Experimental and Theoretical Study of Cu$_2$O Photoelectrode and Cu$_2$O Doped with Ag, Co, Ni and Zn Metals for Water Splitting Application

(Kajian Secara Eksperimental dan Teori Mengenai Fotoelektrod Cu$_2$O dan Cu$_2$O 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 Cu$_2$O thin film via wet chemical oxidation method obeyed the theoretical prediction. However, the Cu$_2$O 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 Cu$_2$O 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 Cu$_2$O due to ionic radii of the dopant affected the shifting of band gap. In this study, Co showed more significant improvement of Cu$_2$O for photoelctrochemical 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

INTRODUCTION

A classic metal oxide semiconductor, the cuprous oxide (Cu$_2$O), recently has been reinvigorated as the material of choice for photoelectrochemical water-splitting study (Li & Delaunay 2013; Paracchino et al. 2011; Salehmim et al. 2017b; Salehmim 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 2015). 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 (CB) being positioned with enough potential to reduce water but insufficient V$_{th}$ potential to oxidize water (Dubale et al. 2014a; Zhang et al. 2013). Ideally, a good photoelectrode...
semiconductor has its conduction band ($C_g$) and valence band ($V_{un}$) straddle the theoretical water redox potential of 1.23 V vs. NHE (Walter et al. 2010).

Considering the needs of extending the $V_{un}$ 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$_2$O by probably increasing the number of nucleation centers and prevents the formation of copper phases other than Cu$_2$O film, thus expecting increase in photocatalytic activity (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$_2$O 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$_2$O composite which was prepared using solvothermal method only demonstrated an improved photocatalytic degradation activity than that achieved by bare Cu$_2$O 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$_2$O was also not affected by doping, instead the Mg doping only improved its photocconductivity and consequently, its performance in solar energy application. With another dopant, a Zn-doped Cu$_2$O 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$_2$O revealed that a 0.07 increment was measured as compared to undoped Cu$_2$O (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$_2$O for photoelectrochemical water-splitting application. Therefore, there is more room to investigate the suitable dopant to considerably shift the $V_{un}$ of Cu$_2$O 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).

According to Ramanathan, Subramanian, and Valantina (2015), the use of hybrid B3LYP to calculate the band gap of bulk Cu$_2$O 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$_2$O $E_g$ (1.9 – 2.2 eV). Interestingly, in the present study, the use of hybrid B3LYP to calculate the $E_g$ of bulk Cu$_2$O 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$_2$O nanowire which will be discussed further in this study. Likewise experimental means, the feasibility of band gap widening of Cu$_2$O 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$_2$O through DFT revealed that band gap widening was achieved due to the coexistence of both N impurity and oxygen vacancy (Min et al. 2012). Alternatively, 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; Martinez 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$_2$O and effect of dopants on Cu$_2$O. The calculated $E_g$, $V_{un}$, and $C_{un}$ of undoped and doped Cu$_2$O 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 $V_{un}$ should be more positive than the oxidation potential of H$_2$O to O$_2$, whilst, the bottom edge of the $C_{un}$ 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$_2$O) 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$_4$)$_2$S$_2$O$_8$ (sigma), 1 ml of NH$_3$, 32% (w/w) and ddH$_2$O. 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 Cu(OH)$_2$ NW TO Cu$_2$O NW

The conversion of Cu(OH)$_2$ NW to Cu$_2$O 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$_2$O 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 Cu Kα 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$_2$SO$_4$ 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$_2$O crystal structure shown in Figure 1. Software Materials Studio 8.0 CASTEP from Accelrys was used to calculate the first principle of Cu$_2$O. One local exchange-correlation functional, LDA, three gradient-corrected exchange correlations functional, GGA (PBE and PW91) and a set of non-local functional (B3 LYP) 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$_2$O.

RESULTS AND DISCUSSION

THE TRANSFORMATION OF Cu(OH)$_2$ NW TO Cu$_2$O NW

The conversion from Cu(OH)$_2$ NW to Cu$_2$O 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 Cu(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$_2$O at 500°C (Hacialioğlu et al. 2012).

STRUCTURAL CHARACTERIZATION

Figure 2 illustrates the FESEM images of sample before and after annealing under inert condition. The Cu(OH)$_2$ NW was first fabricated through chemical oxidation technique (Figure 2a) and completely transformed to Cu$_2$O NW under inert condition (Figure 2b). Morphology changes was noticed where the spiky NW of Cu(OH)$_2$ was transformed to a bendy and slimmer shape of NW after annealing. The length (L) and width (W) (µm) of Cu$_2$O NW was measured to be (L: $4.39 \pm 0.33$, W: $0.32 \pm 0.03$). It was also reported that the bendy Cu$_2$O 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 1. The cubic system of Cu$_2$O (a) undoped Cu$_2$O (b) doped Cu$_2$O

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

The crystal phase of Cu(OH)$_2$ NW and Cu$_2$O NW was determined using thin film XRD, as shown in Figure 3. The XRD of annealed samples shows that no Cu(OH)$_2$ or CuO phase were detected (Figure 3) indicating a complete transformation of Cu(OH)$_2$ to Cu$_2$O 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$_2$O 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$_2$O to Cu. The highest peak of Cu$_2$O 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.
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 \((F(R) \times \text{hv})^2\) 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 \((1-R)^2/2R\) 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; Hsu 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).

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

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).

FIGURE 5. The photocurrent density generated from Cu2O NW photocathode

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 2.093 eV 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,
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$_2$O. 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$_2$O 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$_2$O gave direct band gap.

In addition, the Density of states (DOS) of Cu$_2$O represented the valence and conduction band of Cu$_2$O. The Total DOS had proven the calculation of the band structure of Cu$_2$O and represent the valence band (VB) and conduction band (CB) of Cu$_2$O. The VB of Cu$_2$O 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$_2$O is incompletely filled dz$^2$ orbital. This calculation of density of state was similar with reference.
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$_2$O 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$_2$O UV part ($\lambda < 400$ nm) to form a visible light source.

FIGURE 8. Optical properties of undoped Cu$_2$O

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 (H$_2$O/H$_2$ couple and H$_2$O/O$_2$ couple) are important to achieve efficient photo electrochemical water splitting. The pure Cu$_2$O 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$_2$O straddle for water splitting. However, to improve the band gap of Cu$_2$O to become more reliable for water splitting doping techniques could be used by using DFT method.

EFFECT OF DOPING CO, NI, ZN AND AG ON ELECTRONIC PROPERTIES OF Cu$_2$O

In this study by using the hybrid method, Cu$_2$O which was doped to study the effect of doping on the electronic properties of Cu$_2$O. According Sieberer et al. (2007) the doping of Cu$_2$O 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$_2$O doped with cation may introduce shallow acceptor level in Cu$_2$O and enhances p-type conduction (Hafiel et al. 2006). Figure 9 showed band structure of doped Cu$_2$O.

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$_2$O 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$_2$O band edges and the extent of their hybridization. As compared to (Nolan & Elliott 2008) who reported the band gap of Cu$_2$O 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$_2$O. From this band alignment we could observe Cu$_2$O and doping act as photo catalyst in photo electrochemical water splitting. For the oxidation potential, Cu$_2$O lower than (O$_2$/H$_2$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$_2$O. While, for the reduction potential Cu$_2$O higher than (H$^+$/H$_2$). This make Cu$_2$O straddle for photo electrochemical water splitting. However, as we can see from the Figure 9 and 10, Co doped Cu$_2$O 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$_2$O. Although the band gap of Co doped Cu$_2$O
Figure 9. Band structure of doped Cu$_2$O (a) Cu$_2$O doped by Ag (b) Cu$_2$O doped by Co (c) Cu$_2$O doped by Ni and (d) Cu$_2$O doped by Zn.

Figure 10. Water Redox Potential of Pure Cu$_2$O and Ag, Co, Ni and Zn doped Cu$_2$O.
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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