

There is considerable interest in the pH-dependent, switchable, biocatalytic properties of cerium oxide (CeO₂) nanoparticles (CeNPs) in biomedicine, where these materials exhibit beneficial antioxidant activity against reactive oxygen species (ROS) at basic physiological pH but cytotoxic prooxidant activity in acidic cancer cell pH microenvironment. While the general characteristics of the role of oxygen vacancies are known, the mechanism of their action at the atomic scale under different pH conditions has yet to be elucidated. The present work applies density functional theory (DFT) calculations to interpret, at the atomic scale, the pH-induced behavior of the stable {111} surface of CeO₂ containing oxygen vacancies. For detailed information please refer to the paper¹.

Input:

```

CERIA BULK ----- Title
EXTERNAL ----- Geometry read from the external .gui file
OPTGEOM ----- Geometry optimization
FULLOPTG ----- Both atomic positions and lattice parameters are optimized
FRAGMENT ----- Partial optimization; the following atoms are free to move
82
1 2 3 4 5 6 7 8 9 10
  23 24 25 26 27 28 29
  45 46 47 48 49 50 51
    91 92 93 94 95 96 97
END
END
258 9
INPUT
30. 0 1 1 1 1 1
20.137829 580.083457 0
15.998482 310.302833 0
14.974187 167.813944 0
----- Basis set section

99 0 ----- End of Basis set
CHEMOD ----- Modification of electronic configuration
1
93
2 7 0 0 0
CHARGED ----- Charged system
ENDBS
DFT
BLYP-D3 ----- Use BLYP functional with Grimme D3 correction
HYBRID ----- Use hybrid functional
12 ----- Mix 12 % Hartree Fock in the exchange energy
NONLOCAL ----- Local term parameterization
0.9 0.81
SPIN ----- Spin polarized calculation
ENDM
MPP ----- Massive parallel (MPP) extension
GUESSP ----- Restart from a previous run density matrix
TOLINTEG
7 7 7 7 14
NODIIS
LEVSHIFT
20 1
TOLDEE ----- Convergence on total energy
5
SHRINK ----- Pack-Monkhorst/Gilat shrinking factors
2 2
MAXCYCLE ----- Maximum number of SCF cycles
1024
FMIXING ----- Percent of Fock/KS matrices mixing
65
PPAN ----- Mulliken Population Analysis
SAVEWF ----- Write wave function
ENDSCF

```

Output:

```
MAX GRADIENT      0.000214 THRESHOLD      0.000450 CONVERGED YES
RMS GRADIENT      0.000027 THRESHOLD      0.000300 CONVERGED YES
MAX DISPLAC.      0.000865 THRESHOLD      0.001800 CONVERGED YES
RMS DISPLAC.      0.000220 THRESHOLD      0.001200 CONVERGED YES
```

Geometry optimization
converging criteria

CONVERGENCE TESTS SATISFIED AFTER 55 ENERGY AND GRADIENT CALCULATIONS

```
*****
* OPT END - CONVERGED * E(AU): -1.758444501740E+04 POINTS 55 *
*****
```

Converged total energy

ENERGY CONTRIBUTIONS OF SEMICLASSICAL CORRECTIONS
D3 DISPERSION ENERGY (AU) -1.470017895128E+00

```
ALPHA BAND GAP:      0.3402 eV
BETA BAND GAP:       3.0421 eV
```

Band gap

CHARGE NORMALIZATION FACTOR 1.00000000

TOTAL ATOMIC CHARGES:

```
9.1948841 9.3144570 9.2693357 9.2659110 9.3272587 9.2027513
9.3385839 9.4284884 27.4175772 27.4240843 27.4132421 27.4365928
27.4496394 27.6798339 27.4337185 27.4186776 27.6553188 9.3129207
9.2982522 9.3637794 9.3197586 9.3558272 9.3572487 9.3023331
9.3475153 9.4031584 9.3011337 9.3209620 9.3078683 9.3235100
9.3221859 9.3339348 9.3216051 9.3331111 9.3322963 27.3951248
27.3950470 27.3931713 27.4029665 27.3991881 27.4045522 27.3931199
27.3925672 27.3877054 9.3376817 9.3342727 9.3322626 9.3331170
9.3370757 9.3341715 9.3310810 9.3299895 9.3346779 9.3081648
9.3048413 9.3108329 9.3118923 9.3139638 9.3123244 9.3086768
9.3072140 9.3090599 27.4235623 27.4234520 27.4228079 27.4235731
27.4233917 27.4237238 27.4232693 27.4236241 27.4229624 9.2384708
9.2382890 9.2381775 9.2386285 9.2384635 9.2385134 9.2388404
9.2387240 9.2388561 8.8412805 0.5224998 0.6567045 8.8802370
0.6189496 0.5966147 0.7065368 8.7438488 0.5669845 0.5875759
8.7092969 0.7169499 8.6683804 0.6549230 0.6441037 8.7395441
0.5613005 0.7069849 0.6152033 8.6582425 0.7138511 8.6792636
0.6300091 0.6812700 8.7378423 0.5634018 0.6747776 8.6680244
0.6247998 0.6907717
```

Mulliken charge of each atom

SUMMED SPIN DENSITY

2.00000000

Sum of electron spin in the system

TOTAL ATOMIC SPINS :

```
-0.0022869 -0.0063002 -0.0029883 -0.0019517 -0.0033895 -0.0014703
-0.0014882 -0.0022942 0.0145989 0.0105647 0.0435001 0.0120985
0.0206494 0.8617259 0.0100976 0.0561895 0.8860451 -0.0006614
-0.0019513 -0.0047466 -0.0007096 -0.0028425 -0.0051616 -0.0020750
-0.0043084 -0.0045520 -0.0004224 -0.0005850 -0.0014812 -0.0010110
0.0007332 -0.0057632 -0.0005563 -0.0008424 -0.0024436 0.0007850
0.0028324 0.0141762 0.0013155 0.0304549 0.0672563 0.0023114
0.0060350 0.0236214 -0.0001665 -0.0003559 -0.0007507 -0.0004186
0.0010225 -0.0013670 -0.0001669 -0.0006621 -0.0011056 -0.0000400
-0.0001009 -0.0002405 -0.0000838 -0.0006781 -0.0014428 -0.0000951
-0.0001086 -0.0004559 0.0000364 0.0001117 0.0002283 0.0003890
0.0009661 0.0009880 0.0000595 0.0008526 0.0010544 -0.0000820
-0.0000529 -0.0001015 -0.0000981 -0.0000575 -0.0000749 -0.0000470
-0.0000186 -0.0000477 0.0000508 0.0000182 -0.0002691 0.0018228
0.0001608 0.0001421 0.0000192 -0.0001985 0.0000949 -0.0001414
0.0004837 0.0004927 -0.0000540 -0.0000644 -0.0000103 -0.0001598
0.0005034 0.0000884 0.0000265 -0.0000641 0.0000245 -0.0001179
0.0000119 0.0001545 -0.0000745 -0.0000111 0.0000096 -0.0000765
0.0000099 0.0000063
```

Electron spin of each atom

References

1. Ma, H.; Liu, Z.; Koshy, P.; Sorrell, C. C.; Hart, J. N., DFT Investigation of Biocatalytic Mechanisms from pH-Driven, Multi-Enzyme, Biomimetic Behavior in CeO₂. *arXiv preprint arXiv: 2104.10994* **2021**.