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


Supporting Information for

# Surface-chemistry-driven water dissociation on cobalt-based graphene hybrid from molecular dy- namics simulations

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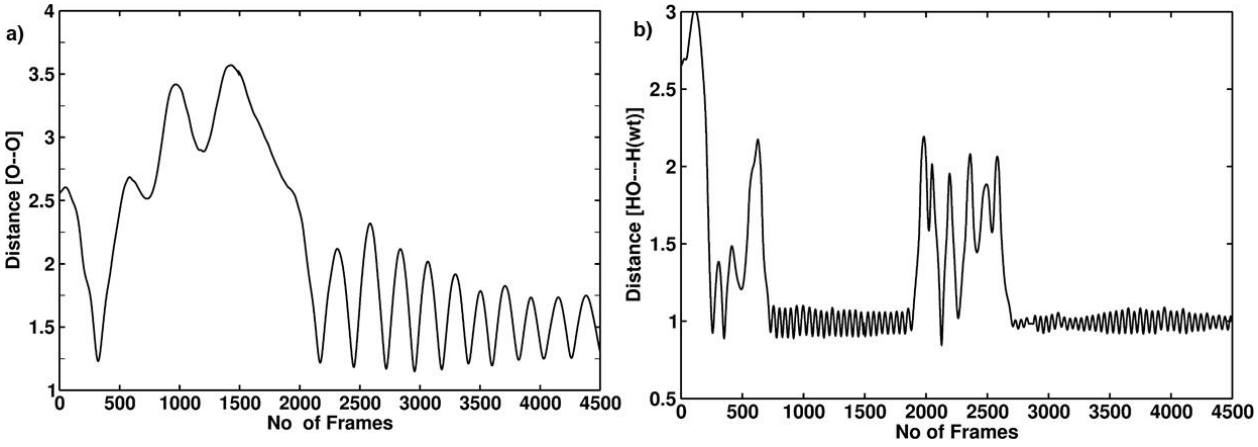


**Figure S1.** Variation of the bond distances (in Å) (a) along the CV1 (b) along the CV2.

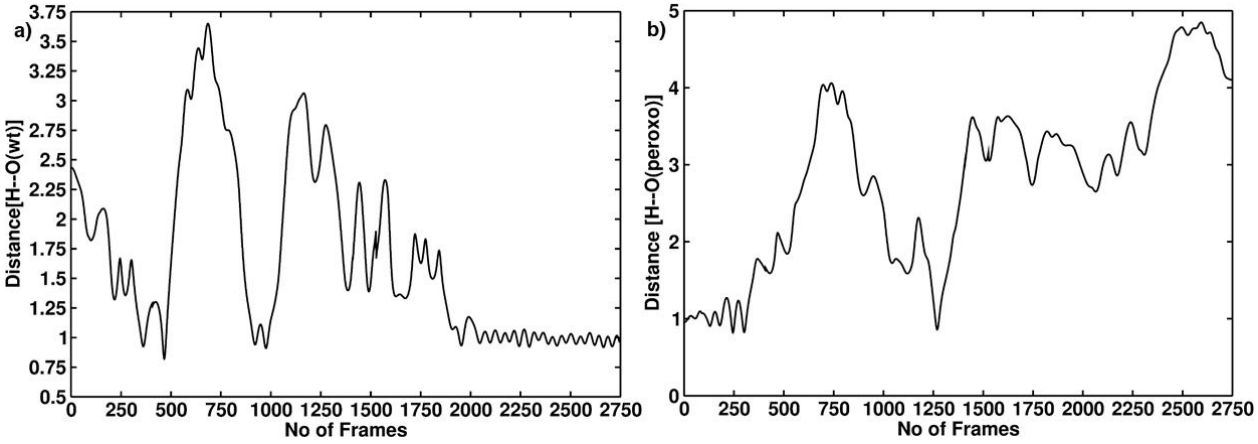


**Figure S2**. Variation of the bond distances (in Å) (a). along the CV1 (b) along the CV2.

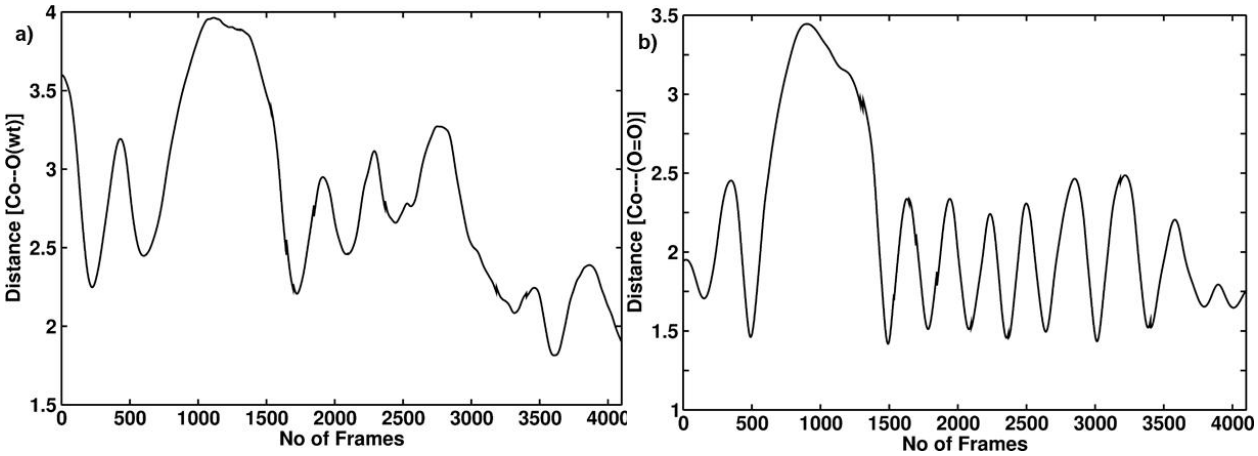


**Figure S3**. Variation of the bond distances (in Å) (a) along the CV1 (b) along the CV2

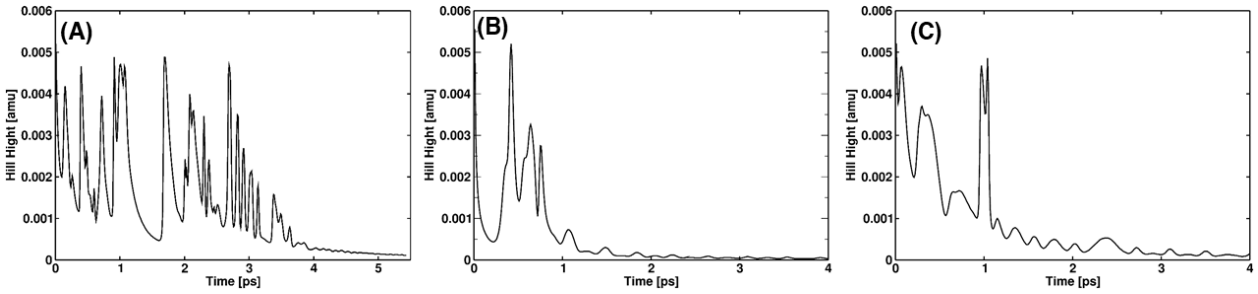


**Figure S4**. Variation of the hill height (in amu) for (A) step1 (B) step2 and (C) step3. All these are run through the Well-Tempered metadynamics, the constant hill size near to zero after formation product gives the evidence for the better convergence of metadynamics simulation.

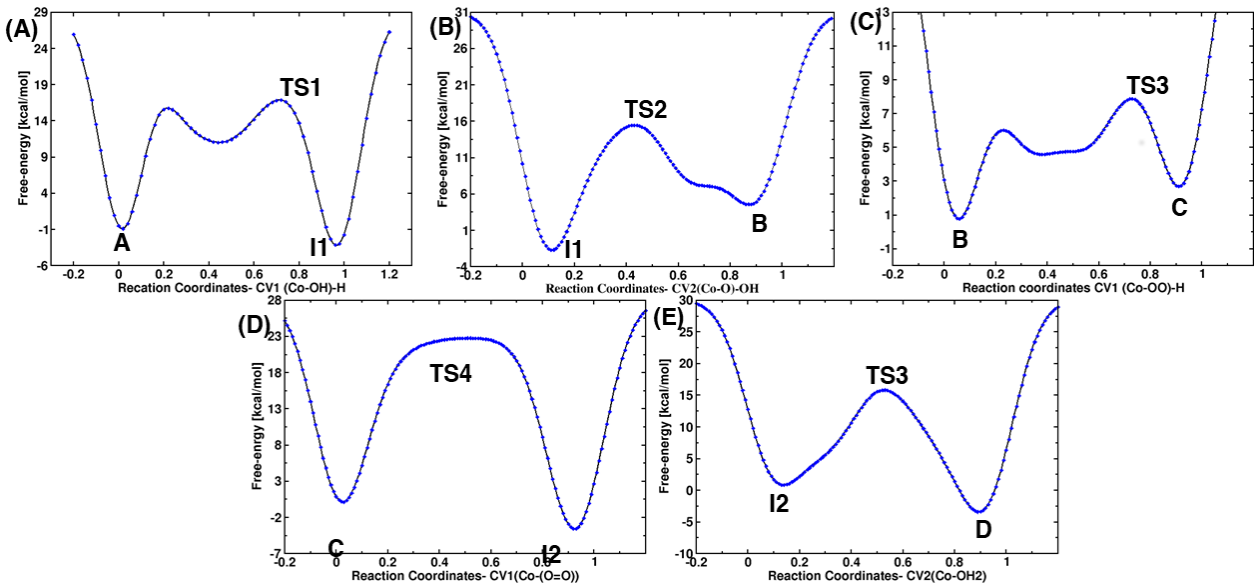


**Figure S5**. 1-D representation of the free-energies along the (A) CV1 of step1 (b) CV2 of step2 (C) CV1 of step 2 (CV1 and CV2 defined for same event) (D) CV1 of step3 (E) CV2 of step3

**Table S1.** Parameters for oxygen-oxygen bond formation.

| | CV1 (Co-$O_b$-$O_c$H bond) | CV2 (Co-$O_a$-H bond) |
|---|---|---|
| NN | 8 | 6 |
| ND | 24 | 18 |
| $R_0$ | 2.10 | 2.10 |
| K (for Quadratic wall) | 5 (wall at 2.80 Å) | 5(wall at 3.00 Å) |
| Time Step | 0.2 | - |
| Height of Gaussian | 5.0 x $e^{-3}$ | - |
| Bias factor for WT mtd | 25 | |
| Scale | 0.1 | 0.1 |
| HILLS added | For 5 steps | For 5steps |
| Temperature (avg. in kelvin) | 299.3 | - |

**Table S2.** Changing of spin moments and charges (Mulliken and Lowdin) during the formation of the oxygen-oxygen bond.

| | | **A** | | **TS1** | | **I1** | | **TS2** | | **B** | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Charge | Spi. mom | Charge | Spi. mom | Charge | Spi. mom | Charge | Spi. mom | Charge | Spi. mom |
| **Co** | Mulliken | 0.4684 | -0.0148 | 0.5285 | -0.3599 | 0.4069 | -0.1154 | 0.5078 | -0.1837 | 0.3895 | -0.0011 |
| | Lowdin | 0.3053 | -0.4337 | 0.4636 | -0.3736 | 0.3420 | -0.1423 | 0.3811 | -0.1828 | 0.3542 | -0.0012 |
| **$O_a$** | Mulliken | -0.4761 | 0.0016 | -0.4927 | -0.0469 | -0.2353 | 0.0006 | -0.3847 | -0.0047 | -0.2909 | 0.0000 |
| | Lowdin | -0.2060 | -0.0001 | -0.2083 | -0.0475 | 0.0008 | 0.0015 | -0.1461 | -0.0064 | -0.0579 | 0.0000 |
| **$O_b$** | Mulliken | -0.4007 | -0.6302 | -0.2153 | -0.3720 | -0.2982 | -1.0424 | -0.3716 | 0.7243 | -0.3274 | 0.0002 |
| | Lowdin | -0.1844 | -0.5923 | 0.0068 | -0.3517 | -0.1455 | -1.0095 | -0.2097 | 0.6972 | -0.1787 | 0.0002 |
| **$O_c$** | Mulliken | -0.3852 | -0.0030 | -0.3026 | -0.4614 | -0.3580 | -0.5462 | -0.3147 | 0.7243 | -0.1906 | 0.0000 |
| | Lowdin | -0.1223 | -0.0030 | -0.0366 | -0.4398 | -0.1153 | -0.5277 | -0.0618 | 0.2783 | -0.0353 | 0.0000 |
| **H** | Mulliken | 0.1423 | 0.0000 | 0.1153 | -0.0000 | 0.1341 | 0.0000 | -0.3147 | 0.2788 | 0.1258 | 0.0000 |
| | Lowdin | 0.0265 | 0.0000 | -0.0000 | 0.0000 | 0.0603 | 0.0000 | 0.0342 | 0.0000 | 0.0390 | 0.0000 |
| **N (bridged)** | Mulliken | -0.2214 | -0.0148 | -0.2317 | -0.1994 | -0.2713 | -0.0369 | -0.0888 | -0.3553 | -0.1951 | 0.0072 |
| | Lowdin | 0.1569 | -0.0129 | 0.1601 | -0.1726 | 0.1258 | -0.0324 | 0.2376 | -0.3018 | 0.1531 | 0.0083 |
| **C (grap)** | Mulliken | 0.0482 | -0.0081 | 0.0316 | -0.0173 | 0.0588 | -0.0044 | 0.0321 | 0.0622 | 0.0409 | 0.0673 |
| | Lowdin | 0.0545 | -0.0074 | 0.0399 | -0.0137 | 0.0672 | -0.0047 | 0.0328 | 0.0446 | 0.0536 | 0.0486 |
| **C(grap) grafted** | Mulliken | -0.1376 | 0.0002 | -0.1202 | 0.0099 | -0.1020 | 0.0026 | -0.1380 | 0.0072 | -0.1244 | -0.0053 |
| | Lowdin | -0.1730 | 0.0001 | -0.1681 | -0.0025 | -0.1496 | -0.0001 | -0.1892 | -0.0061 | -0.1806 | 0.0037 |
| **C(grap)** | Mulliken | 0.0599 | 0.0113 | 0.0487 | -0.0510 | 0.0492 | -0.0256 | 0.0534 | 0.0121 | 0.0434 | 0.0375 |
| | Lowdin | 0.0660 | 0.0071 | 0.0613 | -0.0439 | 0.0706 | -0.0219 | 0.0885 | 0.0012 | 0.0354 | 0.0248 |
| **C(grap)** | Mulliken | 0.0513 | 0.0060 | 0.0158 | 0.0123 | 0.0399 | 0.0096 | 0.0355 | 0.0130 | 0.0347 | 0.0187 |
| | Lowdin | 0.0309 | 0.0032 | 0.0214 | 0.0051 | 0.0263 | 0.0054 | 0.0109 | 0.0040 | 0.0627 | 0.0123 |

**Table S3.** Parameters for the formation of superoxide complex from peroxide complex.

| | CV1 (Co-($O_b$-Oc)-H to $O_dH_2$ bond) | CV2 (Co-($O_b$-$O_c$) to H bond) |
|---|---|---|
| NN | 6 | 6 |
| ND | 18 | 18 |
| $R_0$ | 2.00 | 2.10 |
| Time Step | 0.2 | - |
| Height of Gaussian | 5.0 x $e^{-3}$ | - |
| Bias factor for WT mtd | 25 | |
| Scale | 0.1 | 0.1 |
| HILLS added | For 5 steps | For 5steps |
| Temperature (avg. in kelvin) | 300.5 | - |

**Table S4.** Changing of Mulliken and Lowdin moments and charges during the formation of superoxide complex from peroxide complex.

| | | B | | TS3 | | C | |
|---|---|---|---|---|---|---|---|
| | | Charge | Spi. mom | Charge | Spi. mom | Charge | Spi. mom |
| **Co** | Mulliken | 0.4229 | 0.0883 | 0.4447 | 0.2273 | 0.4009 | 0.2051 |
| | Lowdin | 0.3411 | 0.0910 | 0.3605 | 0.2342 | 0.3137 | 0.2139 |
| **$O_a$** | Mulliken | -0.3171 | 0.0494 | -0.2203 | 0.1186 | -0.2697 | 0.2079 |
| | Lowdin | -0.1495 | 0.0470 | -0.0758 | 0.1117 | -0.1003 | 0.2013 |
| **$O_b$** | Mulliken | -0.1328 | 0.0016 | -0.2090 | 0.0313 | -0.3763 | 0.1959 |
| | Lowdin | 0.0114 | 0.0025 | -0.0980 | 0.0351 | -0.2248 | 0.1946 |
| **$O_c$** | Mulliken | -0.2382 | 0.0021 | -0.1128 | 0.0050 | -0.0400 | 0.0047 |
| | Lowdin | -0.0289 | 0.0026 | 0.0633 | 0.0048 | 0.1439 | 0.0040 |
| **H** | Mulliken | 0.1317 | 0.0006 | 0.1646 | 0.0070 | 0.1524 | 0.0028 |
| | Lowdin | -0.0512 | 0.0005 | 0.0583 | 0.0056 | -0.0086 | 0.0039 |
| **N (bridged)** | Mulliken | -0.0915 | 0.4542 | -0.0801 | 0.4559 | -0.1242 | 0.3229 |
| | Lowdin | 0.2319 | 0.3992 | 0.2406 | 0.4002 | 0.1970 | 0.2858 |
| **C (grap)** | Mulliken | 0.0448 | -0.0183 | 0.0375 | 0.1218 | 0.0425 | 0.1155 |
| | Lowdin | 0.0376 | -0.0131 | 0.0430 | 0.0542 | 0.0484 | 0.0847 |
| **C(grap) grafted** | Mulliken | -0.1367 | -0.0174 | -0.1471 | -0.0255 | -0.1174 | -0.0254 |
| | Lowdin | -0.1929 | 0.0026 | -0.1911 | 0.01843 | -0.1622 | 0.0133 |
| **C(grap)** | Mulliken | 0.0324 | -0.0174 | 0.0317 | 0.0760 | 0.0191 | 0.1173 |
| | Lowdin | 0.0326 | -0.0131 | 0.0430 | 0.0542 | 0.0484 | 0.0847 |
| **C(grap)** | Mulliken | 0.0317 | 0.0446 | 0.0380 | 0.1023 | 0.0402 | 0.1067 |
| | Lowdin | 0.0362 | 0.0395 | 0.0254 | 0.0789 | 0.0383 | 0.0801 |

**Table S5.** Parameters for addition of water molecule with release of dioxygen.

| | **CV1 (Co- $O_eH_2$ bond)** | CV2 (Co-$O_a$-H bond) |
|---|---|---|
| NN | 10 | 6 |
| ND | 30 | 18 |
| $R_0$ | 3.20 | 2.10 |
| K (for Quadratic wall) | 5 (wall at 4.00 Å) | 5(wall at 3.00 Å) |
| Time Step | 0.2 | - |
| Height of Gaussian | 5.0 x $e^{-3}$ | - |
| Bias factor for WT mtd | 25 | |
| Scale | 0.1 | 0.1 |
| HILLS added | For 5 steps | For 5steps |
| Temperature (avg. in kelvin) | 304.6 | - |

**Table S6.** Changing of Mulliken and Lowdin spin moments and charges during the release of the oxygen molecule.

| | | **C** | | **TS4** | | **I2** | | **TS5** | | **D** | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Charge | Spi. mom | Charge | Spi. mom | Charge | Spi. mom | Charge | Spi. mom | Charge | Spi. mom |
| **Co** | Mulliken | 0.4129 | 0.0002 | 0.3310 | -0.0001 | 0.3661 | -0.0003 | 0.6230 | 0.1190 | 0.5621 | 0.2130 |
| | Lowdin | 0.2767 | 0.0002 | 0.2861 | -0.0001 | 0.3215 | -0.0004 | 0.5451 | 0.1141 | 0.5203 | 0.2030 |
| **$O_b$** | Mulliken | -0.3112 | 0.00005 | -0.1891 | 0.00002 | -0.2266 | 0.00001 | -0.0009 | 0.0087 | -0.3663 | -0.1668 |
| | Lowdin | -0.1170 | 0.0001 | -0.0047 | 0.00007 | -0.0159 | 0.00005 | -0.1966 | -0.0901 | -0.2001 | -0.1588 |
| **$O_c$** | Mulliken | -0.2516 | 0.00006 | -0.2518 | 0.00001 | -0.1953 | 0.00002 | -0.1143 | -0.0177 | -0.2369 | -0.0348 |
| | Lowdin | -0.0991 | 0.00007 | -0.1144 | 0.00001 | -0.0615 | 0.00003 | 0.0548 | -0.0183 | -0.0691 | -0.0354 |
| **$O_e$** | Mulliken | -0.2843 | -0.00005 | -0.2518 | 0.00001 | -0.2823 | -0.0000 | -0.2264 | 0.0061 | -0.3081 | 0.0040 |
| | Lowdin | -0.0303 | -0.00001 | -0.0315 | -0.0000 | -0.0236 | -0.0000 | 0.0011 | 0.0068 | -0.0765 | 0.0067 |
| **N (bridged)** | Mulliken | 0.0199 | 0.0160 | -0.0866 | 0.02609 | -0.0255 | 0.0213 | -0.0009 | 0.0087 | -0.0318 | 0.0284 |
| | Lowdin | 0.2407 | 0.0154 | 0.1823 | 0.0254 | 0.2098 | 0.0212 | 0.2110 | 0.0094 | 0.2035 | 0.0279 |
| **C (grap)** | Mulliken | 0.0175 | 0.0161 | 0.0264 | 0.0485 | 0.0224 | 0.0483 | 0.0136 | 0.0250 | 0.0107 | 0.0394 |
| | Lowdin | 0.0335 | 0.0116 | 0.0497 | 0.0352 | 0.0488 | 0.0354 | 0.0237 | 0.0185 | 0.0370 | 0.0288 |
| **C(grap) grafted** | Mulliken | -0.1326 | -0.0037 | -0.0993 | -0.0084 | -0.1012 | -0.0066 | -0.1304 | -0.0030 | -0.1024 | -0.0072 |
| | Lowdin | -0.1390 | 0.0029 | -0.1267 | 0.0067 | -0.1187 | 0.0066 | -0.1489 | 0.0050 | -0.1094 | 0.0068 |
| **C(grap)** | Mulliken | 0.0020 | 0.0606 | -0.0076 | 0.1074 | -0.0218 | 0.0913 | 0.0292 | 0.0791 | 0.0275 | 0.1015 |
| | Lowdin | 0.0164 | 0.0431 | 0.0153 | 0.0776 | -0.0061 | 0.0651 | 0.0536 | 0.0570 | 0.0296 | 0.0726 |
| **C(grap)** | Mulliken | 0.0308 | 0.0053 | 0.0264 | 0.0355 | 0.0248 | 0.0346 | 0.0304 | 0.0093 | 0.0323 | 0.03025 |
| | Lowdin | 0.0188 | 0.0047 | 0.0180 | 0.0265 | 0.0283 | 0.0261 | 0.0237 | 0.0075 | 0.0266 | 0.0226 |