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ReaxFF and Density Functional Theory Studies of Structural and Electronic Properties of Copper Oxide Clusters

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ABSTRACT. In this study, we investigate the structural and electronic properties of copper oxide clusters, Cu_nO_n (n = 9 - 15). To find the lowest energy structures of copper oxide clusters, we use ReaxFF and density functional theory calculations. We calculate many initial copper oxide clusters using ReaxFF quickly. Then we calculate the lowest energy structures of copper oxide clusters using B3LYP/LANL2DZ model chemistry. We examine the atomization energies per atom, average bond angles, Bader charges, ionization potentials, and electronic affinities of copper oxide clusters. In addition, the second difference in energies is investigated for relative energies of copper oxide clusters.

Key words: Copper oxide clusters, Density functional theory, Particulate matter, ReaxFF, Molecular dynamics

INTRODUCTION

Copper oxide clusters have been used in many areas, such as solar cells,[1] organic light emitting diodes (OLED),[2] photo-catalysis,[3] and electrochemical applications.[4] Copper oxide clusters are very useful in industries, being a very well-known the catalyst in promoting the formation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs). Copper oxide clusters have had their structural and electronic properties studied in experiments.[5-18] However, theoretical studies of copper oxide clusters are not much. Small copper oxide clusters have been researched using density functional theory (DFT). CuO_2,[19] CuO_3,[20] CuO_4,[21] CuO_5,[21] CuO_6 clusters[22,23] and their several isomers are calculated with DFT. Cu_nO_n clusters with n = 1 - 8 have been examined using Monte Carlo (MC) simulations and DFT.[24] Also, Cu_3O_n clusters with n = 1 - 6 have been examined using *ab initio* MC simulations and DFT.[25]

In general, DFT calculations need many resources such as CPU time and memory for large molecules. For finding the global minimum energy structures, if the structures of many initial copper oxide clusters need to be calculated using DFT, these procedures are very expensive computationally. Fortunately, the ReaxFF for Cu/O/H interaction were developed by Adri van Duin in 2010.[26] ReaxFF is a bond based force field in Molecular Dynamics simulations. ReaxFF energy terms in the system are in equation (1)

$$E_{system} = E_{bond}+E_{over}+E_{val}+E_{pen}+E_{tors}+E_{conj}+E_{vdWaals}+E_{Coulomb} \quad (1)$$

ReaxFF describes chemical bonding without expensive quantum mechanics (QM) calculations. Therefore, the local energy structures of copper oxide clusters can be calculated with ReaxFF inexpensively. Then, the lowest structures of each copper oxide clusters are optimized using DFT. In this article, we investigate the structures and electronic properties of copper oxide clusters (Cu_nO_n, n = 9 - 15) using ReaxFF and DFT.

METHODS

For finding local minimum energy of copper oxide clusters, we made about 200 initial copper oxide clusters by turning Cu_9O_9 clusters to $Cu_{15}O_{15}$ clusters. We attached a Cu-O unit to an optimized Cu_8O_8 cluster,[24] studied previously for making initial Cu_9O_9 structures. By this process, we made each initial copper oxide clusters from Cu_9O_9 and $Cu_{15}O_{15}$ clusters. All initial structures were calculated using ReaxFF. The LAMMPS program was used for ReaxFF calculations. We used parameters for the Cu-O system.[26,27] The NVE-MD simulations on copper and oxygen were relaxed to 0 K with 100 Å 100 Å × 100 Å. After ReaxFF calculations, we calculated single point calculations using DFT for all initial copper oxide clusters structures to obtain ReaxFF calculations, then, decided the lowest energy structure of each copper oxide cluster. We put single point calculation energies of initial Cu_9O_9 clusters in *Table* S1. We used the B3LYP/LANL2DZ model chemistry to optimize copper oxide cluster calculations, because this model is in very good

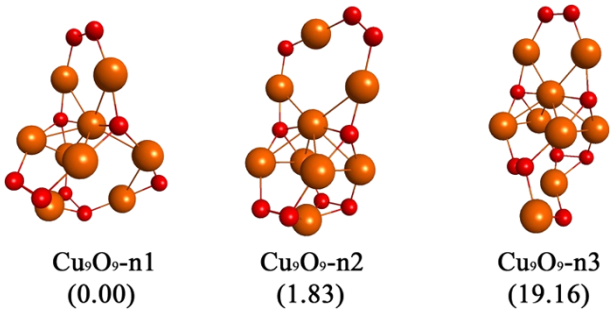

***Figure* 1.** Optimized structures of neutral Cu_9O_9 clusters using the B3LYP/LANL2DZ model chemistry. The numbers in parentheses indicate the relative energies in kcal/mol. Copper/oxygen atoms colored yellow/red.

agreement with experimental data.[24] We also calculated the lowest spin-state energy of copper oxide clusters structures. All calculations were done using the Gaussian 09 program.[28]

RESULTS AND DISCUSSION

The copper oxide clusters, Cu_nO_n (n = 1 - 8), were studied in the previous investigation using *ab initio* Monte Carlo simulations and DFT.[24] *Figure* 2 shows the optimized neutral Cu_nO_n clusters with n = 9 - 15 using the B3LYP/LANL2DZ model chemistry. The numbers of each atom of copper oxide clusters are Bader charges.[29] We calculated doublet and quartet spin states for odd-numbered copper oxide clusters and singlet and triplet spin states for even-numbered copper oxide clusters in neutral copper oxide clusters. *Table* 1 shows the spin states of the lowest energy structures of copper oxide clusters. In neutral copper oxide clusters, odd-numbered copper oxide clusters have quartet spin states and even-numbered copper oxide clusters have triplet spin states. In cationic and anionic copper oxide clusters, odd-numbered copper oxide clusters have triplet spin states and even-numbered copper oxide clusters have quartet spin states.

Neutral Cu_9O_9 cluster, $Cu_{10}O_{10}$ cluster, and $Cu_{11}O_{11}$ cluster have the CuO_4 group at the bottom of each cluster as does the Cu_8O_8 cluster. The copper atoms of CuO_4 groups have a large positive charge. (1.07 for the Cu_9O_9 cluster, 1.10 for the $Cu_{10}O_{10}$ cluster, and 1.11 for the $Cu_{11}O_{11}$ cluster) A neutral Cu_9O_9 cluster was made by adding a Cu-O unit at the bottom of a neutral optimized Cu_8O_8 cluster. The structures of neutral, cationic and anionic Cu_9O_9 clusters are the same (*Figures* 2 - 4). Three isomers are found in the neutral Cu_9O_9 clusters in *Figure* 1. The relative energies of the second and third most stable structures are 1.83 and

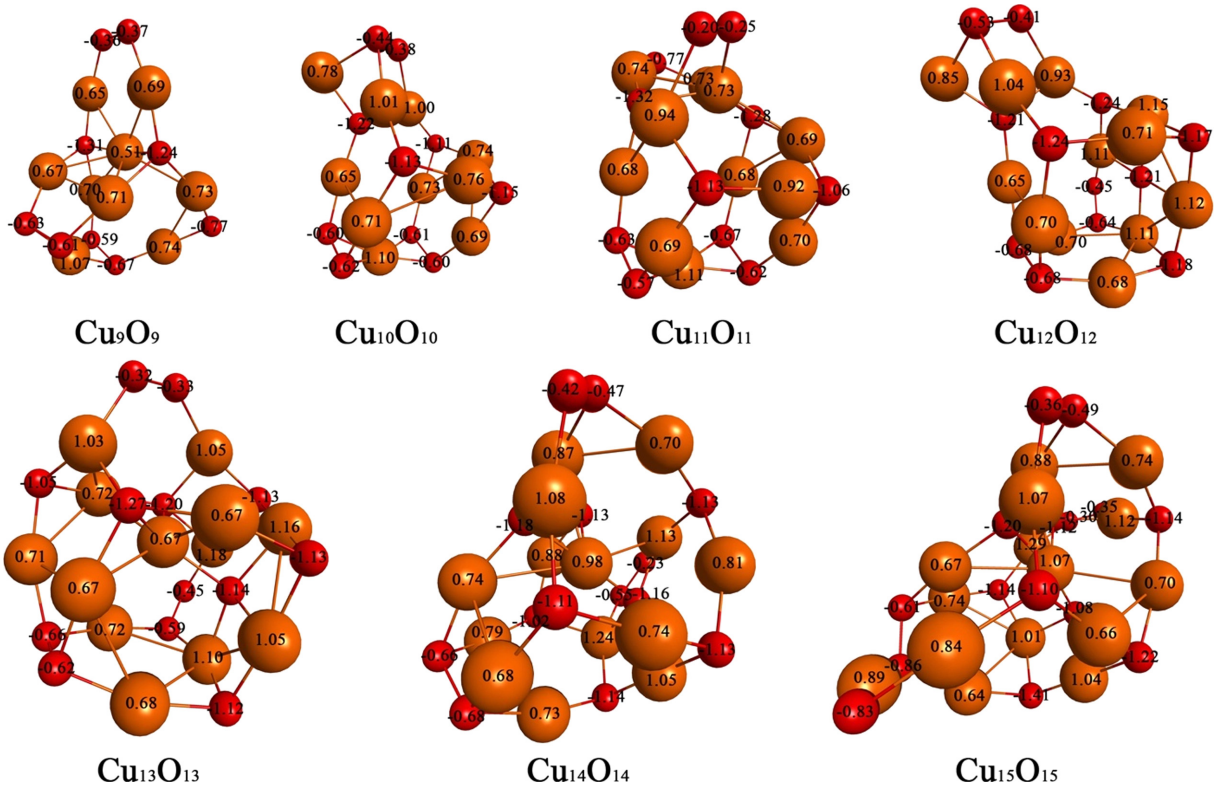

***Figure* 2.** Optimized structures of neutral Cu_nO_n clusters (n = 9 - 15) using the B3LYP/LANL2DZ model chemistry. The numbers of atoms are Bader charges. Copper/oxygen atoms colored yellow/red.

***Table* 1.** Spin states and energy differences between spin states in parentheses of the lowest energy structures of copper oxide clusters

Cluster	Spin States	Cluster	Spin States	Cluster	Spin States
Cu_9O_9	quartet (0.01)	$Cu_9O_9^+$	triplet (31.27)	$Cu_9O_9^-$	triplet (29.04)
$Cu_{10}O_{10}$	triplet (21.22)	$Cu_{10}O_{10}^+$	quartet (3.53)	$Cu_{10}O_{10}^-$	quartet (0.03)
$Cu_{11}O_{11}$	quartet (2.18)	$Cu_{11}O_{11}^+$	triplet (41.63)	$Cu_{11}O_{11}^-$	triplet (25.81)
$Cu_{12}O_{12}$	triplet (22.00)	$Cu_{12}O_{12}^+$	quartet (3.83)	$Cu_{12}O_{12}^-$	quartet (0.35)
$Cu_{13}O_{13}$	quartet (0.65)	$Cu_{13}O_{13}^+$	triplet (40.24)	$Cu_{13}O_{13}^-$	triplet (29.83)
$Cu_{14}O_{14}$	triplet (41.80)	$Cu_{14}O_{14}^+$	quartet (1.25)	$Cu_{14}O_{14}^-$	quartet (1.58)
$Cu_{15}O_{15}$	quartet (2.59)	$Cu_{15}O_{15}^+$	triplet (55.91)	$Cu_{15}O_{15}^-$	triplet (42.72)

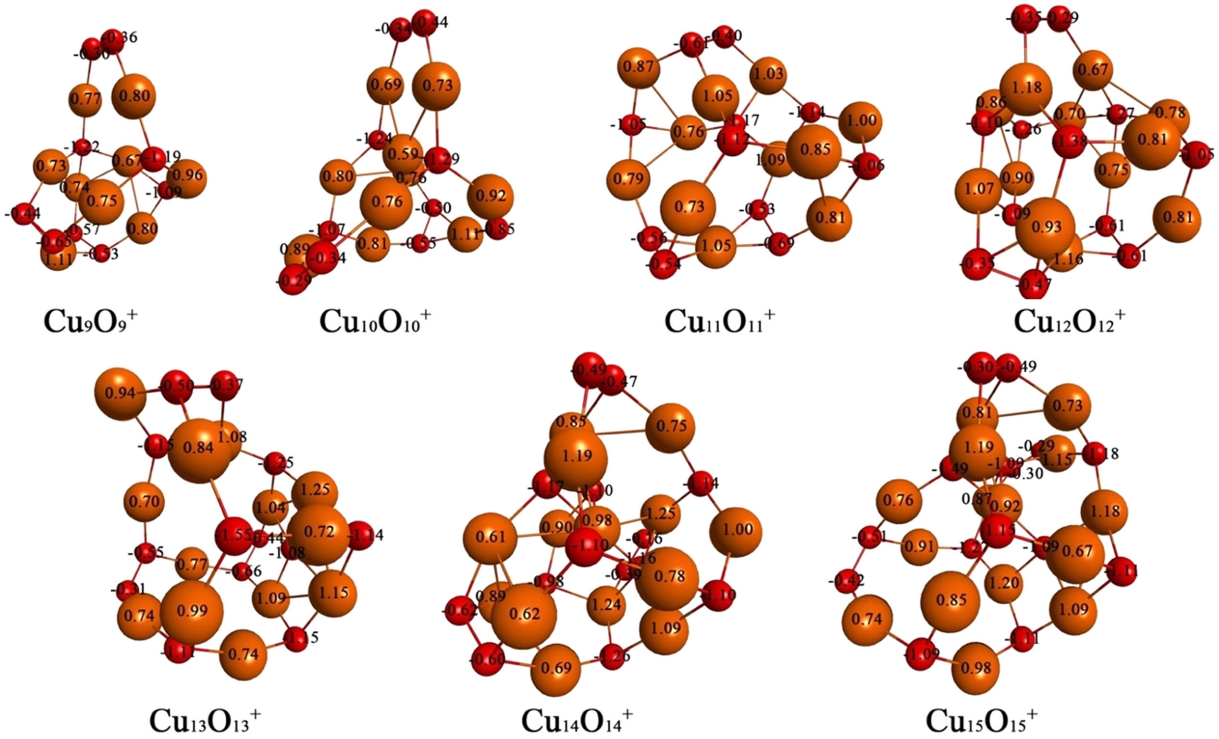

***Figure* 3.** Optimized structures of cationic Cu_nO_n clusters (n = 9 - 15) using the B3LYP/LANL2DZ model chemistry. The numbers of atoms are Bader charges. Copper/oxygen atoms colored yellow/red.

19.16 kcal/mol, respectively.

Figures 3 and 4 shows the optimized structures of cationic and anionic copper oxide clusters (Cu_nO_n with n = 9 - 15), respectively.

Next, a neutral $Cu_{10}O_{10}$ cluster was formed by attaching a Cu-O unit to the top of the neutral optimized Cu_9O_9 cluster. The structure of the neutral $Cu_{10}O_{10}$ cluster is different from that of cationic and anionic $Cu_{10}O_{10}$ clusters. However, the structures of cationic and anionic $Cu_{10}O_{10}$ clusters are the same, and these clusters are made by adding a Cu-O unit at the bottom of the CuO_4 group. Therefore, the CuO_4 group was broken.

In $Cu_{11}O_{11}$ clusters, a Cu-O unit was added at the top of neutral, cationic, and anionic optimized $Cu_{10}O_{10}$ clusters, respectively. The structures of cationic $Cu_{11}O_{11}$ cluster is the same with the structure of anionic $Cu_{11}O_{11}$ cluster. In $Cu_{12}O_{12}$ clusters, the CuO_4 group of the neutral $Cu_{12}O_{12}$ cluster was destroyed, because a Cu-O unit is attached. Cationic and anionic $Cu_{12}O_{12}$ clusters were made by adding a Cu-O unit to the bottom side of the optimized cationic and anionic $Cu_{11}O_{11}$ clusters, but the CuO_4 group still remains for a cationic $Cu_{12}O_{12}$ cluster and is broken for an anionic $Cu_{12}O_{12}$ cluster.

A Cu-O unit is attached to the middle of the back of a neutral $Cu_{12}O_{12}$ cluster to make a $Cu_{13}O_{13}$ cluster, and the structures of neutral, cationic, and anionic $Cu_{13}O_{13}$ clusters are very similar. Neutral $Cu_{14}O_{14}$ was constructed by adding a Cu-O unit to the lower part of the back of neutral opti-

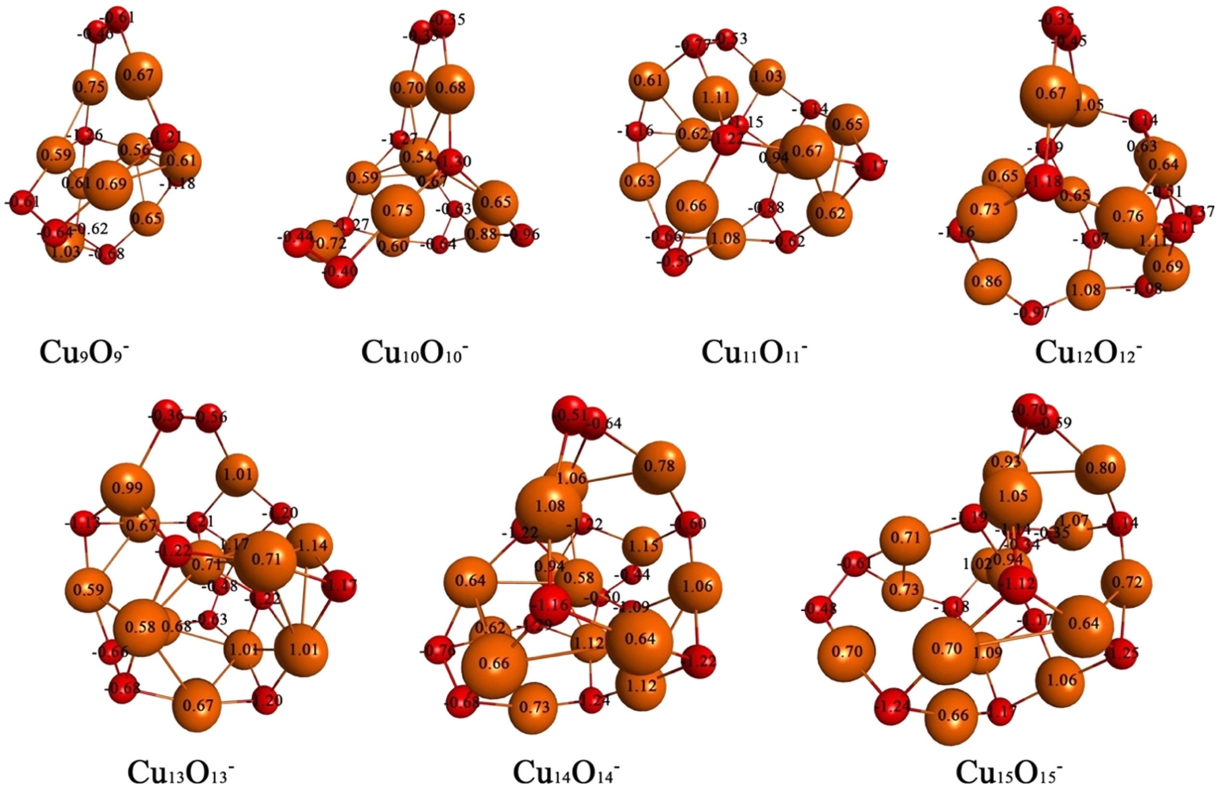

***Figure* 4.** Optimized structures of anionic Cu_nO_n clusters (n = 9 - 15) using the B3LYP/LANL2DZ model chemistry. The numbers of atoms are Bader charges. Copper/oxygen atoms colored yellow/red.

mized $Cu_{13}O_{13}$ clusters. Like $Cu_{13}O_{13}$ clusters, neutral, cationic, and anionic $Cu_{14}O_{14}$ clusters are very similar structurally each other. A neutral $Cu_{15}O_{15}$ cluster was made by attaching the side of a neutral optimized $Cu_{14}O_{14}$ cluster. However, the structure of a neutral $Cu_{15}O_{15}$ cluster is somewhat different from that of cationic and anionic $Cu_{15}O_{15}$ clusters.

Table 2 shows the HOMO-LUMO gaps of neutral $(CuO)_n$ clusters with n = 9 - 15. The Cu_9O_9 cluster has the largest HOMO-LUMO gap (2.10 eV) and the average value of HOMO-LUMO gaps (from $Cu_{10}O_{10}$ to $Cu_{15}O_{15}$ clusters) is 1.54 eV.

Calculated atomization energies per atom are shown in *Figure* 5. Atomization energies per atom are calculated by equation (2).

***Table* 2.** HOMO-LUMO gaps of neutral copper oxide clusters

Cluster	HOMO-LUMO gap (eV)
Cu_9O_9	2.01
$Cu_{10}O_{10}$	1.63
$Cu_{11}O_{11}$	1.60
$Cu_{12}O_{12}$	1.31
$Cu_{13}O_{13}$	1.64
$Cu_{14}O_{14}$	1.49
$Cu_{15}O_{15}$	1.58

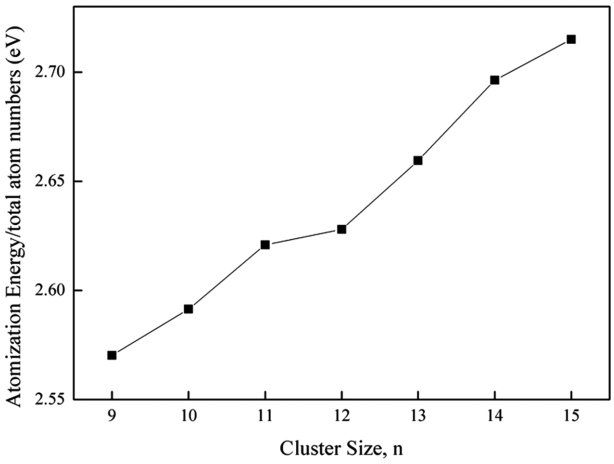

***Figure* 5.** Atomization energies per atom of neutral Cu_nO_n clusters (n = 9 - 15) using the B3LYP/LANL2DZ model chemistry.

$$E_a = [nE(Cu) + nE(O) - E(Cu_nO_n)]/2n \quad (2)$$

The atomization energies per atom are increased as the cluster size increases. However, the atomization energies per atom increase very slowly from the $Cu_{11}O_{11}$ cluster to the $Cu_{12}O_{12}$ cluster. The values of atomization energies per

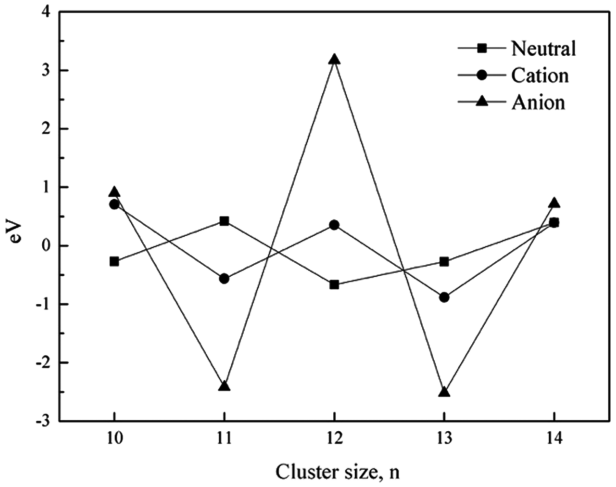

***Figure* 6.** Second difference in energies of neutral, cationic, and anionic copper oxide clusters (Cu_nO_n) with n = 9 - 15. using the B3LYP/LANL2DZ model chemistry.

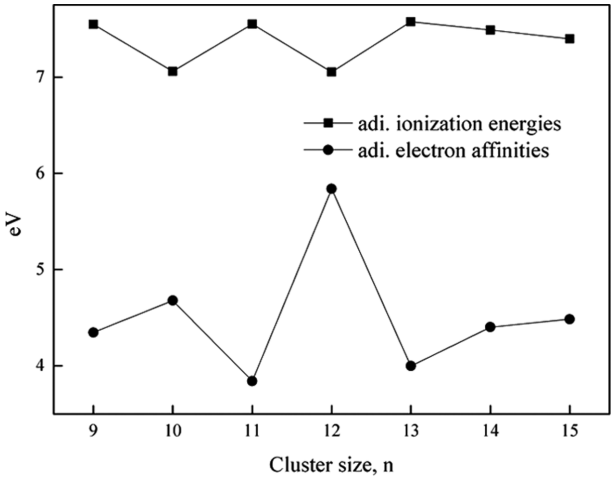

***Figure* 7.** Calculated adiabatic ionization energies and electron affinities of Cu_nO_n clusters (n = 9 - 15) using the B3LYP/LANL2DZ model chemistry.

atom of the $Cu_{11}O_{11}$ and the $Cu_{12}O_{12}$ clusters are 2.62 eV and 2.63 eV, respectively. The atomization energies per atom of copper oxide clusters (Cu_nO_n, n = 1 - 8) rise rapidly from n = 1 to n = 5 and then almost no change at about 2.5 eV.[24] Second difference in energies is calculated from equation (3).

$$\Delta^2E(n) = [E(n + 1) - E(n)] - [E(n) - E(n - 1)] \quad (3)$$

Figure 6 shows the second difference in energies of neutral, cationic, and anionic copper oxide clusters. In general, the second difference in energies tells which a cluster is more stable than other clusters. In neutral copper oxide clusters, odd-numbered copper oxide clusters are more stable than even-numbered copper oxide clusters, except for the $Cu_{14}O_{14}$ cluster. In Cu_nO_n clusters with n = 1 - 8, the odd-numbered copper oxide clusters are more stable than even-numbered copper oxide clusters, because the stability of neutral copper oxide clusters is correlated with a Cu-O-Cu angle from a tetrahedral geometry.[24]

However, in our investigation, the stability of neutral copper oxide clusters cannot be explained by Cu-O-Cu angels. *Table* 3 shows the average Cu-O-Cu angles of neutral copper oxide clusters. The average Cu-O-Cu angles have similar values of about 104.4 degree except for the average Cu-O-Cu angle of the $Cu_{13}O_{13}$ cluster.

***Table* 3.** Average Cu-O-Cu angles of neutral copper oxide clusters

Cluster	Average Cu-O-Cu angles
Cu_9O_9	102.7
$Cu_{10}O_{10}$	104.8
$Cu_{11}O_{11}$	104.5
$Cu_{12}O_{12}$	105.0
$Cu_{13}O_{13}$	98.4
$Cu_{14}O_{14}$	104.5
$Cu_{15}O_{15}$	105.1

We think that the structural stability is correlated with a six-membered ring in our study. Generally, a six-membered ring is more stable than other rings. From the calculated second difference in energies, we know that $Cu_{11}O_{11}$, $Cu_{13}O_{13}$, and $Cu_{14}O_{14}$ clusters are more stable than are the $Cu_{10}O_{10}$ and $Cu_{12}O_{12}$ clusters. The $Cu_{11}O_{11}$, $Cu_{13}O_{13}$, and $Cu_{14}O_{14}$ clusters have one or two six-membered rings, and the $Cu_{10}O_{10}$ and $Cu_{12}O_{12}$ clusters have no six-membered ring.

In cationic and anionic clusters, there is the odd-even oscillation. Even-numbered clusters are more stable than are odd-numbered clusters. It is interesting that an anionic $Cu_{12}O_{12}$ cluster is more stable than other anionic clusters.

Figure 7 shows the calculated adiabatic ionization potentials and electron affinities of copper oxide clusters. There are odd-even oscillations from Cu_9O_9 to $Cu_{13}O_{13}$ clusters. After the $Cu_{13}O_{13}$ cluster, ionization energies and electron affinities are decreased and increased, respectively.

CONCLUSION

We use ReaxFF and DFT calculations for finding the lowest energy copper oxide clusters, Cu_nO_n with n = 9 - 15. Using ReaxFF, we calculated lots of initial copper oxide clusters quickly. Then, the lowest energy structures of neutral, cationic, and anionic copper oxide clusters can be found with DFT. The structures of neutral, cationic, and anionic copper oxide clusters are very similar. (Cu_9O_9, $Cu_{13}O_{13}$,

and $Cu_{14}O_{14}$ clusters) From the second difference in energies, in neutral copper oxide clusters, the $Cu_{11}O_{11}$, $Cu_{13}O_{13}$, and $Cu_{14}O_{14}$ clusters are more stable than are other copper oxide clusters. These clusters have one or two six-membered rings. Whether or not these clusters have a six-membered ring determines their structural stability.

Supporting Information. Single point calculation energies of initial Cu_9O_9 clusters.

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