

DOE Award Number: DE-FG02-07ER15920
Name of Recipient: University of Pennsylvania
Project Title: Exploiting the flexibility and the polarization of ferroelectric perovskite surfaces to achieve efficient photochemistry and enantiospecificity
Name of project director/principal investigator: Andrew M. Rappe
Consortium/teaming members: (none)

This report has been prepared for public distribution. The report includes discussion of a U. S. Patent that has already issued, based on this work.

I Executive summary:

This research project explored the catalytic properties of complex surfaces of functional materials. The PI used first-principles density functional theory (DFT) calculations to explore a tightly integrated set of properties. The physical properties of complex functional materials that influence surface chemistry were explored, including bulk and surface electric dipoles, and surface conductivity. The energetic, compositional, electronic, and chemical properties of the surfaces of these materials were explored in detail, and connections between material properties and chemical reactivity were established.

This project led to 28 publications, including *Nat. Comm.*, *JACS*, 3×*PRL*, 7×*PRB*, 2×*ACS Nano*, 2×*Nano Lett.*, 4×*JPCL*, 2×*JCP*, *Chem. Mater.*, *ACS Appl. Mater. Interfaces*, *Phys. Rev. Appl.*, and a U.S. Patent on surface catalysts.

The key accomplishments in this project involved work in six coordinated areas: pioneering ways to control bulk dipoles in order to dynamically affect catalysis, exploring novel ways of bringing charge to the surface for redox catalysis, nonstoichiometric surfaces offering new sites for heterogeneous catalysis, illustrating how surface catalysis responds to applied pressure, catalytic growth of carbon-based materials, and new computational methods allowing more accurate exploration of molecule-surface interactions.

II Summary of project activities, accomplishments, and products

II.A Pioneering ways to control bulk dipoles in order to dynamically affect catalysis

A major theme of this project was the control of bulk dipoles in order to influence catalytic properties at surfaces, for photochemical, electrochemical, and chemical reactivity. The polarization of a material can bring charge to a surface, drive nonstoichiometric reconstructions (see Sec. II.C), shift surface electronic energy levels, and change surface catalytic pathways. As a result, investigations were conducted to understand the reorientation of dipoles, and the chemical and electronic influence of dipoles on surfaces and vice versa. The ability to change substrate dipoles can offer a novel control of surface catalytic functionality.

The PI examined how forming interfaces between two materials induces distortions that carry over from one to the other.¹ This can be extended to surface catalytic materials, with distortions inherited from a substrate. Next, an investigation of the surface atomic response to bulk dipole was conducted. The PI and team found that each polar state (up-poled, unpoled, down-poled) gives rise to different surface stoichiometries and patterns, offering control over surface reactivity.² The coupling between bulk polar dipole and molecular adsorption was examined for a family BaTiO₃ nanowires. The wire thickness changes the dipole stability, as does the molecular adsorption, so the resulting chemisorption strength can be tuned by material selection, *T*, and material thickness.³ The PI also explored the properties of finite-size oxide nanocubes, such that the polarization can be reoriented easily. The finite size mimics the high-surface-area catalysts required for industrial applications, and the enhanced polarization rotation flexibility in these systems offers catalytic flexibility as well.⁴ The PI extended this theme of surface dipole influencing surface

chemistry by examining H₂O interactions with hybrid perovskite materials. The PI and team found that water binding is stronger on one termination than another, leading to strongly enhanced subsurface water incorporation on this termination.^{5,6}

More recent work in this area includes using light to control the material dipoles and to use surface chemical bonding to control bulk dipoles and light emission. These new directions open up future opportunities in controllable catalysis. The PI explained catalytically triggered changes in photoluminescence from LaAlO₃/SrTiO₃ heterostructures in collaboration with Profs. Mohammed Islam and Jonathan Spanier. The polar LaAlO₃ layer provides a range of electronic energy levels for defects, leading to diffuse photoluminescence. However, theory explains that exposure to water catalyzes reaction and leaves protons on the surface, passivating the surface charges and returning all defects to one energy level, giving sharp photoluminescence.⁷ In a collaboration led by Prof. Aaron Lindenberg, the PI studied ways of reorienting bulk polarization with ultrafast light pulses, suggesting future opportunities to change the surface catalytic state rapidly and reversibly.⁸

II.B Exploring novel ways of bringing charge to the surface for redox catalysis

As part of this project, new materials are sought in order to enhance redox catalysis. In order to support redox catalysis, a substrate must reduce reaction barriers and also transport electrons or holes to and from the surface. As a result, research is focused on developing materials where the surface conductivity is robust, controllable, and interesting.

The PI examined ways to develop new charge ordered materials. Charge ordering involves a material easily undergoing metal to insulator transition, and it is enabled by having the same element existing in different oxidation states in the insulator and the same oxidation state in the metal. The PI studied how to stabilize the charge ordered state through steric templating, since the higher oxidation state ion is smaller than the lower oxidation state ion.⁹ This can make flexible charge flow feasible at catalytically favorable *T*.

The PI also examined topological insulators and topological semimetals, because they have surfaces with unusual and valuable conductivity. Most materials can be oxidized, meaning that the metallic surface states become insulating. However, topological insulators have conductive surface states that are “topologically protected”, meaning that they will always be conductive regardless of the chemisorbed molecules—this is a powerful property! Very few researchers study topological physics and catalysis, and the PI is nearly unique in being able to examine the potential of the conductive surfaces of topological materials and harness them for catalysis. The PI and theory collaborators Profs. Kane and Mele discovered new classes of topological materials, including Dirac line node materials (materials with one-dimensional Fermi surfaces)¹⁰ and layered topological insulators (materials with multiple metal-insulator transitions due to symmetry).¹¹

The PI also conducted an intriguing study on how to use bulk dipoles to control the free charge at a surface. The PI predicted that graphene on polar LiNbO₃ would have its charge and conductivity affected by the oxide dipole. This was confirmed in a beautiful experiment by collaborators Profs. Moonsub Shim and Lane Martin. This ability to influence surface charge via oxide dipole opens up possibilities for controllable redox catalysis.¹²

Silicides form an interesting platform for new research in the area of redox catalysis, since they combine a variety of surface sites with useful bulk conductivity. The PI and team explored varying the Pt:Si atom ratio in order to shift the energies of the Pt 5*d* orbitals and influence surface catalytic reactivity and conductivity.¹³

II.C Nonstoichiometric surfaces offering new sites for heterogeneous catalysis

One of the key findings in this grant period is the discovery of significant reaction barrier lowering due to catalytic reaction on nonstoichiometric surfaces. The PI predicted that the “TiO₂ double layer” surface of SrTiO₃ with two consecutive layers of TiO₂ (instead of the usual alternation of SrO and TiO₂) offers two

undercoordinated Ti sites that work together to catalyze the oxygen evolving reaction (OER) much better than the conventional surface. The PI then led an experimental confirmation of this prediction, collaborating with Profs. Dawn Bonnell and Chris Murray who annealed SrTiO₃ samples to produce the double layer surface and the conventional one. The PI's student conducted electrochemical experiments proving reaction barrier lowering of more than 0.5 eV in quantitative agreement with the predictions.¹⁴ This work led to a U.S. Patent that issued recently.¹⁵

This breakthrough relates to other studies conducted by the PI exploring the chemical, physical, and electronic properties of nonstoichiometric surfaces. Essentially, the consideration of nonstoichiometric surfaces opens up a new platform for catalyst design, providing many surfaces for the same material and facet. The PI studied a range of nonstoichiometric surfaces, including phase transitions between different patterns for the same surface composition.¹⁶ The PI conducted an examination of the surface reactivity of nonstoichiometric BaTiO₃ with H₂O, and the use of H₂O to convert one surface reconstruction to another.¹⁷ A more recent study demonstrated how, for the same material and facet, reconstructions formed at different *T* can give a wide range of surface dipoles, tailoring the band alignment to make materials overlap with the redox potentials for water splitting and other redox reactions.¹⁸ In recent work in this theme, exploration of nonstoichiometric surfaces for catalysis has extended beyond oxides. The PI and his group studied a family of nickel phosphide materials, discovering that under catalytic conditions, these materials show phosphorus-rich surfaces that could be responsible for the excellent hydrogen-evolving reaction (HER) activity in these materials.¹⁹

II.D Illustrating how surface catalysis responds to applied pressure

As part of our search for novel control parameters for heterogeneous catalysis, we explored the influence of mechanical pressure on surface reactivity, on both inert and catalytically active surfaces. The PI examined benzene chemisorption on Au and Pt surfaces, noting the stronger interactions on Pt. Further, the PI demonstrated that as pressure is applied, the benzene molecules can be forced to react, using mechanical pressure to lower the chemical reaction barrier. Au requires much more pressure before reaction can occur, since it binds benzene weakly.^{20;21}

II.E Catalytic growth of carbon-based materials

In concert with the heterogeneous catalytic studies conducted above, the PI examined chemical reactions involved in forming carbon materials and the opportunities for catalysts in these processes. He examined the growth of graphene/BN interfaces in collaboration with Profs. Marija Drndic and Charlie Johnson, finding out that the two types of seams (C-N or C-B) have different chemical and mechanical properties due to changes in antibonding states.²² In addition, the PI provided first-principles chemical bonding insight into reactions of alkyl acrylates. In collaboration with theorist Masoud Soroush (Drexel) who provided macroscopic kinetic modeling knowhow, the PI predicted overall polymer production rates based on first-principles chemical reaction rates.²³

II.F New computational methods allowing more accurate exploration of molecule-surface interactions

To enhance our ability to pursue the heterogeneous catalysis studies above, we developed new electronic and chemical computational methods that provide more accurate results, that include additional interactions, and that provide a clearer picture of chemical bonding.

Van der Waals interactions: Through a sustained collaboration with Jianmin Tao (now a professor at Temple), the PI explored new ways of including van der Waals (vdW) interactions, because this is an im-

portant aspect of chemisorption and a large fraction of the interaction energy. Together they developed a way of using the dynamic multipole polarizability²⁴ to find the leading $1/R^6$ and higher-order interaction coefficients between molecules and surfaces. Next they showed that in solids, the vdW interactions are strongly screened²⁵ and that higher-order corrections again are important. Furthermore, they show that C_6 , C_8 , and C_{10} are all important for inter-molecular²⁶ vdW interactions.

Modeling Mn oxides: As mentioned above, the redox flexibility of Mn makes it promising for nonstoichiometric surface catalytic oxides and in charge-ordered materials. But treating all the different accessible oxidation states poses a difficult challenge for DFT. Accordingly, the PI designed a new pseudopotential²⁷ for Mn including both U and J terms, allowing accurate modeling of MnO, Mn₂O₃, Mn₃O₄, and MnO₂. This opens up accurate catalysis study of mixed redox Mn surfaces.

Quantum pressure to visualize bonding: The “quantum pressure” formalism provides a great way to visualize covalent bonding in complex molecule-surface situations. The PI extends this approach²⁸ to a variety of chemical systems while examining the influence of magnetic fields on bonding.

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