KnE Engineering

ICoSE Conference Proceedings
ICoSE Conference on Instrumentation, Environment and
Renewable Energy (2015), Volume 2016

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Conference Paper

First Principle Calculation of Electronic, Optical Properties and Photocatalytic Potential of CuO Surfaces

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Abstract We have performed DFT calculations of electronic structure, optical properties and photocatalytic potential of the low-index surfaces of CuO. Photocatalytic reaction on the surface of semiconductor requires the appropriate band edge of the semiconductor surface to drive redox reactions. The calculation begins with the electronic structure of bulk system; it aims to determine realistic input parameters and band gap prediction. CuO is an antiferromagnetic material with strong electronic correlations, so that we have applied DFT + U calculation with spin polarized approach, beside it, we also have used GW approximation to get band gap correction. Based on the input parameters obtained, then we calculate surface energy, work function and band edge of the surfaces based on a framework developed by Bendavid et al (J. Phys. Chem. B, 117, 15750-15760) and then they are aligned with redox potential needed for water splitting and CO_2 reduction. Based on the calculations result can be concluded that not all of low-index CuO have appropriate band edge to push reaction of water splitting and CO2 reduction, only the surface CuO(111) and CuO(011) which meets the required band edge. Fortunately, based on the formation energy, CuO(111) and CuO(011) is the most stable surface. The last we calculate electronic structure and optical properties (dielectric function) of low-index surface of CuO, in order to determine the surface state of the most stable surface of CuO.

Keywords: Cupric oxide, DFT, dielectric function, GW approximation, photocatalytic potential.

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Received: 1 August 2016
Accepted: 18 August 2016
Published: 6 September 2016

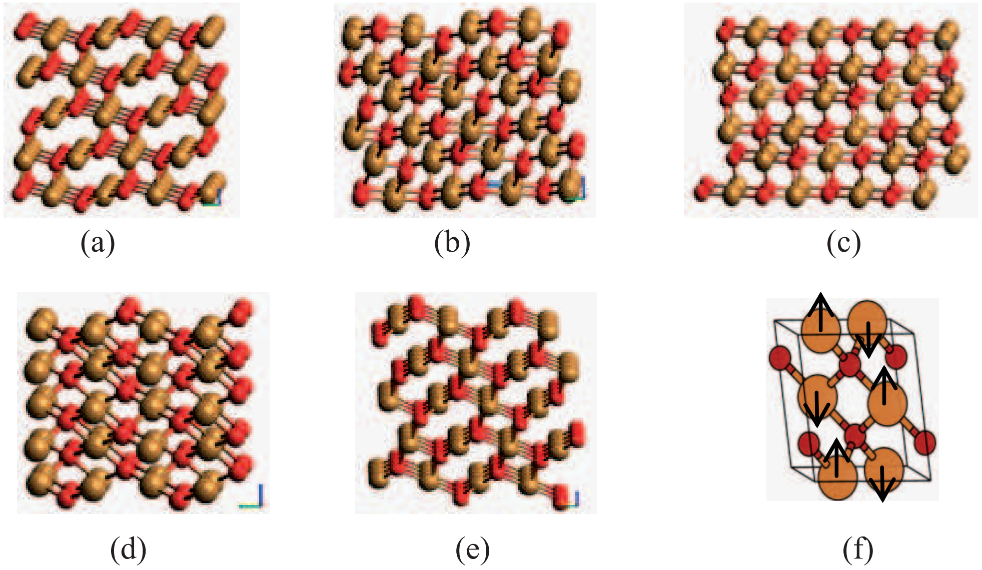
Publishing services provided by Knowledge E

Selection and Peer-review under the responsibility of the ICoSE Conference Committee.

1. Introduction

Photocatalytic reaction on the surface of semiconductor requires the appropriate photocatalytic potential or band edge of the semiconductor surface to drive redox reactions. The necessities that the conduction band minimum (CBM) have to lie above the reduction reaction potential and the valence band maximum (VBM) have to lie below the oxidation reaction potential. DFT calculation provides a theoretical mean to calculate the band edge potential of material. But we cannot perform the calculation through bulk system, because, within a periodic DFT calculation of bulk, the eigenvalues are not properly referenced to any absolute scale. However, when the DFT calculations performed onslabsystem which consists of an infinite surface and vacuum, the eigenvalues will be referring to the vacuum potential [1]. The next problem is

How to cite this article: Faozan Ahmad, M Kemal Agusta, and Hermawan K Dipojono, "First Principle Calculation of Electronic, Optical Properties and Photocatalytic Potential of CuO Surfaces," *KnE Engineering*, vol. 2016, 7 pages. DOI 10.18502/keg.v1i1.504


(a) (b) (c)

(d) (e) (f)

Figure 1: The extended structure of CuO surface (2x2); CuO(111) (a), CuO(011) (b), CuO(101) (c), CuO(010) (d), CuO($\bar{1}$11) (e), and the unit cell of bulk and antiferromagnetic spin ordering (f).

the DFT calculation of VBM and CBM often doesn't show the actual value, because the weakness of the DFT in predicting bandgap of strong electron correlation system. Fortunately, Perdew and Levy showed that the band gap center (BGC) can be predicted exactly using DFT [2].

Cupric oxide or tenorite (CuO) has been attractive attention because of its interesting properties as a p-type semiconductor with a narrow band gap (1.2-1.7 eV). CuO has been used as an effective modifier of photocatalyst TiO2 and ZnO in water splitting and CO2 reduction system. In this paper we will calculate surface energy, work function, photocatalytic potential, electronic and optical properties theoretically from first principle.

2. Computational Method

Spin-polarized calculations based on density functional theory are performed using the Quantum Espresso package [3]. Generalized gradient approximation (GGA) based on the Perdew–Burke–Ernzerhof (PBE) functional is used for the exchange-correlation energy. The projector augmented wave (PAW) and norm conserving (NC) method is used to describe the ionic core pseudopotential. CuO has a monoclinic structure with space group C2/c1 ($a = 4.690$ Å, $b = 3.420$ Å, $c = 5.131$ Åand $\beta = 99.540°$). The CuO surface is modeled by at least five layers a 1×1 unit cell (see Fig.1). The Brillouin zone is sampled using $4 \times 4 \times 1$ Monkhorst–Pack k-points. Surface relaxation is considered by optimizing the two topmost layers of the surface and keeping the other layers in their bulk parameters. One shot GW method or G_0W_0 approximation and optical properties calculation are conducted using Yambo package [4]. Here we have calculated the properties of CuO surface, namely work function, surface formation energy, photocatalytic potential, electronic properties and optical properties

The calculation of electronic structure of bulk is performed using DFT+U and GW method to predict theoretical band gap. Based on the realistic value of computed bandgap, the band edge of CuO is calculated using Eq.1. Band gap center (E_{BGC}) obtained from DFT calculation of CuO surface have to be referenced to vacuum potential that can be calculated by measuring electrostatic potential of the surface [1].

$$\begin{aligned} E_{VBM} &= E_{BGC} - \tfrac{1}{2}E_g, \\ E_{CBM} &= E_{BGC} + \tfrac{1}{2}E_g. \end{aligned} \tag{1}$$

The next calculations are work function (ϕ) and surface energy (γ). Work function is defined as the difference in energy between an electron at rest in the vacuum and an electron at the Fermi level. Whereas, surface energy is defines as the excess energy at the surface of a material compared to the bulk. Fermi level in semiconductor often define as VBM (the highest occupied eigenvalue). Work function and surface energy for stoichiometric surface are calculated using Eq.2 and Eq.3, respectively [1,5].

$$\phi = E_{vac} - E_F, \tag{2}$$

$$\gamma = \frac{1}{2A}\left[E_{surf} - \frac{N_s}{N_b}E_{bulk}\right], \tag{3}$$

where E_{surf} is the total energy of stoichiometric slab, $E_{bulk}$is the total energy of bulk, A is the unit surface area, N_s is the number of atoms in slab, and N_b is the number of atoms in bulk.

3. Photocatalytic Potential

The calculation begins with the electronic structure of bulk to predict theoretical band gap using DFT+U and G_0W_0 method. Hubbard potential (U) in this calculation is applied simultaneously to the Cu 3*d* and O 2*p* state. The G_0W_0correction is carried out on the top of DFT+U calculation. The acceptable value of U is constrained by the valid value of calculated local magnetic moment of atom. The experimental data for band gap of CuO is about 1.67 eV at zero Kelvin temperature [6] and local magnetic moment of atom Cu (μ) is about 0.62 up to 0.74 μ_B [7,8]. Table 1 show that the value of theoretical bandgap calculated in DFT+U method is still underestimate, but the G_0W_0 over DFT+U can open the band gap approaching the experimental result.

To calculate band edge, firstly we have to calculate the reference vacuum potential that can be obtained by calculating electrostatic potential of CuO surfaces in DFT+U framework. The electrostatic potential was averaged in the x and y directions to get the potential along the z direction. Fig. 2 shows a method of how to calculate E_{BGC} and E_{VBM} that are referenced to E_{VAC} of CuO(111) surface from electrostatic potential.

Once we get E_{BGC} and band gap we can calculate the band edge position by applying Eq.1 and based on calculated E_{VBM} (with assumption that $E_F \cong E_{VBM}$), we also can

Method	μ-Cu [μ_B]	Direct band gap [eV]	Indirect band gap [eV]
DFT+U, U=1	0.67	0.63	0.38
DFT+U, U=3	0.74	1.66	1.41
DFT+U+G_0W_0,U=0.3	-	1.50	2.37
DFT+U+G_0W_0,U=0.35	-	1.69	2.47
DFT+U+G_0W_0,U=0.4	-	1.77	2.51

Table 1: Band gap and local magnetic moment of CuO calculated in DFT+U and G_0W_0 method calculations.

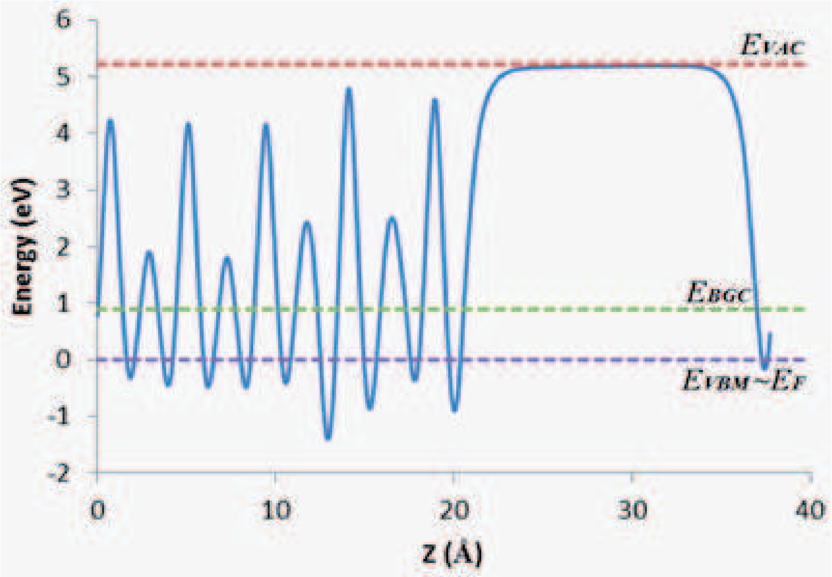


Figure 2: Calculated electropotential along z-axis of CuO(111) surface using DFT+U.

compute work function (ϕ) by following Eq. 2. Finally, to know the most probable or most energetically favorable surface we calculate surface energy through Eq.3. Table 2 shows the calculated work function, E_{BGC}, E_{VBM}, E_{CBM} and surface energy of CuO surfaces. From the result we can see that CuO(111) have the lowest surface energy, this is indicate the CuO(111) is the most stable surface, CuO(101) have the lowest energy needed to extract an electron from the bulk crystal indicated by the lowest work function, CuO($\bar{1}$11) have the lowest E_{VBM}, and CuO(101) have the highest E_{CBM}.

In Fig. 3, we compare the photocatalytic potential of CuO surfaces with redox potential of water and reduction potential of CO2/CH3OH in pH=7.0 (by assumption the

Surface	Work Function (ϕ) [eV]	Band gap Center (E_{BGC}) [eV]	E_{VBM} [eV]	E_{CBM} [eV]	Surface Energy (γ) [J/m^2]
CuO(111)	5.22	-4.82	-5.66	-3.99	0.38
CuO($\bar{1}$11)	5.71	-5.75	-6.58	-4.91	0.82
CuO(010)	5.67	-5.29	-6.13	-4.46	1.02
CuO(101)	4.68	-4.23	-5.07	-3.40	0.89
CuO(011)	5.31	-4.81	-5.64	-3.97	0.60

Table 2: Work Function and Surface Energy of CuO calculated within in DFT+U.

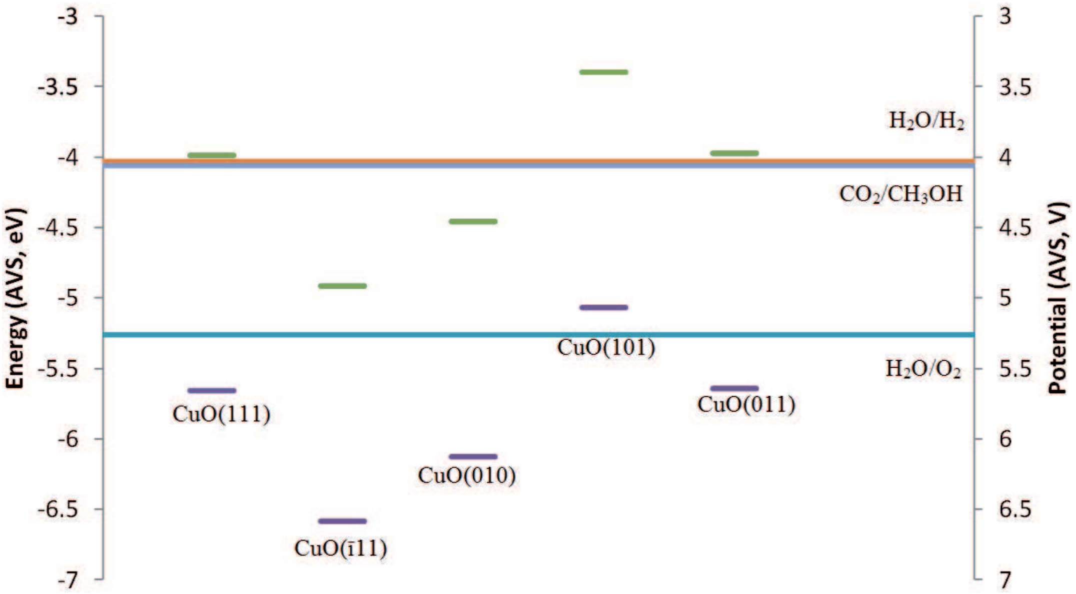


Figure 3: Calculated band-edge position of CuO surfaces in comparison to redox potential of H_2O/O_2, H_2O/H_2, and CO_2/CH_3OH at pH = 7 (refers to AVS: absolute vacuum energy scale).

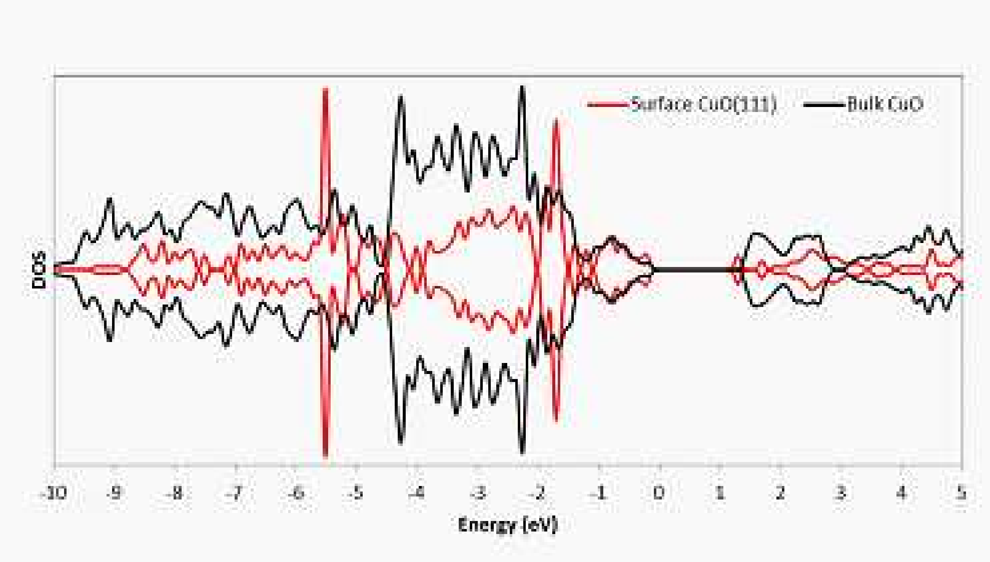


Figure 4: Calculated DOS of surface CuO(111) and bulk.

pH of neutral CuO surfaces are 7.0). It is appears that not all of low-index CuO have appropriate band edge to push reaction of water splitting and CO2 reduction, only the surface CuO(111) and CuO(011) which meets the required band edge. Fortunately, based on the surface energy, CuO(111) and CuO(011) is the most stable surface.

4. Electronic and Optical Properties of Surface

Here we consider electronic and optical properties of the most stable surface CuO(111). The electronic properties are computed using DFT+U, while the optical properties are calculated by solving BSE (Bethe Salpeter Equation).

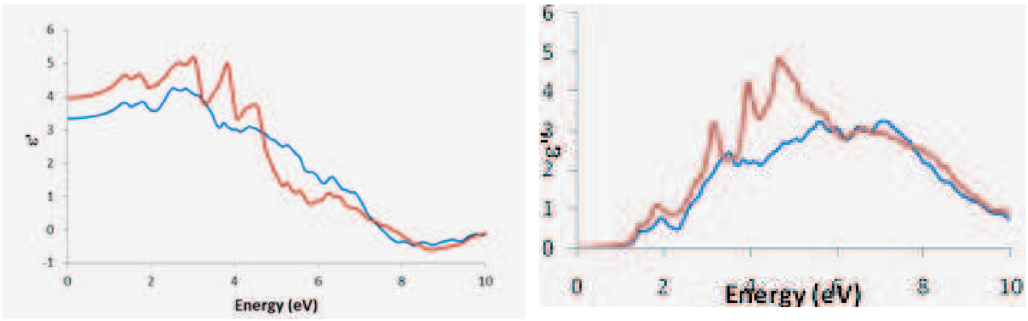


Figure 5: Calculated dieletric function ϵ' (a) and ϵ'' (b) for different light polarization, x-polarization are represented by blue lines and y-polarization are represented by red lines.

In Fig. 4, DOS (density of state) of bulk CuO and surface CuO(111) are presented. It appears a new state or surface state in the band gap. The surface state have important role in photocatalyst, it act as intermediate or trapping state which will reduce recombination rate, so that the electron and hole have more possibility to interact with reactant.

Fig. 5 shows the calculated dielectric function $\epsilon(\omega)$ that consist of ϵ' (dispersive or real part of ϵ) and ϵ'' (absorptive or imaginary part of ϵ). Here we compare between the dielectric function with different light polarization, namely x-polarization (ϵ_{xx}) and y-polarization (ϵ_{yy}). Both of dielectric functions for different polarizations are not identic, this indicates an anisotropy feature of the surface that related (suggested) to the present of surface state [9]. For further analysis of this feature we need RAS (reflected anisotropy spectroscopy).

5. Summary

We have performed DFT calculations of photocatalytic potential, electronic structure, and optical properties of low-index surfaces of CuO. Our calculation show that the calculated photocatalytic potential of CuO (the most stable surface CuO(111)) is sufficient to push reaction of water splitting and CO2 reduction. New state on band gap and anisotropy feature of dielectric function for different light polarization is suggested related to surface state of CuO(111).

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