First-principles calculations for alloyed nanostructures



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To my parents, who for reasons unfathomable to me, continue to support me

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Abstract

ZnO is one of the most popular materials for light-matter interaction applications, including photocatalysis. One of the main advantages of ZnO for such applications is that it possesses a wide band gap which is direct, located at the Γ point of the Brillouin zone.

Surface alloying allows for tailoring carrier concentration at the surface level by modifying adsorption energies and activation energies for catalysis while preserving the superb electronic structure of the bulk material. Even further, surface alloying can alter the workfunction of the material and allow for it to be tuned for specific photocatalytic applications.

First-principles electronic structure calculations are presented for Mn-doped ZnO with various alloying concentrations at the out-most (surface) layer of Zn atoms, while the interior of the material is kept at the ideal wurtzite structure. For each system, the surface energy and surface workfunction are calculated and trends in surface stability and surface electronic structure of this material, as well as its applications in photocatalysis are discussed. It is shown that for specific terminations of the slab tunability of the workfunction is achieved without significant loss in stability.

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1 Introduction

Water scarcity is one of the many facets of climate change, one that rears most apparent in countries with little precipitation such as those of the Mediterranean basin. The problem intensfies further in areas that have been subjected to extensive use of pesticides, heavily disrupting the water cycle [1].

The need is thus imperative to develop new methods for wasterwater reclamation and specifically ones that are compatible with renewable, "green" energy sources. One such process, that takes advantage of the bountiful sunlight usually accompanying the countries with low precipitation rate, is photocatalysis, a variation of regular catalysis that is light-driven instead of temperature-driven [2].

ZnO is one of the most popular materials for light-matter interaction applications, including photocatalysis. One of the main advantages of ZnO for such applications is that it possesses a wide band gap which is direct, located at the Γ point of the Brillouin zone. However due to problems integral to the process large scale use of photocatalysis while feasible is not currently comparable in terms of sheer output with thermal catalysis. Rational designs of high-performance photocatalysts are required for sustainable development. To this end, several methods have been proposed for control over the properties of the photocatalyst .

The method used in this work that attempts to alleviate these difficulties is surface alloying, essentially the doping of a semiconductor slab only in the outer surface layer. This allows for tailoring of carrier concentrations while preserving the superb electronic structure of the bulk material.

The goal of this work is to show how surface modification can play a role in the photocatalytic properties of a material and provide insight towards the rational design of more efficient photocatalysts, thus expanding the potential offered by such a promising method.

2 Theory

2.1 Photocatalysis: A Quick Introduction

Photocatalysis is broadly defined as a type of catalysis that increases the rate of a photoreaction —a chemical reaction that requires the presence of light —by adding substances (photocatalysts) that participate in the chemical reaction without being consumed [3].

The most common types of photocatalysts are semiconductor oxides whose bandgap allows for the necessary light-matter interaction. Most elemental, III-V and IV-VI, semiconductors have band gaps too small to be of use. The two most studied ones are the semiconductor oxides ZnO (Zinc Oxide) and TiO₂ (Titanium Dioxide), both of which are non-toxic, abundant and with suitable enough bandgaps for photocatalysis under the presence of sunlight.

The photodegradation of pollutants by using ZnO is shown schematically in Fig. 1. Photocatalysis occurs when the photocatalyst (ZnO) is irradiated by light with energy larger than its bandgap energy E_g ($h\nu \ge E_g$). Light energy absorption then triggers charge separation by exciting electrons from the valence band to the conduction band of the semiconductor, leaving holes in the valence band. The photogenerateded carriers then move to the surface of the photocatalyst. Simultaneously, electrons and holes undergo recombination, which reduces quantum yield. This recombination rate is affected by many factors related to photocatalyst structures and surface modifications.

The reactive electrons and holes arrive at the surface of ZnO and facilitate oxidation and reduction reactions that generate excess reactive oxygen species, including superoxide anion (O_2^{-}) and hydroxyl radical (\cdot OH). This happens because the bottom of the conduction band of ZnO is more negative than the redox potential of O_2/O_2^{-} . As such, these excited electrons can produce O_2^{-} which is a powerful oxidising agent. Similarly, the top of the valence band of ZnO is more positive than the redox potential of \cdot OH/H₂O. Consequently, H₂O molecules can be oxidized by these holes to form hydroxyl radicals. These highly reactive radical groups (OH,O₂⁻) directly oxidize organic pollutant molecules in solutions by adsorption. Intermediates will eventually be converted to green compounds such as CO₂, H₂O and harmless mineral acids [2],[4],[5],[6],[7].



Figure 1: Basic mechanism of ZnO photocatalysis. $E_{h\nu}$ is the irradiated photon energy, R is the electron acceptor, and D is the electron donor (Picture taken from [6]).

So with just a photocatalyst and sunlight, this process creates oxidizing agents capable of degrading complex pollutants such as organic dyes, and inorganic pollutants such as pesticides. However, not all is peachy.

2.1.1 The Issue

Sunlight consists of about 5 - 7% UV light, 46% visible light and 47% IR radiation. The photocatalytic oxidation in the section above has been carried over ZnO and TiO₂ semiconductor oxides using UV light irradiation since that is the wavelength of light the bandgap of these materials corresponds with. ZnO has a bandgap of about 3.3 eV while TiO₂ has around 3.2 eV [8],[9]. So due to the large bandgaps of these materials, light usable for photocatalysis is higher energetically than most of our sun's light. Yet photocatalysis utilizing a larger part of the spectrum would multiply the speed and efficiency of such processes [10].



Figure 2: Distribution of sunlight across the near-visible part of the electromagnetic spectrum. The UV makes only a small fraction of received sunlight. (Picture taken from [11]).

Past research has been focused on achieving high photocatalytic efficiency in the visible part of the spectrum but so far nothing more efficient than ZnO and TiO₂ has been found. Since the photocatalytic process takes place in air saturated and water rich environments, the employed catalyst should remain stable under these conditions. Narrow band gap semiconductors such as Fe₂O₃ ($E_g = 2.3 \text{ eV}$), GaP ($E_g = 2.23 \text{ eV}$) and GaAs ($E_g = 1.4 \text{ eV}$) which can absorb visible light are unstable in aqueous suspensions and therefore unsuitable for photocatalytic applications.

2.1.2 The Solutions

More recent research has been gravitating towards the modification of the materials that are already good photocatalysts, specifically ZnO and TiO_2 in order to lower their bandgap, while preserving their good photocatalytic properties.

A host of methods have been employed to that end, with varying degrees of success:

Dye sensitization involves the physical adsorption of dyes that occurs through weak Van der Waals interaction between the dye molecule and the surface of semiconductor. It facilitates electron transfer between the dye molecules and the host semiconductor and has been demonstrated as a useful tool to induce visible light photocatalysis on the surface of wide band gap semiconductors like TiO₂ which are otherwise inactive under visible light. Similar techniques include Polymer Sensitization and Surface-Complex Assisted Sensitization [10], [12], [13], [14], [15].

Doping is another popular technique implemented in a multitude of works and with a multitude of results depending on the photocatalyst, dopant and the overall scheme [16], [17]. However, the general consensus is that while doping effectively reduces the bandgap, it does so by creating unwanted states within the bandgap, modifying the good electronic properties of the photocatalyst and thus resulting in reduced efficiency.

One of the more effective methods is the rational design of heterostructures, usually of the metal-semiconductor or semiconductor-semiconductor variety. The first type, called Schottky junction, is formed from the direct and intimate contact of a metal and a semiconductor. The most important property of a Schottky junction is that it allows for only unidirectional electron flow due to the existence of the Schottky barrier at the semiconductor-metal interface facilitating the separation of photogenerated electron-hole pairs.

By taking advantage of an effect called the plasmonic effect which occurs on the surface of a metal if the frequency of incident photons matches the electronic oscillation frequency of the metal surface free electrons. The resonance results in an intense and highly localized electromagnetic field. What essentially happens is that at the interface of the two materials electrons can be excited from metal to the conduction band of the semiconductor. The energy of incident light needed to induce the plasmonic effect is less than the band gap of the semiconductor, so it is feasible to harvest the light energy of the visible part of the spectrum [18], [19], [20].

The semiconductor-semiconductor junction is also highly promising. There are many rational designs with this type of junction, one of the more common ones being called the Z-scheme which is schematically shown in Fig 3. This structure is typically composed of two semiconductors with a staggered alignment of band structures allowing for electrons of the conduction band of one to move to the valence band of the other, allowing for a separation of electron and holes, addressing the issure of recombination.



Figure 3: Schematic illustration of charge transfer driven by photoexcitation of a Z-scheme system (Picture taken from [20]).

In both cases it is important to know and have control over the Fermi energy level or more specifically of the workfunction of the semiconductor (a quantity that will be discussed in great detail later), since it is a crucial factor for the function of both types of structures developed above. Fine-tuning of the workfunction would allow for greater control over what wavelength of light the structure absorbs and thus over the overall efficiency of the process.

2.1.3 Surface Alloying

Many techniques have been developed to address the problem of finetuning the workfunction of a semiconductor persists. Doping, which is the usual way to alter the Fermi energy of a semiconductor, alters the structure of the material and modifies the good electronic properties of our photocatalysts. A very novel technique designed to address this issue in particular is that of Surface Alloying.

Surface Alloying is a novel form of doping, which consists of replacing atoms of our semiconductor only on the outmost, surface layer of the material on slabs of a semiconductor. While the materials as a whole can be said to be doped, due to the quantity of dopant or solvent added, the surface of the material can be said to be alloyed, hence the name. The hope with this work is to use first-principles calculations to determine whether altering the surface chemistry of the material can change the workfunction of the material, while keeping the other electronic properties of the bulk, the ones that make ZnO a good photocatalyst, intact.

As this work proves that is seemingly feasible but how this happens is not trivial. The workfunction is dependent only on the vacuum energy level and the Fermi energy of the slab, so the exact mechanism behind this change is not self-evident. Further discussion can be found in the Consclusions section.

2.1.4 A Broader Picture

Of course the method of Surface Alloying is much more broad than just its photocatalytic applications. While this work was developed with that goal in mind, Surface Alloying as proven by this work should be able to allow for the finetuning of workfunctions while leaving other properties of the bulk intact. The applications of such a technique are wide, from sensors to self-cleaning surfaces [21].

2.2 Zinc Oxide: A Quick Review of our Photocatalyst

We chose Zinc Oxide (ZnO) as our photocatalyst of choice since it is one of the two most popular photocatalysts and is much easier to create and manipulate in real world experiments [8], [22].

ZnO has a direct wide band gap of about 3.3 eV located at the Γ point of its Brillouin Zone. Some of its main advantages are the availability of fairly high-quality ZnO bulk single crystals, high electron mobility and a large exciton binding energy (about 60 meV). Of course the bandgap is not the only determinating factor of a good photocatalyst. It is important for such a material to be transparrent in order to absorb light and to be stable in the aquatic conditions that are usually present in the photocatalytic reactions, both of which conditions ZnO fulfills.

In addition, ZnO can be produced by very easy crystal-growth techniques, allowing for low cost ZnO-based devices. Also ZnO is not toxic for humans and has been used in cosmetics, food supplements and lubricants for years.

ZnO can be found in many forms including wurtzite (B4), zinc-blende (B3) and rocksalt (B1). However at ambient conditions the most stable phase is wurtzite and this is the one studied in this work, as will be discussed in greater detail later.

2.2.1 Workfunction

For complex systems such as the metal-semiconductor heterostructure the charge polarization formed is determined in large part by the two materials' relative workfunctions (ϕ), defined as the minimum energy needed to transfer an electron from the Fermi energy (E_F) to the Vacuum (V) [20], [23].

$$\phi = V - E_F \tag{1}$$

Therefore, the workfunction is a good descriptor for the electron affinity of a facet. Also, the work function can be a highly effective descriptor for identifying the reduction and oxidation facets of a photocatalyst [24]. When placing two semiconductors adjacent to each other the one with the lower workfunction ought to have the higher Fermi energy, so knowing the workfunction allows us to predict the effects of rational designs of these more complex photocatalytic structures.

2.2.2 Surface Energy

However surface alloying comes itself with a cost. Since the concentrations of our solvent need to be much higher than those of usual doping, at least in the surface, there is a decent chance that the material will not be thermodynamically stable [25], [26].

So in addition to the workfunction we calculate another quantity called the Surface Energy of the slab which serves as our measure of stability and is defined as:

$$\gamma = \frac{E_{slab} - N_{bulk} E_{bulk}}{2A} \tag{2}$$

where E_{slab} is the total energy of the slab, N_{bulk} is the number of atoms in the slab, E_{bulk} is the energy of each atom and A is the slab surface area.

Thus the surface energy is defined as the energy of the slab configuration minus the energy of the individual components per measure of surface. If the surface energy is positive it means that the energy of the surface is higher than that of the bulk. That is very desirable because otherwise it would be energetically favorable for the bulk atoms to move to the surface and the slab would disintegrate as negative surface energy would imply [27], [28].

Thus the Surface Energy serves as a measure of the stability of the slab and serves as an indicator on when the surface alloying has interfered with it significantly.

2.3 Quantum Theory

The Schrödinger equation is the fundamental equation of the atomic and subatomic regime dictating the time evolution of the quantum phenomena, including nuclei-electron interactions among others. The time-dependent Schrödinger equation is:

$$\hat{H}\Psi(x,t) = i\hbar \frac{\partial \Psi(x,t)}{\partial t}$$
(3)

where the Hamiltonian term \hat{H} corresponds to the energy operator and $\Psi(x,t)$ is the wavefunction.

When an electronic structure simulation is performed, the modeling of the interactions is required. However in ground state calculations such as these time-dependence is not important, and we are only interested in the lowest-energy eigenstate of the Hamiltonian. We thus need the time-independent Schrödinger equation:

$$\hat{H} \left| \Psi \right\rangle = E \left| \Psi \right\rangle \tag{4}$$

Still solving even the time-independent equation proves difficult when we have a multitude of ions and electrons in our system. This is the generic Hamiltonian for such a system:

$$\hat{H} = \sum_{I} -\frac{\hbar^{2}}{2M_{I}} \nabla_{I}^{2} + \sum_{i} -\frac{\hbar^{2}}{2m_{i}} \nabla_{i}^{2} + \frac{1}{2} \sum_{I,J} \frac{Z_{I} Z_{J} e^{2}}{4\pi\epsilon_{0}} \frac{1}{|\vec{r_{I}} - \vec{r_{J}}|^{2}} + \frac{1}{2} \sum_{i,j} \frac{e^{2}}{4\pi\epsilon_{0}} \frac{1}{|\vec{r_{i}} - \vec{r_{j}}|^{2}} - \frac{1}{2} \sum_{I,i} \frac{Z_{I} e^{2}}{4\pi\epsilon_{0}} \frac{1}{|\vec{r_{I}} - \vec{r_{i}}|^{2}}$$

$$(5)$$

where the capital indices denotes summation over ions and the lower case indices summation over electrons.

It becomes obvious that this problem is too hard to solve for any realistic simulation of atoms or molecules.

2.3.1 The Born-Oppenheimer Approximation

According to this approximation, the terms in Eq. (5) regarding the ions momentum can be excluded since the nuclei are more than 3 orders of magnitude times heavier than the electrons. The electrons are considered to fill the medium which is formed by the static ions. In that case the Hamiltonian becomes:

$$\hat{H}_{BO} = \sum_{i} -\frac{\hbar^2}{2m_i} \nabla_i^2 + \frac{1}{2} \sum_{i,j} \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\vec{r_i} - \vec{r_j}|^2} - \sum_{I,i} \frac{Z_I e^2}{4\pi\epsilon_0} \frac{1}{|\vec{r_I} - \vec{r_i}|^2}$$
(6)

Still with the positions of the nuclei kept fixed, solving this system by calculating the electronic wave functions remains impossible, even on a computer, since too many degrees of freedom are involved. That is due to the interaction term between the electrons. We can make further approximations to write the Hamiltonian as:

$$\hat{H}_{IP} = \sum_{i} \left[-\frac{\hbar^2}{2m_i} \nabla_i^2 + V(\vec{r_i}) \right]$$
(7)

where the potential $V(\vec{r_i})$ is a function of the nuclear potential which we considered static in the Born-Oppenheimer approximation.

So we have effectively written our Hamiltonian as a sum of one-electron Hamiltonians which can be solved relatively easily. However this last approximation was not without cost. The form of $V(\vec{r_i})$ can be quite complicated; in particular, V depends on the wave function ψ on which the IP Hamiltonian is acting. Moreover, V is often a nonlocal operator which means that the value of $V\psi$, evaluated at position r, is determined by the values of ψ at other positions r', and V depends on the energy in some approaches. These complications are the price we have to pay for an independent electron picture. Thus, while the problem has been greatly reduced, it is far from over.

2.3.2 Density Functional Theory

Most electronic structure calculations for solids are based on density functional theory (DFT), which results from the work of Hohenberg, Kohn and Sham [29],[30]. This is an ab initio approach that has also become popular for atoms and molecules. In the density functional theory, the electronic orbitals are solutions to a Schrödinger equation which depends on the electron density rather than on the individual electron orbitals, by considering a non-uniform spatial electron distribution. However, the dependence of the one-particle Hamiltonian on this density is in principle nonlocal. Often, this Hamiltonian is taken to depend on the local value of the density only in what is termed as the local density approximation (LDA). In the vast majority of DFT electronic structure calculations for solids, this approximation is adopted.

This method can be summed up as follows [24]. According to the Hohenberg-Kohn theorems for a system of many electrons there exists a unique potential that one electron sees describing all others, and such a potential is a functional of the density. This potential can be written as follows:

$$V(\vec{r}) = V_H + V_{xc} \tag{8}$$

The V_H term is the Hartree term and is the electrostatic potential generated by the density $n(\vec{r})$. The V_{xc} term is far more complicated and includes the self-interaction correction, the Pauli exchange and the correlation effect of electrons in the Coulomb potential.

While the we know that potential $V(\vec{r})$ exists, there exists no analytical way of calculating it. Here more approximations such as the LDA discussed above or the Generalised Gradient Approximation which we will discuss in the next section come into play, giving us a way to derive this potential from the density functional. There are higher order approximations, giving progressively better results but at the cost of increasingly more computational time.

After calculating the $V(\vec{r})$ we can proceed to solve the Kohn-Sham equations:

$$\left[-\frac{\hbar^2}{2m_i}\nabla_i^2 + V(\vec{r})\right]\psi_i(\vec{r}) = \epsilon_i\psi_i(\vec{r})$$
(9)

Note that while this looks a lot like the time-independent Schrödinger equation for one particle, is not in fact the same, because the $V(\vec{r})$ term is a functional of the density and on itself an operator.

Thus our wavefunctions $\psi_i(\vec{r})$ will be themselves functionals of the density (hence the name of this theory).

From here we can use the calculated wavefunctions to re-evaluate our density $n(\vec{r})$ from the following equation:

$$n'(\vec{r}) = \sum_{i} |\psi_i(\vec{r})|^2$$
(10)

Thus this allows us to use those equations in an iterative scheme, beginning with an educated guess of the value of $n(\vec{r})$ resulting in progressively better results as follows:

- 1. Starting Density $n(\vec{r})$
- 2. Calculate $V(\vec{r})$ from Eq. (8)
- 3. Calculate $\psi_i(\vec{r})$ from Eq. (9)
- 4. New Density $n'(\vec{r})$]
- 5. Move to step 1

This process can be repeated until we have received self-consistent results, meaning that input density $n(\vec{r})$ and output density $n'(\vec{r})$ match and/or the total energy does not change.

DFT is a very powerful predictive tool especially with the current powerful supercomputers and has been used to calculate ab initio a host of different material properties including but not limited to energy levels and bandgaps, chemical reactions, electronic properties and even optical and dynamical properties in more complex schemes of DFT. Thus it is a very good method to calculate the surface properties we require in our work.

2.3.3 Generalised Gradient Approximation

As we discussed previously the Local Density Approximation (LDA) approximation uses the known exchange energy of the free electron gas and considers the total exchange energy of the system as a sum of the energy per particle of a homogeneous electron gas of density n. As expected this is a good approximation for density homogeneous systems.

Generalized gradient approximation (GGA), however, calculates the total exchange energy with respect to the density gradient, providing more accurate results in surface simulations such as those we want to implement in this work. Such functionals have been constructed by multiple groups and in these work we used the functional potentials of Perdew, Burke and Enzerhof known as the PBE potentials [31].

3 Computational Method

There is a wide array of computational software to implement DFT for quantum chemistry and solid state physics purposes. Some of the most widely used are: VASP (Vienna Ab initio Simulation Package), GPAW (Grid based projector augmented wave method), CASTEP (CAmbridge Serial Total Energy Package) and Quantum ESPRESSO. We have used VASP, written in the Fortran lagnuage. The most essential input parameters for our calculations are:

- The k-point grid for the Brillouin Zone sampling that determines the number of Kohn-Sham wavefunctions that will be calculated.
- The plane wave cutoff (ENCUT) which determines the number of basis functions, the planewaves, that are used to represent each wavefunction.

It is thus important to optimize those parameters for our system, since small enough values cost accuracy while larger than necessary cost computational time.

As mentioned above, PBE potentials have been used, along with a dipole correction since the majority of this work is performed on non-stoichiometric slabs.

4 Benchmark Calculations

In this section we present an extensive set of benchmark calculations we performed in order to find the optimum parameters for our simulations. To this end we studied bulk Zn, ZnO in two of its bulk forms, molecular Oxygen and of course our solute Mn in its bulk form.

For each calculation as a first step we kept k-point grids constant and allowed the ENCUT parameter to change, graphing the change in the lattice constant (or other physical parameter) of our system. Then we did the opposite, allowing the k-point grid to change while keeping the ENCUT constant. Both for high k-point grids and for high ENCUT, we observe that the physical parameters converge to a value. Thus higher values of grid or ENCUT only add more computational time.

From these diagrams we proceed to determine a sufficient but minimal ENCUT and k-point grid required to perform the calculation properly with that material.

Finally as a check we calculate the same physical parameters with our new benchmark parameters. The results are summed up in Table 1 at the end of this section.

4.1 Molecular Oxygen

For Molecular Oxygen we study the bond length of the molecule and how it changes with different Energy Cutoff. As is shown in Fig. 4 the bond length converges to a value really close to the experimental one for ENCUT=500 and does not change for higher values of ENCUT. Thus for calculations involving oxygen we should not have to use a higher value.



Figure 4: The bond length of molecular oxygen as a function of the Energy Cutoff (ENCUT)

Molecular Oxygen being a molecule and not a periodic structure requires only a k-point grid of 1x1x1 and thus requires no further investigation there.

4.2 Bulk Zinc

The rest of our materials are bulk so we investigate their lattices constants as a function of both ENCUT and the k-point grid.

In addition bulk Zinc has an hcp structure. Thus we have two lattice constants to check.





Figure 5: Bulk Zn hcp structure



Figure 6: The lattice constant a of the bulk Zn versus the Energy Cutoff (top) and the k-point grid (bottom)



Figure 7: The lattice constant c of the bulk Zn versus the Energy Cutoff (top) and the k-point grid (bottom)

4.3 Zinc Oxide

Zinc Oxide (ZnO) is studied in two separate crystalline forms. In its sphalerite form (ZnO-sph) it has a structure similar to zincblende while in its wurtzite form (ZnO-w) it shows a hcp structure, as shown in Figures 8 and 9. Zincblende/sphalerite is based on a fcc lattice of anions whereas wurtzite is derived from an hcp array of anions. In both structures, the cations occupy one of the two types of tetrahedral holes present. In either structure, the nearest neighbor connections are similar, but the distances and angles to further neighbors differs.

The wurtzite crystal structure is the most thermodynamically stable vari-

ant under atmospheric conditions, and thus the most common. It can be found with non-polar $(1 \ 0 \ \overline{1} \ 1)$ surface termination, with polar $(0 \ 0 \ 0 \ \overline{1})$ Oxygen termination, and with polar $(0 \ 0 \ 0 \ 1)$ Zn-terminated surfaces, which results in different chemical reactivity for different terminations [32], [33].



Figure 8: Sphalerite (zincblende) ZnO structure



Figure 9: Wurtzite ZnO structure

We repeat the above procedure for Zn for each of the two forms.



Figure 10: The sole lattice constant a of the sphalerite structure versus the Energy Cutoff (top) and the k-point grid (bottom).



Figure 11: The lattice constant a versus the Energy Cutoff (top) and the k-point grid (bottom)



Figure 12: The lattice constant c versus the Energy Cutoff (top) and the k-point grid (bottom)

4.4 Bulk Manganese

Finally we examine our solute, manganese. Manganese comes in four forms in nature. Alpha and beta are highly complex forms with many atoms per cell and outside of the scope of this work. Here we examine gamma and delta manganese which are bcc and fcc lattice respectively.



Figure 13: Bcc Mn structure



Figure 14: Fcc Mn structure



Figure 15: The lattice constant a of the bcc Manganese structure versus the Energy Cutoff (top) and the k-point grid (bottom)



Figure 16: The lattice constant a of the fcc Manganese structure versus the Energy Cutoff (top) and the k-point grid (bottom)

4.5 Summing up

A/A	Zn		O_2	ZnO-w		ZnO-sph	bccMn	fccMn
in Å	a	с	1	a	с	a	a	a
theory	2.66	5.00	1.22	3.28	5.33	4.62	3.50	2.78
experiment	2.66	4.95	1.21	3.25	5.21	4.64	3.51	2.80
ENCUT	50	00	500	500		650	450	300
k-point grid	8x8	8x4	1x1x1	4x4x3		8x8x8	5x5x5	4x4x4
Energy/atom	-1.	24	-4.94	-8.93		-8.93	-8.88	-8.82

Table 1: The chemical potentials from early calculations

In summary, our calculations predict lattice constants within 2% or less with the experimental values while requiring minimal computational resources.

We decided to use wurtzite ZnO since while it has very similar energy to sphalerite it requires less resources. In addition we decided to use bcc Manganese over the fcc structure as the base of our solvent because it is more stable energetically.

For our alloyed slab of ZnO with Mn we used a Energy Cutoff of 500 as that seems to be sufficient for all of the materials present.

5 Workfunction and Surface Energy Calculations

5.1 The slab

To perform our calculations we constructed slabs of the following form:



Figure 17: An example of a slab from the side view (left) and top view (right). With red are the Oxygen atoms, blue for Zinc atoms and brown for Manganese. This is the 25% Manganese on the surface case for a stoichiometric slab of 6 layers.

All of our slabs are constructed to have 4 atoms per layer. However since we have periodic boundary conditions on the x and y axes, our system corresponds to an idealised slab 6 layers thick and of infinite size in the x and y axes. One layer is counted as a layer of Oxygen and a layer of Metal. Essentially our slab is a ZnO slab in its wurtzite form, except for our surface solute. On the surface in our example we have one Manganese atom (brown) and three Zinc atoms (blue). This corresponds to a 25% alloying, since in our extended slab, one Zinc atom in four will be replaced with Manganese. Finally we have added a large vacuum on the z-axis of the slab, of the order of 25 Å. This way we will be able to calculate the local potential away from the slab, for reasons that will become apparent in the next section.

5.2 Workfunction

As discussed earlier the Workfunction is defined as the difference between the vacuum energy level away from the slab and the Fermi Energy level of the slab:

$$\phi = V - E_F \tag{11}$$

The Vasp software provides the Fermi Energy and constructs the Local Potential around from the slab.



Figure 18: The Local Potential and the Fermi Energy of a slab.

In the vacuum region, away from the slab, the Local Potential V forms a plateau allowing us to calculate it with very small deviation.

The Fermi Energy is given directly from the Vasp algorithm and while the zero of the scale of energy is arbitarily defined, the difference of these two energies that is the workfunction is without ambiguity.

5.3 Surface Energy

As we discussed in the theory section, the Surface Energy is defined as:

$$\gamma = \frac{E_{slab} - N_{bulk} E_{bulk}}{2A} \tag{12}$$

Note that what here is termed E_{bulk} is essentially the chemical potential of each atom species, so perhaps a better description would be μ_{bulk} instead of E_{bulk} , but Eq 12 is more well-known. For our slab where we have Zinc, Oxygen and potentially Manganese atom this equation becomes:

$$\gamma = \frac{E_{slab} - N_{Zn}E_{Zn} - N_O E_O - N_{Mn}E_{Mn}}{2A} \tag{13}$$

We take the slab Energy E_{slab} directly from Vasp and the energies of the different types of atoms from our benchmark calculations. However, it is unclear as to which energy we should use for each type of atom.

An oxygen atom has a different energy (or more precisely a different chemical potential) inside the oxygen molecule (approximately -4.93 eV) and different inside a ZnO atom (approximately -7.69 eV). Similarly for Zinc, having to choose between the chemical potential of bulk Zinc (-1.24eV) and that of the atom inside ZnO (-4 eV).

To deal with this problem without excluding any scenario we create the following pair of equations:

$$E_{Zn} = x E_{Zn}^{bulk} + (1 - x)(E_{ZnO}^{bulk} - \frac{1}{2}E_{O_2})$$
(14)

$$E_O = y \frac{1}{2} E_{O_2} + (1 - y) (E_{ZnO}^{bulk} - E_{Zn}^{bulk})$$
(15)

where E_{Zn}^{bulk} is the energy of a Zn atom in the Zn bulk, E_{O_2} is the energy of the oxygen molecule and E_{ZnO}^{bulk} the energy of a Zn atom and Oxygen atom in the ZnO cell. This way the energies (or again, more precisely the chemical potentials) of Zinc and Oxygen are calculated from both their bulk or molecular form or from ZnO, weighted with two different factors x and y that move between 0 and 1. Using Eqs 14-15 and values of the chemical potentials gathered from our benchmark calculations and summed up again in Table 2 we are able to

A/A	$E^{ZnO}_{slab}(eV)$	$E_O^{mol/2}(eV)$	$E_{Zn}^{bulk}(eV)$	$E^{bulk}_{ZnO}(eV)$
my calculations	-177.05	-4.93	-1.24	-8.93
database values	-	-4.95	-1.26	-9.10

Table 2: E_{slab}^{ZnO} is the Slab Energy for a regular ZnO calculation. Next are calculated shown the chemical potential from our calculation in the first row and compared with theoretical values from other calculations. Database values taken from materialsproject.org [34].

The results can be summed up on the following contour plot, where the x and y axes give the values x and y from Eqs 14, 15 and the z-axis gives a different value of Surface Energy in terms of color in J/m^2 . Red for the very high values of about 15 J/m^2 and blue for the very low of about $-10 J/m^2$.



Figure 19: The z-axis gives Surface Energy γ of a ZnO slab with colours while the x and y axes are correspondingly the x and y variable from Eqs 14, 15

Realistic values are usually on the low single digits so the green valley on slashing the plot diagonally from the upper left to the bottom right is our desired area. In this specific work we have used $E_{Zn} = (E_{ZnO}^{bulk} - \frac{1}{2}E_{O_2})$ and $E_O = \frac{1}{2}E_{O_2}$ which correspond to x=0, y=1 or the upper left corner of the Fig. 19.

5.4 The Process: Step by Step

For the curious reader the exact process used to calculate the results can be found here. More about the trial and error required to reach this scheme can be found in Appendix A.

We take the Oxygen-terminated case for 25 % Manganese on the surface as an example. VASP has 4 input files required to start a calculation: The POSCAR file where the geometry lies, the INCAR file where the commands are given in the form of tags, the KPOINTS file where the k-point grid is determined and the POTCAR file which contains the pseudopotential for each atomic species used in the calculation as discussed in the DFT part of the Theory section. Out of the four, only the three are provided by hand, POTCAR instead is provided by VASP.

Since our original slabs were created ab initio it is important to perform a relaxation on them, for the atoms to acquire a more relaxed geometry. In order to mimic the bulk structure beneath the surface, the atoms of the outer two layers on each side were fixed while the middle two layers were allowed to be fully relaxed until the total (free) energy change and the band structure energy change between two steps are both smaller than 10^{-7} eV.

A conjugate-gradient algorithm was used to relax the ions into their instantaneous groundstate. In the first step ions (and cell shape) are changed along the direction of the steepest descent (the direction of the calculated forces and stress tensor). From there the algorithm performs in rotation trial steps and corrector steps until the forces are below a given value. A more detailed discussion can be found in Numerical Recipes, by Press et al.

In our case we kept the positions of the inner atoms constant, since they ought to be in good approximation of the bulk ZnO and allowed the positions of the outer layers of atoms where the Mn atoms were to change. Cell shape and cell volume was also kept constant.

0-TERM ZNO 25% MN				
1.00000000000000000				
6.559999999999999	96 0.000000000000000 0	0.0000000000000000000000000000000000000	90	
0.000000000000000	00 5.6811266488259164 0	0.0000000000000000000000000000000000000	90	
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4.9199999999999999999999	4.7342722073549304 24.665320	05128205144 T		#Dipole Correction centering
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Figure 20: The POSCAR file (left) and the INCAR file (right) used for relaxation

Our KPOINTS file is very simple, just a Mohkrost-Pack of a 3x3x1 grid to accound for our system being a slab:



Figure 21: The KPOINTS file used for relaxation

Then we proceed to use the output of the relaxation, essentially a new POSCAR file to calculate the local potential and energies (Fermi and slab), required to determine the workfunction and surface energy. To do that we do a simple convergence calculation along with a 3D plot of the local potential like Fig 18. The KPOINTS file does not change.

O-TERM ZNO 25% MN						l l
1.000000000000000						I
6.55999999999999999	96 0.00000000000	0000 0.0000000000	00000	00		I
0.0000000000000000	00 5.681126648825	9164 0.0000000000	00000	00		I
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2 24 18						I
Selective dynamics						I
Direct						I
-0.00000000000000000	0.3373411403699761	0.3726075339923801	Т	Т	Т	I
-0.00000000000000000	0.3327524815502358	0.6615154842213166	Т	Т	Т	I
-0.00000000000000000	0.3328501929354072	0.3303918538840578	Т	Т	Т	I
0.7516391026559140	0.8324846500683891	0.6068946602113396	Т	Т	Т	I
0.50000000000000000	-0.0041553516092440	0.6764068794023202	Т	Т	Т	I
0.500000000000000000	0.3349616965606357	0.6069640198453794	Т	Т	Т	I
0.75000000000000000	0.50000000000000000	0.5356999330207657	F	F	F	I
0.75000000000000000	0.83333333333333357	0.4643000669792343	F	F	F	I
0.50000000000000000	0.00000000000000000	0.5356999330207657	F	F	F	I
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0.2500554055504050	0.8377292004422352	0.0020102373070724		- T	T	#Dipole Correction
0.2528105520210520	0.5020072444771140	0.3654007356574565	F	F	F	LDIPOL = .TRUE.
0.5000000000000000000000000000000000000	0.333333333333333357	0.4400201930419373	F	F	F	IDIPOL = 3
0.5000000000000000000000000000000000000	0.333333333333333333333	0.910020001009000.				$DIPOL = 0.5 \ 0.5 \ 0.5$
) contoring

Figure 22: The POSCAR file (left) and the INCAR file (right) used for convergence and local potential calculation.

The Vacuum Level energy is then calculated from taking the averaging the potential away from the slab, where its relatively flat as can be show in Fig. 23.



Figure 23: The Local Potential of the slab. Note that the vacuum level has been put in the center of the graph like in Fig. 18.

5.5 The Workfunction as a function of Slab Thickness

We began our calculations by identifying a sufficient slab thickness for us to work with. To do this we calculated the Workfunction and Surface Energy for the 0% Mn case which is essentially a regular ZnO slab, and the 100% case which is essentially a ZnO slab where every Zn atom in the surface has been replaced by a Mn atom.

Our results are summed up on Table 3

# layers of ZnO	Workfunction $\phi_0 - \phi_{100}$	Surface Energy $\gamma_0 - \gamma_{100}$
4	0.0	1.48
6	-0.4	1.52
8	-0.4	1.51
10	-0.5	1.51

Table 3: Workfunction and Surface Energy for increasing slab thickness in Metal-terminated ZnO slab

We see that both of our properties converge relatively well for increasing slab thickness. Thus we take the 6 layer case to be a good enough approximation for higher slab thickness.

5.6 The Workfunction as a function of Surface Manganese Concentration

Working with 6-layer slabs we have identified three configurations with different workfunctions and surface energies presented on Figure 24:



Figure 24: Different configurations of 6 layer ZnO lab with 25% Mn. Stoichiometric (left column), Metalterminated (middle column) and Oxygen-terminated (right column)

The left column is our stoichiometric slab, essentially just a slab of ZnO with our solute. The top end (on the side view) is made of oxygen, while the bottom end is made of metal.

If however we cleave off the top layer of oxygens we create a slab that is Metal-terminated on both ends, as shown in the middle column (it should be noted that when we refer to layers in general we mean a layer of ZnO, while a layer of oxygen or metal is used to reference the upper or bottom half of that). This, as will be demonstrated, leads to very different values on the Workfunction and of course the Surface Energy. By doing the reverse, we cleave off the bottom layer of metal to create, as is shown on the right a slab that is Oxygen-terminated on both ends.

Thus we proceed to calculate the Workfunction and the Surface Energy in these three configurations as a function of the increasing concentration of Manganese on the surface. The results for the Workfunction can be summed up on Figure 25:



Figure 25: The Work function ϕ as a function of the surface concentration of Manganese for the different terminated configurations

As we see changes on the surface concentration do lead in changes in the workfunction of about 1 eV for the Metal-terminated and Stoichiometric cases while for the Oxygen-terminated they are almost 3 eV.

Similarly in Figure 26 we can see the trends of the Surface Energy for these same configurations.



Figure 26: The Surface Energy γ as a function of the surface concentration of Manganese for the different terminated configurations

As is obvious from Figure 26 the Surface Energy or the Oxygen-terminated and stoichiometric slabs starts lower and decreases even further. In fact, for the cases > 25% Mn the Surface Energy is negative, suggesting that these configurations are unstable. However the Metal-terminated case does exemplify small variation in stability for increaseing concentration of Mn.

In Figure 27 we see one of these configurations and as we can see, even from the atom structure, after relaxation our configuration seems largely jungled up.



Figure 27: The O-terminated case with 75% Mn on the surface after relaxation.

The problem with a technique as novel as Surface Alloying is that to the best of our knowledge no experimental work of this configuration has been tried as of the writing of this thesis. However in order to apply some measure of experimental check in our theoretical calculations we compare the work-function of pure ZnO compared to the theoretical and experimental values as provided by Fang-Ling Kuo et al. [35].

This work	Fang-Ling Kuo et al. [35]	Fang-Ling Kuo et al.
	(experiment)	(theory)
4.29 eV	$3.74 \mathrm{~eV}$	5.1 eV

Table 4: Workfunction of ZnO comparison between this work and Fang-Ling Kuo et al.

The difference between our calculation and the experimental value is around 0.5 eV which is not trivial. However it should be noted that workfunction is very hard to measure experimentally because it is dependent on how the material was placed and the exact conditions of the room. In addition the thickness of slabs of real ZnO was much larger than our 6 layered slab.

A second thing that should be noted is that the computational value calculated in the same paper is even further away from the experimental value, suggesting that this difference is to be expected. Fang-Ling Kuo et al. used a very similar scheme as in this work to calculate the workfunction computationally, and the difference between the two values is probably due to how they measured the vacuum energy level, by not applying a dipole correction and instead choosing a point in the middle of the vacuum region, while in the present thesis we average the workfunction in the two plateaus formed by the dipole correction.

6 Conclusions

An issue that needs to be addressed is how the alteration of surface chemistry can change something like the workfunction which seems to be dependent only on bulk properties. The idea is not without precendence. It is known that different facets of the same crystal can sport different workfunctions. The answer lies to the surface states present at the edge of the material.

Those surface states are widely known for pinning the Fermi Energy level, making methods such as doping ineffective in altering the workfunction of the material in applications such as the Schottky junction. With Surface Alloying we completely alter the surface chemistry of the material, and thus the surface states. So we change the local Fermi energy level close to the surface, while leaving the bulk Fermi energy level and thus the rest of the properties of the material intact.

Of course, Surface Alloying is not the only method designed to address the issue of finetuning the workfunction. In Table 5 it is shown that the workfunction range for the stable Metal-terminated case is 0.68 eV. Compared to the work of Sun et al. where they created an inteface of ZnO-MoO₃ and their effective range was around 0.1 eV, our result offer a greater deal more finetuning. In another work by Ghosh et al. they use the combination of two techniques to produce a result of over 1 eV in range.

So we see that Surface Alloying is comparable or better than other similar techniques, and one thing that should be noted in particular is that since we have great control over the amount of Mn in the surface, we have a great deal of control within this effective range, while some of these other techniques are a bit more quantised in their finetuning.

	This work	Sun et al. $[36]$	Ghosh et al. [37]
Method	Surface Alloying	MoO_3 interface	Faceted Au nanostructure
			and oxygen defects
Workfunctions (eV)	4.18 - 4.86	4.10-4.20	3.91 - 4.98
Effective Range (eV)	0.68	0.1	1.07

Table 5: Workfunction ranges for different methods of workfunction tuning.

To conclude, in this work, we studied the effects of Manganese surface alloying on Zinc Oxide slabs with different terminations and for different thicknesses and examined the response of the electronic properties of the material. We calculate the workfunction from the local potential away from the slab and the surface energy from the thermodynamics of its formation. We demonstrated that the surface alloying leads to changes in workfunction, allowing for a measure of tunability on the workfunction for the material, something most desirable for photocatalytic applications. For some terminations, namely the Oxygen termination and the stoichiometric termination, this leads to instability for higher concentrations of manganese. However the Metal termination combines both tunability and stability. In addition, Surface Alloying compares similarly or favorable with similar tehniques, thus ZnO with Surface Alloying makes a great candidate for something like a Z-scheme or Schottky junction rational design.

Additional work could be performed with a different alloy or a different semiconductor, or in even more complex cases co-alloying in the surface, in order to further expand the range of tunability this method provides. In addition experimental work should be performed to verify the results of this work in a realistic setting.

A Appendix: Effects of Computational Parameters

When studying a relatively large system of atoms (of approx. 50 atoms) such as the slabs required for this work, it is crucial for one to choose a suite of computational parameters that fit one's system. And the determination of set of parameters requires a certain trial and error, thus this appendix is devoted to helping any curious reader learn from the mistakes and misteps of the author.

A.1 Dipole Correction

The dipole correction is an artificial correction implemented by the VASP software in order to correct an unphysical error produced by the periodic boundary conditions used in DFT calculations, where not only the total energy converges slowly, but also the potential and the forces are affected by finite size errors.

Most computational software have this option. For VASP that is the LDIPOL tag, which when is set active creates a linear correction and for charged cells a quadratic electrostatic potential is added to the local potential in order to correct the errors introduced by the periodic boundary conditions. For this work the dipole correction was set only on the axis perpendicular to the surface, where the asymmetry exists [38].



Figure 28: 25% Mn Stoichiomtric slab without dipole correction (top) and with dipole correction (bottom).

As should be obvious it is much easier and more accurate to calculate the vacuum energy level and thus the workfunction when the dipole correction is on, forming two relatively flat plateaus instead of a slope.

A.2 The AMIN Parameter

An important parameter for this work was the AMIN tag of the VASP softaware. This parameter specifies the minimal mixing parameter in Kerker's initial approximation to the charge dielectric function used in the Broyden/Pulay mixing scheme and seems rather innocuous.

However for systems where one dimension is far larger than the other, like

in the case of our slab, which along with the vacuum was often close to 50 Å. In VASP this can spoil convergence since charge sloshing might occur along the long lattice vector. It was thus crucial to increase the minimal mixing parameter.

A.3 Magnetic Calculations

Magnetic calculations were performed as a preamble to the main work to determine whether ZnO exhibits any magnetic phenomenon. Both ferromagnetic and the antiferromagnetic structures were studied. The results are summed up in the following table:

	No spin	Ferromagnetic	Antiferromagnetic
workfunction ϕ (eV)	4.0 ± 0.3	4.0 ± 0.3	4.0 ± 0.3
slab energy (eV)	-176.33	-176.36	-176.35

 Table 6: Magnetic Calculations Results

Due to the negligible differences in energy we decided to ignore any magnetic effects.

	Regular DFT	DFT+U
workfunction ϕ (eV)	4.75 ± 0.03	4.79 ± 0.03
slab energy (eV)	-222.45	-218.12

 Table 7: Magnetic Calculations Results

A.4 Different Potential Schemes

Additional Potential schemes were also tried in order to determine whether one offered considerable computational accuracy advantages.

A.4.1 DFT+U

A semi-empirical but effective method is called the DFT+U approach. The basic idea behind DFT+U is to treat the strong on-site Coulomb interaction of localized electrons, which is not correctly described by LDA or GGA, with an additional Hubbard-like term. The on-site Coulomb interactions are particularly strong for localized d and f electrons, but can be also important for

p localized orbitals. The strength of the on-site interactions are usually described by parameters U (on site Coulomb) and J (on site exchange). These parameters U and J can be extracted from ab-initio calculations, but usually are obtained semi-empirically. Its main advantage is the ease with which it can implemented in the existing DFT framework, requiring only an additional parameter. As an example of the effectiveness of the +U correction we calculated bandgap from the density of states of bulk ZnO. This is a problem that DFT is notoriously bad at approaching due to the d electrons of Zinc. While the experimental value of the bandgap of ZnO is close to 3.3 eV as we can see in Figure 29, regular DFT calculates it at roughly 0.7 eV, which is a severe underestimation.



Figure 29: The Density of States of bulk ZnO using regular DFT with PBE potentials

Contrary to that, using only a semi-empirical value of U=6eV in the DFT+U scheme (specifically Dudarev's method) we can calculate a gap of about 2.6 eV, which is a significant improvement for a semi-empirical method.



Figure 30: The Density of States of bulk ZnO using the +U correction in DFT with PBE potentials

However this method's effectiveness diminishes with the addition of Manganese and the slab configuration, providing results that while close to the ones generated by the regular PBE calculations had the additional problems of using semi-empirical parameters.

A.4.2 HSE

Hybrid functionals are a class of approximations to the exchange-correlation energy functional in density functional theory that incorporate a portion of exact exchange from Hartree-Fock theory with the rest of the exchangecorrelation energy from other sources.

The HSE (Heyd-Scuseria-Ernzerhof) exchange-correlation functional uses an error-function-screened Coulomb potential to calculate the exchange portion of the energy in order to improve computational efficiency.

We tried the HSE06 hybrid functional, but to little avail since the computational time required was orders of magnitude more than the plain PBE.

In the end, for our case, both of these methods added little more than additional computational time and were abandoned in favor of the plain PBE potentials.

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