



# Density Functional Theory Study of Water Adsorption on the CoO (100) and CoO (110) Surfaces

Salihah Azemi<sup>1</sup>, Khuzaimah Arifin<sup>2,\*</sup>, Rozan Mohamad Yunus<sup>2</sup>, Sharifah Najihah Timmiati<sup>2</sup>

<sup>1</sup>School of Applied Physics, Faculty of Science and Technology, Universiti Kebangsaan Malaysia 43600 UKM Bangi, Selangor, MALAYSIA

<sup>2</sup>Fuel Cell Institute, Universiti Kebangsaan Malaysia 43600 UKM Bangi, Selangor, MALAYSIA

\*Corresponding Author

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**Abstract:** In this study, density functional theory was used to identify the optimum adsorption sites of H<sub>2</sub>O molecule on the CoO(100) and CoO(110) surfaces. The adsorption of H<sub>2</sub>O molecule is the first step in water molecule splitting on a catalytic surface. CoO bulk crystals were optimised by using generalised gradient approximation-Perdew-Burke-Ernzerhof functional methods through spin orbital interaction calculations. Band structure calculation results show that the indirect and direct bandgaps are 0.23 and 1.6 eV, respectively, which are similar to the reported experimental bandgap. The CoO(100) and CoO(110) surfaces were created from the optimised bulk structure. The CoO(100) surface contains 13 atoms Co vacancy, whereas the CoO(110) surface contains 15 atoms Co vacancy on the top layer surfaces. The adsorption energy of H<sub>2</sub>O on the CoO(100) and CoO(110) surfaces was calculated on the basis of eight configurations. The optimum adsorption energy (5.123 eV) of H<sub>2</sub>O on the CoO(100) surface is in Model 5. Meanwhile, the optimum adsorption energy (2.810 eV) of H<sub>2</sub>O on the CoO (110) surface is in Model 6. This result indicates that H<sub>2</sub>O is easier to absorb on CoO(110) than on CoO(100), and agree to the experiment result reported.

**Keywords:** Cobalt oxide, band structure, PDOS, energy Adsorption

## 1. Introduction

Energy demand is increasing globally with the advances in technology and rising world population. Fossil fuels, including petroleum, coal and natural gas, which are the main current energy sources, are predicted to be exhausted in few years. In addition, the use of fossil fuels causes environmental pollution and triggers global warming because of carbon dioxide emissions. The need to tap alternative and renewable energy sources, including solar energy, wind, geothermal heat, tides, and biomass, is indispensable [1; 2]. The development of carbon-free energy from renewable sources has attracted the attention of researchers primarily because they are low cost and produce clean energy. Hydrogen gas has emerged as an alternative to fossil fuels with the development of fuel cell technology. Fuel cell produces clean and efficient energy, with pure water as a by-product; thus, it may solve global warming and climate change issues [3; 4].

Hydrogen is the most abundant element in the universe. However, hydrogen is rarely found in the form of gas (H<sub>2</sub>) on Earth. It bonds with elements such as water, hydrocarbons and organic matter. Photoelectrochemical water splitting is an environmental-friendly method for producing hydrogen gas and oxygen gas [5]. Over the last three decades, energy storage in chemical bonds has attracted attention as an efficient method [6]. The first report of water splitting

under sunlight was TiO<sub>2</sub> [7]. However, TiO<sub>2</sub> has a large band gap of 3.2 eV under ultraviolet irradiation, which only contributes 4% of the solar energy to reach Earth. In addition, 13.8% of solar energy cannot be used [8]. An ideal semiconductor photoelectrode for water splitting must have (i) an ideal semiconductor energy band gap to absorb sufficient solar energy (1.6 eV < E<sub>g</sub> < 2.2 eV), (ii) efficient light absorption, (iii) high electrical conductivity, (iv) high photoelectrochemical stability in electrolyte solution, (v) edge band gap structure that meets water redox potential criteria and (vi) high carrier mobility [9].

Metal oxide semiconductors have been widely studied for photoelectrochemical water splitting because they are cheaper and more environmentally friendly than other types of semiconductors [10; 11]. Metal oxide is selected as a photocatalytic because it is stable in aqueous solution and has a high photoactivity under visible light [11]. However, the weakness of metal oxide semiconductors is in their large energy gap (TiO<sub>2</sub> = 3.2eV, SnO<sub>2</sub> = 3.5 eV, KTaO<sub>3</sub> = 3.4 eV). In addition, it is only suitable for use in a limited range of ultraviolet wave spectrum. Hence, the production of metal oxide-based semiconductor electrodes with modified energy gap to absorb visible light is expected to be useful in photoelectrochemical water splitting. Recently, cobalt oxide (CoO) has been widely studied because of its many advantages, including its 5% efficiency in solar to hydrogen production, which is the highest efficiency of any single material for photoelectrochemical water splitting [12]. CoO has been reported in rock-salt cubic structure (space group Fm3hm) with octahedral Co<sup>2+</sup> atoms (Fig. 1a) [13]. Among the various surfaces of CoO, CoO(100) is reported as the most probable surface configuration for CoO (Fig. 1b-c).

In this study, we used density functional theory (DFT) methods to investigate the electronic structure and identify the stable adsorption sites of H<sub>2</sub>O molecule on the CoO(100) and CoO(110) surfaces. First-principle DFT calculation is commonly used to assess the properties of molecules and mechanisms on the catalyst surface. It is a reliable, fast and inexpensive technique [14; 15]. The adsorption of H<sub>2</sub>O molecule is the first step in water molecule splitting process. In a catalytic process, a model with absorption energy in the middle among other models is the most preferable model. The highest absorption energy means the H<sub>2</sub>O weakly absorbed and there is not enough interaction with the catalyst surface. While the smallest absorption energy means H<sub>2</sub>O adsorbed strongly on the catalyst surface, causing it difficult to continue the catalytic process.[16].

## 2 Computational Methodology

First-principles calculations were performed based on DFT implemented in The CASTEP module from Biovia Material Studio 2016 software package. Exchange correlation by using the functional of generalised gradient approximation (GGA) with the level theory of the Perdew–Burke–Ernzerhof functional (PBE) was employed for electron–electron interactions [17]. Calculations were spin-polarised using an ultrasoft pseudo-potential. In these calculations, a plane-wave cutoff energy of 340 eV was used. The Monkhorst–Pack grid size for the self-consistent field calculation was 6x6x6. The rock-salt CoO structure was obtained from the Crystallography Open Database (CID No 1000053.cif); the structure of magnesium oxide was changed to CoO. The corresponding optimised crystal structures were used to develop the CoO (100) and CoO(110) surfaces. The vacuum slab layer thickness of the surfaces was set to 15 Å for the structural relaxations of the slabs.

The adsorption energy of H<sub>2</sub>O on the CoO (100) and CoO (110) surfaces was calculated based on eight configurations to identify the optimum sites of H<sub>2</sub>O on the CoO surfaces. The adsorption energy of molecules in different adsorption sites was calculated using the equation (1):

$$E_{\text{ads}} = E_{\text{(molecule on surface)}} - E_{\text{(surface)}} - E_{\text{(molecule)}} \quad (1)$$

where E (molecule on surface) is the total energy of H<sub>2</sub>O adsorbed on the CoO surface, and E(surface) and E(molecule) are the formation energies of the CoO surface and H<sub>2</sub>O molecule, respectively.

## 3. Results and Discussions

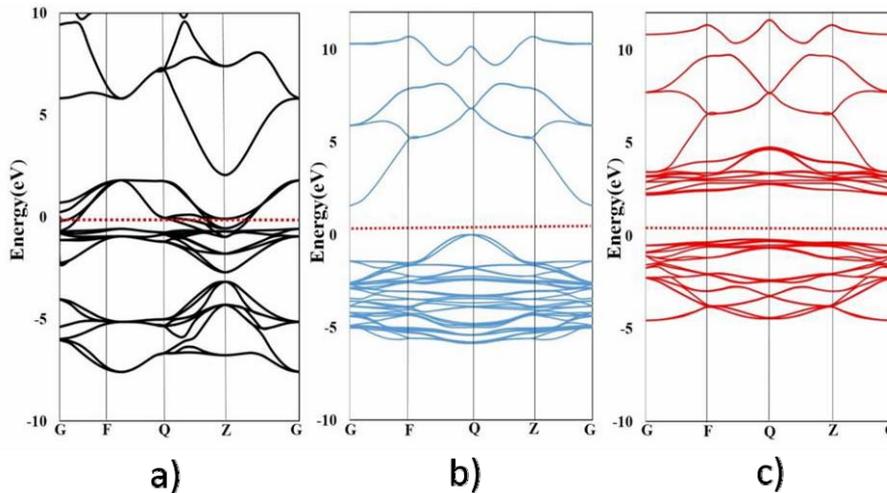
### 3.1 Optimization of CoO and H<sub>2</sub>O structures

All lattice and bonding parameters between cobalt and oxygen atoms, Co-O for CoO bulk, using different methods are given in Table 1. The GGA–PBE method provides a lattice parameter of 4.27387 Å with a deviation value of 0.16% to the experimental value of 4.26 Å [18]. Furthermore, the calculation of bonding between Co-O atoms is 2.137 Å, which is closer to the experimental value of 2.133 Å. The deviation value is 0.19% with a bonding error of 0.0004 Å.

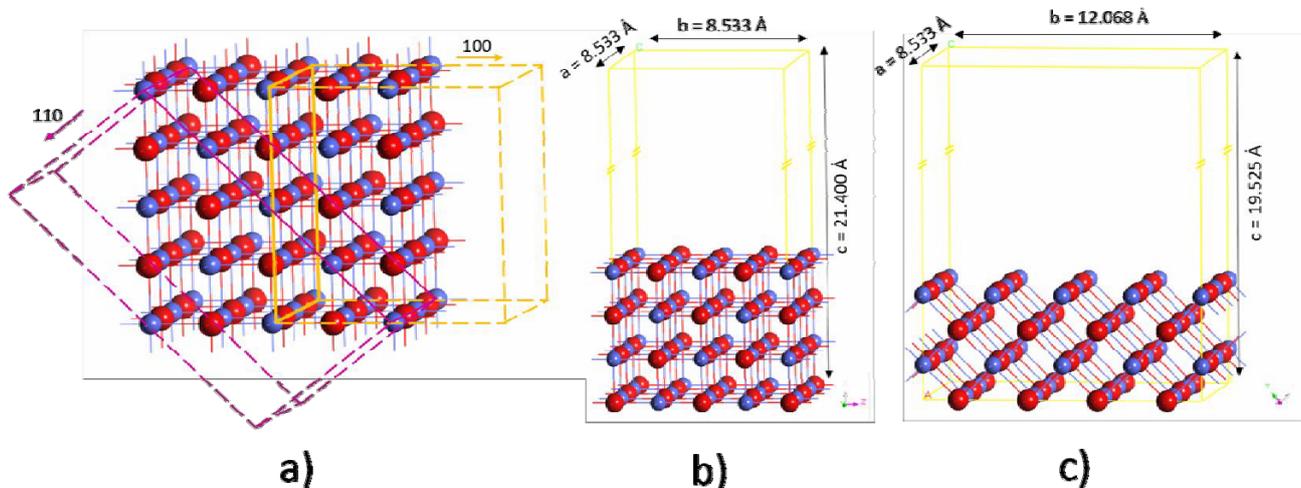
**Table 1 - Lattice parameters of optimised CoO bulk**

		Experimen (Å)	GGA-PBE Value (Å)	Deviation value (%)
Lattice Parameter (Å)	a=b=c	4.274	4.27387	0.
Bonding between atom (Å)	Co-O	2.133	2.137	0.19

Fig. 1(a) shows the calculated band structure of pure CoO without spin orbit interactions, which shows metallic properties. The band structure is similar with reported by many researcher [19-21]. Figs. 1(b) and (c) show the calculated band structures considering spin orbital interactions and the band structures of alpha- and beta-cobalt oxide. The different alpha and beta phases may confirm the magnetic properties of CoO. The spin orbital interactions calculation shows that CoO has indirect and direct bandgaps, which are 0.23 and 1.55 eV, respectively, which are similar to the reported experimental bandgap [22].



**Fig.1 - Calculated band structure of pure CoO (a) without spin polarization, (b-c) with spin polarization and (c) partial density of state**



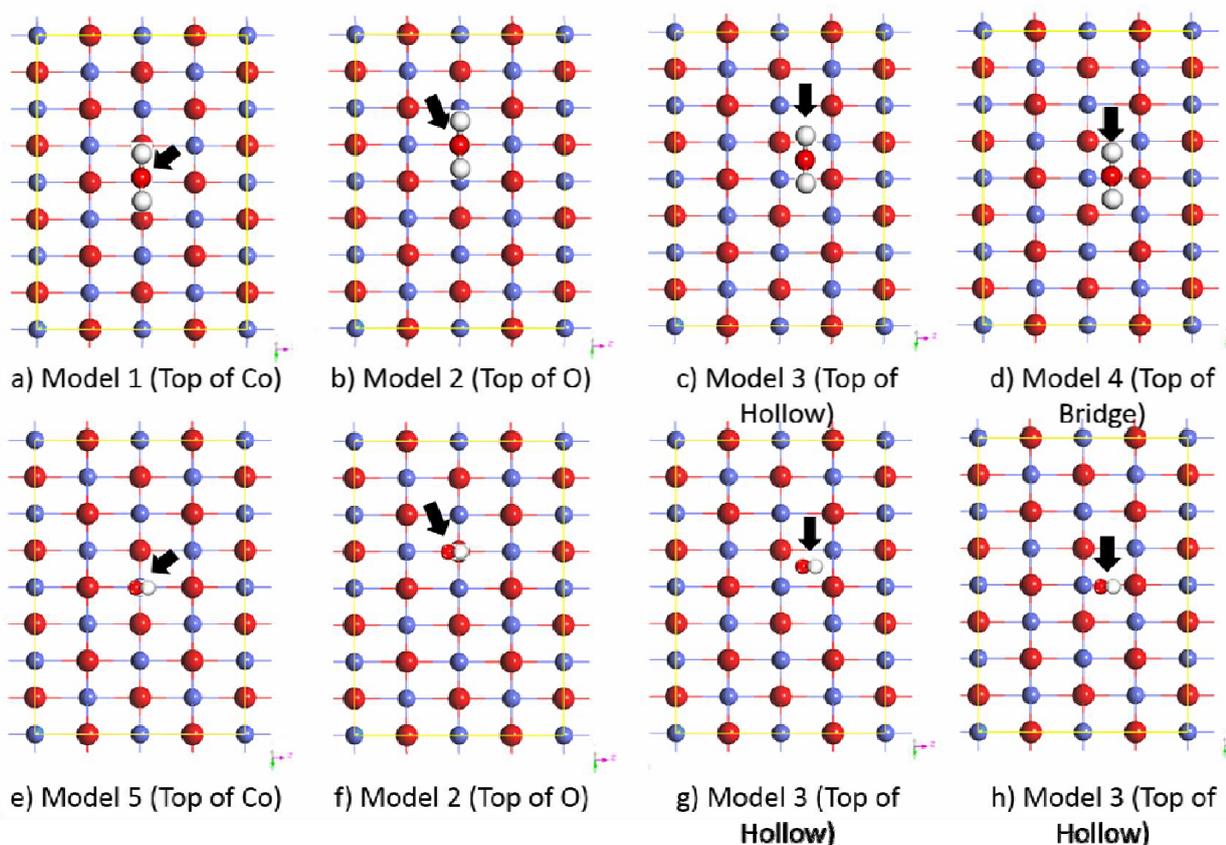
**Fig. 2 - (a) Crystal structure of CoO bulk (Blue: cobalt, Red: oxygen), (b) CoO (100) and (c) CoO (110)**

The CoO (100) and CoO (110) surfaces were created from the 2x2x2 optimized bulk structure. Fig. 2 is the optimized structures of CoO (100) and CoO (110) surfaces, where the CoO (100) has lattice size  $a = b$ , and the atoms position are perpendicular each layer. Meanwhile, CoO (110) surface has lattice size  $a \neq b$  and produce zig-zag layer configuration. From Fig 2, clearly shows that CoO (110) surface has larger compared to the CoO (100) surface in which the CoO (100) surface contains 13 atoms Co atoms at the top layer surfaces, whereas the CoO (110) surface contains 15 atoms Co. However, CoO (100) layer was thicker compared to CoO (110) layer.

### 3.2 Energy Adsorption of water molecule

The water molecule was utilised with the optimum configuration at the adsorption site, such as on top, bridges and along the Co and O atoms to obtain an overview of the nature of the interaction. Fig. 3 shows eight configurations of H<sub>2</sub>O adsorption positions on CoO (100) and CoO (110) that have been investigated using DFT. Figs. 3(a) to 3(d) represent the H<sub>2</sub>O adsorption model on the surface of CoO (110) over the Co and O atoms at Co-O holes and bridge,

respectively. The H<sub>2</sub>O is adsorbed at horizontal position (Fig.4). Meanwhile, Figs. 3(e) to 3(g) show H<sub>2</sub>O molecule at vertical position (Fig. 4). The distance between H<sub>2</sub>O and CoO (100) surface was set to 3.0 Å (Figs. 4). This distance is considered to have an interaction between the H<sub>2</sub>O adsorption and the selected CoO surfaces.



**Fig. 3 - H<sub>2</sub>O adsorption on CoO surface**

Table 3 shows a summary of the H<sub>2</sub>O adsorption on CoO(100). On the basis of the data obtained, the adsorption energies calculated on Model 1, Model 2, Model 3, Model 4, Model 5, Model 6, Model 7 and Model 8 are 5.188, 6.039, 5.729, 5.094, 5.123, 5.691, 5.094 and 5.096 eV, respectively. In a catalytic process, a model with absorption energy in the middle among other models is the most preferable model. The highest absorption energy means the H<sub>2</sub>O weakly absorbed and there is not enough interaction with the catalyst surface. While the smallest absorption energy means H<sub>2</sub>O adsorbed strongly on the catalyst surface, causing it difficult to continue the catalytic process. The H<sub>2</sub>O adsorption energy over the CoO (100) surface has an optimum value of 5.123 eV in Model 5, where the H<sub>2</sub>O position on top of Co atom. This value is taken based on the intermediate energy among them. The other reason is because the adsorption of H<sub>2</sub>O on the site of atom at Co is stronger than at other sites owing to the stable Co<sup>2+</sup> ion structure on the CoO(100) surface. The adsorption on the surface of the holes and bridges causes the H<sub>2</sub>O molecule to move toward the site that contains atoms for optimum energy adsorption. In general, the closer the energy to the d-line at Fermi level, the stronger the binding to the surface [23].

Therefore, adsorption of the H<sub>2</sub>O molecule at the Model 5 site is optimum compared with other models because the bond between the molecules and the surface is the most optimum and easy for water splitting. At the same time, the H<sub>2</sub>O adsorption at the Model 2 site is the least optimum because of the high adsorption energy of 6.039 eV because the distance between H<sub>2</sub>O bonding and surface is too large and causes difficulty for H<sub>2</sub>O to decompose. Table 4 shows a summary of the H<sub>2</sub>O adsorption energy on the CoO (110) surface.

On the basis of the data obtained, the adsorption energies calculated on Model 1, Model 2, Model 3, Model 4, Model 5, Model 6, Model 7 and Model 8 are -2.708, -3.013, -3.006, 3.176, 3.329, 2.810, 2.812 and 3.296 eV, respectively. The H<sub>2</sub>O adsorption energy over the CoO surface (110) has an intermediate value of 2.810 eV in Model 6. Therefore, Model 6 has the most optimum adsorption energy. This value is chosen because it is the optimum energy for H<sub>2</sub>O bonds to decompose during water splitting. The adsorption energy values are not too large and not too small. If the adsorption energy is too low, H<sub>2</sub>O is difficult to decompose, and vice versa. Therefore, the optimum adsorption energy is at the Model 6 site. This result indicates that H<sub>2</sub>O easier to absorb on CoO (110) than on CoO(100).

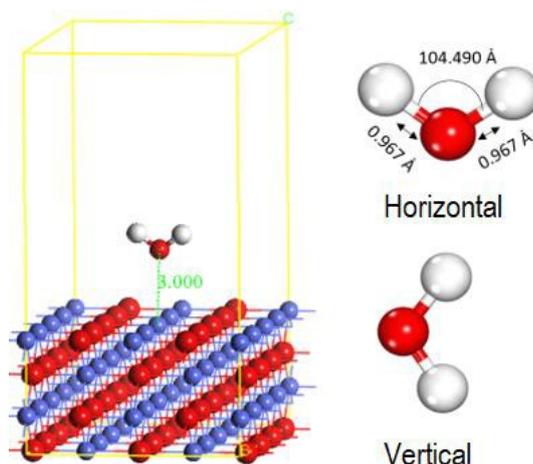


Fig. 4 - Side view of H<sub>2</sub>O adsorption on CoO surface before optimization step

Table 3 - Summary of calculations of CoO (100) adsorption energy.

Model	H <sub>2</sub> O distance with surface (Å)	Energy Adsorption (eV)
Model 1	2.0	5.1
Model 2	2.9	6.0
Model 3	2.1	5.7
Model 4	1.9	5.0
Model 5	2.0	5.1
Model 6	2.6	5.6
Model 7	1.9	5.0
Model 8	2.0	5.0

Table 4 - Summary of calculations of CoO adsorption energy (110).

Model	H <sub>2</sub> O distance with surface (Å)	Energy Adsorption (eV)
Model 1	1.6	-2.708
Model 2	1.5	-3.013
Model 3	1.5	-3.006
Model 4	1.9	3.1
Model 5	1.9	3.3
Model 6	1.6	2.8
Model 7	1.7	2.8
Model 8	1.9	3.2

#### 4. Conclusion

This study was successful built CoO(100) and CoO(110) surfaces and determined the H<sub>2</sub>O adsorption energy on the surfaces by using a DFT calculation method. The surface of CoO(100) has planar atoms configuration, while the CoO(110) surface has zig-zag atoms configuration. The surface area of CoO(110) was found larger than the CoO(100) surface. The H<sub>2</sub>O adsorption energy calculated on both surfaces on basis of eight models. On the CoO(100) surface, the optimum adsorption energy was found at Model 5, in which the H<sub>2</sub>O placed vertically on top of Co atom. The calculated value is 5.123 eV. Meanwhile, the optimum H<sub>2</sub>O adsorption energy on the CoO(110) surface was found at Model 6, where the H<sub>2</sub>O placed horizontally on top of O atom. The calculated value is 2.810 eV. The optimum adsorption energy of H<sub>2</sub>O on CoO(110) was found smaller than H<sub>2</sub>O on CoO(100). It indicates that H<sub>2</sub>O is easier to adsorb on CoO(110) rather than on CoO(100). However, these promising results require further experimental confirmation.

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