

Program Book

December 15~16, 2011 Dr. Poe Lecture Hall IAMS, Academia Sinica, Taipei, Taiwan





■ Sponsors

Institute of Atomic and Molecular Sciences, Academia Sinica, Taiwan PIRE-ECCI Program, UC Santa Barbara, USA Max-Planck-Gesellschaft, Germany National Science Council, Taiwan

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Dr. Susannah Scott (University of California - Santa Barbara, USA)

Dr. Alec Wodtke (University of Göttingen & Max-Planck-Gesellschaft, Germany)

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General Information

■ Venue

Dr. Poe Lecture Hall, IAMS, Academia Sinica

Registration

The registration desk is located in front of the Lecture Hall.

Lunches

Lunch boxes will be provided for participants on December 15 and 16. We will provide lunch tickets for receiving the lunch box to all participants.

■ Dinners (for speakers only)

Thursday, December 15, 18:30~20:00

Café83, Leader Hotel Taipei

Location: The 2F of Leader Hotel Taipei. No. 83, Sec. 4, Roosevelt Rd., Taipei City.

Friday, December 16, 18:30~20:00

Shin Yeh Taiwanese Cuisine, NanXi Branch

Location: 8F, No. 12, Nanjing W. Rd., Taipei City

Transportation: Take MRT Tamsui-Xindian Line at Gongguan (NTU) station and get off at Zhongshan station. Walk to Exit #3 of the station (Shin-Kong Mitsukoshi Building #1). The restaurant is just at 8F of the building.

Fare for single journey: NTD \$20

Duration: 10 minutes between Gongguan station and Zhongshan station)

Route map of Taipei MRT



Program for Sustainable Energy Workshop

December 15, 2011 (Thu) Dr. Poe Lecture Hall, IAMS, Academia Sinica

0830-0900	Registration		
0900-0915	(Dr. Mei-Yi	Opening Remarks in Chou, Dr. Alec Wodtke and Dr. Susannah Scott)	
	Surface and Gas	Dynamics (Chairperson: Dr. K.H. Chen)	
0915-0940	Dr. Alec Wodtke (Phys. Chem., U. Göttingen)	Beam-surface scattering as a probe of chemical reaction dynamics at interfaces	
0940-1005	Dr. Kopin Liu (IAMS, Academia Sinica)	Imaging the steric effects in polyatomic reactions	
1005-1030	Dr. Chi-Kung Ni (IAMS, Academia Sinica)	Energy transfer of highly vibrationally excited molecules and supercollisions	
1030-1100		Coffee Break	
	Surface and Gas Dynamics (Chairperson: Dr. A. Wodtke)		
1100-1125	Dr. Eckart Hasselbrink (Phys. Chem., U. Duisburg- Essen)	Energy conversion from catalytic reactions to hot electrons in thin metal heterostructures	
1125-1150	Dr. Jim Jr-Min Lin (IAMS, Academia Sinica)	ClOOCl and ozone hole — A catalytic cycle that we don't like	
Catalysis			
1150-1215	Dr. Trevor Hayton (Chemistry, UCSB)	Nitric oxide reduction mediated by a nickel complex	
1215-1240	D	iscussions (Chairperson: Dr. A. Wodtke)	
1240-1330		Lunch	

Nanoscience (Chairperson: Dr. D.P. Tsai)		
1330-1355	Dr. Claus Ropers (Physics, U. Göttingen)	Metallic nanostructures for linear and nonlinear light confinement and spectroscopy
1355-1420	Dr. Juen-Kai Wang (IAMS, Academia Sinica)	Nano-photovoltaic project in Academia Sinica
1420-1445	Dr. Michael Gordon (Chem. Engineering, UCSB)	Multi-scale optical, electrical, and chemical interrogation of conjugated polymer films for photovoltaic applications
1445-1515	Coffee Break	
Nanoscience (Chairperson: Dr. M. Gordon)		
1515-1540	Dr. Din Ping Tsai (Physics, NTU)	Plasmonic hot spots of optical disk for photocatalytic reactors
1540-1605	Dr. Steven Buratto (Chemistry, UCSB)	Size-selected vanadium oxide clusters on $TiO2(110)$ -(1×1) and their role in oxidative dehydrogenation of methanol: Every atom counts
1605-1630	Dr. Kuei-Hsien Chen (IAMS, Academia Sinica)	Nanomaterials as catalyst support for hydrogen technology
1630-1700	D	viscussions (Chairperson: Dr. C. Ropers)
1830-2000		Welcome Dinner (Speakers only) Café83, Leader Hotel Taipei (2F)

Catalysis (Chairperson: Dr. S. Cheng)		
0900-0925	Dr. Susannah Scott (Chemistry, UCSB)	Nanostructured catalysts for carbohydrate dehydration
0925-0950	Dr. Shang-Bin Liu (IAMS, Academia Sinica)	Synthesis of highly nitrogen-doped porous carbons and their applications as electrocatalyst materials in proton exchange membrane fuel cells
0950-1015	Dr. Peter Ford (Chemistry, UCSB)	Nanomaterial antennae in photo-delivery of bioactive molecules
1015-1040	Dr. Eric McFarland (Chem. Engineering, UCSB)	Solar production of fuels and chemicals: Are there science- based cost-effective pathways forward?
1040-1100	Coffee Break	
Catalysis (Chairperson: Dr. S. Scott)		
1100-1125	Dr. Soofin Cheng (Chemistry, NTU)	Catalysis for biodiesel synthesis
1125-1150	Dr. Daniel Little (Chemistry, UCSB)	Electron transfer from the electrode up
1150-1215	Dr. Liming Zhang (Chemistry, UCSB)	Establishing the equivalency between alkynes and alpha-diazo ketones via gold catalysis
1215-1240	Discussions (Chairperson: Dr. S. Scott)	
1240-1330	240-1330 Lunch	
Modeling and Simulation (Chairperson: Dr. C.M. Wei)		
1330-1355	Dr. Mei-Yin Chou (IAMS, Academia Sinica)	Catalytic effect of near-surface alloying on hydrogen interaction with the aluminum surface

December 16, 2011 (Fri) Dr. Poe Lecture Hall, IAMS, Academia Sinica

1355-1420	Dr. Luca Ghiringhelli (Fritz-Haber, Max-Planck)	Towards catalysis by gold clusters: Allowed reaction cycles and poisons
1420-1445	Dr. Baron Peters (Chem. Engineering, UCSB)	A systematic ab initio strategy for predicting structure-activity relationships in amorphous catalysts and supports
1445-1515	Coffee Break	
Modeling and Simulation (Chairperson: Dr. L. Ghiringhelli)		
1515-1540	Dr. Ming-Chang Lin (Appl. Chem., NCTU)	Ab initio chemical kinetics of some practically important processes occurring in the gaseous and condensed phases
1540-1605	Dr. Ricardo Mata (Phys. Chem., U. Göttingen)	Correlated wave function methods studies of metal clusters and complexes
1605-1630	Dr. Ching-Ming Wei (IAMS, Academia Sinica)	Material simulations using quantum Monte Carlo
1630-1700	Discussions & Closing Remarks (Chairperson: Dr. M.Y. Chou)	
1830-2000	Dinner with Dr. Y.T. Lee (President, ICSU, UN) (Speakers only) Shin Yeh Taiwanese Cuisine, NanXi Branch	

I01

Beam-surface Scattering as a Probe of Chemical Reaction Dynamics at Interfaces

Alec M. Wodtke

Georg August University, Institute of Physical Chemistry, Göttingen and Max Planck Institute for Biophysical Chemistry, Dynamics at Surfaces, Göttingen, Germany

Email: <u>alec.wodtke@mpibpc.mpg.de</u>

Developing a predictive understanding of surface chemistry based on the first principles of Physics must include possible breakdown of the Born-Oppenheimer approximation. Reaching this goal means progressing beyond what is now possible for gas-phase bimolecular reactive encounters. This represents one of the most important challenges to current research in chemical physics; since, to the extent that the Born-Oppenheimer approximation breaks down, we have no predictive theory of surface chemistry. This means we are working in an exciting environment where new phenomena might be discovered through experiments and inspire new theoretical developments. This lecture will present recent experimental results that demonstrate the importance of Born-Oppenheimer breakdown. I will emphasize quantitative measurement that can be directly compared to dynamical theories that go beyond the Born-Oppenheimer Approximation.

- 1. J.D. White, J. Chen, D. Matsiev, D.J. Auerbach, and A.M. Wodtke, *Nature* 433, 503-505 (2005).
- 2. Y.H. Huang, C.T. Rettner, D.J. Auerbach, and A.M. Wodtke, *Science* 290, 111-114 (2000).
- 3. R. Cooper, I. Rahinov, Z.S. Li, D. Matsiev, D.J. Auerbach, and A.M. Wodtke, Chem. Sci. 1, 55-61 (2010).
- 4. N. Shenvi, S. Roy, and J.C. Tully, *Science* **326**, 829-832 (2009).
- 5. J. Larue, J., T. Schafer, D. Matsiev, L. Velarde, N.H. Nahler, D.J. Auerbach, and A.M. Wodtke, *Phys. Chem. Chem. Phys.* **13**, 97-99 (2011).

Author Biography (Alec M. Wodtke)

Alec M. Wodtke received his Bachelor of Arts degree from the University of Utah (in Chemistry). He obtained his Doctor of Philosophy degree in Physical Chemistry from the University of California, Berkeley. Before he became a Professor at the Georg August University of Göttingen and a Director and Scientific Member of the Max Planck Society, at the Max Planck Institute for Biophysical Chemistry at Göttingen, in 2010, he worked at the University of California, Santa Barbara, in the Chemistry Department. He was Assistant Professor from 1988 to 1993; Associate Professor from 1993 to 1996; Full Professor from 1996 to 2010 and Professor Above Scale since then. Since 2005 he has been the Director of the Partnership for International Research and Education – Electron Chemistry and Catalysis at Interfaces.



Besides being a member of the American Chemical Society and the Deutsche Bunsengesellschaft für physikalische Chemie as well as a fellow of the American Physical Society and the American Association for the Advancement of Science he has been on the Advisory Board of several journals and chaired different program and nominating committees (e.g. US-China partnership workshop on surface science and heterogeneous catalysis in Dalian in 2009) and organized various workshops.

Research Interests:

- Energy dynamics at surfaces
- Photochemical production of cyclic-N3
- Vibrational promotion of electron emission
- Scattering of laser-prepared molecules from metal surfaces

Honors:

Alexander von Humboldt Professorship	2010
Elected Fellow of the American Physical Society	2009
Elected Fellow of the American Association for the Advancement of Science	2007
Alexander von Humboldt Research Award to Senior US Scientists	1998
Alfred P. Sloan Research Fellow	1992
Camille and Henry Dreyfus Teacher Scholar Award	1992
NSF Presidential Young Investigator	1989
U.C. Regents Junior Faculty Fellow	1989
ACS Outstanding Graduate Student Award	1984
NSF Predoctoral Fellow	1982

- Y.H. Huang, C.T. Rettner, D.J. Auerbach, and A.M. Wodtke, *Science* 290, 111-114 (2000).
- J.D. White, J. Chen, D. Matsiev, D.J. Auerbach, and A.M. Wodtke, *Nature* 433, 503-505 (2005).
- N. Shenvi, S. Roy, and J.C. Tully, *Science* **326**, 829-832 (2009).
- R. Cooper, I. Rahinov, Z.S. Li, D. Matsiev, D.J. Auerbach, and A.M. Wodtke, Chem. Sci. 1, 55-61 (2010).

Imaging the steric effects in polyatomic reactions

Kopin Liu

Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan

Email: kliu@pub.iams.sinica.edu.tw

This talk will highlight our recent studies on the reaction of atoms/radicals with methane isotopomers. The experiments were performed under crossed molecular-beam conditions, using a time-sliced, ion velocityimaging detection scheme, which enables us to acquire the quantum-state correlation of the coincidently formed product pairs [1, 2]. Such product pair-correlation measurements can reveal dynamics information that are often hidden or lost by conventional measurements [3]. To explore the mode-specific and bond-selective reactivity, a narrowband IR OPO/OPA was used to prepare a single rotational state of the stretch-excited methane reactants [4-8]. A number of fundamental issues in chemical reaction dynamics will be elucidated when compared to the ground state reactivity. More recently, the polarization property of the IR pumping laser was exploited to investigate the stereo-specific aspects of reactive encounter [9]. Two general approaches to perform a steric-control of molecular collisions are proposed. We will demonstrate in a polarization experiment how to unfold a set of polarization-dependent differential cross sections from images acquired at various experimental geometries. The decoded polarization-dependent differential cross sections provide deeper insights into the stereo-specific reactivity.

- 1. J. J. Lin, J. Zhou, W. Shiu, K. Liu, Rev. Sci. Instrum. 74, 2495-2500 (2003).
- 2. J. J. Lin, J. Zhou, W. Shiu, K. Liu, Science 300, 966-969 (2003).
- 3. K. Liu, Phys. Chem. Chem. Phys. 9, 17-30 (2007).
- 4. S. Yan, Y.-T. Wu, K, Liu, Science 316, 1723-1726 (2007).
- 5. J. Riedel, Y. Yan, H. Kawamata, K. Liu, Rev. Sci. Instrum. 79, 033105 (2008).
- 6. S. Yan, Y.-T. Wu, K, Liu, PNAS 105, 12667-12672 (2008).
- 7. W. Zhang, H. Kawamata, K. Liu, Science 325, 303 (2009).
- 8. F. Wang, K. Liu, Chem. Science 1, 126-133 (2010).
- 9. F. Wang, J.-S. Lin, K. Liu, Science 331, 900-903 (2011).

Author Biography (Kopin Liu)



Kopin Liu received his BS degree from National Tsing Hua University in 1971, and Ph.D. in Chemistry from Ohio State University in 1977. He was a staff scientist at Argonne National Laboratory before joining Institute of Atomic and Molecular Sciences in 1993.

Research Interests:

- Mode- and bond-selective chemistry;
- Correlation and coherent phenomena in molecular collisions;
- Solvation and hydration dynamics.

Honors:

Humboldt Research Award, Alexander von Humboldt Foundation, 2011.

NSC-NRC Eminent Researchers Award, 2010.

Fellow, Academy of Sciences for the Developing World (TWAS), 2005.

Academician, Academia Sinica, 2004.

Distinguished Alumni, National Tsing Hua University, 2002.

The First Presidential Science Prize of Taiwan, 2001.

Fellow, American Physical Society, 1998.

Fellow, Foundation for the Advancement of Outstanding Scholarship, 1996 ~ 2006.

- "Do vibrational excitations of CHD₃ preferentially promote reactivity toward the chlorine atom?" Yan, Y.-T.Wu, B. Zhang, X.-F. Yue, and K. Liu, Science **316**, 1723 (2007).
- "Tracking the energy flow along the reaction path," S. Yan, Y.-T.Wu, and K. Liu, Proc. Natl. Acad. Sci. USA **105**, 12667 (2008).
- "CH stretching excitation in the early barrier F + CHD₃ reaction inhibits CH bond cleavage," W. Zhang, H. Kawamata, and K. Liu, Science **325**, 303 (2009).
- "Steric control of the reaction of CH stretch-excited CHD₃ with chlorine atom," F. Wang, J.-S. Lin, and K. Liu, Science **331**, 900 (2011).

Energy Transfer of Highly Vibrationally Excited Molecules and Supercollisions

Chi-Kung Ni

Institute of Atomic and Molecular Sciences, Academia Sinica Taipei, Taiwan and Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan

Email: ckni@po.iams.sinica.edu.tw

Collisional energy transfer plays a major role in gas phase photochemical, photophysical and thermal processes. Lindemann first discovered the importance of molecular energy transfer in thermal unimolecular decomposition. Recent experiments which utilize spectroscopic methods provide more information about the collisional energy transfer. However, the results are the averages of the outcomes of individual collisions over the entire thermal ensemble of colliding molecules. Detail information about the energy transfer distribution and the mechanism of supercollisions remain unclear. Recently we have studied the energy transfer of highly vibrationally excited molecules (azulene, naphthalene, methylnaphthalene, dimethylnaphthalene, ethylnaphthalene, biphenyl, phenanthrene, diphenylacetylene, and fluoronaphthalene) using crossed-beam /time-of-flight mass spectrometer/time-sliced velocity map ion imaging techniques. Energy transfer distribution functions were obtained directly from the scatterings and energy transfer mechanisms were proposed. In this talk, we will discuss several effects on energy transfer and supercollisions, including complex, initial relative velocity, initial rotation, methylation and alkylation, vibrational frequency and vibrational motion, and attractive potential.

- 1. C. L. Liu, H. C. Hsu, Y.n C. Hsu, and C. K. Ni, Energy transfer of highly vibrationally excited naphthalene I translational collision energy dependence, *J. Chem. Phys.***127**, 104311 (2007).
- 2. C. L. Liu, H. C. Hsu, Y.n C. Hsu, and C. K. Ni, Energy transfer of highly vibrationally excited naphthalene II vibrational energy dependence, isotope effects, and mass effects, *J. Chem. Phys.* **128**, 124320 (2008).
- 3. C. L. Liu, H. C. Hsu, and C. K. Ni, Energy transfer of highly vibrationally excited naphthalene III rotational effects, *J. Chem. Phys.* **128**, 164316 (2008).
- 4. H. C. Hsu, C. L. Liu, Y.n C. Hsu, and C. K. Ni, Energy transfer of highly vibrationally excited 2methylnaphthalene methylation effects, *J. Chem. Phys.* **129**, 044301 (2008).
- 5. H. C. Hsu, Y. A. Dyakov, and C. K. Ni, Energy transfer of highly vibrationally excited biphenyl, *J. Chem. Phys.* **133**, 174315 (2010).
- 6. H. C. Hsu, M. T. Tsai, Y. A. Dyakov, and C. K. Ni, Energy transfer of highly vibrationally excited phenanthrene and diphenylacetylene, *Phys. Chem. Chem. Phys.* **13**, 8313–8321 (2011).
- 7. H. C. Hsu, M. T. Tsai, Y. A. Dyakov, and C. K. Ni, Energy transfer of highly vibrationally excited naphthalene: collisions with CHF₃, CF₄, and Kr, *J. Chem. Phys.* **135**, 054311 (2011).
- 8. H. C. Hsu, M. T. Tsai, Y. A. Dyakov, and C. K. Ni, Alkylation effects on the energy transfer of highly vibrationally excited naphthalene, *Chemistry An Asian Journal* **6**, 3048 (2011).

Author Biography (Chi-Kung Ni)

Chi-Kung Ni received his BS degree from Department of Chemistry, National Tsing Hua University in 1985. He obtained his MS and Ph.D. degrees from Columbia University in 1993. He worked as a postdoctoral research fellow in University of California, Berkeley till 1995 before he joined Academia Sinica, Taiwan. In Institute of Atomic and Molecular Sciences, Academia Sinica, he works on the UV photodissociation, energy transfer of highly vibrationally excited molecules, MALDI mechanism, and X ray photochemistry.



Research Interests:

- UV photodissociation of organic molecules in molecular beam.
- Energy transfer of highly vibrationally excited molecules in crossed-molecular beam.
- Mechanism of matrix-assisted laser desorption ionization (MALDI)
- X ray photochemistry.

Honors:

Dr. Ni received Outstanding Young Scholar Award from Department of Chemistry, National Tsing Hua University in 2007, and National Science Council Outstanding Research Award in 2010.

- "Photodissociation dynamics of small aromatic molecules studied by multimass ion imaging", Chi-Kung Ni, Cheng-Ming Tseng, Ming-Fu Lin, and Yuri Dyakov, *J. Phys. Chem. B* **111**, 12631 (2007) (invited Feature Article)
- "Energy transfer of highly vibrationally excited naphthalene: collisions with CHF₃, CF₄, and Kr", Hsu Chen Hsu, Ming-Tsang Tsai, Yuri A. Dyakov and Chi-Kung Ni, *J. Chem. Phys.* **135**, 054311 (2011).
- "Plume expansion dynamics of matrix-assisted laser desorption ionization", Chi-Wei Liang, Chih-Hao Lee, Yuan-Tseh Lee, and Chi-Kung Ni, *Chemistry An Asian Journal* **6**, 2986 (2011).
- "Photodissociation dynamics of hydroxybenzoic acids", Yi Lin Yang, Yuri A. Dyakov, Yuan T. Lee, Chi-Kung Ni, Yi-Lun Sun, Wei-Ping Hu, *J. Chem. Phys.* **134**, 034314 (2011).

I04

Energy Conversion from Catalytic Reactions to Hot Electrons in Thin Metal Heterostructures

Eckart Hasselbrink

Physical Chemistry, Fakultät für Chemie, Universität Duisburg-Essen, 45141Essen, Germany

Email: Eckart.Hasselbrink@Uni-DuE.de

The direct conversion of chemical energy into electrical power is an attractive concept whose potential is yet largely unexplored. Besides thermoelectricity, the generation of hot electrons excited in the course of a chemical reaction at a metal surface may be a source of electrical power provided that the charges can be separated. Thin metal films as top layers in metal-insulator-metal or metal-insulator-oxide structures may serve for this purpose. We have fabricated devices consisting of a 10 - 20 nm thin metal layer (Au, Ag, Pt) on top of oxidized Ta, Al or Si substrates. The electrochemically prepared 2 -3 nm thin oxide layer serves as barrier. However, electrons excited by chemical reactions at the surface of the top layer may tunnel through this barrier, which can be detected as a macroscopic current [1]. Such a current has been observed for the reaction of hydrogen on and with Au or Ag surfaces and characterized regarding the energy distribution of the underlying electronic excitations [2]. Experiments studying the water formation reaction (2 H2 + O2 -> 2 H2O) are underway. From a fundamental point of view these experiments probe to which extent non-adiabatic events in the surface chemistry contribute to the release of the excess energy [3].

- 1. P. Thissen, B. Schindler, D. Diesing, E. Hasselbrink, Optical response of metal-insulator-metal heterostructures and their application for the detection of chemicurrents, New J. Phys, 12, 113014 (2010).
- 2. B. Schindler, D. Diesing, E. Hasselbrink, Electronic excitations induced by hydrogen surface chemical reactions on gold, J. Chem. Phys. 134, 034705 (2011).
- 3. E. Hasselbrink, How non-adiabatic are surface dynamical processes?, Curr. Opin. Solid State Mater. Sci. 10, 192 (2006).

Author Biography (Eckart Hasselbrink)

1981	Diplom (Physics) University of Göttingen
1985	PhD (Physics) University of Göttingen
1986-1987	Postdoctoral Research Fellow, Stanford University, USA, with
	Prof. R. N. Zare
1988–1996	Group leader, Fritz-Haber-Institut der Max-Plank-Gesellschaft
1993	Habilitation (Physical Chemistry) Free University Berlin
1996–1997	Lektor for Fysik, Odense Universitet
2003-2008	Prorektor for Research of the university
1998-present	Chair for Physical Chemistry, University of Duisburg-Essen



Research Interests:

- Functional ultra-thin oxide layers and organic monolayers
- Laserstructuring of surface layers into functional assemblies
- Chemical reaction dynamics at surfaces
- Surface photochemistry
- Non-adiabatic reaction pathways and energy dissipation
- Sum frequency generation spectroscopy

Honors:

1987 Reimar-Lüst-Stipendium of the Max-Planck-Gesellschaft1992 Karl-Scheel-Preis der Physikalischen Gesellschaft zu Berlin1994 Dozentenstipendium of the Fonds der Chemischen Industrie

- B. Schindler, D. Diesing, E. Hasselbrink, Electronic excitations induced by hydrogen surface chemical reactions on gold, J. Chem. Phys. 134, 034705 (2011).
- N. Hartmann, B. Klingebiel, T. Balgar, S. Franzka, E. Hasselbrink, Laser induced local dehydroxylation on surface-oxidized silicon substrates: Mechanistic aspects and prospects in nanofabrication, Appl. Phys. A 94, 95 (2009).
- Xu Han, T. Balgar, E. Hasselbrink, Vibrational dynamics of hydrogen on Ge surfaces, J. Chem. Phys. 130, 134701 (2009).
- E. Hasselbrink, How non-adiabatic are surface dynamical processes?, Curr. Opin. Solid State Mater. Sci. 10, 192 (2006).

ClOOCl and Ozone Hole — A Catalytic Cycle that We Don't Like

Jim Jr-Min Lin

Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan

Email: jimlin@gate.sinica.edu.tw

The photochemistry of the ClO dimer (ClOOCl) plays a central role in catalytic destruction of polar stratospheric ozone [1-8]. In spite of intense investigations for decades, some of its laboratory photochemical data had not reached the desired accuracy to allow a reliable simulation of the stratospheric ozone loss until recently. Inevitable impurities in ClOOCl samples have obstructed conventional measurements. In particular, an absorption measurement of ClOOCl in 2007 [3] which gave much lower cross sections than previous studies implied that the formation of Ozone Hole cannot be explained with current chemical models. Scientists have wondered if the model is insufficient or the data is erroneous [1,2]. Efforts [4-8] aiming to resolve this controversy will be given in this presentation, emphasizing newly developed experiments to determine two critical photochemical properties of ClOOCl—its absorption cross section and product branching ratio.

References:

- 1. M. von Hobe, Science 318, 1878 (2007).
- 2. Q. Schiermeier, *Nature* **449**, 382 (2007).
- 3. F. D. Pope, J. C. Hansen, K. D. Bayes, R. R. Friedl, and S. P. Sander, J. Phys. Chem. A 111, 4322 (2007).
- 4. H.-Y. Chen, C.-Y. Lien, W.-Y. Lin, Y. T. Lee, and J. J. Lin, Science 324, 781 (2009).
- C.-Y. Lien, W.-Y. Lin, H.-Y. Chen, W.-T. Huang, B. Jin, I-C. Chen, and <u>J. J. Lin</u>, J. Chem. Phys. 131, 174301 (2009).
- 6. B. Jin, I-C. Chen, W.-T. Huang, C.-Y. Lien, N. Guchhait, and J. J. Lin, J. Phys. Chem. A 114, 4791 (2010).
- 7. W.-T. Huang, A. F Chen, I-C. Chen, C.-H. Tsai and J. J. Lin, Phys. Chem. Chem. Phys. 13, 8195-8203 (2011).
- 8. J. J. Lin, A. F Chen, and Y. T. Lee, Chem. Asian J. 6, 1664, (2011) (Focus Review).

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Author Biography (Jim Jr-Min Lin)

Jim J. Lin received his Ph.D. degree From National Taiwan University in 1998, became an Assistant Research Fellow in Institute of Atomic and Molecular Sciences, Academia Sinica in 2001 and is now a Research Fellow since 2010. He involved in developing important detection techniques for crossed molecular beam reactive scattering, including (i) electron-impact ionization in ultrahigh vacuum, (ii) VUV photoionization with synchrotron radiation, (iii) hydrogen-atom Rydberg tagging, and (iv) velocity-map ion imaging. Recently his group has resolved an important issue regarding the validity of current chemical models of Ozone Hole by measuring the photochemical quantities of ClOOCl including the absorption cross sections and product quantum yields at critical wavelengths.



Research Interests:

- Elementary chemical reactions.
- Atmospheric chemistry.
- Reactivity of transient/unstable species.

Honors:

2010 Ta-You Wu Memorial Award, National Science Council, Taiwan; 2010 Y. Z. Hsu Scientific Paper Award (Green Technology), Far Eastern Y. Z. Hsu Science and Technology Memorial Foundation; 2009 The Broida Prize, The 30th International Symposium on Free Radicals; 2009 The CSJ Asian International Symposium: The Distinguished Lectureship Award, The Chemical Society of Japan; 2008 Asian and Oceanian Photochemistry Association Prize for Young Scientists, Asian and Oceanian Photochemistry Association; 2005 Academia Sinica Research Award for Junior Research Investigator, Academia Sinica; 2004 Distinguished Young Chemist Award, Chinese Chemical Society, Taipei, Taiwan

- "UV Photolysis of ClOOCl and the Ozone Hole," Jim J. Lin, Andrew F Chen, and Yuan T. Lee, Chem. Asian J., 6, 1664 (2011) (Focus Review).
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Nitric Oxide Reduction Mediated by a Nickel Complex

Trevor W. Hayton

Department of Chemistry and Biochemistry, University of California Santa Barbara, CA 93106-9510. Tel: 805-893-3392, Fax: 805-893-4120

E-mail: hayton@chem.ucsb.edu

The reduction of NO to N₂O is an important step in the global nitrogen cycle. The key step in the reaction is the creation of an N–N bond via a proposed hyponitrite $([N_2O_2]^{2^-})$ intermediate. However, there is still much debate about the mechanism of N-N bond formation, as the observation of the short-lived hyponitrite ligand is rare. In an effort to address these issues we are exploring the reactivity of a series of nickel nitrosyl complexes. Addition of bipy to $[Ni(NO)(I)(THF)_2]$, followed by anion exchange with AgPF₆ results in generation of three-coordinate $[Ni(NO)(bipy)][PF_6]$ (1). Subsequent addition of bipy to 1 leads to formation of $[Ni(NO)(bipy)_2][PF_6]$ (2) in good yield. Complexes 1 and 2 have been fully characterized, including analysis by X-ray crystallography. On standing, complex 2 slowly converts into $[Ni(bipy)_3][PF_6]_2$ (3) and N₂O, amongst other products. Efforts to understand the mechanism of N₂O formation during the reaction will be presented.

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Author Biography



Trevor Hayton was born in Ottawa, Ontario in 1975. In 1998 he received his B.Sc. in Chemistry from the University of British Columbia, whereupon he began his Ph.D. research, also at UBC, under the direction of Peter Legzdins. After graduating in 2003, he began a postdoctoral fellowship at Los Alamos National Laboratory, working under the direction of James M. Boncella. In 2006 he started a faculty position at University of California, Santa Barbara, where he is currently an Assistant Professor.

Research Interests:

- Actinide and lanthanide coordination chemistry
- Synthesis and reactivity of high oxidation states
- Redox-active ligands sets
- Solar fuel formation

Honors:

2009 Sloan Fellowship

- Schnaars, D. D.; Wu, G.; Hayton, T. W. Borane-Mediated Silylation of a Metal-Oxo Ligand. *Inorg. Chem.* **2011**, *50*, 4695-4697.
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- Wright, A. M.; Wu, G.; Hayton, T. W. Structural Characterization of a Copper Nitrosyl Complex with a {CuNO}¹⁰ Configuration. J. Am. Chem. Soc. **2010**, *132*, 14336-14337.

Metallic nanostructures for linear and nonlinear light confinement and spectroscopy

Claus Ropers

Courant Research Center Nano-Spectroscopy and X-Ray Imaging, University of Göttingen, Germany

Email: cropers@gwdg.de

Metallic nanostructures exhibiting plasmonic resonances offer unique possibilities for tailoring, controlling and concentrating microscopic optical fields. The near-fields associated with such resonances can be used to enhance and spatially confine a multitude of optical phenomena. In this talk, several examples for the localization of linear and nonlinear processes at metallic nanostructures are discussed.

First, linear light confinement to nanometric dimensions using the excitation of propagating surface plasmon modes on the shaft of conical metal tapers is demonstrated. [1] Second, the localization of nonlinear photoelectron emission from the apex of such sharp metallic tips is illustrated, which allows for studying photoelectric effects in their high-intensity limits. [2,3] Finally, resonant plasmonic bow-tie antennas in the presence of atomic gases are shown to enhance multiphoton and strong-field fluorescence.[4]

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- 4. "Nanostructure-based High Harmonic Generation revisited: Predominance of field-enhanced Atomic Line Emission", M. Sivis, M. Duwe, B. Abel and C. Ropers, submitted (2011).

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Author Biography (Claus Ropers)

Claus Ropers studied Physics at the University of Göttingen and the University of California at Berkeley. Conducting his doctoral work at the Max Born Institute (MBI), Berlin, he received his Ph.D. from the Humboldt University Berlin in 2007. In 2008, he was appointed assistant professor at the University of Göttingen, and became associate professor in 2011. His research focuses on ultrafast processes in nanostructures and solid state systems. To this end, his group develops and investigates novel experimental techniques for the observation of ultrafast dynamical behavior on the nanoscale.



Research Interests:

- Ultrafast carrier dynamics in nanostructures and solid state systems; time-resolved optical spectroscopy.
- Linear and nonlinear optics of nanostructures, characterization and control of field enhancements, resonant surface plasmon polariton phenomena.
- Nonlinear photoelectron emission, generation and characterization of femtosecond electron pulses, time-resolved electron imaging.
- Nonlinear pulse propagation in optical fiber and supercontinuum generation.

Honors:

Claus Ropers was awarded the "Carl-Ramsauer-Preis" by the Physical Society of Berlin in 2008, and the "Nanowissenschaftspreis 2008" by the Working Group of the Centers of Competence of Nanotechnology in Germany (AGeNT-D) in 2009.

- "Seeded Supercontinuum Generation with Optical Parametric Down-Conversion", D. R. Solli, B. Jalali, and C. Ropers, Phys. Rev. Lett. **105**, 233902 (2010).
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Nano-photovoltaic Project in Academia Sinica

Juen-Kai Wang

Center for Condensed Matter Sciences, National Taiwan University and Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan

Email: jkwang@ntu.edu.tw and jkwang@po.iams.sinica.edu.tw

Harvesting solar energy – being the single energy source on earth – has a long evolutionary history in supporting our sustainable nature and has become one of major renewable energy sources nowadays. In particular, energy conversion through photovoltaics – converting photon energy into electrical energy – has the advantage of making direct link to modern appliance usages. This talk introduces our endeavors in pursuing high-efficiency, low-cost and long-lifetime solar cells in Academia Sinica via an integrated approach that incorporate expertise of physics, chemistry, material science, engineering, characterization and simulation. We emphasize on realizing such goals through nanomorphological and interface controls that have been recognized to play important roles in biological light-harvesting.

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Author Biography (Juen-Kai Wang)

Juen-Kai Wang received his BS degree from Electrical Engineering, National Taiwan University in 1983. He obtained his MS and Ph.D. degrees from Applied Physics, Harvard University in 1986 and 1992, respectively. After his post-doctoral study of femtochemistry at California Institute of Technology, he joined Center for Condensed Matter Sciences, National Taiwan University in 1994 and has been jointly appointed by Institute of Atomic and Molecular Sciences, Academia Sinica since 2003. His main research endeavor is the development of innovative optical spectroscopic techniques and their applications to various challenging scientific problems.



Research Interests:

- Nanoprobe enhanced optical spectroscopy
- Charge and energy transfer dynamics in photovoltaic systems
- Intense light-matter interaction
- Biomedical vibrational spectroscopy
- Surface vibrational spectroscopy

Honors:

Dr. Wang received the Executive Yuan Award for Outstanding Contributions in Science and Technology and Nano-Tech Award bestowed by Ministry of Economic Affairs in 2010, owing to his contribution in the development of a fast detection platform of microorganisms based on enhanced Raman scattering.

- "Highly Raman-Enhancing Substrates Made of Ag-Nanoparticle Array with Tunable Sub-10 nm Gaps," H.-H. Wang, C.-Y. Liu, S.-B. Wu, N.-W. Liu, C.-Y. Peng, T.-S. Chan, C.-F. Hsu, J.-K. Wang, and Y.-L. Wang, Adv. Mater. 18, 491 (2006).
- "Excited-state dynamics of *trans,trans*-distyrylbenzene: Transient anisotropy and excitation energy dependence," F.-C. Hsu, M. Hayashi, H.-W. Wang, S. H. Lin, and J.-K. Wang, J. Phys. Chem. A **111**, 759 (2007).
- "Direct Near-Field Optical Investigation of Phase-Change Medium in Blue-Ray Recordable and Erasable Disc," J.-Y. Chu, S.-C. Lo, S.-C. Chen, Y.-C. Chang, and J.-K. Wang, Appl. Phys. Lett. **95**, 103105 (2009).
- "A high speed detection platform based on surface-enhanced Raman scattering for monitoring antibiotic-induced chemical changes in bacteria cell wall," T.-T. Liu, Y.-H. Lin, C.-S. Hung, T.-J. Liu, Y. Chen, Y.-C. Huang, T.-H. Tsai, H.-H. Wang, D.-W. Wang, J.-K. Wang, Y.-L. Wang, and C.-H. Lin, PloS ONE 4, e5470 (2009).

Multi-scale Optical, Electrical, and Chemical Interrogation of Conjugated Polymer Films for Photovoltaic Applications

Michael J. Gordon

Department of Chemical Engineering, University of California, Santa Barbara, USA

Email: mjgordon@engr.ucsb.edu

Understanding and controlling carrier transport in conjugated polymer films and composites is critical to the development and widespread application of plastic solar cells. Recent efforts have focused on "bulk heterojunction" (BHJ) structures where a conjugated polymer is mixed at the nanoscale with a fullerene acceptor to achieve large interfacial areas for exciton splitting. It has been seen in these systems that fabrication protocols drastically affect device efficiency and that charge transport is intimately tied to film morphology through local disorder, domain formation, and compositional heterogeneity. Since charge transport in these systems occurs over distances <100 nm, it is no surprise that *local* physicochemical properties have a tremendous impact on photovoltaic behavior. Unfortunately, our understanding of these issues is poor because conventional PV testing on devices tends to "average out" micro- and nanoscale heterogeneities. To this end, we combine device-level testing of BHJ films with confocal/near-field optical and electrical interrogation (conductive AFM and electrostatic force microscopy) to understand how processing affects nanoscale morphology, molecular alignment, chemical structure, and charge transport. In this work, we show that confocal Raman and photoluminescence (PL) imaging of polythiophene and PPV/fullerene blends, when combined with electrical AFM techniques, are highly descriptive means to study donor/acceptor mixing and nanoscale transport. For instance, spatially-correlated PL, Raman, and electrical imaging are combined to differentiate between regions of phase separation, low donor concentration, and polymer chain organization. The talk will also highlight how low temperature PL measurements and analysis of vibronic (electron-phonon) coupling in films can be used to probe local order and crystallinity. Preliminary results on near-field Raman interrogation of surfaces for localized chemical imaging at the nanoscale will also be mentioned.

Author Biography (Michael J. Gordon)

Prof. Mike Gordon received his BS/MS in Chemical Engineering from the Colorado School of Mines in 1994/1995, and went on to receive an MS in Applied Physics (1998) and PhD in Chemical Engineering (2003) from the California Institute of Technology. He then spent two years as a postdoc at the Laboratoire des Technologies de la Microélectronique (LTM-CNRS) in Grenoble, France, and returned to Caltech in 2006 as a visiting scientist, before joining the faculty at UCSB in 2007. The overarching theme of Prof. Gordon's research is to explore, understand, and exploit the unique physicochemical properties and dynamics of nanoscale systems found in material science, microelectronics, catalysis, and biology. His approach focuses on the development and application of "hybrid" scanning probe



of single nanostructures and surfaces to learn how size, confinement, organization, and surface chemistry affect behavior. The majority of his work is "hands-on" experimental science involving a combination of nanostructure synthesis, laser spectroscopy, and scanning probe microscopy techniques (STM/AFM/SNOM).

Research Interests:

- Nanoscale chemical imaging of surfaces using near-field vibrational spectroscopy.
- Developing novel instruments and methods to identify, measure, and manipulate individual molecules, nano-objects, and micro-scale systems.
- Plasmonics; optical enhancement / coupling effects involving nanoparticles & thin films.
- Synthesis of catalytic nanoparticles using solution and plasma-based techniques.
- Fundamental optical and electrical studies of organic materials for solar cell applications.

Honors:

Prof. Gordon was selected as a 2010 Packard Fellow and he received an NSF CAREER grant in 2010 to develop instruments for near-field optical imaging of surfaces. Mike has also received the Northrop Grumman Excellence in Teaching Award in 2009, he was an Intel fellow from 2000-2003, and he received the Constantin G. Economou prize for his PhD research at the California Institute of Technology.

- L.C. Jones, Z. Buras, and M.J. Gordon, **2011** (in submission), "Selective hydrogenation of C₂H₂ on Ag-doped Pt nanoparticle catalysts," JACS.
- M.J. Gordon, T. Baron, F. Dhalluin, P. Gentile, and P. Ferret, **2009**, "Mechanical deformation and fracture of cantilevered silicon nanowires," Nanoletters 9(2), 529.
- M.J. Gordon, X. Qin, A. Kutana, and K.P. Giapis, 2009, "Gas-surface reactions at high collision energies?," JACS 131, 1927.
- M.J. Gordon and T. Baron, **2005**, "Amplitude mode electrostatic force microscopy in UHV: quantification of nanocrystal charge storage," Phys. Rev. B 72, 165420.

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Plasmonic Hot Spots of Optical Disk for Photocatalytic Reactors

Ming Luen Tzeng¹, Yu Lin Chen¹, Pin Chieh Wu¹, Li Chung Kuo¹, Yao Wei Huang¹, Cheng Hung Chu¹, Hung Ji Huang², Jeffrey Chi-Sheng Wu³, Din Ping Tsai^{1,2,4}

¹Department of Physics, National Taiwan University, Taipei 10617 ²Instrument Technology Research Center, National Applied Research Laboratories, Hsinchu 300 ³Department of Chemical Engineering, National Taiwan University, Taipei 10617 ⁴Research Center for Applied Sciences, Academia Sinica, Taipei 11529

E-mail: dptsai@phys.ntu.edu.tw

Environmental applications of plasmonic effects for photo-catalytic chemical reactors will be discussed in this talk. Plasmonic hot spots and their near-field optical interactions are considered to be the novel methods to achieve high efficient photo-catalytic chemical process. The localized and enhanced electromagnetic field of plasmonic nanostructures of nano recording marks of optical disk provide many hot spots. We found the blinking experiments can demonstrate the hot spots of the optical disks used in our photo-catalytic reactor. Results of the photo-catalytic process happened in the plasmonic optical disk photo-chemical reactor successfully demonstrate better efficiency of the decomposition of the Methyl Orange to carbon dioxide and water.

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- J. J. Chen, C. S. Wu, P. C. Wu, D. P. Tsai, "Plasmonic Photocatalyst for H2 Evolution in Photocatalytic Water Splitting," J. Phys. Chem. C 115, 210 (2011).
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Author Biography (Din Ping Tsai)

Din Ping Tsai received his Ph.D degree in Physics from University of Cincinnati, USA in 1990. From 1990 to 1991 he was a Member of Research Staff at Micro Lithography Inc., California, USA. He was a Postdoctoral Fellow and Research Associate at Ontario Laser and Lightwave Research Center, Toronto, Canada from 1991 to 1994. From 1994 to 1999 he was an Associate Professor at National Chung Cheng University, Chia Yi, Taiwan. He joined National Taiwan University (NTU) as an Associate Professor in 1999, and became Professor and Distinguished Professor of Department of Physics at NTU in 2001 and 2006, respectively. He was invited to join Research Center for Applied Sciences, Academia



Sinica as an Adjunct Research Fellow in 2006. He serves as the Director General of the National Instrument Technology Research Center located in Hsinchu Science Park, Taiwan since 2008.

Research Interests:

Nanophotonics, near-field optics, plasmonics, metamaterials and bio-photonics.

Honors:

- Fellows : American Physical Society (APS), 2007 ; Electro Magnetics Academy (EMA), 2007 ; Optical Society of America (OSA), 2006 ; International Society of Optical Engineering (SPIE), 2005.
- "Outstanding Academic Award," Ministry of Education, Taiwan, 2011.
- "Outstanding Research Award," National Taiwan University, Taiwan, 2010.
- "Outstanding Research Award," Pan Wen Yuan Foundation, Taiwan, 2010.
- "Outstanding Research Award," National Science Council (NSC), Taiwan, 2010.
- "Research Achievement Award," Taiwan Information Storage Association, 2009.
- "Ho Chin Tui Awards," Ho Chin Tui Foundation, 2009.
- "Science 50 Award," National Science Council (NSC), 2008.
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- W. M. Zhu, A. Q. Liu, X. M. Zhang, D. P. Tsai, T. Bourouina, J. H. Teng, X. H. Zhang, H. C. Guo, H. Tanoto, T. Mei, G. Q. Lo, D. L. Kwong, "Switchable Magnetic Metamaterials Using Micromachining Processes," Advanced Materials 23, 1792 (2011).
- W. T. Chen, C. J. Chen, P. C. Wu, S. Sun, L. Zhou, G. Y. Guo, C. T. Hsiao, K. Y. Yang, N. I. Zheludev, **D. P. Tsai**, "Optical magnetic response in three-dimensional metamaterial of upright plasmonic meta-molecules," Optics Express **19**(13), 12837 (2011).

Size-Selected Vanadium Oxide Clusters on TiO2(110)-(1×1) and Their Role in Oxidative Dehydrogenation of Methanol: Every Atom Counts

Steven K. Buratto

Department of Chemistry and Biochemistry, University of California, Santa Barbara, CA USA

Email: <u>buratto@chem.ucsb.edu</u>

Vanadium oxides supported on TiO2 are known to catalyze a number of reactions including the oxidative dehydrogenation of methanol to formaldehyde. Although a great deal of work has been carried out in order to study the catalytic activity, several questions related to the exact compositions and structures of the active species remain unanswered. In an effort to gain a fundamental understanding of these catalysts, we deposit mass-selected V_x and V_xO_y clusters on TiO₂(110)-(1×1) in ultra high vacuum (UHV). These model catalysts are then characterized using STM to determine how the clusters bind to the support. We show that V_1 and V_2 clusters remain size-selected upon deposition, that there are clear differences in the morphologies of these clusters, and that the sizes and shapes observed for the clusters are consistent with density functional theory (DFT) calculations. We also show that that VO and VO₂ clusters remain size-selected upon deposition, and adsorb in sites predicted by DFT.



Figure 1: STM image of VO deposited on $TiO_2(110)$ and 300K (left image), STM of water adsorbed to the VO/ TiO_2 surface at 300K (middle image), and lowest energy structure for 3 water molecules bound to the VO/ TiO_2 surface. The first water molecule has a desorption energy of 1.01 eV and the 2nd and 3rd water molecules have a desorption energy of 0.812 eV.

We observed unusual reactivity of the VO-modified $TiO_2(110)$ -(1×1) surface towards water and methanol adsorption. Room-temperature STM images (Figure 1) show adsorbed water molecules form chains along the five-fold coordinated Ti (5c-Ti) rows when a VO/TiO₂ surface is exposed to water. These chains of water molecules have been observed on bare $TiO_2(110)$ at low temperature (~120K), but not at room temperature. Thermal desorption of water from a VO/TiO₂(110) surface shows a desorption state at 395K which is not present for bare TiO₂. These observations are supported by DFT calculations which predict room temperature adsorption of water along the 5c-Ti rows of a VO/TiO₂ surface, with adsorption energies of -0.8 eV to -1.1 eV for each water molecule (see Fig. 2). Finally, we will present our most recent experiments describing the catalytic activity of VO, VO₂ and VO₃ clusters in the oxidation of methanol to produce formaldehyde and water.

Author Biography (Steven K. Buratto)

Prof. Buratto received a BS degree from the University of Puget Sound in 1987 with a double major in chemistry and mathematics. He obtained his Ph.D. in chemical physics from the California Institute of Technology in 1992. He was a Postdoctoral Member of the Technical Staff at AT&T Bell Laboratories from 1992 to 1994. Prof. Buratto was appointed to the faculty in the Department of Chemistry at UCSB in 1994. Prof. Buratto has an interdisciplinary research program utilizing ultra-high resolution microscopy and spectroscopy to probe physical properties of nanoscale materials of all types including molecular semiconductors and quantum dots used in optoelectronics, metal and metal oxide nanoparticle catalysts and polymer membranes used in fuel cells.



Research Interests:

- Metal and metal oxide nanocluster catalysts; combining mass-selection, ion soft-landing and STM to probe the size dependence of the catalytic activity.
- Proton conductance and interconnectivity in polymer electrolyte membranes used in fuel cells.
- Reducing the catalyst loading in fuel cells by electrodeposition of catalyst particles through the ionomer membrane.
- High resolution chemical imaging of molecular semiconductor films and blends.

Honors:

Prof. Buratto received Camille and Henry Dreyfus New Faculty Award in 1994, an NSF Career Award in 1995, a David and Lucille Packard Fellowship in Science and Engineering in 1997 and an Alfred P. Sloan Fellowship in 1998.

- S.P. Price, X. Tong, C. Ridge, V. Shapovalov, Z.P. Hu, P. Kemper, H. Metiu, M.T. Bowers, S.K. Buratto, "STM Characterization of Size-Selected V-1, V-2, VO and VO₂ Clusters on a TiO₂ (110)-(1 x 1) Surface at Room Temperature" Surf. Sci. 605 (9-10), 972-976 (2011).
- X. Tong, L. Benz, S. Chretien, H. Metiu, M.T. Bowers, S.K. Buratto, "Direct Visualization of Water-Induced Relocation of Au Atoms from Oxygen Vacancies on a TiO₂ (110) Surface" J Phys Chem C 114, (9), 3987-3990 (2010).
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Nanomaterials as Catalyst Support for Hydrogen Technology

Kuei-Hsien Chen

Institute of Atomic and Molecular Sciences, Academia Sinica and Center for Condensed Matter Sciences, National Taiwan University, Taipei, Taiwan

Email: chenkh@pub.iams.sinica.edu.tw

One-dimensional carbon and ZnO with large surface area and continuous transport path offer excellent support of catalysts in hydrogen energy conversion. First, Cu NP/ZnO NW nanocomposite shows enhanced methanol to hydrogen reforming at lower temperature.[1-2] Detailed XAS study shows change transfer between Cu and ZnO, which might result in enhanced catalytic activity. Similar approach for water splitting has been carried out using GaN NW as the photo cathode. Up to 0.91% conversion efficiency has been achieved using NW comparative to the 0.35% for thin film GaN. [3] Second, nitrogen doped CNT (N-CNT) is excellent for Pt nanoparticle loading. Much uniform and mono-dispersed Pt particles can be deposited on N-CNTs directly grown on carbon cloth (CC). It is demonstrated that higher power output (150%) can be achieved at much lower (20%) Pt catalyst loading. A maximum output power of 1.1 Wcm⁻² has been achieved using the Pt/CNTs/CC electrode.[4-5] Furthermore, the newly developed Pt/graphene nanowalls (Pt/GNW) is shown to deliver much enhanced activity for methanol oxidation, which is correlated with the residual strain of graphene after growth.[6] Detailed characterization and simulation of this system is underway.

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Author Biography (Kuei-Hsien Chen)

Kuei-Hsien Chen received his BS degree from Electrical Engineering, NTU in 1981. He obtained his MS and Ph.D. degrees from Applied Science, Harvard University in 1989. He worked on CVD diamond at the R&D Center in General Electric Coorporation till 1992 before he joined Academia Sinica, Taiwan. In Institute of Atomic and Molecular Sciences, Academia Sinica, he works on the synthesis and application of advanced materials, particularly one-dimentional nanomaterials such as carbon nanotubes, graphene, ZnO and GaN nanowires, and their composites. The energy applications of these new materials are the major thrusts of his laboratory.



Research Interests:

- Advanced materials synthesis including CVD, MBE, and ALD for thin film and 1D carbon and semiconductors.
- Nanomaterials for electrocatalysis, gas reforming, solar hydrogen, and thermoelectric applications.
- Transport properties of 1D and 2D materials.

Honors:

Dr. Chen received Academia Sinica Young Scholar Research Award in 2000, NSC Outstanding Research Award in 2005, and Outstanding Scholar Awards of the Foundation for the Advancement of Outstanding Scholarship in 2008. Moreover, the artworks of his group have been awarded First Prize in Science as Art Contest in AVS-2007 and MRS-2008.

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Nanostructured Catalysts for Carbohydrate Dehydration

Susannah Scott

Department of Chemical Engineering and Department of Chemistry & Biochemistry University of California, Santa Barbara

Email: <u>sscott@engineering.ucsb.edu</u>

Biorenewable feedstocks are potential carbon-neutral sources of chemical feedstocks. Specifically, 5hydroxymethylfurfural (HMF) and its derivatives may be utilized as petroleum substitutes or additives, or as replacements for petrochemicals. HMF is produced by the acid-catalyzed dehydration of carbohydrates. Mineral acid catalysts show limited selectivity in complex solvent mixtures, and product separation is complicated. Solid acid catalysts are desired for large-scale processing, however, typical strong solid acids such as Amberlyst 70 show low selectivity. We explored the use of propylsulfonic acid groups incorporated into SBA-15-type mesoporous ordered silicas (MOS) by co-condensation. The functional groups in cocondensed silicas are more hydrothermally stable than comparable grafted sites. To further increase stability and promote selectivity towards HMF, the acid sites were incorporated into periodic mesoporous silicas (PMO) containing organic groups in the framework.

A MOS dehydration catalyst based on SBA-15 containing co-condensed propylsulfonic acid groups (SBA-15-PrSO₃H) showed a significant loss of surface area and, more importantly, functional groups (FG) under typical reaction conditions. Changes in the powder XRD and SEM/TEM images are consistent with disruption of mesopore ordering, while the solid-state NMR spectra (¹³C and ²⁹Si) confirmed that cleavage of the organic functional groups from the silica had occurred. In contrast, PMO materials containing 40 or 90 mol% ethylene linkers in the framework (SBA-15-45%Et-PrSO₃H and SBA-15-90%Et-PrSO₃H, respectively) show little change after exposure to the same conditions, consistent with greater higher hydrothermal stability in the hydrophobic channels. The catalytic activity in fructose dehydration was examined for all three materials under flow conditions. While the MOS catalyst SBA-15-PrSO₃H is more robust than a non-ordered mesoporous catalyst (propylsulfonic acid-modified silica from Silicycle), the PMO-based catalysts showed superior resistance to deactivation.



Author Biography (Susannah Scott)

Prof. Scott received her B.Sc. in Chemistry from the University of Alberta (Canada) in 1987, and her Ph.D. in Inorganic Chemistry from Iowa State University in 1991, where she worked with J. Espenson and A. Bakac on the activation of O_2 and organic oxidations. She was a NATO Postdoctoral Fellow with Jean-Marie Basset at the Institut de recherches sur la catalyse (CNRS) in Lyon, France, before joining the faculty of the University of Ottawa (Canada) in 1994 as an Assistant Professor of Chemistry. She moved to the University of California, Santa Barbara in 2003. She directs the NSF-sponsored Partnership for International Research and Education in Electron Chemistry and Catalysis at Interfaces, a partnership between UCSB and several prominent catalysis research groups in China.



Research Interests:

- Redox reactions catalyzed by PGM-substituted complex oxides
- Controlled, autocatalytic synthesis of supported metal nanoparticles
- Well-defined supported catalysts for olefin metathesis and tandem alkane metathesis
- Creating and understanding supported olefin polymerization catalysts and cocatalysts
- Surface structure and chemistry of oxides
- Catalytic routes to polymer nanocomposites
- Catalysts for converting biomass to fuels and chemicals
- New spectroscopic and kinetic methods for studying heterogeneous catalysts

Honors:

Prof. Scott was awarded an NSERC Women's Faculty Award, a Cottrell Scholar Award, two Union Carbide Innovation Awards and was named a Canada Research Chair in Catalyst Design. She was a Miller Visiting Research Professor at the University of California, Berkeley and has won the John Charles Polanyi Prize in Chemistry.

- "Acid-Functionalized SBA-15-Type Silica Catalysts for Carbohydrate Dehydration", A. J. Crisci, M. H. Tucker, M.-Y. Lee, S. G. Jang, J. A. Dumesic, and S. L. Scott, ACS Catal, 2011, 1, 719-728.
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- "Evidence for the Pairwise Disposition of Grafting Sites on Highly Dehydroxylated Silicas, via their Reactions with Ga(CH₃)₃", S. D. Fleischman, S. L. Scott, J. Am. Chem. Soc., 2011, 133, 4847-4855; featured on the journal cover.
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Synthesis of Highly Nitrogen-doped Porous Carbons and their Applications as Electrocatalyst Materials in Proton Exchange Membrane Fuel Cells

Shang-Bin Liu

Institute of Atomic and Molecular Sciences, Academia Sinica and Department of Chemistry, National Taiwan Normal University, Taipei, Taiwan

E-mail: <u>sbliu@sinica.edu.tw</u>

A comprehensive study on synthesis, characterization, and electrocatalytic applications of nitrogen-doped nanostructured carbon materials has been made. The highly (> 7.5 wt%) N-doped carbons were fabricated by first preparing various carbon-silicate (C-Si) composites by co-condensation method using melamine-formaldehyde resin oligomer (MFRO) as the primary carbon source, triblock copolymer surfactant (P123) as the soft template, and sodium silicate as the hard template while varying the synthesis conditions, viz. duration of polymerization, C/Si ratio, and severity of hydrothermal treatment. Subsequently, the N-doped carbon matrixes may be obtained by graphitizing the Si-C composites at elevated temperatures (600-900 °C) followed by removal of the silica template by acid treatment. The N-doped carbons so fabricated were found to possess superior electrochemical activities and excellent stability during oxygen reduction reaction (ORR) even in the absence of a novel metal catalyst, surpassing the commercial Pt-C electrocatalysts commonly used in direct methanol fuel cells (DMFCs).

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Author Biography (Shang-Bin Liu)

Prof./Dr. Shang-Bin Liu obtained his M.S. (1982) and Ph.D. (1985) in Physics from College of William and Mary, USA. After his postdoctoral research (1985-1987), which was jointly appointed by the Dept. of Chemistry, Univ. of California, Berkeley (under Prof. Alexander Pines) and Dept. of Geology, Stanford Univ. (under Prof. Jonathan F. Stebbins), he has been affiliated with Institute of Atomic and Molecular Sciences, Academia Sinica as an Associate Research Fellow (1987-1993) and Research Fellow (1993-present). At present, he is jointly appointed as a professor in the Dept. of Chemistry, National Taiwan Normal Univ. His research interests include developments of solidstate NMR techniques for porosity and acidity characterization of porous



catalytic and adsorptive materials and synthesis and modification of novel porous silica and carbon materials for applications as electrocatalysts in fuel cells and/or as adsorbents in fuel storage and CO₂ capture.

Research Interests:

- Solid-state Nuclear Magnetic Resonance (NMR) spectroscopy and its applications in porosity and acidity characterization of porous materials.
- Synthesis and surface functionalization of porous silicas and their applications in CO₂ capture and fuel storage.
- Synthesis and modification of porous carbon materials and their applications in fuel cells.

Honors:

Dr. Liu received Excellent Research Awards (1993-1994), The 45th Science and Technology Award for Short-term Oversea Research (2007), and Special Talents Award (2010-2011) from National Science Council (NSC), Taiwan.

- "Fabrication and Characterization of Well-Dispersed and Highly Stable PtRu Nanoparticles on Carbon Mesoporous Material for Applications in Direct Methanol Fuel Cell," S.H. Liu, W.Y. Yu, C.H. Chen, A.Y. Lo, B.J. Hwang, S.H. Chien, and S.B. Liu,* Chem. Mater. 20, 1622-1628 (2008).
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Nanomaterial Antennae in Photo-delivery of Bioactive Molecules

Peter C. Ford

Department of Chemistry and Biochemistry, University of California, Santa Barbara Santa Barbara, CA, 93106-9510 USA

Email: ford@chem.ucsb.edu

Our laboratory has been developing photochemical strategies for the delivery of bioactive agents such as NO and CO to physiological targets that would allow one to control the location, timing, and dosage of such delivery. In this context, we have explored the photoreactions of small molecule precursors including the iron/sulfur/nitrosyl clusters $Fe_2(\mu-SR)_2(NO)_4$ and the Cr(III) nitrito complex *trans*-Cr(cyclam)(ONO)₂⁺. These release NO under visible irradiation but have poor absorbance properties at longer wavelengths. To address this issue, we have designed new complexes with pendant dyes and supramolecular assemblies with water-soluble semiconductor quantum dots to serve as antennae for light absorption and photosensitization of reactions from analogous precursors. These polychromophoric systems demonstrate much greater light absorbance and increase rates of NO release using longer wavelength visible light. Certain antennae have high two photon cross-sections, a feature that allows use of NIR light (where tissue transmission is maximized) to sensitize photoreactions of these systems.



Acknowledgement: This research is sponsored by the US National Science Foundation

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Author Biography (Peter C. Ford)

Peter Ford joined the UCSB faculty in 1967 after earning a Ph.D. in physical organic chemistry with Kenneth B. Wiberg at Yale and serving as a NSF Postdoctoral Fellow in inorganic chemistry with Henry Taube at Stanford. He has also been a Visiting Fellow at the Australian National U. (1974), a Guest Professor at the U. Copenhagen (1981), an Alexander von Humboldt US Senior Scientist Researcher in Germany (1992, 1999 & 2010) and Guest Investigator at the US National Cancer Institute (1994). At UCSB, Professor Ford has served as Research Advisor for 60 Ph.D. graduates and numerous B.S., M.S. and postdoctoral students.



Research Interests:

- Applications of photochemistry for small molecule bioregulator delivery to physiological targets. Applications of nanomaterials as antennae.
- Fundamental reaction mechanisms of small molecule bioregulators, (CO, NO, etc.)
- Catalytic conversion of biomass to chemicals and fuels. .

Honors:

Prof. Ford's research has been recognized with a Dreyfus Foundation-Teacher Scholar award, a Senior Fulbright Fellowship, an A. von Humboldt-Stiftung US Senior Scientist Research Prize (1992, 2010), the 1992 Richard C. Tolman Medal of the American Chemical Society, election as a Fellow of the AAAS (1993) and the 2008 Award in Photochemistry of the InterAmerican Photochemical Society.

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- Nitric Oxide Photogeneration from *trans*-Cr(cyclam)(ONO)₂⁺ in a Reducing Environment. Activation of Soluble Guanylyl Cyclase and Arterial Vasorelaxation, with A. D. Ostrowski et al, *J. Med. Chem.*, **2010**, *53*, 715-722.^{*}
- One-Pot Catalytic Conversion of Cellulose and of Woody Biomass Solids to Liquid Fuels. with T. D. Matson, et al, *J. Am. Chem. Soc.* **2011**, *133*, 14090-14097.

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Solar Production of Fuels and Chemicals: Are there Science-based Cost-effective Pathways Forward?

Eric McFarland

Department of Chemical Engineering, University of California, Santa Barbara, CA USA

Email: <u>ewmcfar@engineering.ucsb.edu</u>

Thermal radiation from nuclear reactions in our sun is the sunlight which sustains life on earth today and powered the photosynthetic processes responsible for the inexpensive fossil fuels which made possible mankind's present prosperity. Investigations of photoelectrocatalysts for artificial solar photosynthesis have been ongoing for decades and the fundamental processes involved are well known. Highly efficient semiconductor device structures have been demonstrated, nonetheless there are no cost-effective material systems or processes capable of significant commercial production of electricity or chemicals. Research on improved photoelectrocatalyst material systems comprised of earth abundant materials in cost-effective system configurations will be discussed and how theory guided materials discovery has been utilized to improve the efficiency of light absorption and energy transfer in photoelectrochemical conversion. The impact of fundamental economic constraints on practical reactors and processes will be highlighted and suggestions made for science based approaches which might make meaningful progress towards meeting one of mankind's greatest challenges.

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Author Biography (Eric McFarland)

Eric McFarland received his Ph.D. from the Massachusetts Institute of Technology and M.D. from Harvard Medical School. He obtained his B.S. and M.S. degrees from U.C. Berkeley in Nuclear Engineering. Following an internship in General Surgery, he joined the Nuclear Engineering faculty at MIT. In 1991 he moved to the University of California at Santa Barbara where he is a Professor of Chemical Engineering. McFarland has worked closely with industry and developed a number of technologies related to the chemical industry. From 1996-1998 he took a leave of absence to be a founding technical director for Symyx Technologies a chemical technology company devoted to combinatorial material science and he has recently served



as President of GRT Inc. a catalysis based energy company. His research is focused on coupling fundamental chemical processes at surfaces with novel material systems for applications to the production and interconversion of fuels and energy. In particular, fundamental surface chemical-electrical phenomena related to catalysis, photoelectrocatalysis, and chemo-electronic devices.

Research Interests:

- Nanostructures for solar photochemical conversion, catalysis, and electrocatalysis applications.
- Advanced materials synthesis.
- Theory guided material system design.

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Catalysis for Biodiesel Synthesis

Soofin Cheng

Department of Chemistry, National Taiwan University, Taipei, Taiwan

Email: chem1031@ntu.edu.tw

Biodiesels are long chain alkyl esters (or fatty acid alkyl esters) synthesized by transesterification of triglycerides with short chain alcohols, such as methanol, ethanol and propanol. The production of first generation biodiesel by transesterification requires high quality vegetable oils with low carboxylic acid content (< 0.5 wt%) as feedstock, which is competition for food supply. Recycled cooking grease and oils can be used as feedstock after removal of carboxylic acids by a previous esterification process, which is a complement to the main transesterification reaction used to product biodiesel.¹ Industrially, strong liquid acids, such as H₂SO₄, HCl and *para*-toluenesulfonic acid, are used as the esterification catalysts and they are corrosive and difficult to be recycled.^{1,2} Furthermore, the sulfur-containing biodiesels are corrosive to the fuel tanks and their combustion generates exhaust pollution. These problems can be solved by replacing the hazardous liquid acids with solid acid catalysts.¹⁻³ Sulfonic acid-functionalized platelet SBA-15 materials (SA-SBA-15-p) with ordered short mesochannels (150-350 nm) and acid capacities up to 1.2 mmol H⁺/g co-condensation of tetraethyl orthosilicate (TEOS) were synthesized by one-pot and 3mercaptopropyltrimethoxysilane (MPTMS) in the presence of appropriate amounts of Zr(IV) ions and H₂O₂. The SA-SBA-15-p materials were efficient catalysts for biodiesel synthesis through esterification of long chain carboxylic acids with methanol. The short-channel SA-SBA-15 materials showed higher catalytic activities than the conventional rod-like or fiber-like analogues, due to better molecular diffusion. Moreover, the used SA-SBA-15-p materials could be easily regenerated by ethanol extraction and the catalytic activities were retained after several recycle runs.⁴

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- 4. S.-Y. Chen, T. Yokoi, C.-Y. Tang, L.-Y. Jang, T. Tatsumi, J.C.C. Chan, S. Cheng, *Green Chem.*, **13**, 2920 (2011).

Author Biography (Soofin Cheng)

Soofin Cheng received her BS degree from Department of Chemistry, National Tsinghua University in 1975. She obtained her Ph.D. degree from Texas A&M University in 1982. After doing Postdoctoral research at TAMU for three years, she joined National Taiwan University as an Associate Professor, then promoted to Professor in 1989. Her researches are mainly in preparation, characterization and applications of novel nano-porous materials and composite materials.



Research Interests:

- Preparation of novel nano-porous materials for the applications in catalysis, photo-catalysis and electrocatalysis
- Preparation of organic/inorganic nano-composites of special photo and magnetic functionalities
- Heterogeneous catalysis for fine chemical synthesis
- Catalysis for renewable energies
- Key materials for solid oxide and direct methanol fuel cells

- "Sulfonic acid-functionalized platelet SBA-15 materials as efficient catalysts for biodiesel synthesis" S.-Y. Chen, T. Yokoi, C.-Y. Tang, L.-Y. Jang, T. Tatsumi, J.C.C. Chan, S. Cheng,* *Green Chem.*, **13**, 2920 (2011).
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- "Pinacol-type rearrangement catalyzed by Zr-incorporated SBA-15" S.-Y. Chen, J.-F. Lee, S. Cheng,* J. Catal. 270, 196 (2010)
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Electron Transfer from the Electrode Up

R. Daniel Little,^{*a} Cheng-Chu Zeng,^b Randi Gbur,^a Seung Joon Yoo ^a

^a Department of Chemistry and Biochemistry, University of California, Santa Barbara CA

^b College of Life Science & Bioengineering, Beijing University of Technology, Beijing, China

Email: little@chem.ucsb.edu

One focal point of our research is upon the design, synthesis and exploration of new electron transfer mediators.[1-3] Efficient electron transfer allows the mediator to be used catalytically and generally requires less energy, since a lower potential is necessary to effect the desired transformation than a direct process at the electrode. We have recently uncovered a new class of mediators based upon the triarylimidazole framework. They are metal-free yet span a relatively wide range of potentials. Some of their chemistry will be discussed. Efforts are also underway to attach mediators capable of achieving either reduction or oxidation to electrode surfaces. In addition, we have begun to explore the use of copolymers consisting of a mediator and a polyelectrolyte in order to reduce waste by achieving electron transfer without the need for a supporting electrolyte.

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- 3. "A Highly Selective Rearrangement of a Housane-derived Cation Radical; an Electrochemically Mediated Transformation", Y.S. Park, S.C. Wang, D.J. Tantillo and R.D. Little, *J. Org. Chem.* **72**, 4351-4357 (2007).

Author Biography (R. Daniel Little)

Dan Little received his B.S. degree in chemistry and mathematics from the Wisconsin State University in Superior, and his Ph.D. from the University of Wisconsin. Following postdoctoral studies at Yale he joined the faculty of the University of California in Santa Barbara; he is a past Department Chair.

Research Interests:

- Mediated electron transfer processes
- Green electrochemistry
- The pseudopterosin marine natural products
- Diradicals related to trimethylenemethane
- Molecule-assisted homolysis

Honors:

In addition to serving on a variety of review panels for the National Science Foundation and the National Institutes of Health, Dr. Little was named an outstanding alumnus of the University of Wisconsin, Superior, a fellow of the Alfred P. Sloan Foundation and the Wisconsin Alumni Research Foundation, a recipient of the Harold J. Plous Award (UCSB), and was named an outstanding faculty member by the UCSB student affiliates of the American Chemical Society.

- "Exploration and Determination of the Redox Properties of the Pseudopterosin Class of Marine Natural Products", W. Zhong and R.D. Little, *Tetrahedron Symposium in Print (Electron Transfer)*, **65**, 10784-10790 (2009).
- "A General Mechanistic Scheme for Intramolecular Electrochemical Hydrocyclizations. Mechanism of the Electroreductive Cyclization of ω -Keto- α , β -Unsaturated Esters", A.J. Fry, R.D. Little and J. Leonetti, *J. Org. Chem.* **59**, 5017-5026 (1994).
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Establishing the Equivalency between Alkynes and alpha-Diazo Ketones via Gold Catalysis

Liming Zhang

Department of Chemistry and Biochemistry, University of California Santa Barbara, California, USA

Email: zhang@chem.ucsb.edu

 α -Oxo metal carbenes/carbenoids are highly reactive intermediates and can undergo a wide range of reactions including difficult transformations (e.g., C-H insertion and cyclopropanations). Decomposition of α -diazo ketones by metal complexes is the principal method for their generations. However, α -diazo ketones are



hazardous, potentially explosive, and seldom commercially available. The development of safe and readily available equivalents of these dangerous chemicals would be of tremendous practical benefits and advantages and may dramatically facilitate the application of these metal carbene chemistry. By using a gold-catalyzed intermolecular oxidation of alkynes, α -oxo gold carbenes are formed as reactive intermediates. Since these gold intermediates can also be formed via gold-promoted

decomposition of α -diazo ketones. This alkyne oxidation effectively makes benign and easily available alkynes equivalent to dangerous α -diazo ketones. The application of this strategy in organic synthesis has led to the development of several highly efficient synthetic methods,¹⁻⁵ which will be discussed in the oral presentation.

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Author Biography (Liming Zhang)

Liming Zhang received his BS degree in Chemistry from Nanchang University in 1993, his MS degrees in Organic Chemistry from Nankai University in 1996 and the University of Alabama in 1998, and his Ph.D. degree in Medicinal Chemistry from the University of Michigan in 2003. He was a postdoctoral researcher working with Professor Sergey Kozmin at the University of Chicago between 2003 and 2005. He joined the Department of Chemistry, University of Nevada, Reno as an Assistant Professor in 2005. He moved to the Department of Chemistry and Biochemistry, University of California, Santa Barbara in 2009 and



was promoted to Associate Professor in 2011. His independent work has been centered on the understanding of homogeneous gold catalysis and its application in the development of highly efficient synthetic methodologies.

Research Interests:

- Homogeneous transition metal catalysis especially gold catalysis
- Heterogeneous catalysis
- Synthetic methodology and reaction mechanism
- Natural product total synthesis

Honors:

2009 Alfred P. Sloan Research Fellow; Spring 2009 CAPA (Chinese American Chemistry & Chemical Biology Professor Association) Distinguished Junior Faculty Award; 2008 Mousel-Feltner Award for Excellence in Research and/or Creative Activity (University of Nevada, Reno); 2008 NSF CAREER Award; 2008 Amgen Young Investigator's Award; 2007 Thieme Journal Award.

- Ye, L.; Cui, L.; Zhang, G.; Zhang, L. "Alkynes as Equivalents of α-Diazo Ketones in Generating α-Oxo Metal Carbenes: A Gold-Catalyzed Expedient Synthesis of Dihydrofuran-3-ones" *J. Am. Chem. Soc.* **2010**, *ASAP*.
- Zhang, G.; Peng, Y.; Cui, L.; Zhang, L. "Gold-Catalyzed Homogeneous Oxidative Cross -Coupling Reactions" *Angew. Chem. Int. Ed.* **2009**, *48*, 3112-3115.
- Cui, L.; Peng, Y.; Zhang, L. "A Two-Step, Formal [4 + 2] Approach toward Piperidin-4-ones via Au Catalysis" *J. Am. Chem. Soc.* **2009**, *131*, 8394-8395.
- Zhang, L. "Tandem Au-catalyzed 3,3-Rearrangement-[2+2] Cycloadditions of Propargylic Esters: Expeditious Access to Highly Functionalized 2,3-Indoline-fused Cyclobutanes" J. Am. Chem. Soc. 2005, 127, 16804–16805.

Catalytic Effect of Near-Surface Alloying on Hydrogen Interaction with the Aluminum Surface

Feng Zhang¹, Yan Wang¹, and Mei-Yin Chou^{1,2}

¹School of Physics, Georgia Institute of Technology, Atlanta, Georgia 30332, USA ²Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan

Email: mychou6@gate.sinica.edu.tw

Complex metal hydrides such as sodium alanate (NaAlH₄) containing light metals and hydrogen have been considered as promising candidates for hydrogen storage because of their high gravimetric and volumetric density of hydrogen. It was found that a small amount of catalyst, such as Ti, added to sodium alanate could greatly improve the kinetics of hydrogen desorption and recharge reactions in this prototypical complex metal hydride, giving rise to a reversible hydrogen storage system with favorable temperature and pressure conditions. The mechanism of this important catalytic process is a topic of intensive studies in the recent decade. We have proposed a near-surface alloying mechanism [1] based on detailed analysis of available experimental data as well as first-principles calculations. The calculated results indicate that the catalyst remains at subsurface sites near the Al surface, and its presence reduces the dissociation energy barrier of H₂. The binding between Ti and Al modifies the surface charge distribution, which facilitates hydrogen adsorption and enhances hydrogen mobility on the surface. This catalytic reaction is also expected to help the formation of alane, another important lightweight hydrogen storage material. In addition, we have found by first-principles calculations that a neutral AlH₃ vacancy induces a few isolated vibrational modes that are highly localized in the vacancy region with frequencies in the phonon gaps of pure NaAlH₄ in both the α and γ phases [2]. In contrast, isolated vibrational modes in the phonon gap region are not found for the systems containing charged AlH₄ vacancies. Therefore, the proposed existence of AlH₃ vacancies in the dehydrogenation reaction of NaAlH₄ can be possibly confirmed by the experimental detection of these unique vibrational modes associated with the AlH₃ vacancy. Possible diffusion paths of the AlH₃ vacancy in bulk NaAlH₄ are also identified for both phases.

- 1. "Catalytic Effect of near-Surface Alloying on Hydrogen Interaction on the Aluminum Surface," Y. Wang, F. Zhang, P. Lin, R. Stumpf, and M. Y. Chou, *Phys. Rev. B* **83**, 195419 (2011).
- 2. "Theoretical Study of the Vibrational Properties of NaAlH₄ with AlH₃ Vacancies," Feng Zhang, Yan Wang, and M. Y. Chou, *Faraday Discussion* **151**, 243-251 (2011).

Author Biography (Mei-Yin Chou)

Mei-Yin Chou obtained her Ph.D. in Theoretical Condensed Matter Physics from the University of California at Berkeley in 1986. After working for Exxon Research and Engineering Company in New Jersey as a postdoctoral fellow, she accepted an Assistant Professor position at Georgia Institute of Technology in 1989. She was promoted to Associate Professor in 1993 and to Professor in 1998. In addition, she was the ADVANCE Professor of Science at Georgia Tech in 2002-2006, and Chair of the School of Physics in 2005-2010. She became Director and a Distinguished Research Fellow of the Institute of Atomic and Molecular Sciences at Academia Sinica in January 2011, and an Adjunct



Professor at National Taiwan University in August 2011. Chou is an expert in computational materials physics with extensive experience in atomistic simulations of the structural and dynamical properties of solids, clusters, surfaces, and nanostructures. She served as Vice Chair (2006), Chair-Elect (2007), Chair (2008), and Past-Chair (2009) of the Division of Computational Physics in the American Physical Society.

Research Interests:

First-principles calculations aiming to provide unambiguous explanations for various interesting phenomena observed experimentally and to make reliable predictions of new material properties from microscopic quantum theories. The research topics have included the electronic and structural properties of solids, surfaces, interfaces, clusters, and hydrogen storage materials.

Honors:

Dr. Chou received the Alfred P. Sloan Research Fellowship in 1990-1992, the David and Lucile Packard Fellowship in 1990-1995; and the Presidential Young Investigator Award from National Science Foundation in 1991-1996. She also won the Sigma Xi Young Faculty Award at Georgia Institute of Technology in 1993 and was the ADVANCE Professor of Science from 2002 to 2006.

She was elected Fellow of the American Physical Society in 2002.

- "Lattice Vibrational Modes and their Frequency Shifts in Semiconductor Nanowires," L. Yang and M. Y. Chou, *Nano Lett.* **11**, 2618-2621 (2011).
- "Quantum Size Effects on the Work Function of Metallic Thin-Film Nanostructures," J. Kim, S. Qin, W. Yao, Q. Niu, M. Y. Chou, and C.-K. Shih, *Proc. Natl. Acad. Sci.* <u>79</u>, 12761-12765 (2010).
- "Effects of Metallic Contacts on Electron Transport through Graphene," S. Barraza-Lopez, M. Vanevic, M. Kindermann, and M. Y. Chou, *Phys. Rev. Lett.* **104**, 076807 (2010).
- "Structural and Electronic Properties of Oxidized Graphene," J.-A. Yan, L. Xian, and M. Y. Chou, *Phys. Rev. Lett.* 103, 086802 (2009).

Towards Catalysis by Gold Clusters: Allowed Reaction Cycles and Poisons

Luca M. Ghiringhelli

Fritz Haber Institute of the Max Planck Society, Berlin, Germany Theory Department

Email: ghiringhelli@fhi-berlin.mpg.de

Nanosized gold particles are good catalysts in a variety of oxidation reactions [1,2]. These reactions, for which oxidation of CO to CO₂ serves as a paradigm, imply a transition in the total spin and therefore do not occur spontaneously in the gas phase. In the catalytic process, the catalyst clusters are exposed to an atmosphere of gas-phase O_2 and CO reactants at finite temperature and pressure. We have thus modeled free gold clusters in contact with an atmosphere composed of O_2 and CO by means of DFT calculations (PBE functional), and accounted for both temperature and pressure effects employing *ab initio* atomistic thermodynamics [3]. On the basis of this analysis, we could recognize the thermodynamic driving force of the catalytic CO oxidation process and single out the possible (*p*,*T*)-dependent reaction cycles and those paths leading to stable structures that poison the catalytic process. This as a useful (exploratory) theoretical step, before taking chemical reaction kinetics into consideration. In the proposed reaction paths, the total spin is conserved in each elementary step, and it is the adsorption of an incoming O_2 molecule that drives the catalyst cluster from the singlet to the triplet spin state, and vice versa.

- 1. M. Haruta, T. Kobayashi, H. Sano, and N. Yamada, Chem. Lett. 2, 405 (1987).
- 2. A. S. K. Hashmi and G. J. Hutchings, Gold Catalysis, Angew. Chem. Int. Ed. 45, 7896 (2006).
- 3. E.C. Beret, L.M. Ghiringhelli, and M. Scheffler, *Free gold clusters: Beyond the static, mono-structure description.* Faraday Discuss. **152 (1)**, 153-167 (2011).

Author Biography (Luca M. Ghiringhelli)

Luca M. Ghiringhelli received his MS degree in Nuclear Engineering from the Politecnico of Milano (Italy) in 2000.

He obtained his PhD in Natural Sciences from the Van 't Hoff Institute, University of Amsterdam (The Netherlands), under the supervision of Evert Jan Meijer and Daan Frenkel. The thesis was on liquid-liquid phase transitions in covalent fluids.

From 2005 to 2008 he was at the Max Planck Institute for Polymers in Mainz (Germany) as a post-doc fellow, where he worked on adsorption of organi molecules on metal surfaces.

Since 2009 he has been at the Fritz Haber Institute in Berlin, where he became a project leader in 2011. In Berlin, partially funded by the "Unifying concepts in catalysis" (Unicat) initiative, he works on *ab initio* statistical mechanics of cluster catalysis and corrosion.



Research Interests:

- Finite temperature and pressure configurational sampling of transition metal nanoclusters and comparison with experiments via vibrational analysis
- Development of accelerated schemes for the efficient sampling of the configurational space of atomic clusters
- Finite temperature calculations of rates (e.g. for nucleation, chemical reactions)
- Kinetic energy functional for orbital-free DFT

Honors:

Alexander von Humboldt fellowship for the period November 2006 - April 2008.

- L. M. Ghiringhelli, J. H. Los, E. J. Meijer, A. Fasolino, and D. Frenkel, *Modelling the phase diagram of carbon*, Phys. Rev. Lett. 94, 145701 (2005).
- L. M. Ghiringhelli, C. Valeriani, E. J. Meijer, and D. Frenkel *Local structure of liquid carbon controls diamond nucleation*, Phys. Rev. Lett 99, 055702 (2007).
- L. M. Ghiringhelli and L. Delle Site, *Phenylalanine near Inorganic Surfaces: Conformational statistics vs specific chemistry*, J. Am. Chem. Soc 130, 2634 (2008).
- L. M. Ghiringhelli, I. P. Hamilton, and L. Delle Site *Interacting electrons, spin statistics, and information theory*, J. Chem. Phys. 123, 014106 (2010).

A systematic ab initio strategy for predicting structure-activity relationships in amorphous catalysts and supports

Bryan Goldsmith and Baron Peters

Department of Chemical Engineering, University of California Santa Barbara, USA

Email: <u>baronp@engineering.ucsb.edu</u>

Modeling isolated sites on amorphous catalyst supports remains a major challenge. Typical strategies use arbitrarily chosen constraints to model the rigid solid, or else they use no constraints which results in sites with unrealistic flexibility. We present a systematic ab initio method to model isolated sites on amorphous supports with small cluster models. To avoid arbitrary constraints while still retaining influences from the extended solid structure, we introduce a novel structural embedding scheme based on the reversible work theorem. A sequential quadratic programming framework then helps us test mechanistic hypotheses and relate chemical properties such as activation energy and Lewis acidity to active site structure. The algorithm is illustrated for an empirical valence bond model system. We then use the algorithm to model a key step for ethene metathesis by isolated molybdena on an amorphous silica support. As a second example, we model shifted hydrolysis on amorphous-silica alumina as studied previously by Chizallet and Raybaud.

Author Biography (Baron Peters)



BS: Chemical Engineering, University of Missouri - Columbia (1999)B.S. Mathematics, University of Missouri - Columbia (1999)PhD: Chemical Engineering, University of California - Berkeley (2004)

Research Interests:

The kinetics of nucleation, electron transfer, and catalytic reactions depend on the properties of short-lived and rarely-visited transition states that cannot be directly observed in experiments. We gain insight into the properties of transition states using molecular simulation and electronic structure theory. Examples include the effects of solution additives on nucleation rates for crystallization, the dominant electron transfer conduits in realistic fluctuating environments, and catalytic reaction mechanisms. When applications pose new challenges beyond the scope of available techniques, we develop theories and algorithms to address those challenges. In particular, we specialize in path sampling methods for free energies and reaction coordinate identification, metrics for reaction coordinate error, methods to obtain accurate rate constants, and multiscale simulation approaches.

Honors:

NSF graduate fellowship (2000)

Ab Initio Chemical Kinetics of Some Practically Important Processes Occurring in the Gaseous and Condensed Phases

M. C. Lin

Department of Applied Chemistry, National Chiao Tung University, Hsinchu, Taiwan and Department of Chemistry, Emory University, Atlanta, GA, USA

Email: chemmcl@emory.edu

Quantitative prediction of kinetics and mechanisms of chemical processes, including experimentally hard to measure product branching ratios, by ab initio quantum and statistical theory calculations can be routinely carried out since the past decade or so. In the past several years, we have investigated a variety of processes occurring in the gaseous (such as combustion and atmosphere reactions) and the condensed phases (such as sublimation of ammonium salts and the reduction of O_2 in SOFC and PEMFC).

In this presentation, some of the reaction systems studied at Emory University and National Chiao Tung University will be discussed.

- 1. R. S. Zhu and M. C. Lin, "Ab initio chemical kinetics for ClO reactions with HO_x, ClO_x, and NO_x (x=1,2): A review", *Comput. Theort. Chem.*, **965(2-3)**, 328-339 (2011).
- 2. R. S. Zhu and M. C. Lin, "The Mechanism and Kinetics for Ammonium Perchlorate Sublimation: A First-Principles Study", *Journal of Physical Chemistry C*, **112(37)**, 14481-14485 (2008).
- 3. Zhe Cheng, Jeng-Han Wang, YongMan Choi, Lei Yang, M. C. Lin and Meilin Liu, "From Ni-YSZ to Sulfur-Tolerant Anode Materials for SOFCs: Electrochemical Behavior, in situ Characterization, Modeling, and Future Perspectives", *Energy and Eviron. Sci.*, **4**, 4380-4409 (2011).

Author Biography (M. C. Lin)

2005/8~ R. W. Woodruff Prof., Emeritus, Emory Univ., USA
2005/6~ NSC Distinguished Visiting Prof., Nat'l Chiao Tung Univ.
2004/2~ Chair Professor, Nat'l Chiao Tung University
2003/7~ Director of CIMS, Nat'l Chiao Tung University
2005-2011 TSMC Distinguished Prof., Nat'l Chiao Tung Univ.
1988-2005 Robert W. Woodruff Professor, Emory University
1982-1988 Senior Scientist for Chemical Kinetics, NRL, USA
1981-1988 Adjunct Prof. of Chem., The Catholic Univ. of America
1974-1982 Supervisory Research Chemist; Head, NRL, USA
1970-1974 Research Chemist, Naval Research Laboratory, USA
1965-1967 Postdoctoral Research Associate, Cornell University, USA
1962-1965 Ph.D., University of Ottawa, Canada
1955-1959 B.Sc., Taiwan Normal University



Research Interests:

We employ state-of-the-art experimental and computational techniques to investigate a new generation of quantum dot and nanoparitcle films for solar energy conversion by photovoltaic and photo-electrochemical water splitting for hydrogen generation, ethanol to hydrogen conversion by heterogeneous catalysis, and chemical kinetic studies of atmospheric chemistry and hydrocarbon and propellant combustion processes.

Honors:

Fellow of the Royal Society of Chemistry, UK (2009), Captain Robert Dexter Conrad Award for Scientific Achievement of U.S. Navy (1998), JSPS Fellow of Japan Society for the Promotion of Science (1991), Taiwanese-American Foundation Prize for Science and Technology of Taiwanese-American Foundation (1989), Alexander von Humboldt Award of A. von Humboldt Foundation, Germany (1982), Guggenheim Fellow of John Simon Guggenheim Foundation (1982), Navy Meritorious Civilian Service Award of U.S. Navy (1979), Pure Science Award of Sigma Xi, NRL Chapter (1978), Physical Sciences Award and Fellow of the Washington Academy of Sciences, USA (1976) and Hillebrand Prize of Chemical Society of Washington (1975).

- "Ab initio chemical kinetics for ClO reactions with HOx, ClOx, and NOx (x=1,2): A review", R. S. Zhu and M. C. Lin, *Comput. Theort. Chem.*, **965(2-3)**, 328-339 (2011).
- "The Mechanism and Kinetics for Ammonium Perchlorate Sublimation: A First-Principles Study", R. S. Zhu and M. C. Lin, *Journal of Physical Chemistry C*, **112(37)**, 14481-14485 (2008).
- "From Ni-YSZ to Sulfur-Tolerant Anode Materials for SOFCs: Electrochemical Behavior, in situ Characterization, Modeling, and Future Perspectives", Zhe Cheng, Jeng-Han Wang, YongMan Choi, Lei Yang, M. C. Lin and Meilin Liu, Energy and Eviron. Sci., 4, 4380-4409 (2011).
- "Roaming-mediated isomerization in the photodissociation of nitrobenzene", Michael L. Hause, Nuradhika Herath, Rongshun Zhu, M. C. Lin and Arthur G. Suits, *Nature Chemistry*, **3**, 932–937 (2011).

Correlated wave function methods studies of metal clusters and complexes

Ricardo Mata

Institute of Physical Chemistry, University of Göttingen, Göttingen, Germany

Email: <u>rmata@gwdg.de</u>

Metals are ubiquitous in the context of catalysis, may this be in the form of a metal complex inside an enzyme pocket or a complete surface, adsorbing reactants and facilitating reaction pathways. The idea of in silico quantitative predictions for such systems is certainly tempting, but faces several challenges. On one hand, high accuracy is warranted in the theoretical predictions. An error of only a few kJ/mol can be enough to tip the balance in favor of the wrong structural isomer or reaction mechanism. On the other hand, it is difficult to create reduced models for such systems. A metallic cluster has completely different properties from an extended metal surface. Likewise, enzymatic activity is controlled not only by the active center, but also by the neighboring residues.

In this talk, the use of hybrid local correlation methods for the treatment of metal clusters and complexes will be discussed. The idea behind the method is to apply different levels of theory to different regions of the system, thereby focusing the theoretical description on the chemical process at hand. Examples are given for the calculation of adsorption processes at surfaces and enzymatic catalysis. Furthermore, the use of general gaussian force fields for the description of metal-metal interactions will be discussed. The latter allow for the mapping of theoretical results to an analytical cheap potential which can then be used to extensively explore the energy landscape of metal clusters.

References:

- 1. R. A. Mata, H.-J. Werner, and M. Schütz, J. Chem. Phys. 128, 144106 (2008).
- 2. J. M. Dieterich, H.-J. Werner, R. A. Mata, S. Metz, and W. Thiel, J. Chem. Phys. 132, 035101 (2010).
- 3. U. Ryde, R. A. Mata, and S. Grimme, Dalton Trans. 40, 11176-11183 (2011).

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Author Biography (Ricardo Mata)

Ricardo Mata graduated in Chemistry at the University of Lisbon in 2003. Later that year, he moved to the Institute of Theoretical Chemistry at the University of Stuttgart where he carried out his PhD studies. He received his degree in 2007. Soon afterwards, he was awarded a postdoctoral fellowship and returned to the University of Lisbon as a member of the Group of Mathematical Physics. In Fall 2009, he was appointed Junior Professor and leader of the Free-Floater Junior Research Group "Computational Chemistry and Biochemistry" at the University of Göttingen. His current work focuses on wave function



studies of general reactivity and electronic properties of molecules, from model peptides to bioinorganic complexes.

Research Interests:

- Local and incremental correlation methods for the theoretical description of weak molecular interactions and electronic excitation spectra.
- Application of hybrid quantum mechanical/molecular mechanics methods to enzymatic reactivity.
- Theoretical treatment of solvent-specific effects.

- "High-accuracy computation of reaction barriers in enzymes", F. Claeyssens, J. N. Harvey, F. R. Manby, R. A. Mata, A. J. Mulholland, K. E. Ranaghan, M. Schütz, S. Thiel, W. Thiel, and H.-J. Werner, Angew. Chem. Int. Ed. 45, 6856 (2006).
- "Correlation regions within a localized molecular orbital approach", R. A. Mata, M. Schütz, and H.-J. Werner, J. Chem. Phys. 128, 144106 (2008).
- "Assessing the accuracy of many-body expansions for the computation of solvatochromic shifts", R. A. Mata, Mol. Phys. 108, 381 (2010).
- "An incremental correlation approach to excited state energies based on natural transition/localized orbitals", R. A. Mata, and H. Stoll, J. Chem. Phys. 134, 034122 (2011).

Material Simulations Using Quantum Monte Carlo

Ching-Ming Wei

Institute of Atomic and Molecular Sciences, Academia Sinica, 106 Taipei, Taiwan

Email: cmw@phys.sinica.edu.tw

Density functional theory (DFT) is one of the most commonly used theoretical methods for real material simulations. However, DFT results might actually depend on the choice of approximate exchange-correlation (XC) functionals, casting doubt on the reliability of the DFT methods, and thus the correctness of DFT needs to be checked systematically by highly accurate theoretical methods. Since Quantum Monte Carlo (QMC) [1] methods can treat electron-electron exchange-correlation effects correctly, it can be used to examine the accuracy of various XC functionals such as LDA, GGA, and hybrid functionals. In this talk, I will present the QMC results in the study of surface energy and surface adsorption. For surface energy, the systems studied include NaCl(100), MgO(100), CaO(100), TiO₂(110), Si(100)-(2x2), C(100)-(2x2), and Ge(100)-(2x2) surfaces. Our results indicate that (i) the surface energy by QMC is always larger than the surface energy by LDA; and (ii) the surface energy by LDA is always larger than the surface energy by GGA. For NaCl(100) and MgO(100) surface, QMC results reproduce the experimental measured surface energies within a few percentages. By comparing the surface energies obtained from DFT and DMC, the results predicted by DFT using either LDA or GGA functional are underestimated. For surface adsorptions, the systems examined include H₂O and OH adsorptions on various types of surfaces such as NaCl(100), MgO(100), TiO₂(110), graphene, Si(100), and Al(100). By comparing GGA (PBE) results with QMC, our results indicate that (i) for the H₂O adsorption, PBE predicts the correct adsorption energies; (ii) for the OH adsorption, PBE has predicted a large over-binding effect except on graphene and Si(100) surfaces. These QMC results strongly suggest that one needs to be very cautious when using DFT to study the surface adsorptions of OH free radical.

References:

1. W. M. C. Foulkes, L. Mitás, R.J. Needs and G. Rajagopal, Rev. Mod. Phys. 73, 33 (2001).

Author Biography (Ching-Ming Wei)

Ching-Ming Wei received his BS and MS degrees from Dept. of Physics, NTU in 1982 and 1984. He obtained his Ph.D degree from Dept. of Physics, Univ. of Wiscionsin at Milwaukee in 1990. After one year teaching in Tamkang University, he joined Institue of Physics, Academia Sinica, Taiwan in 1991 and worked on the development of theoretical surface structural tools by direct inversion of diffraction patterns. In 1996, he began to use DFT to tackle the subjects related surface structure and diffusing, surface magic cluster, and quantum size effect of metal thin



films. In 2004, he moved into Institute of Atomic and Molecular Sciences, Academia Sinica. In 2006, he began to use and develop Quantum Monte Carlo studies in real material simulations.

Research Interests:

- Surface Magic Clusters
- Quantum Size Effects in metal thin films
- Material Simulations using Quantum Monte Carlo

Honors:

Dr. Wei received Academia Sinica Young Scholar Research Award in 1996, NSC Outstanding Research Award in 1994, 1999, and 2004, and Achievement in Asia Award of Oversea Chinese Physics Association in 1996. He was elected as the Fellow of Taiwan (ROC) Physical Society in 1997 and the fellow of American Physical Society in Nov. 2011.

- *"Theory of quantum size effects in thin Pb(111) films"*, <u>C.M. Wei</u> and M. Y. Chou, Phys. Rev. B 66, 233408 (2002).
- *"Magic Numbers of Atoms in Surface-Supported Planar Clusters"*, Y.-P. Chiu, L.-W. Huang, <u>C.M. Wei</u>, C. S. Chang, and Tien T. Tsong, Phys. Rev. Lett. 97, 165504 (2006).
- "Quantum Monte Carlo Calculation of Clusters: Accuracy of Density Functional Approximation", C. R. Hsing, <u>C.M. Wei</u>, N. D. Drummond, and R. J. Needs, Phys. Rev. B79 (24), 245401(2009).
- "Broken Even-Odd Symmetry in Self-Selection of Distances between Nanoclusters due to the Presence or Absence of Topological Solitons", M. Y. Lai, J. P. Chou, O. A. Utas, N. V. Denisov, V. G. Kotlyar, D. Gruznev, A. Matetsky, A. V. Zotov, A. A. Saranin, <u>C. M. Wei</u>, and Y. L. Wang, Phys. Rev. Lett. 106, 166101 (2011).

IAMS, Academia Sinica P.O. Box 23-166, Taipei, Taiwan Tel: 886-2-2362-0212 Fax: 886-2-2362-0200 http://sew2011.iams.sinica.edu.tw