DESIGNING NEW MATERIALS FOR CONVERTING SOLAR ENERGY TO FUELS VIA QUANTUM MECHANICS

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Final Report

to

the Air Force Office of Scientific Research

by

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Executive Summary

This grant was the first to the PI to use first principles quantum mechanics to characterize key atomic-scale elementary processes involved in photocatalysis by novel materials comprised of abundant elements. In particular, we performed computer simulations to evaluate the efficacy of doped and alloyed first-row transition metal oxides for use as catalysts for renewable fuels production. Our work began with extensive testing of methods to calculate properties of interest in photocatalytic production of fuels. These preliminary studies were necessary to establish a quantitatively accurate set of theories to employ when performing photocatalyst modeling, which entails a complicated series of events starting from sunlight absorption to produce electronic excited states (electron-hole pairs), subsequent electron-hole pair separation and transport, followed by redox chemistry at the surface of the catalyst to produce fuels. Properties to be optimized include the material's band gap (which determines the amount of sunlight absorbed), valence and conduction band edge positions (which control whether, e.g., photocatalytic water splitting is thermodynamically allowed), electron-hole pair lifetimes and charge carrier mobilities (which determine whether the charge carriers survive to reach an interface where they can react), and overpotentials for redox reactions at the surfaces of catalysts (which largely control the kinetics of the photoelectrocatalysis). We have examined all of these properties for a number of candidate catalyst materials, and have elucidated important design principles from these studies for future optimization of photocatalysts.

The optimal electronic structure methods to calculate these key quantities vary depending on the property of interest (in practice there is no universal theory that can address all of them). We settled on the following set of techniques, based on extensive benchmarking and in some cases some methodological developments:

- We are concerned here with materials based on mid-to-late, first-row, transition metal oxides; standard density functional approximations fail for such materials for well-known reasons. Consequently, we compute *material structure and band edge character* using *ab initio DFT+U or hybrid DF theories* in order to properly treat intra-atomic exchange interactions between the d-electrons of the transition metal ions. By *ab initio DFT+U*, we mean DFT+U using our method for deriving U from *ab initio* wavefunction calculations. By band edge character, we mean determining whether the band edge is, e.g., dominated by oxygen p-states or metal d- or s-states. Knowing this character has implications both for excited state lifetime and transport

mechanisms.

- The fundamental band gap derived from photoemission-inverse photoemission experiments can be calculated via Green's function methods, namely the GW approximation. We have shown that with accurate ground state eigenvalues and wavefunctions as input, *we can accurately compute transition metal oxide band gaps with the perturbative G0W0 method.*

- If we are interested in local optical excitations, we use embedded correlated wavefunction theory - typically electrostatic embedding for transition metal oxides is sufficient – to compute both electronic excited states and their lifetimes. This is a less expensive and complementary approach to the Bethe-Salpeter equation, which delivers band-to-band single excitation optical spectra.

- Localized charge carrier transport is evaluated using embedded UHF/CASSCF wavefunctions and the small polaron model to calculate mobilities. Delocalized carriers are characterized qualitatively from band structures, densities of states, and the electron densities derived from DFT+U or hybrid DFT calculations.

- Absolute positions of the band edges are determined by a combination of surface work function and bulk fundamental gap calculations. The work function is calculated using DFT+U or hybrid DFT using a periodic slab model to represent the surface. The position of the band gap center with respect to the vacuum level delivers the work function. This value, combined with the fundamental gap computed with G0W0 theory on a bulk sample, allows the band edges to be placed with respect to vacuum. Knowing the absolute positions of the band edges tells us the free energy of the electrons and holes in those levels. Their free energy relative to the reaction free energies for reduction and oxidation determines whether photocatalysis is thermodynamically allowed.

- Finally, we calculate surface redox chemistry using *ab initio* DFT+U theory; for explicit calculation of charge transfer events, we use embedded correlated wavefunction theory.

Our key published findings based on using these methods are as follows:

- Through a simple quantum mechanical analysis, we proposed that the best elements with which to dope parent transition metal oxides are closed or half-filled shell metal ions, since they should not act as traps for charge carriers due to their inherent stability (maximal intra-atomic exchange stabilization).

- We then showed with quantum mechanical simulations that *band gaps and positions of the band*

edges can indeed be tuned by alloying with such closed/half-filled shell metal ions (e.g., Li(I) in NiO, Zn(II) in MnO) to optimize light absorption and the thermodynamic driving force for, e.g., water splitting to produce hydrogen and oxygen.

- Closed or half-filled shell dopants can also be exploited to increase charge carrier concentration without creating traps and hence improve the conductivity of these materials (e.g., Mn(II) in hematite for hole transport, Y(III) in MnO:ZnO for electron transport).

- We discovered that dopants derived from covalent oxides (e.g., Si from silica, as a dopant in hematite) can also be used to increase charge carrier density without creating traps. Charge carriers stay away from such dopants because they would have to occupy high-energy antibonding levels.

- We also found that closed-shell dopants can be used to suppress intrinsic vacancy defects that act as charge carrier traps (e.g., Li(I) in Cu_2O), thereby suggesting a means to improve photoconductivity of cuprous oxide, a material that has garnered intense interest for solar energy conversion because of its optimal band gap and well-placed band edges.

- Finally, we showed the importance of balancing the stability of O, OH, OOH adsorbates for water oxidation (e.g., Co, Ni dopants at hematite surfaces).

During this grant, 17 research articles and two review articles were published. Two utility patents, along with eight provisional patents, were filed during this grant period. 19 invited seminars on this research were given at universities, federal agencies, and national laboratories, and 27 contributed talks and posters were given by graduate students and postdoctoral fellows on this research during the grant period. The PI gave 22 invited and plenary lectures at conferences and workshops on this research during the grant period. Three graduate students who worked solar energy conversion materials research, Ms. Peilin Liao, Ms. Dalal Kanan, and Ms. Leah Isseroff Bendavid, submitted their Ph.D. theses in March 2012, April 2013, and August 2013, respectively. Peilin, Dalal, and Leah are now postdoctoral fellows at Northwestern University, Columbia University, and Stanford University, respectively. Other members of the research team included former postdocs Dr. Maytal Caspary Toroker (now an Assistant Professor at the Technion in Israel) and Dr. John Keith (now an Assistant Professor at the University of Pittsburgh). A former graduate student, Dr. Sahar Sharifzadeh, contributed to one of the publications; she is starting as an Assistant Professor at Boston University. Mr. Nima Alidoust will finish his dissertation this fall; others continue. Publications, patents, and presentations stemming from this work are listed at the report's end.

4

Research Accomplishments

Efficient (photo)electrochemical production of fuels is one of the great technological challenges of our time. Such processes offer the possibility of renewable fuel sources based on either solar or wind energy. However, no viable catalysts exist yet. Over the duration of this grant, we applied first principles quantum mechanics techniques to help identify robust, efficient, and inexpensive materials for photocatalytic electrodes that can convert sunlight, carbon dioxide, and water into fuels. We focused on the physics and chemistry of transition metal oxide semiconductor electrodes, in particular those that have been or could be used as anodes (e.g., hematite) or cathodes (e.g., cuprous oxide) in photoelectrochemical cells to split water. Given the inherent experimental difficulties with probing molecular species at semiconductor electrodes immersed in water, our calculations offer the means to fill the knowledge gap regarding how to optimize light absorption and charge transport, and how to tune the relative stability and reactivity of various photoelectrochemical intermediates, to improve overall efficiency. Armed with such knowledge, it has been possible, to suggest additives to enhance solar energy conversion generally and water splitting in particular. The ability to manufacture renewable hydrogen from sunlight and a proper catalyst is a critical part of the portfolio needed to achieve a fossil-fuel-free future, given that largely all hydrogen today is produced from fossil fuels with carbon dioxide as a byproduct. While hydrogen can be used directly as a fuel, a more important prospective use of renewable hydrogen is in the conversion of biomass to fuels. That process generally requires an enormous amount of hydrogen due to the high oxygen content of biomass that must be removed via hydrogenation to make an energy-dense fuel. So searching for an effective, commercially viable water-splitting catalyst should be a priority for a petroleum-free future for the Air Force.

Our strategy has been to use validated first principles quantum mechanics calculations to test hypotheses we postulate regarding means to improve solar energy conversion efficiency, to explore variations in materials via doping and alloying parent transition metal oxides, and to extract design principles aimed at future materials design of photoelectrocatalysts. We spent years validating different electronic structure methods to determine which ones furnished the accuracy required to make reliable predictions of each property of interest across multiple materials. Given the transition metal oxides we focused on – from the first row and toward the right of the transition series – methods beyond standard density functional theory (DFT)

approximations to electron exchange-correlation are required to capture the correct physics associated with exact exchange for the tightly held 3d electrons in these metals.

In what follows, we outline the insights we gleaned from these extensive systematic studies of methods and properties of pure, doped, and alloyed transition metal oxides relevant for solar energy conversion. We then list the personnel involved, the articles published, patents filed, dissertations submitted, and presentations given during the grant period associated with this research. Numbered citations refer to the publication list.

Band Gaps and Band Edge Positions

We started by evaluating relevant properties of five candidate parent materials: manganese oxide (MnO), wüstite (FeO), hematite (Fe_2O_3), nickel oxide (NiO), and cuprous oxide (Cu_2O). In their pure form, each of these materials has positive features but also major drawbacks. Specifically, while MnO has among the highest conductivity of transition metal oxides and NiO has already been used a co-catalyst in water-splitting, they both have band gaps that are too large to absorb any significant fraction of the solar spectrum. While FeO has a band gap in the visible region, it is unstable at room temperature, among other issues. Fe_2O_3 is already being explored as a photoanode for water splitting because it has a nearly ideal band gap for maximum sunlight absorption but has low conductivity. Finally Cu_2O also has a near perfect band gap and has been used in experimental solar cells, but like FeO and NiO, it naturally contains metal vacancy defects that harm its photoconductivity. Our work pointed toward ways to overcome these problems by materials engineering, either by doping or alloying with another oxide, as well as working at the nanoscale.

We devised a first principles scheme to calculate absolute band edge positions. We demonstrated this scheme in the above five transition metal oxides and also assessed the thermodynamic feasibility of using these materials in photoelectrochemical cells to produce fuels, including hydrogen, methane, methanol, and formic acid. Methanol can be converted by known means – zeolite catalysis – to energy-dense, higher hydrocarbon fuels. The position of the valence band maximum (conduction band minimum) must lie lower (higher) in energy than the oxidation (reduction) reaction free energy in order for these reactions to be thermodynamically favorable. The fundamental property known as the band gap center was determined by calculating the work function of a periodic slab model of a surface. The valence band maximum (conduction band minimum) is then set by subtracting (adding) half of the

fundamental gap obtained from a G0W0 calculation on the bulk crystal. The results for manganese(II) oxide, iron(II) oxide, iron(III) oxide, copper(I) oxide, and nickel(II) oxide were found to be in quite good agreement with experiment [1], thus validating this scheme for determining band edge positions in previously uncharacterized engineered materials discussed later in this report.

During our methods benchmarking, we tested various GW perturbation theory approximations on cuprous oxide and manganese oxide to determine which methods will deliver the best photoemission/inverse photoemission band gaps. As the results of any perturbative method are heavily dependent on the reference state, we identified the appropriate reference Hamiltonian by evaluating the performance of DFT-based input wave functions and eigenvalues generated with varying exchange-correlation functionals. For cuprous oxide and manganese oxide, we found that a reference Hamiltonian employing the hybrid Heyd-Scuseria-Ernzerhof (HSE) hybrid functional used in conjunction with "one-shot" G0W0 produced the most accurate photoemission/inverse-photoemission band gap and photoemission spectrum [2,3]. We note that for some other transition metal oxides we have studied, DFT+U/G0W0 proved superior. The physical origin of why a hybrid functional was required for the zeroth-order wave function was identified, e.g., giving insight into the unique electronic structure of Cu_2O and MnO in comparison to other transition-metal oxides [2]. In particular, Cu_2O is more covalent than many of the other oxides, and therefore it is insufficient to use DFT+U which only corrects the approximate exchange interactions within the d-electron manifold whereas the exchange corrections in a more covalent material are needed globally, as provided by the HSE functional. For MnO, the superior performance of the HSE functional can be traced to the predicted mixed O/Mn character at the valence band maximum [3]. DFT+U only incorporates exact exchange for the Mn d electrons whereas HSE accounts for short-range exact exchange throughout. Consequently, the HSE functional also permits the oxygen p-electrons to reduce their self-interaction to better describe the Mn–O bonding, thereby lowering the valence band edge and increasing the band gap beyond that found with DFT+U/G0W0.

Next we explored band gap/edge engineering via alloying metal oxides. Multiple reasons exist for doing so; one was already mentioned, namely that the band gap of certain oxides, like MnO and NiO, are too large to absorb much sunlight. Others, such as FeO, have conduction

and valence band edges with the same orbital character that could lead to unfavorably high electron–hole recombination rates (hence the need to establish the band edge character as noted earlier). Another limitation of FeO is that the calculated valence band edge is not positioned well for oxidizing water. We have argued that key properties, including band gaps, band edge positions, and possibly electron–hole recombination rates, may be improved by alloying transition metal oxides that have different band alignments. *We introduced a new metric, the band gap center offset, to rapidly screen potential parent materials.* The concept was illustrated by calculating the electronic structure of binary oxide alloys that contain manganese, nickel, iron, zinc, and/or magnesium, within density functional theory (DFT)+U and hybrid DFT theories. We concluded that alloys of FeO are worth evaluating further as solar energy conversion materials, both because they will stabilize FeO under ambient conditions (its instability at room temperature was noted above) and because of favorable changes in band edge character and positions that should extend electron-hole pair lifetimes and permit greater light absorption and suitability for water splitting [4].

We also examined whether alloying MnO with ZnO in varying solid solutions could move its band gap into the visible range. We predicted that alloying MnO with ZnO with increasing amounts of ZnO systematically reduces MnO's band gap for more efficient light absorption while maintaining advantageous band edge placements. The 1:1 alloy of MnO and ZnO was identified as a new (2.6 eV band gap) visible-light-absorbing material with band edges suitably placed with respect to both water-oxidation and CO2-reduction reactions, making it a compelling candidate for solar fuel catalysis [3].

Most recently we explored alloying NiO with ZnO and Li_2O to see if either could reduce NiO's large (~4.0 eV) band gap down into the visible range (~1.5-2.0 eV is optimal for various applications). NiO is an inexpensive yet promising solar fuels candidate. *Using a simple quantum mechanics argument, we suggested that its charge-transfer character may lead to longer carrier lifetimes needed for higher efficiencies.* Moreover, its conduction band edge is suitable for driving hydrogen evolution via water-splitting. Our calculations indicated that *band gaps should dramatically decrease to ~2.0 eV when NiO is alloyed with Li_2O.* We showed that $Li_xNi_{1-x}O$ alloys (with x = 0.125 and 0.25) are p-type semiconductors appropriate for photocathodes, contain states with no impurity levels in the gap that would act as traps and maintain NiO's desirable charge-transfer character that should extend electron-hole pair lifetimes. Lastly, we found that

the alloys have potential for photoelectrochemical applications, with band edges well-placed for photocatalytic hydrogen production and CO_2 reduction, as well as for use in tandem dye-sensitized solar cells as a photocathode [5,5'].

Electronic Excited States in Metal Oxides

Culmination of our work in this area is presented in a review article that outlined and assessed methods for calculating electronic excited states in transition metal oxides [6]. Characterization of excitations in transition metal oxides is a crucial step in the development of these materials for photonic and optoelectronic applications. However, many transition metal oxides are considered to be strongly correlated materials, and their complex electronic structure is challenging to model with many established quantum mechanical techniques. We reviewed state-of-the-art first-principles methods to calculate charged and neutral excited states in extended materials, and discussed their application to transition metal oxides. We briefly discussed developments in DFT to calculate fundamental band gaps, and introduced time-dependent DFT, which can model neutral excitations. Charged excitations can be described within the framework of many-body perturbation theory based on Green's functions techniques, which predominantly employs the *GW* approximation to the self-energy to facilitate a feasible solution to the quasiparticle equations. We reviewed the various implementations of the *GW* approximation and evaluated each approach in its calculation of fundamental band gaps of many transition metal oxides. We also briefly reviewed the related Bethe–Salpeter equation (BSE), which introduces an electron–hole interaction between *GW*-derived quasiparticles to describe accurately neutral excitations. Embedded correlated wavefunction theory is another framework used to model localized neutral or charged excitations in extended materials. Here, the electronic structure of a small cluster is modeled within correlated wavefunction theory, while its coupling to its environment is represented by an embedding potential. We reviewed a number of techniques to represent this background potential, including electrostatic representations and electron density-based methods, and assessed their application to transition metal oxides.

Early on, in the validation stage of this grant, we compared embedded correlated wavefunction approaches for predicting neutral excited states within MgO as a prototypical metal oxide [7]. As mentioned above, the crystal is partitioned into a cluster treated with *ab initio* correlated wavefunction methods and a background described by various electrostatic or

9

orbital-free-DFT-based embedding potentials. Excited singlet and triplet states were found to be nearly degenerate and of charge-transfer type, consistent with experiment. Although the prediction of excitation energies by embedded correlated wavefunction theory with an electrostatic description of the background falls slightly short of much more expensive Green's function methods, it offers a significant improvement over standard DFT or non-embedded correlated wavefunction methods. As this method is much more economical and sufficiently accurate, we use this method – electrostatically embedded correlated wavefunction theory – to evaluate excited states in transition metal oxides in our subsequent work.

For example, we examined neutral optical excitations in MnO:ZnO and pure MnO using electrostatically embedded cluster models treated with complete active space second order perturbation (CASPT2) theory [8]. We predicted excitation energies, character of excitations, and their lifetime. The lowest-lying excitations in MnO are predicted to be single Mn d $\rightarrow$ d ligand field excitations ($\sim$2.6 eV, $\sim 10^8$ s lifetime), followed by double d $\rightarrow$ d excitations ($\sim$5.2 eV, $\sim 10^6$ s lifetime), Mn 3d $\rightarrow$ 4s excitations ($\sim$6.3 eV, $\sim 10^{-3}$ s lifetime), and higher-lying O 2p $\rightarrow$ Mn 3d ligand-to-metal charge-transfer (LMCT) excitations ($\sim$10.1 eV, $\sim 10^{-4}$ s lifetime). The longer-lived transitions should exhibit better electron–hole pair separation and enhance photoconductivity depending on ease of charge carrier transport. Alloying MnO with ZnO notably lowers the LMCT transition to $\sim$8.3 eV with the metal orbital comprised mainly of Zn 4s states, leaving most other absorption properties relatively unchanged. We find near degeneracies among spin-allowed and spin-forbidden LMCT states that could facilitate intersystem crossing resulting in longer lifetimes. We suggest seeking other materials that exhibit similar LMCT excitations but that are visible-light activated as a design strategy for further enhancing photon conversion efficiencies.

Charge Transport in Transition Metal Oxides

Once the electron-hole pair is formed upon light absorption, if it lives long enough to begin to separate, one must evaluate the mobility of electrons and holes in these materials as another key metric that will determine their efficacy in solar energy conversion. We began a series of studies of how dopants and vacancy defects either help or harm transport in these oxides, as we describe next.

Doping hematite (Fe_2O_3) to make it either p-type or n-type is known to enhance its conductivity. We used electrostatically embedded wavefunction theory combined with small

polaron theory to understand how titanium, zirconium, silicon, or germanium n-type doping affects the electron transport mechanism in hematite. Our results suggested that zirconium, silicon, or germanium doping is superior to titanium doping because the former dopants do not act as electron trapping sites due to the higher instability of Zr(III) compared to Ti(III) and the more covalent interactions between silicon (germanium) and oxygen. This suggests that *use of n-type dopants that easily ionize completely or promote covalent bonds to oxygen can provide more charge carriers while not inhibiting transport* [9].

We went on to propose ways to enhance the conductivity of wüstite (naturally p-type FeO). Unfortunately, the conversion efficiency of FeO is inhibited by its low hole conductivity. Increasing the iron vacancy concentration or adding p-type dopants will improve FeO conductivity by increasing the number of holes; however, it was not known which strategy introduces larger energy traps that would hinder hole conductivity. We again employed the small polaron model along with *ab initio* calculations on electrostatically embedded clusters to analyze the local trapping effects of iron vacancies and several substitutional p-type dopants that are soluble in FeO, including copper, nitrogen, lithium, and sodium, and also hydrogen as an interstitial dopant for comparison. We found that vacancies create stronger traps than dopants and that copper and nitrogen dopants form deeper traps than lithium, sodium, or hydrogen. Furthermore, hydrogen repels the hole and substantially decreases the trap formed by an iron vacancy. Because of the shallower traps formed compared to vacancies, we concluded that *lithium-, sodium-, or hydrogen-doped, nanostructured or alloyed FeO may be worth evaluating as a p-type semiconductor for solar energy conversion applications* [10,10'].

Our last example that employs electrostatically embedded clusters and the small polaron model (localized charge carrier hopping) evaluated mobility of both holes and electrons in pure and doped MnO and the MnO:ZnO alloy [11,11']. Poor measured hole conductivity in undoped MnO:ZnO alloys (with up to 10% ZnO) severely limits this material's utility in electronic devices, and its electron conductivity has not yet been characterized. We assessed the effects of Al, Ga, In, Sc, Y, Ti, Sb, Gd, F (n-type dopants) and Li (a p-type dopant) to determine which may enhance conductivity in MnO:ZnO. Our findings indicated that Ga, Sc, Ti, F, and Sb dopants create deep traps whereas In forms shallower traps that merit further investigation. *Y, Al, Gd, and Li dopants should increase the carrier concentration while maintaining favorable electron and hole transport pathways in MnO:ZnO.* The latter are recommended for

11

increasing the conductivity of MnO:ZnO and its effectiveness for solar energy conversion.

Finally, we examined properties affecting electron transport in naturally p-type cuprous oxide. As the conduction band edge in cuprous oxide does not consist of localized states, the small polaron model does not apply. Cuprous oxide's photoconductivity is limited by minority carrier (electron) recombination caused by native defect trap states. We examined the creation of trap states by cation vacancies, using DFT+U and hybrid DFT to analyze the electronic structure and calculate formation energies. With several DFT-based methods, a simple vacancy was predicted to be consistently more stable than a split vacancy by 0.21 ± 0.03 eV. Hybrid DFT was used to analyze the density of states and charge density distribution, predicting a delocalized hole for the simple vacancy and a localized hole for the split vacancy, in contrast to previously reported results. The differing character of the two defects indicates that they contribute to conduction via different mechanisms, with the split vacancy as the origin of the acceptor states that trap minority carriers. We explored methods of improving photoconductivity by doping Cu_2O with Li, Mg, Mn, and Zn, analyzing their impact on vacancy formation energies and electronic structures. Results suggest that *the Li dopant has the greatest potential to improve the photoconductivity of cuprous oxide by inhibiting the creation of trap states* [12, 12'].

Surface Chemistry of Transition Metal Oxides

Our work in this area consists of a systematic characterization of the properties of pure and surface-modified (dopants, hydroxylation, etc.) transition metal oxide surfaces, including their ability to split water. We report below on properties related to cuprous oxide, MnO:ZnO, and hematite surfaces.

As mentioned earlier, for a photocatalytic reaction to be thermodynamically allowed, a semiconductor's band edges need to be placed appropriately relative to the reaction redox potentials. We applied our scheme for calculating band edges with DFT-based methods to Cu_2O, evaluating its available thermodynamic overpotential for redox reactions such as water splitting and conversion of CO_2 to methanol. Because these calculations are surface dependent, we first studied the low-index surfaces of Cu_2O using periodic DFT+U theory to characterize and identify the most stable surface, which should be the most catalytically relevant. We employed various techniques to calculate the surface energy, including *ab initio* atomistic thermodynamics. The $Cu_2O(111)$ surface with (1×1) periodicity and surface copper vacancies

was identified as the most stable at all oxygen partial pressures, although the ideal stoichiometric $Cu_2O(111)$ surface is relatively close in energy under oxygen-poor conditions. These surfaces were then used to calculate the band edges. Comparison of the band edges to redox potentials reveals that Cu_2O is thermodynamically capable of photocatalytic reduction of CO_2 to methanol and the reduction and oxidation of water [13].

Cuprous oxide can be unstable with respect to reduction to metallic copper or oxidation to form cupric oxide. Therefore we also considered whether deposition of cuprous oxide on a similar but stable substrate (wurtzite ZnO) might stabilize the cuprous oxide phase. We again employed DFT-based methods 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 thicknesses. We first established an accurate model of the ZnO substrate, validating DFT + U theory against the more accurate hybrid-DFT to calculate properties of bulk wurtzite ZnO and the $ZnO(10\bar{1}0)$ surface. DFT + U theory was 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 was found to be only weakly interacting, with a DFT + U– derived adhesion energy of 0.85 ± 0.07 J/m^2. Electron density analysis revealed that some interface stabilization occurs because of local Zn-O and Cu-O bonding interactions at the interface. The overall impact of the ZnO substrate on the electronic structure of the Cu_2O overlayer is to reduce the Cu_2O band gap [14]. Thus ZnO can potentially act as a reasonable substrate on which to deposit Cu_2O, without harming its favorable properties.

The last stage of our work considered adsorption and reaction of water – and one study of carbon dioxide - with transition metal oxide surfaces, including cuprous oxide, MnO:ZnO, and hematite. We review that work next.

We investigated the adsorption of CO_2 on the $Cu_2O(111)$ surface using DFT + U theory with and without dispersion corrections (the latter was considered since CO_2 is expected to primarily bind via weak physisorption, which is dominated by dispersion forces). A number of adsorbate geometries were considered on four different surface terminations that included the bulk-terminated surface and surfaces with oxygen and/or copper vacancies. CO_2 was found to adsorb most strongly as a tilted linear molecule coordinated to an unsaturated surface cation. Surface vacancies allow for bent adsorbate configurations to be accessed but

they are all less stable than the linear adsorbate. Bader analysis confirmed that adsorption of bent CO_2 is accompanied by charge transfer from the surface to the molecule, whereas minimal charge transfer occurs in linear physisorption. We show that surface oxygen vacancies have a small impact on adsorption free energies, while surface copper vacancies result in a significant reduction of CO_2 adsorption. Including dispersion corrections increases the stability of adsorbed CO_2, but adsorption is mostly endoergic at 298.15 K and 1 atm. Our findings reveal *that adsorption of CO_2 on cuprous oxide is contingent on the presence of copper cations at the surface. Thus, this surface's chemistry is dominated by Lewis acidity, in contrast to other oxide surfaces where oxygen anions may act as Lewis bases to form carbonates. The suppression of carbonate formation is important, as it confirms that this surface may be useful for CO_2 reduction to fuels* [15].

We also investigated the interaction of water with cuprous oxide surfaces, in a joint collaboration with surface science experimentalists [20]. Hydrogen-bonded cyclic water clusters were observed and their electronic structure (dI/dV) was mapped via scanning probe techniques. The measurements and our calculations suggest that a new type of cyclic water cluster forms, characterized by simultaneous and cooperative bonding interactions among the molecules as well as with both metal and oxygen surface sites. DFT + U calculations confirmed the stability of these clusters and were used to discuss other potential water-oxide bonding scenarios. The calculations show that the spatial and energetic distributions of electronic states in the system are similar in character to those of the lowest unoccupied molecular orbitals of hydrogen-bonded water molecules. In addition, through experimental observations and thermodynamic arguments, the analysis provided shows that water molecules on copper oxide act as a probe of the underlying structure, revealing that a single structural model is insufficient to fully describe oxides that grow on Cu(111). In particular, experiment and theory together conclude that *Cu vacancies in the growing islands of cuprous oxide inhibit water adsorption in the center of the islands (that have reached thermodynamic equilibrium), while the stoichiometric (but less stable!) cuprous oxide that exists at the island edges (growth front) selectively binds these water clusters*.

Water reactions on pure and doped, hydroxylated hematite represented our first foray into a full catalytic modeling of water splitting. In photoelectrochemical cells, sunlight may be converted into chemical energy by splitting water into hydrogen and oxygen molecules. Hematite (α-Fe_2O_3) is a promising photoanode material for the water oxidation component of

14

this process. Numerous research groups have attempted to improve hematite's photocatalytic efficiency despite a lack of foundational knowledge regarding its surface reaction kinetics. To elucidate detailed reaction mechanisms and energetics, we performed periodic DFT + U calculations for the water oxidation reaction on the fully hydroxylated hematite (0001) surface, with and without dopants [16]. We investigated two different concentrations of surface reactive sites. Our best model involves calculating water oxidation mechanisms on a pure (1×1) hydroxylated hematite slab (corresponding to 1/3 ML of reactive sites) with an additional overlayer of water molecules to model solvation effects. This yielded an overpotential of 0.77 V, a value only slightly above the 0.5–0.6 V experimental range. To explore whether doped hematite can exhibit an even lower overpotential, we considered cation doping by substitution of Fe by Ti, Mn, Co, Ni, or Si and F anion doping by replacing O on the fully hydroxylated surface. The reaction energetics on pure or doped hematite surfaces were described using a volcano plot. *The relative stabilities of holes on the active O anions were identified as the underlying cause for trends in energetics predicted for different dopants.* We found that *moderately charged O anions give rise to smaller overpotentials. Co- or Ni-doped hematite surfaces give the most thermodynamically favored reaction pathway (lowest minimum overpotential) among all dopants considered* [16']. Measurements that appeared at the same time as our paper (*Electrochim. Acta* **2012**, *59*, 121–127) reported improved reactivity with Ni doping, further validating our predictions.

Lastly, we used *ab initio* DFT + *U* theory to investigate the structure and energetics of water adsorption and reaction on MnO:ZnO(001). Our calculations showed that there is a preference for molecular adsorption at water coverages of less than half a monolayer (ML). At higher coverages, cooperative water–water interactions facilitate water dissociation at the interface. The work function is very sensitive to water dipole orientation and/or presence of hydroxyls on the surface. The computed phase diagram revealed the surface to be fairly hydrophilic with a preference for the first water ML to be 33% dissociated at 0.75 ML, 50% dissociated at 1 ML, and 50% dissociated at 2 ML water coverage under various conditions away from water-poor conditions [17]. In our study of water oxidation by this metal oxide alloy [18], we confirmed that previously established scaling relationships between the binding energies of reaction intermediates are valid. The predicted electrochemical overpotential for water oxidation under experimentally relevant conditions (0.82 V versus the standard

hydrogen electrode) is slightly higher than those values reported for manganese oxides but comparable to our previously calculated values for hematite photoanodes, suggesting that this material is worth exploring further for photocatalysis, given its improved conductivity properties compared to hematite.

Summary

Concepts and findings developed during this grant were recently shared with the community in an invited review article [19]. In this review, we discussed how theory can be applied to investigate various aspects of a photocatalytic cycle: light absorption, electron/hole transport, band edge alignments of semiconductors, and surface chemistry. Emphasis was placed on identifying accurate models for specific properties and furnishing theoretical insights in terms of design principles for improving photocatalytic performance. The executive summary above lists the insights we gleaned from our work, so we do not repeat them here.

Personnel

Faculty: Emily A. Carter, P.I.

Postdoctoral Fellows: Dr. Maytal Toroker, Dr. John Keith, Dr. Christoph Riplinger, Dr. Kuang Yu

Graduate Students: Peilin Liao, Dalal Kanan, Leah Isseroff Bendavid, Nima Alidoust, Jin Cheng, Alexander Tkalych

Archival articles and patents published during reporting period:

[0] Emily A. Carter and Ivan Milas, *Barium-Doped Bond Coats for Thermal Barrier Coatings.* Utility patent filed on August 26, 2008 (United States). Patent Application No.: 12/194,813. Patent No.: US 7,927,714. Issued April 19, 2011. (Issued during this grant; research funded by prior AFOSR grant; added here for completeness.)

[1] M. Caspary Toroker, D. K. Kanan, N. Alidoust, L. Y. Isseroff, P. Liao and E. A. Carter, "First Principles Scheme to Evaluate Band Edge Positions in Potential Transition Metal Oxide Photocatalysts and Photoelectrodes," *Phys. Chem. Chem. Phys.*, **13**, 16644 (2011). doi: 10.1039/c1cp22128k

[2] L. Y. Isseroff and E. A. Carter, "Importance of Reference Hamiltonians Containing Exact Exchange for Accurate One-Shot GW Calculations of Cu_2O," *Phys. Rev. B*, **85**, 235142 (2012).

doi: 10.1103/PhysRevB.85.235142

[3] D. K. Kanan and E. A. Carter, "Band Gap Engineering of MnO via ZnO Alloying: A Potential New Visible-Light Photocatalyst," *J. Phys. Chem. C*, **116**, 9876 (2012). doi: 10.1021/jp300590d

[4] M. C. Toroker and E. A. Carter, "Transition Metal Oxide Alloys as Potential Solar Energy Conversion Materials," *J. Mater. Chem. A*, **1**, 2474 (2013). doi: 10.1039/C2TA00816E

[5] N. Alidoust, M. C. Toroker, J. A. Keith, and E. A. Carter, "Significant Reduction in Nickel(II) Oxide Band Gap Upon Alloying with Lithium Oxide: Applications to Solar Energy Conversion," *ChemSusChem*, **7**, 195 (2014). doi: 10.1002/cssc.201300595.

[6] L. Isseroff Bendavid and E. A. Carter, "Status in Calculating Electronic Excited States in Transition Metal Oxides from First Principles," in *Topics in Current Chemistry*, C. Di Valentin, S. Botti, and M. Cococcioni, Eds. (Springer, Germany) (2014). doi: 10.1007/128_2013_503

[7] D. K. Kanan, S. Sharifzadeh and E. A. Carter, "Quantum Mechanical Modeling of Electronic Excitations in Metal Oxides: Magnesia as a Prototype," *Chem. Phys. Lett.*, **519**, 18 (2012). doi: 10.1016/j.cplett.2011.11.003

[8] D. K. Kanan and E. A. Carter, "Optical Excitations in MnO and MnO:ZnO via Embedded CASPT2 Theory and their Implications for Solar Energy Conversion," *J. Phys. Chem. C*, **117**, 13816 (2013). doi: 10.1021/jp4024475

[9] P. Liao, M. Caspary Toroker, and E. A. Carter, "Electron Transport in Pure and Doped Hematite," *Nano Letters*, **11**, 1775 (2011). doi: 10.1021/nl200356n

[10] M. C. Toroker and E. A. Carter, "Hole Transport in Non-Stoichiometric and Doped Wüstite," *J. Phys. Chem. C*, **116**, 17403 (2012). doi: 10.1021/jp3047664

[11] D. K. Kanan and E. A. Carter, "*Ab Initio* Study of Electron and Hole Transport in Pure and Doped MnO and MnO:ZnO Alloy," *J. Mater. Chem. A*, **1**, 9246 (2013). doi: 10.1039/C3TA11265A

[12] L. Y. Isseroff and E. A. Carter, "Electronic Structure of Pure and Doped Cuprous Oxide with Copper Vacancies: Suppression of Trap States," *Chem. Mater.*, **25**, 253 (2013). doi: 10.1021/cm3040278

[13] L. Isseroff Bendavid and E. A. Carter, "First Principles Predictions of the Structure, Stability, and Photocatalytic Potential of Cu_2O Surfaces," *J. Phys. Chem. B,* **117**, 15750 (2013). doi: 10.1021/jp406454c

[14] L. Isseroff Bendavid and E. A. Carter, "First Principles Study of Bonding, Adhesion, and

Electronic Structure at the $Cu_2O(111)/ZnO(1010)$ Interface," *Surf. Sci.*, **618**, 62 (2013). doi: 10.1016/j.susc.2013.07.027

[15] L. Isseroff Bendavid and E. A. Carter, "CO_2 Adsorption on $Cu_2O(111)$: A DFT+U and DFT-D study," *J. Phys. Chem. C*, **117**, 26048 (2013). doi: 10.1021/jp407468t

[16] P. Liao, J. A. Keith, and E. A. Carter, "Water Oxidation on Pure and Doped Hematite (0001) Surfaces: Prediction of Co and Ni as Effective Dopants for Photocatalysis," *J. Am. Chem. Soc.*, **134**, 13296 (2012). doi: 10.1021/ja301567f

[17] D. K. Kanan, J. A. Keith, and E. A. Carter, "Water Adsorption on MnO:ZnO(001) – From Single Molecules to Bilayer Coverage," *Surf. Sci.*, **617**, 218 (2013). doi: 10.1016/j.susc.2013.07.023

[18] D. K. Kanan, J. A. Keith, and E. A. Carter, "First Principles Modeling of Electrochemical Water Oxidation on MnO:ZnO(001)," *ChemElectroChem*, **1**, 407 (2014). doi: 10.1002/celc.201300089

[19] P. Liao and E. A. Carter, "New Concepts and Modeling Strategies to Design and Evaluate Photo-electro-catalysts Based on Transition Metal Oxides," *Chem. Soc. Rev.*, **42**, 2401 (2013). doi: 10.1039/C2CS35267B

Submitted Publications and Patents

[5'] Emily A. Carter, Nima Alidoust and Maytal C. Toroker, *Nickel-Lithium-Oxides for Solar Energy Conversion Devices.* Provisional Patent Application No.: 61691120 filed on August 20, 2012. Provisional Patent re-filed as *Nickel-Lithium-Oxides for Solar Energy Conversion Devices and Substitutionally Alloying Nickel Oxide with Lithium in High Concentrations in the Rocksalt Structure for Use in Tandem Dye-Sensitized Solar Cells and Photocatalysis*, Application No.: 61865257 filed on August 16, 2013.

[10'] Emily A. Carter and Maytal C. Toroker, *Wustite-Based Photoelectrodes with Lithium, Hydrogen, Sodium, Magnesium, Manganese, Zinc, and Nickel Additives.* Provisional Patents: Application No.: 61578342 filed on December 21, 2011; Application No.: 61578600 filed on December 21, 2011; Application No.: 61649601 filed on May 22, 2012. Utility Application No.: 13/899,049 filed on May 21, 2013.

[11'] Emily A. Carter and Dalal K. Kanan, *Doped MnO:ZnO Alloys as Visible Light Absorbing Solar Energy Conversion Materials.* Provisional Patent Application No.: 61600319 filed on February 17,

2012.

[12'] Emily A. Carter and Leah Y. Isseroff, Doped Cuprous Oxide as a Semiconductor for Solar Energy Conversion Devices. Provisional Patent Application No: 61603545 filed on February 27, 2012. Provisional Patent Application No.: 61751116 re-filed on January 10, 2013.

[16'] Emily A. Carter, Peilin Liao and John Andrew Keith, *Hematite-Based Photoanodes with Manganese, Cobalt, and Nickel Additives*. Provisional Patent Application No.: 61554287 filed on October 19, 2011. Utility Patent Application No.: 13666662 filed on November 1, 2012.

[20] C. X. Kronawitter, C. Riplinger, X. He, P. Zahl, E. A. Carter, P. Sutter, and B. E. Koel, "Hydrogen-bonded cyclic water clusters nucleated on an oxide surface," *J. Am. Chem. Soc.*, submitted, (2014).

Ph.D. Dissertations

Peilin Liao, Princeton University Ph.D. 2012. Dissertation Title: Mechanical, Optical, Transport, and Catalytic Properties of Iron Oxides from First Principles.

Dalal K. Kanan, Princeton University Ph.D. 2013. Dissertation Title: Methods and Strategies for the *Ab Initio* Design of Novel Mn Oxide-Based Water Splitting Photocatalyst Materials.

Leah Isseroff Bendavid, Princeton University Ph.D. 2013. Dissertation Title: First Principles Evaluation of the Photocatalytic Properties of Cuprous Oxide

These dissertations are available upon request from

http://library.princeton.edu/databases/subject/dissertationstheses

Invited Seminars by the P. I.

Mar.10, 2014   "Running Combustion Backwards: Fuels from Sunlight, From First Principles," Stanford Chemical Engineering Student-Sponsored Colloquium, Stanford University, Stanford, CA

Feb. 11, 2014   "Running Combustion Backwards: Fuels from Sunlight, From First Principles," The Linnett Lecture (General), Department of Chemistry, University of Cambridge, Cambridge, UK

Dec. 4, 2013   "How Quantum Mechanics Can Help Solve the World's Energy Problems," 2013 Hoyt C. Hottel Lecture in Chemical Engineering, Massachussetts Institute of Technology, Cambridge, MA

Oct.22, 2013   "Running Combustion Backwards: Fuels from Sunlight, from First Principles," Lord Chemistry Lecture, Department of Chemistry, Allegheny College, Meadville, PA

Oct.21, 2013   "How Quantum Mechanics Can Help Solve the World's Energy Problems," Lord Public Lecture, Department of Chemistry, Allegheny College, Meadville, PA

May 1, 2013   "A Quantum Search for Fuels from Sunlight," Francis Clifford Phillips Lectures, Xi Chapter of the Phi Lambda Upsilon National Honorary Chemical Society and the Department of Chemistry, University of Pittsburgh, Pittsburgh, PA.

Mar.28, 2013   "Quantum Mechanical Evaluation of Energy Conversion Materials for Generating Electricity and Fuels," Chemistry Colloquium Speaker, Columbia University, New York, NY.

Mar.14, 2013   "Quantum Mechanical Evaluation of Electron and Ion Transport in Metal Oxides," Distinguished Lecture, Naval Research Laboratory Chemistry Division Colloquium, Washington, DC.

Mar. 1, 2013   "The Role of Science in Moving the Planet to Green Energy and a Sustainable Future," W. Allan Powell Lecture, Virginia Section of the American Chemical Society and the University of Richmond, Richmond, VA.

Oct. 5, 2012   "Quantum Mechanical Evaluation of Energy Conversion Materials for Generating Electricity and Fuels," Institute of Mechanical Engineering Seminar, École Polytechnique Fédérale de Lausanne, Lausanne, Switzerland.

Sept.13, 2012   "The Role of Science in Solving Our Planet's Energy Problems," Rutgers Energy Institute and Bloustein School of Planning and Public Policy Energy Policy Seminar, Rutgers University, New Brunswick, NJ.

Mar. 5, 2012   "How Quantum Mechanics Can Help Solve the World's Energy Problems," David Bradford Seminar in Science, Technology, and Environmental Policy, Princeton University, Princeton, NJ.

Feb. 24, 2012   "Role of Science in Moving the Planet to Green Energy and a Sustainable Future," Honorary Mathematical and Physical Sciences Distinguished Lecture, National Science Foundation, Arlington, VA.

Feb. 2, 2012	"Quantum Mechanical Evaluation of Energy Conversion Materials for Generating Electricity and Fuels," Dean's Distinguished Lecture, College of Science and Technology, Temple University, Philadelphia, PA.
Dec.16, 2011	"How Quantum Mechanics Can Help Solve the World's Energy Problems," Community Auditing Program Lecture, Princeton University, Princeton, NJ.
June 2, 2011	"Quantum Mechanical Evaluation of Energy Conversion Materials for Generating Electricity and Fuels," Jerome B. Cohen Lecture, Department of Materials Science and Engineering, Northwestern University, Evanston, IL.
Mar. 4, 2011	"How Quantum Mechanics Can Help Solve Our Energy Problems," Davidson Lectureship, Department of Chemistry, University of North Texas, Denton, TX.
Feb. 22, 2011	"A Tale of Two Visions: Building the Andlinger Center and Fuels from Sunlight," Nanotechnology for Clean Energy IGERT Seminar, Rutgers University, New Brunswick, NJ.
Nov 2, 2010	"Quantum Mechanics Based Design Concepts for Improved Materials for Energy Applications," Molecular Foundry Distinguished Lecture, Lawrence Berkeley National Laboratory, Berkeley, CA.

Invited Lectures by the P. I.

Mar.19, 2014	"First principles quantum simulations of (photo)electrocatalysis at semiconductor surfaces, " at the *247th ACS Spring National Meeting*, Dallas, TX
Mar.16, 2014	"First principles quantum mechanical evaluation of mixed electron-ion conductors and the oxygen reduction reaction," at the *247th ACS Spring National Meeting*, Dallas, TX
Nov. 4, 2013	"Quantum Mechanics and the Future of the Planet," *Mathematics of Planet Earth 2013 Simons Public Lecture* at the *Institute for Pure and Applied Mathematics Workshop III: Batteries and Fuel Cells*, Los Angeles, CA
Sept.27, 2013	"Mechanisms of Photoelectrochemical Reduction of Carbon Dioxide and Water Splitting from First Principles," at the *Avogadro Colloquia (second edition) on Challenges for theoretical and computational chemistry in Horizon2020*, Pisa, Italy

Aug.27, 2013   "How Quantum Mechanics Can Help Solve the World's Energy Problems," plenary lecture at the *Applied Mathematics, Modeling and Computational Science (AMMCS) 2013 International Conference*, Waterloo, ON, Canada

Dec.13, 2012   "Materials Genome Initiative: Hard Condensed Matter for Energy Applications," at the *NSF Materials Genome Initiative Workshop*, Arlington, VA.

Aug.14, 2012   "Quantum Mechanical Design and Evaluation of New Solar Energy Conversion Materials," keynote lecture at the *SPIE Optics & Photonics 2012*, San Diego, CA.

June 8, 2012   "The Role of Science in Moving the Planet to Green Energy and a Sustainable Future," keynote address at the *2012 Midwest Theoretical Chemistry Conference*, Madison, WI.

May 25, 2012   "Quantum Mechanical Evaluation of Photoelectrochemical and Solid Oxide Fuel Cells," keynote lecture at the *11th Spring Meeting of the International Society of Electrochemistry*, Washington, DC.

Mar.25, 2012   "Quantum Mechanical Evaluation of New Solar Energy Conversion Materials," at the ACS Spring 2012 National Meeting & Exposition, San Diego, CA.

Feb. 27, 2012   "Transport In and Chemistry On Transition Metal Oxides for Energy Conversion," at the American Physical Society March Meeting 2012, Boston, MA.

Sept. 4, 2011   "How Quantum Mechanics Can Help Solve the World's Energy Problems," Plenary Lecture at GDCh Chemistry Forum, Bremen, Germany.

June 13, 2011   "Quantum Mechanical Evaluation of New Solar Energy Conversion Materials," at the Seventh Condensed Phase and Interfacial Molecular Sciences (CPIMS) Research Meeting, Baltimore, MD.

May 19, 2011   "First Principles Evaluation of Potential Photo-catalytic Electrodes for Water Splitting and Carbon Dioxide Reduction," at the AFOSR Molecular Dynamics Contractor's Meeting, Pasadena, CA.

May 5, 2011   "Quantum Mechanical Evaluation of Energy Conversion Materials," at the Institute for Pure and Applied Mathematics Workshop: Materials Design in Chemical Compound Space, Los Angeles, CA.

April29, 2011   "Moving the Planet to Green Energy," at the She Roars: Celebrating Women at Princeton Conference, Princeton, NJ.

Jan. 14, 2011   "A Tale of Two Visions: Building the Andlinger Center and Fuels from Sunlight," at The Planet and Our Future: A Princeton Conference on Environmental Challenges and Solutions, Guanacaste, Costa Rica.

Dec.15, 2010   "Ab Initio Predictions of Excited States and Transport in Metal Oxides," at the Pacifichem 2010 Congress, Honolulu, HI.

Oct.21, 2010   "Solar Energy Conversion Materials: Sunlight to Electricity or Fuels," at the Future Directions in CO2 Conversion Chemistry Workshop, Princeton, NJ.

Sept.30, 2010   "How Quantum Mechanics Can Help Solve Our Energy Problems," at the Frontiers in Renewable Energy Sciences and Technologies Workshop, Cambridge, MA.

Sept.10, 2010   "Solar Energy Conversion Materials," at the Second Chemical Sciences and Society Symposia (CS3) on Sustainable Materials, London, England.

Aug.26, 2010   "How Quantum Mechanics Can Help Solve Our Energy Problems," at the Meeting of the NRC Board on Chemical Sciences and Technology, Woods Hole, MA.

Contributed Presentations by Postdocs and Graduate Students

Nov. 5, 2013   "Modeling Photoelectrochemical Water Oxidation and CO_2 Reduction With DFT+U, DFT+D, and Heterogeneous Solvation," talk at the *2013 AIChE Annual Meeting*, San Francisco, CA. (presented by John Keith)

Nov. 5, 2013   "Insights Into the Performance of Cu_2O in Photocatalytic CO_2 Conversion," talk at the *2013 AIChE Annual Meeting*, San Francisco, CA. (presented by Leah Isseroff Bendavid)

April10, 2013   "Band Gap Engineering of Nickel(II) Oxide via Degenerate Alloying with Li_2O for Solar Energy Conversion: A Theoretical Study," talk at the *ACS National Meeting & Exposition*, New Orleans, LA. (presented by Nima Alidoust)

Dec. 6, 2012   "New Solar Energy Conversion Materials," talk at the *New Jersey Technology Council 2012 Regional Commercialization Conference*, Wilmington, DE. (presented by Leah Isseroff)

Nov.29, 2012   "New Solar Energy Conversion Materials," talk at *Celebrate Princeton Invention 2012*, Princeton, NJ. (presented by Nima Alidoust, Leah Isseroff, and John Keith)

Nov.12, 2012	"Band Gap Engineering of Nickel Oxide for Solar Energy Applications," poster at the *Synergize 2012 Inaugural Annual Meeting of the Princeton Energy & Environmental Corporate Affiliates Program*, Princeton, NJ. (presented by Nima Alidoust)
Aug.21, 2012	"Band Gap Engineering of Nickel Oxide for Solar Energy Applications," poster at the *Summer School on Inorganic Materials for Energy Conversion and Storage*, Santa Barbara, CA. (presented by Nima Alidoust)
July 23 and July 25, 2012	"Electronic Structure of Pure and Doped Cuprous Oxide with Copper Vacancies: Suppression of Trap States," poster at the *Gordon Research Conference on Computational Chemistry*, Mount Snow, VT. (presented by Leah Isseroff)
May 22, 2012	"First Principles Evaluation of Optical, Transport, and Catalytic Properties of Pure and Doped Hematite for Photocatalytic Water Splitting," poster at the *AFOSR Molecular Dynamics Contractor's Meeting*, Arlington, VA. (presented by Peilin Liao)
Mar.27, 2012	"Quantum Mechanical Investigation of Photo-electrochemical Water Oxidation on MnO(001) and MnO:ZnO(001)," talk at the *ACS Spring 2012 National Meeting & Exposition*, San Diego, CA. (presented by Dalal Kanan)
Dec. 3, 2011	"Ab Initio Study of Electron and Hole Transport in Pure and Doped MnO/ZnO Alloys," poster at the *Princeton Research Symposium*, Princeton, NJ. (presented by Dalal Kanan)
Dec. 3, 2011	"Designing Cheap Materials that Produce Fuels from Water and Sunlight Using Quantum Mechanics," talk at the *Princeton Research Symposium*, Princeton, NJ. (presented by Dalal Kanan)
July 20, 2011	"Quantum Mechanical Studies of Copper(I) Oxide for Photocatalysis," poster at the *American Conference on Theoretical Chemistry (ACTC) 2011*, Telluride Science Research Center, Telluride, CO. (presented by Leah Isseroff)
July 20, 2011	"Ab initio Study of Electron and Hole Transport in Pure and Doped MnO/ZnO alloys," poster at the *American Conference on Theoretical Chemistry (ACTC) 2011*, Telluride Science Research Center, Telluride, CO. (presented by Dalal Kanan)
June7-8, 2011	"First Principles Scheme to Evaluate Band Edge Positions in Potential Transition Metal Oxides Photocatalysts and Photoelectrodes," poster at the *ES11: The 23rd Annual Workshop on Electronic Structure Methods*, The University of Pennsylvania, Philadelphia, PA. (presented by Maytal Toroker)

Mar.30, 2011 "Ab-initio Calculation of Band Positions for Transition Metal Oxides Reveals Potential Materials for Photoelectricity," talk at the *241st American Chemical Society National Meeting and Exposition*, Anaheim, CA. (presented by Maytal Toroker)

Mar.30, 2011 "Analysis of Cuprous Oxide as a Possible Photocatalyst for Carbon Dioxide Reduction," talk at the *241st American Chemical Society National Meeting and Exposition*, Anaheim, CA. (presented by Leah Isseroff)

Dec.12, 2010 "Quantum Mechanical Studies of Copper (I) Oxide for Solar Energy Conversion Applications," talk at the *Tokyo Institute of Technology Energy Global COE International Forum on Multidisciplinary Education and Research for Energy Science*, Tokyo, Japan. (presented by Leah Isseroff)

Nov.20, 2010 "Band Gap Optimization in Transition Metal Oxide Alloys," poster at the *Princeton Research Symposium*, Princeton, NJ. (presented by Maytal Toroker)

Nov.20, 2010 "Quantum Mechanical Evaluation of Nickel Oxide Properties for Solar Energy Applications," poster at the *Princeton Research Symposium*, Princeton, NJ. (presented by Nima Alidoust)

Nov. 8, 2010 "Quantum Mechanical Studies of Copper(I) Oxide for Solar Energy Conversion Applications," poster at the Advanced Energy 2010 Conference, Stony Brook, NY. (presented by Leah Isseroff)

Oct.21, 2010 "Quantum Mechanics Modeling of Electronic Excitations in Metal Oxides," poster at the *Future Directions in CO2 Conversion Chemistry Workshop*, Princeton, NJ. (presented by Dalal Kanan)

Oct.21, 2010 "Band Gap Optimization of Transition Metal Oxide Alloys," poster at the *Future Directions in CO2 Conversion Chemistry Workshop*, Princeton, NJ. (presented by Maytal Toroker)

Oct.21, 2010 "Local and Band-to-Band Excited States in Hematite From Quantum Mechanics," poster at the *Future Directions in CO2 Conversion Chemistry Workshop*, Princeton, NJ. (presented by Peilin Liao)

Sept.30, 2010 "Band Gap Optimization of Transition Metal Oxide Alloys," poster at the *Frontiers in Renewable Energy Sciences and Technologies Workshop*, Cambridge, MA. (presented by Maytal Toroker)

Aug.17, 2010   "Band Gap Optimization of Transition Metal Oxide Alloys," poster at the *Gordon Research Conference on Solid State Studies in Ceramics*, New London, NH. (presented by Maytal Toroker)

Aug.16, 2010   "Local and Band-to-Band Excited States in Hematite from Quantum Mechanics," poster at the *Gordon Research Conference on Solid State Studies in Ceramics*, New London, NH. (presented by Peilin Liao)

May 24, 2010   "Quantum Mechanics Modeling of Electronic Excitations in Metal Oxides," poster at the *AFOSR Molecular Dynamics and Theoretical Chemistry Contractor's Meeting*, Chantilly, VA. (presented by Dalal Kanan)