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First principles study of bonding, adhesion, and electronic structure at the $Cu_2O(111)/ZnO(10\bar{1}0)$ interface

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ABSTRACT

Density functional theory (DFT)-based methods are used to understand atomic level interactions and calculate adhesion energies of the $Cu_2O(111)/ZnO(10\bar{1}0)$ interface with varying Cu_2O coating thickness. We first establish an accurate model of the ZnO substrate, validating DFT + U against the more accurate hybrid-DFT to calculate properties of bulk wurtzite ZnO and the $ZnO(10\bar{1}0)$ surface. DFT + U is then used to analyze the structure of the $Cu_2O(111)$ surface, characterizing the formation of surface copper dimers. The $Cu_2O(111)/ZnO(10\bar{1}0)$ interface is found to be only weakly interacting, with a DFT + U–derived adhesion energy of 0.85 ± 0.07 J/m^2. Charge density analysis reveals that some interface stabilization occurs because of local Zn – O and Cu – O bonding interactions at the interface. We find that the overall impact of the ZnO substrate on the electronic structure of the Cu_2O overlayer is to reduce the Cu_2O band gap.

1. Introduction

The reduction of CO_2 to methanol is attractive as a renewable source of a fuel precursor and a means of reducing CO_2 concentrations in the atmosphere. Methanol can be readily converted into gasoline by the well-known zeolite-based Mobil process [1–3]. Commercial production of methanol typically uses a Cu/ZnO catalyst with syngas and CO_2 feeds [4]. While there is some uncertainty regarding the nature of the active site on the Cu/ZnO catalyst, oxidized Cu(I) sites are thought to promote catalytic activity and selectivity toward methanol production [4–7]. To increase catalytic activity and potentially create a photochemically-driven catalyst, Cu_2O has been proposed as an enhanced catalyst for methanol synthesis, as its surface contains Cu(I) ions that may strongly bind reactant molecules while acting as reduction sites [8,9]. Cu_2O is also characterized by optical properties that may enable catalysis to be driven photochemically without an external bias, as has been employed in photocatalytic water splitting [10].

Early studies of the electrochemical activity of Cu_2O for CO_2 reduction have exhibited increased methanol yields and Faradaic efficiencies, but Cu_2O also degrades in the process due to its simultaneous reduction to Cu [8,9]. Stabilization of Cu_2O during catalysis is crucial for it to be a sustainable catalyst. Greater catalyst stability was achieved recently using hybrid CuO–Cu_2O semiconductor nanorod arrays [11]. Another method of stabilization derives motivation from the role of the ZnO substrate in the Cu/ZnO catalyst, where ZnO is presumed to stabilize the oxidized Cu(I) active sites [4–7]. Stabilization of a Cu_2O catalyst might therefore be accomplished via the deposition of Cu_2O on a ZnO substrate, which might act to stabilize the oxidized Cu(I) ions of Cu_2O in a similar manner as in the Cu/ZnO catalyst. This demands a better understanding of the stability and electronic properties of the Cu_2O/ZnO interface, which we undertake using methods based on first-principles density functional theory (DFT). A study of Cu_2O/ZnO interfaces will also contribute insight into Cu_2O/ZnO heterojunction solar cells.

We chose to study the interface comprised of the two nonpolar, low-energy surfaces of its components, where the surfaces considered are unreconstructed and bulk terminated (i.e., no surface vacancies). There are three stable phases for ZnO — rocksalt, zinc blende, and wurtzite. The wurtzite structure is the most stable under ambient conditions, and is therefore the relevant phase for our applications. Wurtzite ZnO is dominated by low index surfaces, specifically, the nonpolar $(10\bar{1}0)$ and $(11\bar{2}0)$ surfaces and the polar zinc-terminated (0001)–Zn and oxygen-terminated $(000\bar{1})$–O basal plane surfaces. Early qualitative low-energy electron diffraction (LEED) experiments identified the nonpolar $(10\bar{1}0)$ surface as the most stable face [12], which was verified by a number of DFT-based calculations of surface cleavage energies [13–16]. Cu_2O is stable in the cuprite crystal structure, and only the (111) and (100) surfaces have been characterized experimentally

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[17]. Using DFT + U, we have shown elsewhere that the ideal bulk-terminated (111) surface is lower in energy than the ideal (100) surface [18]. We therefore studied the $Cu_2O(111)/ZnO(10\bar{1}0)$ interface. Here we consider the stoichiometric $Cu_2O(111)$ surface, although future work will be needed to consider interfaces containing copper vacancies thought to be favorable on the (111) surface [18–21].

First row, mid-to-late transition-metal oxides are strongly correlated materials that are challenging to model with Kohn-Sham DFT, largely due to the self-interaction error of local and semilocal exchange-correlation (XC) functionals. In modeling the $Cu_2O(111)/ZnO(10\bar{1}0)$ interface, it may be important to use variants of DFT that incorporate a fraction of exact nonlocal exchange, such as hybrid XC functionals [22–24], or that introduce a parameterized approximation to exact exchange, such as the DFT + U method [25,26]. DFT with the Heyd–Scuseria–Ernzerhof (HSE) screened exchange hybrid functional was previously employed in accurate modeling of bulk Cu_2O, while the DFT + U method with the Perdew–Burke–Ernzerhof (PBE) generalized gradient expansion (GGA) XC functional [27,28] was identified as an alternative method for accurate structural predictions [29]. Bulk wurtzite ZnO has been studied using a number of DFT XC functionals, including the local density approximation (LDA) XC functional [30–32], PBE, the Tao–Perdew–Staroverov–Scuseria (TPSS) nonempirical meta-GGA functional [33,34], and HSE [16,35]. DFT-HSE predicted accurate lattice constants and bulk moduli, with improved electronic and optical properties in comparison to predictions with other functionals, and is therefore the best method with which to model ZnO. While DFT-HSE offers the ideal accuracy for both materials, it is unfeasible to use DFT-HSE when modeling large system sizes such as interfaces due to its computational cost. Here we explore the use of PBE + U as a less computationally expensive method than DFT-HSE that may offer similar accuracy in structural and electronic properties.

Prior to simulating the interface, it is first necessary to have a model of the ZnO substrate that accurately describes its unique surface properties. The nonpolar $ZnO(10\bar{1}0)$ surface is characterized by surface Zn–O dimers whose bulk fourfold coordination is reduced to threefold coordination. The nature of the surface dimer relaxation offers insight into the bonding character of the material [36]. If ZnO is dominated by ionic character, both atoms of the surface dimer would relax inward toward the bulk from their bulk-terminated positions and reduce the dimer bond length to obtain better screening. However, if the bonding is dominated by covalent character, the cation would surpass the anion in its inward relaxation so that it lies in a plane with its three anionic neighbors, effectively rehybridizing from sp^3 to sp^2. This would result in a strong tilt of the surface dimer with little change to the bond length. Fig. 1 shows the geometry of the surface dimer and the structural parameters used to describe its distortion. The nonpolar $ZnO(10\bar{1}0)$ surface was characterized through LEED analysis by Duke et al., who showed that the surface is not reconstructed but undergoes significant inward relaxation of the surface dimer with the Zn−O bond rotating with respect to the ideal surface plane [37]. They observed a relatively small tilt angle, θ, of 11.5 ± 5°, implying that chemical bonding in ZnO is primarily ionic with some covalent contributions, in agreement with the description of ZnO as being at the borderline between ionic and covalent solids [38].

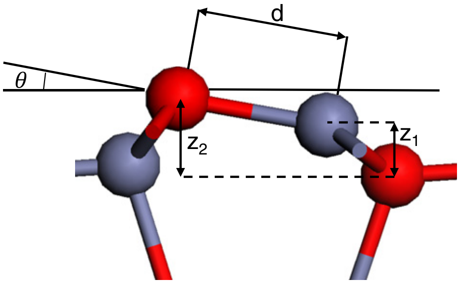

Fig. 1. Diagram of the surface geometry and independent structural parameters used to describe the distortion of the surface dimer on $ZnO(10\bar{1}0)$. Red and gray spheres represent the O and Zn ions, respectively.

Early theoretical calculations of the $ZnO(10\bar{1}0)$ surface used an empirical periodic tight-binding (TB) model, which predicted an overestimated tilt angle of 17.2° [39]. Later first-principles periodic Hartree–Fock (HF) [40], DFT-LDA [41], and DFT-B3LYP [14] calculations predicted much lower tilt angles of 2.48°, 3.59°, and 5.20°, respectively. Their underestimation of the tilt angle was explained as most likely due to unconverged geometries, as these calculations used thin slabs, frozen middle layers, or restricted the relaxation of Zn surface atoms to perpendicular to the surface [16]. More accurate tilt angles of 10.7° and 10.1° were calculated with DFT-LDA and DFT-PBE, respectively, when thicker slabs were used and the atoms in all layers were fully relaxed, illustrating the importance of a fully converged model [16]. Here we study how PBE + U and DFT-HSE compare to earlier theoretical approaches in the modeling of the ZnO surface, and further analyze the character of its chemical bonding.

It is also necessary to develop an accurate model of the $Cu_2O(111)$ surface. Schulz and Cox characterized the $Cu_2O(111)$ surface using LEED and X-ray and ultraviolet photoemission spectroscopies, leading to proposed models of an ideal stoichiometric O-terminated (1×1) surface and a reconstructed $(\sqrt{3} \times \sqrt{3})R30°$ surface with 1/3 monolayer of oxygen vacancies [42]. They did not report the nature of surface relaxation in either termination, prompting further examination of the structure of the ideal $Cu_2O(111)$ surface via theory. DFT-PBE calculations of the ideal surface showed negligible surface relaxation, with a slight contraction of the bonds at the surface and minimal extension of some subsurface bonds to create a more compact surface trilayer [19,43,44]. We use PBE + U in this study, as it showed greater accuracy than DFT-PBE in predicting the ground state properties of bulk Cu_2O [29]. While it would have been best to compare the PBE + U model of the surface to DFT-HSE, this comparison is not feasible due to computational expense, as the $Cu_2O(111)$ slab is too large to be relaxed with the more expensive hybrid functional. Instead we analyze the $Cu_2O(111)$ surface structure predicted with the PBE + U model and compare it to earlier results with DFT-PBE.

Very little is known about the $Cu_2O(111)/ZnO(10\bar{1}0)$ interface, as most previous work has focused on copper oxide coatings on the ZnO(0001) surface, probably because there is evidence that the O-terminated ZnO(0001) surface is the most catalytically active face in methanol synthesis from syngas [45]. $Cu_2O(111)$ overlayers have been experimentally observed on Zn-terminated ZnO(0001) [46,47], and DFT-PBE has been used to characterize the most stable Cu-oxide surface structures on ZnO(0001) [48]. This study will therefore provide insight into a previously uncharacterized interface.

We first compare the performance of PBE + U and DFT-HSE for bulk and surface calculations of ZnO to evaluate the viability of PBE + U for modeling the $Cu_2O(111)/ZnO(10\bar{1}0)$ interface. Our investigation of the $ZnO(10\bar{1}0)$ surface not only establishes a viable model for the ZnO substrate to be used in the interface, but also contributes to understanding its unique bonding character and structural properties. We also use PBE + U to analyze the structure of the unsupported $Cu_2O(111)$ surface and to evaluate its stability. After we validate the performance of PBE + U and develop a suitable model for both the substrate and coating, we then study the energetics and electronic structure of the $Cu_2O(111)/ZnO(10\bar{1}0)$ interface for various coating thicknesses.

2. Methods

The Vienna Ab-initio Simulation Package (VASP version 5.2.2) [49] was used to perform all DFT and DFT + U calculations. Blöchl's all-electron, frozen-core projector augmented wave (PAW) method [50]