

## II.F.7 Photoelectrochemical Materials: Theory and Modeling

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### Fiscal Year (FY) 2012 Objectives

For FY 2012, the main goal of this project was to improve materials efficiency by understanding and hence tuning the following by theoretical/computational modeling

- optical gaps and
- absorption probabilities
- conduction properties

This allows us to devise materials selection criteria for photoelectrodes for photoelectrochemical (PEC) energy conversion.

### Technical Barriers

This project addresses the following technical barriers from the Production section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (Y) Materials Efficiency
- (Z) Materials Durability

### Technical Targets

This project is intended to provide (i) a theoretical understanding of the performance of current PEC materials and provide feedback and guidance for performance

improvement; (ii) materials prediction for photocatalysts by computational approach.

### FY 2012 Accomplishments

- Theoretically studied the Cu-based delafossites materials and their nano-crystal phases to predict efficient photocatalysts for hydrogen production.
- We have shown that a set of unique and highly stable delafossite nano-crystals can be designed with tunable band gap.
- We have further investigated the optical absorption probabilities of these nano-crystals and determined a fundamental barrier in efficient optical absorptions for these oxide materials.



### Introduction

Numerous metal oxides have been tried as photocatalysts for the last four decades to produce hydrogen [1-4] by water splitting through PEC process. Simple band engineering approaches to tune the band structure of naturally occurring oxides have not been so far very successful to generate hydrogen efficiently [5]. Alternate strategies, such as nanostructured photocatalysts have shown promises to split water to produce hydrogen [6-8]. Favorable focus on the nanostructure materials are due to the fact that their electronic structures are tunable, charge carrier scatterings are small and in many cases relatively low cost synthesis procedures available. However, to facilitate and control any redox reaction, such as to split water efficiently, the basic understanding of the nature of 'band' gap of the nanostructures and the electrons excitation across the gap is essential. The present study of the self-passivated and charge compensated nano-structures were performed with density functional theory (DFT) [9,10] and time-dependent DFT (TDDFT) [11,12]. These are very useful methods to study the ground state electronic structure and excitation energy, respectively, for the nanostructures.

Cu delafossites,  $\text{CuMO}_2$  ( $M =$  group 13 and 3 metals), have received great attention recently. These are stable in most aqueous solutions and have good  $p$ -type conductivity [13]. PEC response to split water for hydrogen has already been demonstrated for Cu-delafossites [16,17]. Recent theoretical studies have revealed that due to their crystal structure, Cu-delafossites have some undesirable features for PEC applications, such as indirect band gap and very weak optical absorption at the minimum band gap [14,15].

However, though the absorption can be improved by breaking the inversion symmetry of the crystals, [15] even after doping or alloying the band gap of delafossites remained indirect [16]. One way to go beyond this limitation is to consider nano-crystals. As the energy levels of the nano-structures are discrete and dispersionless, these structures do not suffer from indirect band gap problem. So it would be interesting to see if the minimum gap of nano-crystals enhances the optical absorptions.

## Approach

$\text{CuYO}_2$  nano-crystals have been considered here as the prototype delafossite. These nanostructures were modeled in such a way that the basic structural features of delafossite have been retained. In delafossite structures, O and Cu form linear bonds along the  $c$ -axis, and O– $M$  ( $M$  = transition metal atoms, such as Y) form distorted octahedrons. These octahedrons are connected by the Cu–O chain. All the nano-crystals considered here have oxygen terminated surfaces on both the lower and upper face (Figure 1). Upon several testing, it has been found that Y-terminated structures (either on both or one side) are heavily distorted and are less stable.

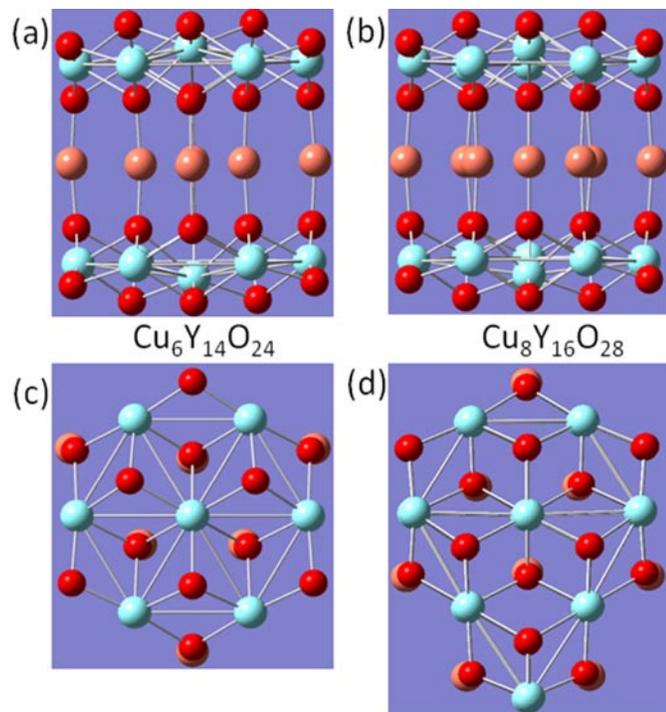
For the present report, *Gaussian03* code [17] has been used to calculate the electronic structures of  $\text{CuYO}_2$  nano-crystals. Hybrid density functional theory with B3LYP

functional [18-20] was used with the LANL double  $\zeta$  basis set and effective core potential [21] to study the delafossite nanocrystals. Hybrid functionals are in general found to be relatively accurate in reproducing the band gaps of semiconductors and insulators [22] for both DFT and TDDFT [23]. Full geometry optimizations with different spin-states were performed to obtain the lowest energy configurations. In addition, to obtain a better description of the optical gap or the electron transition energies from occupied to unoccupied states, we have used TDDFT as implemented in Gaussian03 [24]. All computations were performed at the high performance supercomputing center facilities of the University of Texas at Arlington.

## Results

A charge compensated ionic structure,  $\text{Cu}_m\text{Y}_n\text{O}_l$ , should have  $m+3n-2l=0$ ; where 1, 3 and  $-2$  are the oxidation states of Cu, Y and O atoms in delafossite structure, respectively. Though the overall structure is neutral, a charge uncompensated nanocrystal will have local charged ions and which would lead to charged defect-states in the highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO-LUMO) gap. Another interesting aspect of these nano-crystals is, in addition to charge compensation, the top and the bottom layer of the nano-crystals are self-passivated by extra Y–Y bonds (Figure 1), which are not found in the corresponding bulk structure [14]. These self-passivated and charge compensated metal-oxide nano-crystals are a unique set of nano-materials with very high chemical stability. It is very challenging to model such nano-crystals with basic delafossite features. Figures 1(a) and (b) show the relaxed structures of two of the charge compensated nanocrystals, and the top views are shown in Figure 1(c) and (d). Extra Y–Y bonds are seen here, which saturate the Y–O octahedrons and resulting in no unpassivated dangling bonds. Even at this small level, the basic delafossite structure, i.e., O–Cu–O linear chain-like bonds bounded by O–Y octahedrons are visible.

**Binding Energies:** The binding energies were calculated with respect to the infinite separation limit of the constituent atoms at their ground state spin configurations. First of all, the binding energies per atom are considerably high, implying that in general these nano-crystals are stable. Binding energy per atom is slightly higher for  $\text{Cu}_6\text{Y}_{14}\text{O}_{24}$ , which is charge compensated with zero dipole moment. It has binding energy of 5.408 eV/atom. On the other hand charge neutral, but non-zero dipole moment structure has little lower binding energy, for instance 5.390 eV/atom for  $\text{Cu}_8\text{Y}_{16}\text{O}_{28}$ . In fact this has a little higher dipole moment of 14.820 Debye which contributes to the polar nature of the structure. On the other hand, the charge uncompensated structure, such as  $\text{Cu}_8\text{Y}_{16}\text{O}_{24}$ , has relatively much lower binding energy of 5.165 eV/atom. To see how much charge imbalance affects the stability, we further show binding energy of another



**FIGURE 1.** Relaxed structures of two charge compensated delafossite nanostructures: (a)  $\text{Cu}_6\text{Y}_{14}\text{O}_{24}$  and (b)  $\text{Cu}_8\text{Y}_{16}\text{O}_{28}$ . Structures in (c) and (d) are the top-views of structures presented in (a) and (b), respectively. Orange, red and light green balls represents Cu, O and Y atoms, respectively.

non-charge balanced structure,  $\text{Cu}_8\text{Y}_{18}\text{O}_{32}$ , 5.351 eV/atom. However, in the former case the unsaturated charge is +8, in the later the it is only -2. It can be argued here that *the more charge balanced a structure is, the higher the binding energy*.

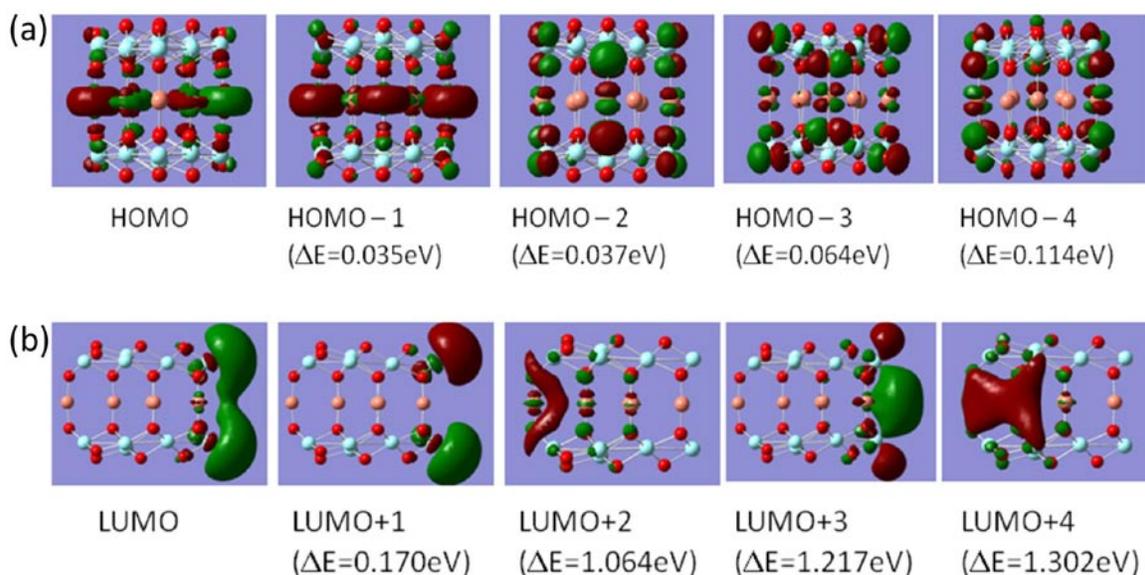
**HOMO and LUMO:** Figure 2(a) shows the structure of the topmost five occupied orbitals for  $\text{Cu}_8\text{Y}_{16}\text{O}_{28}$  structures. This structure is especially chosen for the fact that it is a charge compensated structures with non-zero dipole moment, hence will represent a more general case. Here the HOMO is mainly situated around the Cu atoms in the middle with some contributions from O-atoms which are bonded with Cu. The outer O-atoms (top and bottom surfaces) do not have any significant contributions to these top occupied orbitals. The shape of the HOMO around the Cu atoms is clearly indicative of  $3d_{z^2}$  orbital. The same is true for the HOMO-1 orbital which is only 35 meV lower than the HOMO. These features can be directly compared with the bulk delafossite structures where valence band maximum is mainly composed by Cu-d with O-p hybridization [14]. From HOMO-2 orbital and further below, the  $3d_{z^2}$  structure is no longer seen; rather mixed components of  $3d$  orbitals get prominent. As expected, Y has practically no contribution to these orbitals. In case of ionization, an electron will be taken out from the HOMO. Our calculated adiabatic ionization potential is 6.557 eV which is very high.

Similarly, we have also studied the first five unoccupied orbitals, i.e., LUMO, LUMO+1, etc. and are presented in Figure 2(b). Unlike the position of HOMO, LUMO is mainly situated on one side of the structure and have major contributions from all the three types of atoms, while the

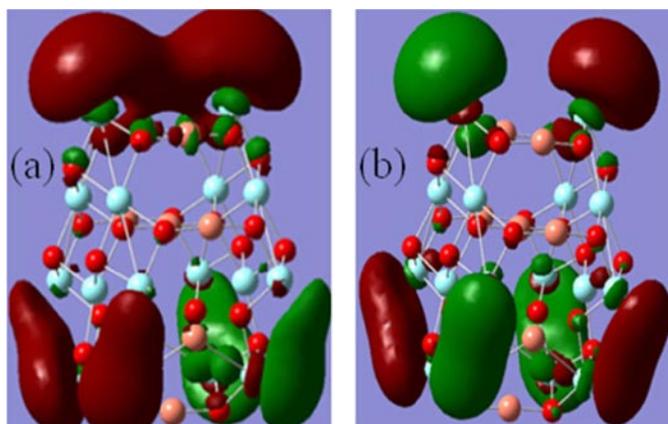
contribution from corner Y atoms is higher. The almost sole contribution from Y atoms was found at LUMO+1 which is 170 meV higher than LUMO. It does not distribute itself throughout the structure, rather situated in two corners. LUMO+2 and above have considerably higher energies, hence may not contribute much on the chemical properties of this structure. It is important to note, the distribution of HOMO is almost over all the Cu atoms, however LUMO is only on the Y atoms which are in one side of the structure. The apparent asymmetric distribution of LUMO could be highly structure dependent. If an extra electron is received by this LUMO, the electron will occupy an unfilled Y-orbital, and the corresponding electron affinity is considerably higher, 1.818 eV.

Next we discuss briefly HOMO and LUMO for a charge uncompensated structure,  $\text{Cu}_8\text{O}_{24}\text{Y}_{16}$ , as shown in Figure 3(a) and (b), respectively. In contrast to the charge compensated structure discussed above, Cu atoms do not contribute much to the HOMO for  $\text{Cu}_8\text{O}_{24}\text{Y}_{16}$ . The largest contribution to both HOMO and LUMO comes from the under-coordinated Y atoms. This under-coordination of Y atoms is also responsible for the distorted Cu-Y bond as seen in here. Hence these HOMO and LUMO can mainly be considered as charge defect states. Here again, the Y-O octahedrons do not contribute to the HOMO and LUMO. The atomic sites and the relative sizes of HOMO and LUMO do not differ much for this charge uncompensated structure. The energy difference between the HOMO and LUMO is only 0.582 eV.

**Optical gaps by TDDFT:** The first excitation energy calculated by TDDFT [24] with non-zero oscillator strength would give an estimation of the optical gap for the nano-



**FIGURE 2.** (a) Valence band (HOMO) composition for  $\text{CuYO-52}$  ( $\text{Cu}_8\text{Y}_{16}\text{O}_{28}$ ) nano-structures is shown here. HOMO-n refers to the  $n$ th orbital below the HOMO.  $\Delta E$  is the energy difference between the HOMO and HOMO-n orbitals. Here we have shown the first five occupied orbitals. (b) Similarly, LUMO is shown here for the same structure. Here LUMO+n refers to the  $n$ th orbital above the LUMO.



**FIGURE 3.** (Color online) (a) HOMO and (b) LUMO of fully optimized  $\text{Cu}_8\text{Y}_{24}\text{O}_{16}$  structure is shown here.

crystals. For example, the first excitation energy for  $\text{Cu}_8\text{Y}_{16}\text{O}_{28}$  was found to be 2.734 eV which is less than its hybrid DFT HOMO-LUMO gap of 3.165 eV. Interestingly, this transition is not allowed as the oscillator strength was found to be zero here. This can be compared to the bulk  $\text{CuYO}_2$  where the optical absorption is symmetry forbidden at the minimum direct gap as well [15]. In fact, for  $\text{Cu}_8\text{Y}_{16}\text{O}_{28}$  the first five excitations have all zero oscillator strength, implying that none of the low energy transition is possible. Similarly, the first excitation probabilities (oscillator strengths) of other structures were also found to be zero. However, for  $\text{Cu}_6\text{Y}_{14}\text{O}_{24}$  the third excitation showed non-zero oscillator strength at energy of 2.931 eV, which is 0.020 eV higher than the first excitation gap. For charge uncompensated structure, like  $\text{Cu}_8\text{Y}_{16}\text{O}_{24}$ , the oscillator strength in the first excitation energy was very small, almost zero. However, this excitation is between the charge defect states, and predominantly on the Y-site.

## Conclusions and Future Directions

A set of self-passivated and charge-compensated nano-crystalline delafossites structures have been presented here. The goal was to (i) model these nano-crystals and find out their stability, and (ii) whether the nanocrystals would enhance the suppressed optical absorption found in delafossite bulk crystals. It has been found that the  $\text{C}_m\text{Y}_n\text{O}_l$  nano-crystals have, in general, high binding energies which are more than 5 eV/atom. The stability of these delafossite nano-crystals is ensured by the Y-Y bonds to passivate the terminating surfaces. The HOMO-LUMO gaps are, in general, higher for the charge-compensated structures. For instances, both the charge-compensated structures has gaps more than 2.7 eV calculated by TDDFT. Interestingly, the absorption probabilities for the first few excitation energies are zero for these nano-crystals. This implies that the enhancement of optical absorption at nano-level compared to bulk can be challenging. This conclusion may apply for

other metal-oxide nano-crystals with inversion symmetries. To test this hypothesis, we will further investigate optical absorptions of other nanocrystals in the next year, such as  $\alpha\text{-Fe}_2\text{O}_3$  and  $\text{MoS}_2$ . Other future plans include:

- Transport properties calculation.
- Electron hopping to the surface, and transfer of electrons from the surface will be studied.
- Doped nano-crystals will be considered.
- Detail orbital analysis will be performed to understand and predict other nano-structures for photo-catalysts.

## FY 2012 Publications/Presentations

1. *Mott insulators: An early selection criterion for materials for photoelectrochemical  $\text{H}_2$  production.* **M.H. Huda**, M.M. Al-Jassim and J.A. Turner. *Journal of Renewable and Sustainable Energy*, **3**, 053101 (2011).
2. *The effect of Bi alloying in Cu delafossites.* M.N. Huda, Y. Yan and M.M. Al-Jassim, *Journal of Applied Physics*, **109**, 113710 (2011).
3. *The electronic structures of Cu delafossites nanocrystals for PEC hydrogen production: A density functional theory study.* **M.N. Huda**, Y. Yan and M.M. Al-Jassim. American Physical Society Meeting, Dallas, Texas (2011).
4. *A first principle study of noble metal atoms doped in Si nanocrystals.* M.N. Huda and C.L. Mayfield. 23<sup>rd</sup> Annual Workshop on Electronic Structure Methods, University of Pennsylvania (2011).

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