REPORT DOCUMENTATION PAGE

Form Approved OMB NO. 0704-0188

1. REPORT DATE (DD-MM-YYYY) 15-10-2018	2. REPORT TYPE Final Report	3. DATES COVERED (From - To) 15-Aug-2011 - 14-Aug-2016

4. TITLE AND SUBTITLE
Final Report: Stress-Controlled Catalysis via Engineering Nanostructures

5a. CONTRACT NUMBER
W911NF-11-1-0353

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
611103

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

6. AUTHORS

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES
Brown University
Office of Sponsored Projects
Box 1929
Providence, RI 02912 -9093

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES)
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSOR/MONITOR'S ACRONYM(S)
ARO

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
59724-MS-MUR.43

12. DISTRIBUTION AVAILIBILITY STATEMENT
Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Pradeep Guduru
UU	UU	UU	UU		19b. TELEPHONE NUMBER 401-863-3362

RPPR Final Report
as of 17-Aug-2020

Agency Code:

Proposal Number: 59724MSMUR **Agreement Number: W911NF-11-1-0353**
INVESTIGATOR(S):

Name: Pradeep R Guduru
Email: pradeep_guduru@brown.edu
Phone Number: 4018633362
Principal: Y

Organization: **Brown University**
Address: Office of Sponsored Projects, Providence, RI 029129093
Country: USA
DUNS Number: 001785542 EIN: 050258809
Report Date: 13-Mar-2015 Date Received: 15-Oct-2018
Final Report for Period Beginning 15-Aug-2011 and Ending 14-Aug-2016
Title: Stress-Controlled Catalysis via Engineering Nanostructures
Begin Performance Period: 15-Aug-2011 **End Performance Period:** 14-Aug-2017
Report Term: 0-Other
Submitted By: Pradeep Guduru Email: pradeep_guduru@brown.edu
Phone: (401) 863-3362
Distribution Statement: 1-Approved for public release; distribution is unlimited.

STEM Degrees: 0 **STEM Participants:** 3

Major Goals: Major Goals
The need to control – either enhancing or retarding - chemical reactions is ubiquitous across a range of technologies, including chemical synthesis via catalysis, chemical sensing via adsorption and reaction, chemical embrittlement in structural materials, and microstructure and precipitate evolution in structural materials. It is commonly thought that mechanical energies cannot compete with chemical energies, so that “Chemistry” and “Mechanics” have little overlap. Roughly, chemical energies are on the order of eV while the mechanical energies are on the order of meV, as loosely estimated by where p is typical mechanical load (~100 MPa) and a typical misfit volume (~ few A3) for a “reaction” process. However, mechanical energy can be harvested from a large volume by relaxing elastic strains or, equivalently, be concentrated near a defect such as a crack tip or dislocation, generating stresses approaching the theoretical material strengths (~10 GPa) and thus provide energies that can alter chemical reactions. More subtly but of equal importance is the fact that mechanical energy can tip the energy landscape to drive reactions or diffusive processes preferentially in one “direction”. The role of stress or strain in influencing reactions appears across a broad range of materials applications such as strained-layer superlattice, self-organization of quantum dot structures in Si-Ge, dynamic strain aging in Al-Mg alloys, and stress corrosion cracking. The role of stress in modifying reactions, broadly construed, is thus well-founded within materials science.
Why is gaining active control over catalytic reactions so important? The application of stress can both tune and modulate reactions, and therefore may overcome the barrier implied in “Sabatier’s Principle” that is manifested in the “Volcano Effect”, two widely held concepts in catalysis. Further, self-equilibrating mismatch strains, arising in core/shell systems or epitaxial monolayers, are subject to relaxation over long times and elevated temperatures, moving an initially optimal system (achieved by some combination of alloying and applied stress, for instance) away from optimality. An externally applied stress can correct for slow changes in the catalyst due to structural relaxation. Such corrections can be accomplished on-the-fly: by measuring the variation of catalytic production rate as a function of small stress variations, the average stress can continually be adjusted to maximize the production rate. All of the above issues further suggest that, with stress as an external driving variable, entirely new materials with greatly enhanced performance and reduced cost are possible, changing the landscape of catalyst design.

With the above background, the major objectives of the MURI effort are:

(i) Develop a scientific basis for controlling chemical reactions using externally applied stress with particular application to catalytic processes.
(ii) Demonstrate the scientific underpinnings of stress controlled catalysis in model experiments (e.g. thin films, nano-pillars) for select reactions of scientific and technological interest (e.g. oxygen reduction reaction, hydrogen

evolution reaction, methanation of carbon monoxide).
(iii) Develop novel multiscale simulation methods that bridge the length scales between the density functional theory and practically used nano-particle catalysts.
(iv) The main outcome of the project is unambiguous demonstration that stress can be used to substantially modify and control chemical reactions, along with possible engineering paths, via both thin film and bulk metallic glass nanostructures, for implementing stress control across a wide material space.

Accomplishments: See Final Report Upload

Training Opportunities: Nothing to Report

Results Dissemination: See Products

Honors and Awards: Shouheng Sun (faculty):
Vernon K. Krieble Professor of Chemistry, Brown University (2016)
Highly Cited Researchers in Chemistry and Materials Science, Thomson Reuters (2015)
Fellow, the Royal Society of Chemistry (2015)
Highly Cited Researchers in Chemistry and Materials Science, Thomson Reuters (2014)
The International Precious Metals Institute (IPMI) Faculty Advisor Award (2013)

Shaojun Guo (Postdoc):
J. Robert Oppenheimer Distinguished Postdoctoral Fellow, LANL (2015)

Huiyuan Zhu (graduate student):
Liane Russell Fellow, Oak Ridge National Lab (2014)
Chinese Government Award for Outstanding Students Abroad (2014)

Xu Zhang (graduate student):
Best Presentation Award, MRS Fall Meeting 2015.

M.F.Francis (Postdoc):
Currently Director's Fellow post-doc at Los Alamos National Laboratory

Sharvan Kumar (Faculty):
Alexander von Humboldt Research Prize, Germany 2015.

Protocol Activity Status:

Technology Transfer: Patents Filed:

“Co/CoO Nanoparticles on Graphene, Method of Manufacture and Use” S.Sun, S. Guo, S. Zhang, L. Wu, pending.

“Multimetallic nanoparticle catalysts with enhanced electrooxidation”, S.Sun, S. Zhang, S. Guo, and H. Zhu, US Patent 9093715.

PARTICIPANTS:

Participant Type: PD/PI
Participant: Pradeep Guduru
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Co-Investigator

Participant: Shouheng Sun
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Benjamin Johnson
Person Months Worked: 12.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Alireza Khorsidi
Person Months Worked: 10.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Zheng Xi
Person Months Worked: 6.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)
Participant: Kai Yan
Person Months Worked: 10.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)
Participant: Yiyi Yan
Person Months Worked: 12.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

ARTICLES:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Applied Physics Letters
Publication Identifier Type: DOI Publication Identifier: 10.1063/1.3695332
Volume: 100 Issue: 11 First Page #: 0
Date Submitted: Date Published:
Publication Location:
Article Title: Misfit dislocations in multimetallic core-shelled nanoparticles
Authors:
Keywords: catalysis, dislocations, gold, iron alloys, lattice constants, metallic thin films, nanoparticles, platinum alloys
Abstract: Core-shelled multimetallic nanoparticles have unique catalytic properties compared to their single-element counterparts. Due to the different lattice parameters of the core and shell, the strain field is built up at the interface between the two phases. As for thin films, a formation of misfit and threading dislocations is an approach to release interface strain. However, for two-phase nanoparticles especially when their sizes are at nanometer scale, their dislocation formation in the volume remains to be investigated owing to the large surface-to-volume ratio. Here, we confirmed the existence of dislocations in the Au-FePt core-shelled nanoparticles of sizes less than 10?nm. It is suggested that the different atom sizes of the core and the shell materials are likely to be a key factor to generate and lock dislocations inside the nanoparticles.
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Journal of the American Chemical Society
Publication Identifier Type: DOI Publication Identifier: 10.1021/ja406091p
Volume: 135 Issue: 37 First Page #: 13879
Date Submitted: Date Published:
Publication Location:
Article Title: Seed-Mediated Synthesis of Core/Shell FePtM/FePt (M = Pd, Au) Nanowires and Their Electrocatalysis for Oxygen Reduction Reaction
Authors:
Keywords: Electrochemical, Radiational, and Thermal Energy Technology
Abstract: We report a new seed-mediated growth of FePt over 2.5 nm wide FePtM (M = Pd, Au) nanowires (NWs) into core/shell FePtM/FePt NWs with controlled FePt shell thickness from 0.3 to 1.3 nm. These FePtM/FePt NWs show shell thickness and core composition-dependent electrocatalytic activity for oxygen reduction reaction (ORR) in 0.1 M HClO4. These core/shell FePtM/FePt NWs are generally more active and durable than the corresponding alloy NWs. Among FePtM/FePt NWs, FePt NWs, FePtPd NWs, and commercial Pt studied, the FePtPd/FePt NWs (0.8 nm shell) show the specific activity of 3.47 mA·cm–2 and the mass activity of 1.68 A/mg Pt at 0.5 V (vs. Ag/AgCl), superior to all other NWs (less than 1.59 mA/cm2 and 0.82 A/mg Pt for FePtAu/FePt and FePt) as well as the commercial Pt (0.24 mA/cm2 and 0.141 A/mg Pt). The FePtM/FePt (0.8 nm shell) NWs are also stable in the ORR condition and show no activity decrease after 5000 potential sweeps between 0.4 and 0.8 V (vs Ag/AgCl). They are the most efficient na
Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors
Acknowledged Federal Support:

RPPR Final Report
as of 17-Aug-2020

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Physical Review B
Publication Identifier Type: DOI Publication Identifier: 10.1103/PhysRevB.87.054113
Volume: 87 Issue: 5 First Page #: 54113
Date Submitted: Date Published:
Publication Location:
Article Title: Multiscale quantum/atomistic coupling using constrained density functional theory
Authors:
Keywords: atomistic coupling
Abstract: Multiscale coupling of a quantum mechanical (QM) domain to a coarser-scale material description in a larger surrounding domain should yield forces and energies in the QM domain that are the same as would be achieved in a QM simulation of the entire system. Here, such a coupling is achieved by using constrained density functional theory (DFT) in which the quantum mechanical interaction between the domains is captured via a constraint potential arising from an imposed constraint on the charge density in a boundary region between the two domains. The implementation of the method, including the construction of the constraint charge density and the calculation of the constraint potential, is presented. The method is applied to problems in three different metals (Al, Fe, and Pd) and is validated against periodic DFT calculations. The method reproduces the QM charge density and magnetic moments of bulk materials, produces a reasonable edge dislocation core structure for Fe, and also gives acc
Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors
Acknowledged Federal Support:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Nano Letters
Publication Identifier Type: DOI Publication Identifier: 10.1021/nl401325u
Volume: 13 Issue: 6 First Page #: 2947
Date Submitted: Date Published:
Publication Location:
Article Title: Monodisperse MxFe3-xO4 (M=Fe, Cu, Co, Mn) Nanoparticles and Their Electrocatalysis for Oxygen Reduction Reaction
Authors:
Keywords: Ferrite nanoparticles; solution phase synthesis; electrocatalysis; oxygen reduction reaction
Abstract: Sub-10 nm nanoparticles (NPs) of M(II)-substituted magnetite MxFe3–xO4 (MxFe1–xO•Fe2O3) (M = Mn, Fe, Co, Cu) were synthesized and studied as electrocatalysts for oxygen reduction reaction (ORR) in 0.1 M KOH solution. Loaded on commercial carbon support, these MxFe3–xO4 NPs showed the M(II)-dependent ORR catalytic activities with MnxFe3–xO4 being the most active followed by CoxFe3–xO4, CuxFe3–xO4, and Fe3O4. The ORR activity of the MnxFe3–xO4 was further tuned by controlling x and MnFe2O4 NPs were found to be as efficient as the commercial Pt in catalyzing ORR. The MnFe2O4 NPs represent a new class of highly efficient non-Pt catalyst for ORR in alkaline media.
Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors
Acknowledged Federal Support:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Journal of the American Chemical Society
Publication Identifier Type: DOI Publication Identifier: 10.1021/ja403041g
Volume: 135 Issue: 19 First Page #: 7130
Date Submitted: Date Published:
Publication Location:
Article Title: Synthetic Control of FePtM Nanorods (M = Cu, Ni) To Enhance the Oxygen Reduction Reaction
Authors:
Keywords: None Noted
Abstract: To further enhance the catalytic activity and durability of nanocatalysts for the oxygen reduction reaction (ORR), we synthesized a new class of 20 nm × 2 nm ternary alloy FePtM (M = Cu, Ni) nanorods (NRs) with controlled compositions. Supported on carbon support and treated with acetic acid as well as electrochemical etching, these FePtM NRs were converted into core/shell FePtM/Pt NRs. These core/shell NRs, especially FePtCu/Pt NRs, exhibited much improved ORR activity and durability. The Fe10Pt75Cu15 NRs showed a mass current densities of 1.034 A/mgPt at 512 mV vs Ag/AgCl and 0.222 A/mgPt at 557 mV vs Ag/AgCl, which are much higher than those for a commercial Pt catalyst (0.138 and 0.035 A/mgPt, respectively). Our controlled synthesis provides a general approach to core/shell NRs with enhanced catalysis for the ORR or other chemical reactions.
Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors
Acknowledged Federal Support:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Angewandte Chemie
Publication Identifier Type: DOI Publication Identifier: 10.1002/ange.201300276
Volume: 125 Issue: 13 First Page #: 3769
Date Submitted: Date Published:
Publication Location:
Article Title: Monodisperse AgPd Alloy Nanoparticles and Their Superior Catalysis for the Dehydrogenation of Formic Acid
Authors:
Keywords: alloys · heterogeneous catalysis · hydrogen storage ·nanoparticles
Abstract: Formic acid (FA, HCOOH) is a common small organic acid with a melting point of 8.4 8C and boiling point of 100.8 8C. It can undergo a dehydrogenation reaction, HCOOH!H2+ CO2, releasing H2 that will be important for hydrogen-based energy applications.[1] Traditionally, the dehydrogenation of FA is catalyzed by metal complexes dissolved in an organic solvent and the catalysis is enhanced by adding an additive, such as sodium formate or amine adducts.[2] To make more practical catalyst for the dehydrogenation reaction of FA, heterogeneous catalysts based on metal nanoparticles (NPs) have been developed. These catalysts are generally more stable but much less active than the homogeneous ones.[3] Recently, bimetallic NP catalysts were found to be more active than their single component counterparts for the dehydrogenation of FA.[4] For example, AgPd NPs supported on cerium oxide or AuPd NPs immobilized in a metal–organic framework showed an enhanced FA dehydrogenation catalysis with the ini
Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors
Acknowledged Federal Support:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Angewandte Chemie International Edition
Publication Identifier Type: DOI Publication Identifier: 10.1002/anie.201207186
Volume: 52 Issue: 33 First Page #: 8526
Date Submitted: Date Published:
Publication Location:
Article Title: Tuning Nanoparticle Catalysis for the Oxygen Reduction Reaction
Authors:
Keywords: alloys;core–shell nanoparticles;fuel cells;oxygen reduction reaction;platinum
Abstract: Advances in chemical syntheses have led to the formation of various kinds of nanoparticles (NPs) with more rational control of size, shape, composition, structure and catalysis. This review highlights recent efforts in the development of Pt and non-Pt based NPs into advanced nanocatalysts for efficient oxygen reduction reaction (ORR) under fuel-cell reaction conditions. It first outlines the shape controlled synthesis of Pt NPs and their shape-dependent ORR. Then it summarizes the studies of alloy and core–shell NPs with controlled electronic (alloying) and strain (geometric) effects for tuning ORR catalysis. It further provides a brief overview of ORR catalytic enhancement with Pt-based NPs supported on graphene and coated with an ionic liquid. The review finally introduces some non-Pt NPs as a new generation of catalysts for ORR. The reported new syntheses with NP parameter-tuning capability should pave the way for future development of highly efficient catalysts for applications in
Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors
Acknowledged Federal Support:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Nano Research
Publication Identifier Type: DOI Publication Identifier: 10.1007/s12274-012-0276-4
Volume: 6 Issue: 1 First Page #: 10
Date Submitted: Date Published:
Publication Location:
Article Title: Ni/Pd core/shell nanoparticles supported on graphene as a highly active and reusable catalyst for Suzuki-Miyaura cross-coupling reaction
Authors:
Keywords: nickel,palladium,core/shell nanoparticles,catalysis,Suzuki–Miyaura crosscoupling
Abstract: Monodisperse Ni/Pd core/shell nanoparticles (NPs) have been synthesized by sequential reduction of nickel(II) acetate and palladium(II) bromide in oleylamine (OAm) and trioctylphosphine (TOP). The Ni/Pd NPs have a narrow size distribution with a mean particle size of 10 nm and a standard deviation of 5% with respect to the particle diameter. Mechanistic studies showed that the presence of TOP was essential to control the reductive decomposition of Ni–TOP and Pd–TOP, and the formation of Ni/Pd core/shell NPs. Using the current synthetic protocol, the composition of the Ni/Pd within the core/shell structure can be readily tuned by simply controlling the initial molar ratio of the Ni and Pd salts. The as-synthesized Ni/Pd core/shell NPs were supported on graphene (G) and used as catalyst in Suzuki–Miyaura cross-coupling reactions. Among three different kinds of Ni/Pd NPs tested, the Ni/Pd (Ni/Pd = 3/2) NPs were found to be the most active catalyst for the Suzuki–Miyaura cross-coupling of
Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors
Acknowledged Federal Support:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Nanoscale
Publication Identifier Type: DOI Publication Identifier: 10.1039/c2nr33637e
Volume: 5 Issue: 3 First Page #: 910
Date Submitted: Date Published:
Publication Location:
Article Title: Monodisperse gold–palladium alloy nanoparticles and their composition-controlled catalysis in formic acid dehydrogenation under mild conditions
Authors:
Keywords: None Noted
Abstract: Monodisperse 4 nm AuPd alloy nanoparticles with controlled composition were synthesized by co-reduction of hydrogen tetrachloroaurate(III) hydrate and palladium(II) acetylacetonate with a borane-morpholine complex in oleylamine. These NPs showed high activity (TOF = 230 h(-1)) and stability in catalyzing formic acid dehydrogenation and hydrogen production in water at 50 °C without any additives.
Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors
Acknowledged Federal Support:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: The Journal of Physical Chemistry C
Publication Identifier Type: DOI Publication Identifier: 10.1021/jp4121035
Volume: 118 Issue: 8 First Page #: 0
Date Submitted: Date Published:
Publication Location:
Article Title: Understanding Strain and Ligand Effects in Hydrogen Evolution over Pd(111) Surfaces
Authors:
Keywords: OXYGEN REDUCTION REACTION; CORE-SHELL NANOPARTICLES; CATALYTIC-ACTIVITY; BIMETALLIC SYSTEMS; METAL-SURFACES; ELECTRONIC-STRUCTURE; CHEMICAL-PROPERTIES; REACTION-RATES; FORMIC-ACID; ADSORPTION
Abstract: Pseudomorphic catalytic systems can exhibit enhanced or inhibited activity relative to the pure surface parent metal, based on a combination of strain and ligand effects. In contrast, mechanically strained and dealloyed systems can exhibit pure strain effects. Density functional calculations for hydrogen adsorption at different coverages between 0.25 and 1 monolayer on biaxially strained Pd(111) are carried out to illustrate its comparison to selected pseudomorphic Pd overlayers (Pd/M). The differing catalytic behavior for the hydrogen evolution reaction (HER) in separation of the ligand and strain effects present in Pd/M pseudomorphs and the consequent modification of the binding strengths caused by them individually are estimated. The strain exhibits a systematic contribution to binding energy changes while the ligand effect can act to either intensify or weaken the strain effect. In certain systems (e.g., Pd/Ir) the ligand effect is more pronounced than the strain. effect while in o
Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors
Acknowledged Federal Support:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: ACS Catalysis
Publication Identifier Type: DOI Publication Identifier: 10.1021/cs500167k
Volume: 4 Issue: 6 First Page #: 0
Date Submitted: Date Published:
Publication Location:
Article Title: Tandem Dehydrogenation of Ammonia Borane and Hydrogenation of Nitro/Nitrile Compounds Catalyzed by Graphene-Supported NiPd Alloy Nanoparticles
Authors:
Keywords: PALLADIUM NANOPARTICLES; CHEMOSELECTIVE HYDROGENATION; HYDROLYTIC DEHYDROGENATION; GOLD NANOPARTICLES; CARBONYL-COMPOUNDS; LATTICE MISMATCH; FACILE REDUCTION; MOLECULAR-SIEVES; NITROARENES; NITRO
Abstract: We report a facile synthesis of monodisperse NiPd alloy nanoparticles (NPs) and their assembly on graphene (G) to catalyze the tandem dehydrogenation of ammonia borane (AB) and hydrogenation of R-NO2 and/or R-CN to R-NH2 in aqueous methanol solutions at room temperature. The 3.4 nm NiPd alloy NPs were prepared by coreduction of nickel(II) acetate and palladium(H) acetlyacetonate by borane-tert-butylamine in oleylamine and deposition on G via a solution phase self-assembly process. G-NiPd showed composition-dependent catalysis on the tandem reaction with G-Ni30Pd70 being the most active. A variety of R-NO2 and/or R-CN derivatives were reduced selectively into R-NH2 via G-Ni30Pd70 catalyzed tandem reaction in 5-30 mm reaction time with the conversion yields reaching up to 100%. Our study demonstrates a new approach to G-NiPd-catalyzed dehydrogenation of AB and hydrogenation of R-NO2 and R-CN. The G-NiPd NP catalyst is efficient and reusable, and the reaction can be performed in an enviro
Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors
Acknowledged Federal Support:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Nanoscale
Publication Identifier Type: DOI Publication Identifier: 10.1039/c4nr01107d
Volume: 6 Issue: 12 First Page #: 0
Date Submitted: Date Published:
Publication Location:
Article Title: A facile route to monodisperse MPd (M = Co or Cu) alloy nanoparticles and their catalysis for electrooxidation of formic acid
Authors:
Keywords: PD NANOPARTICLES; PALLADIUM NANOPARTICLES; CARBON NANOTUBES; AMMONIA BORANE; ELECTROCATALYTIC ACTIVITIES; OXIDATION; DEHYDROGENATION; REDUCTION; EFFICIENT; GRAPHENE
Abstract: MPd (M = Co, or Cu) nanoparticles (NPs) were synthesized by borane-amine reduction of metal acetylacetonates. The size of the MPd NPs was controlled at 3.5 nm and their compositions were tuned by the molar ratios of the metal precursors. These MPd NPs were active catalysts for electrochemical oxidation of formic acid and the Cu30Pd70 NPs showed the highest mass activity at 1192.9 A g(Pd)(-1), much higher than 552.6 A g (Pd)(-1) obtained from the 3.5 nm Pd NPs. Our synthesis provides a facile route to MPd NPs, allowing further investigation of MPd NP catalysts for electrochemical oxidation and many other chemical reactions.
Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors
Acknowledged Federal Support:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Journal of the American Chemical Society
Publication Identifier Type: DOI Publication Identifier: 10.1021/ja500590n
Volume: 136 Issue: 15 First Page #: 0
Date Submitted: Date Published:
Publication Location:
Article Title: Core/Shell Au/CuPt Nanoparticles and Their Dual Electrocatalysis for Both Reduction and Oxidation Reactions
Authors:
Keywords: SHAPE-CONTROLLED SYNTHESIS; OXYGEN-REDUCTION; PLATINUM; CATALYSTS; NANOCRYSTALS; MONODISPERSE; METHANOL; SHELL; FUEL; ENHANCEMENT
Abstract: We report a facile synthesis of monodisperse core/shell 5/1.5 nm Au/CuPt nanoparticles by coreduction of platinum acetylacetonate and copper acetylacetonate in the presence of 5 nm Au nanoparticles. The CuPt alloy effect and core/shell interactions make these Au/CuPt nanoparticles a promising catalyst for both oxygen reduction reaction and methanol oxidation reaction in 0.1 M HClO4 solution. Their specific (mass) reduction and oxidation activities reach 2.72 mA/cm(2) (1500 mA/mg (pt)) at 0.9 V and 0.755 mA/cm(2) (441 mA/mg (pt)) at 0.8 V (vs reversible hydrogen electrode), respectively. Our studies show that the existence of the Au nanoparticle core not only minimizes the Pt usage but also improves the stability of the Au/CuPt catalyst for fuel cell reactions. The results suggest that the core/shell design is indeed effective for optimizing nanoparticle catalysis. The same concept may be extended to other multimetallic nanoparticle systems, making it possible to tune nanoparticle catal
Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors
Acknowledged Federal Support:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Journal of the American Chemical Society
Publication Identifier Type: DOI Publication Identifier: 10.1021/ja5030172
Volume: 136 Issue: 21 First Page #: 0
Date Submitted: Date Published:
Publication Location:
Article Title: Tuning Nanoparticle Structure and Surface Strain for Catalysis Optimization
Authors:
Keywords: OXYGEN REDUCTION REACTION; ALLOY NANOPARTICLES; MAGNETIC-PROPERTIES; FEPT NANOPARTICLES; FORMIC-ACID; ELECTROCATALYSTS; CORE; PD; CU; ELECTROOXIDATION
Abstract: Controlling nanoparticle (NP) surface strain, i.e. compression (or stretch) of surface atoms, is an important approach to tune NP surface chemistry and to optimize NP catalysis for chemical reactions. Here we show that surface Pt strain in the core/shell FePt/Pt NPs with Pt in three atomic layers can be rationally tuned via core structural transition from cubic solid solution [denoted as face centered cubic (fcc)] structure to tetragonal intermetallic [denoted as face centered tetragonal (fct)] structure. The high activity observed from the fct-FePt/Pt NPs for oxygen reduction reaction (ORR) is due to the release of the overcompressed Pt strain by the fct-FePt as suggested by quantum mechanics-molecular mechanics (QM-MM) simulations. The Pt strain effect on ORR can be further optimized when Fe in FePt is partially replaced by Cu. As a result, the fct-FeCuPt/Pt NPs become the most efficient catalyst for ORR and are nearly 10 times more active in specific activity than the commercial Pt
Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors
Acknowledged Federal Support:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: The Journal of Physical Chemistry Letters
Publication Identifier Type: DOI Publication Identifier: 10.1021/jz4024699
Volume: 5 Issue: 2 First Page #: 0
Date Submitted: Date Published:
Publication Location:
Article Title: Computational Design of Core/Shell Nanoparticles for Oxygen Reduction Reactions
Authors:
Keywords: DEALLOYED PT-CU; ELECTROCATALYSTS; PLATINUM; SURFACES; METALS; ALLOY; MONOLAYER; CATALYST; STRAIN
Abstract: A computational strategy to design core/shell nanoparticle catalysts for oxygen reduction reactions (ORRs) is proposed based on multiscale modeling. Using a quantum mechanics/molecular mechanics (QM/MM) coupling method, we have studied the ORR on Pt-Cu core/shell nanoparticles with the size ranging from 3 to 8 nm. We have calculated the oxygen adsorption energy on the nanoparticle surface (a descriptor for ORR activity) as a function of the nanoparticle size and thickness of the Pt shell. We find that the Pt-Cu core/shell nanoparticles exhibit higher ORR activities than flat Pt(iii) surfaces, consistent with experimental observations. We predict that the diameter of the core/shell nanoparticles should be larger than 7 nm to reach the peak of ORR activities. By examining the effects of ligand, quantum confinement, and surface strain, we confirm that the strain plays the dominant role on ORR activities for the core/shell nanoparticles. A universal relation between the surface strain and
Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors
Acknowledged Federal Support:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Chem. Sci.
Publication Identifier Type: DOI Publication Identifier: 10.1039/C5SC02667A
Volume: 0 Issue: 0 First Page #: 0
Date Submitted: Date Published:
Publication Location:
Article Title: Overpotential for CO2 electroreduction lowered on strained penta-twinned Cu nanowires
Authors:
Keywords: Not cited in publication
Abstract: Based on first-principles calculations, we predict that penta-twinned Cu nanowires (NWs) are superior to conventional Cu catalysts for CO2 electroreduction. The penta-twinned NWs possess a combination of ultrahigh mechanical strength, large surface-to-volume ratios and an abundance of undercoordinated adsorption sites, all desirable for CO2 electroreduction. In particular, we show that the penta-twinned Cu NWs can withstand elastic strains orders of magnitude higher than their conventional counterpart, and as a result their CO2 electroreduction activities can be significantly enhanced by elastic tensile strains. With a moderate tensile strain, the bias potential for methane production at a decent current density (2 mA cm?2) can be reduced by 50%. On the other hand, the competing hydrogen evolution reaction can be suppressed by the tensile strains. The presence of H at the NW surface is found to have a minor effect on CO2 electroreduction. Finally, we propose to use graphene as a substr
Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors
Acknowledged Federal Support:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Small
Publication Identifier Type: DOI Publication Identifier: 10.1002/smll.201500330
Volume: 1.1E+001 Issue: 2.9E+001 First Page #: 0
Date Submitted: Date Published:
Publication Location:
Article Title: Surface Profile Control of FeNiPt/Pt Core/Shell Nanowires for Oxygen Reduction Reaction
Authors:
Keywords: None cited in publication
Abstract: Monodisperse core/shell FeNiPt/FePt nanowires (4.5 × 20–50 nm) are synthesized by seed-mediated growth of FePt over the pre-made 2.5 nm wide FeNiPt nanowires. The surface profile of the FeNiPt/FePt nanowires is tailored by acid and thermal treatment. The FeNiPt/Pt-skin nanowires show higher activities than the FeNiPt/Pt-skeleton nanowires.
Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors
Acknowledged Federal Support:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Nature Communications
Publication Identifier Type: DOI Publication Identifier: 10.1038/ncomms7261
Volume: 6.0E+000 Issue: 0 First Page #: 0
Date Submitted: Date Published:
Publication Location:
Article Title: Mechanical work makes important contributions to surface chemistry at steps
Authors:
Keywords: Chemical sciences Catalysis Materials science Physical chemistry
Abstract: The effect of mechanical strain on the binding energy of adsorbates to late transition metals is believed to be entirely controlled by electronic factors, with tensile stress inducing stronger binding. Here we show, via computation, that mechanical strain of late transition metals can modify binding at stepped surfaces opposite to well-established trends on flat surfaces. The mechanism driving the trend is mechanical, arising from the relaxation of stored mechanical energy. The mechanical energy change can be larger than, and of opposite sign than, the energy changes due to electronic effects and leads to a violation of trends predicted by the widely accepted electronic ‘d-band’ model. This trend has a direct impact on catalytic activity, which is demonstrated here for methanation, where biaxial tension is predicted to shift the activity of ?nickel significantly, reaching the peak of the volcano plot and comparable to ?cobalt and ?ruthenium
Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors
Acknowledged Federal Support:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Modelling and Simulation in Materials Science and Engineering
Publication Identifier Type: DOI Publication Identifier: 10.1088/0965-0393/23/1/015004
Volume: 2.3E+001 Issue: 1.0E+000 First Page #: 0
Date Submitted: Date Published:
Publication Location:
Article Title: Magnesium interatomic potential for simulating plasticity and fracture phenomena
Authors:
Keywords: magnesium, dislocations, fracture, empirical potentials, moleculardynamics simulations
Abstract: Magnesium has multiple dislocation and twinning systems with starkly different properties, which make its plastic deformation strongly anisotropic and highly complex. Existing empirical interatomic potentials fail to capture the full scope of these properties, making current molecular statics and dynamics simulation results of limited quantitative and predictive use. Here, based on the work by Kim et al, a new modified embedded-atom method potential for magnesium is introduced and rigorously validated against existing ab initio, continuum theory and experimental results. The new potential satisfactorily reproduces all the necessary mechanical properties for plastic deformation, including the various generalized stacking fault energy surfaces, dislocations core structures, Peierls stresses, surface energies and basal plane cohesive strength. The capability of this potential to accurately describe all the important slip systems and fracture behavior makes it valuable for future realistic
Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors
Acknowledged Federal Support:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Physical Review Letters
Publication Identifier Type: DOI Publication Identifier: 10.1103/PhysRevLett.112.225701
Volume: 1.12E+002 Issue: 2.2E+001 First Page #: 0
Date Submitted: Date Published:
Publication Location:
Article Title: Diffusion on Demand to Control Precipitation Aging: Application to Al-Mg-Si Alloys
Authors:
Keywords: Not cited in publication
Abstract: We demonstrate experimentally that a part-per-million addition of Sn solutes in Al-Mg-Si alloys can inhibit natural aging and enhance artificial aging. The mechanism controlling the aging is argued to be vacancy diffusion, with solutes trapping vacancies at low temperature and releasing them at elevated temperature, which is supported by a thermodynamic model and first-principles computations of Sn-vacancy binding. This diffusion on demand solves the long-standing problem of detrimental natural aging in Al-Mg-Si alloys, which is of great scientific and industrial importance. Moreover, the mechanism of controlled buffering and release of excess vacancies is generally applicable to modulate diffusion in other metallic systems.
Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors
Acknowledged Federal Support:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: The Journal of Physical Chemistry C
Publication Identifier Type: DOI Publication Identifier: 10.1021/jp508636y
Volume: 1.18E+002 Issue: 4.9E+001 First Page #: 0
Date Submitted: Date Published:
Publication Location:
Article Title: First-Principles Prediction of Oxygen Reduction Activity on Pd–Cu–Si Metallic Glasses
Authors:
Keywords: Not found in article
Abstract: We carry out first-principles simulations to assess the potential of Pd–Cu–Si metallic glasses as catalysts for oxygen reduction reaction (ORR) using oxygen adsorption energy (EO) as a descriptor. We find that the substitution of Cu on crystalline Pd(111) surface improves the ORR activity while the substitution of Si on the surface is in general detrimental to the ORR activity. Compressive strains are found to weaken oxygen binding on the surface and thus enhance the ORR activity. On the basis of the analysis of EO distribution on the Pd metallic glasses surfaces, we find that for Si-deficient adsorption sites, the local ORR activity could exceed that on pure Pd surface, while Si-rich sites exhibit a rather poor ORR activity. The Pd metallic glasses can sustain a much higher compression than the crystalline counterpart, thus their ORR activity can be improved substantially under a large compression. It is predicted that low-Si Pd metallic glasses could be excellent ORR catalysts under
Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors
Acknowledged Federal Support:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Advanced Materials
Publication Identifier Type: DOI Publication Identifier: 10.1002/adma.201502725
Volume: 0 Issue: 0 First Page #: 0
Date Submitted: Date Published:
Publication Location:
Article Title: A General Method for Multimetallic Platinum Alloy Nanowires as Highly Active and Stable Oxygen Reduction Catalysts
Authors:
Keywords: Not cited in publication
Abstract: An unconventional class of high-performance Pt Alloy nanowires: A general method is used to produce an unconventional class of multimetallic alloy nanowires (NWs). The obtained PtNi NWs exhibit amazingly specific and mass oxygen reduction reaction (ORR) activities with improvement factors of 51.1 and 34.6 over commercial Pt/C catalysts, respectively, and are also stable in ORR conditions, making them among the most efficient electrocatalysts for ORR.
Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors
Acknowledged Federal Support:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Journal of the American Chemical Society
Publication Identifier Type: DOI Publication Identifier: 10.1021/jacs.5b01100
Volume: 1.37E+002 Issue: 1.8E+001 First Page #: 0
Date Submitted: Date Published:
Publication Location:
Article Title: A New Core/Shell NiAu/Au Nanoparticle Catalyst with Pt-like Activity for Hydrogen Evolution Reaction
Authors:
Keywords: None cited in publication
Abstract: We report a general approach to NiAu alloy nanoparticles (NPs) by co-reduction of Ni(acac)2 (acac = acetylacetonate) and HAuCl4·3H2O at 220 °C in the presence of oleylamine and oleic acid. Subject to potential cycling between 0.6 and 1.0 V (vs reversible hydrogen electrode) in 0.5 M H2SO4, the NiAu NPs are transformed into core/shell NiAu/Au NPs that show much enhanced catalysis for hydrogen evolution reaction (HER) with Ptlike activity and much robust durability. The firstprinciples calculations suggest that the high activity arises from the formation of Au sites with low coordination numbers around the shell. Our synthesis is not limited to NiAu but can be extended to FeAu and CoAu as well, providing a general approach to MAu/Au NPs as a class of new catalyst superior to Pt for water splitting and hydrogen generation.
Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors
Acknowledged Federal Support:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Journal of the American Chemical Society
Publication Identifier Type: DOI Publication Identifier: 10.1021/ja508256g
Volume: 1.36E+002 Issue: 4.2E+001 First Page #: 0
Date Submitted: Date Published:
Publication Location:
Article Title: Nanocatalyst Superior to Pt for Oxygen Reduction Reactions: The Case of Core/Shell Ag(Au)/CuPd Nanoparticles
Authors:
Keywords: None cited in the publication
Abstract: Controlling the electronic structure and surface strain of a nanoparticle catalyst has become an important strategy to tune and to optimize its catalytic efficiency for a chemical reaction. Using density functional theory (DFT) calculations, we predicted that core/shell M/CuPd (M = Ag, Au) NPs with a 0.8 or 1.2 nm CuPd2 shell have similar but optimal surface strain and composition and may surpass Pt in catalyzing oxygen reduction reactions. We synthesized monodisperse M/CuPd NPs by the coreduction of palladium acetylacetonate and copper acetylacetonate in the presence of Ag (or Au) nanoparticles with controlled shell thicknesses of 0.4, 0.75, and 1.1 nm and CuPd compositions and evaluated their catalysis for the oxygen reduction reaction in 0.1 M KOH solution. As predicted, our Ag/Cu37Pd63 and Au/Cu40Pd60 catalysts with 0.75 and 1.1 nm shells were more efficient catalysts than the commercial Pt catalyst (Fuel Cells Store), with their mass activity reaching 0.20 A/mg of noble metal at ?
Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors
Acknowledged Federal Support:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: ACS Nano
Publication Identifier Type: DOI Publication Identifier: 10.1021/acsnano.5b04361
Volume: 0 Issue: 0 First Page #: 0
Date Submitted: Date Published:
Publication Location:
Article Title: Core/Shell Face-Centered Tetragonal FePd/Pd Nanoparticles as an Efficient Non-Pt Catalyst for the Oxygen Reduction Reaction
Authors:
Keywords: FePd; face-centered tetragonal structure; core/shell nanoparticles; electrocatalysis; oxygen reduction reaction
Abstract: We report the synthesis of core/shell face-centered tetragonal (fct)-FePd/Pd nanoparticles (NPs) via reductive annealing of core/shell Pd/Fe3O4 NPs followed by temperature-controlled Fe etching in acetic acid. Among three different kinds of core/shell FePd/Pd NPs studied (FePd core at ?8 nm and Pd shell at 0.27, 0.65, or 0.81 nm), the fct-FePd/Pd-0.65 NPs are the most efficient catalyst for the oxygen reduction reaction (ORR) in 0.1 M HClO4 with Pt-like activity and durability. This enhanced ORR catalysis arises from the desired Pd lattice compression in the 0.65 nm Pd shell induced by the fct-FePd core. Our study offers a general approach to enhance Pd catalysis in acid for ORR.
Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors
Acknowledged Federal Support:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: The Journal of Physical Chemistry C
Publication Identifier Type: DOI Publication Identifier: 10.1021/acs.jpcc.5b06096
Volume: 1.19E+002 Issue: 3.3E+001 First Page #: 0
Date Submitted: Date Published:
Publication Location:
Article Title: Role of Elastic Strain on Electrocatalysis of Oxygen Reduction Reaction on Pt
Authors:
Keywords: None cited in publication
Abstract: The effect of elastic strain on catalytic activity of platinum (Pt) toward oxygen reduction reaction (ORR) is investigated through dealloyed Pt–Cu thin films; stress evolution in the dealloyed layer and the mass of the Cu removed are measured in real-time during electrochemical dealloying of (111)-textured thin-film PtCu (1:1, atomic ratio) electrodes. In situ stress measurements are made using the cantilever-deflection method, and nanogravimetric measurements are made using an electrochemical quartz crystal nanobalance. Upon dealloying via successive voltammetric sweeps between ?0.05 and 1.15 V vs standard hydrogen electrode, compressive stress develops in the dealloyed Pt layer at the surface of thin-film PtCu electrodes. The dealloyed films also exhibit enhanced catalytic activity toward ORR compared with polycrystalline Pt. In situ nanogravimetric measurements reveal that the mass of dealloyed Cu is approximately 210 ± 46 ng/cm2, which corresponds to a dealloyed layer thickness of
Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors
Acknowledged Federal Support:

Publication Type: Journal Article Peer Reviewed: N **Publication Status:** 1-Published
Journal: Angewandte Chemie
Publication Identifier Type: DOI Publication Identifier: 10.1002/anie.201508613
Volume: 55 Issue: 21 First Page #: 6175
Date Submitted: 10/3/18 12:00AM Date Published: 5/17/16 4:00PM
Publication Location:
Article Title: The influence of elastic strain on catalytic activity towards the hydrogen evolution reaction
Authors: Kai Yan, Tuhina Adit Maark, Alireza Khorshidi, Vijay A. Sethuraman, Andrew A. Peterson, Pradeep R. G
Keywords: None cited in publication
Abstract: Understanding the role of elastic strain in modifying catalytic reaction rates is crucial for catalyst design, but experimentally, this effect is often coupled with a ligand effect. To isolate the strain effect, we have successfully investigated the influence of externally applied elastic strain on catalytic activity of metal films towards the hydrogen evolution reaction (HER). We show that elastic strain tunes the catalytic activity in a controlled and predictable way. Both theory and experiment show strain controls reactivity in a controlled manner consistent with the qualitative predictions of the HER volcano plot and the d-band theory: Ni and Pt's activity were accelerated by compression, while Cu's activity was accelerated by tension. By isolating the elastic strain effect from the ligand effect, this study provides a greater insight into the role of elastic strain in controlling electrocatalytic activity.
Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors
Acknowledged Federal Support: **Y**

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Journal of the American Chemical Society
Publication Identifier Type: DOI Publication Identifier: 10.1021/jacs.5b04142
Volume: 1.37E+002 Issue: 2.2E+001 First Page #: 0
Date Submitted: Date Published:
Publication Location:
Article Title: Stable Cobalt Nanoparticles and Their Monolayer Array as an Efficient Electrocatalyst for Oxygen Evolution Reaction
Authors:
Keywords: None cited in publication
Abstract: Monodisperse cobalt (Co) nanoparticles (NPs) were synthesized and stabilized against oxidation via reductive annealing at 600 °C. The stable Co NPs are active for catalyzing the oxygen evolution reaction (OER) in 0.1 M KOH, producing a current density of 10 mA/cm2 at an overpotential of 0.39 V (1.62 V vs RHE, no iR-correction). Their catalysis is superior to the commercial Ir catalyst in both activity and stability. These Co NPs are also assembled into a monolayer array on the working electrode, allowing the detailed study of their intrinsic OER activity. The Co NPs in the monolayer array show 15 times higher turnover frequency (2.13 s–1) and mass activity (1949 A/g) than the NPs deposited on conventional carbon black (0.14 s–1 and 126 A/g, respectively) at an overpotential of 0.4 V. These stable Co NPs are a promising new class of noble-metal-free catalyst for water splitting.
Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors
Acknowledged Federal Support:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Nano Letters
Publication Identifier Type: DOI Publication Identifier: 10.1021/acs.nanolett.5b00320
Volume: 1.5E+001 Issue: 4.0E+000 First Page #: 0
Date Submitted: Date Published:
Publication Location:
Article Title: New Approach to Fully Ordered fct-FePt Nanoparticles for Much Enhanced Electrocatalysis in Acid
Authors:
Keywords: face-centered tetragonal structure, nanoparticles, electrocatalysis, oxygen reduction, hydrogen evolution
Abstract: Fully ordered face-centered tetragonal (fct) FePt nanoparticles (NPs) are synthesized by thermal annealing of the MgO-coated dumbbell-like FePt-Fe3O4 NPs followed by acid washing to remove MgO. These fct-FePt NPs show strong ferromagnetism with room temperature coercivity reaching 33 kOe. They serve as a robust electrocatalyst for the oxygen reduction reaction (ORR) in 0.1 M HClO4 and hydrogen evolution reaction (HER) in 0.5 M H2SO4 with much enhanced activity (the most active fct-structured alloy NP catalyst ever reported) and stability (no obvious Fe loss and NP degradation after 20 000 cycles between 0.6 and 1.0 V (vs RHE)). Our work demonstrates a reliable approach to FePt NPs with much improved fct-ordering and catalytic efficiency for ORR and HER.
Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors
Acknowledged Federal Support:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Journal of the American Chemical Society
Publication Identifier Type: DOI Publication Identifier: 10.1021/ja5099066
Volume: 1.36E+002 Issue: 4.5E+001 First Page #: 0
Date Submitted: Date Published:
Publication Location:
Article Title: Monodisperse Core/Shell Ni/FePt Nanoparticles and Their Conversion to Ni/Pt to Catalyze Oxygen Reduction
Authors:
Keywords: None to cite in publication
Abstract: We report a size-controllable synthesis of monodisperse core/shell Ni/FePt nanoparticles (NPs) via a seed-mediated growth and their subsequent conversion to Ni/Pt NPs. Preventing surface oxidation of the Ni seeds is essential for the growth of uniform FePt shells. These Ni/FePt NPs have a thin (?1 nm) FePt shell and can be converted to Ni/Pt by acetic acid wash to yield active catalysts for oxygen reduction reaction (ORR). Tuning the core size allows the optimization of their electrocatalytic activity. The specific activity and mass activity of 4.2/0.8 nm core/shell Ni/FePt after acetic acid wash reach 1.95 mA/cm2 and 490 mA/mgPt at 0.9 V (vs reversible hydrogen electrode), which are much higher than those of benchmark commercial Pt catalyst (0.34 mA/cm2 and 92 mA/mgPt at 0.9 V). Our studies provide a robust approach to monodisperse core/shell NPs with nonprecious metal core, making it possible to develop advanced NP catalysts with ultralow Pt content for ORR and many other heterogeneo
Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors
Acknowledged Federal Support:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Nano Today
Publication Identifier Type: DOI Publication Identifier: 10.1016/j.nantod.2014.09.002
Volume: 9.0E+000 Issue: 5.0E+000 First Page #: 0
Date Submitted: Date Published:
Publication Location:
Article Title: Graphene and its composites with nanoparticles for electrochemical energy applications
Authors:
Keywords: Graphene; Doped-graphene; Liquid phase exfoliation; Graphene–nanoparticle composites; Energy storage; Energy conversion

Abstract: Graphene is a two dimensional (2D) planar and hexagonal array of carbon atoms and has been studied extensively as advanced nanomaterials for important technological applications. This review summarizes the recent developments in chemistry, materials and energy applications of graphene, doped graphene and their composites with nanoparticles (NPs). It first highlights the new chemistry used to synthesize high quality graphene. It then outlines the methodologies developed to dope graphene with heteroatoms to modify and control graphene properties. It further describes the general approaches to graphene–NP composites via either direct NP growth onto graphene or self-assembly of the pre-formed NPs on graphene surface. These graphene–NP composites provide some ideal systems for studying synergistic effects between graphene and NPs on catalysis. The review focuses on applications of graphene–NP composites in increasing electrochemical energy storage density and in catalyzing chemical reaction

Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors
Acknowledged Federal Support:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Nano Letters
Publication Identifier Type: DOI Publication Identifier: 10.1021/acs.nanolett.5b01154
Volume: 1.5E+001 Issue: 6.0E+000 First Page #: 0
Date Submitted: Date Published:
Publication Location:
Article Title: Computational Design of Strain in Core–Shell Nanoparticles for Optimizing Catalytic Activity
Authors:
Keywords: Surface effects; interface effects; core?shell nanoparticle; oxygen reduction reaction; finite elements

Abstract: Surface strains in core–shell nanoparticles modify catalytic activity. Here, a continuum-based strategy enables accurate surface-strain-based screening and design of core–shell systems using minimal input as a means to enhance catalytic activity. The approach is validated here for Pt shells on CuxPt(1–x) cores and used to interpret experimental results on the oxygen reduction reaction in the same system. The analysis shows that precise control of particle sizes and shell thicknesses is required to achieve peak activity, rationalizing the limited increases in activity observed in experiments. The method is also applied to core–shell nanorods to demonstrate its wide applicability.

Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors
Acknowledged Federal Support:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Phys. Chem. Chem. Phys.
Publication Identifier Type: DOI Publication Identifier: 10.1039/C4CP04924A
Volume: 1.7E+001 Issue: 3.0E+000 First Page #: 0
Date Submitted: Date Published:
Publication Location:
Article Title: Elastic strain effects on catalysis of a PdCuSi metallic glass thin film
Authors:
Keywords: None cited in publication
Abstract: The influence of strain on catalytic activity has previously been examined directly by calculations and indirectly by experiments. The origin of the phenomenon has been attributed to strain-induced changes in the catalyst electronic structure. By employing a Pd-based metallic glass film capable of large elastic strains, we provide direct experimental evidence for catalytic activity being differently influenced by mechanically applied uniaxial tensile and compressive strains. We demonstrate the effect on the oxygen reduction reaction with cyclic voltammetry (CV) curves at different strain levels and compare X-ray photoelectron spectrometry (XPS) results for unstrained and strained (in uniaxial tension) specimens to confirm valence electron band shifts. The experimental findings are complemented by electronic structure calculations on single crystal Pd, as well as alloys with Cu and Si. The CV and XPS shifts observed in the experiments are consistent in both direction and magnitude to th
Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors
Acknowledged Federal Support:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Computer Physics Communications
Publication Identifier Type: DOI Publication Identifier: 10.1016/j.cpc.2016.05.010
Volume: 207 Issue: First Page #: 310
Date Submitted: 9/26/16 12:00AM Date Published: 10/1/16 12:00AM
Publication Location:
Article Title: Amp: A modular approach to machine learning in atomistic simulations
Authors: Alireza Khorshidi, Andrew A. Peterson
Keywords: Potential energy surface; Neural networks; Atomic Simulation Environment (ASE); Density functional theory; Zernike polynomials
Abstract: Electronic structure calculations, such as those employing Kohn–Sham density functional theory or ab initio wavefunction theories, have allowed for atomistic-level understandings of a wide variety of phenomena and properties of matter at small scales. However, the computational cost of electronic structure methods drastically increases with length and time scales, which makes these methods difficult for long time-scale molecular dynamics simulations or large-sized systems. Machine-learning techniques can provide accurate potentials that can match the quality of electronic structure calculations, provided sufficient training data. These potentials can then be used to rapidly simulate large and long time-scale phenomena at similar quality to the parent electronic structure approach. Machine-learning potentials usually take a bias-free mathematical form and can be readily developed for a wide variety of systems. Electronic structure calculations have favorable properties—namely that they
Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors
Acknowledged Federal Support: **Y**

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published

Journal: Angewandte Chemie International Edition

Publication Identifier Type: DOI Publication Identifier: 10.1002/anie.201603022

Volume: 55 Issue: 31 First Page #: 9030

Date Submitted: 9/26/16 12:00AM Date Published: 7/1/16 4:00AM

Publication Location:

Article Title: Ordered PdCu-Based Nanoparticles as Bifunctional Oxygen-Reduction and Ethanol-Oxidation Electrocatalysts

Authors: Kezhu Jiang, Pengtang Wang, Shaojun Guo, Xu Zhang, Xuan Shen, Gang Lu, Dong Su, Xiaoqing Huar

Keywords: None mentioned in publication.

Abstract: The development of superior non-platinum electrocatalysts for enhancing the electrocatalytic activity and stability for the oxygen-reduction reaction (ORR) and liquid fuel oxidation reaction is very important for the commercialization of fuel cells, but still a great challenge. Herein, we demonstrate a new colloidal chemistry technique for making structurally ordered PdCu-based nanoparticles (NPs) with composition control from PdCu to PdCuNi and PtCuCo. Under the dual tuning on the composition and intermetallic phase, the ordered PdCuCo NPs exhibit better activity and much enhanced stability for ORR and ethanol-oxidation reaction (EOR) than those of disordered PdCuM NPs, the commercial Pt/C and Pd/C catalysts. The density functional theory (DFT) calculations reveal that the improved ORR activity on the PdCuM NPs stems from the catalytically active hollow sites arising from the ligand effect and the compressive strain on the Pd surface owing to the smaller atomic size of Cu, Co, and Ni.

Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors

Acknowledged Federal Support: **Y**

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published

Journal: Nano Energy

Publication Identifier Type: DOI Publication Identifier: 10.1016/j.nanoen.2016.03.024

Volume: 24 Issue: First Page #: 1

Date Submitted: 9/29/16 12:00AM Date Published: 6/1/16 4:00AM

Publication Location:

Article Title: Controlled assembly of Cu nanoparticles on pyridinic-N rich graphene for electrochemical reduction of CO2 to ethylene

Authors: Qing Li, Wenlei Zhu, Jiaju Fu, Hongyi Zhang, Gang Wu, Shouheng Sun

Keywords: Cu nanoparticles; Self-assembly; Graphene; Nitrogen doping; CO2 reduction; Electrocatalysis

Abstract: Monodisperse Cu nanoparticles (NPs) assembled on a pyridinic-N rich graphene (p-NG) support show a Cu NP mass- and size-dependent catalysis for the selective electrochemical reduction of CO2 to ethylene (C2H4). For the 7 nm Cu NPs assembled on the p-NG with the p-NG/Cu mass ratio of 1:1, the C2H4 formation Faradaic efficiency and hydrocarbon selectivity reach 19% and 79% respectively at ?0.9 V (vs reversible hydrogen electrode). The p-NG itself can catalyze the CO2 reduction to formate, but in the composite p-NG-Cu structure, the pyridinic-N functions as a CO2 and proton absorber, facilitating hydrogenation and carbon–carbon coupling reactions on Cu for the formation of C2H4. The work demonstrates a new strategy to improve Cu NP catalytic activity and selectivity for the electrochemical reduction of CO2 for sustainable chemistry and energy applications.

Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors

Acknowledged Federal Support: **Y**

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Nanoscale
Publication Identifier Type: DOI Publication Identifier: 10.1039/C5NR06492A
Volume: 8 Issue: 5 First Page #: 2626
Date Submitted: 9/29/16 12:00AM Date Published:
Publication Location:
Article Title: Controlling core/shell Au/FePt nanoparticle electrocatalysis via changing the core size and shell thickness
Authors: Xiaolian Sun, Dongguo Li, Shaojun Guo, Wenlei Zhu, Shouheng Sun
Keywords: None included in article
Abstract: Using a modified seed-mediated method, we synthesized core/shell Au/FePt nanoparticles (NPs) with Au sizes of 4, 7, and 9 nm and the FePt shell was controlled to have similar FePt compositions and 0.5, 1, and 2 nm thickness. We studied both core and shell effects on electrochemical and electrocatalytic properties of the Au/FePt NPs, and found that the Au core did change the redox chemistry of the FePt shell and promoted its electrochemical oxidation of methanol. The catalytic activity was dependent on the FePt thicknesses, but not much on the Au core sizes, and the 1 nm FePt shell was found to be the optimal thickness for catalyzing methanol oxidation in 0.1 M HClO4 + 0.1 M methanol, offering not only high activity (1.19 mA cm?2 at 0.5 V vs. Ag/AgCl), but also enhanced stability. Our studies demonstrate a general approach to the design and tuning of shell catalysis in the core/shell structure to achieve optimal catalysis for important electrochemical reactions.
Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors
Acknowledged Federal Support: **Y**

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Nature Communications
Publication Identifier Type: DOI Publication Identifier: 10.1038/ncomms11850
Volume: 7 Issue: First Page #: 11850
Date Submitted: 9/29/16 12:00AM Date Published: 6/1/16 12:00AM
Publication Location:
Article Title: Surface engineering of hierarchical platinum-cobalt nanowires for efficient electrocatalysis
Authors: Lingzheng Bu, Shaojun Guo, Xu Zhang, Xuan Shen, Dong Su, Gang Lu, Xing Zhu, Jianlin Yao, Jun Gu
Keywords: chemical sciences, material sciences, physical chemistry
Abstract: Despite intense research in past decades, the lack of high-performance catalysts for fuel cell reactions remains a challenge in realizing fuel cell technologies for transportation applications. Here we report a facile strategy for synthesizing hierarchical platinum-cobalt nanowires with high-index, platinum-rich facets and ordered intermetallic structure. These structural features enable unprecedented performance for the oxygen reduction and alcohol oxidation reactions. The specific/mass activities of the platinum-cobalt nanowires for oxygen reduction reaction are 39.6/33.7 times higher than commercial Pt/C catalyst, respectively. Density functional theory simulations reveal that the active threefold hollow sites on the platinum-rich high-index facets provide an additional factor in enhancing oxygen reduction reaction activities. The nanowires are stable in the electrochemical conditions and also thermally stable. This work may represent a key step towards scalable production of high-p
Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors
Acknowledged Federal Support: **Y**

RPPR Final Report
as of 17-Aug-2020

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Angewandte Chemie International Edition
Publication Identifier Type: DOI Publication Identifier: 10.1002/anie.201603022
Volume: 55 Issue: 31 First Page #: 9030
Date Submitted: 9/29/16 12:00AM Date Published: 7/1/16 4:00AM
Publication Location:
Article Title: Ordered PdCu-Based Nanoparticles as Bifunctional Oxygen-Reduction and Ethanol-Oxidation Electrocatalysts
Authors: Kezhu Jiang, Pengtang Wang, Shaojun Guo, Xu Zhang, Xuan Shen, Gang Lu, Dong Su, Xiaoqing Huar
Keywords: None in article
Abstract: The development of superior non-platinum electrocatalysts for enhancing the electrocatalytic activity and stability for the oxygen-reduction reaction (ORR) and liquid fuel oxidation reaction is very important for the commercialization of fuel cells, but still a great challenge. Herein, we demonstrate a new colloidal chemistry technique for making structurally ordered PdCu-based nanoparticles (NPs) with composition control from PdCu to PdCuNi and PtCuCo. Under the dual tuning on the composition and intermetallic phase, the ordered PdCuCo NPs exhibit better activity and much enhanced stability for ORR and ethanol-oxidation reaction (EOR) than those of disordered PdCuM NPs, the commercial Pt/C and Pd/C catalysts. The density functional theory (DFT) calculations reveal that the improved ORR activity on the PdCuM NPs stems from the catalytically active hollow sites arising from the ligand effect and the compressive strain on the Pd surface owing to the smaller atomic size of Cu, Co, and Ni.
Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors
Acknowledged Federal Support: **Y**

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Angewandte Chemie
Publication Identifier Type: DOI Publication Identifier: 10.1002/ange.201406281
Volume: 126 Issue: 46 First Page #: 12716
Date Submitted: 9/29/16 12:00AM Date Published: 11/1/14 4:00AM
Publication Location:
Article Title: Core/Shell Au/MnO Nanoparticles Prepared Through Controlled Oxidation of AuMn as an Electrocatalyst for Sensitive H
Authors: Huiyuan Zhu, Aruna Sigdel, Sen Zhang, Dong Su, Zheng Xi, Qing Li, Shouheng Sun
Keywords: Gold; Mangan; Nanopartikel; Sensoren; Wasserstoffperoxid
Abstract: Monodisperse 5?nm AuMn nanoparticles were synthesized by hydride reduction of manganese acetylacetonate in the presence of Au nanoparticles. The alloy was formed through fast Mn diffusion into the Au structure. The AuMn nanoparticles were converted to Au-MnO composite particles through air annealing at 170?° C. These Au-MnO particles, especially the core/shell Au/MnO nanoparticles, were active for the electrochemical reduction of H2O2, with a detection limit reaching 8?nM. This highly sensitive electrochemical sensor based on the Au/MnO nanoparticles was used to monitor H2O2 concentrations released from living cells, from which tumorigenic cells were discovered to release higher levels of H2O2 than the non-tumorigenic cells.
Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors
Acknowledged Federal Support: **Y**

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: The Journal of Physical Chemistry C
Publication Identifier Type: DOI Publication Identifier: 10.1021/acs.jpcc.7b00281
Volume: 121 Issue: 11 First Page #: 6177
Date Submitted: 10/3/18 12:00AM Date Published: 3/1/17 10:00AM
Publication Location:
Article Title: High Elastic Strain Directly Tunes the Hydrogen Evolution Reaction on Tungsten Carbide
Authors: Kai Yan, Seok Ki Kim, Alireza Khorshidi, Pradeep R. Guduru, Andrew A. Peterson
Keywords: None cited
Abstract: Elastic strain provides a direct means to tune a material’s electronic structure from both computational and experimental vantage points and can thus provide insights into surface reactivity via changes induced by electronic structure shifts. Here we investigate the role of elastic strain on the catalytic activity of tungsten carbide (WC) in the hydrogen evolution reaction. WC makes an interesting material for such investigations as it is an inherently promising catalyst that can sustain larger elastic strains (e.g., ?1.4 to 1.4%) than common transition-metal catalysts, such as Pt or Ni (e.g., ?0.4 to 0.4%). On the basis of density functional theory calculations, a compressive uniaxial strain is expected to cause weakening of the surface–hydrogen interaction of 10–15 meV per percent strain, while a tensile strain is calculated to strengthen the surface–hydrogen interaction by a similar magnitude. Sabatier analysis suggests that weakening of the surface-hydrogen interaction would enhanc
Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors
Acknowledged Federal Support: **Y**

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Chemical Reviews
Publication Identifier Type: DOI Publication Identifier: 10.1021/acs.chemrev.5b00687
Volume: 116 Issue: 18 First Page #: 10473
Date Submitted: 10/3/18 12:00AM Date Published: 6/1/16 4:00AM
Publication Location:
Article Title: Organic Phase Syntheses of Magnetic Nanoparticles and Their Applications
Authors: Liheng Wu, Adriana Mendoza-Garcia, Qing Li, Shouheng Sun
Keywords: None cited
Abstract: In the past two decades, the synthetic development of magnetic nanoparticles (NPs) has been intensively explored for both fundamental scientific research and technological applications. Different from the bulk magnet, magnetic NPs exhibit unique magnetism, which enables the tuning of their magnetism by systematic nanoscale engineering. In this review, we first briefly discuss the fundamental features of magnetic NPs. We then summarize the synthesis of various magnetic NPs, including magnetic metal, metallic alloy, metal oxide, and multifunctional NPs. We focus on the organic phase syntheses of magnetic NPs with precise control over their sizes, shapes, compositions, and structures. Finally we discuss the applications of various magnetic NPs in sensitive diagnostics and therapeutics, high-density magnetic data recording and energy storage, as well as in highly efficient catalysis.
Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors
Acknowledged Federal Support: **Y**

RPPR Final Report
as of 17-Aug-2020

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published

Journal: Nano Energy

Publication Identifier Type: DOI Publication Identifier: 10.1016/j.nanoen.2016.02.030

Volume: 29 Issue: First Page #: 178

Date Submitted: 10/3/18 12:00AM Date Published: 11/1/16 4:00AM

Publication Location:

Article Title: Recent advances in the organic solution phase synthesis of metal nanoparticles and their electrocatalysis for energy conversion reactions

Authors: Qing Li, Shouheng Sun

Keywords: Metal nanoparticles; Solution phasesynthesis; Electrocatalysis; Energy conversions

Abstract: Metalnanoparticles(MNPs)areessentialcatalyst componentsinelectrochemicalenergyconversion andstoragedevices,includingfuelcells,Li-airbatteries andwater-splittingsystems.Synthesesof monodisperseMNPswithcontrolledsizes,shapes and structuresiskeytofullyharvestingtheir catalyticcapabilities. Thisreview first outlinesthefundamentalsofthesynthesisofmonodisperse MNPs byorganicsolutionphasereactions. Itthensummariescommonstrategiesappliedtotailor MNP size,shapeandstructure. Thereviewfurtherhighlightsrecentadvancesofusing MNPsas efficient catalyststocatalyzesomerepresentativereactionsthatrelatedtoenergyconversions, including oxygenreductionreaction,hydrogenevolutionreaction,CO2 reduction reaction, methanol/formicacidoxidationreaction,andoxygenevolutionreaction.

Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors

Acknowledged Federal Support: **Y**

Final (Sixth) Progress Report
No Cost Extension Period August 15, 2016 to August 14, 2017

Stress-Controlled Catalysis via Engineering Nanostructures

W911NF-11-1-0353

Institute for Molecular and Nanoscale Innovation

October 1, 2018

PI: Pradeep R. Guduru
Brown University
182 Hope Street
Box M
Providence, RI 02912

3.0 SCIENTIFIC PROGRESS AND ACCOMPLISHMENTS

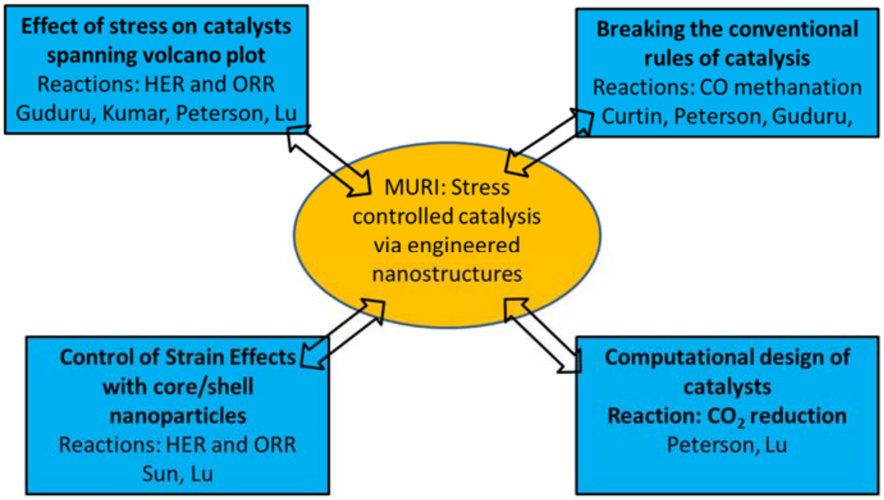
3.1 Background: Enhanced control of chemical reactions has enormous and broad implications for energy generation and conversion, chemical synthesis, sensing, and material degradation. The use of mechanical stress or strain to augment traditional alloying methods provides an avenue both for fine-tuning reaction specificity and/or selectivity and for active control during processes. The focus of this MURI effort is to explore the fundamental principles of stress controlled catalysis through closely coupled experimental and computational investigations.

3.2 MURI objectives:

(i) Develop a scientific basis for controlling chemical reactions using externally applied stress with particular application to catalytic processes.
(ii) Demonstrate the scientific underpinnings of stress controlled catalysis in model experiments (e.g. thin films, nano-pillars) for select reactions of scientific and technological interest (e.g. oxygen reduction reaction, hydrogen evolution reaction, methanation of carbon monoxide).
(iii) Develop novel multiscale simulation methods that bridge the length scales between the density functional theory and practically used nano-particle catalysts.
(iv) The main outcome of the project is unambiguous demonstration that stress can be used to substantially modify and control chemical reactions, along with possible engineering paths, via both thin film and bulk metallic glass nanostructures, for implementing stress control across a wide material space.

3.3 Program organization: The MURI effort was organized into four complementary research thrusts, each of which has computational and experimental investigations.

(i) Effect of stress on catalysts spanning volcano plot
(ii) Control of Strain Effects with core/shell nanoparticles
(iii) Breaking the conventional rules of catalysis
(iv) Computational design of catalysts (Reaction: CO_2 reduction)



3.4 Summary of highlights

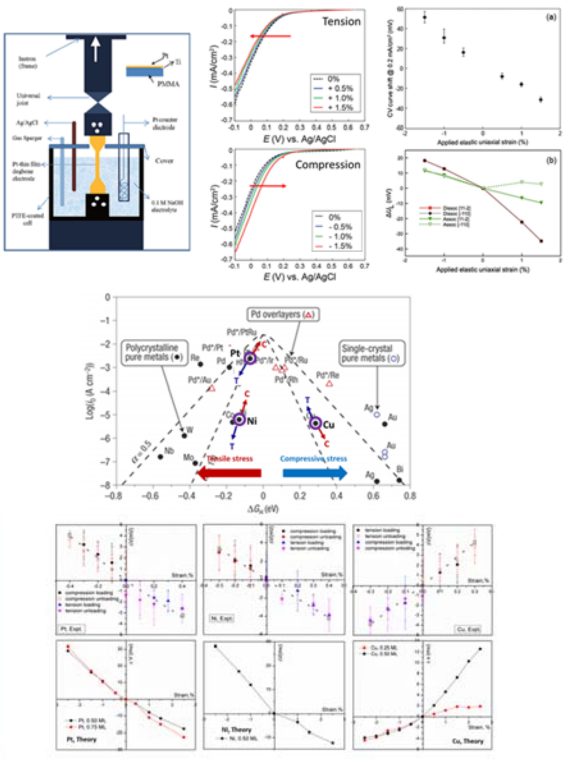
(i) Conclusive demonstration of the systematic effect of stress on catalytic activity

Summary

- Developed new in situ experimental capabilities/approaches to conclusively demonstrate the systematic effect of stress on catalysis in a variety of catalysts.
- Metallic glasses; HER and ORR catalysts that span the volcano plot.
- Close interaction between experiments and theory/computation.
- Provides a quantitatively predictive basis to design catalyst nanostructures that can exploit the stress effect for improved performance in technologically relevant reactions, i.e., elastic strain is another coordinate in catalyst design space.

Future outlook

- Systematic studies that span the full spectrum of multiaxial stress states
- Applications to more complex (multi-step) reactions
- Identify reactions where stress effects can be large and transformative.
- Practical strategies for active straining, i.e., how to translate the basic science results demonstrated here into a practically usable system.



(ii) Rational design of core-shell nano-particle catalysts

Summary

- Traditional computational methods in catalysis that employ density functional theory (DFT) are limited to small collection of atoms. However, in order to predict the catalytic behavior of nano-particles, it is necessary to model the entire structure, which is beyond the capabilities of DFT. We developed a [illegible] method, [illegible] molecular mechanics [illegible] (QM/MM [illegible] of predicting catalytic [illegible] nanoparticles (>10 nm) [illegible] mechanics.
- We employed the multiscale modeling tool to understand and guide the design of core-shell nano-particle catalysts.
- We apply the QM/MM method to establish optimal shell thickness in fct-FePd/Pd nanoparticle catalyst for oxygen reduction reaction (ORR) which is validated by experimental measurements.
- QM-MM calculations predicted that Pt surface strain can be further tuned to optimization in a fct-FeCuPt/Pt structure.
- We synthesized fct-FeCuPt/Pt NPs and found to be more active than fct-FePt/Pt in catalyzing ORR!
- Through a combined experimental and computational effort, we have developed a new catalyst. It provides a rational catalyst design tool at the scale of nanoparticles.
- A new, fast computational design tool for fast screening of material combinations and core-shell configurations.

Future Outlook

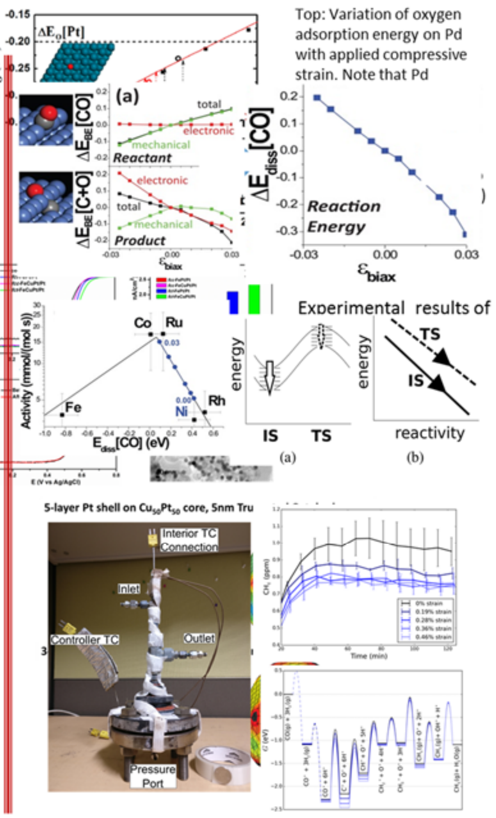
- The QM/MM method that we developed is a powerful tool to design new nanoparticle catalysts by screening for a range of compositions, particle sizes and shell thicknesses.
- Applications to more complex reactions to study stress and alloying effects.

Summary

- In all prior investigations of catalysis on terraces of metals, the strain effect is primarily through the changes that strain causes to the surface electronic structure and the consequent changes in the adsorption energies of reactant and product species. In contrast, we discovered that there is a mechanical contribution to the change in adsorption energy at surface steps in addition to the electronic structure effect. This is due to a stronger coupling between the applied stress and the strain induced by adsorption/desorption process. As a result, the strain effect at such sites can be much greater than that on terraces.
- We predict that tensile strain on Ni surface steps can substantially improve its catalytic activity towards methanation, moving it closer to the volcano peak.
- Carried out an experimental investigation of the stress effect on Ni for methanation.
- The experiments show an opposite trend. Further analysis reveals the possibility of stress changing the descriptor for catalytic activity and the need to investigate the role of stress on the entire reaction, not just the conventionally used single descriptor.

Future outlook

- Identify reactions in which mechanical interaction has a bigger role to play.
- Generalize the role of mechanical interaction in catalysis
- Further experimental investigations to expand upon the methanation studies on Ni.



Top: Variation of oxygen adsorption energy on Pd with applied compressive strain. Note that Pd

Experimental results of

(iii) Breaking the conventional rules in catalysis: can stress help us go beyond the d-band theory predictions?

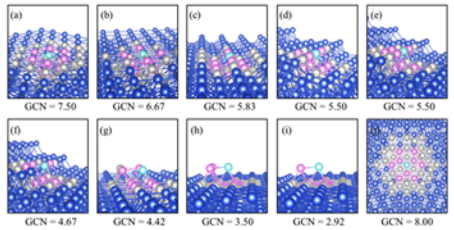
(iv) Computational Design of Catalysts

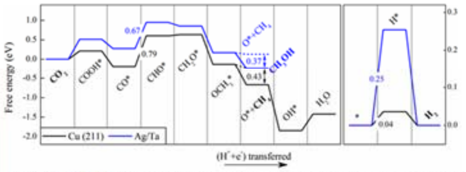
Summary

- The powerful computational modeling tools developed in this program have applications beyond the context in which they have been developed. Useful tool for new catalyst design.
- Model reaction:CO_2 reduction.
- We find that the generalized coordination number (GCN) is a good descriptor for CO_2 reduction on Cu. Using GCN, we can estimate the theoretical limit of the overpotential on (modified) Cu surfaces.
- We predict Ni/Ti and Cu*/Ni NSAs are excellent catalysts for formic acid production – they have 100% selectivity and very low overpotentials.
- We predict Au/Hf as a selective catalyst for HCOOH without HER.
- We predict Ag/Ta as a unique catalyst for CH_3OH production with a relatively high overpotential for HER.
- Some of the results of NSAs could be translated to core/shell NPs, where stress effect could be important. Needs further investigations.

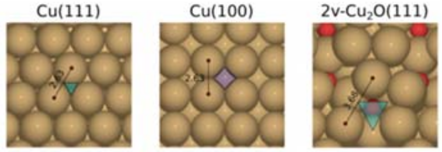
Future outlook

- Experiments guided by the specific computational predictions.
- Discover reactions and systems in which stress plays a significant role.





We predict **Ag/Ta** as an unique catalyst that can reduce CO_2 to CH_3OH at a relatively low overpotential (0.67 V vs. RHE) compared with 0.79 V on Cu (211). The overpotential for HER on Ag/Ta, however, is about six times higher than that on Cu (211).



In the following sections, we expand upon a selected set of accomplishments to underscore the summary provided above.

3.5 Conclusive demonstration of the effect of strain on catalytic activity; model reaction: Hydrogen Evolution Reaction (HER)

The electrochemical production of hydrogen is considered one of the key enabling technologies to transform our energy economy into a more sustainable and carbon-neutral form. [1, 2]. As a result, the hydrogen evolution reaction, below, has gained prominence [3, 4]:

$$2H^+ + 2e^- \rightarrow H_2 \qquad (1)$$

We have systematically (both experimentally and computationally) studied the effect of externally applied elastic strain on the catalytic activity of pure metal films towards HER. HER is ideally suited for studying the effect of elastic strain as it is well established that the binding energy of H----expressed as the free-energy change of hydrogen adsorption (ΔG_H)----is a primary predictor of the effectiveness of an electrocatalyst for HER, with an ideal catalyst having ΔG_H of about 0 eV. In this investigation, we choose three metals that span the volcano plot: Ni (left of the peak), Pt (near the peak) and Cu (right of the peak), which provide a representative set to investigate the effect of elastic strain and the predictions of the d-band model.[5-7] The metal films are subjected to externally apply compressive and tensile loading while they are participating in HER.

Experimentally, thin films of the three metals under consideration (Pt, Ni and Cu) were synthesized by sputtering and/or e-beam evaporation on PMMA (polymethylmethacrylate) substrates. Elastic strains were applied on the films by subjecting the PMMA substrates to uniaxial tensile and compressive loading. An electrochemical cell was designed to be integrated with a universal mechanical testing machine. The activity of the films for HER was studied at each load value through cyclic voltammetry (CV) in 0.1 M NaOH electrolyte by monitoring the shifts in the potential at specified values of HER current. Following assembly, the electrochemical cell was subjected to 30 CV scans at a sweep rate of 50 mV/s to ascertain that a steady state was established. The PMMA substrates were then subjected to a strain cycle. First, the sample was subjected to progressively higher compressive loads corresponding to nominal elastic strains (that is, percent elongation or compression) of 0.1%, 0.2%, 0.3% and 0.4%; the sample was held at each constant strain while five CV scans were collected.

Simultaneously, we performed density functional theory (DFT) calculations on Pt, Ni, and Cu(111) surfaces under various loading conditions to more precisely quantify the theoretical predictions, and further interpret the experimental measurements in terms of changes in the H binding energy. We assumed the thin metal film experiences the same in-plane response, in terms of uniaxial strain and Poisson response, as that of the substrate. For the loading configuration shown, the substrate experiences a strain of ε in the axial direction (i.e. loading direction) and a transverse strain of $-\nu_{PMMA} * \varepsilon$, where ν_{PMMA} of 0.38 is the Poisson's ratio of the PMMA. In the direction normal to the plane, the catalyst was allowed to relax without constraint, as would be expected in the physical sample. At the atomic scale, each metal surface was constructed using a 2×2 non-orthogonal unit cell with four layers and 20 Å vacuum, employing the corresponding DFT bulk lattice constants, calculated as 4.021 Å for Pt, 3.552 Å for Ni, and 3.710 Å for Cu. The free energies for H adsorption (ΔG_H) at 298 K are calculated via the computational hydrogen electrode model as:

$$\Delta G_H(\theta_H) = \Delta E_H(\theta_H) + \Delta E_{ZPE} - T\Delta S + \Delta G_V \qquad (2)$$

where $\Delta E_H(\theta_H)$ is the differential hydrogen adsorption energy[6]:

$$\Delta E_H(\theta_H) = E(nH*) - E((n-1)H*) - \frac{1}{2}E_{H_2} \qquad (3)$$

In the above equations θ_H is the H coverage (0.25-1 monolayer, ML). To make a quantitative connection to the experiments, we define the limiting potential V_L as the electrode potential at which the free energy change of all unit steps in the reaction is less than or equal to zero, i.e., the reaction becomes downhill in the free energy landscape. It can be seen from Figure 1 that V_L is given by -(ΔG_H of the most uphill step)/e where e is the charge of an electron. Although the energy barriers for the unit steps are ignored, the difference between the equilibrium potential and the limiting potential has often been found to give an indication of the overpotential requirement for the catalytic reaction. Hence, the change in the limiting potential with strain, i.e., $\Delta V = V_L$(strained) - V_L(unstrained), can be compared with the experimentally observed shift in the CV curves with strain. Figure 1 (d) to (f) plot the computed ΔV with strain for the three metals (for different

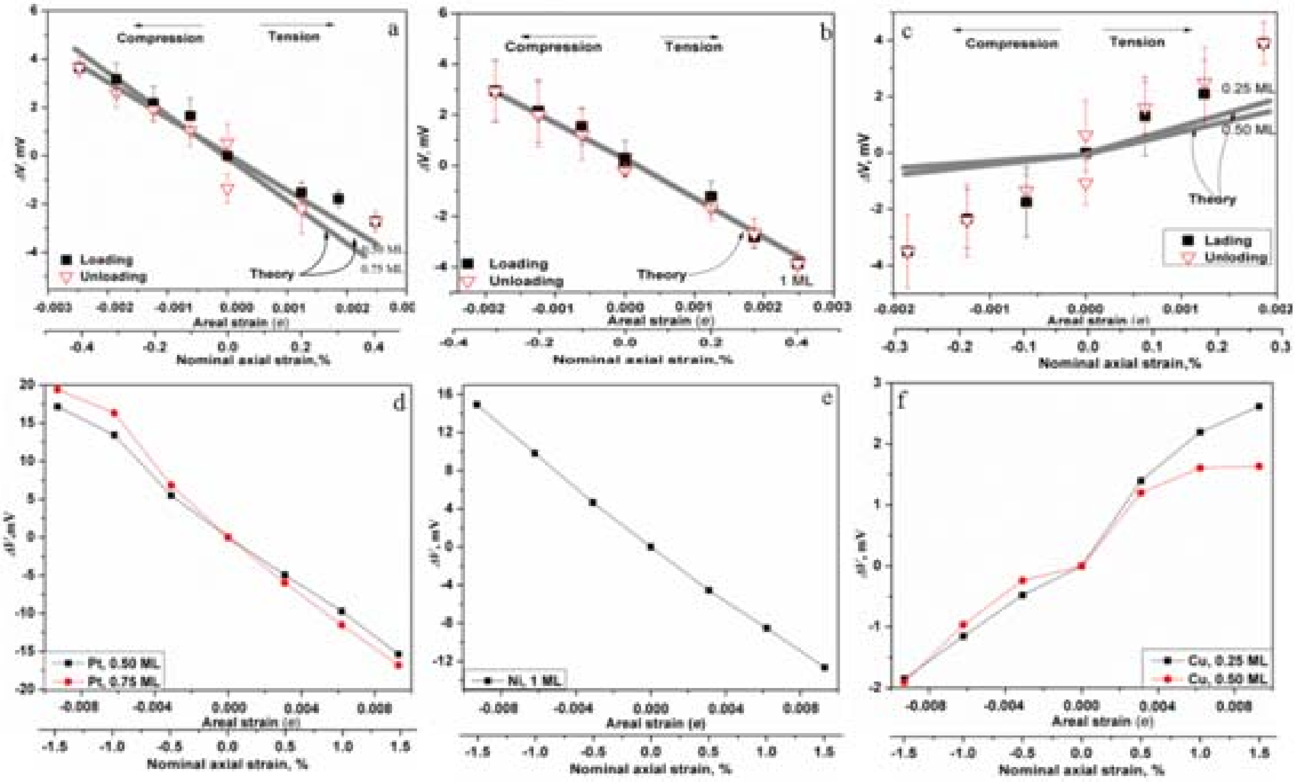


Figure 1. CV-curve shifts relative to the zero strain level as a function of applied elastic strain for (a) Pt, (b) Ni and (c) Cu. A positive potential shift denotes a reduction in overpotential and vice versa. Note the qualitative difference between Cu and the other two metals; compressive strain increases catalytic activity for Pt and Ni whereas the effect is opposite for Cu, which is on the other side of the volcano peak. The solid lines (gray color) on the experimental data represent the computational results from the bottom row of figures. The bottom row shows the potential shifts obtained computationally for (d) Pt(111), (e) Ni(111), and (f) Cu(111) surfaces at different hydrogen coverages as a function of in-plane predominantly uniaxial strain. Areal strain, e = ΔA / A0, where ΔA and A0 are the changed area under nominal axial strain and the initially physical area of the electrode, respectively. The plots shown are average responses for straining along perpendicular in-plane directions. Note that the computationally accessible range of strain values is much larger than what was experimentally accessible.

coverages) in the strain range of -2.5% to 1.5%. We note that the plotted results represent the average response corresponding to multiple loading directions in the (111) plane. The computational results within the experimental loading range were superposed on the experimental data in Figure 1 (a) to (c) as gray solid lines. Despite the simplicity of the computational model, the agreement with the experimental data is remarkably good in all three cases. In particular the computations also capture the reversal in the strain effect on HER activity of Cu compared to that of Pt and Ni. This also suggests that the peak of the volcano plot is correctly placed to the right of Pt; that is, Pt binds H slightly too strongly.

In summary, we experimentally demonstrated that externally applied elastic strain can influence the HER activity of Pt, Ni and Cu thin-film catalysts in a predictable way, consistent with the predictions of the d-band model and with the hydrogen-evolution volcano. By separating the strain effect from the ligand effect, we demonstrated that the effect of strain on metals on opposite sides of the volcano peak is reversed, *i.e.*, compressive strain increases the catalytic activity of metals to the left of the volcano peak and reduces that of the metals to the right. Tensile strain has the opposite effect. The experimental observations match theoretical calculations qualitatively and quantitatively.

3.6 Rational Design of Nano-particle Catalysts:

Our earlier work demonstrated that intermetallic FePt in the core/shell structured FePt/Pt nanoparticles (NPs) can help to enhance Pt catalysis for the oxygen reduction reaction (ORR). To improve the intermetallic ordering in FePt, we first prepared the dumbbell-like Fe_3O_4-FePt NPs with Fe/Pt ratio controlled to close to 1. We then coated the dumbbell NPs with MgO, which is necessary to stabilize NPs against sintering in high temperature reductive annealing condition. Once annealed in Ar + 4% H_2 at 700°C for >5 h, fully ordered intermetallic FePt NPs were obtained. The crystal ordering was characterized by X-ray diffraction peaks from the typical intermetallic FePt structure and by the large room temperature coercivity (>3 T). The MgO coating was removed by washing the product with 0.1 M $HClO_4$ solution at room temperature. This washing also lead to the formation of core/shell FePt/Pt NPs due to the controlled etching of surface Fe from the NPs. The carbon supported FePt/Pt NPs show much enhanced catalysis for ORR in 0.1 M $HClO_4$ at room temperature. However, once tested in the 0.1 M $HClO_4$ solution at 60°C, close to real operation temperature of a polymer electrolyte membrane fuel cells fuel cell (40-80°C), the FePt/Pt catalyst became unstable, and its activity dropped near 50% after 5000 potential cycling between 0.6 and 1.0 V in an O_2-saturated 0.1 M $HClO_4$ (**Figure 2 a&b**).

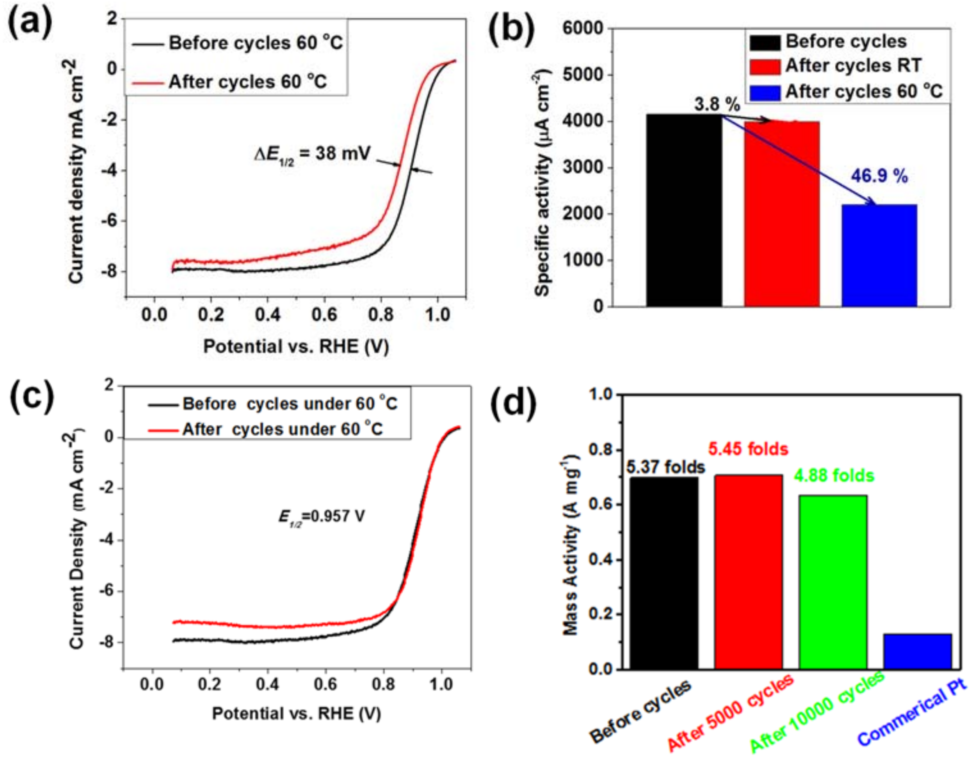


Figure 2. (**a**) ORR polarization curves (before and after 5000 potential cycling) of the FePt/Pt NPs prepared from room temperature acid washing; (**b**) specific activity changes of the (**a**) NP core/shell NP catalyst after potential cycling at different temperatures; (**c**) ORR polarization curves (before and after 10000 potential cycling) of the FePt/Pt NPs prepared as in (**a**) and annealed at 400°C; (**d**) mass activity changes of the (**c**) core/shell NP catalyst after different potential cycling at 60°C.

Considering that the FePt/Pt structure was formed from room temperature washing with 0.1 M $HClO_4$ solution, we hypothesized that the Pt shell formed under this room temperature condition might not be defect-free, and this defected surface might not prevent Fe from further Fe etching or the defected surface might deactivate its catalysis for the ORR at 60°C, leading to the observed activity drop. To overcome this problem, we chose to further anneal the FePt/Pt NPs at 400°C in Ar + 4% H_2. We expected that this annealing would help to "heal" the defected Pt shell to make it defect-free and to stabilize the FePt/Pt structure at 60°C. Indeed, after this simple annealing treatment, we found that the FePt/Pt NPs were both active and stable (Figure 1 c&d). After 5000 potential cycling between 0.6-1.1 V, the activity did not drop - it was actually increased about 10%. After 10000 cycling, the activity dropped only less than 10%. Our data in this group of experiments proved that 1) Fe is more efficiently stabilized in the fully ordered intermetallic FePt structure; 2) the intermetallic FePt core helps to compress the surface Pt (2-3 atomic layers) in the FePt/Pt structure, enhancing the Pt catalysis for the ORR; 3) the higher degree the FePt ordering, the better the activity and stability of the FePt/Pt structure; 4) proper thermal treatment (400°C in our test) can help to further smoothen the Pt shell, making the FePt/Pt active and stable at 60°C for the ORR.

We have scaled-up the synthesis of the FePt/Pt NPs and have shipped a few grams of the NP catalyst to the fuel cell testing lab located in the Los Alamos National Lab to test the catalyst's activity and long term stability in a real membrane electrolyte assembly environment.

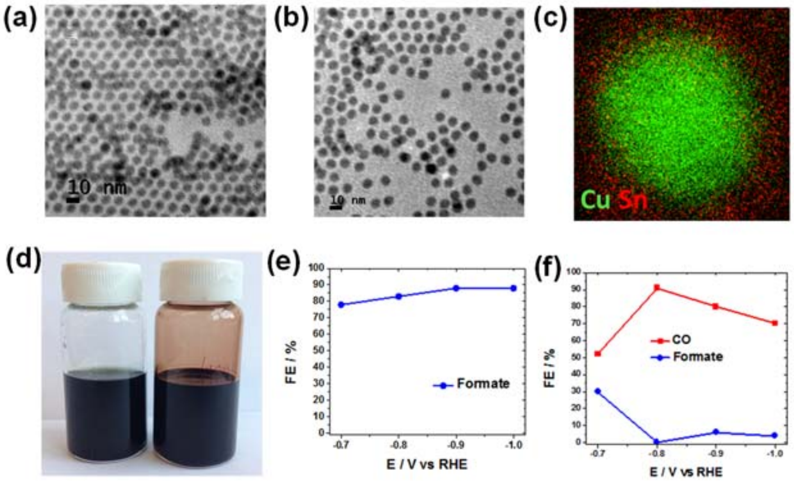


Figure 3. TEM images of (**a**) 7/0.8 nm, (**b**) 7/1/8 nm Cu/Sn NPs; (**c**) elemental mapping of a single 7/0.8 nm Cu/Sn NP; (**d**) photograph of the 7 nm Cu (left) and 7/0.8 nm Cu/Sn NP dispersions in hexane; (**e,f**) reduction potential dependent Faradaic efficiency (FE) in electrochemical reduction of CO_2 in the presence of (**e**) 7/1.8 nm and (**f**) 7/0.8 nm NPs.

Encouraged by the results we obtained from the core/shell NPs, we started to work on the tuning of electrocatalysis for the CO_2 reduction. We tested our synthesis of Au/Cu and Ag/Cu as described in the proposal but our initial synthetic efforts did not yield high quality core/shell structure. We switched our focus on core/shell Cu/Sn NPs. Cu is known to be the most active catalyst for electrochemical reduction of CO_2 to CO and hydrocarbons. The issue of Cu catalysis is its selectivity. Sn is a good catalyst for the CO_2 reduction to formic acid. By combing these two known systems, we may come out with a new catalyst for the CO_2 reduction. Our initial synthesis tended to yield mixture of Cu and SnO_2 NPs. We solved this problem by heating $Sn(acac)_2$ at 250°C in the presence of 7 nm Cu NPs, trioctylamine and tetradecylphosphonic acid. By controlling the amount of $Sn(acac)_2$, Sn coating thickness was controlled. For the study, we made the 0.8 nm and 1.8 nm coating. Figure 3 shows the TEM images of 7/0.8 (Figure 3a), 7/1.8 nm (Figure 3b) Cu/Sn NPs, elemental mapping of a single 7/0.8 nm NP (Figure 3c), and the photo of 7 nm Cu and 7/0.8 nm Cu/Sn NP dispersions in hexane (Figure 3d). When tested as the catalyst for the electrochemical reduction of CO_2 in 0.5 M $KHCO_3$ solution, we noticed that the 7/1.8 nm Cu/Sn functioned similarly to the Sn NPs, forming formate as a major reduction product (Figure 3e). However, for the 7/0.8 nm Cu/Sn NPs, the reduction gave the main product of CO with formate as a very minor product (Figure 3f). Considering the CO_2 reduction to CO is often catalyzed by Au or Ag catalyst, the Sn shell effect on the Cu/Sn catalysis for the selective reduction of CO_2 to formate (from the 1.8 nm Sn shell) or CO (from 0.8 nm Sn shell) offers a new strategy in using core/shell NPs to tune shell catalysis for CO_2 reduction. We are working with the theory group to explain why the Cu/Sn NPs show the specific catalysis as observed.

Looking into next year, we will continue to work on core/shell NP catalyst for electrochemical reactions. Our focus will be on the electrochemical reduction of oxygen (for fuel cell applications) and CO_2 (for the formation of a specific hydrocarbon). In addition, we will start to study core/shell NP catalyst for the CO_2 activation in a thermocatalytic condition. We intend to demonstrate that the core/shell design concept developed in the electrocatalysis can be extended to thermocatalysis as well.

Multiscale Computational Design of Core/Shell Nanoparticles for Electrocatalysis

Core/shell nanoparticles (NPs) are a class of promising catalysts for electrochemical reactions, such as oxygen reduction reaction (ORR) [8], hydrogen evolution reaction (HER) [9], and CO_2 reduction [10], to name but a few. The mismatch between core/shell lattice constants results in non-uniform surface strain distribution, which can be tuned to modulate catalytic activity on NPs for a given reaction. It is well known that surface strain on a core/shell NP depends on its shape, size, shell thickness and chemical composition, thus a prediction of the surface strain as function of geometric and materials parameters is of crucial importance to the design of core/shell NPs. As strain is deeply rooted in the field of Mechanics while catalysis is primarily a subject of Chemistry, we need to combine quantum mechanics with molecular or continuum mechanics to capture mechano-chemistry that underlies stress-controlled catalysis on core/shell NPs. To this end, we have developed a multiscale strategy to computationally design core/shell NPs for electrocatalysis.

It has been established that oxygen adsorption energy on a metal surface, E_O, is a good descriptor of ORR and the ORR reaction rate r on an active site can be expressed as [11, 12]:

$$r = f_0 \exp[-|1.8E_O(\varepsilon)+1.96|/k_BT] \tag{1}$$

where E_O is a function of local strain ε. The overall ORR rate of a given NP, r_{NP}, is thus the average of the reaction rates on all active sites:

$$r_{NP} = \frac{1}{N}\sum_i r_i , \tag{2}$$

including those on the facets and edges of the NP. As E_O on different facets and edges exhibits different dependences on ε, one would have to determine such dependence for each relevant facet and edge of the NP. Specifically, we have carried out first-principles DFT calculations to determine E_O as a function of ε on facets, and QM/MM calculations [13] on edges. Moreover, we performed Molecular Dynamics (MD) simulations with EAM potential [14] to relax the atomic structure of a given NP, from which we can determine the surface strain on the NP. With the information of the strain distribution on the NP and the E_O dependence on the strain for all active sites, one can estimate the overall ORR rate on the NP according to equation (1) and (2).

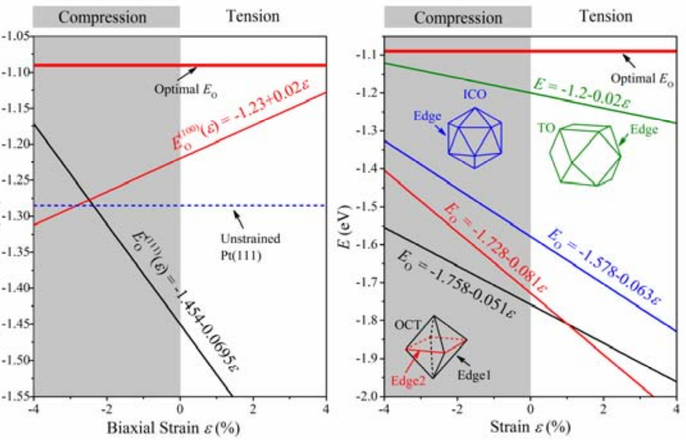


Figure 4. $E_O(\varepsilon)$ on Pd (111), (100) facets and four edges as a function of strain for NPs. The optimal value of E_O is shown as a horizontal red line.

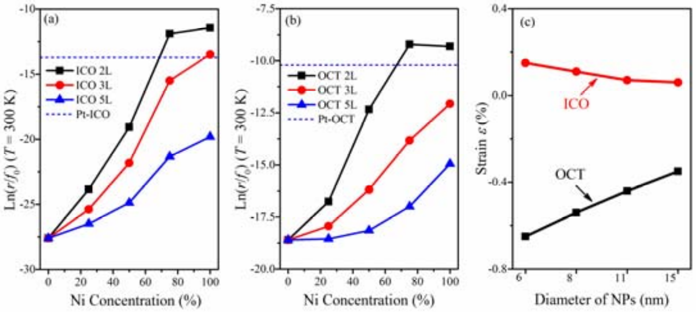


Figure 5. Logarithm of the reaction rate for (a) ICO and (b) OCT NPs, respectively, as a function of Ni concentration in the core. (c) Surface strain of pure Pd NPs as a function of NP diameter.

We have applied this multiscale strategy to design Pd-based core/shell NPs with the goal to replace commercial Pt catalysts for ORR. We focused on NPs in three different shapes, i.e., octahedron (OCT), icosahedron (ICO) and truncated octahedron (TO), as shown in the inset of Fig. 4. The OCT and ICO NPs possess (111) facets only, while the TO NPs have both (111) and (100) facets. In Fig. 4, we display $E_O(\varepsilon)$ on all relevant facets and edges of the NPs. By comparing the left and right panels - both against the optimal E_O, we find that the edges of the OCT and ICO NPs have lower ORR activity than the

Pd (111) facet, while the edges of the TO NPs have a comparable activity as the Pd (100) facet. Moreover, all edges can be activated by compressive strains. In particular, Pd (100) facet is more active than (111) facet for most of the strains. Interestingly, the two facets have opposite dependence of E_O on strain: tension enhances ORR activity on (100) facet while compression promotes the activity on (111) facet. Since a TO NP consists of both (111) and (100) facets, we need to consider their competing effect.

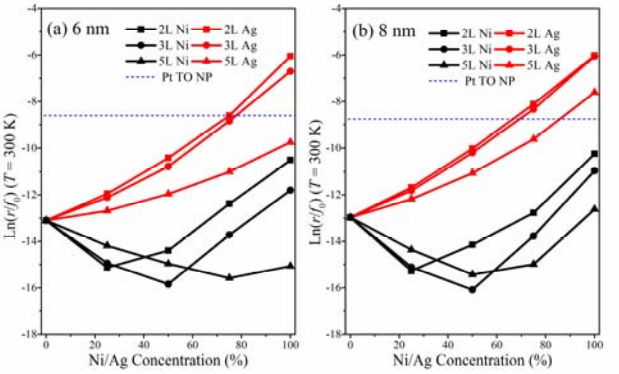


Figure 6. Logarithm of the reaction rate as a function of Ni or Ag concentration in the core for the TO NP with a diameter of (a) 6 nm and (b) 8 nm.

In the following, we focus on Ni_xPd_{1-x} and Ag_xPd_{1-x} cores for the OCT and ICO NPs because our MD simulations showed that the former could supply strong compressions while the latter could provide tensions on the NP surface. In Fig. 5, we present the overall ORR activity (r_{NP}) on the OCT and ICO NPs with a diameter of 8 nm at 300 K. The dashed horizontal line indicates r_{NP} on the pure Pt TO NPs. We find that both higher Ni concentration in the core and thinner Pd-shell can increase ORR activity. More importantly, we predict that the OCT and ICO NPs with 2-layer of Pd-shell and 75% or higher Ni concentration in the core would result in higher ORR activity than a pure Pt NP in the same size and shape. Fig. 5 also highlights the importance of NP shape on ORR activity. For example, the OCT and ICO NPs have intrinsic compressive and tensile strains, respectively as shown in Fig. 5 (c), which significantly influence their ORR activity.

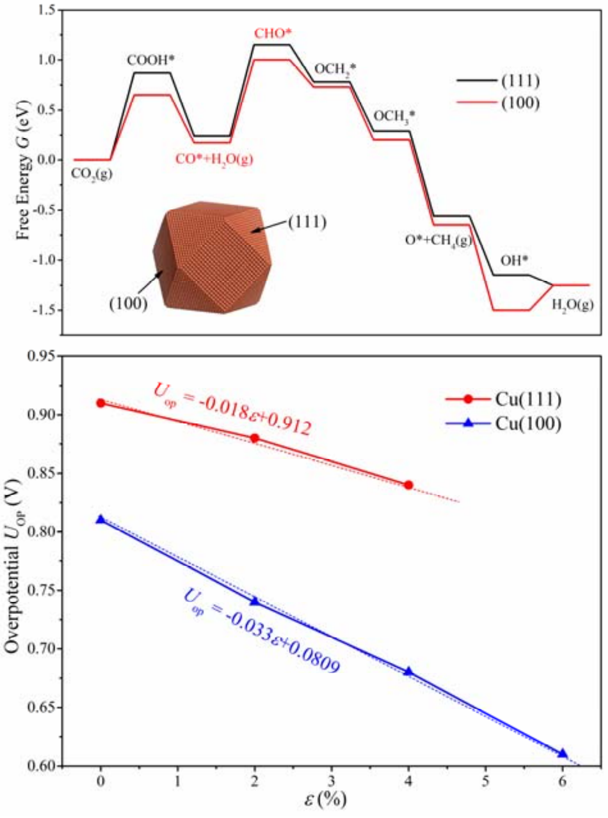


Figure 7. Top: Reaction pathways on Cu (111) and (100) facets. Bottom: U_{OP} as a function of strain ε.

Fig. 6 shows the overall ORR activity (r_{NP}) on the TO NPs with a diameter of 6 nm and 8 nm at 300 K. We find that Ag_xPd_{1-x} core outperforms Ni_xPd_{1-x} significantly, indicating that the enhancement on (100) facet due to tension overrides the retardation on (111) facet due to compression. Thanks to the presence of (100) facets, the TO NPs exhibit much higher ORR activity than the OCT and ICO NPs. For 2 or 3 layers of Pd-shell and 75% or higher Ag concentration in the core, the TO NPs can be as active as the pure Pt NPs in the same shape. Among all NPs examined, we conclude that Ag/Pd NPs in the TO shape with 2 or 3 layer Pd-shell have the highest ORR performance.

We have also studied Cu-based core/shell NPs in the TO shape for CO_2 methanation. Fig. 7(a) shows that both Cu (100) and (111) surfaces share the same reaction pathway for $CO_2 \rightarrow CH_4$. The overpotential (U_{OP}) on (100) is -0.81 V, lower in absolute value than that on (111) surface which is -0.91 V. In Fig. 7(b), we show U_{OP} as a function of strain ε, and tension is found to lower U_{OP} on both surfaces. Therefore, we focus on five FCC metals (Ag, Au, Al, Pt and Pd), which have larger lattice constants than that of Cu to supply tension on the surface. Using MD simulations, we examined the maximum concentration of X (X= Ag, Au, Al, Pt and Pd) as core alloy CuX. In Table I, we list the maximum concentration for each element and the corresponding strain on (111) and (100) facets.

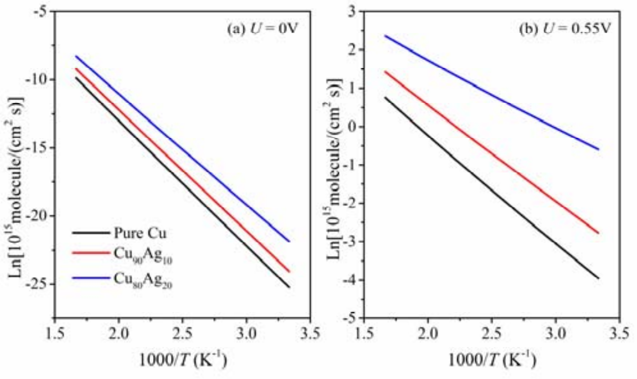


Figure 8. Arrhenius plot for the rate of CH_4 production under (a) U = 0 V and (b) U = 0.55 V on pure Cu, $Cu_{90}Ag_{10}$ and $Cu_{80}Ag_{20}$ NPs.

Table 1 Surface strain on Cu-based core/shell NPs. The core is an alloy of CuX (X= Ag, Pd, Al, Pt and Au).

X	Ag	Pd	Al	Pt	Au
Max. Concentration	20%	40%	25%	37%	20%
ε(111) (%)	2.4	2.2	2.1	2.4	2.7
ε(100) (%)	6.5	6.1	6.7	5.6	6.5

Based on the MD result, we then choose $Cu_{1-x}Ag_x$ as core materials and compute the overall rate (r_{TO}) for CH_4 production on the TO NPs using the following equation [15]:

$$r_{\mathrm{TO}} = \frac{1}{A}\sum_{i,i\in(111)} k_0 e^{-E_{\mathrm{diss}}^{(111)}(i)/k_BT} + \frac{1}{A}\sum_{j,j\in(100)} k_0 e^{-E_{\mathrm{diss}}^{(100)}(j)/k_BT} + \frac{1}{A}\sum_{k,k\in\mathrm{edge}} k_0 e^{-E_{\mathrm{diss}}^{\mathrm{edge}}(k)/k_BT} \quad (3)$$

Fig. 8 shows that r_{TO} increases with Ag concentration in the core. In fact, $Cu_{80}Ag_{20}$ core can offer 29-fold increase in the reaction rate than pure Cu NPs at T = 300 K. If CH_4 is the dominant product in CO_2 reduction, the current density on $Cu_{80}Ag_{20}$/Cu NPs would reach 0.7 mA/cm^2 at 0.55 V and 300 K, much higher than the corresponding value of 0.025 mA/cm^2 on pure Cu NPs in the same condition.

3.7 Theory of anomalous effect of uniaxial strain on surface reactions

The general function of a catalyst is to change the rate and selectivity of a chemical reaction pathway. The rate of an elementary step is largely dictated by the energy levels of the transition state relative to that of the initial state, as can be estimated with transition-state theory. This, in turn, dictates the activity of a catalyst [16]. However, catalysts typically do not give individual control of reaction barriers relative to the endstates [17-19], but rather exhibit highly correlated behavior. Generally, transition states have been calculated to follow relationships such as transition-state scaling (TSS). In the TSS, the transition state---or more formally, the saddle point that represents the highest point along the minimum energy pathway linking initial and final states---is considered as an adsorbate, just as are the initial and final states[20, 21]. In this manner, a more reactive surface binds all adsorbates (transition state, initial state, and final state) more strongly than a more noble surface, and the TSS can be considered as a special case of the adsorbate scaling relations[22]. This can create limitations in catalyst design[17-19] : for example, if one wishes to reduce a reaction barrier by choosing a more reactive metal that binds adsorbates more tightly, then the initial state is also bound more tightly and the barrier relative to the initial state is only marginally changed. This is illustrated in 9.

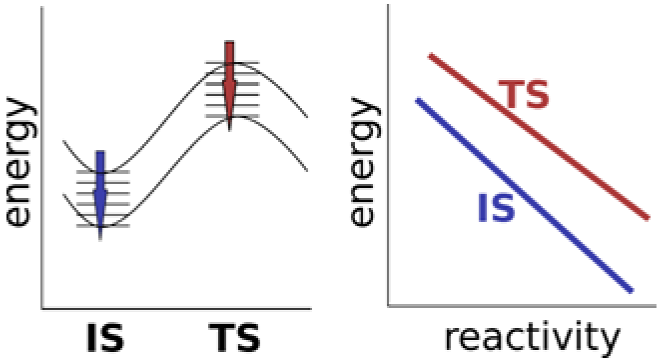


Figure 9. (a) Illustration of transition-state scaling (TSS). If a more reactive catalyst surface is chosen, both the initial state (IS) and transition state (TS) bind to the surface more strongly in a correlated fashion. One must exploit subtle differences in the slopes of the response to change the net barrier.

We discovered an important class of exceptions to the rule of transition-state scaling under conditions of uniaxial loading. When a material is put under tensile strain, the interatomic spacing of the surface atoms increases, leading to less overlap of the d orbitals and a narrower d-band width. Because the number of d electrons is unchanged, the fractional filling of the d band remains constant and the central moment of the d band (the d-band center) shifts upward. By the d-band theory, this higher central moment leads to a strengthening of adsorbate--surface interactions, and the net result is that tensile strain leads to stronger binding of reactive intermediates, while compressive strain leads to weaker binding. However, when individual binding sites are considered, the picture is more subtle. [23, 24] A general rule of thumb is that the higher the coordination number of the binding site, the stronger the response to strain. For example, a bridge (2-fold) site has higher strain susceptibility than does an ontop (1-fold) site, and a three-fold hollow site has a higher strain susceptibility than a bridge site.

Importantly for the current discussion, when strain is applied in one direction, a Poisson response is expected in the orthogonal directions. For example, if uniaxial compression is applied in the x direction, a compensating expansion is observed in the y and z directions which can be quantified with Poisson's ratio. If the compression is applied in line with the material surface, one dimension of the contraction also takes place on the surface of the material. This is illustrated in 10 (a) for an fcc(100) surface in which compression is applied in the *x* direction; in this case, a Poisson response is observed in the *y* (shown) and *z* (not shown) directions. This response can be substantial: in the case of Ag, the contraction in the y direction is about 39 per cent of the applied displacement in the x direction (as dictated by Poisson's ratio).

This results in fundamentally different behavior between the types of sites present in 10. In a fourfold hollow site (labeled "**IS**"" in Figure), a net compression takes place at the binding site, resulting in an encroachment of the surface metal atoms on the binding site; although the transverse (*y* direction) metal atoms move away from the adsorbate the inline metal atoms overwhelm this effect, and an adsorbate at this site would feel the expected weakening of the surface-adsorbate bond with the applied compressive load. However, for an atom located at a bridge site ("**TS**"), the local effect is one of tension: the two metal-adsorbate bonds lengthen and the adsorbate would in net feel a weakening of its binding strength to the metal with the applied tensile strain—which is qualitatively opposite to what is conventionally expected.

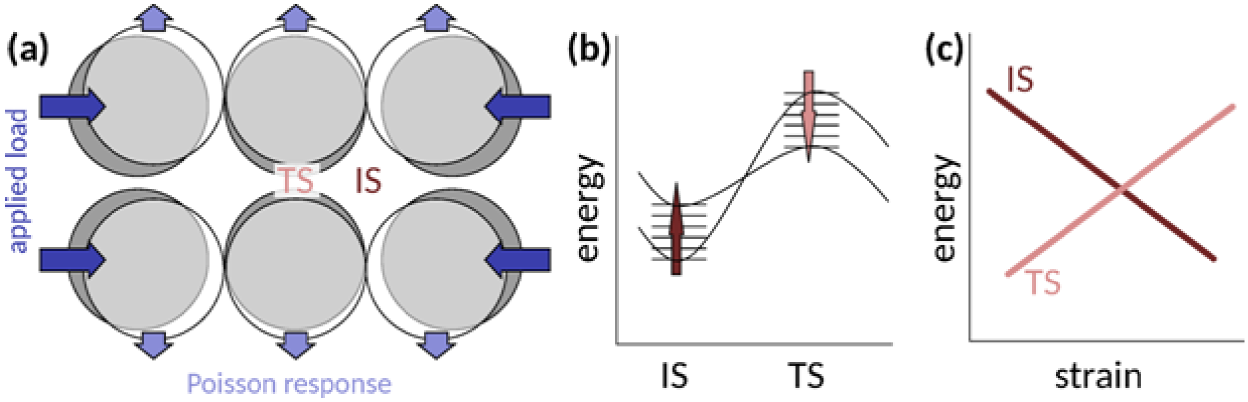


Figure 10. (a) Schematic of applying uniaxial tension to an fcc(100) surface. (b) Qualitative picture of the energy level changes of the initial state (IS) and transition state (TS) with the applied loading. (c) When plotted versus strain, we expect a violation of transition-state scaling.

This scenario can be a rather powerful exception to transition-state scaling, if the initial state (IS) is in the fourfold site and the transition state (TS) is at the bridge site. Under compression, the IS feels a weakening of the surface--adsorbate interaction, resulting in an increase of its energy as shown in 10 (b). Meanwhile, due to the Poisson response, the TS's surface--adsorbate interaction is just the opposite: it is strengthened. The implication of this for the reaction pathway is shown in 10 (b) to (c): the net reaction barrier can be expected to decrease much more significantly than if the IS and TS were correlated as normal. Since reaction rates are exponentially related to changes in barrier height, even rather small deviations to TSS might be expected to have rather large impacts on a catalyst's activity and selectivity.

We used electronic structure calculations to quantify such expectations, devising example reactions in which the IS and FS structures have appropriate site locations to feel the suggested effect. First, we examined the dimerization of two O adsorbates to form O_2 on a Ag(100) surface; this is a type of reaction that can be of importance in the oxygen evolution reaction. For this problem, we used planewave density functional theory and the climbing-image nudged elastic band (CI-NEB) with 5 discrete images along the band to find the minimum energy pathway. At strain levels of 0% and ±3%, we allowed the system to relax in the transverse directions to the applied load in order to calculate the Poisson ratio self-consistently. The initial state consists of two O monomers each adsorbed at a fourfold hollow site, where the effect of compression is to weaken the bonding (*i.e.*, the normal strain effect). However, the reaction pathway leads the dimer to form over the twofold bridge site, which is experiencing a Poisson-driven response to the applied uniaxial loading. The result of these CI-NEB calculations is shown in 11, in which we see the net barrier decreasing as a result of the IS and TS being effected in opposite directions. Specifically, under compressive loading, the elementary reaction becomes more facile as the IS-surface bond weakens and the TS--surface bond strengthens. This anomalous result is an exception to the TSS relations.

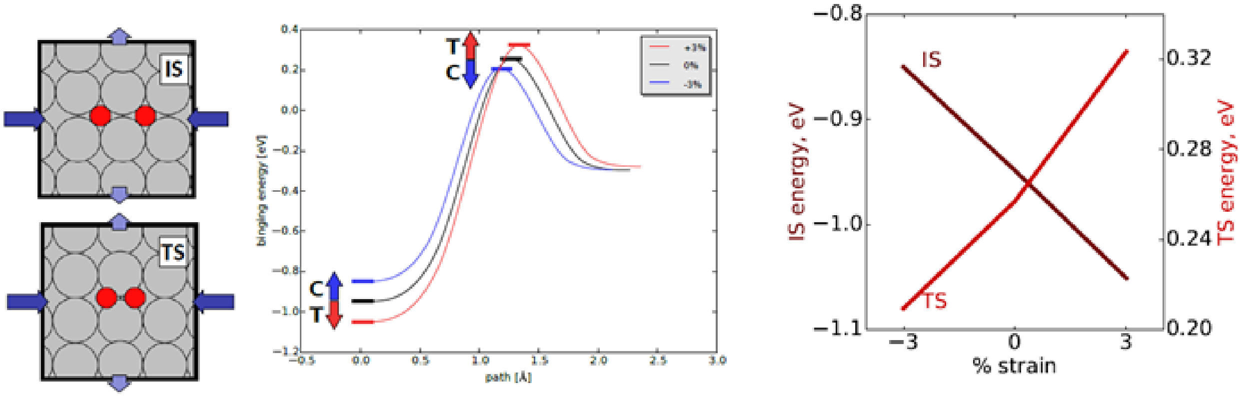


Figure 11. (a) Schematic of O2 association reaction initial state (IS) and transition state (TS). (b) Result of NEB calculations showing the response to compressive (C) and tensile (T) strain. (c) Response of IS and TS binding energies to strain.

As a second type of phenomenon, we examined surface self-diffusion of an adatom on a symmetric Cu 100 surface under uniaxial strain, as shown in 12. In this case, the most stable site for an adatom is the fourfold site, which serves as both the IS and final state (FS) for this reaction. However, although the surface is initially symmetric, we can expect the bridge site relating to diffusion inline (“**I**”) with the strain will behave very differently than that corresponding to diffusion transverse (“**T**”) to the strain, as the former feels a net expansion during compressive load and the latter feels only compression. Again, we performed CI-NEB to trace the minimum energy pathway of the elementary reaction, but this time we performed calculations in the simple EMT representation, which is well-suited for such problems. The results are shown in 13. For inline diffusion, this ends up being a very similar process to that described for the associative desorption process described above for diffusion in the direction parallel to the applied load: the IS feels the conventional response to strain, while the TS feels the reverse response, again representing an exception to TSS. However, for transverse diffusion, a conventional response would take place for the TS: that is, the bridge site will be subject to the same qualitative strain response as the fourfold IS site. Interestingly, this leads to the prediction that the surface diffusion should be strongly enhanced in the direction of the applied compressive load, and retarded in the direction orthogonal to this load.

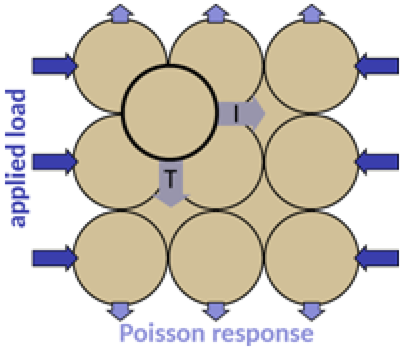


Figure 12. Cu monomer diffusion on Cu(100) surface.

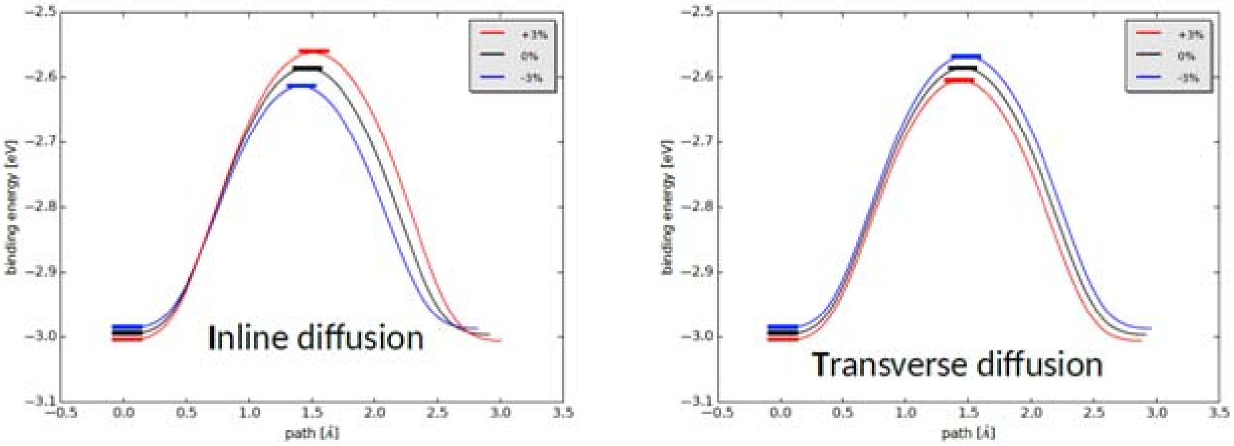


Figure 13. Energy pathway for (a) diffusion along the axis of applied load, and (b) diffusion perpendicular to the axis of applied load.

3.8 Towards Computational Discovery of Catalysts for CO_2 Electrochemical Reduction

Surface Coordination Number as Descriptor for CO_2 Reduction on Cu

Electroreduction of CO_2 is an attractive technology that recycles CO_2 into renewable fuels and useful chemicals [25]. Cu is the only metal that is capable of producing significant quantities of hydrocarbons from CO_2. However, high overpotentials (close to 1 V) and poor product selectivity (16 different products) are two outstanding problems on Cu [26, 27]. In order to overcome these two problems, surface engineering of Cu has been widely explored [28, 29]. Here, we propose a descriptor which can characterize the reactivity on possible Cu surface sites and more importantly predict a theoretical limit of overpotential on Cu. This work provides the roadmap and theoretical limit to lower the overpotential on Cu.

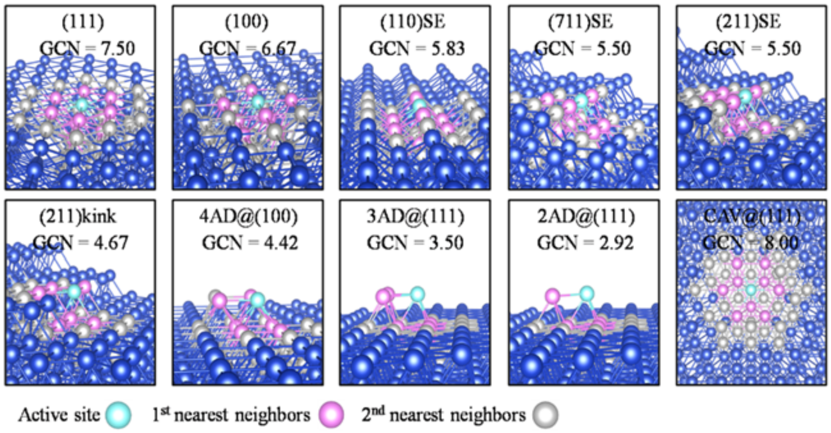


Figure 14. Catalog of active sites and generalized coordination number (GCN) on Cu.

It is well known that the activity of a surface site is correlated to its coordination number (*cn*), i.e., the number of its nearest neighbors. However, *cn* itself is not a good descriptor for CO_2 reduction. For example, the top sites on (110) and (211) step edges have the same (seven) nearest neighbors, but their reactivity for CO_2 reduction is orders of magnitude different [15]. Here, we propose that a generalized coordination number (GCN) can be used as a descriptor for CO_2 reduction, which is an extension of *cn* to include the 2^{nd} nearest neighbor contribution of an active site [30]:

$$\mathrm{GCN}(i)=\sum_{j=1}^{n_i}\frac{cn(j)}{cn_{\max}} \quad (4)$$

where j is the 1st nearest neighbor of the active site i; $cn_{\max}$ is the maximum number of j in bulk. To provide a wide range of possible GCN on Cu, we have included ten active sites as shown in Figure 14. A set of linear scaling relations between GCN and the binding energy of reaction intermediates on the ten active sites has been established for $CO_2 \rightarrow CH_4$ (Figure 15). The free energy of the reaction intermediates, therefore, can be calculated as a function of GCN as well. Based on the free energy-GCN relations, we can determine the limiting potential (U_L) for a given reaction step (e.g., $CO^* + [H^+ + e^-] \rightarrow CHO^*$) as a function of GCN:

$$U_{\mathrm{L}}=-\frac{G[\mathrm{CHO^*}]-G[\mathrm{CO^*}]-G[\mathrm{H^+ + e^-}](U=0\mathrm{V_{RHE}})}{e} \quad (5)$$

which can be used to construct the volcano plot (Figure 25). From the volcano plot, we observe that the overpotential for CH_4 production on Cu decreases with smaller GCN and approaches the volcano top when GCN equals to 3.1. The theoretical limit of the overpotential on Cu is thus estimated as 0.62 V, which is 35% lower than that on (111) surface and 14% lower than that on the (211) step edge. These findings suggest that there is room to further reduce overpotential on Cu by modifying its surface morphology. We predict that dimerized (111) Cu surface could reach the lowest-possible overpotential on Cu. However, to go beyond 0.62 V, one would have to either alloy Cu or applying strains (with core/shell NPs or active straining) to the surface.

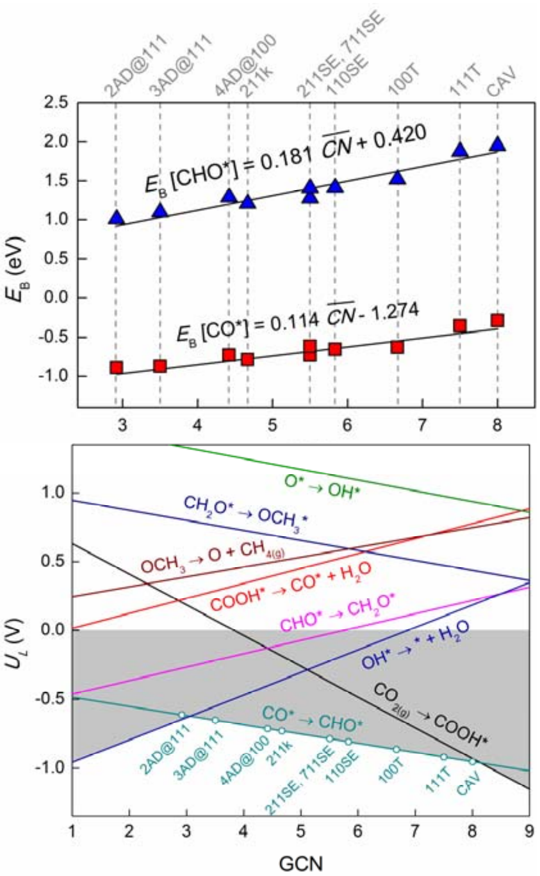


Figure 15. (Top) Binding energies of CO* and CHO* intermediates as a function of GCN. (Bottom) Activity volcano plot for CO_2 reduction to CH_4.

Computational Design of Catalysts for CO_2 Reduction to Formic Acid

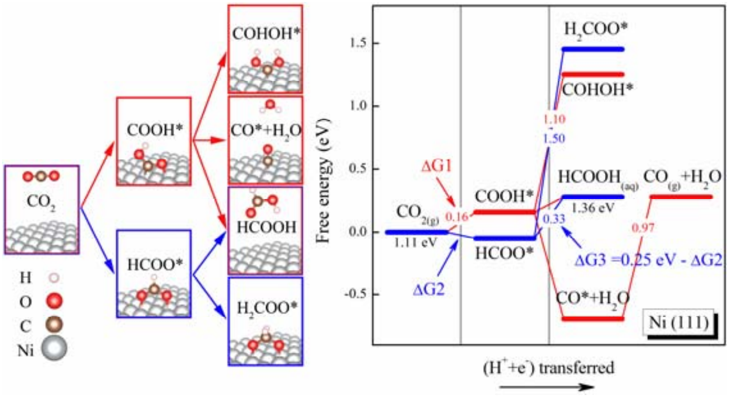


Figure 16. Reaction pathway and the free energy diagram for the reduction of CO_2 to HCOOH on Ni (111).

Ni and other metal catalysts such as Pt, Fe, and Co with strong binding to CO, are considered as poor catalysts for CO_2 reduction because CO can poison surface [27, 31, 32]. In this work, we provide theoretical insight into the mechanism of CO_2 reduction to formic acid on Ni (111) surface and explore possible routes to transform Ni into highly active and selective catalyst.

The reaction pathways and free energy diagram are displayed in Figure 16 obtained from first-principles calculations. There are two competing electrochemical pathways converting CO_2 to formic acid (HCOOH): via COOH* (red) and via HCOO* (blue). On Ni (111), the COOH* pathway is favored due to its lower overpotential (0.16 V) comparing to the HCOO* pathway (0.33 V). Along this preferred pathway, however, prior to the production of HCOOH, the intermediate (COOH*) has to be first reduced to CO* owing to the large free energy drop. The produced CO* is strongly bound to the surface and its desorption requires a very high overpotential of 1 V (Figure 16). Hence, CO* will poison Ni (111) surface and as a result, no HCOOH can be produced.

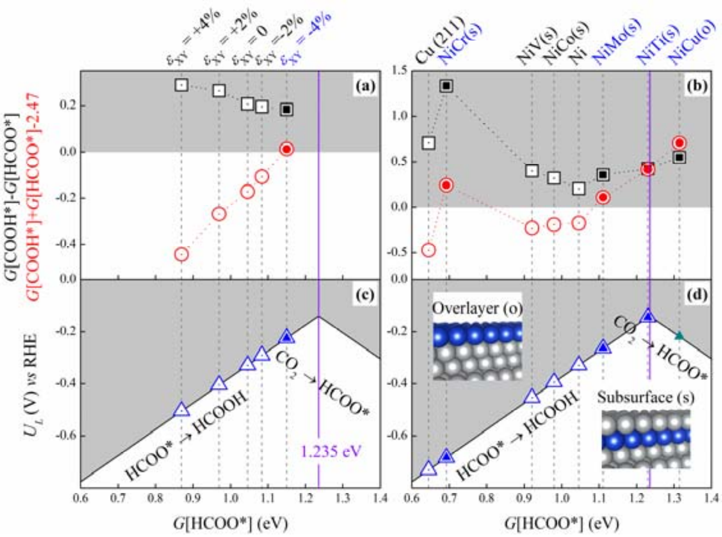


Figure 17. The free energy changes of the reaction intermediates (a) under biaxial strains and (b) for different NSAs. The data points above the zero line meet the design criteria. The corresponding volcano plots are shown in (c) and (d). Schematics for overlayer and subsurface NSAs are shown in insets.

We propose that CO poisoning can be eliminated by switching off the COOH* (blue) pathway and, simultaneously, by activating the HCOO* (red) pathway. To turn off the COOH* pathway on the "designed" catalyst, the limiting potential ΔG1 for the proton-transfer step: $CO_2 \rightarrow COOH^*$ must be higher than ΔG2 for the step: $CO_2 \rightarrow HCOO^*$ and ΔG3 for the step: $HCOO^* \rightarrow HCOOH$, as shown in the free energy diagram. Note that the adsorption of CO_2 and HCOOH is weak and their free energy is calculated as 1.11 and 1.36 eV, respectively [33]. Thus, ΔG3 is equal to 0.25 eV - ΔG2 and the following criteria are required to ensure 100% selectivity (selectivity criteria):

$$G[\mathrm{COOH}^*] - G[\mathrm{HCOO}^*] > 0 \tag{6}$$

$$G[\mathrm{COOH}^*] + G[\mathrm{HCOO}^*] - 2.47\ \mathrm{eV} > 0 \tag{7}$$

Furthermore, in order to achieve the lowest overpotential along the desirable HCOO* pathway, we require ΔG2 = ΔG3 (activity criterion):

$$G[\mathrm{HCOO}^*] = (G[\mathrm{CO}_2] + G[\mathrm{HCOOH}])/2 = 1.235\ \mathrm{eV} \tag{8}$$

Using both criteria, we can computationally design Ni-based catalysts for formic acid production. More specifically, the designed catalysts should activate the HCOO* pathway by satisfying the equation (6) and (7), and should meet the criterion (8) as close as possible. According to these criteria, two possibilities are emerged. The first is to compress pure Ni surface with > 4% biaxial strain (Figure 17a, c), which could turn Ni into highly selective and active catalyst. The second route is to form near-surface-alloys (NSAs) on Ni (Figure 27b, d). We predict that NiTi (Ti as subsurface) and NiCu (Cu as overlayer) NSAs are two promising catalysts for HCOOH production that have very low overpotentials (< 0.3V) and 100% selectivity.

References

1. Zheng, Yao, et al., *Advancing the Electrochemistry of the Hydrogen-Evolution Reaction through Combining Experiment and Theory.* Angewandte Chemie International Edition, 2015. **54**: p. 52-65.
2. Michalsky, Ronald, Yin-Jia Zhang, and Andrew A. Peterson, *Trends in the Hydrogen Evolution Activity of Metal Carbide Catalysts.* ACS Catalysis, 2014. **4**(5): p. 1274-1278.
3. Weissmüller, Jörg and Christian Lemier, *Lattice Constants of Solid Solution Microstructures: The Case of Nanocrystalline Pd-H.* Physical Review Letters, 1999. **82**(1): p. 213-216.
4. Deng, Qibo, Maxim Smetanin, and Jörg Weissmüller, *Mechanical modulation of reaction rates in electrocatalysis.* Journal of Catalysis, 2014. **309**(0): p. 351-361.
5. Greeley, Jeff, et al., *Hydrogen Evolution Over Bimetallic Systems: Understanding the Trends.* ChemPhysChem, 2006. **7**(5): p. 1032-1035.
6. Jeff Greeley, Thomas F. Jaramillo, Jacob Bonde, Ib Chorkendorff, Jens K. Nørskov, *Computational high-throughput screening of electrocatalytic materials for hydrogen evolution.* Nature Materials, 2006. **5**: p. 909-913.
7. Kibler, Ludwig A., et al., *Tuning Reaction Rates by Lateral Strain in a Palladium Monolayer.* Angewandte Chemie International Edition, 2005. **44**(14): p. 2080-2084.
8. Zhang, Sen, et al., *Tuning Nanoparticle Structure and Surface Strain for Catalysis Optimization.* Journal of the American Chemical Society, 2014. **136**(21): p. 7734-7739.
9. Lv, Haifeng, et al., *A New Core/Shell NiAu/Au Nanoparticle Catalyst with Pt-like Activity for Hydrogen Evolution Reaction.* Journal of the American Chemical Society, 2015. **137**(18): p. 5859-5862.
10. Monzo, J., et al., *Enhanced electrocatalytic activity of Au@Cu core@shell nanoparticles towards CO2 reduction.* Journal of Materials Chemistry A, 2015. **3**(47): p. 23690-23698.
11. Nørskov, J. K., et al., *Origin of the Overpotential for Oxygen Reduction at a Fuel-Cell Cathode.* The Journal of Physical Chemistry B, 2004. **108**(46): p. 17886-17892.
12. Nørskov, J. K., et al., *Universality in Heterogeneous Catalysis.* Journal of Catalysis, 2002. **209**(2): p. 275-278.
13. Zhang, Xu and Gang Lu, *Electronic origin of void formation in fcc metals.* Physical Review B, 2008. **77**(17): p. 174102.
14. Zhou, X. W., R. A. Johnson, and H. N. G. Wadley, *Misfit-energy-increasing dislocations in vapor-deposited CoFe/NiFe multilayers.* Physical Review B, 2004. **69**(14): p. 144113.
15. Chen, Zhengzheng, Xu Zhang, and Gang Lu, *Overpotential for CO2 electroreduction lowered on strained penta-twinned Cu nanowires.* Chemical Science, 2015. **6**(12): p. 6829-6835.
16. Stegelmann, Carsten, Anders Andreasen, and Charles T Campbell, *Degree of rate control: How much the energies of intermediates and transition states control rates.* Journal of the American Chemical Society, 2009. **131**(23): p. 8077-8082.
17. Nørskov, Jens Kehlet, et al., *Trends in the exchange current for hydrogen evolution.* Journal of the Electrochemical Society, 2005. **152**(3): p. J23-J26.
18. Nørskov, Jens Kehlet, Thomas Bligaard, and Jesper Kleis, *Rate control and reaction engineering.* Science, 2009. **324**(5935): p. 1655-1656.
19. Avanesian, Talin and Phillip Christopher, *Scaled Degree of Rate Control: Identifying Elementary Steps That Control Differences in Performance of Transition-Metal Catalysts.* ACS Catalysis, 2016. **6**: p. 5268-5272.
20. Sutton, Jonathan E and Dionisios G Vlachos, *A theoretical and computational analysis of linear free energy relations for the estimation of activation energies.* ACS Catalysis, 2012. **2**(8): p. 1624-1634.
21. Wang, Shengguang, et al., *Universal transition state scaling relations for (de) hydrogenation over transition metals.* Physical Chemistry Chemical Physics, 2011. **13**(46): p. 20760-20765.
22. Abild-Pedersen, Frank, et al., *Mechanisms for catalytic carbon nanofiber growth studied by ab initio density functional theory calculations.* Physical Review B, 2006. **73**(11): p. 115419.
23. Maark, Tuhina Adit and Andrew A. Peterson, *Understanding Strain and Ligand Effects in Hydrogen Evolution over Pd(111) Surfaces.* The Journal of Physical Chemistry C, 2014. **118**(8): p. 4275-4281.
24. Mavrikakis, M., B. Hammer, and J. K. Nørskov, *Effect of Strain on the Reactivity of Metal Surfaces.* Physical Review Letters, 1998. **81**(13): p. 2819-2822.
25. Jhong, Huei-Ru “Molly”, Sichao Ma, and Paul J. A. Kenis, *Electrochemical conversion of CO2 to useful chemicals: current status, remaining challenges, and future opportunities.* Current Opinion in Chemical Engineering, 2013. **2**(2): p. 191-199.
26. Kuhl, Kendra P., et al., *New insights into the electrochemical reduction of carbon dioxide on metallic copper surfaces.* Energy & Environmental Science, 2012. **5**(5): p. 7050-7059.

27. Kuhl, Kendra P., et al., *Electrocatalytic Conversion of Carbon Dioxide to Methane and Methanol on Transition Metal Surfaces.* Journal of the American Chemical Society, 2014. **136**(40): p. 14107-14113.
28. Tang, Wei, et al., *The importance of surface morphology in controlling the selectivity of polycrystalline copper for CO2 electroreduction.* Physical Chemistry Chemical Physics, 2012. **14**(1): p. 76-81.
29. Durand, William J., et al., *Structure effects on the energetics of the electrochemical reduction of CO2 by copper surfaces.* Surface Science, 2011. **605**(15–16): p. 1354-1359.
30. Calle-Vallejo, Federico, et al., *Finding optimal surface sites on heterogeneous catalysts by counting nearest neighbors.* Science, 2015. **350**(6257): p. 185-189.
31. Akhade, Sneha A., et al., *Poisoning effect of adsorbed CO during CO2 electroreduction on late transition metals.* Physical Chemistry Chemical Physics, 2014. **16**(38): p. 20429-20435.
32. Hori, Yoshio, et al., *Electrocatalytic process of CO selectivity in electrochemical reduction of CO2 at metal electrodes in aqueous media.* Electrochimica Acta, 1994. **39**(11): p. 1833-1839.
33. Peterson, Andrew A., et al., *How copper catalyzes the electroreduction of carbon dioxide into hydrocarbon fuels.* Energy & Environmental Science, 2010. **3**(9): p. 1311-1315.