Density Functional Theory Study on the Electronic Properties of Doped-Cobalt Oxide (CoO)

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ABSTRACT

Cobalt oxide (CoO) has been widely studied for photocatalyst of water splitting and displaying a high-efficiency material. This paper reports a Density Functional Theory (DFT) study on the electronic properties of rock-salt CoO and analyzes effects of cations (Ni and Fe) and anions (N and F) dopants on the electronic properties. For this purpose, CASTEP software used for first principles plane-wave pseudo-potential calculations at different functional, i.e: GGA-PW91 and LDA. The electronic calculations of the CoO optimized structure showed a metallic structure if without considering spin-orbital interactions. After considering the spin-orbital interaction calculation, the CoO band structure possessed indirect and direct band gaps. The direct bandgap by GGA-PW91 calculation is 2.10 eV, it was agreed to the experimentally reported value of approximately 1.9-2.6 eV. Meanwhile, Ni, Fe, and F-doped CoO, demonstrating decreased CoO direct band gaps to 1.70 eV, 1.80 eV, and 1.73 eV, respectively. While N-doped CoO increased the CoO direct bandgap to 3.05 eV. All dopants shifted the conduction and valence bands position, where Ni-doped CoO band edges keep straddle to the redox potential of water splitting. Among other elements in this study, Ni is a more desirable dopant of CoO to enhance photoelectrochemical hydrogen production.

Keywords: Density Functional Theory; Cobalt oxide; photoelectrochemical; hydrogen production; bandgap

ABSTRAK

Kobalt oksida (CoO) telah dikaji secara meluas untuk fotomangkin pembelahan molekul air dan menunjukkan kecekapan bahan yang tinggi. Kertas ini melaporkan kajian teori fungsi ketumpatan (DFT) untuk menganalisis sifat-sifat elektronik CoO-garam batu dan kesan pendopan kation (Ni dan Fe) dan anion (N dan F) pada sifat elektronik CoO. Untuk tujuan ini, perisian CASTEP telah digunakan dengan kaedah plane-wave pseudo-potential pada fungsian berbeza, iaitu: GGA-PW91 dan LDA. Pengiraan elektronik menunjukkan bahawa struktur CoO yang telah dioptimal menunjukkan sifat magnet apabila tanpa mengambil kira interaksi orbital spin. Apabila interaksi orbital spin digunakan, CoO tulen mempunyai jurang jalur tidak langsung dan langsung. Jurang jalur langsung dari hasil pengiraan GGA-PW91 adalah 2.10 eV sesuai dengan nilai yang dilaporkan secara eksperimen kira-kira 1.9-2.6 eV. CoO yang di dop dengan Ni, Fe dan F menunjukkan penurunan jurang jalur langsung CoO masing-masing kepada 1.70 eV, 1.80 eV dan 1.73 eV. Sementara N-doped CoO meningkatkan jurang jalur langsung CoO kepada 3.05 eV. Semua dopan mengalihkan kedudukan jalur pengaliran dan valence, di mana tepi jalur CoO yang didop dengan Ni kekal menjangkang keupayaan redoks pembelahan molekul air. Di antara elemen pendopan dalam kajian ini, Ni adalah element dop terbaik bagi CoO untuk meningkatkan pengeluaran hidrogen fotoelektrik kimia.

Kata kunci: Teori Fungsian Ketumpatan; kobalt oksida; photoelektrokimia; penghasilan hidrogen; jurang jalur

INTRODUCTION

Nowadays, electrical energy derived from the conversion of chemical energy mostly is based-on fossil fuels, in which the resources are non-renewable and depleting progressively. In addition, the combustion of fossil fuel releases CO_2 that causes global warming. Hydrogen has been considered as an ideal future energy carrier to replace fossil fuels. Phoelectrochemical (PEC) water splitting using direct solar energy is envisioned to be the most prospective method to produce hydrogen, in which the main components, i.e. water and sunlight are abundant and available

everywhere (Salehmin et al. 2019). The PEC cell need a semiconductor material as a photoelectrode. However, most of semiconductor material like TiO$_2$ has wide bandgap and limits its optical absorption in the ultraviolet (UV) spectrum (Adnan et al. 2018). Recently, Cobalt oxide (CoO) has been widely studied due to its many advantages, such as high efficiency of solar to hydrogen (STH) production, stable in acid environment, etc (Moridon et al. 2019; Yusof et al. 2018). However, pure CoO, which has a bandgap of 2.0 to 3.0 eV, does not absorb visible light very well and only becomes excited under UV-light irradiation (Zhou et al. 2010). Additionally, the excited charge carriers in CoO recombine quickly and only a small fraction of the excited carriers are transferred to the CoO surface and participate in the subsequent photocatalytic process (Wdowik&Legut 2008).

CoO has been reported in several structural forms, such as rock salt, wurtzite and zinc blende. The rock-salt cubic structure (space group Fm3hm) with octahedral Co^{2+} atoms is the most stable phase of CoO (Liu et al. 2015; Wdowik & Legut 2008; Youmbi & Calvayrac 2014). Based on a previous study, CoO is also known to possess magnetism properties as a charge-transfer antiferromagnetic (AFM) insulator (Wdowik&Parlinski 2008). However, CoO exhibits type II AFM ordering (AFII) when below the respective Neel temperature (TN). In addition, the magnetic cell is twice as large as the crystallographic unit cell because the spin-up and spin-down Co ions constitute two magnetic sub lattices (Wdowik&Parlinski 2008). Interestingly, most computational studies have shown that CoO is an AFM material with a metallic band structure (Dalverny et al. 2010; Yin et al. 2014). In this paper, we focus on modify the CoO electronic structure by doping with other elements. Doping is a fundamental method used to stabilize specific crystallographic phases, modify electronic properties, and tune absorption properties (Gao et al. 2016; Nguyen et al. 2017). Computational studies based on density functional

theory (DFT) was used to investigate the molecular band structure of CoO and the effects of Nickel (Ni), iron (Fe), nitrogen (N) and fluorine (F) elements doping on the band structure. Computational investigations have received substantial attention in materials science and chemistry to predict and understand the relationships of the band structures of materials with their properties and behaviors (Moridon et al. 2018). Computational study has the advantages of cost-effectiveness due to limited use of materials and chemicals and reduced time requirements for experimental screening, thus improving efficiency and overcoming difficult problems in materials exploration (Arifin, Daud, et al. 2014; Arifin, Minggu, et al. 2014).

COMPUTATIONAL METHOD

The CASTEP module from Biovia Material Studio 2016 software package was used to perform DFT calculations on electronic structures. The rock-salt CoO cubic structure (symmetry group of Fm3m) was obtained from the Crystallography Open Database (CID No 1000053.cif); the structure of magnesium oxide was changed to CoO (Wdowik&Parlinski 2008). Calculations were performed using various DFT functions, such as local density approximation - Ceperley–Alder–Perdew–Zunger (LDA-CAPZ) and generalized gradient approximation (GGA) with the level theory Pardew-Wang 1991 (GGA-PW91). In these calculations, Ultrasoft pseudopotential with 489 eV energy cutoff was used. The k points set use a custom grid parameters with the Monkhorst-Pack (MP) grid size of 6x6x6. The cell contained 14 cobalt and 13 oxygen atoms, as shown in Figure 1. The Ni and Fe dopants were substituted at two Co sites labeled with a yellow color, while N and F dopants were substituted at O atom in the center. The corresponding optimized crystal structures, electronic structures and optical properties were calculated.

TABLE 1. Optimization results of rock-salt CoO

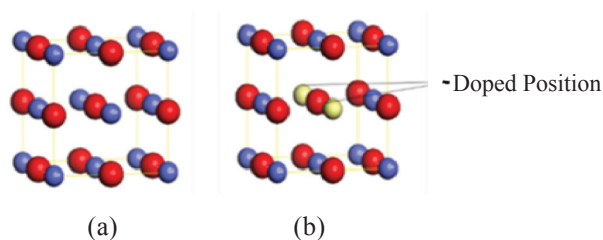|	Dirent Band gap (eV)	Conduction band CB(eV)	Valence band VB(eV)	Lattice constant (A)
CoO				
LDA – CAPZ	3.10	-0.35	2.75	a=b=c=4.24
GGA-PW91	2.10	-0.05	2.05	a=b=c= 4.29
Experiments (Moridon et al. 2019; Zhan et al. 2014)	1.90	-	-	a=b=c=4.27
Doped-CoO (GGA- PW91)				
Ni-doped	1.70	-0.10	1.60	a=b=c= 4.18
Fe-doped	1.80	0.05	1.85	a=b=c= 4.35
N-doped	3.05	0.10	3.15	a=b=c= 4.41
F-doped	1.73	0.05	1.78	a=b=c= 4.21

FIGURE 1. CoO models: (a) undoped CoO and (b) doped CoO

RESULTS AND DISCUSSION

ELECTRONIC PROPERTIES OF PURE COO

The Cobalt oxide (CoO) model initially has a space group of Fm3m and an NaCl cubic type of structure, as shown in Figure 1. CoO crystallizes in a conventional cubic cell with a lattice constant a=b=c: 4.271 and shows a type II AFM ground state. In this work, crystal geometry optimization was performed to select suitable functions of the CASTEP module for CoO calculations. The optimization results are listed in Table 1. The calculated CoO produced a structure with a lattice constant 4. 29 Å for GGA–PW91 method and 4. 24 Å for *LDA–CAPZ* method. The deviation of the lattice to the experiment value is 0.047% and 0.7%, respectively. Furthermore, the calculations bandgap of the CoO were 3.10 eV and 2.10 eV for LDA − CAPZ and GGA– PW91 methods. Meanwhile, the reported band gap experiment for the CoO is around 1.90 eV. Based on the lattice parameter and bandgap calculation results, GGA-PW91 was the most suitable method compared to the experiment result (Moridon et al. 2019).

Figure 2a shows the calculated band structure of pure CoO, which clearly shows that CoO has direct and indirect bandgaps, which is suitable with the experimentally results (Gao et al. 2016). However, here, the discussion will focus only to the direct bandgap of each models. Pure CoO has direct bandgaps of 2.10 eV, in which the valence band (VB) and conduction band (CB) positions were straddle to
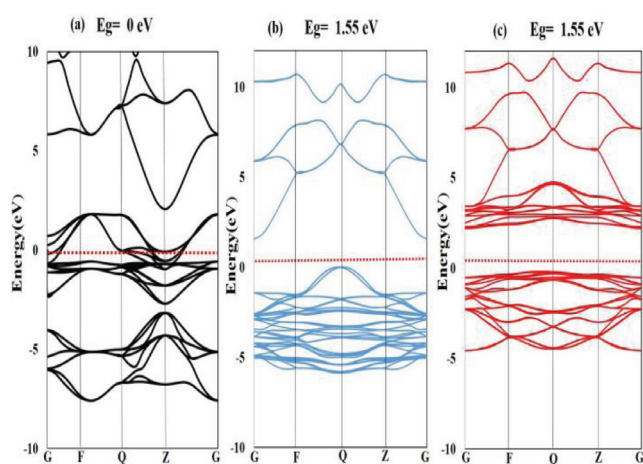

FIGURE 2. The calculated band structure of pure CoO by using GGA-PBE (a) without spin polarization, (b) with spin polarization alpha (c) spin polarization beta
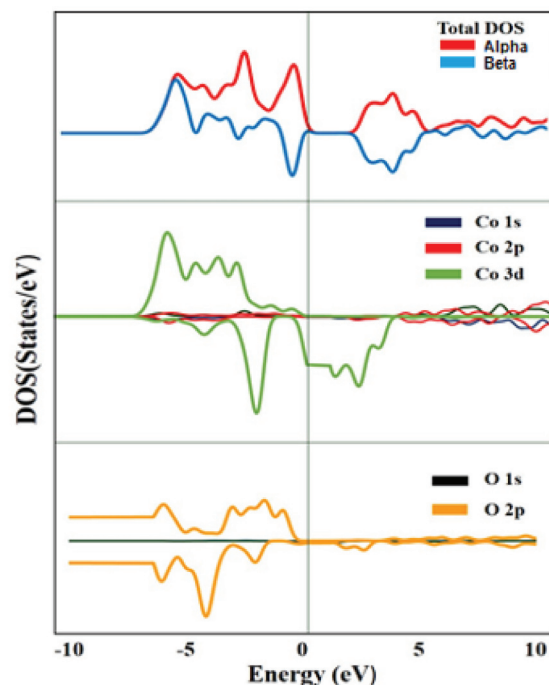

FIGURE 3. Partial density of state (PDOS) of CoO

redox potential of water splitting, which is fulfill the main criteria of material for photoelectrode in PEC water splitting application. According to a few researchers, CoO shows a metallic band structure if the calculation does not include spin–orbit interactions (Gillen & Robertson 2013; Yin et al. 2014). Figure 2a shows the calculated band structure of pure CoO without spin orbit interactions, which shows metallic properties. Figure 2a clearly shows that the calculated band gap is 0 eV because CoO is a magnetic material. Figure 2b and c show the calculated band structures considering spin orbital interactions and the band structures of alpha- and beta-cobalt oxide. The band structure reflects a 1.55 eV band gap. The alpha and beta phases may confirm the magnetic properties of CoO. The alpha and beta phases are the spin states of cobalt, representing +1/2 (alpha) and -1/2 (beta), which are influenced by the valence state and coordination number. Cobalt ions demonstrate dissimilar functions in their different valence states.

As an example, a Co^{2+} ion in its high-spin state can form a small polar force because an electron is easily localized on the surface and can create a small amount of energy for transfer to the conduction band (CB). Due to limited energy, Co^{2+} was difficult to excite to the high-spin Co^{3+}, causing the pure Co^{2+} oxides of CoO to be magnetic insulators. Figure 3 shows the partial density of state (PDOS) of CoO, again confirming that CoO exhibits the 2p and Co 3d states for the valence band (VB), while the CB derives from the Co 3d state. The O 2p state overlapped with the Co 3d state near the Fermi level, indicating a strong exchange interaction. The strong exchange interaction between Co and O contributes to the AFM ordering of CoO.
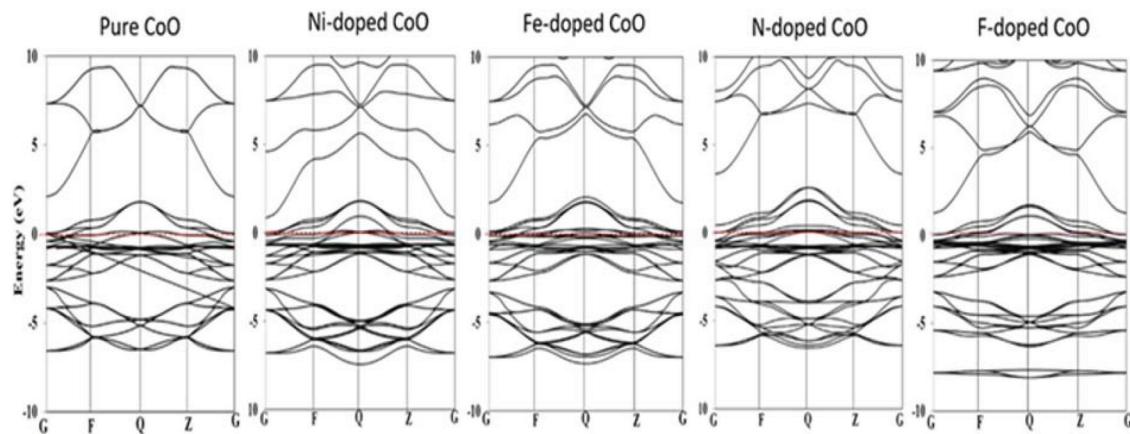
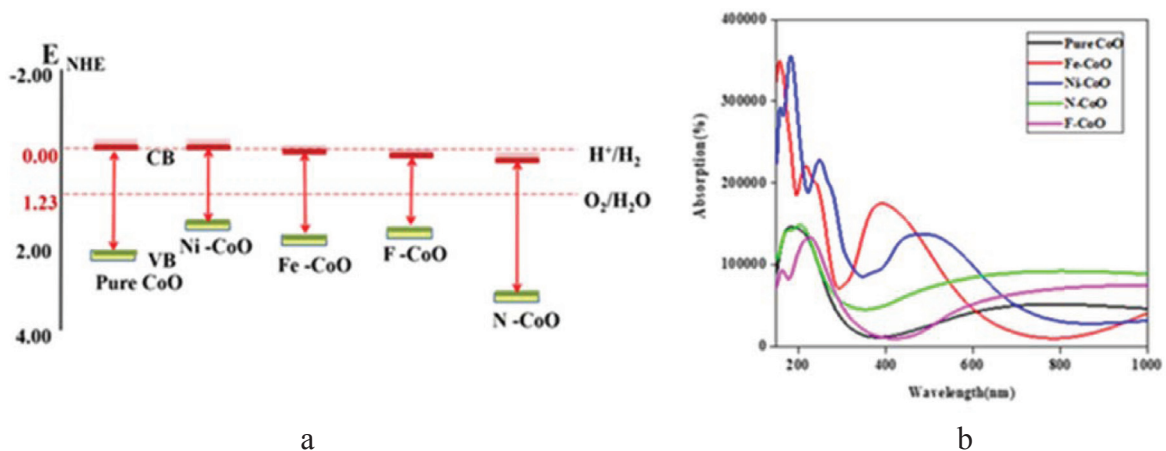FIGURE 4. The calculated band structure of pure and doped CoO by using GGA-PW91

a   b

FIGURE 5. Band alignment of CoO and doped CoO against to water redox potential (a) and optical properties
of CoO and doped CoO

ELECTRONIC PROPERTIES OF DOPED CoO

In this study, the effects of cation and anion doping on the electronic structure and photocatalytic activity of CoO were investigated. Figure 4 shows the band gap shift upon doping the CoO structure with Ni, Fe, N and F elements. According to previous reports, cations can modify the CB edge due to their different atomic d-orbital energies compared with those of Co. The electron transition energy change reduces the band gap compared to that of pure CoO (Zhang et al. 2016). The band gap of undoped CoO was calculated to be approximately 2.10 eV. The calculations indicated that the band gap changed after doping, which induced widened and improved band gaps for PEC water splitting. According to Kiraly et al. 2017, the addition of acceptor impurities contributes to hole levels at low energy in the semiconductor band gap, allowing electrons to be easily excited from the VB into these levels and thus leaving mobile holes in the VB. These holes shift the effective Fermi level to a point approximately halfway between the acceptor levels and the VB (Kiraly et al. 2017; Kriegel et al. 2017).

RELATIONSHIPS OF THE ELECTRONIC PROPERTIES OF PURE AND DOPED COO WITH PEC WATER SPLITTING ENERGIES

To design an efficient photo catalyst for PEC water splitting to produce hydrogen, a few characteristics should be considered, such as band structure, band energy and absorption of the photo catalyst. However, fabrication of semiconductor composites and substitution of impurities to achieve extended absorbance are also important. First, for the band structure, along with a suitable band gap in the range of 1.23 eV-2.00 eV, suitable band-edge positions (CB and VB) with respect to the water redox potentials (the H_2O/H_2 couple and H_2O/O_2 couple) are important to achieve efficient PEC water splitting (Figure 5a). Pure CoO showed a band gap of 2.10 eV with a VB at 2.05 eV lower than the water oxidation potential and a CB of 0.05 eV, which is close to the hydrogen reduction potential, resulting in a band alignment of CoO straddling the threshold for water splitting. Ni-doped CoO resulting a bandgap of 1.70 eV with VB decrease compared with pure-CoO without changing CB position. Furthermore, a bandgap of 1.83 was obtain by Fe-doped CoO, with VB position at 1.80 eV while the CB slightly below potential reduction of water. While F-doped

CoO resulting similar result with Fe-doped CoO with bandgap of 1.80 eV. Contrastly, N-doped CoO showing a wider bandgap compared pure CoO, where CB decrease about 0.05 eV below reduction potential of water, while the VB also increase up to 3.15eV. In addition, for optical absorption, the semiconducting nanoparticles should be exposed to incident UV-visible photons in the wavelength range of 200-800 nm. In this analysis, showed that pure and doped CoO were absorb in UV-vis wavelength range. Ni, Fe and F doping of CoO extend the absorption of light to wider wavelength. While N doped CoO was slightly shifted the absorption peak position as shown in Figure 5b. We can conclude that Ni potentially to transform pure CoO band structure into a more favorable photocatalyst for PEC water splitting and enhance the PEC hydrogen production of CoO. Furthermore, lab experimental is needed to prove the DFT calculation results.

CONCLUSION

Calculations based on the first-principles DFT reveal the strong crystallographic phase dependence of the photocatalytic activity. The present study was designed to determine the electronic properties of pure CoO and the effects of Ni, Fe, N and F monodoping on the electronic structure of CoO. These calculations confirmed that the band gap of CoO changed after doping. The direct band gap of undoped CoO was 2.10 eV, which changed to 1.70 eV, 1.80 eV and 1.73 eV when doped with Ni, Fe and F, respectively. Based on the electronic properties calculated from CASTEP, Ni more desirable dopant to enhance the photoelectrochemical hydrogen production of CoO.

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