DFT + U study of H₂O adsorption and dissociation on stoichiometric and nonstoichiometric CuO(111) surfaces

Faozan Ahmad¹,²,³,⁵, Mohammad Kemal Agusta¹,³, Ryo Maezono⁴ and Hermawan Kresno Dipojono¹,³,⁵

¹ Engineering Physics Research Group, Faculty of Industrial Technology, Institut Teknologi Bandung, Jl. Ganesha 10, Bandung, Indonesia
² Theoretical Physics Division, Department of Physics, Bogor Agricultural University, Jl. Raya Darmaga, Bogor, Indonesia
³ Research Center for Nanoscience and Nanotechnology, Institut Teknologi Bandung, Jl. Ganesha 10, Bandung, Indonesia
⁴ School of Information Science, Japan Advanced Institute of Science and Technology, Asahidai 1-1, Nomi, Ishikawa 923-1292, Japan

E-mail: faozan@apps.ipb.ac.id (FA) and dipojono@tf.itb.ac.id (HKD)

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Abstract
Surface interaction through adsorption and dissociation between H₂O and metal oxides plays an important role in many industrial as well as fundamental processes. To gain further insights on the interaction, this study performs dispersion-corrected Hubbard-corrected density functional theory calculations in H₂O adsorption and dissociation on stoichiometric and nonstoichiometric CuO(111) surfaces. The nonstoichiometric surfaces consist of oxygen vacancy defect and oxygen-preadsorbed surfaces. This study finds that H₂O is chemically adsorbed on the top of Cu₉sub and Cu₉sub-Cu₉sub bridge due to the interaction of its p orbital with d orbital of Cu. The adsorption is found to be the strongest on the surface with the oxygen vacancy defect, followed by the stoichiometric surface, and the oxygen-preadsorbed surface. The oxygen vacancy increases the reactivity for H₂O adsorption and reduces the reaction energy required for H₂O dissociation on the surface. However, the surface modification by the oxygen-preadsorbed significantly reduces the barrier energy for H₂O dissociation when compared with the other surfaces.

Keywords: CuO(111), H₂O adsorption, H₂O dissociation, dispersion-corrected DFT + U

Supplementary material for this article is available online
(Some figures may appear in colour only in the online journal)

1. Introduction

Disclosing the physicochemical phenomena of adsorption and dissociation of H₂O on metal oxide is of great importance for both industrial applications as well as fundamental studies. From industrial point of view, there are many catalytic processes involving H₂O with metal oxides as a catalyst [1–3] in which H₂O could be a reactant as well as a product [4–7]. From fundamental perspectives, over the past decade, many theoretical studies have been conducted to investigate adsorption and dissociation of H₂O on catalyst surfaces such as TiO₂ [8], Cu₂O [9], CeO₂ [10], SrTiO₃ [11], goethite [12], and CoO [13]. In general, the studies focussed on the adsorption and
The stability [15]. The activity of Cu$_2$O catalysts in reactions reported adsorption of H$_2$O on CuO(1 1 1) with high coverage strongly influenced by the Hubbard potential ($U$). Yu et al [30] observed that the calculation of adsorption energy is [22] reported the effect of H$_2$O adsorption on the CuO et al [31] investigated the H$_2$O dissociation on the stoichiometric et al [32] which what processes are involved in H$_2$O adsorption and dissociation on the stoichiometric and nonstoichiometric CuO(1 1 1) surfaces.

Figure 1. The CuO bulk and surface structures. (a) Bulk magnetic cell unit, (b) surface supercell, (c) H$_2$O adsorption sites on the CuO(1 1 1) surface, (d) stoichiometric surface, (e) oxygen vacancy defect surface, and (f) oxygen-preadsorbed surface.

paper would unravel the following questions: (a) how the Hubbard $U$ parameter is determined, (b) how the stoichiometric and nonstoichiometric surfaces are constructed, (c) what processes are involved in H$_2$O adsorption and dissociation on the stoichiometric and nonstoichiometric CuO(1 1 1) surfaces.

2. Computational methods and models

2.1. Computational methods

All calculations are carried out using spin-polarized Kohn–Sham DFT [37, 38] with Hubbard [39] and Van der Waals dispersion corrections of Grimme [40] using Quantum ESPRESSO package [41]. Exchange and correlation functions are expressed by GGA (generalized gradient approximation) based on functional PBE (Perdew–Burke–Ernzerhoff) [42]. Core ions are represented by using projector augmented wave (PAW) [43]. Integration of the Brillouin zone is done on a $4 \times 4 \times 1$ k-points grid sampled by Monkhorst–Pack scheme [44]. A cut-off energy of 500 eV is used to limit the plane wave basis set. The appropriate $U$ value is selected for the localized 3$d$ electrons correction of Cu.

The surface $U$ parameter can be determined using at least two different empirical approaches, first by reproducing bulk properties and second by reproducing surface experimental data. Mishra et al [25] and Maimaiti et al [26] employed the first approach and found that U of 7 eV could reproduce bulk
properties such as the local magnetic moment of Cu atoms and the bandgap of CuO. Trinh et al [45] and Bhola et al [46], who applied the second approach by comparing the x-ray photoelectron spectroscopy and enthalpy data for the H2 adsorption on CuO surfaces with DFT + U calculations, suggested low U values (4.0–4.5 eV). Maimaiti et al also showed that the variation of U did not change the energetic preferences of different oxygen vacancies on CuO(1 1 1). Hence, they concluded that for CuO(1 1 1), the U value of 7 eV was adequate to describe the appropriate electronic structure and reaction energetics.

In this study, the effective U value (U_{eff}) is determined using the first approach, i.e. by calculating the U dependence of the bandgap and atomic magnetic moment (μ). Based on the calculation results (see figure 1 in the electronic supplementary information (ESI) available online at stacks.iop.org/JPhysCM/32/045001/mmedia), the values of bandgap and μCu increase as the value of U increases. Conversely however the value of μO decreases as the value of U increases. By comparing the results with the experimental data of bandgap and μCu that are 1.34 (at 300 K)–1.67 eV (at 0 K) [47] and 0.64–0.74 μB [48], respectively, we obtain that U_{eff} = 7 eV is the appropriate value for U. Although our U is derived for the bulk CuO however the fact that Cu 3d orbitals are quite localized, this study also adopts this U for the surface too. Moreover, this approach have been used successfully by previous researchers as well [22, 25, 26]. To convince further on the correctness of U, at the end of this report, we discuss the effect of different U values by applying U = 0 eV (plain DFT), U = 4.5 eV, and U = 7 eV on H2O dissociation on the stoichiometric and nonstoichiometric CuO(1 1 1) surface.

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**Table 1.** Adsorption energies and geometric parameters of H2O adsorption on the stoichiometric CuO(1 1 1) surface.

| No | Conf. | Adsorption energy (eV) | d (O–H) (Å) | α (H–O–H) (°) |
|----|-------|------------------------|-------------|----------------|
| 1  | A     | -0.87                  | 1.02/0.98   | 103.10         |
|    |       | -0.77<sup>a</sup>      | 1.02/0.98<sup>a</sup> | 102.50<sup>a</sup> |
| 2  | B     | -0.79                  | 1.02/0.98   | 105.50         |
|    |       | -0.64<sup>a</sup>      | 1.02/0.98<sup>a</sup> | 105.50<sup>a</sup> |
| 3  | C     | -0.48                  | 0.99/0.97   | 106.00         |
| 4  | D     | -0.52                  | 0.98/0.98   | 102.10         |
| 5  | E     | -0.35                  | 0.98/0.98   | 104.00         |
| 6  | F     | -0.56                  | 0.99/0.98   | 101.10         |

<sup>a</sup> Without dispersion correction.

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**Figure 2.** H2O adsorption configurations on the stoichiometric CuO(1 1 1) surface.

**Figure 3.** The charge density difference plots for H2O adsorption on the stoichiometric CuO(1 1 1) surfaces (configuration A): (a) between H_{E,O} and O_{surf} and (b) between O_{H,O} and Cu_{sub}.
2.2. Computational models

2.2.1. Stoichiometric CuO(111) surface. Previous studies reported that low index CuO(111) surface had the lowest surface energy [22, 49]. CuO(111) is nonpolar which means it has no net dipole perpendicular to the surface. In this study, CuO(111) surfaces are built based on the bulk structure of CuO with the experimental lattice parameters are given by \(a = 4.68 \text{ Å}, b = 3.42 \text{ Å}, c = 5.13 \text{ Å} \) and \(\beta = 99.54^\circ\) [50]. The experimental lattice parameters are preferred to be used to avoid spurious effects [33]. The magnetic unit cell of bulk CuO is represented in a unit cell consisting of eight formula units of CuO [51] generated based on lattice vector transformations by \(d' = a - c, b' = b, \) and \(c' = a + c\) (see figure 1(a)) [33, 52]. The CuO(111) surface is modeled by a slab comprising of three layers with \((1 \times 2)\) supercell size and a vacuum (see figure 1(d)). The sufficiency for the number of layers is confirmed by the density of states profile (see figure 2 in ESI). The vacuum space between slabs is about 15 Å which is large enough to eliminate spurious effect due to periodic boundary condition [22, 25]. Magnetic spin ordering for the surface follows a bulk-like model [22] (see figure 1(b)). Further, surface optimization is achieved by relaxing the two top layers and fixing the bottom layer in bulk condition.

In the top layer, there are two types of Cu and O atoms, including coordinatively unsaturated and fully coordinated atoms. The first ones are Cu_{3c} (Cu_{sub}) and O_{3c} (O_{suf}), both coordinate with three neighbor atoms. The second ones consist of Cu_{4c} (Cu_{sub}) and O_{4c} (O_{suf}), coordinate with four neighbor atoms. The subscript ‘sub’ and ‘suf’ are used to label subsurface and outer-most atoms, respectively. We define six adsorption sites namely Cu_{sub}–Cu_{sub} bridge, Cu_{sub}–Cu_{suf} bridge, Cu_{suf}, O_{suf}–O_{sub} bridge, and O_{suf}–O_{suf} bridge, which are denoted by A, B, C, D, E, and F, respectively (figure 1(c)).

2.2.2. Oxygen vacancy defect CuO(111) surface. The oxygen vacancy defect CuO(111) surface is modeled by removing an oxygen atom from the stoichiometric surface. This study chooses to remove O_{suf} (O_{suf}) from the outer most layer because it is under-coordinated and, thus, weakly bonded to its surrounding. The removal also leaves Cu_{3c} with more dangling bonds (see figure 1(e)). The stability of this slab model is confirmed by the previous work of Maimati et al [26]. Physically, the structure can be formed through surface reduction by hydrogen [26].

2.2.3. Oxygen-preadsorbed CuO(111) surface. The oxygen-preadsorbed CuO(111) surface is modeled by placing an oxygen adatom on the site A of the stoichiometric surface (see figure 1(f)). Physically, the structure can be formed through adsorption of oxygen molecule over CuO(111) with an oxygen vacancy defect. Our preliminary work found that such mechanism could proceed with low activation energy of 0.12 eV and exothermic by \(-1.21\) eV (see Figure 3 in ESI).

2.2.4. H2O adsorption on CuO(111) surfaces. H2O adsorption is modeled by placing one H2O molecule as an adsorbate on the above mentioned \((1 \times 2)\) super-cell which corresponds to 1/2 ML adsorption coverage. The molecule is allowed to relax in all degrees of freedom along with the two atomic layers of the surface during the optimization. H2O adsorbate is placed on the previously defined sites on the respective surface. These sites are chosen due to the presence of unstable dangling bonds that tend to interact with the adsorbates and are expected to play an important role in the process of adsorption, activation, or dissociation [53].

The interaction strength of H2O and CuO(111) surface is described by the magnitude of adsorption energy \(E_{ads}\) that is calculated by the following equation (1).

\[
E_{ads} = E_{sub/sorb} - (E_{sub} + E_{sorb});
\]  

(1)

where \(E_{sub/sorb}, E_{sub}, \) and \(E_{sorb}\) denote the total energies of surface and adsorbed molecule system, the energy of clean surface, and energy of a free adsorbed molecule in a vacuum, respectively. Based on this definition, negative value of \(E_{ads}\) indicates a stable adsorption.
2.2.5. H$_2$O dissociation on CuO(1 1 1) surfaces. The dissociations of H$_2$O into OH and H species are studied on the surfaces mentioned above. The previously obtained most stable H$_2$O adsorption on each of the surfaces is used as the initial state (IS), while co-adsorbed OH and H are used as the final state (FS). The transition state (TS) between IS and FS is determined via the climbing image nudged elastic band method [54]; this calculation provides the activation energy ($E_{\text{act}}$) and the reaction energy ($\Delta E$) as the potential barrier between IS and TS and the total energy difference between IS and FS, respectively. They are expressed as follows:

$$E_{\text{act}} = E_{\text{TS}} - E_R,$$

$$\Delta E = E_P - E_R,$$

with $E_{\text{act}}$ is the activation energy, $E_{\text{TS}}$ is the energy of the TS, $E_R$ is the energy of the IS and $E_P$ is the energy of the FS. In addition, a vibrational frequency analysis is performed [55] to validate the transition state (TS) where it shall have only one imaginary frequency.

3. Results and discussions

Initially, we study the energetic and electronic structure of H$_2$O adsorption on the stoichiometric and nonstoichiometric CuO(1 1 1) surfaces. Then, we investigate H$_2$O dissociation over the same surfaces by observing bond weakening and energy pathway analysis.

3.1. H$_2$O adsorption on the CuO(1 1 1) surfaces

3.1.1. Adsorption on the stoichiometric CuO(1 1 1) surface. The optimized structures of H$_2$O adsorption on the A, B, C, D, E and F sites of the stoichiometric CuO(1 1 1) surface are shown in figure 2. The values of the adsorption energy are listed in table 1 along with some geometrical parameters. Adsorption on site A is the configuration with the strongest adsorption ($E_{\text{ads}} = -0.87$ eV) where O$_{\text{HLO}}$ atom is adsorbed on the top Cu$_{\text{sub}}$-Cu$_{\text{sub}}$ bridge and both of H$_{\text{HLO}}$ are attracted to two different O$_{\text{sub}}$. The trend on adsorption energy magnitude with respect to adsorption site is A > B > F > D > C > E. It can be inferred that adsorption near unsaturated Cu$_{3c}$ and O$_{3c}$ (A and B) sites is more favored as compared to the saturated ones and it proves that unsaturated sites tend to stabilize themselves by binding to the surrounding atoms. H$_2$O adsorption on unsaturated sites tends to be chemisorption character, whereas on saturated ones tend to be physisorption character. Unsaturated Cu atom (Cu$_{3c}$) gains more electrons from O$_{\text{HLO}}$, whereas unsaturated O atom (O$_{3c}$) gives more electrons to H$_{\text{HLO}}$ than saturated ones. The adsorption is also accompanied by elongation of O–H bond of H$_2$O. The bond elongation correlates quite well with the adsorption strength. Note that the listed dispersion effect of the calculation in table 1 is only shown for configuration A and B, by comparing with
the calculation without incorporating dispersion correction. Clearly, the dispersion correction provides better adsorption energies than that without the correction for the same configuration. It is also obvious that the strongest adsorption is on site A.

The weakening of the O–H bond is further confirmed by the vibrational analysis. Table 2 shows the comparison between the calculated vibrational frequencies H2O molecule in the isolated and adsorbed phase. It is easy to see a significant redshift of stretching vibration frequencies related to the modes with notable OH\textsubscript{H2O} bond length elongation.

Charge redistribution due to the interaction can be studied from charge density difference (\(\Delta \rho\)) obtained from the following formula:

\[
\Delta \rho = \rho_{\text{CuO}(111) + \text{H}_2\text{O}} - \rho_{\text{CuO}(111)} - \rho_{\text{H}_2\text{O}} \tag{4}
\]

where \(\rho_{\text{CuO}(111) + \text{H}_2\text{O}}\) is the total charge density of H\(_2\)O adsorption system while \(\rho_{\text{CuO}(111)}\) and \(\rho_{\text{H}_2\text{O}}\) are total charge density of clean stoichiometric CuO(1 1 1) surface and isolated H\(_2\)O molecule, respectively. By this definition, the positive values of \(\Delta \rho\) correspond to charge accumulation while negative values correspond to charge depletion.

The results of \(\Delta \rho\) for H\(_2\)O adsorption on site A is plotted in figure 3. Obviously there are some charge depletions in the oxygen lone-pair orbital along with charge accumulation in the bonding region between O\(_{\text{H}_2\text{O}}\) and Cu\(_{\text{sub}}\). There is also a strong charge accumulation in between H\(_{\text{H}_2\text{O}}\) atom and O\(_{\text{surf}}\). This is the origin of the O–H bond elongation upon the adsorption.

### 3.1.2. Electronic structure of the H\(_2\)O adsorbed on stoichiometric surface.

Local density of states (LDOS) of adsorption on site A and isolated H\(_2\)O are shown in figure 4. The LDOS are projected on the \(p\) orbitals of O\(_{\text{H}_2\text{O}}\) and \(d\) orbitals of surface Cu\(_{\text{sub}}\). The LDOS of isolated H\(_2\)O molecule shows five peaks that correspond to molecular orbitals (MO) comprising of three occupied valence orbitals: 1b\(_2\), 3a\(_1\), and 1b\(_1\) (the highest occupied molecular orbital, HOMO) and two unoccupied orbitals: 4a\(_1\) (the lowest unoccupied molecular orbital, LUMO), and (2b\(_2\)) [22]. These MO shift toward lower energy from the initial energy position in the gas phase, while Cu 3\(d\) shifts toward higher energy. The sign of chemisorption can be seen from the delocalization of H\(_2\)O MO’s 1b\(_1\) and 3a\(_1\) with oxygen lone pair character upon the adsorption and its mixing with Cu 3\(d\) states. It indicates that orbital interaction of H\(_2\)O adsorption on CuO(1 1 1) is dominated by chemical bonding between oxygen atom of H\(_2\)O and Cu 3\(d\) electronic states of the surface. On the other hand, O–H bonding character orbital (1b\(_2\)) is relatively localized, shifted and hibridized with O 2\(p\) states of surface. This is related to a slight weakening of the O–H bond. The HOMO (1b\(_1\)) of H\(_2\)O is broaden with its higher energy tail touching the Fermi-level, while a new state appears in the unoccupied region, hybridizes with the Cu 3\(d\) states. It simply indicates the occurrence of charge transfer and the formation of new bonding and anti-bonding states between H\(_2\)O and the surface.

The position of the electronic orbitals of Cu\(_{\text{sub}}\) atoms and H\(_2\)O before and after adsorption is shown in orbital energy diagram [56] (see figure 5). It appears that Cu 3\(d\)(up) states...
shift towards higher energy and H\textsubscript{2}O orbitals shift toward lower energy. Hybridization of H\textsubscript{2}O molecular orbitals with the surface is shown by splitting 1\textsubscript{b} and 3\textsubscript{a} orbitals until its energy levels match to that of Cu 3d. These become an important interface of charge transfer between surface and H\textsubscript{2}O molecule. The charge transfer from 1\textsubscript{b} orbitals of H\textsubscript{2}O to Cu 3d states is shown by the emergence of unoccupied 1\textsubscript{b} splitted orbitals on the conduction band with energy levels equal to that of Cu 3d states.

The bonding and anti-bonding states can be seen from overlapping orbital in crystal orbital overlap population (COOP) plot [57] as shown in figure 6. The positive sign of COOP of H\textsubscript{2}O–O\textsubscript{surf} and O\textsubscript{H\textsubscript{2}O}–Cu\textsubscript{sub} pairs shows bonding state formation between them and this in turn indicating their bonds are strengthened and negative sign of COOP of H\textsubscript{2}O–O\textsubscript{O\textsubscript{H\textsubscript{2}O}} shows anti-bonding state formation that indicates its bonds are weakened.

### 3.1.3. Adsorption on the oxygen vacancy defect surface

Table 3 lists the values of adsorption energy along with some structural parameters of H\textsubscript{2}O adsorption on sites A, B and C of the CuO(111) surface with oxygen vacancy. We found that H\textsubscript{2}O is strongly adsorbed on the surface with adsorption energy $-1.06 \text{eV}$ on site C. The trend of the adsorption strength is C > B > A with their structural geometry are shown in figure 7. The bond length O\textsubscript{H\textsubscript{2}O}–Cu\textsubscript{sub} and the shortest distance between O\textsubscript{H\textsubscript{2}O}–O\textsubscript{surf} are 2.06 Å and 1.99 Å, respectively (see figure 8(a)). Based on charge density difference as depicted in figure 8(b), it is found that O\textsubscript{H\textsubscript{2}O} loses its electrons to the surface.

The origin of the strong bonding can be traced from the electronic structure. The presence of an oxygen vacancy defect on CuO(111) surface leads to electron deficiencies on the surface. It increases the local radical characteristic of the dangling bond on the surface. We could see it from LDOS plot of the system as given in figure 9. The LDOS are projected to O\textsubscript{H\textsubscript{2}O} p orbital, surface Cu d orbital and O\textsubscript{surf} p orbital. Unlike the case of adsorption on stoichiometric surface, the H\textsubscript{2}O molecular orbitals are largely shifted down albeit remain localized in energy. There is only a small amount of mixing with d-states that can be found on higher energy, close to the Fermi-level, as well as mixing on lower and higher energy that can be found with O\textsubscript{surf} p orbital. It suggests that the interaction is a radical type. The shifting down of H\textsubscript{2}O molecular orbitals corresponds to the stabilization interactions due to coupling with surface oxygen p orbital which is responsible for the strong adsorption. However, this type of stabilizing interaction usually results in a stronger adsorption molecular structural integrity. Indeed, considerably higher vibrational frequency of symmetric O–H stretching mode (table 4) as compared to the adsorption on stoichiometric surface (table 3) is found for this adsorption. The formation of new bonding state H\textsubscript{H\textsubscript{2}O}–O\textsubscript{H\textsubscript{2}O} in lower energy confirms the structural integrity of H\textsubscript{2}O and the reduction of bonding strength in H\textsubscript{2}O–O\textsubscript{H\textsubscript{2}O} on higher energy below Fermi-level is compensated by increasing the bonding overlap in H\textsubscript{H\textsubscript{2}O}–O\textsubscript{surf} (see figure 4 in ESI).

3.1.4. Adsorption on the oxygen-preadsorbed surface

Values of adsorption energy and some structural parameters of H\textsubscript{2}O adsorption on A, B and C sites on the oxygen-preadsorbed CuO(111) surface are listed on table 5. The configurations of each of those structures are shown in figure 10. The strongest adsorption is found on site C with adsorption energy of $-0.83 \text{eV}$ where H\textsubscript{2}O is adsorbed on Cu\textsubscript{sub}–Cu\textsubscript{sub} bridge. The shortest distance of O\textsubscript{H\textsubscript{2}O}–Cu\textsubscript{sub} and H\textsubscript{H\textsubscript{2}O}–O\textsubscript{pre} are 2.29 Å and 1.73 Å, respectively (see figure 11(a)). The two O–H bond lengths of H\textsubscript{2}O are 1.02 and 0.98 Å with H–O–H angle is 107.20°. Based on charge density difference as depicted in figure 11(b), it is found that O\textsubscript{H\textsubscript{2}O} loses its electron to the surface.

LDOS plot of the adsorption system is given in figure 12. The LDOS are projected on the p orbitals of O\textsubscript{H\textsubscript{2}O} and O\textsubscript{pre} atoms, and d orbital of Cu\textsubscript{sub}. The LDOS profiles share some similarities with the adsorption on stoichiometric surface such as the broadening of peak of H\textsubscript{2}O HOMO toward Fermi level and the splitting of the orbital into unoccupied state. It indicates that H\textsubscript{2}O molecule is adsorbed strongly enough and its O–H bond is weakened. This similarity can also be found in the magnitudes of vibrational frequencies of H\textsubscript{2}O shown in table 4 that comparably close to the ones for the case of adsorption in stoichiometric surface.

However, the presence of preadsorbed oxygen induced a new unoccupied state above the Fermi level, which will attract an electron donor, in this case, the H atom of the H\textsubscript{2}O adsorbate. Thus, it may interact with O\textsubscript{pre}, as indicated by the broadening of peak of H\textsubscript{2}O HOMO toward Fermi level and the splitting of the orbital into unoccupied state. This feature is found to be important in the H\textsubscript{2}O dissociation process described later. Based on COOP analysis, it appears that there is no bonding overlap between H\textsubscript{H\textsubscript{2}O} and O\textsubscript{pre}. This in turn indicates hydrogen bond or Coulombic interaction between them is dominant (see figure 4 in ESI).

Table 6 compares the results of this study with previous reports [14, 21, 22]. The discrepancies are mainly due to the

### Table 4. Vibrational frequencies of H\textsubscript{2}O adsorbed on the nonstoichiometric CuO(111) surfaces.

| No | Vibrational mode | H\textsubscript{2}O on CuO(111) + O\textsubscript{vac} (cm\textsuperscript{-1}) | H\textsubscript{2}O on CuO(111) + O\textsubscript{pre} (cm\textsuperscript{-1}) |
|----|-----------------|-------------------------------------------------|-------------------------------------------------|
| 1  | Sym             | 3433.60                                          | 2938.60                                          |
| 2  | Bend            | 1535.40                                          | 1544.90                                          |
| 3  | Anti-Sym        | 3631.40                                          | 3746.10                                          |

### Table 5. Adsorption energies and geometric parameters of the H\textsubscript{2}O adsorption configurations on the oxygen-preadsorbed CuO(111) surfaces.

| No | Conf. | Adsorption energy (eV) | d (O–H) (Å) | α (H–O–H) (°) |
|----|-------|------------------------|-------------|---------------|
| 1  | A     | 0.21                   | 0.99/0.98   | 102.70        |
| 2  | B     | −0.02                  | 1.01/0.98   | 103.60        |
| 3  | C     | −0.83                  | 1.02/0.98   | 107.20        |
different computational methods and adsorption models (such as H$_2$O coverage). Hu et al used an adsorption model with 1/4 ML coverage via the DFT + U method, whereas Zhang et al performed plain DFT at a coverage of 1/6 ML. The $E_{ads}$ magnitudes from these previous works are comparable with our results despite the higher adsorption coverage of our model (1/2 ML). Fronzi et al utilized DFT + U and a similar coverage but the exclusion of the dispersion correction is responsible for a difference of 0.2 eV with our results. Furthermore, all the calculations confirm that H$_2$O loses an electron, and the O–H bond on top of the CuO(1 1 1) surface is weakened.

3.2. H$_2$O dissociation on the stoichiometric and nonstoichiometric CuO(1 1 1) surfaces.

We proceed to study the dissociation reactions on the stoichiometric and nonstoichiometric surfaces similar to the case of adsorption. The structures for the initial (IS), transition (TS) and final state (FS) are shown in figure 13. The FS structure for reaction on the stoichiometric surface is obtained from relaxed co-adsorption of O and OH on O$_{sub}$ and Cu$_{sub}$–Cu$_{sub}$ bridge, respectively. In case of the oxygen vacancy defects, because the OH-dissociated product is assumed to fill the vacancy, its structure is obtained by relaxing two H atoms on top of two O$_{sub}$ sites of a stoichiometric surface. Finally, for the oxygen-preadsorbed case, the FS structure is obtained by relaxing two co-adsorbed OH on each Cu$_{sub}$ site, assuming that the dissociated H atom was attracted by the preadsorbed O atom to form OH.

The comparison for energetic of the reactions is shown in the energy diagram in figure 14. Dissociation on the stoichiometric and oxygen vacancy defects surface results in almost similar amount of activation energies of 0.18 eV and 0.17 eV. However, dissociation on the oxygen vacancy defect surface
is much more exothermic (\(−0.74\) eV) as compared to the stoichiometric surface (\(−0.29\) eV). The more exothermic reaction can be attributed to the larger stabilization of the FS due to the filling of the vacancy by the dissociated OH.

The smallest activation energy is observed for the oxygen-preadsorbed surface case; the barrier was only 0.04 eV, and the reaction was exothermic by \(−0.30\) eV. The presence of O atom on the surface is thus important in water dissociation on CuO(1 1 1) as also suggested by the interaction between O and \(\text{H}_{2}\text{O}\) in the adsorption phase. Nevertheless, if we include the activation energy for the formation of the oxygen-preadsorbed surface mentioned previously (0.12 eV), the total activation energy is 0.17 eV. This is very close with the activation energy for dissociation on the stoichiometric and oxygen vacancy defect surfaces.

Finally, the CuO(111) surface exhibits a strong catalytic activity for \(\text{H}_{2}\text{O}\) dissociation, with a considerably small activation barrier (<0.2 eV). The surface modification enhances the \(\text{H}_{2}\text{O}\) binding and improves the \(\text{H}_{2}\text{O}\) dissociation activity. Thermodynamically, the oxygen vacancy defect CuO(111) is the most favorable surface which will attract \(\text{H}_{2}\text{O}\) reactants effectively, thus ensuring the availability of reactants on the surface. Kinetically, the oxygen-preadsorbed CuO(111) act

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### Table 6. The direct comparison of the calculation results of this study and previous reports.

| No | Parameter                        | \(\text{H}_{2}\text{O}\) on stoichiometric | \(\text{H}_{2}\text{O}\) on nonstoichiometric |
|----|----------------------------------|------------------------------------------|---------------------------------------------|
|    |                                  | Adsorption energy (eV)                   | Oxygen vacancy                          | Oxygen-pre-adsorbed |
| 1  |                                  | −0.87<sup>a</sup>                       | −1.06<sup>a</sup>                       | −0.83<sup>a</sup> |
|    |                                  | −1.24<sup>b</sup>                       | −1.29<sup>c</sup>                       | −0.97<sup>c</sup> |
|    |                                  | −0.90<sup>c</sup>                       |                                          |                  |
|    |                                  | −0.61<sup>d</sup>                       |                                          |                  |
| 2  | Vibrational frequencies:         |                                          |                                          |                  |
|    | Sym (cm\(^{-1}\))               | 2922.70<sup>a</sup>                     | 3433.60<sup>a</sup>                     | 2938.60<sup>a</sup> |
|    |                                  | 3232.00<sup>a</sup>                     | 2944.00<sup>a</sup>                     | 3454.00<sup>a</sup> |
|    |                                  | 1577.80<sup>a</sup>                     | 1535.40<sup>a</sup>                     | 1544.90<sup>a</sup> |
|    |                                  | 1640.00<sup>a</sup>                     | 1576.00<sup>a</sup>                     | 1600.00<sup>a</sup> |
|    | Bend (cm\(^{-1}\))              | 3679.20<sup>a</sup>                     | 3631.40<sup>a</sup>                     | 3746.10<sup>a</sup> |
|    |                                  | 3636.00<sup>a</sup>                     | 37 180<sup>a</sup>                      | 3642.00<sup>a</sup> |
|    | Anti-sym (cm\(^{-1}\))          |                                          |                                          |                  |
|    |                                  |                                          |                                          |                  |

<sup>a</sup> This study.
<sup>b</sup> Hu <em>et al</em> [22].
<sup>c</sup> Zhang <em>et al</em> [31].
<sup>d</sup> Fronzi and Nolan [29].
as a promoter toward H$_2$O dissociation with the lowest activation barrier; however, it is less able to ensure the presence of H$_2$O on the surface. So we can expect that under surface equilibrium, the concentration of dissociated H$_2$O on the oxygen vacancy defect surface should be much higher than that of molecular H$_2$O, and its relative concentration should also be much higher than those on the other two types of investigated surfaces. Therefore, H$_2$O dissociation is expected to be most strongly promoted on the oxygen vacancy defect CuO(1 1 1) surface.

The effect of Hubbard $U$ parameter on energy preferences in H$_2$O dissociation on CuO(1 1 1) surfaces are examined by applying different U values. The different U values produce slightly different optimized geometric of IS and FS (see figures 5–7 in ESI). Furthermore, the different U also lead the different thermodynamics and kinetics of the reactions. In H$_2$O dissociation on the stoichiometric surface, the addition of U potential lowers activation barrier and changes thermodynamic of the reaction from endothermic at $U = 0$ eV (as obtained by Zhang et al [23]) to exothermic at $U = 4.5$ eV and $U = 7.0$ eV, whereas, on the nonstoichiometric surfaces the addition of U causes decrease in both activation and reaction energies, except for $U = 7.0$ eV on the oxygen vacancy defect surface due to significant difference of its IS geometric. If we compare between $U = 4.5$ eV and $U = 7.0$ eV, $U = 4.5$ eV is more effective in reducing activation barrier in the nonstoichiometric surface than $U = 7.0$ but vice versa on the stoichiometric surface. This result is slightly different from that obtained by Miamiati et al [27] which reported that Hubbard variation does not change energetic preferences in case of oxygen vacancy formation.

4. Conclusions

The dispersion-corrected Hubbard-corrected density functional theory is performed on H$_2$O adsorption and dissociation on the stoichiometric and nonstoichiometric CuO(1 1 1) surface. H$_2$O is favorably adsorbed on the top Cu$_{\text{buck}}$–Cu$_{\text{buck}}$ bridge in the stoichiometric and oxygen-preadsorbed surface and on the top of Cu$_{\text{buck}}$ (Cu$_{\text{top}}$) in the oxygen vacancy surface. Based on changes in OH bond length and angle distortion, we conclude that the adsorption of H$_2$O on the oxygen-preadsorbed CuO(1 1 1) surface leads to the weakening of OH bond more significantly as compared to H$_2$O adsorption on the stoichiometric and oxygen vacancy defect CuO(1 1 1). The H$_2$O molecule is strongly adsorbed on the oxygen vacancy defect surface with the adsorption energy of $-1.06$ eV, followed by the stoichiometric surface ($-0.87$ eV) and the oxygen-preadsorbed surface ($-0.83$ eV). Charge transfer occurs through electron transfer from the H$_2$O molecule to the CuO(1 1 1) surfaces. The dissociation of H$_2$O into OH and H species on CuO(1 1 1) surfaces are exothermic with the lowest reaction energy ($-0.74$ eV) is observed on the oxygen vacancy defect surface, followed by cases of the oxygen-preadsorbed surface ($-0.31$ eV) and stoichiometric surface ($-0.29$ eV). Surface modification of CuO(1 1 1) with the oxygen-preadsorbed significantly reduces the barrier energy of H$_2$O dissociation up to 0.04 eV as compared to the stoichiometric surface of 0.18 eV and the oxygen vacancy defect surface of 0.17 eV. These results indicate that CuO(1 1 1) surface exhibits a strong catalytic activity for H$_2$O dissociation and the surface modification of CuO(1 1 1) with the oxygen-preadsorbed significantly reduces the barrier energy of H$_2$O dissociation and with the oxygen vacancy defect can increase the reactivity of surface in H$_2$O adsorption.

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ORCID iDs

Faozam Ahmad https://orcid.org/0000-0001-6182-0780
Hermawan Kresno Dipojono https://orcid.org/0000-0002-1391-3533

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