19
Pd      -2.664748476    2.549013314    9.761816320 CORE   20 Pd Pd    0.0000   20
Pd      -1.197777980    4.964811495    8.753153263 CORE   21 Pd Pd    0.0000   21
Pd       0.270793033    1.105795364    3.732330112 CORE   22 Pd Pd    0.0000   22
Pd      -2.652191086    0.022600213    6.279624463 CORE   23 Pd Pd    0.0000   23
Pd       0.285547943    5.953919422    3.677103388 CORE   24 Pd Pd    0.0000   24
end
end
```

PdB:

```
!BIOSYM archive 2
PBC=ON

!DATE
PBC      5.4183      8.5939      6.0289   100.0118   106.1264    80.0027
B        0.544007901   -0.088865954    5.287452216 CORE    1 B   B    0.0000    1
B       -0.887600358    3.004152236    5.300092118 CORE    2 B   B    0.0000    2
B        2.546439424    0.844115572    2.831905575 CORE    3 B   B    0.0000    3
B        1.113902858    3.937009425    2.844254982 CORE    4 B   B    0.0000    4
B        2.240514144   -0.679044032    5.714983509 CORE    5 B   B    0.0000    5
B       -0.254731202    4.691143835    5.701609038 CORE    6 B   B    0.0000    6
B        3.405099868    7.620768628    2.430074245 CORE    7 B   B    0.0000    7
B        4.835597581    4.527176363    2.416918109 CORE    8 B   B    0.0000    8
B        0.726282368    4.443838413    1.209389220 CORE    9 B   B    0.0000    9
B        2.606288824    0.174306734    1.182013248 CORE   10 B   B    0.0000   10
B       -0.194600508    4.021119899    4.051725752 CORE   11 B   B    0.0000   11
B        1.852983511   -0.172479346    4.080082515 CORE   12 B   B    0.0000   12
Pd       1.666027812    2.308788807    1.196385649 CORE   13 Pd Pd    0.0000   13
Pd       5.121354240    6.540535745    1.196426425 CORE   14 Pd Pd    0.0000   14
Pd       1.716813894    4.931972111    4.730806661 CORE   15 Pd Pd    0.0000   15
Pd       3.798461556    0.759675577    4.775023075 CORE   16 Pd Pd    0.0000   16
Pd       2.153580914    7.702427927    0.486908005 CORE   17 Pd Pd    0.0000   17
Pd       4.234948270    3.529001587    0.531392249 CORE   18 Pd Pd    0.0000   18
Pd       1.435060706    7.376477179    3.401722451 CORE   19 Pd Pd    0.0000   19
Pd       3.279223400    3.086097572    3.357007700 CORE   20 Pd Pd    0.0000   20
Pd       4.284107840    6.155902122    4.066162967 CORE   21 Pd Pd    0.0000   21
Pd       0.829169287    1.924099371    4.066709100 CORE   22 Pd Pd    0.0000   22
Pd       4.517817694    1.084981170    1.861031490 CORE   23 Pd Pd    0.0000   23
Pd       2.672032085    5.375743340    1.904507754 CORE   24 Pd Pd    0.0000   24
end
end
```

$Pd_{0.5}B$:

```
!BIOSYM archive 2
```

PBC=ON

!DATE
PBC 2.9427 7.5865 10.2745 90.4501 90.0355 90.0823
B 1.429360108 6.104555410 1.445780225 CORE 1 B B 0.0000 1
B 2.911995815 0.166489968 4.016373107 CORE 2 B B 0.0000 2
B 2.914440035 1.093213439 0.608084022 CORE 3 B B 0.0000 3
B 1.425766570 6.950580665 8.311526380 CORE 4 B B 0.0000 4
B 1.442225397 0.186780110 1.447945881 CORE 5 B B 0.0000 5
B 2.901760111 7.010989080 0.605890080 CORE 6 B B 0.0000 6
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B 1.426327827 6.064459853 6.582768851 CORE 13 B B 0.0000 13
B 2.908881247 0.126431665 9.153410026 CORE 14 B B 0.0000 14
B 2.911401167 1.053023105 5.745178287 CORE 15 B B 0.0000 15
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Pd 2.898314878 4.741857192 5.704678524 CORE 17 Pd Pd 0.0000 17
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Pd 2.909008728 2.355234487 9.191704140 CORE 20 Pd Pd 0.0000 20
Pd 1.425351101 4.721696088 8.272943301 CORE 21 Pd Pd 0.0000 21
Pd 1.439245625 2.375480870 6.623018403 CORE 22 Pd Pd 0.0000 22
Pd 1.428430703 4.761801241 3.136169242 CORE 23 Pd Pd 0.0000 23
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end
end

α-B:

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B 0.930120329 1.773197918 3.760198361 CORE 2 B B 0.0000 2
B 3.431571613 3.650893053 5.575879270 CORE 3 B B 0.0000 3
B 1.091823899 2.647042612 1.026060769 CORE 4 B B 0.0000 4
B 2.460941750 0.195048354 6.024331100 CORE 5 B B 0.0000 5
B -0.177743737 1.642581818 6.618024630 CORE 6 B B 0.0000 6
B 0.794871119 0.195550454 6.169565228 CORE 7 B B 0.0000 7
B -0.053627593 4.224594164 4.917161434 CORE 8 B B 0.0000 8
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B 1.055295936 4.094026359 2.059591945 CORE 10 B B 0.0000 10
B 0.082908270 0.196067079 0.618634059 CORE 11 B B 0.0000 11
B 3.602708661 4.224990589 0.243788570 CORE 12 B B 0.0000 12
B 3.433124299 1.642236029 5.575985925 CORE 13 B B 0.0000 13
B 1.055736249 1.199812478 2.059481237 CORE 14 B B 0.0000 14
B 2.495278270 1.200157263 3.101513257 CORE 15 B B 0.0000 15
B -0.052130881 1.069200125 4.917293690 CORE 16 B B 0.0000 16

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B       3.469652766   0.195252366   4.542468700 CORE   18 B   B   0.0000   18
B       0.929619420   3.520671381   3.760328971 CORE   19 B   B   0.0000   19
B       3.467454466   2.647341718   2.653147129 CORE   20 B   B   0.0000   20
B       2.620952257   1.773514881   1.400761028 CORE   21 B   B   0.0000   21
B       3.604192417   1.069595237   0.243950786 CORE   22 B   B   0.0000   22
B       0.083109277   2.646839685   2.507952117 CORE   23 B   B   0.0000   23
B       2.458742970   2.647146391   4.135041312 CORE   24 B   B   0.0000   24
end
end
```

2. Details about the relative formation energy diagram and the results of Rh_xB

The phase stabilities of M_xB_y (M = Pd or Rh) compounds can be investigated by calculating their formation energies relative to the products of dissociation into constituent elements. For each phase identified from the SSW trajectory, its relative formation energy (ΔE) can be calculated by the following equation:

$$\Delta E = (E_{M_xB_y} - x\,E_M - y\,E_B)/(x + y)$$

In equation, $E_{M_xB_y}$ is the DFT calculated energy. E_M and E_B are the single atom energies of constituent elements. Here the face centered cubic (*fcc*) structure of elemental Pd/Rh and the α-B were used to obtain E_M and E_B. In general, a structure whose formation energy lies on the phase stability line (i.e., the convex hull) is deemed stable with respect to decomposition into other M_xB_y compounds or elemental solids and thus can be experimentally synthesized.

The relative formation energy of Rh_xB borides are shown in Fig. S2. With the increase of B content, the formation energy (ΔE) first decreases, then increases. Only Rh_2B and RhB appear in the convex hull and thus are the thermodynamically stable alloy composition. Theory predicts that RhB is the highest boron content Rh_xB alloy that can be achieved experimentally. The phase diagram of RhB in 1960s also shows two major Rh_xB alloys, i.e. $Rh_{1.1}B$ and Rh_7B_3, and no B contents higher than RhB is found in experiment. Being similar with that in Pd_xB system, from Rh to RhB, the GM structures of RhB also transform from the fcc structures to the hcp structures. The GM structure of RhB (Z=1, #194, P63/mmc) has a hcp Rh sublattice with the B atoms sitting at the distorted interstitial O_h sites (shown in Fig. S2b).

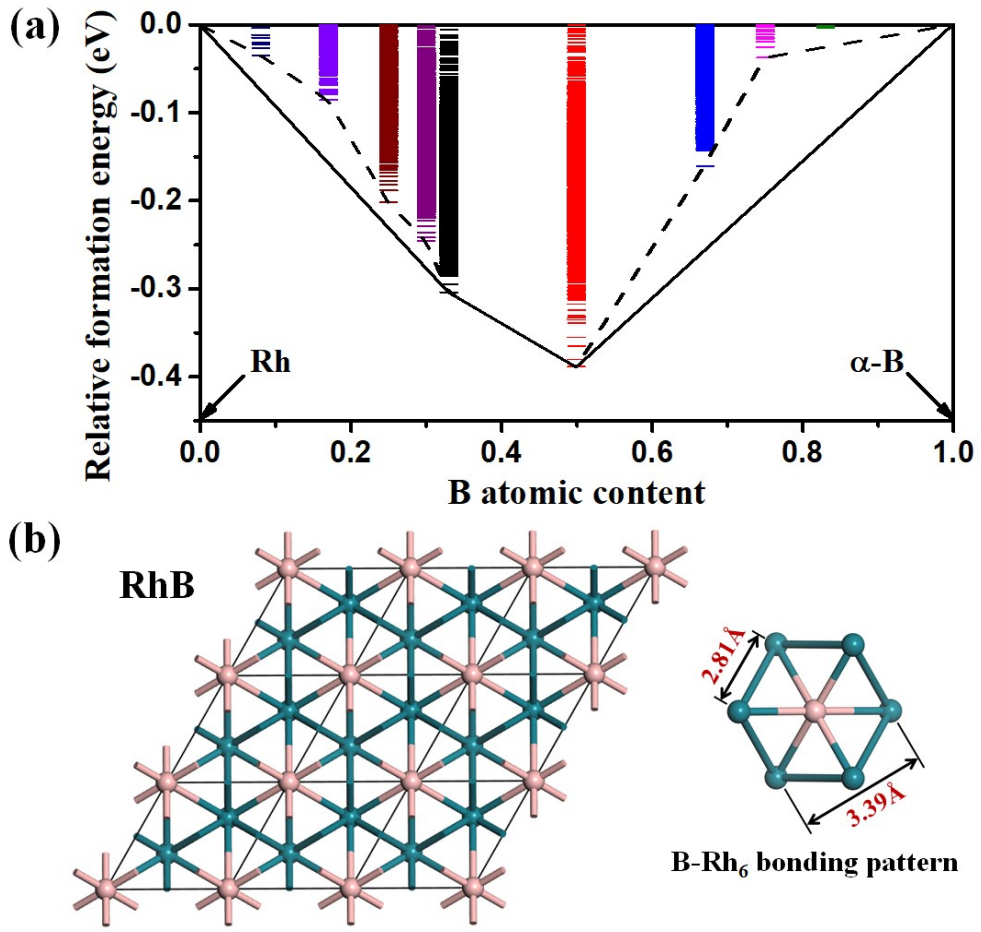

Fig S2. (a) The relative formation energy of Rh_xB borides with respect to pure Rh (*fcc*) and α-B. The convex hulls are shown by solid lines. Dotted lines connect the most stable structure for each composition obtained from SSW search. (b) The GM structures of RhB (viewed from the normal direction of the close-packed plane) and the B-Rh_6 distorted octahedron bonding patten.

The coordinates of the GM structures of RhB are listed below in .arc file format:

```
!BIOSYM archive 2
PBC=ON

!DATE
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B          0.000000000      0.000000000      2.079719708 CORE       2 B    B       0.0000     2
Rh         0.000000000      1.954653893      1.039859854 CORE       3 Rh Rh        0.0000     3
Rh         1.692779927      0.977326947      3.119579563 CORE       4 Rh Rh        0.0000     4
end
end
```

3. Surface phase diagram and H adsorption structures on Pd_xB

The thermodynamic equilibrium H coverage under electrochemical potentials can be determined by constructing the surface phase diagram using DFT.[1-3] Detailed calculation setups can be found in our previous study.[3, 4] It should be mentioned that the water environment for all structures has been considered implicitly with a continuum solvation model, which is solved using the Poisson-Boltzmann equation with a smooth dielectric function as implemented recently.[5-8]

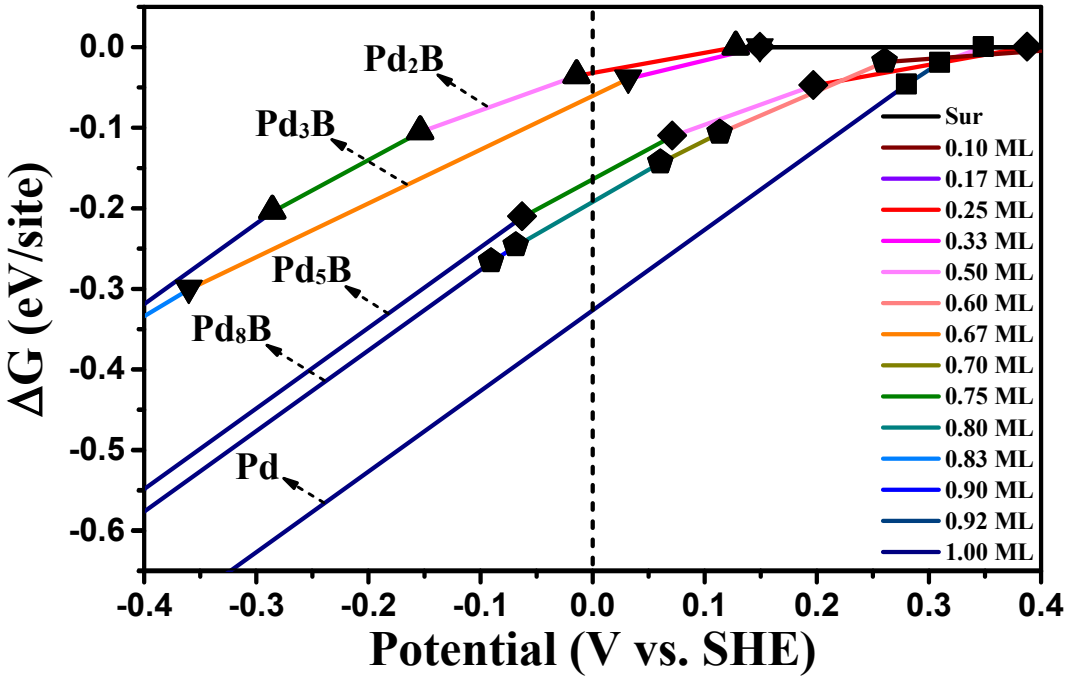

Fig S3. The H surface phase grams of the Pd_xB at different potentials. With the increase of B contents, the equilibrium H coverage at 0 V gradually decreases from the 1ML on Pd(111) to 0.25 ML on Pd_2B. This is mainly due to the fact that the H atoms donot adsorb on the fcc sites directly above the subsurface B.

Table S1. The hydrogen adsorption free energies (ΔG_H) on Pd, Rh, Pt and Pd-/Rh- B surfaces at low coverages (0.2~0.25 ML H coverage).

surface	ΔG_H (eV)	surface	ΔG_H (eV)	surface	ΔG_H (eV)
Pd(111)	-0.38	Rh(111)	-0.34	Pt(111)	-0.33
Pd_8B(010)	-0.39	Rh_2B(100)	-0.40		
$Pd_5B(\bar{1}02)$	-0.40	RhB(001)	-0.26		
Pd_3B(010)	-0.26				
Pd_2B(010)	-0.13				

4. Structure snapshots of the key reaction intermediates on Pd_xB

We investigated the kinetics for two surface H coupling to form H_2 molecule on Pt and Pd_xB surfaces follow the Tafel mechanism. The reaction is starting from the equilibrium H coverage condition where all Hs are at the hollow sites (H_{ad} in Fig. S4), one additional H comes from solution (proton) to adsorb (IS_{H-H} in Fig. S4). As shown in Fig. S4, this additional H trends to sit on the atop site on Pd(111) and on the hollow site above subsurface B on Pd_xB surfaces. The difference can be attributed to the reduced H coverage on Pd_xB, which let more unoccupied hollows sites expose. At the TS, the additional H reacts with the nearby hollow site H, forming a [H-H] complex nearby a top site. The distances between the reacting Hs at TSs on Pd(111) is 0.83 Å. Interestingly, although the reaction barriers (ΔG_a) on Pd_xB are generally lower than that on Pd, the H-H distance of the TSs on Pd_xB are very close to that on Pd(111), which is in the range of 0.84~0.86 Å. This implies that the subsurface B may plays the critical role for the reduce of ΔG_a on Pd_xB surfaces.

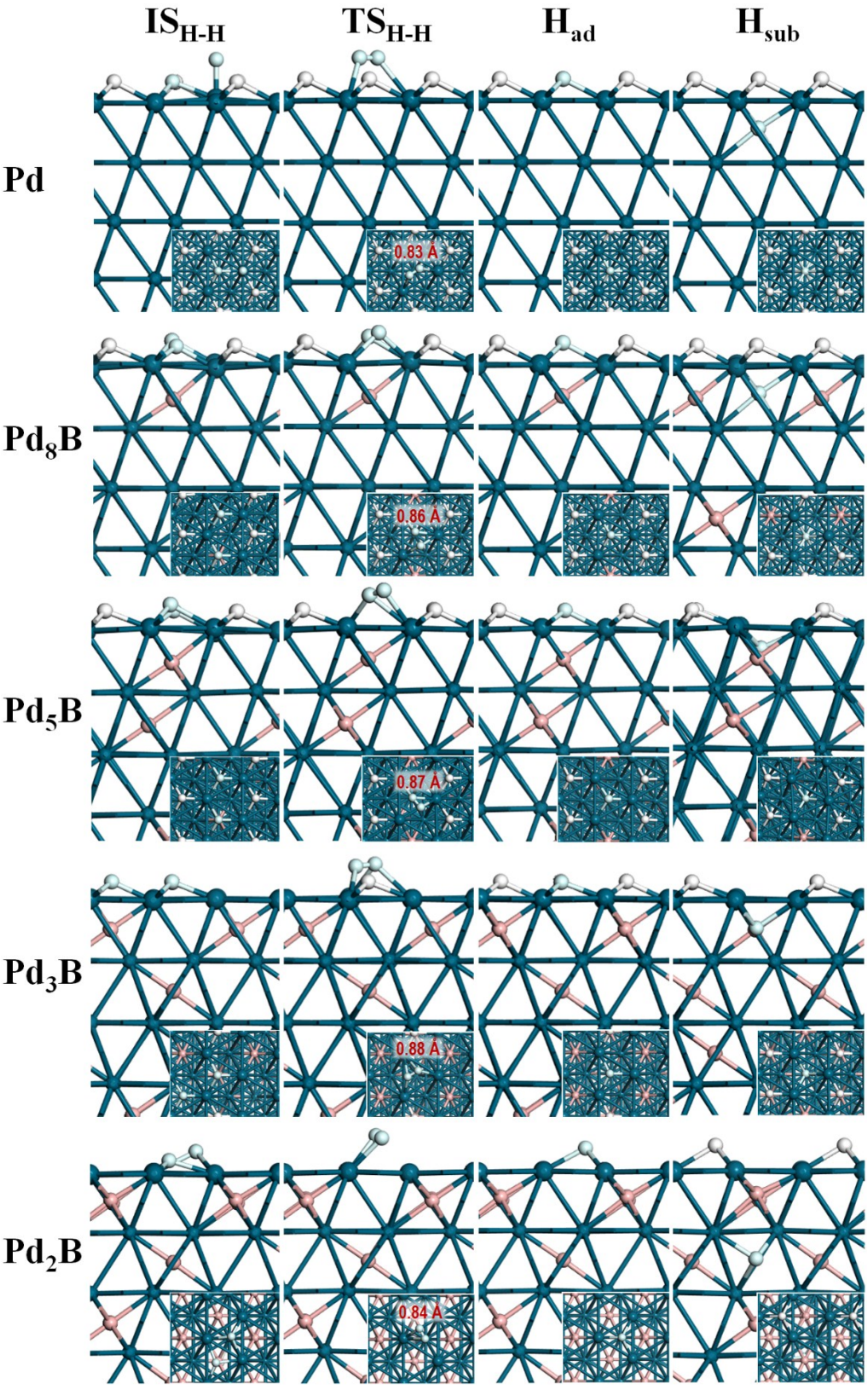

Fig S4. The side and top views for the structures of key reaction intermediates on Pd(111) and Pd$_x$B surfaces. Left two columns: ISs and TSs (H-H distance are indicated by the red numbers) of HER; right two columns: The H covered surfaces with and without subsurface H. The dark cyan ball represents Pd; the pink ball represents B; the write ball represents the surface adsorbed H; the light cyan ball represents the reacting H.

5. The reaction profile for Tafel reaction (H-H coupling)

The free energy profile of hydrogen evolution reaction ($2H^+ + 2e^- \rightarrow H_2(g)$) on the Pd, Pd_5B, Pd_2B, Rh and RhB are shown in Fig S5. According to our results, Pd_2B show high HER activity with the lowest barrier for H-H coupling (0.35 eV).

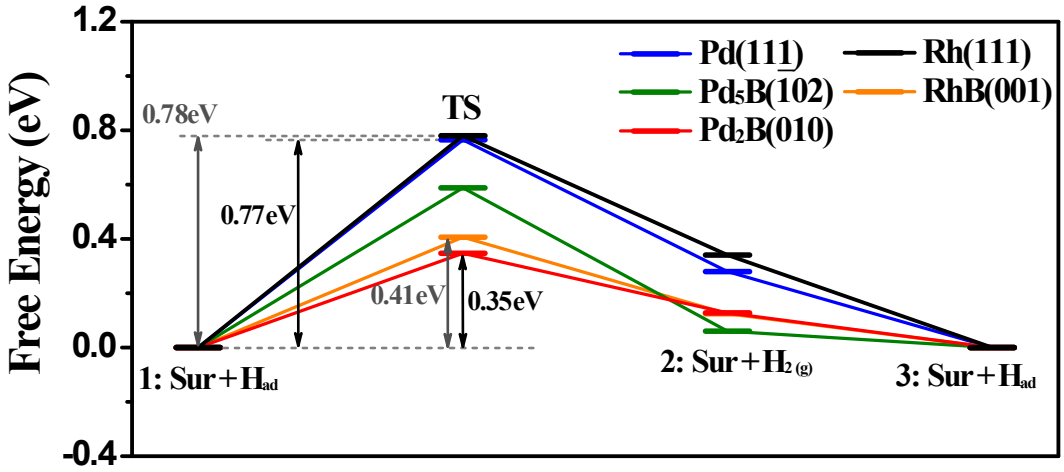

Fig S5. The free energy profile of Tafel reaction ($2H_{ad} \rightarrow H_2$) on Pd(111), Rh(111) and Pd-/Rh- boron surfaces at 0 V.

6. The polarization curves from theory

The currents were calculated by using the equation: $i = -nFS^{-1}N_A^{-1}\times A\ \exp(-\Delta G_a/RT)\theta_{site}$, where A is the pre-exponential factor (6.25×10^{12} at 300 K from classic TS theory); ΔG_a is the estimated free energy barrier according to the data in Figure 2a and ref[9], i.e. 0.35 eV for Pd_2B surface sites, 0.48 eV for the apex sites on Pt_{NP}; θ_{site} is the number of the active sites on the surface(in this work, for ease of comparison, θ_{site} was estimated to be 1/2000, due to the low density of apex sites on Pt_{NP}. The θ_{site} on Pd_2B was in fact underestimated.); S is the surface area. Comparing with the Pt_{NP}, Pd_2B can further reduce HER overpotential by ~21 mV at the current density of -30 mA/cm^2.

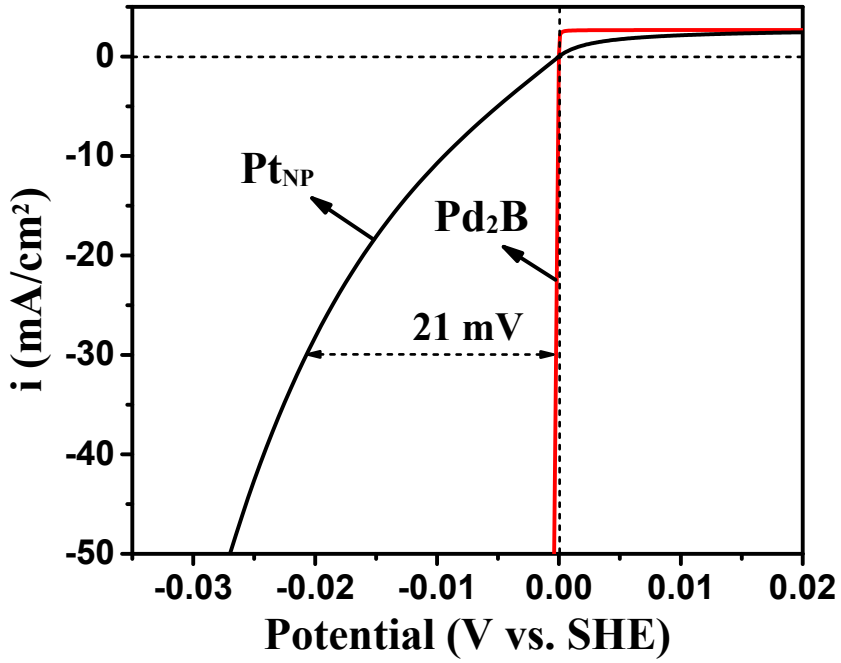

Fig S6. The theoretical predicted polarization curve of Pd_2B and Pt nanoparticle(Pt_{NP}).

7. Subsurface H formation

The formation of subsurface H is closely related to the hydrogen corrosion. We utilized the energy cost for the subsurface H formation (ΔG_{sub}) to evaluate the stability of Pd- and Rh- borides under HER conditions. The most stable adsorption site for the subsurface H were shown in Fig. S4. Obviously, both the subsurface B and the subsurface H prefer to stay the interstitial O_h sites. We note that the too-close contact (<2 Å) between H and B is thermodynamically prohibited. In the Pd_2B, as half interstitial O_h sites has already been occupied by B, the subsurface H on $Pd_2B(010)$ can only be stable beneath the second-layer Pd. This is similar for H in RhB(001): all the interstitial O_h sites are occupied by B, which forces the subsurface H atoms to enter the tetrahedral void of Rh sublattice beneath the second-layer Rh.

Table S2. Calculated free energy change of subsurface hydrogen formation (ΔG_{sub}) on Pd, Rh and Pd-/Rh- B surfaces. All ΔG_{sub} are calculated for the equilibrium H coverage at o V.

surface	ΔG_{sub} (eV)	surface	ΔG_{sub} (eV)	surface	ΔG_{sub} (eV)
Pd(111)	0.02	Rh(111)	0.45	Pt(111)	0.94
Pd_8B(010)	0.16	Rh_2B(100)	0.08		
$Pd_5B(\bar{1}02)$	0.21	RhB(001)	0.97		
Pd_3B(010)	0.15				
Pd_2B(010)	0.74				

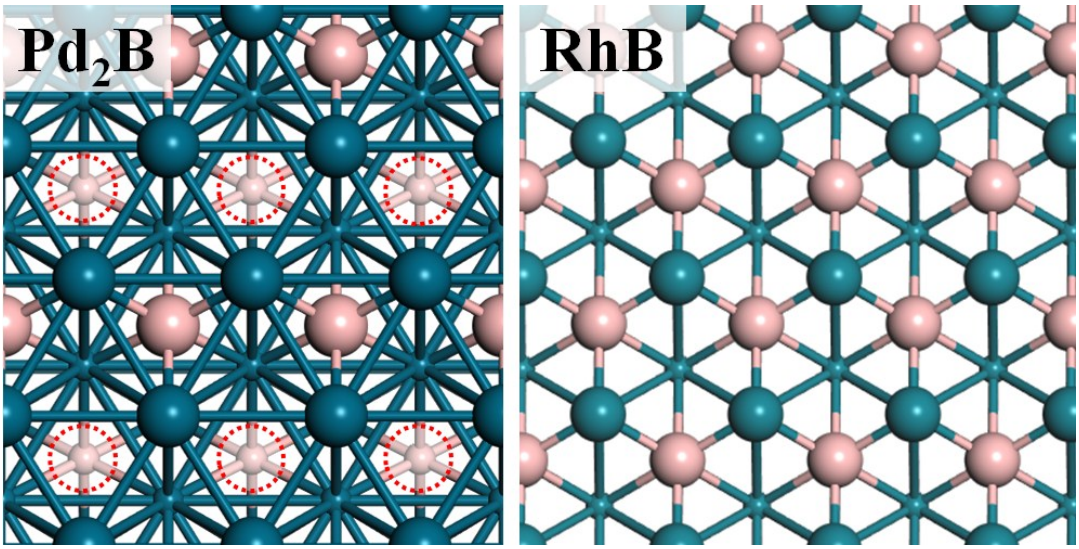

Fig S7. The illustration of $Pd_2B(010)$ and RhB(001) surface. In Pd_2B all the subsurface octahedral voids are just above the B occupied interstitial O_h sites, which are indicated by the red dashed circles. In RhB all octahedal void sites are already occupied by B.

References:

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