Experimental evidence shows that small Cu$_2$O nanoparticles exhibit ferromagnetic or paramagnetic properties, allowing for the promising possibility to recycle the catalyst Cu$_2$O easily in wastewater treatment. In this paper, theoretical calculation studying the magnetic property of copper/oxide clusters is reported. A series of Cu$_{m}$O$_{n}$ clusters (m, n = (4, 1); (4, 2); (4, 5); (16, 15); (28, 15); (44, 15); (28, 27)) were investigated using generalized gradient approximation (GGA) and the Hubbard U (GGA+U) method within density functional theory (DFT). It is found that the electronic structures of bulk Cu$_2$O calculated by the GGA and GGA+U are similar. The structures of Cu$_{m}$O$_{n}$ ((m, n) = (4, 1); (4, 2); (4, 5)) are all planar. For the bulk-product Cu$_{m}$O$_{n}$ ((m, n) = (16, 15); (28, 15); (44, 15); (28, 27)), O atoms prefer to be the outermost atoms. We classified two types of clusters on the basis of their O to Cu atomic ratios. One is O-rich clusters, i.e., Cu$_{48}$O$_{59}$, Cu$_{16}$O$_{15}$, and Cu$_{28}$O$_{27}$. The other is O-poor clusters, i.e., Cu$_{4}$O, Cu$_{4}$O$_{2}$, Cu$_{28}$O$_{15}$, and Cu$_{44}$O$_{15}$. The calculation results show that the O-rich clusters have longer average Cu–Cu bonds and larger binding energy than those of the O-poor ones. More interestingly, the former are magnetic and give ferromagnetic ordering while the latter are nonmagnetic. The hydrogenation of O-terminated clusters can improve its stability but suppress its magnetism. The study may be extremely useful for the potential applications of Cu$_2$O nanoparticles in the catalysis and semiconductor fields.

1. Introduction

During the past decades, metal oxides, especially transition-metal oxide nanoparticles, have attracted more and more attention because of their wide applications in catalysis, fuel cell, sensor technology, magnetic materials, etc. The structures of small clusters containing a few to hundreds of atoms are different from bulk materials. In an atomic cluster, most of the atoms are located at the surface. Its structural crossover phenomena and electronic confinement effects determine physical and chemical properties of materials. With the increase of cluster sizes, more atoms can be considered to share the same characteristics and be positioned as that of solid material. In the center of large clusters, condensed phases are formed in correspondence to bulk modification.

Cu$_2$O is of great interest in catalysis and semiconductor fields due to its material abundance, preparation simplicity, nontoxicity, and suitable band gap. Its p-type conduction property and broad response to visible light (VL) suggest that one of the most important applications of Cu$_2$O is its function as a component in a photovoltaic solar cell. It was found that by combining Cu$_2$O with an n-type semiconductor, such as TiO$_2$ or ZnO, the new composite materials show good energy conversion efficiency, implying that it is an economical candidate to replace the traditional high-cost crystalline silicon solar cell. In addition, it is also a promising material able to be applied in developing transparent conducting electronic devices by alloying with alkaline-earth oxide. As a catalyst, Cu$_2$O has been found to degrade organic pollutants in wastewater under visible light.

When catalysts hybridize with magnetic materials such as Fe, it is believed to benefit the recycling of the catalysts in solution. If Cu$_2$O has magnetic properties as well, it will become an even better photocatalyst.

With the growing interest in the new and exciting field of "oxide spintronics", magnetic oxide semiconductors are attracting more attention as a potential candidate for materials in spintronics-related technology. More recently, there is new evidence indicating that Cu$_2$O nanoparticles (~10–100 nm) surprisingly have a native ferromagnetic property. In our group, we have succeeded in synthesizing a series of Cu$_2$O nanomaterials including nanowhiskers, nanorods, nanowires, aligned nanosheets arrays, nanoflowers, and nanoparticles. They are composed of super small Cu$_2$O particles within the size range of ~2–8 nm. However, the magnetic properties of the tiny Cu$_2$O nanoparticles (~2–8 nm) demonstrate the paramagnetic characteristics shown in Figure S1 (Supporting Information). Oxygen concentration and particle size are proposed to be related to the magnetic properties. Bulk native point defects and surface properties from theoretical studies are indicated to be the origin of the Cu$_2$O native magnetism. However, the kind of study has not been consid-
ered due to the complexity of the electronic structure, which would require post-DFT approaches, such as DFT+U. Therefore, it remains to investigate the puzzling magnetic properties relative to the sizes and compositions of those cluster materials further. Moreover, the study of Cu₂Oₙ clusters could also shed light on our present knowledge of Cu₂O photocatalysis and magnetic properties as well as highlight the application of cuprous oxide-based nanomaterials.

The small spherical nanoparticles of Cu₂O synthesized in our group have a cuprite crystal structure. Therefore, the clusters under investigation here are truncated from bulk Cu₂O. Bulk Cu₂O has been well studied using first principles methods ranging from 5 to 59 atoms. Because the (−OH) group was detected in the samples of Cu₂O nanoparticles in our experiment, the hydrogenation of the O-terminated cluster is also calculated to check the hydrogenation effect on the cluster. We have considered both O- and Cu-terminated clusters with different oxygen concentrations. Furthermore, both bulk Cu₂O and clusters are calculated using density functional theory (DFT) with GGA-PW91 approaches. Considering the nonstoichiometry of clusters, especially the O-rich oxides that induce the Cu d orbitals to be partially occupied, the DFT+U approach is also used for all the bulk and clusters calculations. The results obtained by the two methods are compared.

2. Computational Details

The calculations were performed using the Vienna ab initio simulation package (VASP) based on self-consistent density functional theory (DFT). We used a frozen-core projector augmented wave (PAW) approach to describe core–valence interaction and Perdew and Wang (PW91)-type GGA for the exchange–correlation functional. To explore strong on-site Coulomb repulsion among localized Cu 3d electrons, GGA+U formalism given by Dudarev et al. was used:

\[ E_{\text{LSDA+U}} = E_{\text{LSDA}} + \frac{(U - J)}{2} \sum_{\sigma} \left[ \left( \sum_{m_1} n_{m_1,m_1}^\sigma - \sum_{m_1,m_2} \delta_{m_1,m_2}^\sigma \delta_{m_2,m_1}^\sigma \right) \right] \]

where the expression in square brackets is the total number of d electrons \( N_\sigma \), while \( U \) and \( J \) are respectively the spherically averaged matrix elements of screened Coulomb and exchange energy. \( \sigma \) represents spin and \( m \) is the magnetic quantum number of the d orbital. Since only the difference \( (U - J) \), it is relevant, we have treated them as one single parameter labeled as \( U \).

To achieve appropriate parameters for cluster calculation, our calculations began with bulk Cu₂O. We used a plane wave cutoff energy of 508 eV for all calculations to ensure accurate results. For the cubic bulk unit cell Cu₂O, we used a 7 × 7 × 7 Monkhorst–Pack k-point sampling scheme with 20 irreducible k-points. For the density of states (DOS) calculation, k-points were performed using tetrahedron method with a 15 × 15 × 15 Monkhorst–Pack grid (120 irreducible k-points). A smear-

### Table 1: Structural Parameters of Bulk Cu₂O Calculated by GGA-PW91 (G-P), GGA+U (G+U), Hatree–Fock, and GGA-PBE Methods

<table>
<thead>
<tr>
<th></th>
<th>G-P</th>
<th>G+U</th>
<th>HP</th>
<th>PBE</th>
<th>Exp</th>
</tr>
</thead>
<tbody>
<tr>
<td>lattice (Å)</td>
<td>4.30</td>
<td>4.26</td>
<td>4.28</td>
<td>4.34/4.29</td>
<td>4.27</td>
</tr>
<tr>
<td>Cu–O (Å)</td>
<td>1.86</td>
<td>1.85</td>
<td>1.85</td>
<td>1.88/1.86</td>
<td>1.85</td>
</tr>
<tr>
<td>Cu–Cu (Å)</td>
<td>3.04</td>
<td>3.01</td>
<td>3.03</td>
<td>3.07</td>
<td>3.01</td>
</tr>
</tbody>
</table>

*The experimental values are also listed for comparison. From ref 19. From refs 6 and 22. From ref 40.*
However, it is significantly lower than the experimental value 2.0 eV due to a well-known DFT limitation, which is the self-interaction error. 

The calculated band structures of bulk Cu$_2$O using GGA-PW91 (panel a) and GGA-PW91 (panel b) are shown in Figure 2. The direct band gap at Γ-point is 0.51 eV using DFT-PW91. The calculated band gap agrees well with 0.52 eV using LDA and 0.47 eV using DFT-PBE. However, it is significantly lower than the experimental value 2.0 eV due to a well-known DFT error. The band gap increases to 0.80 eV using GGA+U, as shown in Figure 2a. Because of the closed 3d shell, Cu$_2$O is not considered to be a strongly correlated material. The GGA+U method partially improves the accuracy of band gap calculation, although the improvement is not pronounced. On the basis of the above bulk results, we began our theoretical cluster work. For nonstoichiometric clusters, especially the O-rich copper clusters that induce the Cu d states to be partially occupied, the DFT+$U$ approach is also necessary and used for cluster calculations.

### 3.2. Clusters of Cu$_{m}$O$_n$

We generated six O-centered spherical clusters of Cu$_{4}$O, Cu$_{4}$O$_{2}$, Cu$_{4}$O$_{5}$, Cu$_{4}$O$_{15}$, Cu$_{4}$O$_{15}$, and Cu$_{4}$O$_{27}$ from cubic bulk Cu$_2$O. Both Cu terminations and O concentrations are taken into account. Figure 3a shows a schematic picture of how to cut the O-centered Cu$_2$O spherical clusters from the bulk. Cu$_{4}$O$_{15}$ (radii $R = 4.30$ Å), Cu$_{4}$O$_{15}$ ($R = 4.69$ Å), and Cu$_{4}$O$_{27}$ are terminated by Cu atoms and possess low O weight percentages. Cu$_{4}$O$_{2}$, Cu$_{4}$O$_{15}$, and Cu$_{28}$O$_{27}$ are truncated by O atoms and have high O weight percentages. Because it is difficult to obtain clusters with high O weight percentages, Cu$_{28}$O$_{27}$ is made by removing some outer Cu atoms.

#### 3.2.1. Cu$_{4}$On ($n = 1, 2, 5$)

We considered a large number of isomers as reasonable initial structures for Cu$_{4}$O and Cu$_{4}$O$_{5}$ clusters. Additionally, we investigated the relationship between oxygen concentration and cluster properties, stoichiometric cluster Cu$_{4}$O$_{5}$ is also considered. All the isomers of the three clusters, we have studied tend to form 2D structures. The stable structures of Cu$_{4}$O, Cu$_{4}$O$_{2}$, and Cu$_{4}$O$_{5}$ are shown in Figure 3b. All of them have $C_1$ point symmetry. The bond length and bond angles of these clusters are similar to those of reported copper oxide cluster calculations. (mol) For (I) Cu$_{4}$O, 4 copper atoms form a dense configuration and tightly bond to each other, all the Cu–Cu bond lengths are shorter than that of bulk metal copper, 2.540 Å in experiment. The average Cu–Cu bond length is 2.395 Å and the O atom joins two copper atoms for the formation of a (Cu$_2$O) unit. For (II) Cu$_{4}$O$_{2}$, the tightly bonded 4 copper atoms are disturbed by inserting two O atoms to form two (Cu$_2$O) units. This structure is in accordance with ref 43. For (III) Cu$_{4}$O$_{5}$, the tightly bonded 4 copper framework is thoroughly destroyed. One O atom inserts into the center of copper framework and the other 4 O atoms attach to two copper atoms for the formation of (Cu$_2$O) units (Figure 3b). From this result, it can be concluded that the (Cu$_2$O) unit plays a very important role in small cluster formation, which agrees well with other cluster studies.

Semiconductor clusters can also possess considerably different electronic properties from the bulk owing to the quantum confinement effect. The energy gap between the highest-occupied molecular orbital (HOMO) and the lowest-unoccupied molecular orbital (LUMO) plays a very important role to characterize cluster properties. To study the electronic properties of the clusters in detail, we performed spin-polarized calculations and plotted their electronic density of states in Figure 4 (I, Cu$_{4}$O; II, Cu$_{4}$O$_{2}$; III, Cu$_{4}$O$_{5}$). The band gaps for the three clusters using GGA-PW91 are 0.70, 0.50, and 0.50 eV, respectively. The band gap becomes wider when the O concentration decreases. Besides, no magnetism is found for these small clusters by GGA-PW91. Using the GGA+U method, the band gap is increased to 1.12 and 1.09 eV for Cu$_{4}$O and Cu$_{4}$O$_{2}$, respectively, and again no magnetism is found. However, for Cu$_{4}$O$_{5}$, the spin-
up and spin-down plot is split with a gap of 1.28 eV for spin-up and 0.96 eV for spin-down. The local spin moment on a Cu atom can go up to 0.29 \( \mu_B \) and on an O atom be slightly polarized to 0.15 \( \mu_B \), leading to ferromagnetism in Cu\(_4\)O\(_5\) with a total spin moment of 2 \( \mu_B \).

### 3.2.2. Large Clusters Cu\(_{n}\)O\(_m\)

Considering a large number of isomers for the larger clusters, we focused on bulk-generated clusters for the remaining clusters. After relaxation, (a) Cu\(_{16}\)O\(_{15}\) and (b) Cu\(_{28}\)O\(_{15}\) clusters have \( T_d \) space group, (c) Cu\(_{44}\)O\(_{15}\) has \( C_3 \) point symmetry, and (d) Cu\(_{28}\)O\(_{27}\) has \( C_1 \) point symmetry.

The initial and optimized structures of the large clusters are shown in Figure 5. Geometric optimization shows that the O-rich clusters are different from the O-poor clusters. For the O-rich clusters, the outermost atoms remain O-terminated. For (a) Cu\(_{16}\)O\(_{15}\), the surface atoms form new Cu–O and Cu–Cu bonds, which makes the cluster exhibit moderate contraction. The average Cu–O bond length \( d_{\text{Cu-O}} \) is 1.79 Å (GGA+U: 1.77 Å), showing -3.76% (GGA+U: -4.84%) variation compared to the bulk. The average Cu–Cu bond length \( d_{\text{Cu-Cu}} \) is 2.85 Å (GGA+U: 2.81 Å), which is longer than the Cu–Cu distance 2.55 Å in Cu metal. For (d) Cu\(_{28}\)O\(_{27}\), the cluster undergoes a drastic contraction because of the copper vacancies resulting from removing Cu atoms at the outer surface. The formation of new Cu–O and Cu–Cu bonds is observed at the outermost surface and drives the cluster’s drastic reconstruction. The average \( d_{\text{Cu-Cu}} \) is 2.68 Å (GGA+U: 2.70 Å).

For the O-poor clusters, (b) Cu\(_{28}\)O\(_{15}\) and (c) Cu\(_{44}\)O\(_{15}\), drastic structure reconstruction is exhibited at the outermost surface of the cluster, in which Cu atoms move inward while O atoms become the outermost atoms of the clusters. After relaxation, the new Cu–Cu and Cu–O bonds at the cluster surface are formed and, finally, O atoms become the outmost surface atoms for all the large clusters. The large displacement of the atoms at the surface is due to the large electronic affinity of O atoms and the tendency to form Cu–O covalent bonds, which drives the Cu atoms at the surface to move deeper into cluster. Hence, an O-rich surface is formed. The different behavior of the oxygen group element and metal atoms is similar to that of other semiconductor clusters, especially the CdS nanocrystal. The average \( d_{\text{Cu-Cu}} \) for the two clusters is 2.58 and 2.57 Å (GGA+U: 2.54 Å), respectively. For bulk-product Cu\(_n\)O\(_m\) (\( m/n = (16, 15); (28, 15); (44, 15); (28, 27) \)), O atoms prefer to be the outermost too.

The two types of clusters present different electronic properties. The O-rich clusters (a) Cu\(_{16}\)O\(_{15}\) and (d) Cu\(_{28}\)O\(_{27}\) are found to be magnetic, while the O-poor clusters are nonmagnetic. We performed spin polarized calculations, and the resulting electronic density of states is shown in Figure 6. For (a) Cu\(_{16}\)O\(_{15}\) and (d) Cu\(_{28}\)O\(_{27}\), the majority and minority spin DOS splits. The PDOS of the cluster (a) (not given here) shows that the

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**Figure 4.** DOS plot for the clusters studied: I, Cu\(_4\)O; II, Cu\(_4\)O\(_2\); III, Cu\(_4\)O\(_5\). The Fermi level is set to zero; the solid and dashed lines are the results from GGA-PW91 and GGA+U.

**Figure 5.** Structure of large clusters studied. The middle and right columns show each nanocluster in its initial and relaxation configurations, respectively. (a) Cu\(_{16}\)O\(_{15}\) and (d) Cu\(_{28}\)O\(_{27}\) possess high O/Cu ratios. (b) Cu\(_{28}\)O\(_{15}\) and (c) Cu\(_{44}\)O\(_{15}\) possess low O/Cu ratios. Cu atoms: green spheres. O atoms: red spheres.

**Figure 6.** DOS plot for the clusters studied. (a) Cu\(_{16}\)O\(_{15}\) and (d) Cu\(_{28}\)O\(_{27}\) possess high O/Cu ratios. (b) Cu\(_{28}\)O\(_{15}\) and (c) Cu\(_{44}\)O\(_{15}\) possess low O/Cu ratios. The Fermi level is set to zero; the solid line stands for the GGA-PW91 result.
Table 3: Properties of Cu_{n}O_{m} Clusters Calculated by GGA-PW91 (G-P) and GGA+U (G+U)

<table>
<thead>
<tr>
<th>Clusters</th>
<th>G-P D_{c_{Cu}} (Å)</th>
<th>G-P D_{c_{O}} (Å)</th>
<th>G-P E_{b} (eV)</th>
<th>G-P M (μB)</th>
<th>G+U D_{c_{Cu}} (Å)</th>
<th>G+U D_{c_{O}} (Å)</th>
<th>G+U E_{b} (eV)</th>
<th>G+U M (μB)</th>
</tr>
</thead>
<tbody>
<tr>
<td>bulk CuO</td>
<td>3.04</td>
<td>3.01</td>
<td>1.86</td>
<td>1.85</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Cu_{16}O_{15}</td>
<td>2.39</td>
<td>2.40</td>
<td>1.78</td>
<td>1.76</td>
<td>2.274</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Cu_{28}O_{27}</td>
<td>2.38</td>
<td>2.32</td>
<td>1.86</td>
<td>1.84</td>
<td>2.562</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Cu_{4}O_{5}</td>
<td>2.75</td>
<td>2.71</td>
<td>1.84</td>
<td>1.83</td>
<td>3.413</td>
<td>0</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>Cu_{28}O_{15}</td>
<td>2.85</td>
<td>2.81</td>
<td>1.79</td>
<td>1.77</td>
<td>3.461</td>
<td>14</td>
<td>14</td>
<td>14</td>
</tr>
<tr>
<td>Cu_{44}O_{15}</td>
<td>2.58</td>
<td>2.54</td>
<td>1.84</td>
<td>1.85</td>
<td>3.477</td>
<td>0</td>
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<tr>
<td>Cu_{28}O_{27}</td>
<td>2.57</td>
<td>2.53</td>
<td>1.97</td>
<td>1.97</td>
<td>3.354</td>
<td>0</td>
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</tr>
<tr>
<td>Cu_{16}O_{15}H_{4}</td>
<td>2.68</td>
<td>2.70</td>
<td>1.95</td>
<td>1.94</td>
<td>3.713</td>
<td>3.95</td>
<td>22</td>
<td></td>
</tr>
</tbody>
</table>

*E_{b} (eV)* represents the average binding energy of Cu_{n}O_{m} clusters. D_{c_{Cu}} (Å) and D_{c_{O}} (Å) are the average Cu–Cu bond and Cu–O bond length of the clusters, and *M (μB)* denotes the magnetization.

4. Conclusions

First principles can be used to investigate the structural and electronic properties of a series of Cu_{n}O_{m} clusters. GGA and GGA+U methods lead to similar results for Cu_{4}O. The O-rich clusters (Cu_{16}O_{15}, Cu_{28}O_{15}, and Cu_{28}O_{27}) have longer average Cu–Cu bond lengths and higher stabilities. Due to the size and geometrical effects, the formation of copper vacancy (oxidation process) is obviously much easier, implying even more effective catalysis of these clusters. Moreover, these O-rich clusters are magnetic. When the clusters are hydrogenated, the magnetism can be reduced and the stability of the clusters can be improved further. This study will give a new understanding of the Cu_{n}O_{m} clusters, facilitate further investigation of Cu_{n}O_{m} materials, and guide the controllable preparation of cuprous oxide nanomaterials.

Acknowledgment. This work is financially supported by the National Natural Science Foundation of China (Nos. 20973070 and 50804035), the Key Project of Chinese Ministry of Education (No. 109116), National Basic Research Program of China (No. 2009CB939704), the Natural Science Foundation of Hubei Province, China (No. 2009CBDB004), and the Program of Introducing Talents of Discipline to Universities (No. B08033).

Supporting Information Available: Figure S1 showing the ZFC/FC magnetization as a function of temperature. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes
