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Research Article

The interaction of copper oxide(001) and carbon: An Ab initio calculation

Nguyen Minh Phi[1,2], **Tran Thi Thu Hanh**[1,2,*]

ABSTRACT

Copper oxide (CuO) can be biosynthesized using plant extracts, which has sparked an interest in theoretical studies of the interaction between CuO and carbon, a common component found within plant cells. Through density functional theory simulations, the monoclinic structure of CuO has been successfully created and demonstrated to be stable. Monoclinic CuO exhibits metallic properties, characterized by a small overlap of energy states at the Γ point. This structure was further used to create the CuO(001) facet with 14 atomic layers to study carbon atom adsorption. The most favorable site for carbon adsorption on the CuO(001) facet is the bridge site. The bonding between surface Cu and C was found to be non-ionic. This led to some structure change in the surface layer of the CuO lattice, with copper atoms being displaced by a distance ranging from 0.176 to 0.373 Å. Carbon was demonstrated to reach a 1:4 adsorption ratio on the CuO(001) surface. The binding energy of carbon to the CuO(001) surface was calculated to be -5.783 eV. This highly negative value signifies a strong attractive force between carbon and CuO, potentially lead to the formation of electronic bonds between them. The carbon atom appears to have modified some electronic and optical properties of CuO. However, to fully understand the extent of these modifications, further calculations and investigations are warranted. This research paves the way for a deeper understanding of how plant-based materials might influence the properties of metal oxides, opening doors for the development of novel materials with tailored functionalities.

Key words: Density functional theory, metal oxide, simulation, SIESTA.

[1] *Laboratory of Computational Physics, Faculty of Applied Science, Ho Chi Minh City University of Technology (HCMUT), VNU-HCM, Ho Chi Minh City, Vietnam*

[2] *Viet Nam National University Ho Chi Minh City, Vietnam*

Correspondence

Tran Thi Thu Hanh, Laboratory of Computational Physics, Faculty of Applied Science, Ho Chi Minh City University of Technology (HCMUT), VNU-HCM, Ho Chi Minh City, Vietnam

Viet Nam National University Ho Chi Minh City, Vietnam

Email: thuhanhsp@hcmut.edu.vn

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INTRODUCTION

Metal oxides play critical roles in numerous technological advancements and continue to be the focus of research and development efforts across various disciplines. Their applications range from gas sensors, batteries, catalysis, and solar panels [1], to applications in the medical field as antimicrobial agents, disinfectants, cosmetics, etc. [2]. In the field of materials science, metal oxides are of interest due to their close-packed structure, catalytic activity, optical properties, and chemical reactivity. The properties of metal oxides can change dramatically depending on their components, shape and size.

Copper oxide is a type of metal oxide that can be found in nature as tenorite, composed of deeply oxidized copper. CuO exhibits p-type semi-conductor behavior and plays a crucial role as a small bandgap semiconductor [3]. The bonding between Cu and O is expected to be a combination of covalent and ionic bonds, mostly from the interaction of O-2s, O-2p, and Cu-3d orbitals [4]. CuO crystals can be found in cubic or monoclinic structures; cubic CuO exhibits semiconductor behavior, while monoclinic CuO is metallic. Monoclinic is the more common structure type of CuO. Some applications of CuO include methanol sensing [5], antimicrobials [6], and batteries [3]. Although CuO(110) surface is good for CH_4 sensing, with strong adsorption energy at all sites [7]. CuO(001) has been shown to have the largest surface energy, followed by the (110) facet [8]. Therefore, the CuO(001) surface will be the focus of our study due to its high reactivity.

To synthesize metal oxides, various methods can be employed, ranging from bottom-up approaches such as liquid-phase exfoliation and electrochemical exfoliation, to top-down approaches including pulsed laser deposition and chemical vapor deposition [5]. Among these methods, biosynthesis stands out as particularly exciting, where metal oxide nanoparticles are synthesized from plants, fungi, bacteria, or algae [2]. The green synthesis approach holds promise due to its accessibility, environmental sustainability, and minimal energy and material requirements. Using this approach, copper oxide and carbon nanoparticles have been discovered in the leaf extract of plants such as *Ficus religiosa* [6] and *Adhatoda vasica* [9]. In this process, the plant extracts acted as both reducing and capping agents—reducing copper sulfate pentahydrate to CuO, while organic molecules formed protective lay-

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ers, preventing aggregation and maintaining a uniform size and shape of the CuO nanoparticles. Carbon has been chosen for this study because it is the most common elemental component in plant extracts and has the ability to form nanocomposites with CuO after the biosynthesis process, as confirmed in experiments[6,9]. Meanwhile, elements like oxygen, nitrogen, and hydrogen may be suitable for further in-depth studies.

This led to the interest in theoretically studying the interaction between copper oxide and natural carbon present in plants using ab initio simulation.

CALCULATION METHODS

To investigate the interaction of carbon atoms with CuO material, a Density Functional Theory study was conducted using the SIESTA simulation software package. SIESTA, short for the Spanish Initiative for Electronic Simulations with Thousands of Atoms, utilizes the self-consistent field loop method to solve the Kohn-Sham equation in a plane wave basic set[10]. The double-zeta polarization basic set size, and norm conserving approximation for pseudopotentials were employed. For the exchange-correlation functional correction, the generalized gradient approximation method of Perdew, Burke and Ernzerhof was utilized[11]. Optimized geometry for all models was achieved using the conjugate gradient algorithm on total energy, the calculation is stopped when the maximum stress component is less than 0.02 eV/Å. Additionally, a cutoff energy of 200 Ry was used for all calculations.

Three models of CuO were investigated, including a monoclinic CuO unit cell, a monoclinic CuO(001) slab with 14 layers, and a CuO(001) slab with a carbon atom adsorbed on top of the surface. The CuO unit cell model was employed to investigate the band structure, phonon properties, and the correct bond length of Cu-O. Therefore, a large number of k-points (10×10×10 Monkhorst-Pack) was used in this model. For the CuO slab and CuO/C model, a smaller k-point mesh (3×3×3 Monkhorst-Pack) was used to minimize the calculation time.

RESULTS AND DISCUSSION

The CuO unit cell model

The parameter for the initial Cu and O atom coordinate was sourced from the Material Project database[12] to provide a closer representation of the monoclinic crystals. The in-plane directions were set to a = 4.25Å and b = 4.0Å, with the out-of-plane direction set to c = 5.16 Å. Following this notion, the α and γ angles were 90°, and uniquely for the monoclinic structure, the β angle was 92.50°.

After the geometric optimization, the relaxed lattice for monoclinic CuO was found to be a = 4.279Å, b = 4.169Å, c = 5.313Å, and β = 91.6704°. The monoclinic structure is preserved after the simulation, as the β angle differs from the 90° angle of the cubic structure. The average bond length of Cu-O was determined to be 2.0Å. These results are well agreed with the other experimental and theories study[3,13] (See Table 1). The relaxed structure can be seen in Figure 1.

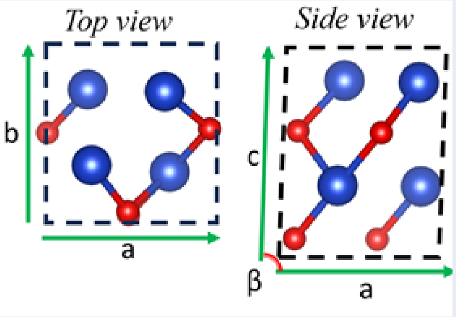

Figure 1: The top and side views of themonoclinic CuO structure, with copper atoms represented in blue and oxygen inred. [Source: Authors]

Table 1: The calculated lattice parameters (Å) and angle β (°) for the monoclinic CuO.

Lattice parameters	a (Å)	b (Å)	c (Å)	β (°)
This work	4.279	4.169	5.313	91.670
Ref.[3]	4.274	4.04	5.182	91.648
Ref.[13]	4.683	3.421	5.129	99.567

The band structure and phonon band structure were analyzed along the directions of the monoclinic system's Brillouin zone in reciprocal space (Z−Γ−Y−S−X). Fermi energy correction was applied to the band structure results (See Figure 2). The band structure of monoclinic CuO reveals metallic properties with a small overlap across the Fermi levels of electronic states at the Γ point, while showing a small gap in other directions. The phonon dispersion curves (displayed in Figure 3) demonstrate the dynamic stability of the CuO structure. Three acoustic branches, including longitudinal, transverse, and flexural modes, are observed at frequencies ranging from 80 to 150 cm^{-1}. A phonon gap is observed at around 300 to 400 cm^{-1} with no negative phonon branch across the entire Brillouin zone. These results confirm the thermodynamic stability of our CuO structure.

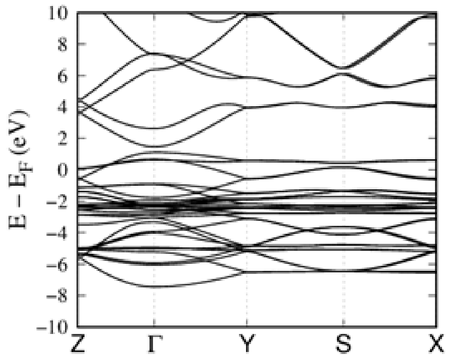

Figure 2: The band structure of the monoclinic CuO. [Source: Authors]

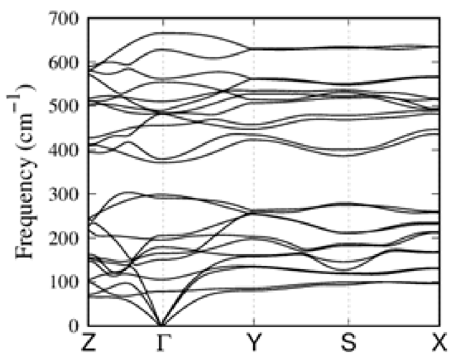

Figure 3: The phonon band structure of the monoclinic CuO. [Source: Authors]

The CuO(001) slab model

The relaxed unit cell parameters were further used to construct the CuO slab. The CuO slab consists of 14 layers of Cu/O, with a total of 28 atoms per unit lattice (14 Cu atoms and 14 O atoms). In chemical vapor deposition, the thickness of CuO can be controlled by the precursor flow rate, deposition time, and temperature[14]. In biosynthesis, the thickness of CuO may depend on the concentration and type of plant extract used[2].

Periodic boundary conditions were applied along the a and b lattice directions. The c direction was exposed to a large vacuum space of 40 Å before the periodic unit cell was repeated to eliminate periodic interactions in the c directionn. This setup resulted in the creation of the monoclinic CuO structure with the (001) facet exposed (See Figure 4).

The CuO/C model

To investigate the interaction between the CuO(001) and carbon, a carbon atom was initially placed on top of the CuO slab with a distance of 1.0 Å to the first exposed layer. The 10 layers at the bottom of the CuO(001) facet were fixed, while the remaining 4 surface layers were allowed to move freely to interact with the carbon atom (See Figure 4).

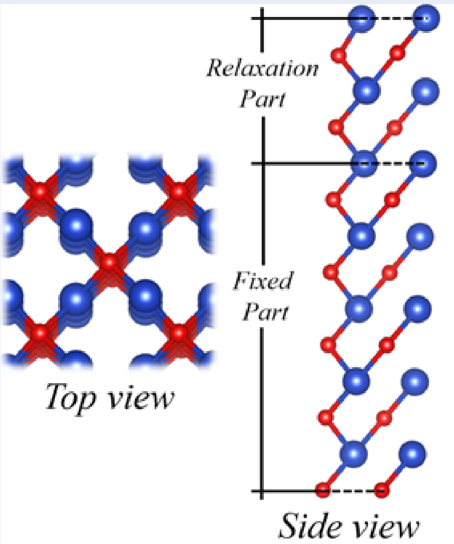

Figure 4: The surface structure of the CuO(001) and the side view of the CuO slab. [Source: Authors]

After relaxation, the carbon atom has moved from the top of the Cu atom site to the more favorable bridge site, located between two Cu atoms (See Figure 5). This could be attributed to the specific dictional properties of covalent bonding between C and Cu. The *Mulliken* population analysis indicates a small charge transfer of 0.057e from the surface Cu atoms to the carbon atom, further suggesting this is a neutral bonding type. A slight displacement of Cu atoms on the surface is observed when bonding with carbon. The displacement ranges from 0.176 to 0.373Å, with the Cu atoms being pull out of the CuO lattice. This model also confirms that the surface coverage ratio of carbon on CuO(001) could reach a 1:4 ratio (See Figure 6).

The binding energy of a carbon atom to the CuO(001) surface was calculated using the following formula:

$$E_{binding} = E_{C/CuO} - E_C - E_{CuO},$$

where $E_{C/CuO}$ represents the total energy of the CuO adsorbed carbon model, E_C denotes the total energy of an isolated carbon atom and E_{CuO} is the total energy of the CuO slab. The calculated binding energy

Table 2: The displacements of atoms (Å) along three dimensions in the first and second layers of CuO(001).

Layer	Atom	x-axis	y-axis	z-axis	Total
1	Cu	0.247	0.279	0.023	0.373
1	Cu	0.160	0.070	0.015	0.176
2	O	0.010	0.004	0.059	0.060
2	O	0.024	0.000	0.036	0.043

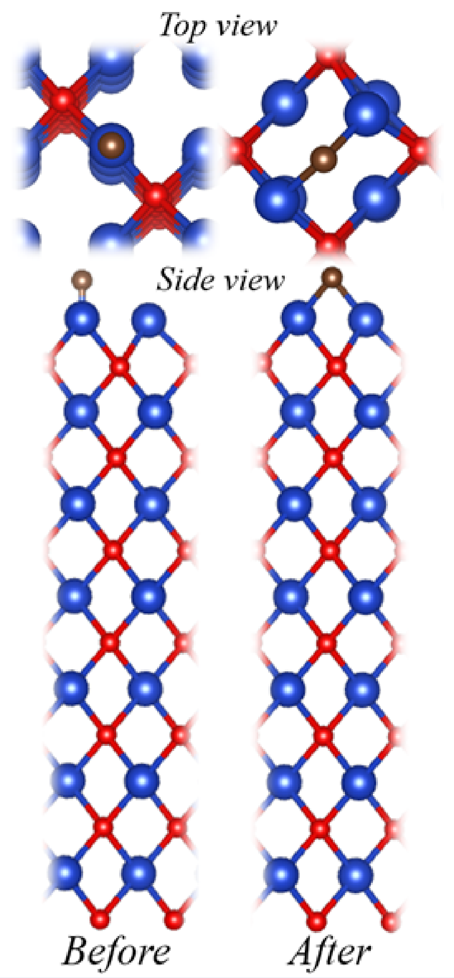

Figure 5: The carbon position on the CuO slabbefore and after relaxation. Carbon is brown. [Source: Authors]

is −5.783 eV. This negative value suggests that the reaction between CuO and carbon will occur spontaneously, as it is exothermic. The binding energy is also a lot stronger than the physisorption threshold of 0.5 eV, indicating chemisorption processes wherein the CuO surface forms a strong electronic bond with carbon.

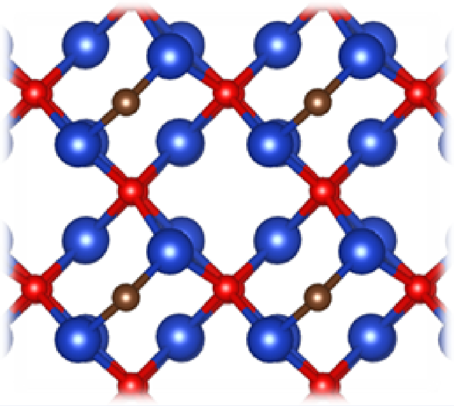

Figure 6: The overall ratio of carbon on the surface of CuO(001). [Source: Authors]

CONCLUSIONS

This paper has investigated the interaction between CuO and carbon through a series of density functional theory calculations. The stable monoclinic CuO model was obtained with the metal properties. A CuO(001) slab with 14 layers was created based on the relaxed parameters and then applied to the carbon atom adsorption reaction. The favorable adsorption site for the carbon atom on the CuO(001) surface is the bridge site, located between the two topmost Cu atoms. This interaction slightly pulls the Cu atoms out of the periodic lattice. The adsorption model was fully relaxed, demonstrating that carbon could occupy the surface with a 1:4 ratio on the CuO(001) surface. Using the total energy results, the binding energy of carbon was calculated as −5.783 eV. This negative value suggests a strong attractive interaction between carbon and CuO(001). Conducting a larger-scale calculation regarding CuO(001) adsorbed carbon would be worthwhile to gain a deeper understanding of the impact of carbon on the electronic, optical, and mechanical properties of CuO.

COMPETING INTERESTS

The authors declare that there are no conflicts of interest related to this work.

AUTHORS' CONTRIBUTIONS

All authors contributed equally to the conception, model design, data analysis, and writing of the manuscript.

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Bài nghiên cứu

Nghiên cứu tương tác giữa CuO(001) và cacbon: Tính toán nguyên lý ban đầu

Nguyễn Minh Phi[1,2], **Trần Thị Thu Hạnh**[1,2,*]

TÓM TẮT

Đồng oxít (CuO) có thể được tổng hợp sinh học từ chiết xuất thực vật, tạo động lực cho việc nghiên cứu lý thuyết về sự tương tác giữa CuO và cacbon, vốn là một thành phần phổ biến được tìm thấy trong thực vật. Qua các tính toán DFT, cấu trúc monoclinic của CuO đã được mô phỏng thành công và chứng minh là ổn định. Cấu trúc monoclinic của CuO thể hiện tính chất kim loại, được đặc trưng bởi sự chồng chất các mức lượng năng lượng tại điểm Γ. Cấu trúc này đã được sử dụng để tạo ra bề mặt CuO(001) với 14 lớp nguyên tử để nghiên cứu hấp thụ nguyên tử cacbon. Vị trí trên bề mặt CuO(001) thuận lợi nhất cho sự hấp thụ cacbon là vị trí cầu. Liên kết giữa đồng và cacbon được chỉ là liên kết không có sự ion hóa. Việc hấp phụ này dẫn đến một số thay đổi cấu trúc trong lớp bề mặt của mạng lưới CuO, với Cu bị dịch chuyển trong khoảng 0.17 đến 0.35 Å. Mô hình này đã chứng minh cacbon đạt được tỷ lệ hấp thụ 1:4 trên bề mặt CuO(001). Năng lượng liên kết của cacbon với bề mặt CuO(001) được tìm thấy là -5.783 eV. Điều này thể hiện có một lực hút mạnh mẽ giữa cacbon và CuO, thể hiện tính liên kết điện tử. Chúng tôi tin rằng nguyên tử cacbon đã sửa đổi một số tính chất điện tử và tính chất quang của CuO. Cần thêm các tính toán bổ sung để hiểu sâu hơn về cách các vật liệu dựa trên thực vật có thể ảnh hưởng đến các tính chất của oxit kim loại, mở ra cánh cửa cho việc phát triển các vật liệu mới.

Từ khoá: DFT, mô phỏng, SIESTA, oxít kim loại.

[1] *Phòng Thí nghiệm Vật lý Tính toán, Khoa Khoa học Ứng dụng, Trường Đại học Bách Khoa, Việt Nam*

[2] *Đại học Quốc gia TP. Hồ Chí Minh, 268 Lý Thường Kiệt, Phường Diên Hồng, TP. Hồ Chí Minh, Việt Nam.*

Liên hệ

Trần Thị Thu Hạnh, Phòng Thí nghiệm Vật lý Tính toán, Khoa Khoa học Ứng dụng, Trường Đại học Bách Khoa, Việt Nam

Đại học Quốc gia TP. Hồ Chí Minh, 268 Lý Thường Kiệt, Phường Diên Hồng, TP. Hồ Chí Minh, Việt Nam.

Email: thuhanhsp@hcmut.edu.vn

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