Supporting information: Ab-initio Simulations of Copper Oxide Nanowires and Clusters on TiO_2 (101) Anatase Surface

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Supporting Information

This supporting information shows optimized bulk Cu_2O and CuO structures with their thermodynamic stabilities with respect to oxygen pressure in the subsequent figure. Tables of formation energies of three stable 3L and 2L Cu_2O/TiO_2 and CuO/TiO_2 structures and three optimized 2L structures of Cu_2O/TiO_2 and CuO/TiO2 clusters are shown. In addition, Tables showing Löwdin analysis determined from the PDOS of bulk Cu oxides and their respective nanowires, Cu_2O/TiO_2 and CuO/TiO_2 nanowire systems are included.

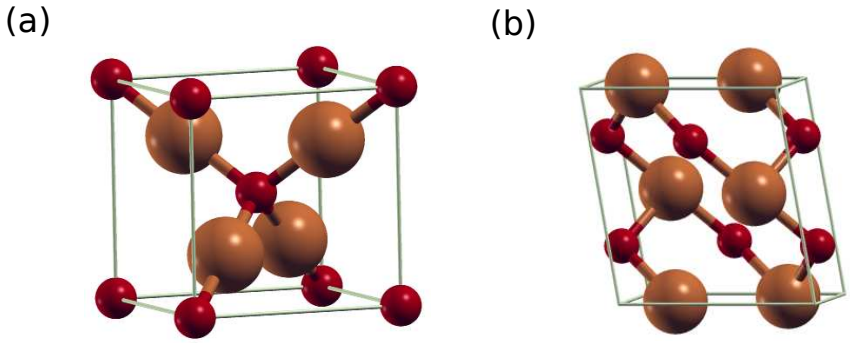

Figure 1: Optimized crystal structures of bulk copper oxides: (a) Cu_2O and (b) CuO. Red balls: oxygen; red-brown ball: copper.

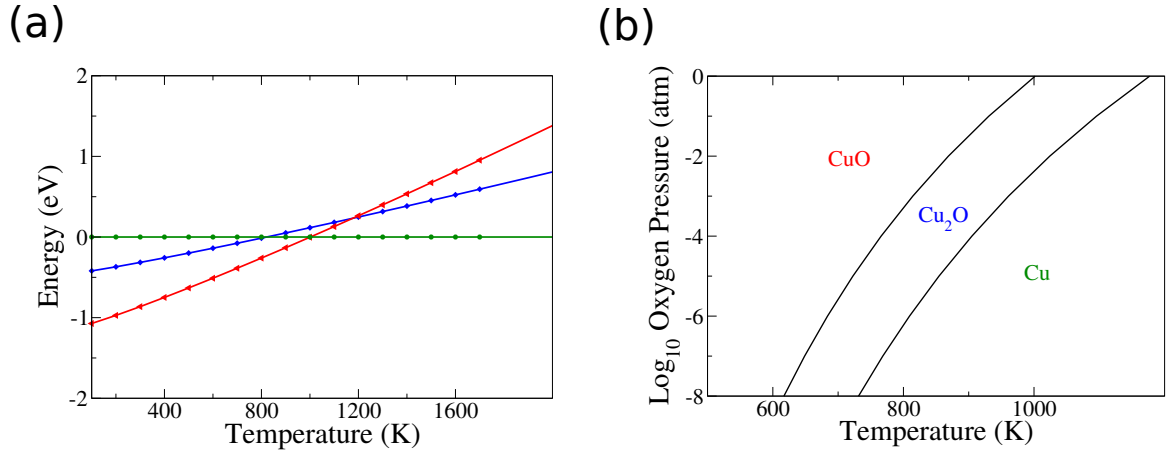

Figure 2: (a) Calculated Gibb's free energy of CuO (red line with triangles), Cu_2O (blue line with diamonds) and Cu (green line with circles) at 1 atm oxygen pressure as a function of temperature. Metallic copper has 0 eV free energy. (b) Phase diagram showing the pressure and temperature ranges of bulk copper oxides.

Table 1: Calculated formation energies of the three most stable structures of 3L (see Fig. 1: main text) and 2L Cu_2O/TiO_2 (see Fig. 3: SI) structures

Structures	Formation energies (eV)	
	3L (10 Å× 7.57 Å)	2L (10 Å× 15.15 Å)
a	-5.45	-4.58
b	-4.30	-4.21
c	-3.93	-3.78

Table 2: Calculated formation energies of the three most stable structures of 3L (see Fig. 2: main text) and 2L CuO/TiO_2 (see Fig. 4: SI) structures

Structures	Formation energies (eV)	
	3L (10 Å× 7.57 Å)	2L (10 Å× 15.15 Å)
b(3L) and a(2L)	-2.56	-2.35
a(3L) and b(2L)	-2.48	-1.41
d(3L) and c(2L)	-1.46	-1.39

From optimized structure shown in Fig. 1a, a planar Cu_3 trimer formed from two Cu-Cu dimers in the initial structure seems to stabilize the Cu_2O nanowire on TiO_2 (101) surface. The Cu_3 triangular cluster is bound on each side with an O atom which binds the cluster to the TiO_2 surface forming 3 Cu_2O units. The tetrahedral Cu_2O cluster (Fig. 1b) with total energy difference of 1.15 eV, has two O atoms bound on the sides of tetrahedral Cu_4 cluster. The O atom at the top of the tetrahedral is bound to triangular Cu atoms while the other O atom is bound between two Cu atoms and a Ti surface atom.

The Cu_2O cluster shown in Fig. 1c which has a calculated DFT total energy difference of 1.52 eV, is slightly rotated compared to the tetrahedral Cu_2O cluster (Fig. 1b), with the top most O atom being bound to 3 Cu atoms. The Cu_2O cluster shown in Fig. 1d with an energy difference of 2.10 eV, forms 3 Cu_2O units. For the Cu_2O cluster in Fig. 1e with the highest energy difference of 3.54 eV, hence least stable, one O atom inserts itself into the center of a tetrahedral Cu framework and the other O atom attaches to one Cu atom. The Cu_2O cluster binds to the TiO_2 surface through Cu-Ti bond and two Cu-O bonds.

The optimized CuO cluster on TiO_2 surface shown in Fig. 2b with $\triangle$E=0.13 eV was cut as a planar structure from bulk CuO. The atomic structure of the cluster is very similar to the CuO

nanowire on the (101) TiO_2 surface shown in Fig. 2a, except for the separation distance between the replica of at least 4.0 Å, that makes it not to form a nanowire. The CuO nanowire on TiO_2 surface shown in Fig. 2c with a DFT energy difference of 0.49 eV is a modification of Fig. 2a. One oxygen atom has been removed from the top of the triangular Cu atoms and anchored on Cu atom to make it coordinated to four O atoms as in the bulk. For the optimized structure in Fig. 2d with DFT energy difference of 1.23 eV, two O atoms were added to the Cu_2O/TiO_2 cluster shown in Fig. 1b, with each O atom being placed on the side of the triangular Cu atoms. This resulted into 3 sets of tetrahedra each with 3 Cu atoms at the base and one O atom at the vertex.

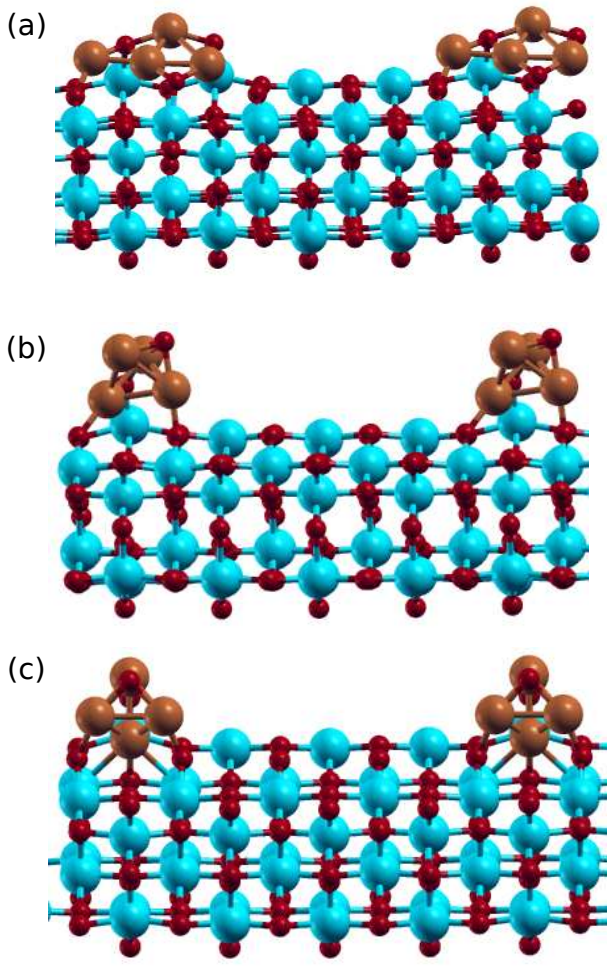

Figure 3: 2L optimized Cu_2O clusters on TiO_2 (101) surface. The total energy differences are with respect to that of the most stable structure (a). (a) $\triangle$E=0 eV; (b) $\triangle$E=0.37 eV; (c) $\triangle$E= 0.80 eV. Blue balls; titanium, red balls; oxygen, red-brown balls; copper. The two Cu_2O clusters on TiO_2 anatase (101) surface are replicas of each other.

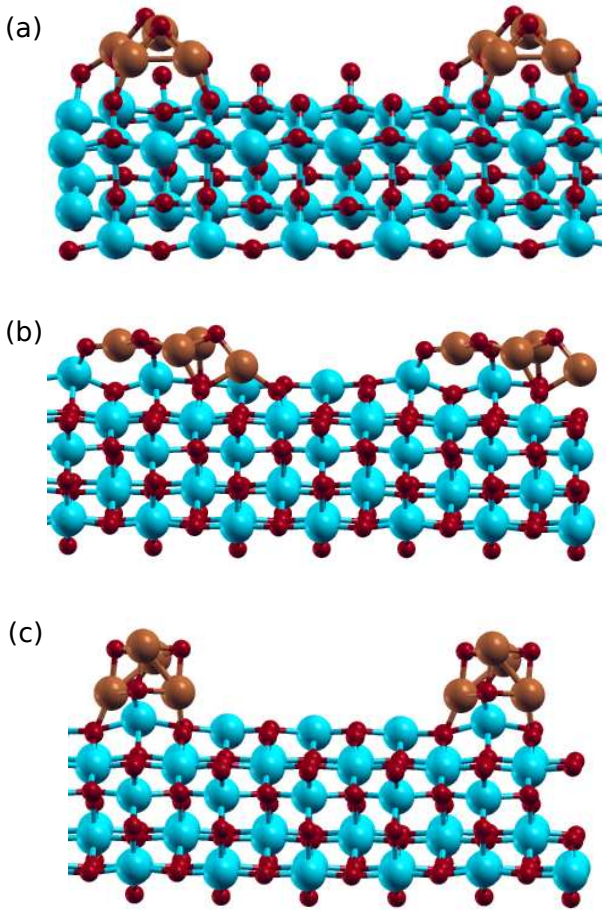

Figure 4: 2L optimized CuO clusters on TiO_2 (101) surface with their respective total energy differences referenced to the most stable structure, (a). (a) $\triangle$E=0 eV; (b) $\triangle$E=0.94 eV; (c) $\triangle$E= 0.96 eV. Colour code as in Fig. 3. The two CuO clusters on TiO_2 anatase (101) surface are replicas of each other.

Table 3: Total Löwdin charge (Q) and Polarization (μ) of Cu and O atoms in bulk Cu_2O, isolated Cu_2O nanowire (NW) and Cu_2O/TiO_2 nanowire (NW) as calculated from their respective PDOS.

Atm species	Löwdin charge (|e|)			Polarization (μ_B)		
Cu/O	Cu_2O-bulk	Cu_2O-NW	Cu_2O/TiO_2-NW	Cu_2O-bulk	Cu_2O-NW	Cu_2O/TiO_2-NW
Cu	10.80	10.80	10.83	0.00	0.00	0.00
Cu	10.80	10.77	10.94	0.00	0.00	0.00
Cu	10.80	10.72	10.94	0.00	0.00	0.00
Cu	10.80	10.65	10.86	0.00	0.00	0.00
O	6.37	6.44	6.55	0.00	0.00	0.00
O	6.37	6.47	6.55	0.00	0.00	0.00

Table 4: Total Löwdin charge (Q) and Polarization (μ) of Cu and O atoms in bulk CuO, isolated CuO nanowire (NW) and CuO/TiO_2 nanowire (NW) as calculated from their respective PDOS.

Atm species	Löwdin charge (|e|)			Polarization (μ_B)		
Cu/O	CuO-bulk	CuO-NW	CuO/TiO_2-NW	CuO-bulk	CuO-NW	CuO/TiO_2-NW
Cu	10.63	10.62	10.72	0.25	0.22	0.43
Cu	10.63	10.63	10.66	-0.25	0.20	-0.30
Cu	10.63	10.63	10.66	-0.25	0.20	0.43
Cu	10.63	10.51	10.65	0.25	0.38	0.37
O	6.36	6.48	6.38	0.00	0.36	0.39
O	6.36	6.32	6.36	0.00	0.93	0.02
O	6.36	6.33	6.55	0.00	0.91	0.25
O	6.36	6.35	6.55	0.00	0.85	0.31

Table 5: Change in total Löwdin charge ($\triangle$Q) and Polarization ($\triangle\mu$) of Cu and O atoms in clean Cu_2O nanowire and Cu_2O/TiO_2 nanowire with respect to Cu_2O bulk as calculated from their respective PDOS.

Atomic species	$\triangle$Q(|e|)		$\triangle\mu(\mu_B)$	
Cu/O	Cu_2O-NW	Cu_2O/TiO_2-NW	Cu_2O-NW	Cu_2O/TiO_2-NW
Cu	0.00	0.00	0.00	0.00
Cu	0.03	0.14	0.00	0.00
Cu	0.08	0.14	0.00	0.00
Cu	0.15	0.06	0.00	0.00
O	0.07	0.18	0.00	0.00
O	0.10	0.18	0.00	0.00

Table 6: Change in total Löwdin charge ($\triangle$Q) and Polarization ($\triangle\mu$) of Cu and O atoms in isolated CuO nanowire and CuO/TiO_2 nanowire with respect to CuO bulk as calculated from their respective PDOS.

Atomic species	$\triangle$Q(|e|)		$\triangle\mu(\mu_B)$	
Cu/O	CuO-NW	CuO/TiO_2-NW	CuO-NW	CuO/TiO_2-NW
Cu	0.01	0.09	0.03	0.18
Cu	0.00	0.03	0.45	0.05
Cu	0.00	0.03	0.45	0.68
Cu	0.12	0.02	0.13	0.12
O	0.12	0.02	0.36	0.39
O	0.04	0.00	0.93	0.02
O	0.03	0.19	0.91	0.25
O	0.01	0.19	0.85	0.31

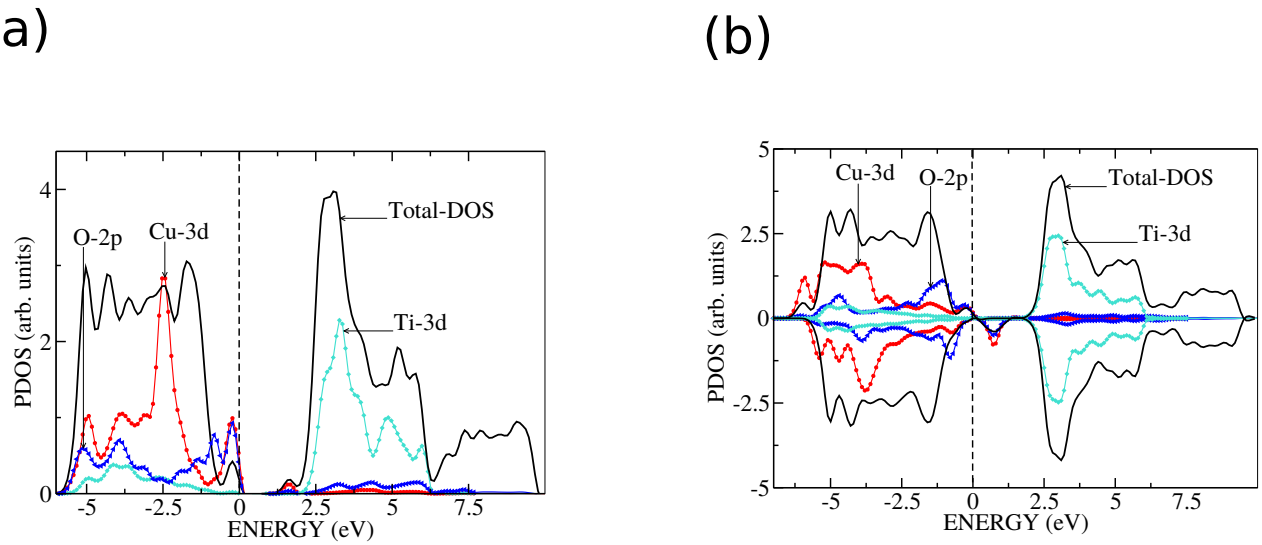

Figure 5: TDOS and PDOS of most stable clusters; (a) Cu_2O on TiO_2 (see Fig. 1b: main text) and (b) CuO on TiO_2 (see Fig. 2b: main text)(101) anatase surface. Black solid line: total DOS; red line with circles: Cu-3d; blue line with triangles: O-2p; turquoise line with diamonds: Ti-3d. Fermi level is set at 0 eV. The Total-DOS has been scaled down to be on the same scale as the PDOS.

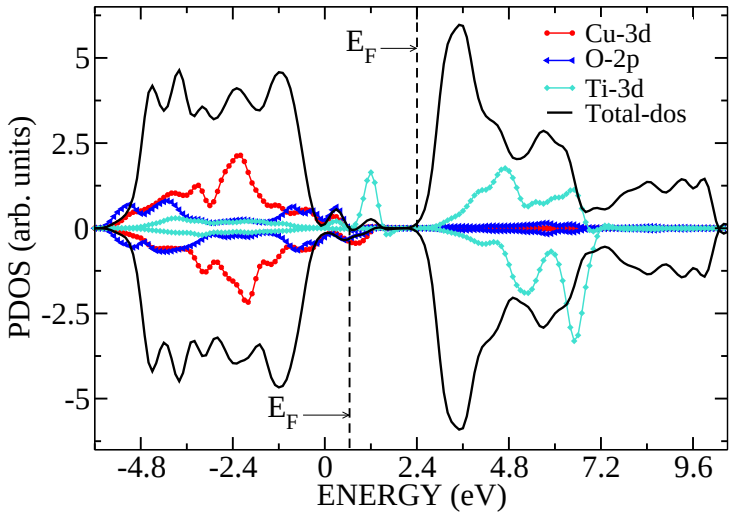

Figure 6: TDOS and PDOS of most stable Cu_2O/TiO_2 (101) anatase nanowire system with an excited electron leading to a polaronic state. Fermi level is set to 0 eV. The total DOS has been reduced to be on the same scale as PDOS.