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MATERIALS DESIGN OF CORE-SHELL NANOSTRUCTURE CATALYSTS AND NEW QUANTUM MONTE CARLO METHODS, WITH APPLICATION TO COMBUSTION

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14. ABSTRACT

During the current grant period, we completed projects designed to understand the surface chemistry of polar oxides. We showed how oxide dipoles change bare and supported-metal chemistry, imparting charge to "switchable nanocatalysts". We showed how changing gaseous conditions above oxides can change the bulk and surface structure, controlling surface chemistry. We also investigated how doping oxides changes their catalytic and light absorption properties. We demonstrated that metal cations can be incorporated accompanied by vacancies, leading to recycling of catalytic met- als as "intelligent catalysts". We showed that this effect enhances catalysis and improves visible light absorption for possible solar applications. We have developed new methods for improved modeling of surface chemical and light absorption properties. We showed the importance of going beyond the d-band center approximation to understand metal catal- ysis, and created new pseudopotentials to facilitate use of hybrid functionals for extended solids. Because oxides offer both visible light absorption and fruitful surface chemistry, some preliminary activities relating to water splitting reactivity have been undertaken toward the end of the grant period. Diffusion and reactivity of water fragments has been

15. SUBJECT TERMS

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To: technicalreports@afosr.af.mil

Subject: Annual Progress Statement to Dr. Michael Berman

Contract/Grant Title: Materials Design of Core-Shell Nanostructure Catalysts

Contract/Grant #: FA9550-07-1-0397

Reporting Period: 01-05-2007 to 30-11-2009

Honors and Highlights:

- Named founding co-director of Pennergy: the Penn Center for Energy Innovation (September 2009)
- Named to Energy Advisory Committee, Ben Franklin Technology Partners of Southeast Pennsylvania
- 14 papers published under AFOSR support, including *Nature Materials*, *J Am Chem Soc*, 3 *Phys Rev Lett*, 3 *J Phys Chem*, and *Chem of Materials*.
- 2009 *Phys Rev Lett* on theory/experiment collaboration showing chemical control of oxide surfaces (AFOSR supported) selected for an entire "highlight article" in *Physics*.
- Organized symposium "Solar Energy Capture and Conversion: Materials, Challenges, and Breakthroughs" (also presented AFOSR-supported research as invited speaker) (February 2009)
- Named to MRSEC advisory board, Ohio State University MRSEC
- Chaired MRSEC review panel, NSF
- Secretary/Treasurer, Division of Chemical Physics, APS (2007-2010)
- Secondary appointment with voting rights, Materials Science and Engineering Department, University of Pennsylvania (2008-2011)
- First major AFOSR-sponsored paper with Penn undergraduate (Liz Sokol, 2009)

Highlights of current-grant published work (AFOSR supported)

- Predicted that polar thin-film **oxides** can have anomalous **surface chemistry**, and predicted ways to alter reactivity controllably
  - Showed that catalytic activity of oxide-supported metals can be dramatically affected by oxide dipole direction, which can be harnessed in "switchable nanocatalysts" [PRL 2007, #2 below].
  - Collaboration with experimental colleagues at Penn provided first demonstration that the polar state of bare oxides influences physisorption of CO_2 and CH_3OH, molecules relevant for proposed work in photocatalysis [Nat. Mat. 2008, #8 below].
  - Collaboration with experimental colleagues at Penn demonstrates that changing temperature and gas environment causes important changes in surface stoichiometry [Phys. Rev. Lett. 2008, #9 below].
  - Collaboration with experimental colleagues at Argonne National Lab confirmed our prediction of the strong coupling between surface chemistry and bulk oxide dipole [Phys. Rev. Lett. 2009, #12 below].
  - Computational demonstration of how metal clusters on metal-oxide substrates can interact with the cations and the oxygen of the substrate, leading to "dipolar metal nanoclusters" [J. Phys. Chem. 2009, #13 below].
- Predicted that **doping oxides with metals** with different valence changes their chemistry
  - Collaboration with experimental colleagues at UCSanta Barbara showed that Pd can be incorporated in $BaCeO_3$ by binding an oxygen vacancy, explaining the "intelligent catalyst" effect [Chem. Mater. 2008, #3 below].
  - Predicted that incorporating Pt, Pd, or Ni into $PbTiO_3$ increases its visible light absorption, making it a promising solar material [JACS 2008, #11 below].
- Pioneered **new methods** to understand surface catalysis and light absorption of photoelectrochemical materials
  - Developed new pseudopotentials that enable efficient Hartree-Fock or hybrid functional calculations by reducing plane-wave cutoffs [PRB 2008, #6 below].
  - Demonstrated orbital-specific density of states analysis to understand reactivity of metal clusters on oxides [JPC 2008, #7 below].

Highlights of work in progress (unpublished):

- Building on our **surface oxide chemistry** work....
  - Just completed a study of OH diffusion across oxide surfaces. Examination of water fragment binding and mobility is a key step toward microkinetic modeling of water splitting on oxides.
  - Started a study of H_2O and OH on the 3×1 reconstruction containing undercoordinated (and not fully oxidized) Ti ions. Will examine reactivity of these Ti ions for water splitting, perhaps considering other reconstructions.
- Building on our **doped oxides** for changing materials chemistry work...
  - At least four experimental groups (Oak Ridge, Wisconsin, Drexel, Penn) are currently working to synthesize and characterize solar oxide $Pb(Ti,Ni)O_3$ predicted and published under current AFOSR support
  - Predicted improved solar light absorption for several new oxide materials (writing patent disclosures this week; manuscript ready to submit)
  - Applying first-principles thermodynamics to determine the range of conditions under which a dopant will bind an oxygen vacancy, giving rise to the favorable solar and catalytic properties discovered in the current grant period.
- Building on our **methodology** work...
  - Using hybrid DFT functionals, LDA+U, screened exchange, and self-consistent GW methods to improve electronic structure description for photoelectrochemical predictions.
  - Launched collaboration with Mike Fayer to model ultrafast dynamics of organic molecules in solution, modeling 2DIR results.

Annual accomplishments (200 words max): During the current grant period, we completed projects designed to understand the surface chemistry of polar oxides. We showed how oxide dipoles change bare and supported-metal chemistry, imparting charge to "switchable nanocatalysts". We showed how changing gaseous conditions above oxides can change the bulk and surface structure, controlling surface chemistry. We also investigated how doping oxides changes their catalytic and light absorption properties. We demonstrated that metal cations can be incorporated accompanied by vacancies, leading to recycling of catalytic metals as "intelligent catalysts". We showed that this effect enhances catalysis and improves visible light absorption for possible solar applications. We have developed new methods for improved modeling of surface chemical and light absorption properties. We showed the importance of going beyond the d-band center approximation to understand metal catalysis, and created new pseudopotentials to facilitate use of hybrid functionals for extended solids. Because oxides offer both visible light absorption and fruitful surface chemistry, some preliminary activities relating to water splitting reactivity have been undertaken toward the end of the grant period. Diffusion and reactivity of water fragments has been explored, beyond-DFT methods for band-gap prediction have been applied, and new doping strategies for improving visible light absorption have been studied.

Archival publications (published with AFOSR support) during reporting period:

1. M. W. Lee, M. Mella, and A. M. Rappe, "Electronic quantum Monte Carlo calculations of energies and atomic forces for diatomic and polyatomic molecules", Advances in Quantum Monte Carlo, J. B. Anderson and S. M. Rothstein, eds. ACS Symposium Series, No. 953, Oxford Univ Press, pp. 69–79 (2007).
2. A. M. Kolpak, I. Grinberg, and A. M. Rappe, "Polarization effects on the surface chemistry of $PbTiO_3$-supported Pt films", Phys. Rev. Lett. **98** 166101 1–4 (2007).
3. J. Li, U. G. Singh, J. W. Bennett, K. Page, J. Weaver, J.-P. Zhang, T. Proffen, A. M. Rappe, S. Scott, and R. Seshadri, "$BaCe_{1-x}Pd_xO_3$ ($0 \leq x \leq 0.1$): Redox controlled ingress and egress of palladium in a perovskite", Chem. Mater. **19**, 1418–26 (2007).
4. M. W. Lee, S. V. Levchenko, and A. M. Rappe, "Force calculation of polyatomic molecules in quantum Monte Carlo using Pulay's corrections", Mol. Phys. **105**, 2493–7 (2007).
5. I. Grinberg, A. M. Kolpak, Y.-H. Shin, and A. M. Rappe, "Modeling of Materials for Naval SONAR, Pollution Control, and Nonvolatile Memory Applications", Proceedings of the DoD High Performance Computing Modernization Program Users Group Conference, IEEE, pp. 177–184, (2007).
6. W. A. Al-Saidi, E. J. Walter, and A. M. Rappe, "Optimized norm-conserving Hartree-Fock pseudopotentials for plane-wave calculations", Phys. Rev. B **77**, 075112 1–10 (2008).
7. S. E. Mason, I. Grinberg, and A. M. Rappe, "Orbital-specific Analysis of Chemisorption on Transition-Metal Surfaces", J. Phys. Chem. C **112**, 1963–6 (2008).
8. D. Li, M. H. Zhao, J. Garra, A. M. Kolpak, A. M. Rappe, D. A. Bonnell, and J. M. Vohs, "Direct *in situ* determination of the polarization dependence of physisorption on ferroelectric surfaces," Nat. Mat. **7** 473–7 (2008).
9. A. M. Kolpak, D. Li, R. Shao, A. M. Rappe, and D. A. Bonnell, "Evolution of the structure and thermodynamic stability of the $BaTiO_3$ (001) surface", Phys. Rev. Lett. **101**, 036102 1–4 (2008).
10. J. W. Bennett, I. Grinberg, Y.-H. Shin, and A. M. Rappe, "Modeling of materials for naval SONAR, pollution control and nonvolatile memory application", 2008 DoD HPCMP Users Group Conference, 214–20 (2008).
11. J. W. Bennett, I. Grinberg, and A. M. Rappe, "New Highly Polar Semiconductor Ferroelectrics through d^8 Cation-O Vacancy Substitution into $PbTiO_3$: A Theoretical Study", J. Am. Chem. Soc. **130**, 17409–12 (2008).
12. R. V. Wang, D. D. Fong, F. Jiang, M. J. Highland, P. H. Fuoss, C. Thompson, A. M. Kolpak, J. A. Eastman, S. K. Streiffer, A. M. Rappe, and G. B. Stephenson, "Reversible chemical switching of a ferroelectric film", Phys. Rev. Lett. **102**, 047601 1–4 (2009). Selected for a *Viewpoint* by J. Hlinka, "Switching a ferroelectric film by asphyxiation", Physics **2**, 8 1–2 (2009).
13. S. E. Mason, E. A. Sokol, V. R. Cooper, and A. M. Rappe, "Spontaneous Formation

of Dipolar Metal Nanoclusters", J. Phys. Chem. A **113**, 4134-7 (2009).

14. S. Srinivasan, M. W. Lee, M. C. Grady, M. Soroush, and A. M. Rappe, "Computational Study of the Self-Initiation Mechanism in Thermal Polymerization of Methyl Acrylate", J. Phys. Chem. A **113**, 10787-94 (2009).

Changes in research objectives, if any: none

Change in AFOSR program manager, if any: none

Extensions granted or milestones slipped, if any: none

Include any new discoveries, inventions, or patent disclosures during this reporting period (if none, report none): new oxide solid solutions for visible light absorption and carrier separation