

Supporting Information for Decoupling CO₂ Reduction and Hydrogen Evolution Reaction on CuZn Alloys by Constructing Asymmetric Active Microenvironments

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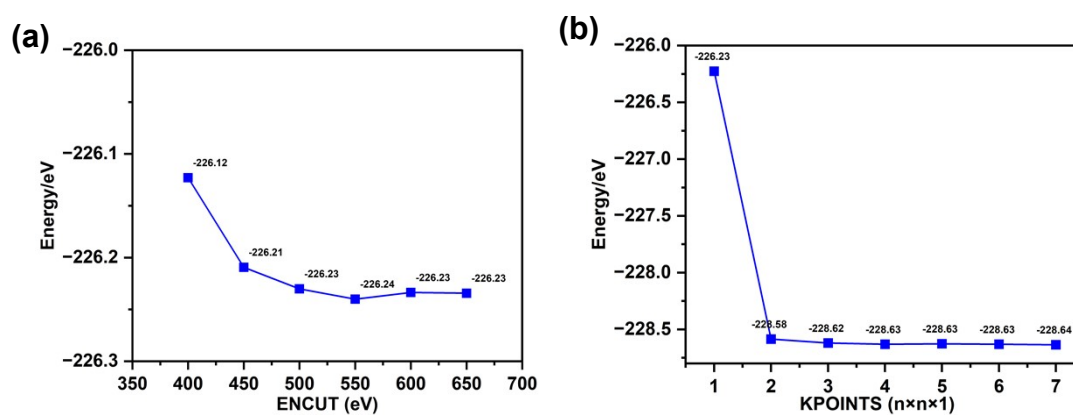
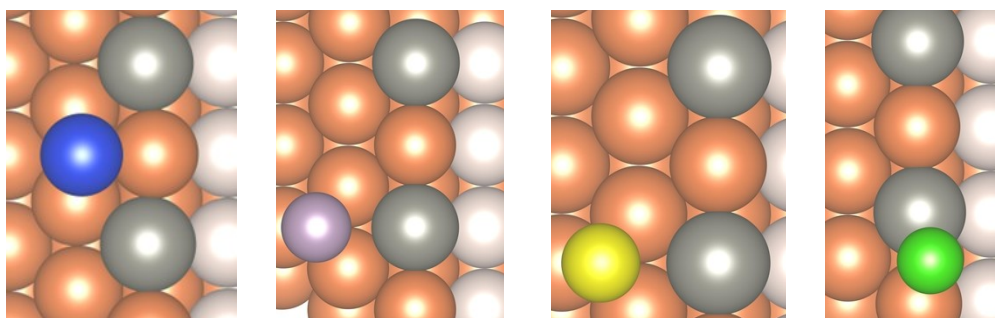


Figure S1. (a) Tests of the cutoff energy and (b) the K-point mesh.



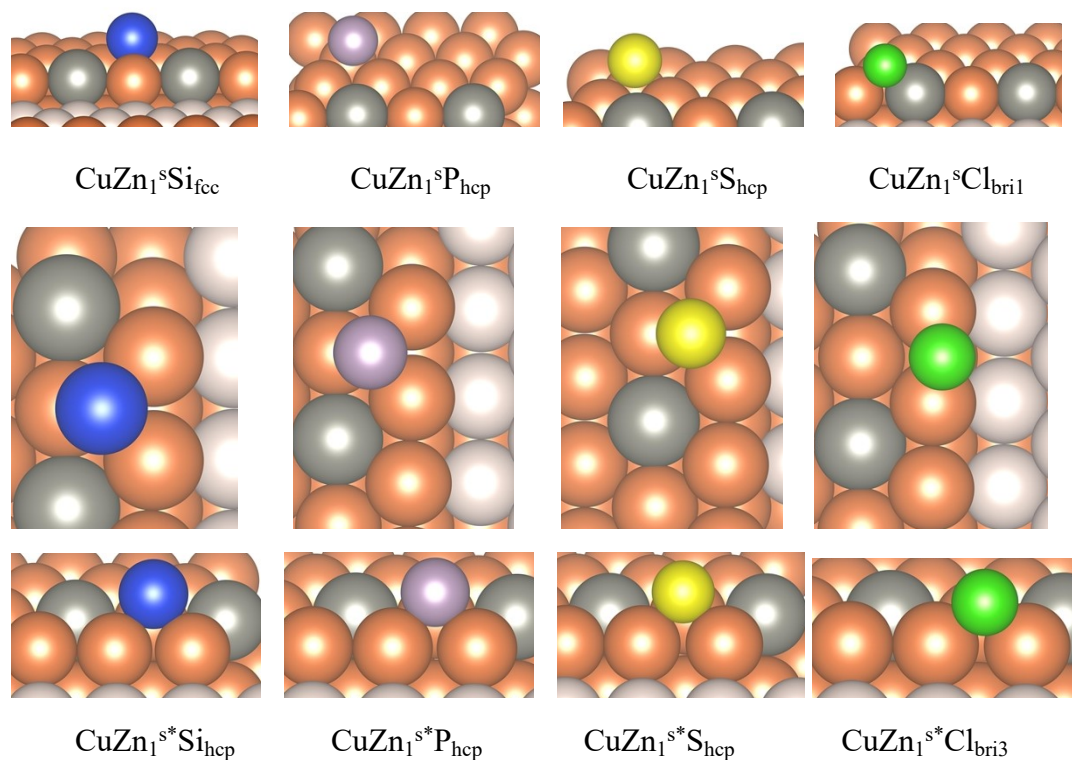


Figure S2. Top and side views of CuZnX structures ($X = \text{Si}, \text{P}, \text{S}, \text{Cl}$).

Table S1. Formation energies of oxidized and reduced Zn clusters under solvation conditions ($\epsilon=78.4$). All data were obtained at $\Delta\mu_{\text{O}} = -2.5$ eV, i.e., under a hydrogen-rich environment.

| Cluster | Formation/eV ($\Delta\mu_{\text{O}} = -2.5$ eV) |
|---------------------------|--|
| ZnO^{a} | -0.07 |
| ZnOH^{a} | -1.37 |
| Zn_1^{a} | -1.52 |
| Zn_1^{s} | -1.73 |
| $\text{Zn}_1^{\text{s}*}$ | -1.71 |
| Zn_2^{s} | -1.68 |
| $\text{Zn}_2^{\text{s}*}$ | -1.61 |

Table S2. Vibrational frequencies of *COOH, *CO, COH, and H on CuZnX.

| Catalyst | intermediate | Vibrational frequencies | | | | | |
|--|---------------------|-------------------------|----------------|------------------------------|------------------------------|----------------|--|
| Zn ₁ ^s Si _{fcc} | *COOH | 1 f = 105.481447 THz | 662.759479 THz | 2PiTHz | 3518.482243 cm ⁻¹ | 436.236357 meV | |
| | | 2 f = 50.343474 THz | 316.317379 THz | 2PiTHz | 1679.277497 cm ⁻¹ | 208.203949 meV | |
| | | 3 f = 36.739770 THz | 230.842795 THz | 2PiTHz | 1225.506786 cm ⁻¹ | 151.943531 meV | |
| | | 4 f = 29.229666 THz | 183.655410 THz | 2PiTHz | 974.996692 cm ⁻¹ | 120.884227 meV | |
| | | 5 f = 19.902008 THz | 125.048001 THz | 2PiTHz | 663.859494 cm ⁻¹ | 82.308117 meV | |
| | | 6 f = 18.986982 THz | 119.298728 THz | 2PiTHz | 633.337535 cm ⁻¹ | 78.523875 meV | |
| | | 7 f = 11.173135 THz | 70.202878 THz | 2PiTHz | 372.695655 cm ⁻¹ | 46.208389 meV | |
| | | 8 f = 8.226528 THz | 51.688798 THz | 2PiTHz | 274.407419 cm ⁻¹ | 34.022196 meV | |
| | | 9 f = 7.397706 THz | 46.481158 THz | 2PiTHz | 246.760903 cm ⁻¹ | 30.594464 meV | |
| | | 10 f = 4.352971 THz | 27.350522 THz | 2PiTHz | 145.199474 cm ⁻¹ | 18.002447 meV | |
| | | 11 f = 3.744141 THz | 23.525132 THz | 2PiTHz | 124.891099 cm ⁻¹ | 15.484528 meV | |
| | | 12 f = 0.956966 THz | 6.012794 THz | 2PiTHz | 31.920943 cm ⁻¹ | 3.957694 meV | |
| | *CO | 1 f = 60.295599 THz | 378.848421 THz | 2PiTHz | 2011.244629 cm ⁻¹ | 249.362643 meV | |
| | | 2 f = 10.363543 THz | 65.116060 THz | 2PiTHz | 345.690569 cm ⁻¹ | 42.860183 meV | |
| | | 3 f = 9.692328 THz | 60.898693 THz | 2PiTHz | 323.301253 cm ⁻¹ | 40.084261 meV | |
| | | 4 f = 8.083065 THz | 50.787393 THz | 2PiTHz | 269.622007 cm ⁻¹ | 33.428880 meV | |
| 5 f = 5.036220 THz | | 31.643506 THz | 2PiTHz | 167.990225 cm ⁻¹ | 20.828141 meV | | |
| 6 f = 2.653569 THz | | 16.672869 THz | 2PiTHz | 88.513547 cm ⁻¹ | 10.974285 meV | | |
| *COH | 1 f = 80.065180 THz | 503.064362 THz | 2PiTHz | 2670.686848 cm ⁻¹ | 331.123087 meV | | |
| | 2 f = 51.103738 THz | 321.094255 THz | 2PiTHz | 1704.637154 cm ⁻¹ | 211.348147 meV | | |
| | 3 f = 36.003226 THz | 226.214944 THz | 2PiTHz | 1200.938330 cm ⁻¹ | 148.897430 meV | | |
| | 4 f = 19.412949 THz | 121.975153 THz | 2PiTHz | 647.546243 cm ⁻¹ | 80.285531 meV | | |
| | 5 f = 12.974406 THz | 81.520600 THz | 2PiTHz | 432.779601 cm ⁻¹ | 53.657851 meV | | |
| | 6 f = 8.617801 THz | 54.147243 THz | 2PiTHz | 287.458901 cm ⁻¹ | 35.640374 meV | | |
| | 7 f = 4.935239 THz | 31.009022 THz | 2PiTHz | 164.621853 cm ⁻¹ | 20.410516 meV | | |
| | 8 f = 3.090788 THz | 19.419993 THz | 2PiTHz | 103.097584 cm ⁻¹ | 12.782476 meV | | |
| | 9 f = 1.943754 THz | 12.212967 THz | 2PiTHz | 64.836654 cm ⁻¹ | 8.038723 meV | | |
| *H | 1 f = 41.778533 THz | 262.502266 THz | 2PiTHz | 1393.581818 cm ⁻¹ | 172.782187 meV | | |
| | 2 f = 23.519639 THz | 147.778248 THz | 2PiTHz | 784.530674 cm ⁻¹ | 97.269442 meV | | |
| | 3 f = 9.100224 THz | 57.178396 THz | 2PiTHz | 303.550802 cm ⁻¹ | 37.635516 meV | | |
| Zn ₁ ^s Si _{hcp} | *COOH | 1 f = 105.620468 THz | 663.632974 THz | 2PiTHz | 3523.119484 cm ⁻¹ | 436.811302 meV | |
| | | 2 f = 48.689049 THz | 305.922318 THz | 2PiTHz | 1624.091813 cm ⁻¹ | 201.361794 meV | |
| | | 3 f = 36.674879 THz | 230.435058 THz | 2PiTHz | 1223.342229 cm ⁻¹ | 151.675160 meV | |
| | | 4 f = 29.009816 THz | 182.217499 THz | 2PiTHz | 967.363055 cm ⁻¹ | 119.937776 meV | |
| | | 5 f = 19.054684 THz | 119.724111 THz | 2PiTHz | 635.595824 cm ⁻¹ | 78.803867 meV | |
| | | 6 f = 18.666937 THz | 117.287827 THz | 2PiTHz | 622.661992 cm ⁻¹ | 77.200276 meV | |
| | | 7 f = 8.171328 THz | 51.341965 THz | 2PiTHz | 272.566138 cm ⁻¹ | 33.793906 meV | |
| | | 8 f = 7.602265 THz | 47.766438 THz | 2PiTHz | 253.584250 cm ⁻¹ | 31.440451 meV | |
| | | 9 f = 6.488804 THz | 40.770359 THz | 2PiTHz | 216.443202 cm ⁻¹ | 26.835547 meV | |
| | | 10 f = 4.435724 THz | 27.870477 THz | 2PiTHz | 147.959827 cm ⁻¹ | 18.344687 meV | |
| | | 11 f = 3.242246 THz | 20.371629 THz | 2PiTHz | 108.149665 cm ⁻¹ | 13.408854 meV | |
| | | 12 f = 3.182594 THz | 19.996827 THz | 2PiTHz | 106.159899 cm ⁻¹ | 13.162155 meV | |
| | *CO | 1 f = 56.071124 THz | 352.305260 THz | 2PiTHz | 1870.331304 cm ⁻¹ | 231.891611 meV | |
| | | 2 f = 12.472362 THz | 78.366161 THz | 2PiTHz | 416.033197 cm ⁻¹ | 51.581561 meV | |
| | | 3 f = 10.291156 THz | 64.661242 THz | 2PiTHz | 343.276016 cm ⁻¹ | 42.560817 meV | |
| | | 4 f = 10.004472 THz | 62.859950 THz | 2PiTHz | 333.713246 cm ⁻¹ | 41.375184 meV | |
| 5 f = 5.463886 THz | | 34.330606 THz | 2PiTHz | 182.255603 cm ⁻¹ | 22.596823 meV | | |
| 6 f = 1.000002 THz | | 6.283197 THz | 2PiTHz | 33.356468 cm ⁻¹ | 4.135676 meV | | |
| *COH | 1 f = 82.238166 THz | 516.717635 THz | 2PiTHz | 2743.169853 cm ⁻¹ | 340.109837 meV | | |
| | 2 f = 47.857090 THz | 300.694964 THz | 2PiTHz | 1596.340641 cm ⁻¹ | 197.921086 meV | | |
| | 3 f = 35.957030 THz | 225.924683 THz | 2PiTHz | 1199.397381 cm ⁻¹ | 148.706376 meV | | |
| | 4 f = 17.206770 THz | 108.113324 THz | 2PiTHz | 573.956046 cm ⁻¹ | 71.161506 meV | | |
| | 5 f = 12.413325 THz | 77.995220 THz | 2PiTHz | 414.063935 cm ⁻¹ | 51.337404 meV | | |
| | 6 f = 6.241671 THz | 39.215758 THz | 2PiTHz | 208.199743 cm ⁻¹ | 25.813487 meV | | |
| | 7 f = 6.217431 THz | 39.065270 THz | 2PiTHz | 207.391164 cm ⁻¹ | 25.713236 meV | | |
| | 8 f = 4.298941 THz | 27.011040 THz | 2PiTHz | 143.397217 cm ⁻¹ | 17.778995 meV | | |
| | 9 f = 0.649853 THz | 4.083144 THz | 2PiTHz | 21.676746 cm ⁻¹ | 2.687575 meV | | |
| *H | 1 f = 37.813268 THz | 237.587768 THz | 2PiTHz | 1261.314805 cm ⁻¹ | 156.383161 meV | | |
| | 2 f = 36.533564 THz | 229.547152 THz | 2PiTHz | 1218.628482 cm ⁻¹ | 151.090730 meV | | |
| | 3 f = 7.957204 THz | 49.996585 THz | 2PiTHz | 265.423733 cm ⁻¹ | 32.908361 meV | | |
| Zn ₁ ^s P _{hcp} | *COOH | 1 f = 104.565257 THz | 657.002888 THz | 2PiTHz | 3487.921438 cm ⁻¹ | 432.447299 meV | |
| | | 2 f = 43.511222 THz | 273.389072 THz | 2PiTHz | 1451.378104 cm ⁻¹ | 179.948015 meV | |
| | | 3 f = 38.160701 THz | 239.770756 THz | 2PiTHz | 1272.903932 cm ⁻¹ | 157.820930 meV | |
| | | 4 f = 33.323933 THz | 209.380446 THz | 2PiTHz | 1111.566720 cm ⁻¹ | 137.816758 meV | |
| | | 5 f = 21.063246 THz | 132.344280 THz | 2PiTHz | 702.594250 cm ⁻¹ | 87.110616 meV | |
| | | 6 f = 20.300131 THz | 127.549485 THz | 2PiTHz | 677.130461 cm ⁻¹ | 83.954623 meV | |
| | | 7 f = 11.834014 THz | 74.355303 THz | 2PiTHz | 394.740206 cm ⁻¹ | 48.941566 meV | |
| | | 8 f = 9.333397 THz | 58.643463 THz | 2PiTHz | 311.328604 cm ⁻¹ | 38.599841 meV | |
| | | 9 f = 6.830286 THz | 42.915951 THz | 2PiTHz | 227.833801 cm ⁻¹ | 28.247801 meV | |
| | | 10 f = 4.685443 THz | 29.439508 THz | 2PiTHz | 156.289560 cm ⁻¹ | 19.377443 meV | |
| | | 11 f = 3.443685 THz | 21.637311 THz | 2PiTHz | 114.868962 cm ⁻¹ | 14.241941 meV | |
| | | 12 f = 2.866366 THz | 18.009906 THz | 2PiTHz | 95.611662 cm ⁻¹ | 11.854340 meV | |
| | *CO | 1 f = 60.486242 THz | 380.046264 THz | 2PiTHz | 2017.603781 cm ⁻¹ | 250.151077 meV | |
| | | 2 f = 11.012046 THz | 69.190726 THz | 2PiTHz | 367.322309 cm ⁻¹ | 45.542178 meV | |
| | | 3 f = 9.725086 THz | 61.104516 THz | 2PiTHz | 324.393932 cm ⁻¹ | 40.219736 meV | |
| | | 4 f = 8.783265 THz | 55.186884 THz | 2PiTHz | 292.978190 cm ⁻¹ | 36.324679 meV | |
| 5 f = 3.556083 THz | | 22.343526 THz | 2PiTHz | 118.618142 cm ⁻¹ | 14.706780 meV | | |
| 6 f = 3.206639 THz | | 20.147906 THz | 2PiTHz | 106.961953 cm ⁻¹ | 13.261597 meV | | |
| *COH | 1 f = 84.271671 THz | 529.494524 THz | 2PiTHz | 2811.080279 cm ⁻¹ | 348.519741 meV | | |
| | 2 f = 44.365827 THz | 273.788710 THz | 2PiTHz | 1479.884636 cm ⁻¹ | 183.482376 meV | | |
| | 3 f = 38.138999 THz | 239.592245 THz | 2PiTHz | 1271.993158 cm ⁻¹ | 157.695950 meV | | |
| | 4 f = 21.347397 THz | 134.129649 THz | 2PiTHz | 712.072481 cm ⁻¹ | 88.285767 meV | | |
| | 5 f = 14.164545 THz | 88.998460 THz | 2PiTHz | 472.478346 cm ⁻¹ | 58.579870 meV | | |
| | 6 f = 8.517548 THz | 53.517335 THz | 2PiTHz | 284.114822 cm ⁻¹ | 35.225761 meV | | |
| | 7 f = 6.383065 THz | 40.105980 THz | 2PiTHz | 212.916124 cm ⁻¹ | 26.398244 meV | | |
| | 8 f = 5.310562 THz | 33.367243 THz | 2PiTHz | 177.141263 cm ⁻¹ | 21.962725 meV | | |
| | 9 f = 3.368582 THz | 21.165426 THz | 2PiTHz | 112.363803 cm ⁻¹ | 13.931341 meV | | |
| *H | 1 f = 32.554995 THz | 204.549060 THz | 2PiTHz | 1085.017721 cm ⁻¹ | 134.636686 meV | | |
| | 2 f = 26.671668 THz | 167.583932 THz | 2PiTHz | 889.671050 cm ⁻¹ | 110.305192 meV | | |
| | 3 f = 23.990834 THz | 150.738958 THz | 2PiTHz | 800.248073 cm ⁻¹ | 99.218151 meV | | |

| | | |
|--|-------|---|
| Zn ₁ ^s *P _{hcp} | *COOH | 1 f = 104.819031 THz 658.597395 2P _i THz 3496.386414 cm-1 433.496822 meV 2 f = 44.500297 THz 279.603614 2P _i THz 1484.370093 cm-1 184.038502 meV 3 f = 37.231596 THz 233.933019 2P _i THz 1241.912335 cm-1 153.977561 meV 4 f = 32.143204 THz 201.961706 2P _i THz 1072.181839 cm-1 132.933654 meV 5 f = 20.428879 THz 128.358432 2P _i THz 681.434029 cm-1 84.487082 meV 6 f = 19.168313 THz 120.438061 2P _i THz 639.386069 cm-1 79.273798 meV 7 f = 10.714182 THz 67.319193 2P _i THz 357.386642 cm-1 44.310312 meV 8 f = 6.833177 THz 42.934119 2P _i THz 227.930254 cm-1 28.259760 meV 9 f = 6.299788 THz 39.582734 2P _i THz 210.138294 cm-1 26.053837 meV 10 f = 3.325887 THz 20.897165 2P _i THz 110.939659 cm-1 13.754768 meV 11 f = 1.448177 THz 9.099167 2P _i THz 48.305977 cm-1 5.989182 meV 12 f = 1.240532 THz 7.794495 2P _i THz 41.379706 cm-1 5.130432 meV |
| | *CO | 1 f = 60.192582 THz 378.201146 2P _i THz 2007.808351 cm-1 248.936598 meV 2 f = 10.482134 THz 65.861188 2P _i THz 349.646329 cm-1 43.350635 meV 3 f = 9.133083 THz 57.384851 2P _i THz 304.646837 cm-1 37.771407 meV 4 f = 7.828181 THz 49.185912 2P _i THz 261.120006 cm-1 32.374766 meV 5 f = 4.394400 THz 27.610830 2P _i THz 146.581405 cm-1 18.173784 meV 6 f = 3.461563 THz 21.749643 2P _i THz 115.465317 cm-1 14.315880 meV |
| | *COH | 1 f = 67.189440 THz 422.163699 2P _i THz 2241.198391 cm-1 277.873286 meV 2 f = 51.817684 THz 325.580113 2P _i THz 1728.451849 cm-1 214.300794 meV 3 f = 34.179253 THz 214.754582 2P _i THz 1140.097134 cm-1 141.354080 meV 4 f = 18.710164 THz 117.559425 2P _i THz 624.103861 cm-1 77.379045 meV 5 f = 11.212909 THz 70.452788 2P _i THz 374.022387 cm-1 46.372882 meV 6 f = 6.761561 THz 42.484141 2P _i THz 225.541394 cm-1 27.963579 meV 7 f = 4.705261 THz 29.564026 2P _i THz 156.950603 cm-1 19.459402 meV 8 f = 4.347086 THz 27.313547 2P _i THz 145.003178 cm-1 17.978109 meV 9 f = 3.273961 THz 20.570905 2P _i THz 109.207588 cm-1 13.540020 meV |
| | *H | 1 f = 39.772928 THz 249.900679 2P _i THz 1326.682046 cm-1 164.487669 meV 2 f = 36.051957 THz 226.521128 2P _i THz 1202.563812 cm-1 149.098964 meV 3 f = 7.204784 THz 45.268993 2P _i THz 240.325720 cm-1 29.796602 meV |
| Zn ₁ ^s S _{hcp} | *COOH | 1 f = 105.648753 THz 663.810695 2P _i THz 3524.062976 cm-1 436.928280 meV 2 f = 49.785340 THz 312.810516 2P _i THz 1660.660134 cm-1 205.895689 meV 3 f = 37.021901 THz 232.615467 2P _i THz 1234.917669 cm-1 153.110332 meV 4 f = 29.406500 THz 185.331978 2P _i THz 983.897319 cm-1 121.987764 meV 5 f = 19.330315 THz 121.455953 2P _i THz 644.789891 cm-1 79.943786 meV 6 f = 18.881861 THz 118.638231 2P _i THz 629.831063 cm-1 78.089128 meV 7 f = 11.182993 THz 70.264815 2P _i THz 373.024473 cm-1 46.249157 meV 8 f = 7.152978 THz 44.943487 2P _i THz 238.597659 cm-1 29.582350 meV 9 f = 5.772513 THz 36.269769 2P _i THz 192.550305 cm-1 23.873204 meV 10 f = 4.340004 THz 27.269048 2P _i THz 144.766940 cm-1 17.948820 meV 11 f = 3.164860 THz 19.885401 2P _i THz 105.568359 cm-1 13.088813 meV 12 f = 0.611036 THz 3.839255 2P _i THz 20.381982 cm-1 2.527045 meV |
| | *CO | 1 f = 60.592980 THz 380.716922 2P _i THz 2021.164193 cm-1 250.592512 meV 2 f = 10.892019 THz 68.436573 2P _i THz 363.318631 cm-1 45.045785 meV 3 f = 9.804700 THz 62.107404 2P _i THz 329.718103 cm-1 40.879849 meV 4 f = 8.517143 THz 53.514790 2P _i THz 284.101315 cm-1 35.224086 meV 5 f = 4.555906 THz 28.625601 2P _i THz 151.968659 cm-1 18.841719 meV 6 f = 3.861044 THz 24.259467 2P _i THz 128.789564 cm-1 15.967877 meV |
| | *COH | 1 f = 80.902833 THz 508.327491 2P _i THz 2698.627943 cm-1 334.587342 meV 2 f = 50.798616 THz 319.177118 2P _i THz 1694.459388 cm-1 210.086264 meV 3 f = 35.298689 THz 221.788202 2P _i THz 1177.437479 cm-1 145.983694 meV 4 f = 19.504157 THz 122.548230 2P _i THz 650.588612 cm-1 80.662737 meV 5 f = 11.067933 THz 74.588424 2P _i THz 395.871629 cm-1 49.081844 meV 6 f = 7.459763 THz 46.864790 2P _i THz 248.797545 cm-1 30.846975 meV 7 f = 4.752244 THz 29.859227 2P _i THz 158.517770 cm-1 19.653707 meV 8 f = 3.748268 THz 23.551062 2P _i THz 125.028757 cm-1 15.501506 meV 9 f = 2.716063 THz 17.065524 2P _i THz 90.598092 cm-1 11.232736 meV |
| | *H | 1 f = 32.373810 THz 203.410650 2P _i THz 1079.874045 cm-1 133.887366 meV 2 f = 27.234779 THz 171.121161 2P _i THz 908.454402 cm-1 112.634031 meV 3 f = 24.509943 THz 154.000515 2P _i THz 817.563678 cm-1 101.365014 meV |
| Zn ₁ ^s *S _{hcp} | *COOH | 1 f = 105.065024 THz 660.143013 2P _i THz 3504.591851 cm-1 434.514167 meV 2 f = 49.024451 THz 308.029713 2P _i THz 1635.279629 cm-1 202.748907 meV 3 f = 36.509871 THz 229.398286 2P _i THz 1217.838174 cm-1 150.992744 meV 4 f = 29.440659 THz 184.981116 2P _i THz 982.034648 cm-1 121.756822 meV 5 f = 19.490304 THz 122.461189 2P _i THz 650.126528 cm-1 80.605445 meV 6 f = 18.804145 THz 118.149926 2P _i THz 627.238736 cm-1 77.767720 meV 7 f = 10.917732 THz 68.598130 2P _i THz 364.176312 cm-1 45.152124 meV 8 f = 7.503282 THz 47.144510 2P _i THz 250.282533 cm-1 31.031090 meV 9 f = 6.105876 THz 38.364353 2P _i THz 203.670108 cm-1 25.251884 meV 10 f = 4.693333 THz 29.489080 2P _i THz 156.552726 cm-1 19.410071 meV 11 f = 3.605518 THz 22.654136 2P _i THz 120.267122 cm-1 14.911228 meV 12 f = 1.322495 THz 8.309481 2P _i THz 44.113684 cm-1 5.469402 meV |
| | *CO | 1 f = 60.007747 THz 377.039795 2P _i THz 2001.642927 cm-1 248.172183 meV 2 f = 10.623037 THz 66.746511 2P _i THz 354.346365 cm-1 43.933366 meV 3 f = 8.912066 THz 55.996163 2P _i THz 297.274518 cm-1 36.857356 meV 4 f = 7.538649 THz 47.366729 2P _i THz 251.462259 cm-1 31.177358 meV 5 f = 5.805409 THz 36.476462 2P _i THz 193.647602 cm-1 24.009251 meV 6 f = 2.805869 THz 17.629792 2P _i THz 93.593696 cm-1 11.604144 meV |
| | *COH | 1 f = 73.009573 THz 458.732678 2P _i THz 2435.337148 cm-1 301.943433 meV 2 f = 50.818956 THz 319.304292 2P _i THz 1695.134533 cm-1 210.169072 meV 3 f = 34.657641 THz 217.760383 2P _i THz 1156.054441 cm-1 143.332535 meV 4 f = 18.529595 THz 116.424816 2P _i THz 618.080406 cm-1 76.632321 meV 5 f = 11.365641 THz 71.412428 2P _i THz 379.116964 cm-1 47.004530 meV 6 f = 4.998283 THz 31.405137 2P _i THz 166.724763 cm-1 20.671244 meV 7 f = 4.188328 THz 26.316039 2P _i THz 139.707570 cm-1 17.321537 meV 8 f = 4.392024 THz 27.595899 2P _i THz 146.502138 cm-1 18.163957 meV 9 f = 1.024320 THz 6.435994 2P _i THz 34.167644 cm-1 4.236249 meV |
| | *H | 1 f = 33.054071 THz 207.684855 2P _i THz 1102.565106 cm-1 136.700700 meV 2 f = 29.428381 THz 184.903971 2P _i THz 981.625099 cm-1 121.706045 meV 3 f = 23.000863 THz 144.518683 2P _i THz 767.226174 cm-1 95.123956 meV |

| | | |
|---|-------|--|
| Zn ₁ ^s Cl _{bril} | *COOH | 1 f = 104.813875 THz 658.565002 2P _i THz 3496.214444 cm ⁻¹ 433.475501 meV 2 f = 43.972572 THz 276.287820 2P _i THz 1466.767084 cm ⁻¹ 181.856006 meV 3 f = 37.767021 THz 237.297194 2P _i THz 1259.772192 cm ⁻¹ 156.191901 meV 4 f = 32.338398 THz 203.188149 2P _i THz 1078.692826 cm ⁻¹ 133.740913 meV 5 f = 20.102488 THz 126.307655 2P _i THz 670.546791 cm ⁻¹ 83.137236 meV 6 f = 19.825048 THz 124.564447 2P _i THz 661.292383 cm ⁻¹ 81.989835 meV 7 f = 10.924816 THz 68.642646 2P _i THz 364.412637 cm ⁻¹ 45.181425 meV 8 f = 9.156890 THz 57.534439 2P _i THz 305.440978 cm ⁻¹ 37.869868 meV 9 f = 6.910827 THz 43.422007 2P _i THz 230.520370 cm ⁻¹ 28.530894 meV 10 f = 5.909205 THz 37.128627 2P _i THz 197.109842 cm ⁻¹ 24.438515 meV 11 f = 5.066605 THz 31.835675 2P _i THz 169.010417 cm ⁻¹ 20.954629 meV 12 f = 2.782841 THz 17.485108 2P _i THz 92.825592 cm ⁻¹ 11.508911 meV |
| | *CO | 1 f = 53.576913 THz 336.633676 2P _i THz 1787.133413 cm ⁻¹ 221.576383 meV 2 f = 8.812312 THz 55.369389 2P _i THz 293.947077 cm ⁻¹ 36.444806 meV 3 f = 8.676272 THz 54.514626 2P _i THz 289.409278 cm ⁻¹ 35.882190 meV 4 f = 7.823036 THz 49.153587 2P _i THz 260.948396 cm ⁻¹ 32.353489 meV 5 f = 5.189590 THz 32.607156 2P _i THz 173.106083 cm ⁻¹ 21.462427 meV 6 f = 4.199959 THz 26.389122 2P _i THz 140.095556 cm ⁻¹ 17.369641 meV |
| | *COH | 1 f = 83.497917 THz 524.632885 2P _i THz 2785.190627 cm ⁻¹ 345.319751 meV 2 f = 49.564422 THz 311.422451 2P _i THz 1653.291124 cm ⁻¹ 204.982048 meV 3 f = 36.533398 THz 229.546109 2P _i THz 1218.622945 cm ⁻¹ 151.090043 meV 4 f = 20.265265 THz 127.330418 2P _i THz 675.976474 cm ⁻¹ 83.810431 meV 5 f = 12.873750 THz 80.888160 2P _i THz 429.422080 cm ⁻¹ 53.241571 meV 6 f = 7.701657 THz 48.390939 2P _i THz 256.899624 cm ⁻¹ 31.851505 meV 7 f = 5.400103 THz 33.929846 2P _i THz 180.128033 cm ⁻¹ 22.333038 meV 8 f = 4.608274 THz 28.954641 2P _i THz 153.715477 cm ⁻¹ 19.058297 meV 9 f = 4.056064 THz 25.485005 2P _i THz 135.295743 cm ⁻¹ 16.774540 meV |
| | *H | 1 f = 32.282596 THz 202.837534 2P _i THz 1076.831464 cm ⁻¹ 133.510134 meV 2 f = 26.430394 THz 166.067066 2P _i THz 881.623036 cm ⁻¹ 109.307365 meV 3 f = 24.361535 THz 153.068040 2P _i THz 812.613322 cm ⁻¹ 100.751247 meV |
| Zn ₁ ^s *Cl _{bril3} | *COOH | 1 f = 105.364230 THz 662.022980 2P _i THz 3514.572288 cm ⁻¹ 435.751584 meV 2 f = 51.412102 THz 323.031765 2P _i THz 1714.923083 cm ⁻¹ 212.623440 meV 3 f = 35.430428 THz 222.615942 2P _i THz 1181.831816 cm ⁻¹ 146.528523 meV 4 f = 27.142975 THz 170.544342 2P _i THz 905.392164 cm ⁻¹ 112.254362 meV 5 f = 18.495415 THz 116.210117 2P _i THz 616.940605 cm ⁻¹ 76.490914 meV 6 f = 17.492146 THz 109.906397 2P _i THz 583.475179 cm ⁻¹ 72.341728 meV 7 f = 10.667927 THz 67.028560 2P _i THz 355.843719 cm ⁻¹ 44.119014 meV 8 f = 7.267966 THz 45.665978 2P _i THz 242.433250 cm ⁻¹ 30.057903 meV 9 f = 6.625250 THz 41.627671 2P _i THz 220.994531 cm ⁻¹ 27.399840 meV 10 f = 3.732247 THz 23.450402 2P _i THz 124.404370 cm ⁻¹ 15.435340 meV 11 f = 2.807924 THz 17.642784 2P _i THz 93.662244 cm ⁻¹ 11.612642 meV 12 f = 2.112118 THz 13.270830 2P _i THz 70.452678 cm ⁻¹ 8.735022 meV |
| | *CO | 1 f = 60.961940 THz 383.035167 2P _i THz 2033.471382 cm ⁻¹ 252.118410 meV 2 f = 10.925820 THz 68.648955 2P _i THz 364.446131 cm ⁻¹ 45.185578 meV 3 f = 9.385269 THz 58.969382 2P _i THz 313.058852 cm ⁻¹ 38.814365 meV 4 f = 7.985034 THz 50.171450 2P _i THz 266.352066 cm ⁻¹ 33.023459 meV 5 f = 5.673931 THz 35.650358 2P _i THz 189.261948 cm ⁻¹ 23.465499 meV 6 f = 1.673745 THz 10.516452 2P _i THz 55.830131 cm ⁻¹ 6.922057 meV |
| | *COH | 1 f = 81.474700 THz 511.920638 2P _i THz 2717.703374 cm ⁻¹ 336.952395 meV 2 f = 51.001157 THz 320.449720 2P _i THz 1701.215425 cm ⁻¹ 210.923906 meV 3 f = 35.092458 THz 220.492417 2P _i THz 1170.558369 cm ⁻¹ 145.130793 meV 4 f = 19.390480 THz 121.833982 2P _i THz 646.796787 cm ⁻¹ 80.192610 meV 5 f = 12.486679 THz 78.456116 2P _i THz 416.510755 cm ⁻¹ 51.640771 meV 6 f = 7.368235 THz 46.295984 2P _i THz 245.777848 cm ⁻¹ 30.472580 meV 7 f = 4.095171 THz 25.730720 2P _i THz 136.600208 cm ⁻¹ 16.936273 meV 8 f = 2.652494 THz 16.666114 2P _i THz 88.477687 cm ⁻¹ 10.969839 meV 9 f = 1.851806 THz 11.635242 2P _i THz 61.769606 cm ⁻¹ 7.658458 meV |
| | *H | 1 f = 43.072222 THz 270.630755 2P _i THz 1436.734648 cm ⁻¹ 178.132458 meV 2 f = 34.870338 THz 219.096793 2P _i THz 1163.149224 cm ⁻¹ 144.212176 meV 3 f = 4.148571 THz 26.066237 2P _i THz 138.381412 cm ⁻¹ 17.157115 meV |

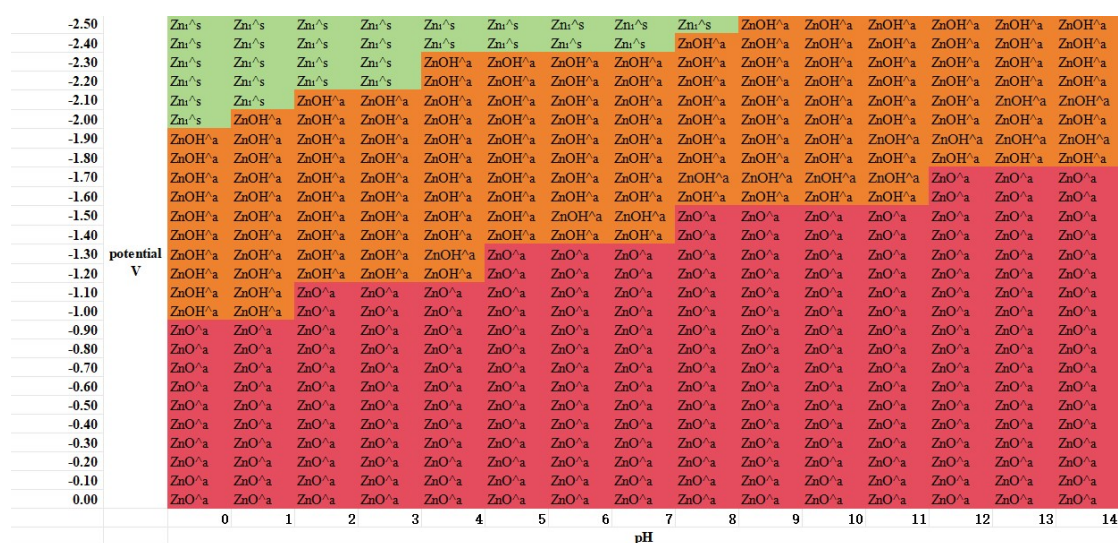


Figure S3. Distribution of oxidized and reduced clusters formed under different pH and reduction potentials.

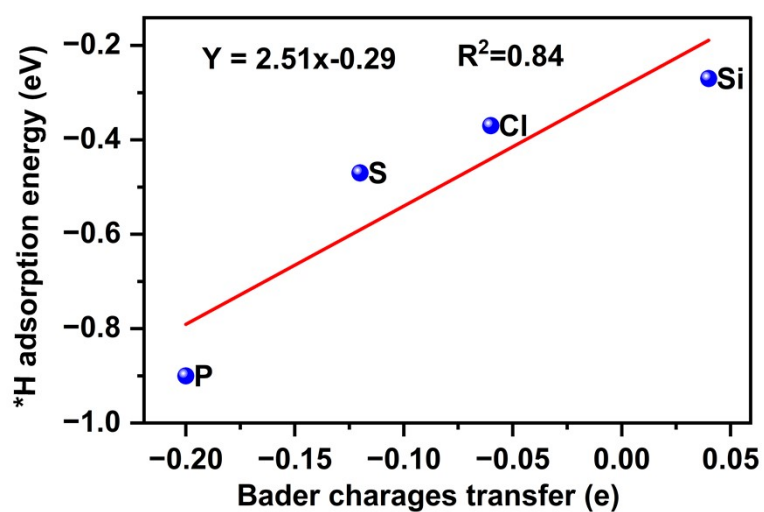


Figure S4 Functional relationship between H adsorption energy and Bader charge transfer in CuZn_1^sX .

Table S3. Gibbs Free Energies of Reaction Intermediates (in eV).

| intermediates CuZnX | *COOH | *CO | *COH | *H |
|---|-------|-------|------|-------|
| $\text{CuZn}_1^s\text{Si}_{\text{fcc}}$ | 0.51 | 0.30 | 1.28 | -0.12 |
| $\text{CuZn}_1^s\text{P}_{\text{hcp}}$ | -0.16 | -0.24 | 0.22 | -0.74 |
| $\text{CuZn}_1^s\text{S}_{\text{hcp}}$ | 0.46 | 0.38 | 1.04 | -0.31 |
| $\text{CuZn}_1^s\text{Cl}_{\text{bri1}}$ | 0.75 | 0.31 | 1.13 | -0.21 |
| CuZn_1^s | 0.86 | 0.36 | 1.16 | -0.21 |
| $\text{CuZn}_1^{s*}\text{Si}_{\text{hcp}}$ | 0.82 | 0.35 | 0.96 | -0.08 |
| $\text{CuZn}_1^{s*}\text{P}_{\text{hcp}}$ | 1.13 | 0.27 | 1.41 | -0.12 |
| $\text{CuZn}_1^{s*}\text{S}_{\text{hcp}}$ | 1.20 | 0.35 | 1.46 | -0.17 |
| $\text{CuZn}_1^{s*}\text{Cl}_{\text{bri3}}$ | 0.88 | 0.34 | 1.07 | 0.10 |
| CuZn_1^{s*} | 0.46 | 0.32 | 1.08 | -0.23 |