

Experimental and Theoretical Study of Cu₂O Photoelectrode and Cu₂O Doped with Ag, Co, Ni and Zn Metals for Water Splitting Application

(Kajian Secara Eksperimental dan Teori Mengenai Fotoelektrod Cu₂O dan Cu₂O Didop Logam Ag, Co, Ni dan Zn untuk Aplikasi Pembelahan Molekul Air)

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ABSTRACT

In the present study, cuprous oxide nanowire fabricated using wet chemical oxidation method was proven to produce high photoactive film for photoelectrochemical (PEC) water splitting. A relatively high photocurrent density of -5mA cm^{-2} at 0.6V vs Ag/AgCl was generated. The PEC performance is the reflection of intrinsic light absorption capacity at visible region which correspond to 2.0eV , an ideal band gap for PEC water splitting. Comparison with calculated data based on density functional theory using CASTEP shows that the band gap and light absorption capacity obtained from experimental work exhibited a close match. Hence, this study suggested that the preparation of Cu₂O thin film via wet chemical oxidation method obeyed the theoretical prediction. However, the Cu₂O is limited with poor stability in PEC condition attributed to the insufficient potential of its valence band to oxidize water. Therefore, an effort was directed to address the feasibility of shifting the valence band by modeling a doped Cu₂O with several dopants using DFT technique. The selected dopants were Ag, Co, Ni and Zn. Preliminary conclusion of this study indicated that doping could be used to tune the band gap of Cu₂O due to ionic radii of the dopant affected the shifting of band gap. In this study, Co showed more significant improvement of Cu₂O for photoelectrochemical water splitting process. However, to validate the simulation, further study should be carried out experimentally.

Keywords: Copper Oxide; Chemical oxidation; band structure; Photo electrochemical; Hydrogen production

ABSTRAK

Kuprous oksida telah dihasilkan dengan menggunakan kaedah pengoksidaan kimia basah dan terbukti menghasilkan filem fotoaktif yang tinggi untuk pembelahan molekul air secara fotoelectrochemical (PEC). Dalam kajian ini, ketumpatan fotostatat tinggi -5mA cm^{-2} pada 0.6V vs Ag/AgCl dihasilkan. Prestasi PEC tinggi ini adalah pantulan keupayaan penyerapan cahaya intrinsik di rantau yang kelihatan sesuai dengan 2.0eV , jurang band yang ideal untuk pemisahan air PEC. Berbanding dengan data yang dikira berdasarkan teori fungsian ketumpatan menggunakan CASTEP, jalur jurang dan kapasiti penyerapan cahaya yang diperolehi daripada kerja eksperimen menunjukkan hasil yang hampir sama. Oleh itu, kajian ini mencadangkan bahawa penyediaan filem nipis Cu₂O melalui kaedah pengoksidaan kimia basah mematuhi ramalan teoritis. Walau bagaimanapun, Cu₂O adalah terhad dengan kestabilan miskin dalam keadaan PEC disebabkan oleh potensi yang tidak mencukupi bagi jalur valensinya untuk mengoksidasi air. Usaha seterusnya telah diarahkan untuk menangani kelayakan mengalihkan band valensi dengan memodelkan Cu₂O yang doped dengan beberapa dopan menggunakan teknik DFT. Dopan yang dipilih ialah Ag, Co, Ni dan Zn. Dalam mencari pemahaman tentang bagaimana doping dapat digunakan untuk menyesuaikan jalur jurang Cu₂O kita dapat menyimpulkan radius ion dopan mempengaruhi peralihan jalur jurang. Kajian ini berjaya mengkaji dopan yang dapat meningkatkan prestasi Cu₂O dalam pembelahan molekul air secara fotoelektrokimia iaitu Co. Walau bagaimanapun, untuk mengesahkan simulasi, satu kajian selanjutnya harus dijalankan secara eksperimen.

Kata kunci: Tembaga oksida; Pengoksidaan kimia; Struktur band; Foto elektrokimia; Pengeluaran hidrogen

INTRODUCTION

A classic metal oxide semiconductor, the cuprous oxide (Cu₂O), recently has been reinvigorated as the material of choice for photoelectrochemical water-splitting study (Li & Delaunay 2013; Paracchino et al. 2011; Salehmin et al. 2017b; Salehmin et al. 2018). Researchers found that a copper based photoelectrode is attractive not only it is an earth-abundant and non-toxic material, it also theoretically characterized as a

robust photocatalyst with high photo conversion efficiency for hydrogen evolution (Wick & Tilley 015). Being prominently high in efficiency, however, its stability under PEC condition is substantially poor, subsequently hinders its application into practicality. The problem lies in the band gap (E_g) alignment against water redox potential where its conduction band (C_B) being positioned with enough potential to reduce water but insufficient V_B potential to oxidize water (Dubale et al. 2014a; Zhang et al. 2013). Ideally, a good photoelectrode

semiconductor has its conduction band (C_B) and valence band (V_B) straddle the theoretical water redox potential of 1.23 V vs. NHE (Walter et al. 2010).

Considering the needs of extending the V_B position to be more positive than water oxidation potential, elemental doping is one of the frequent approaches that has been attempted (Heng et al. 2012; Kardarian et al. 2016; M Sieberer et al. 2007). An elemental doping will affect the crystallite size of Cu_2O by probably increasing the number of nucleation centers and prevents the formation of copper phases other than Cu_2O film, thus expecting increase in photoactivity (Kardarian et al. 2016). Through doping, the electronic properties of semiconductor would also be altered (Nolan & Elliott, 2008). However, reported studies have shown that the addition of dopant into Cu_2O might not necessarily alter the band gap value. This drawback might be due to similar ionic radii and/or minimal structural distortion that would not disrupt Cu-Cu interaction (Kardarian et al. 2016). For example, Sn-doped Cu_2O composite which was prepared using solvothermal method only demonstrated an improved photocatalytic degradation activity than that achieved by bare Cu_2O counterpart (Deng et al. 2015a). The doping effort towards band gap adjustment was not discussed, assuming that the band gap widening was not achieved. Similarly, the band gap energy of Mg-doped Cu_2O was also not affected by doping, instead the Mg doping only improved its photoconductivity and consequently, its performance in solar energy application. With another dopant, a Zn-doped Cu_2O has shown an increased in band gap value and enhanced photoluminescence properties (Heng et al. 2012). The determination of band gap of Zn-doped Cu_2O revealed that a 0.07 increment was measured as compared to undoped Cu_2O (2.10 eV). Although no deliberation on band edges position over the water redox potential, the response on enhanced photoluminescence properties remarked the achievable of band gap tuning through elemental doping.

Literature survey ascertained that no significant experimental data has been reported on the effort of band gap widening through doping that could benefitted the stability of Cu_2O for photoelectrochemical water-splitting application. Therefore, there is more room to investigate the suitable dopant to considerably shift the V_B of Cu_2O to be more positive relative to water redox potential. Alternatively, since there are large number of atoms for combination and the long time scales, an effective theoretical calculation of density functional theory has been commonly applied (Yang & Ayers, 2003).

However, the computational analysis by using material studio software could clarify effects of doping on the crystal and electronic structure. CASTEP is a first principles electronic structure code for predicting properties of materials. It employs the density functional theory plane-wave pseudopotential method, which allows performing first-principles quantum mechanics calculations that explore the properties of crystals and surfaces in materials such as semiconductors, ceramics, metals, minerals, and zeolites

According to Ramanathan, Subramanian, and Valantina (2015), the use of hybrid B3LYP to calculate the band gap of bulk Cu_2O found that the value of 0.86, 1.21, 0.59 eV were obtained. This E_g is rather much deviated from actual range of reported Cu_2O E_g (1.9 – 2.2 eV). Interestingly, in the present study, the use of hybrid B3LYP to calculate the E_g of bulk Cu_2O has resulted in proximity as compared to experimental E_g value to be 2.09 and 2.05 eV, respectively. The finding remarked the adoption of hybrid B3LYP to calculate Cu_2O nanowire which will be discussed further in this study. Likewise experimental means, the feasibility of band gap widening of Cu_2O as an effect of dopant through theoretical calculation for PEC water splitting application has also not been proven. Notwithstanding, the DFT calculation of N-doped Cu_2O through DFT revealed that band gap widening was achieved due to the coexistence of both N impurity and oxygen vacancy (Min et al. 2012). Although the dopant such as Ag, Ni, Zn, Mn, Fe, Co, and Sn have been calculated for measuring the E_g value using DFT, but none of the studies examine the band edges alignment against water redox potential (Deng et al. 2015b; Martínez et al. 2003; M Sieberer et al. 2007).

Therefore, we have performed the computational analysis by using one local exchange-correlation functional, LDA, three gradient-corrected exchange correlations functional, GGA and a set of non-local functional to study the electronic band structure and density of states of undoped Cu_2O and effect of dopants on Cu_2O . The calculated E_g , V_B and C_B of undoped and doped Cu_2O were then aligned against water redox potential to provide information on resulted E_g widening. For an efficient water-splitting reaction to occur, the top-edge position of the semiconductor's V_B should be more positive than the oxidation potential of H_2O to O_2 , whilst, the bottom edge of the C_B should be more negative than the reduction potential (Ahmad et al. 2015; Mohamed et al. 2018).

METHODOLOGY

THE FABRICATION OF $Cu(OH)_2$ NW

Cuprous hydroxide $Cu(OH)_2$ nanowire (NW) as precursor was fabricated using slightly modified chemical oxidation method (Salehmin et al. 2018). Prior to fabrication, a cleaned Cu foil was prepared by sonicating the metal foil in acetone, ethanol, and double distilled water (ddH_2O) for 5 min each. Then the foil was immediately dried with nitrogen flow. The growth composition was prepared with 2.67 M NaOH (Macro) and 0.133 M $(NH_4)_2S_2O_8$ (sigma), 1 ml of NH_3 32% (w/w) and ddH_2O . To initiate the NW growth process, the Cu foil was immediately immersed in the growth solution for 25 min. Finally, the reaction was ceased by taking out the sample before rinsing with deionized water and drying in air.

THE TRANSFORMATION OF $\text{Cu}(\text{OH})_2$ NW TO Cu_2O NW

The conversion of $\text{Cu}(\text{OH})_2$ NW to Cu_2O NW was conducted through annealing under nitrogen at 500°C for 2 hours. The air inside the furnace was first evacuated by purging the tube with nitrogen and vacuuming alternately, for three cycles.

MATERIAL CHARACTERIZATION

The structural formations of Cu_2O NW were characterized using a field-emission scanning electron microscope (FESEM) (Zeiss AM10). The crystallite phase of the samples were determined by X-ray diffractometer (XRD) (Bruker D8 Advance), using $\text{Cu K}\alpha$ radiation. Whereas, the photoresponse of the samples were measured using UV-vis spectra with diffuse reflectance mode (Perkin Elmer, Lambda 950).

PHOTOELECTROCHEMICAL MEASUREMENT

The photocurrent density was measured using potentiostat (Versastat V4) with three electrodes configuration. The photocathode sample, a saturated Ag/AgCl in 3M KCl solution, and platinum coil were connected to working, reference, and counter electrode cable, respectively. Those electrodes were immersed in a 0.5M Na_2SO_4 which contained in a photocell with exposed area of 1 cm^2 . The photocurrent density was acquired under simulated AM 1.5G of 100 mW cm^{-2} illumination power density.

COMPUTATIONAL MODEL AND METHODS

The cubic system of Cu_2O crystal structure shown in Figure 1. Software Materials Studio 8.0 CASTEP from Accelrys was used to calculate the first principle of Cu_2O . One local exchange-correlation functional, LDA, three gradient-corrected exchange correlations functional, GGA (PBE and PW91) and a set of non-local functional (B3LYP) were used to perform the optimization calculations. With several DFT-based methods, Hybrid (B3LYP) DFT is used to analyze the density of states and other electronic properties of Cu_2O . Pseudo potential reciprocal space was used to treat the core electron for $\text{Cu } 3d^{10} 4s^1$. The computational lattice parameters are $a=b=c: 4.269600\text{ \AA}$ and plane wave basis set cut-off was 700.0000 eV . In this case Cu doping was adopted as shown in Figure 1. Cu atom was replaced by Co, Ni, Zn and Ag to study effect of doping.

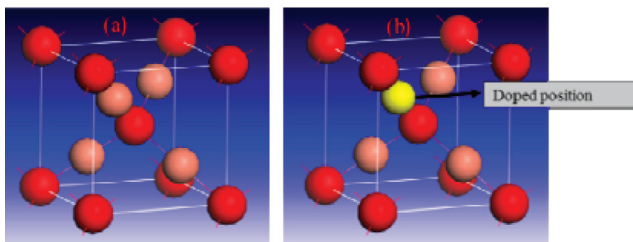


FIGURE 1. The cubic system of Cu_2O (a) undoped Cu_2O (b) doped Cu_2O

RESULTS AND DISCUSSION

THE TRANSFORMATION OF $\text{Cu}(\text{OH})_2$ NW TO Cu_2O NW

The conversion from $\text{Cu}(\text{OH})_2$ NW to Cu_2O through annealing in inert condition was reported to be achieved at 500°C at different annealing time (Dubale et al. 2014b; Salehmin et al. 2017a; Suria, 2017). It involves changing of phases during annealing which is initiated with dehydration of $\text{Cu}(\text{OH})_2$ at 120°C , followed by oxidation to CuO around 180 to 200°C (Kargar et al. 2014) and deoxidization of CuO to Cu_2O at 500°C (Hacialioglu et al. 2012).

STRUCTURAL CHARACTERIZATION

Figure 2 illustrates the FESEM images of sample before and after annealing under inert condition. The $\text{Cu}(\text{OH})_2$ NW was first fabricated through chemical oxidation technique (Figure 2a) and completely transformed to Cu_2O NW under inert condition (Figure 2b). Morphology changes was noticed where the spiky NW of $\text{Cu}(\text{OH})_2$ was transformed to a bendy and slimmer shape of NW after annealing. The length (L) and width (W) (μm) of Cu_2O NW was measured to be (L: 4.39 ± 0.33 , W: 0.32 ± 0.03). It was also reported that the bendy Cu_2O NW which resulted after annealing was due to the stress of phase changes resulted from oxygen separation from the lattice of CuO (Ahmad et al. 2015).

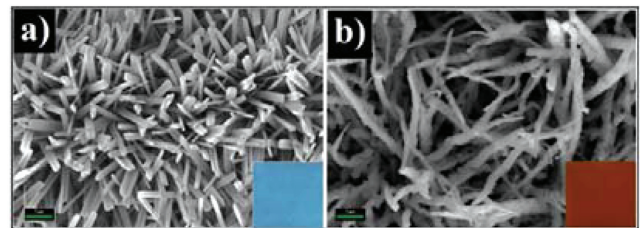


FIGURE 2. FESEM images of a) $\text{Cu}(\text{OH})_2$ NW fabricated using chemical oxidation method and corresponding Cu_2O which transformed via annealing and Cu_2O NW annealed in inert condition

The crystal phase of $\text{Cu}(\text{OH})_2$ NW and Cu_2O NW was determined using thin film XRD, as shown in Figure 3. The XRD of annealed samples shows that no $\text{Cu}(\text{OH})_2$ or CuO phase were detected (Figure 3) indicating a complete transformation of $\text{Cu}(\text{OH})_2$ to Cu_2O at 500°C for 2 hours under nitrogen atmosphere. Similar observation also has been reported by other studies (Dubale et al. 2014a; Li et al. 2013; sHsu et al. 2013). Each annealed sample exposes Cu_2O phase with the co-existence of metallic Cu phase (200, 200) under thermal reduction. Such observation is caused by the unavoidable and rapid deoxidization process of Cu_2O to Cu . The highest peak of Cu_2O crystal phase (111) is known to be responsible for photoconductivity as reported by many (Kim et al. 2014; Kim et al. 2015; sHsu et al. 2013), which will be discussed in PEC measurement section.

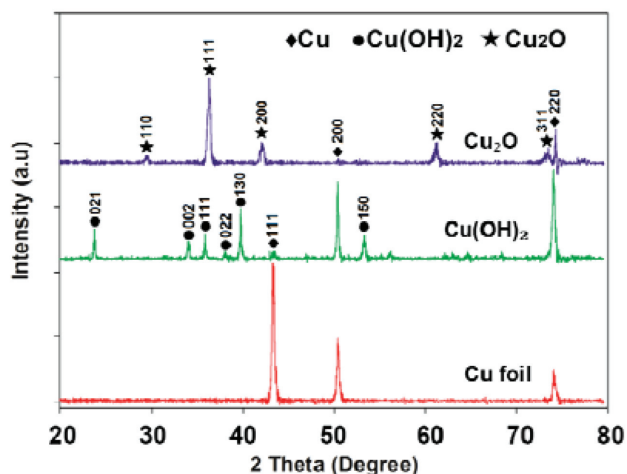


FIGURE 3. The XRD of Cu foil, Cu(OH)₂ NW and Cu₂O NW

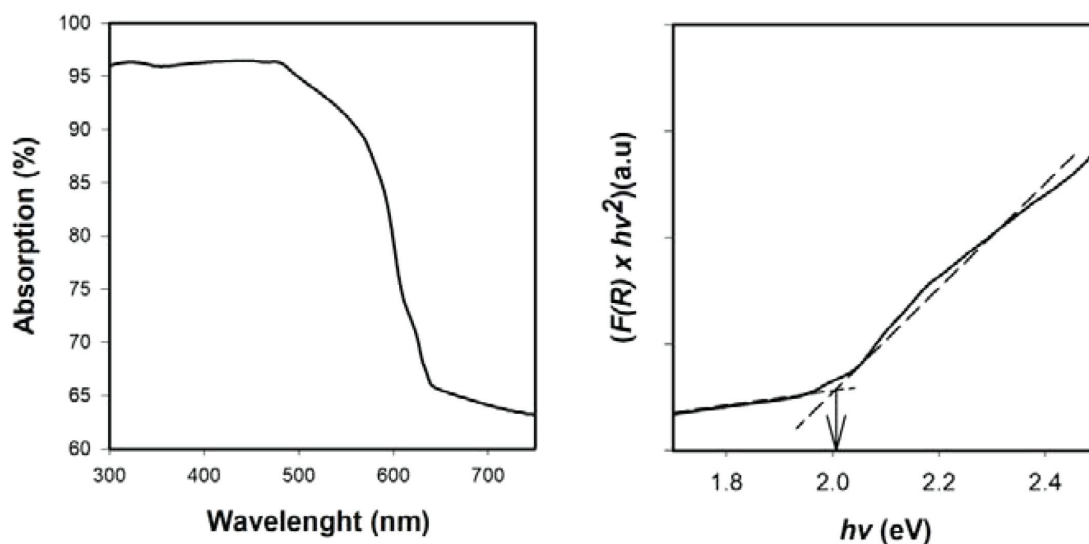


FIGURE 4. a) The diffuse reflection spectra, and b) The corresponding conversion of Kubelka-Munk function vs. band gap energy

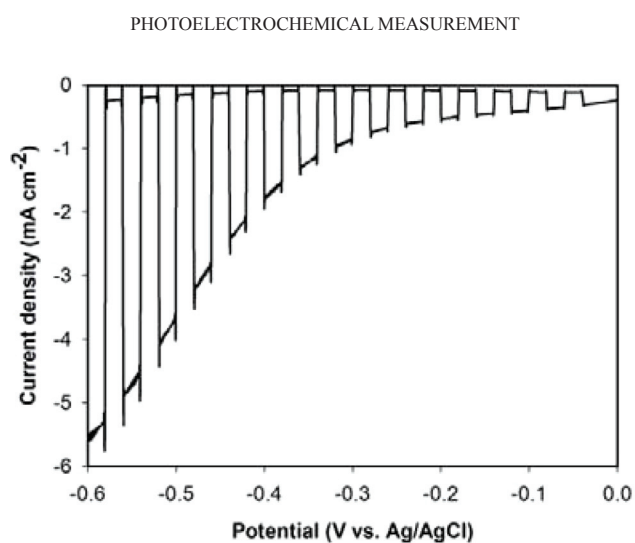


FIGURE 5. The photocurrent density generated from Cu₂O NW photocathode

The optical property of Cu₂O NW sample was measured by UV-vis absorption spectra as illustrated in Figure 4a). To determine the band gap for each annealed sample, Kubelka-Munk (K-M) equation was applied where $(F(R) \times hv)^2$ values was adopted for a direct band gap material (Dai et al. 2014), were plotted against excitation energy (eV). The $F(R)$ is defined as $(1-R)/2R$ where R is the reflectance value of the sample. The corresponding K-M plot as shown in Figure 4b has determined an E_g value of 2.0 eV. The resulted E_g is in agreement with the reported band gap energy for Cu₂O NW (1.8 to 2.1 eV) (Dubale et al. 2014a; Li et al. 2013; Lu et al. 2004; sHsu et al. 2013). It is noteworthy that the mentioned range of E_g of a semiconductor is promising to affect high photoconversion efficiency (Murphy et al. 2006; Solar 2018).

The photocurrent generation of Cu₂O NW is illustrated in Figure 5. For a single unprotected Cu₂O photocathode, the PEC performance presented in this study is declared to be the highest ever reported. The recorded current density of -5.45 mA cm⁻² at -0.6V vs. Ag/AgCl is corresponding to 6% applied bias potential efficiency (ABPE).

COMPUTATIONAL STUDY; ELECTRONIC PROPERTIES OF PURE CU₂O

The electronic properties of Cu₂O were investigated by using the local exchange-correlation and non-local functional DFT (density functional theory). Optimization calculations were performed by LDA, GGA (PW91, PBE), LDA+U and B3LYP (hybrid). The Cu₂O gave the direct band gap 0.735, 0.503, 0.490, 0.843 and 2.093eV as shown in Figure 7. LDA and GGA (PW91 and PBE) typically underestimate the electronic structure of Cu₂O. According to (Nilius et al.2016) LDA depends on the density only, while the GGA depends on the density and gradient. GGA usually provide a better result,

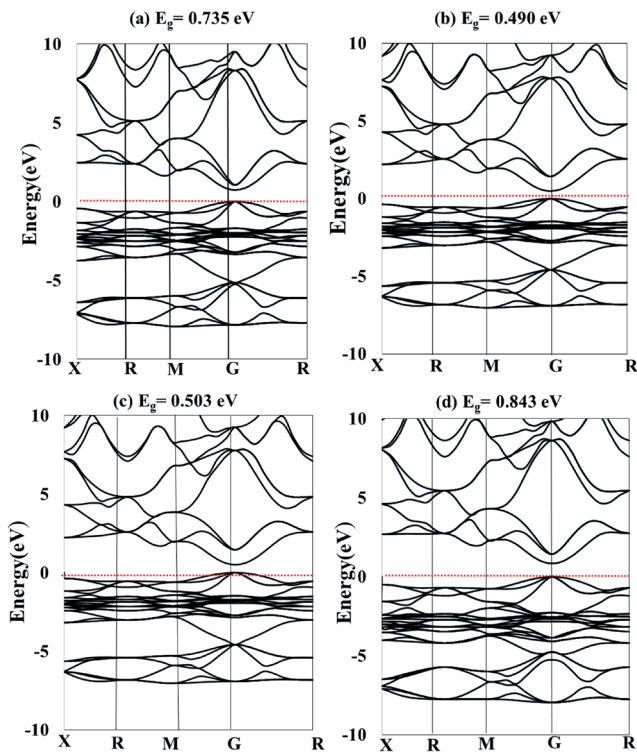
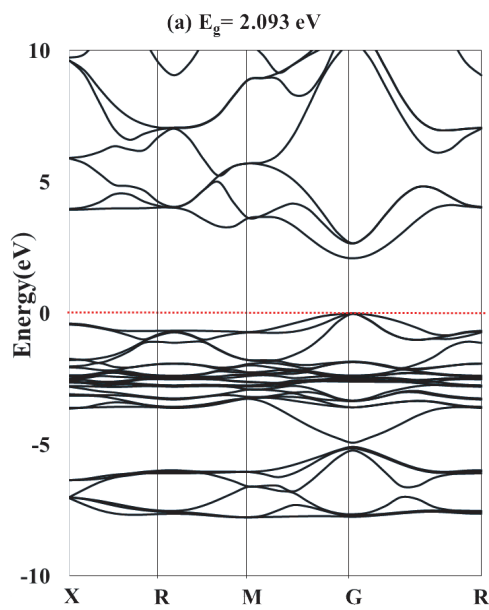


FIGURE 6. Band structure of undoped Cu_2O by different method of calculation (a) LDA (b) GGA-PBE (c) GGA-PW91 (d) LDA + U

however in the case of Cu_2O , local exchange-correlation functional (LDA or GGA), which fail to correctly reproduce band-gaps and absolute positions of the band edges. GGA method failed in description of oxide electronic properties due to their impact on the surface thermodynamics problem and principally concerns polar/non-stoichiometric surfaces, and may lead to an erroneous estimation of their stability (Haftel & Gall 2006).



Next +U supplemented LDA functional are expected to show even greater overestimations of cell volumes however LDA+U give the same general behavior whereas underestimates electronic properties qualitatively. Although addition of an empirical Hubbard term (LDA+U) partially corrects the problem in cases where transition metal atoms are involved, this approach turns out to be inefficient for compounds with simple sp atoms or closed cationic d (or f) shells (Isseroff & Carter 2013)

Non-local functional hybrid (B3LYP) functional used to construct the initial geometries for slabs, to relax structures, and to calculate surface energies, as the hybrid (B3LYP) functional was shown to be most accurate result of the electronic properties of Cu_2O . B3LYP was the functional with the combination of Hartree-Fock exchange with DFT exchange-correlation. Hybrid can give very much better dissociation energies and are now widely used in molecular calculations; there is strong evidence that they also give much better adsorption energies. The Hybrid result of Cu_2O band structure shown in Figure 8(a) which showed 2.09eV this value is close to the previous calculations using DFT by (Martínez-Ruiz et al. 2003; Sieberer et al. 2007) and our the experimental value. Results for band structures show that the top of the valence band and bottom of the conduction band lies at the G point of the Brillouin zone and Cu_2O gave direct band gap.

In addition, the Density of states (DOS) of Cu_2O represented the valance and conduction band of Cu_2O . The Total DOS had proven the calculation of the band structure of Cu_2O and represent the valance band (VB) and conduction band (CB) of Cu_2O . The VB of Cu_2O is mainly contributed by Cu 3d orbital and O 2p orbital as shown in Figure 8(b). Cu 3d and O 2p states mainly contribute to the valence band, while Cu 2s state contributes to the CB. One of the reasons for the stability of Cu_2O is incompletely filled dz2 orbital. This calculation of density of state was similar with reference.

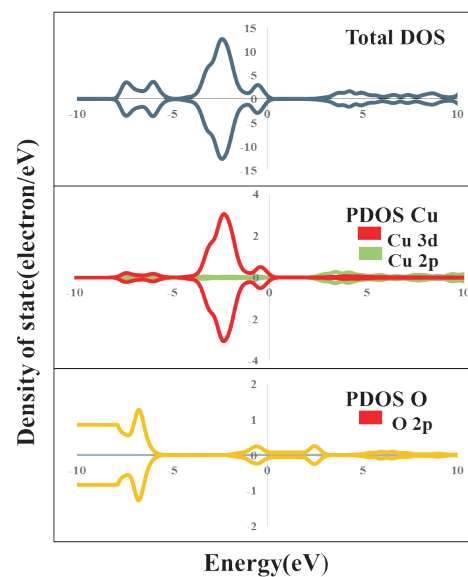


FIGURE 7. Band structure and the Density of states (DOS) of undoped Cu_2O by using hybrid method (B3LYP)

Optical absorption behavior is one of the very important fundamental properties in revealing the energy structures and applications in photo catalysis. Figure 8 shows the UV-visible absorbance spectra of DFT calculation. The calculated optical properties of pure Cu_2O are fully consistent with the experimental measurements as showed in Figure 4(a). In addition, for the optical absorption case, it is important for the exposure of semiconducting nanoparticles to incident UV-visible photons in the wavelength range of 200–800 nm (energy is 1.5–6.5 eV or 150–600 kJ mol⁻¹), to make sure for absorption to occur (Pemendakan, 2015). In this analysis, the photocatalytic activity of the Cu_2O UV part ($\lambda < 400$ nm) to form a visible light source.

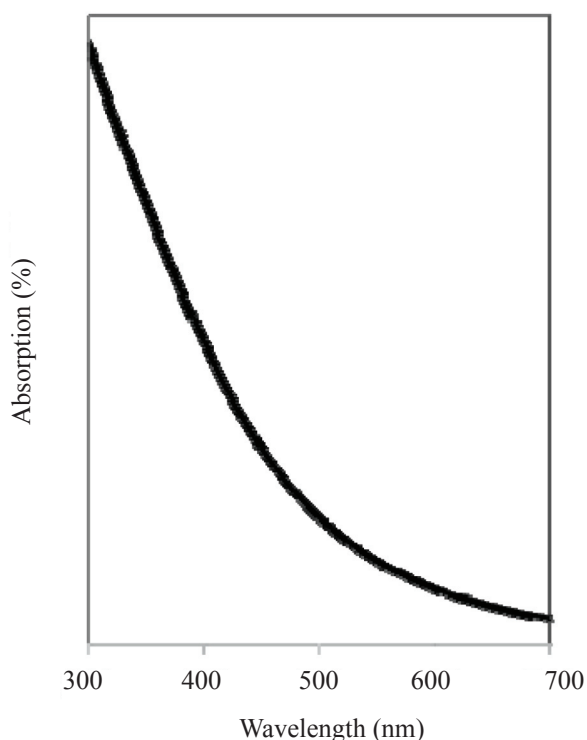


FIGURE 8. Optical properties of undoped Cu_2O

To design an efficient photo catalyst for photo electrochemical water splitting to produce hydrogen, a few characteristic should be consider such as, band structure, band energy and absorption of photo catalyst. However, the fabrication of semiconductor composites and substitution of impurities for achieving extended absorbance also play and importance factor. Firstly, for the band structure, along with a suitable band gap which in range of 1.23eV-2.00eV, suitable band-edge positions (CB and VB) with respect to the water redox potentials ($\text{H}_2\text{O}/\text{H}_2$ couple and $\text{H}_2\text{O}/\text{O}_2$ couple) are important to achieve efficient photo electrochemical water splitting. The pure Cu_2O gave the band gap 2.093eV with the VB and CB higher than the water oxidation potential and the hydrogen reduction potential, whereas the band alignments of Cu_2O straddle for water splitting. However, to improve the band gap of Cu_2O to become more reliable for water splitting doping techniques could be used by using DFT method.

In this study by using the hybrid method, Cu_2O which was doped to study the effect of doping on the electronic properties of Cu_2O . According Sieberer et al. (2007) the doping of Cu_2O with impurities, both cations and anions, has been attempted in order to control the properties. According to Kikuchi & Tonooka (2005) it is desirable to use cations as a dopant in doping for practical applications because carrier generation by the cation doping is more stable. To confirm the statements and investigate the stability, one Cu atom replacing by the cation transitions element such as Co, Ni, Zn and Ag. The study suggested that Cu_2O doped with cation may introduce shallow acceptor level in Cu_2O and enhances p-type conduction (Haftel et al. 2006). Figure 9 showed band structure of doped Cu_2O .

However, it was found that the impact of the dopant depended on its ionic radius, its oxidation state, and the detailed electronic structure of the dopant and the host. Substitution by cations with a larger ionic radius such as Co and Ni led to smaller band gap from 2.01eV to 0.94eV and 0.35eV respectively, Cobalt preferred oxidation state is +2 and, it substitutes to the copper, and behaves as a donor. While Ni behaves as acceptors and doping with Ni gives rise to a p-type semiconductor with the impurity levels above the valence band maximum. Next, Cu_2O was doped with Zn and Ag, both Zn and Ag have a small ionic radius than Cu. Doping with Zn resulted in the reduction of band gap to 1.20eV, causing the material to become metallic and having n-type semiconductor (properties such as high impurity level than conduction band minimum), with impurity levels above the conduction band minimum. Doping with Ag resulted in increasing (value of) the band gap 2.18eV, Ag elements should behave as donors. However, the effect on the gap was mainly dependent on the alignment of dopant electronic states with Cu_2O band edges and the extent of their hybridization. As compared to (Nolan & Elliott 2008) who reported the band gap of Cu_2O can be both increased or decreased by a suitable choice of dopant. They had doped with Ba^{2+} , Sn^{2+} , Cd^{2+} , In^{3+} , La^{3+} , and Ce^{4+} who had larger ionic radii and produce small band gap. Moreover, doped with as Al^{3+} , Ga^{3+} , Ti^{4+} , and Cr^{4+} , who had small ionic radii's and show increasing in band gap.

The Figure 10 showed the band alignment of water redox potential of pure and doped Cu_2O . From this band alignment we could observe Cu_2O and doping act as photo catalyst in photo electrochemical water splitting. For the oxidation potential, Cu_2O lower than ($\text{O}_2/\text{H}_2\text{O}$) at pH=0, indicating they are resistant to the hole oxidation and stable in the solution, these are reasons for the easier oxidation of Cu_2O . While, for the reduction potential Cu_2O higher than (H^+/H_2). This make Cu_2O straddle for photo electrochemical water splitting. However, as we can see from the Figure 9 and 10, Co doped Cu_2O was the most suitable dopant to improve the efficiency of the water splitting characteristic's because there was a reduction in band gap and does not changed properties of Cu_2O . Although the band gap of Co doped Cu_2O

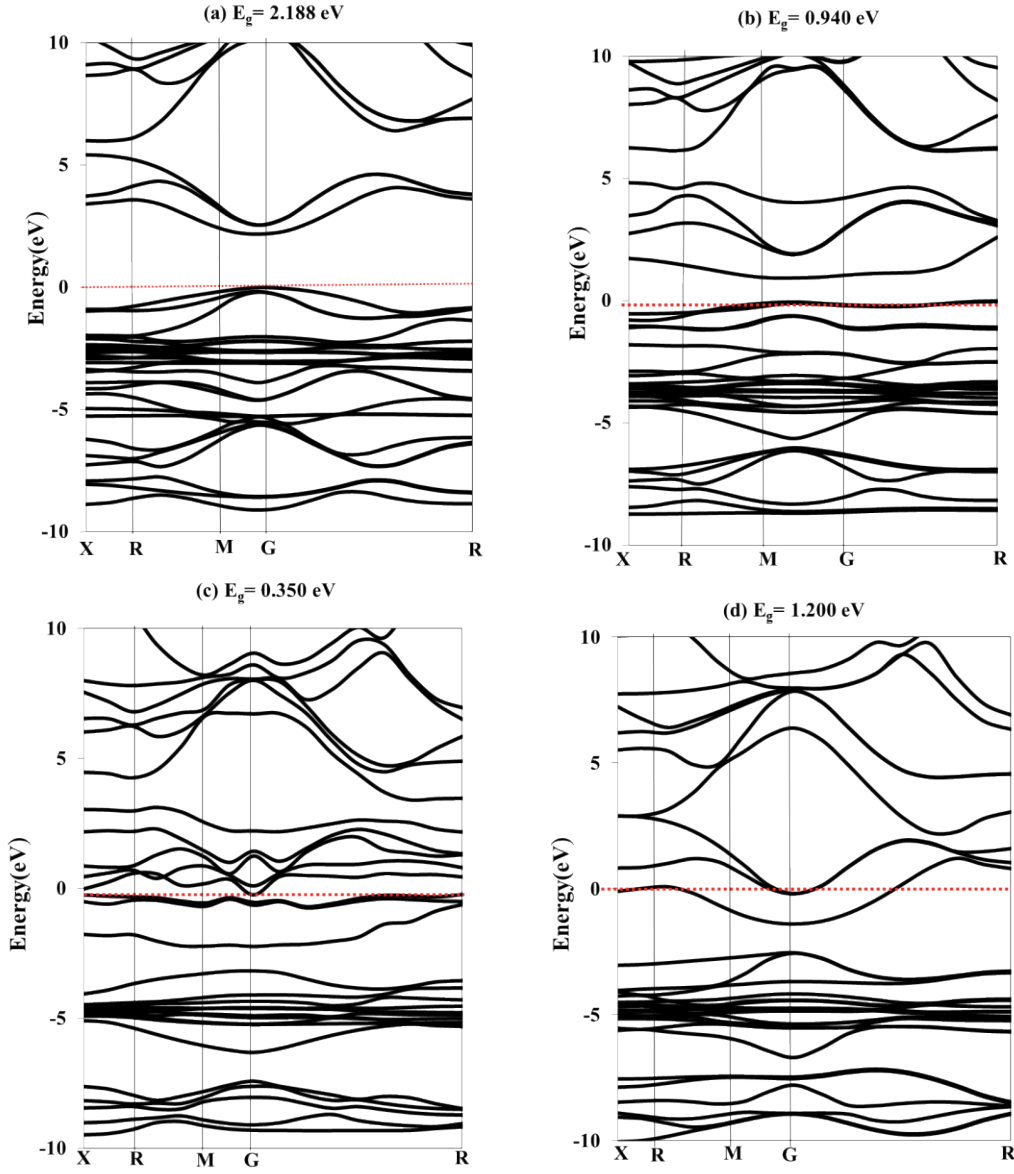


FIGURE 9. Band structure of doped Cu_2O (a) Cu_2O doped by Ag (b) Cu_2O doped by Co (c) Cu_2O doped by Ni and (d) Cu_2O doped by Zn

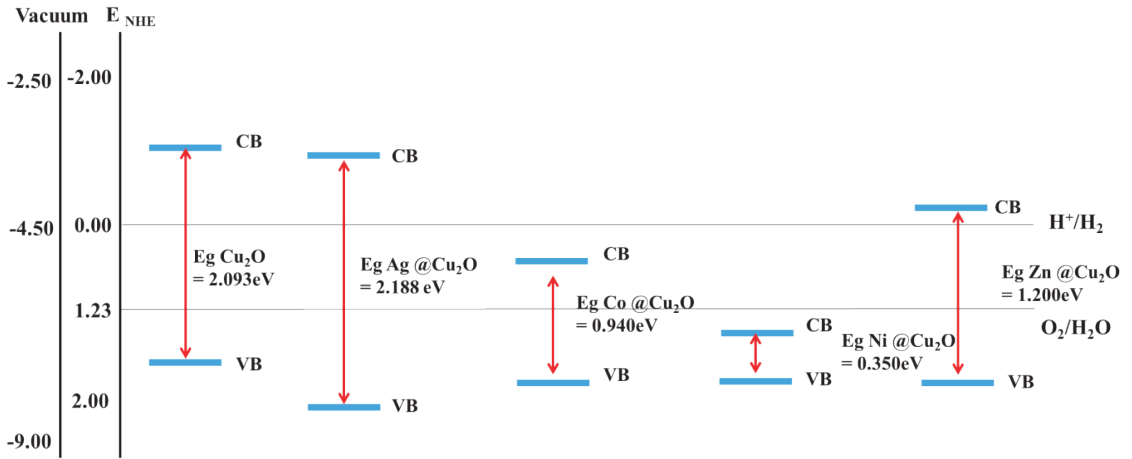


FIGURE 10. Water Redox Potential of Pure Cu_2O and Ag, Co, Ni and Zn doped Cu_2O .

less than minimum band gap of the water splitting condition (1.23eV-2.00eV), an experimental study should be carried out to study the affect and prove the ability of Co as dopant. Moreover, even Zn as dopant makes the VB and CB line near to oxidation and reduction line, Zn also make the material become metallic and appearance of indirect band gap which was not favorable in PEC water splitting. In addition for Ni reduces the band gap to small and not straddle for oxidation and reduction line, while for Ag as dopant increase the band gap, increasing in band gap will cause higher change of recombination and lower the PEC efficiency.

CONCLUSION

In summary, the fabrication Cu₂O NW through wet chemical oxidation method was experimentally characterized to have a direct band gap of 2.05eV which well predicted via DFT study. In seeking an understanding of how doping can be used to tune the band gap of Cu₂O we could conclude that there are two conditions related to the dopant that are key for increasing the band gap. The first is that dopants with larger ionic radii than Cu⁺ and another key are dopants with ionic radii smaller than Cu⁺. This study successfully study dopant that could improve Cu₂O in Photoelectrochemical water splitting which is Co. However, to validate the simulation, a further study will be carried out experimentally.

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