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

Supporting Information

Evolution of the Atomic and Electronic Structures of CuO Clusters: A Comprehensive Study Using DFT Approach

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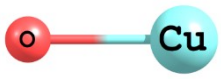
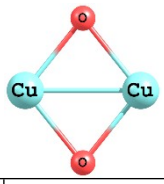
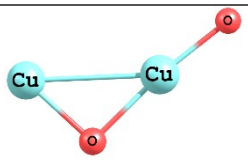
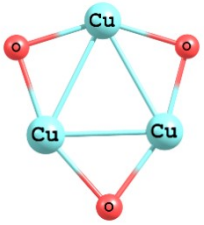
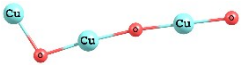
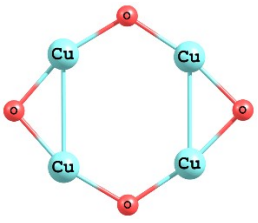
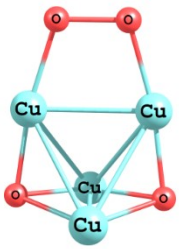
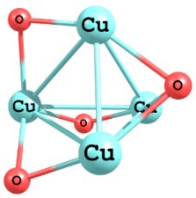
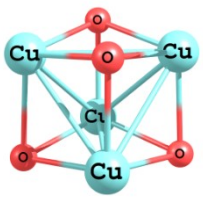
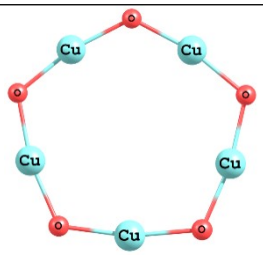
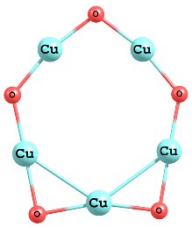
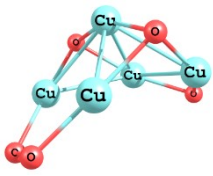
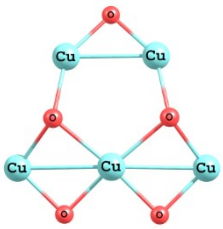
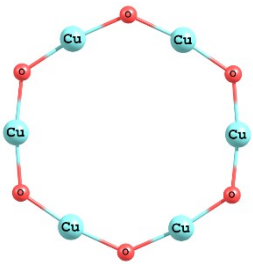
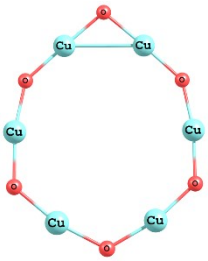
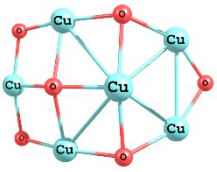
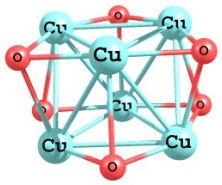
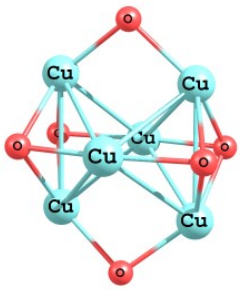
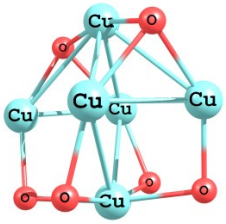
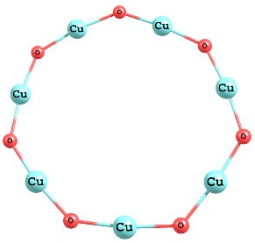
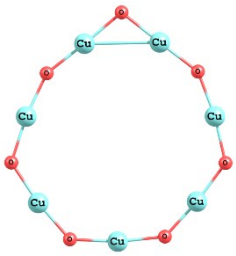
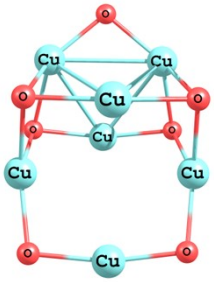
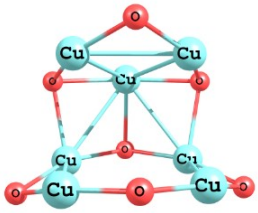
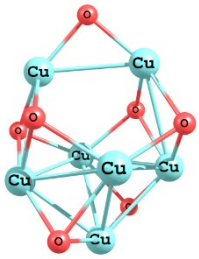
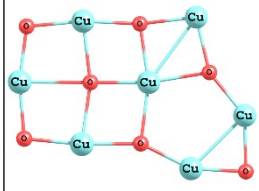
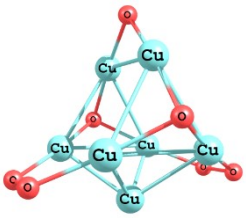
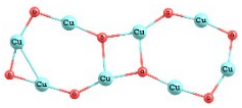
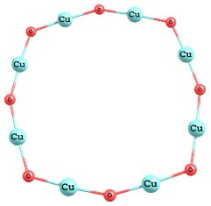
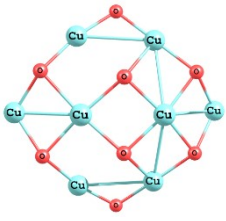
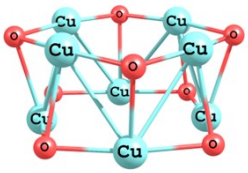
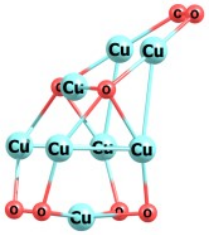
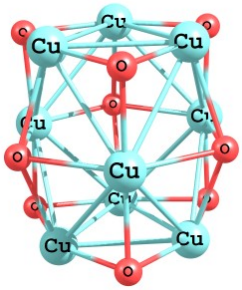
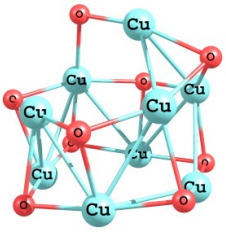
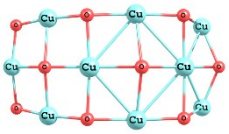
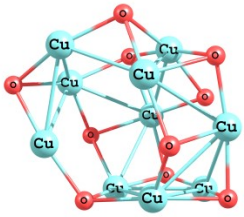
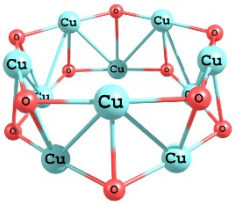
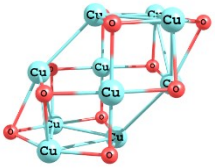
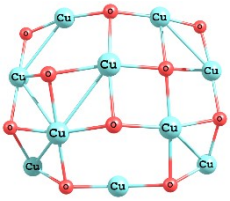
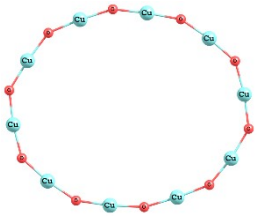
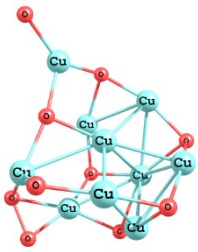
Table S1: Relative energy of different isomers of $(CuO)_n$ clusters (n=1-12) using PBE functional

CuO cluster	Relative energy of different isomeric structure (in eV)							
CuO								
	1a	**0.00**						
$(CuO)_2$								
	2a	**0.00**	2b	**0.01**				
$(CuO)_3$								
	3a	**0.00**	3b	**1.29**				
$(CuO)_4$								
	4a	**0.00**	4b	**1.54**	4c	**1.56**	4d	**2.49**

$(CuO)_5$		5a	**0.00**		5b	**0.18**		5c	**0.74**		5d	**2.59**
$(CuO)_6$		6a	**0.00**		6b	**0.07**		6c	**0.35**		6d	**0.81**
		6e	**1.14**		6f	**1.75**						
$(CuO)_7$		7a	**0.00**		7b	**0.04**		7c	**0.21**		7d	**0.62**
		7e	**0.65**		7f	**0.66**		7g	**1.46**			
$(CuO)_8$												

								
	8a	**0.00**	8b	**0.73**	8c	**0.76**	8d	**1.08**
								
	8e	**3.21**						
$(CuO)_9$								
	9a	**0.00**	9b	**0.44**	9c	**1.15**	9d	**1.33**
$(CuO)_{10}$								
	10a	**0.00**	10b	**0.16**	10c	**0.36**	10d	**0.94**
								
	10e	**1.33**	10f	**2.09**				

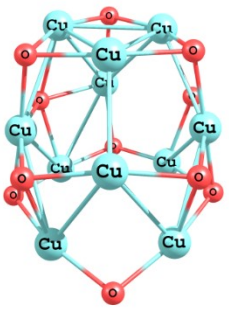
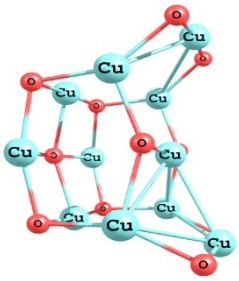
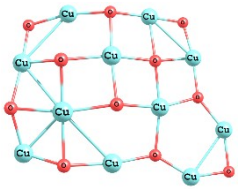
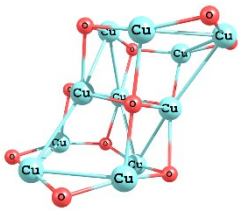
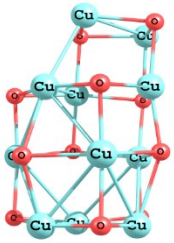
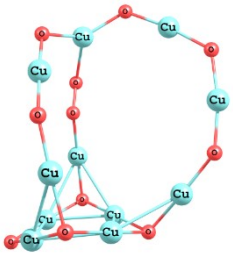
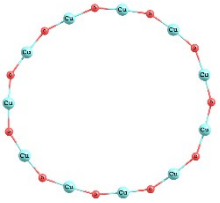
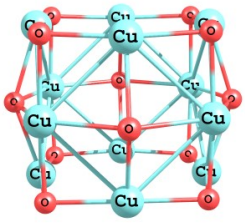
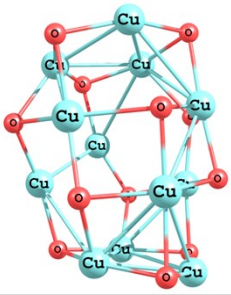
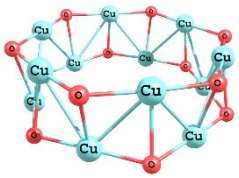
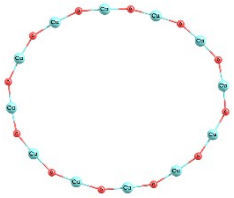
$(CuO)_{11}$		11a	**0.00**		11b	**1.08**		11c	**1.47**		11d	**1.51**
		11e	**1.89**		11f	**1.98**		11g	**2.4**			
$(CuO)_{12}$		12a	**0.00**		12b	**0.93**		12c	**2.00**		12d	**3.82**

Table S2: Geometric parameters (Cu-O and Cu-Cu interatomic distances and Cu-O-Cu bond angle) of the lowest energy isomers of $(CuO)_n$ clusters (n=1-12) and bulk CuO using PBE functional.

Cluster size (n)	PBE method				
	Cu-O		Cu-Cu		Average Cu-O-Cu bond angle (degree)
	Avg. Interatomic distance (Å)	No of bonds	Avg. Interatomic distance (Å)	No of bonds	
1	1.70	1			
2	1.84	4	2.30	1	77.3
3	1.80	6	2.46	3	86.7
4	1.75	8	2.75	4	104.8
5	1.74	10	2.98	5	119.9
6	1.73	12	3.15	*	130.4
7	1.72	14	3.18	*	136.3
8	1.95	24	2.58, 2.82	16	81.8, 101.9
9	1.96	30	2.53, 3.50	18	85.2, 112.5
10	1.91	30	2.54	10	83.3, 94.4, 106.5, 113.2, 118.2
11	1.95	34	2.62	22	84.3, 96.5, 102.3, 125.6, 140.3
12	1.83, 1.89, 2.01	40	2.64, 2.75	24	97.4, 124.6
Bulk	1.96	4	2.63	4	102.0, 119.0

* Cu-Cu interatomic distance up to 3 Å is considered as a bond

Table S3: Comparative results (present calculation and reported values) of bond length and binding energy per atom of dimer and bulk species.

Species	Bond length (Å)	Binding energy /atom (eV)
Cu_2 dimer	2.24* (Cu-Cu) 2.22[1] (Cu-Cu)	0.94 * 1.03 [2]
Cu bulk	2.56 * (Cu-Cu) 2.56 [2] (Cu-Cu)	3.44 * 3.50 [3]
CuO Monomer	1.73* (Cu-O) 1.72 [4] (Cu-O)	1.41 * 1.22 [4]
CuO bulk	1.96 * (Cu-O)	3.77 *

* Present work using hybrid method

(1) *J. Chem. Phys.* 1987, **86**, 1715 - 1726.
(2) *J. Chem. Phys* 1978, **68**, 1744 - 1751.
(3) *Phys. Rev. B* 1983, **27,** 2132 - 2144.
(4) *J. Phys. Chem.* 1991, **95**, 3460 – 3463.
(5) *Phys. Rev. B* 2013, **87**, 115111.

Table S4: Vibrational frequency obtained for optimised structure of CuO clusters (n=1-12) using GAMESS. No imaginary frequency was obtained for any of the optimised structure of CuO clusters

Vibrational frequencies (in cm^{-1}) of optimised structure of neutral CuO clusters					
CuO	**$(CuO)_2$**	**$(CuO)_3$**	**$(CuO)_4$**	**$(CuO)_5$**	**$(CuO)_6$**
37.819	0.027	21.621	7.612	17.820	11.340
33.198	0.027	0.019	0.019	4.728	3.455
0.027	0.027	0.021	0.021	0.015	0.015
0.027	8.461	0.025	0.025	0.024	0.020
0.027	37.619	19.910	18.482	0.031	0.026
582.011	60.158	40.661	27.698	13.285	4.857
	200.839	57.251	64.632	41.253	12.606
	223.353	116.846	68.806	43.440	21.634
	284.792	135.603	90.719	52.883	24.575
	329.504	142.511	103.698	60.870	29.169
	385.443	166.430	136.769	87.886	45.466
	561.692	194.557	139.951	102.795	49.876
		412.004	160.838	112.968	58.196
		436.067	179.814	118.952	62.590
		468.397	194.533	131.967	76.929
		508.171	224.092	150.508	97.409
		575.227	409.912	169.690	106.171
		589.665	420.543	191.225	110.993
			434.933	230.220	129.653
			515.482	241.827	133.014
			524.801	368.267	147.108
			575.943	389.744	150.821
			599.325	401.741	184.484
			660.205	472.989	192.732
				473.867	216.491
				597.112	235.948
				621.377	241.007
				665.977	246.062
				714.874	334.988
				720.544	339.068
					341.222
					364.528
					409.362
					464.307
					469.085
					644.413
					656.853
					710.171
					735.029
					763.673
					789.557
					794.762

Vibrational frequencies (in cm^{-1}) of optimised structure of neutral CuO clusters					
$(CuO)_7$	$(CuO)_8$	$(CuO)_9$	$(CuO)_{10}$	$(CuO)_{11}$	$(CuO)_{12}$
11.340	47.470	44.901	16.990	0.013	38.313
3.455	22.961	0.007	0.018	0.015	27.242
0.015	0.020	0.014	0.020	0.018	0.019
0.020	0.021	0.019	0.025	11.132	0.019
0.026	0.022	27.680	2.990	35.494	0.020
4.857	14.228	46.510	26.063	40.510	26.219
12.606	52.103	71.793	36.745	63.644	56.677
21.634	69.629	85.237	43.604	73.592	57.140
24.575	79.671	100.674	65.243	78.461	70.917
29.169	88.008	112.015	77.280	91.448	87.534
45.466	99.926	118.999	83.755	97.810	94.823
49.876	107.144	125.997	90.239	106.935	97.628
58.196	119.628	137.448	96.138	119.387	100.056
62.590	135.323	140.994	99.398	122.664	107.461
76.929	141.306	169.080	107.304	129.590	121.644
97.409	146.737	174.604	127.766	131.237	128.968
106.171	167.487	182.697	133.560	145.823	138.077
110.993	178.420	185.495	142.271	155.958	141.409
129.653	183.304	194.903	151.193	165.093	144.705
133.014	191.264	202.934	154.972	167.481	149.497
147.108	198.166	208.029	164.700	176.957	154.864
150.821	223.863	214.836	174.634	179.129	160.180
184.484	227.716	229.059	183.506	184.318	167.060
192.732	234.833	235.659	187.549	198.857	170.265
216.491	248.310	255.368	189.149	208.733	173.906
235.948	255.011	265.111	198.401	212.140	187.970
241.007	256.453	269.582	206.758	220.998	191.624
246.062	271.744	279.502	216.450	226.001	201.340
334.988	290.950	307.545	235.233	232.997	204.823
339.068	306.873	331.508	242.396	242.083	217.080
341.222	316.064	360.229	292.121	250.682	218.900
364.528	342.922	377.069	310.921	259.868	228.621
409.362	416.985	384.649	325.347	269.019	230.582
464.307	428.881	390.283	335.891	270.709	235.247
469.085	438.631	398.764	341.499	279.136	256.694
644.413	443.586	411.544	354.114	333.819	266.687
656.853	451.091	421.905	359.779	346.801	291.789
710.171	467.079	436.697	368.926	372.114	298.432
735.029	473.730	446.529	372.049	382.579	311.183
763.673	491.396	465.207	373.998	393.003	324.530
789.557	525.576	471.836	383.202	408.579	329.432
794.762	535.965	473.530	387.260	412.148	352.662
	547.113	493.421	393.041	419.511	367.180
	548.488	504.251	397.676	425.538	387.249
	566.878	509.220	414.324	432.000	402.247
	567.065	511.358	421.788	436.004	411.353
	572.254	518.647	427.464	445.715	423.373
	577.494	534.734	440.620	454.309	427.614

		535.735 546.038 557.112 566.969 582.528 607.779	443.287 450.595 546.567 584.626 591.593 609.263 618.852 625.257 641.406 653.516 661.246 666.364	460.394 479.063 486.726 491.006 498.188 511.492 519.585 526.878 530.158 537.404 543.243 546.178 550.126 562.000 575.496 584.289 587.568 603.637	433.651 443.326 448.221 451.406 452.432 457.147 466.548 477.152 482.584 492.416 501.373 503.425 506.353 526.714 556.601 558.414 564.229 567.468 574.879 575.986 582.890 593.033 594.449 598.686

Table S5: Optimized structure of neutral, cation and anion of copper oxide clusters [$(CuO)_n$, n=1-12] using LCAO-MO approach

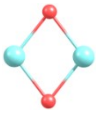
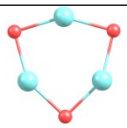
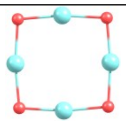
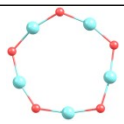
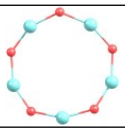
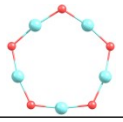
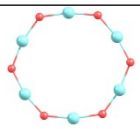
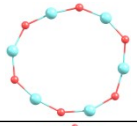
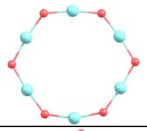
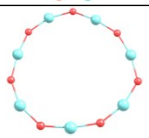
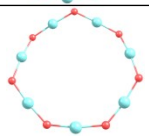
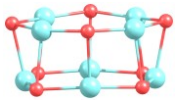
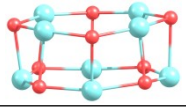
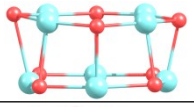
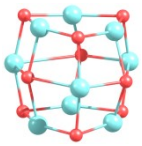
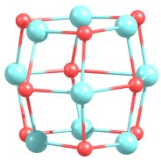
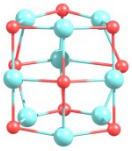
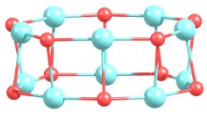
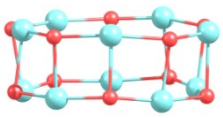
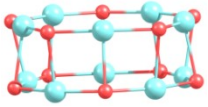
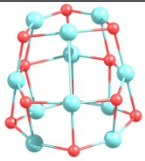
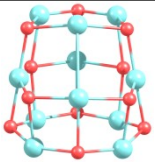
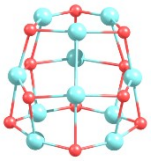
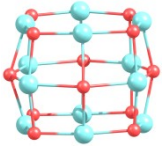
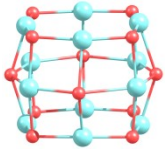
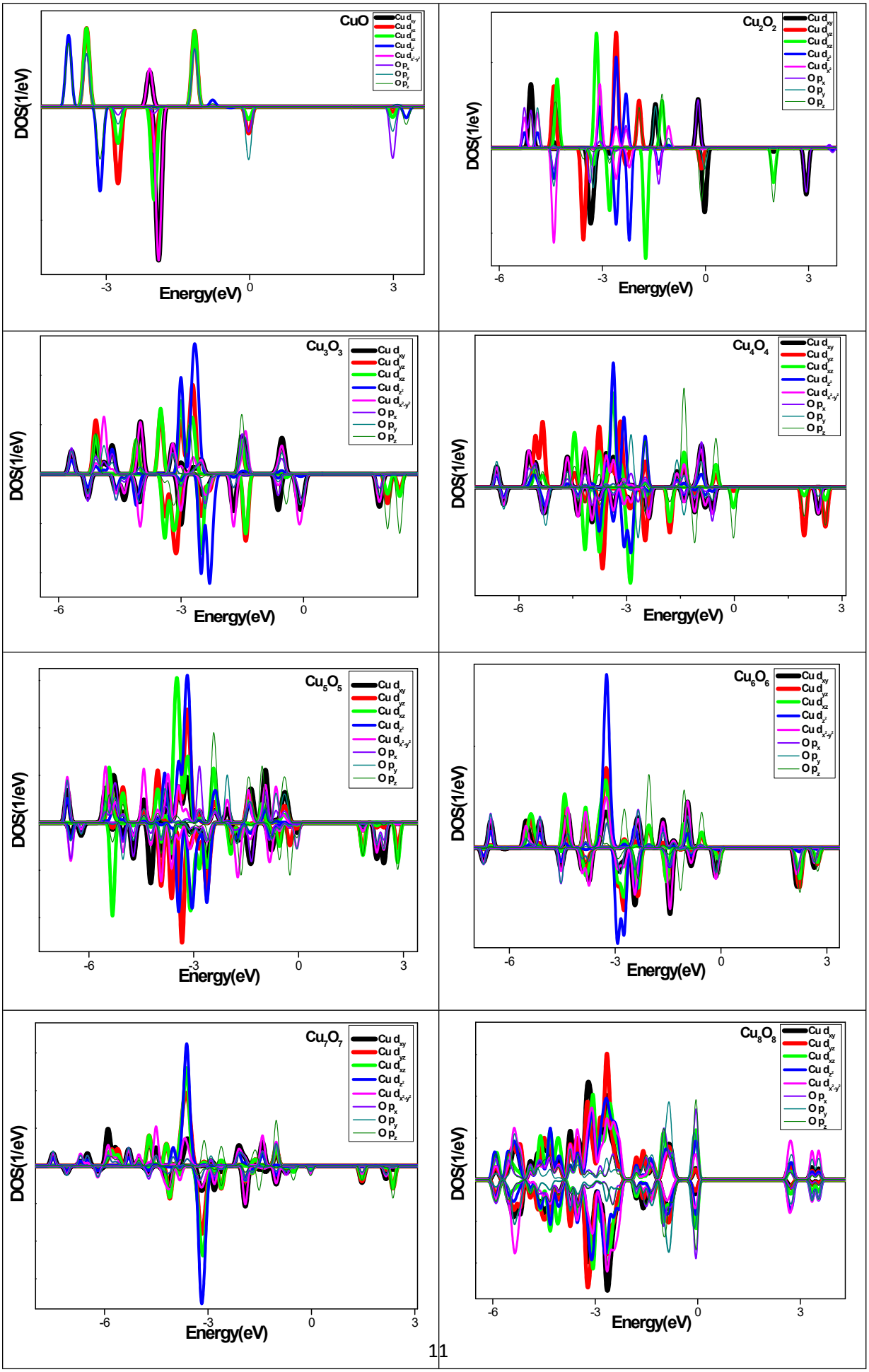
Species	Neutral	Cation	Anion
CuO			
$(CuO)_2$			
$(CuO)_3$			
$(CuO)_4$			
$(CuO)_5$			
$(CuO)_6$			
$(CuO)_7$			
$(CuO)_8$			
$(CuO)_9$			
$(CuO)_{10}$			
$(CuO)_{11}$			
$(CuO)_{12}$			

Table S6: Bader Charges of copper atoms in copper oxide clusters (n = 1-12) and in CuO bulk

Clusters	q Cu				Average charge
CuO	0.60				0.60
$(CuO)_2$	0.90	0.89			0.89
$(CuO)_3$	0.86	0.94	0.87		0.89
$(CuO)_4$	1.01	0.97	1.00	1.01	1.00
$(CuO)_5$	0.98	0.98	1.06	1.01	1.00
	0.97				
$(CuO)_6$	0.95	1.03	1.02	1.02	1.00
	1.02	0.99			
$(CuO)_7$	1.00	1.01	1.02	1.03	1.02
	1.03	1.02	1.03		
$(CuO)_8$	1.10	1.11	1.11	1.12	1.11
	1.11	1.10	1.09	1.10	
$(CuO)_9$	1.07	1.03	1.09	1.15	1.11
	1.07	1.10	1.07	1.24	
	1.14				
$(CuO)_{10}$	1.14	1.12	1.13	1.11	1.12
	1.12	1.10	1.12	1.12	
	1.12	1.14			
$(CuO)_{11}$	1.08	1.09	0.78	1.34	1.07
	1.36	1.11	1.23	1.05	
	0.76	0.93	1.04		
$(CuO)_{12}$	1.23	1.21	1.11	1.13	1.16
	1.14	1.22	1.14	1.21	
	1.15	1.12	1.13	1.15	
CuO Bulk	1.08	1.08	1.08	1.08	1.08


CuO
Cu2O2
Cu3O3
Cu4O4
Cu5O5
Cu6O6
Cu7O7
Cu8O8
Cu d
O p
DOS(1/eV)
Energy(eV)

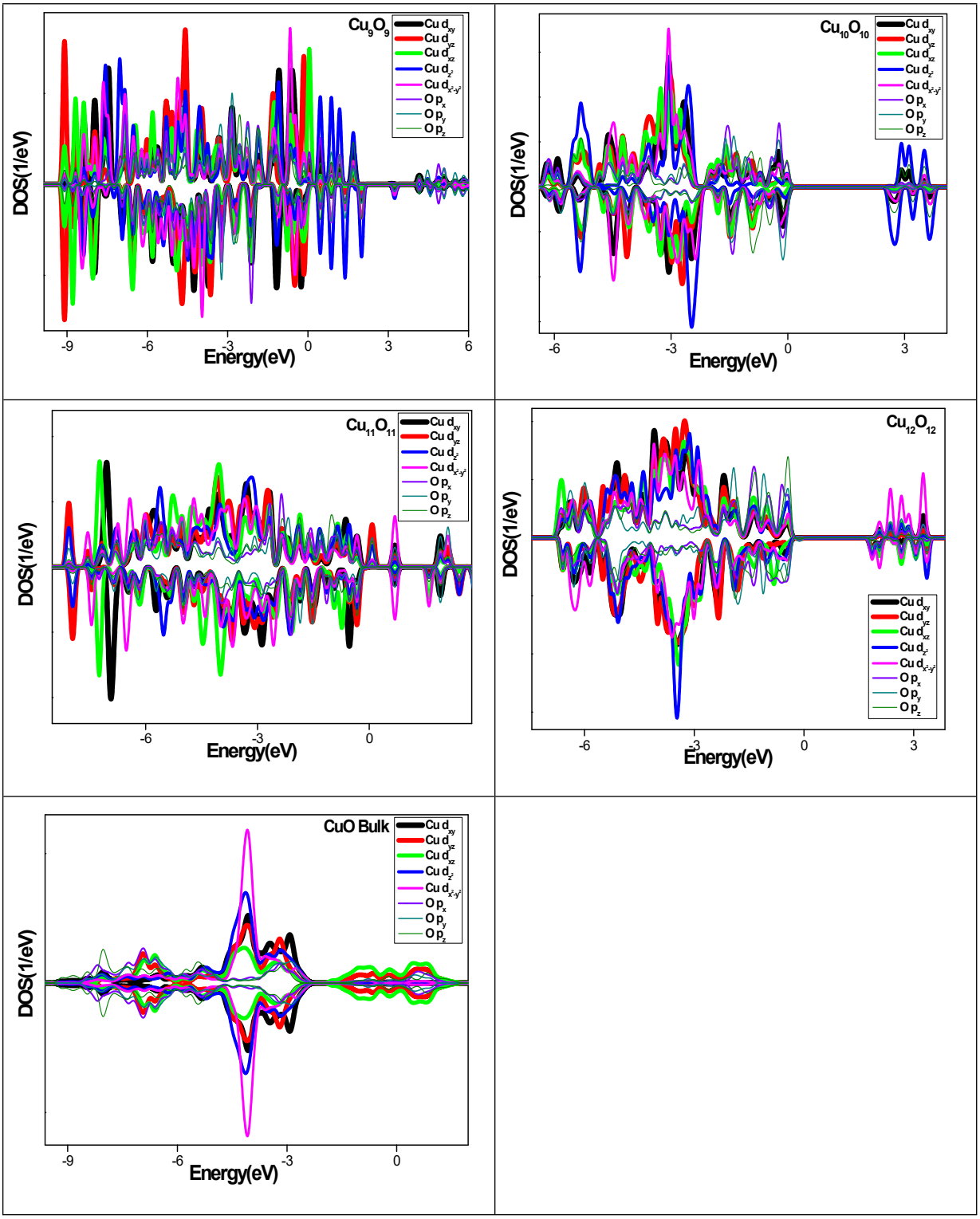


Figure S1: Projected density of states (PDOS) as a function of energy of copper oxide clusters $(CuO)_n$ (n=1-12) and CuO bulk using hybrid functional