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Major Goals: The overall objective of the research proposed was to develop a holistic understanding of energy transfer by direct photoexcitation of adsorbate-metal bonds on metal nanoparticle surfaces and the knowhow to exploit this phenomenon to manipulate reaction selectivity in a rational manner. The specific objectives are:
(1) Develop relationships between adsorbate/metal electronic structure and the impact of bond formation on the optical properties of sub 5-nanometer meal particles.
(2) Uncover governing factors that control the efficiency of direct energy transfer driven photocatalysis using adsorbates that are ubiquitous in heterogeneous catalysis.
(3) Demonstrate control of reaction selectivity by targeting adsorbate specific electronic transitions with monochromatic visible photon excitation.

Accomplishments: The first goal was to “Develop relationships between adsorbate/metal electronic structure and the impact of bond formation on the optical properties of sub 5-nanometer meal particles.” Accomplishments associated with this goal are described below.

Using a combination of in-situ diffuse reflectance UV-Vis spectroscopy and linear response time dependent density functional theory (DFT) calculations it was identified that the bond formed between Pt nanoparticles and CO molecules renormalizes the orbitals associated with these species, forming a dipole-allowable resonant electronic transition at ~2.7 eV (450 nm) from Pt−CO bonding orbitals with predominantly metal character to antibonding Pt−CO orbitals of mostly molecule character. On the other hand, it was found that the formation of a bond between Pt nanoparticles and an O atom does not renormalize orbitals to allow for electronic transitions localized on this bond. This is due to the diffuse nature of the orbitals involved in Pt-O bond formation, which is differentiated from the more localized orbitals involved in Pt-CO bond formation.

The second goal was to “Uncover governing factors that control the efficiency of direct energy transfer driven photocatalysis using adsorbates that are ubiquitous in heterogeneous catalysis.” Accomplishments associated with this goal are described below.

Using CO oxidation under kinetically controlled conditions where the rate is strictly limited by the activation of Pt-CO bonds to free Pt sites for O_2 dissociation it was found that 450 nm photoexcitation was more efficient for driving Pt-CO bond breaking as compared to 400 nm or 600 nm photons. For example, efficiency for Pt-CO bond breaking was ~1.4x greater for 450 nm photons than 400 nm photons and 3x greater than 600 nm photons. A similar resonant phenomenon was not observed for the H_2 oxidation reaction under kinetically controlled conditions where the H_2 oxidation rate was controlled by the rate of Pt-O bond activation. Instead, the rate of photocatalytic Pt-O activation was controlled by the light absorption properties of bulk Pt. The results indicate that the resonant electronic transitions existing at Pt-CO bonds allow for an efficient bond-breaking pathway that does not exist in off resonant conditions, or for the activation of Pt-O bonds. Further it was demonstrated that the efficiency of photon driven catalysis at metal surfaces driven by photoexcitation of electronic transitions and metal-adsorbate interfaces is enhanced significantly by reducing the size of the nanoparticle. It is hypothesized that the increase surface area to volume ratio found with decreasing nanoparticle sizes geometrically provides a larger probability for excitation electronic transitions at the nanoparticle surface. Thus, it was identified that if a metal-adsorbate bond can be characterized by localized bonding and anti-bonding states that span the system Fermi level and that small (< 5 nm diameter) nanoparticles are used as photocatalysts, then direct photoexcitation of the metal adsorbate bond is the most efficient mechanism of bond activation.

The third major goal of this research was to “Demonstrate control of reaction selectivity by targeting adsorbate specific electronic transitions with monochromatic visible photon excitation.” Accomplishments associated with this goal are described below.

It was demonstrated that the unique resonant electronic transitions existing at Pt-CO interfaces, which do not exist at Pt-O bonds could be exploited to control the outcome of the preferential CO oxidation reaction. In this reaction a small amount of CO in an H_2 rich stream is desired to be oxidized by O_2 to produce a highly pure H_2 stream for fuel cell applications. We demonstrated that 450 nm photoexcitation of 2.3 nm Pt nanoparticles operating preferential CO oxidation induced a 40% increase in CO_2 production selectivity (from 40 to 80%). A similar impact was not observed on larger particles, or off resonant excitation, corroborating our hypothesized mechanism of selectivity control by photoexcitation of targeted bonds.

Following our achievement of the project goals, we were interested in understanding how the local geometry of metal sites creating bonds with the adsorbates influenced the photoexcitation process. Before addressing this question we needed to develop quantitative insights into the nature and distribution of exposed metal sites on metal nanostructures. This issue is complicated by the reconstruction of metal surfaces that is induced reactive adsorption. To address this we developed approaches to quantitatively measure the distribution of different exposed metal (Pt) site geometries on nanoparticles of varying size before and after molecular (CO) adsorption.

A quantitative IR spectroscopy approach was developed to identify the fraction of exposed Pt sites existing as well-coordinated and under-coordinated Pt atoms, by exploiting site specific vibrational frequencies of CO bound to each type of site, deconvoluting and integrating the contributions of site specific vibrational stretches to the IR spectra and normalizing the relative intensities by the site-specific extinction coefficients for each stretch. Using this measurement approach we calculated that at room temperature 1.8 nm Pt nanoparticles have 39% of exposed atoms existing as well-coordinated sites and 61% as under-coordinated sites, whereas 17 nm Pt particles have 77% terrace sites and 23% defect sites, in quantitative agreement with predictive geometric models. The agreement between IR based analysis of site distributions and the predictive geometric model justifies the quantitative nature of the approach.

Using our approach, it was identified that as temperature was raised for Pt nanoparticles with saturation coverage of CO, the IR stretch associated with adsorption on under-coordinated Pt sites increased in intensity, suggesting reconstruction that is consistent with particle roughening. The roughening increased defect site density by 5-20% dependent on particle size and conditions. By exploiting quantitative IR measurements under CO oxidation conditions where the Pt surface was poisoned in CO the well-coordinated Pt site density on working catalysts was correlated to turn over frequency for the reaction, conclusively demonstrating that CO oxidation occurs on well coordinated Pt atoms when operating at CO saturation conditions (these conditions are common in PEM cells with >100 PPM CO, in automotive catalytic convertors and were used for our photocatalysis studies).

To understand the CO induced Pt nanoparticle surface reconstruction at an atomic level, DFT calculations of Pt surface energies for various facets as a function of CO coverage were executed. The calculations showed that at saturation CO coverage, (100) facets of Pt reconstruct into “roughened” surfaces, while (111) facets stay intact. To visually corroborate the predications in-situ scanning transmission electron microscopy was utilized to observe Pt nanoparticle reconstruction due to CO adsorption. Atomic resolution images showed almost quantitative agreement with theoretical predictions, providing evidence of the proposed facet selective adsorbate induced reconstruction. These results were further corroborated by using quantitative IR. The quantitative agreement between calculations and IR measurements, accompanied by the visual agreement between calculations and microscopy provide convincing evidence that we have completely described the structure of Pt nanoparticles following CO induced roughening, where (100) facets reconstruct into higher index facets, while (111) facets remain intact. These results strongly suggest that in our examination of photons activating Pt-CO bonds through resonant photoexcitation, we were observing photochemistry associated with CO molecules adsorbed to (111) facets.

Training Opportunities: Matthew Kale and Talin Avanesian were the primary PhD students involved in this project. Through execution of the project each of them gained significant fundamental understanding of phenomena controlling catalytic and photocatalytic processes on metal nanostructures. Matthew Kale was trained in: (1) the synthesis of catalytic metal particles with controlled sizes, (2) execution of wavelength and intensity dependent photocatalytic measurements, (3) execution of kinetic measurements of thermocatalytic processes, (4) the use of in-situ IR and UV-Vis spectroscopy for understanding interactions at adsorbate-metal interfaces and (5) the use of in-situ IR to provide quantitative measurements of metal reconstruction and site distributions at the metal surface. Talin Avanesian was trained in: (1) using electronically excited state density functional theory based calculations for understanding potential energy surfaces associated with adsorbate motion on metal surface in response to photoexcitation, (2) coupling first principles calculations with inelastic scattering calculations to predict wavelength resolved photocatalytic measurements, (3) using density functional theory calculations to examine adsorbate induced reconstruction of metal surfaces. Both Talin and Matt were also trained in the dissemination of scientific results through authoring publications and delivering scientific lectures at national meetings. Both Talin and Matt completed their Dissertations and earned PhD’s in part based on their work on this project.

Results Dissemination: 6 papers were published in top journals in the field of physical chemistry, materials, and catalysis (JPC Lett, JPCC, ACS Cat, JACS, Nano Lett, Ann Rev Phys Chem) based on the research performed for this project.

15 Invited and 8 contributed lectures at national meetings (ACS, MRS), department seminars (Ohio U, UCLA, UCI, ASU) and international meetings (Pacifichem, DIET-15, Chemical Reactions Under External Fields) were delivered based on the research performed for this project.

Honors and Awards: PI Received NSF CAREER Award

Matthew Kale received the Dissertation Year Fellowship (2015-2016) and Graduate Research Mentorship Fellowship (2014-2015) from University of California, Riverside.

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Technology Transfer: Nothing to Report

PARTICIPANTS:

Participant Type: Graduate Student (research assistant)
Participant: Matthew J Kale
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: Talin Avanesian
Person Months Worked: 5.00 **Funding Support:**
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RPPR Final Report
as of 06-Jul-2018

Participant Type: PD/PI
Participant: Phillip Christopher
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Authors: Talin Avanesian
Acknowledged Federal Support: **N**

Project Summary - Grant # W911NF-14-1-0347
(Reporting Period: September 2014 – September 2017)

Chemical transformations via photon induced metal-to-molecule electron transfer on metal nanocrystal surfaces

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Objective

In this project we are broadly studying the impact of visible photon excitation on the rate and selectivity of catalytic processes at metal nanoparticle surfaces. We are specifically interested in the possibility of photons exciting electronic transitions localized at adsorbate-metal nanoparticle interfaces and the potential exploitation of these events to control the outcome of selective catalytic reactions. It is hypothesized that resonant electronic transitions at adsorbate metal interfaces may be ubiquitous, with resonant energies and transition dipole strengths depending on characteristics of the bond being formed (on the metal and adsorbate). Further it is hypothesized that by matching the energy of a photon flux to resonant photoexcitation energy of targeted adsorbate metal bonds, the outcome of chemical process could be controlled. The proposed research is intended to introduce novel selective pathways for important fuel and chemical production reactions that cannot be achieved with current classes of heterogeneous electron, photon or thermally driven catalytic processes. *The overall objective of the research proposed here is to develop a holistic understanding of catalysis by direct photoexcitation of adsorbate-metal bonds on metal nanoparticle surfaces and the knowhow to exploit this phenomenon to manipulate reaction selectivity in a rational manner. The specific objectives are:*

(1) Develop relationships between adsorbate/metal electronic structure and the impact of bond formation on the optical properties of sub 5-nanometer meal particles.
(2) *Uncover governing factors that control the efficiency of direct photoexcitation driven photocatalysis using adsorbates that are ubiquitous in heterogeneous catalysis.*
(3) *Demonstrate control of reaction selectivity by targeting adsorbate specific electronic transitions with monochromatic visible photon excitation.*

Accomplishments (The results describe below were previously published in: *Nano Letters*, **2014**, 14, 5405-5412; *J. Phys. Chem. C*, **2014** 118, 28017-28031; *ACS Catalysis*, **2016**, 6, 5599-5609; *Journal of the American Chemical Society*, **2017**, 139, 4551-4558; *Annual Review of Physical Chemistry*, **2017**, 68, 379-398; *Journal of Physical Chemistry Letters*, **2017**, 8, 2526-2534)

The transfer of energy from a photon flux to an adsorbate molecule, which could then result in chemical conversion, can occur through three primary pathways: (1) substrate mediated photoexcitation, (2) direct photon absorption by homo-lumo states in the adsorbate and (3) direct photon absorption by hybrid states localized at the metal-adsorbate bond. Substrate mediated photoexcitation of adsorbates or adsorbate−metal bonds occurs through photon absorption in the metal bulk, creating a distribution of energetic electrons and holes that undergo carrier−carrier scattering while migrating toward the surface, where they transiently transfer into unoccupied adsorbate resonances, see Figure 1(A). Direct photoexcitation of intramolecular HOMO−LUMO transitions in weakly chemisorbed systems resembles photoexcitation of their gas phase counterparts, although electronic states are typically broadened and stabilized and exhibit reduced band gaps, see Figure 1(B). Hybridization between metal d-states and molecular states forms bonding and antibonding states through either charge donation from the adsorbate or back-donation from the metal, which can be directly photoexcited, Figure 1(C). While mechanisms (1) and (2), above, have thoroughly been demonstrated to drive photochemistry on metal surfaces, to the involvement of mechanism (3) in photon-mediated catalysis at metal surfaces has been scarcely discussed. This mechanism has the potential to exhibit resonant photochemistry in the visible photon range, enabling control over the outcome of chemical reactions by targeted activation of adsorbate-metal bond with photons.

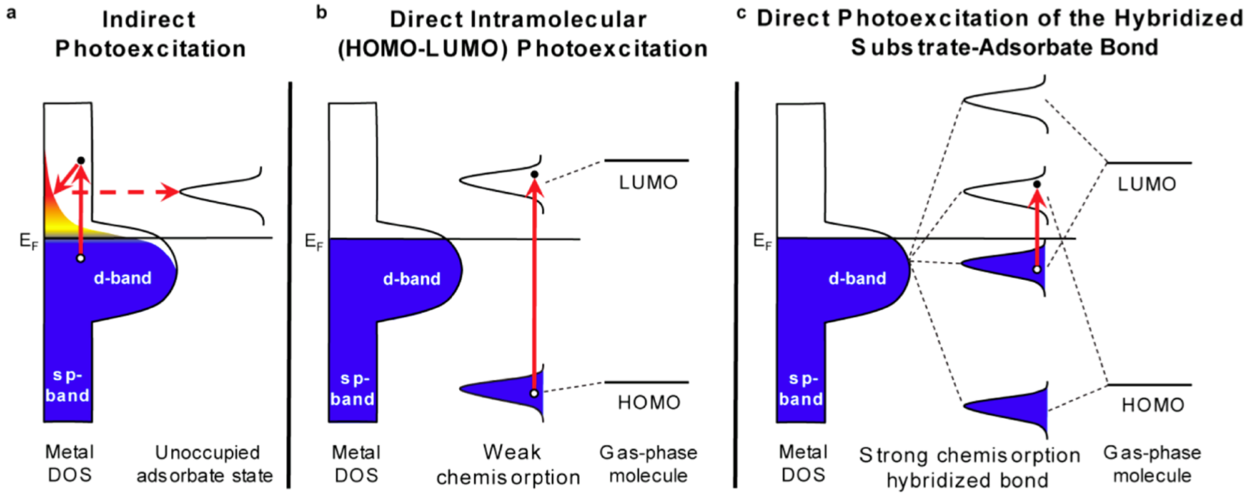

Figure 1. Schematic of adsorbate or adsorbate−metal bond photoexcitation on metal surfaces. (a) Substrate mediated photoexcitation of adsorbates or adsorbate−metal bonds. (b) Direct photoexcitation of intramolecular HOMO−LUMO transitions in weakly chemisorbed systems. (c) Direct photoexcitation of bonds formed between metal surfaces and strongly chemisorbed adsorbates involves resonant electronic transitions between hybridized metal and adsorbate states. Adapted from *Nano Letters*, **2014**, 14, 5405-5412.

The first goal of this project was to "Develop relationships between adsorbate/metal electronic structure and the impact of bond formation on the optical properties of sub 5-nanometer meal particles." Accomplishments associated with this goal are described below.

Figure 2(A) shows *in-situ* diffuse reflectance UV-Vis absorption spectra on 2.3 nm Pt clusters that are clean (no adsorbates) covered in CO and covered in O. The difference spectra between the clean and adsorbate covered Pt nanoparticles are shown in Figure 2(B), where it is clearly seen that CO induces new electronic transitions forming a dipole-allowable resonant electronic transition at ~2.7 eV (450 nm), whereas O adsorption has very little influence on the Pt cluster optical absorption. Using linear response time dependent density functional theory (DFT) calculations it was identified that the bond formed between Pt nanoparticles and CO molecules renormalizes the orbitals associated with these species, introducing resonant electronic transition from Pt−CO bonding orbitals with predominantly metal character to antibonding Pt−CO orbitals of mostly molecule character, Figure 2(C). The DFT predicted energy is ~0.6 eV lower than the observed transition which is within reasonable error, given the simplicity of the model system. On the other hand, it was found that the formation of a bond between Pt nanoparticles and an O atom does not renormalize orbitals to allow for electronic transitions localized on this bond, Figure 2(C). This is due to the diffuse nature of the orbitals involved in Pt-O bond formation, which is differentiated from the more localized orbitals involved in Pt-CO bond formation. Thus it was demonstrated that the formation of metal adsorbate bonds could influence the optical properties of small metal clusters by introducing new interfacial electronic transitions and that this process is highly dependent on the nature of the molecule.

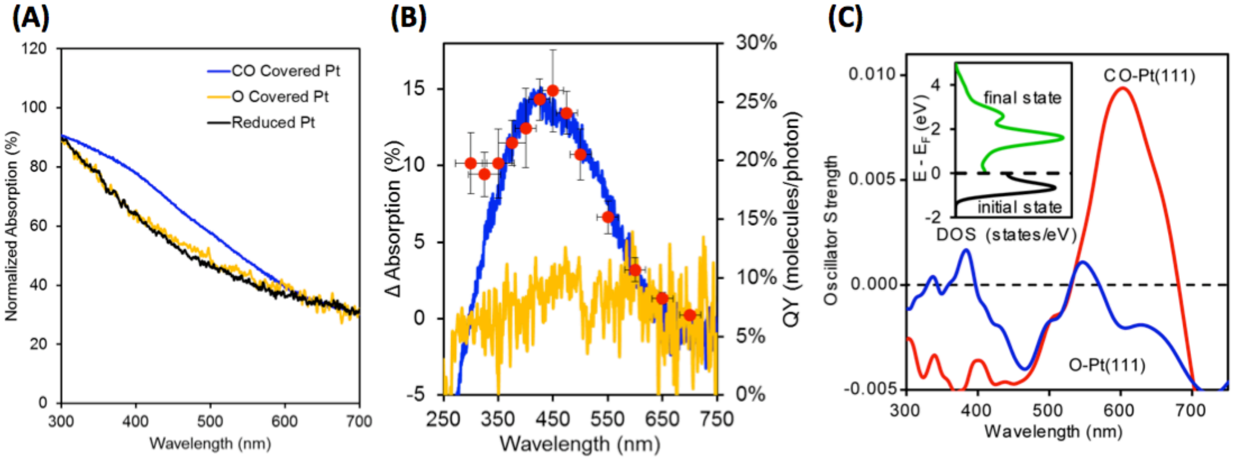

Figure 2. The influence of CO and O adsorption on the optical properties of 2.3 nm Pt clusters. (A) *in-situ* diffuse reflectance UV-Vis absorption spectra of 2.3 nm Pt clusters in a reduced (adsorbate free), O covered and CO covered condition. (B) Difference spectra calculated from (A) showing the influence of CO and O adsorption on the absorption spectra of the Pt particles. (C) linear response time dependent DFT calculations of the oscillator strengths for adsorbate induced electron excitations on a Pt(111) surface. The inset shows the electronic states involved in the resonant electronic transitions localized at the Pt-CO interface. Adapted from *Nano Letters*, **2014**, 14, 5405-5412.

The second goal was to "Uncover governing factors that control the efficiency of direct energy transfer driven photocatalysis using adsorbates that are ubiquitous in heterogeneous catalysis." Accomplishments associated with this goal are described below.

Using CO oxidation under kinetically controlled conditions where the rate is strictly limited by the activation of Pt-CO bonds to free Pt sites for O_2 dissociation it was found that 450 nm photoexcitation was more efficient for driving Pt-CO bond breaking as compared to 400 nm or 600 nm photons, but only when using small (< 5 nm) Pt nanoparticles as photocatalysts, see Figure 3(A). For example, efficiency for Pt-CO bond breaking was ~1.4x greater for 450 nm photons than 400 nm photons and 3x greater than 600 nm photons. When using larger Pt particles a majority of photons are absorbed in the Pt bulk and thus can only drive chemistry through a substrate-mediated mechanism shown in Figure 1(A). A similar resonant phenomenon was not observed for the H_2 oxidation reaction under kinetically controlled conditions where the H_2 oxidation rate was controlled by the rate of Pt-O bond activation. Instead, the rate of photocatalytic Pt-O activation was controlled by the light absorption properties of bulk Pt, regardless of Pt particle size, see Figure 3(B).

The results indicate that the resonant electronic transitions existing at Pt-CO bonds allow for an efficient bond-breaking pathway that does not exist in off resonant conditions, or for the activation of Pt-O bonds. Further it was demonstrated that the efficiency of photon driven catalysis at metal surfaces driven by photoexcitation of electronic transitions and metal-adsorbate interfaces is enhanced significantly by reducing the size of the nanoparticle. It is hypothesized that the increase surface area to volume ratio found with decreasing nanoparticle sizes geometrically provides a larger probability for excitation electronic transitions at the nanoparticle surface. Thus, it was identified that if a metal-adsorbate bond can be characterized by localized bonding and anti-bonding states that span the system Fermi level and that small (< 5 nm diameter) nanoparticles are used as photocatalysts, then direct photoexcitation of the metal adsorbate bond is the most efficient mechanism of bond activation.

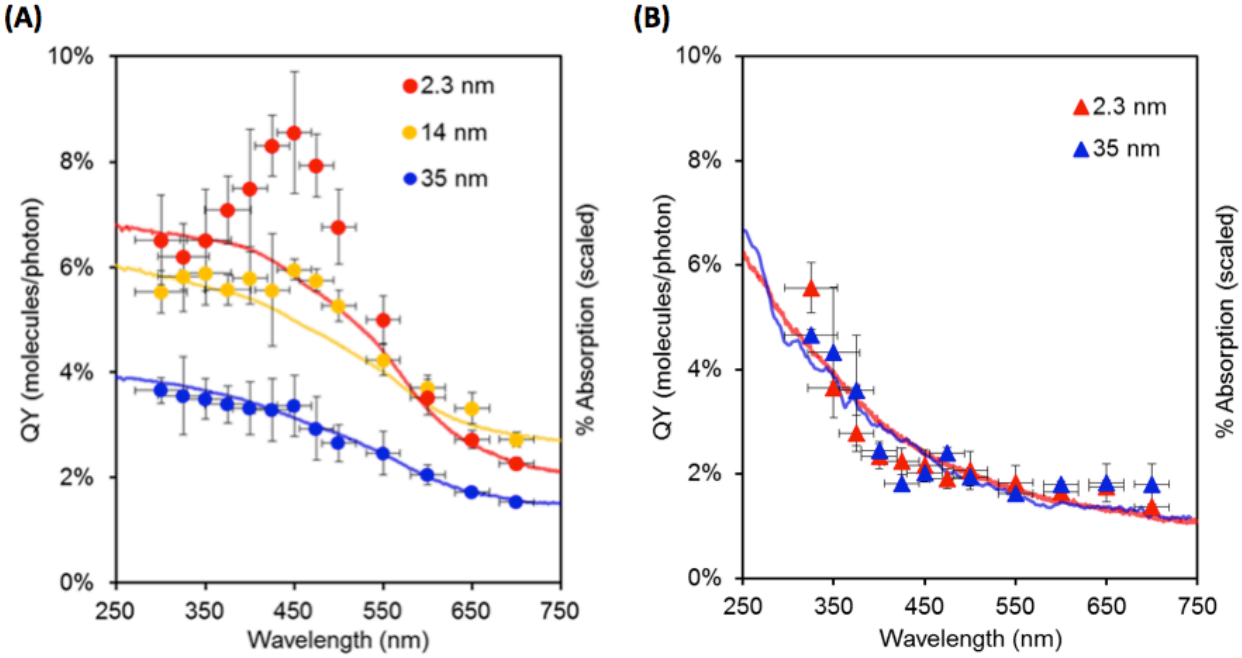

Figure 3. The influence of Pt particle size on Pt-CO and Pt-O bond activation by photoexcitation. (A) Quantum Yield (QY) for Pt-CO bond activation (measured via CO oxidation) as a function of photon excitation wavelength for Pt particles of varying size. (B) QY for Pt-O bond activation (measure via H_2 oxidation) as a function of photon excitation wavelength for Pt particles of varying size. The solid lines in each plot represent the absorption spectra measured for each catalyst under reaction conditions.

The third major goal of this research was to "Demonstrate control of reaction selectivity by targeting adsorbate specific electronic transitions with monochromatic visible photon excitation." Accomplishments associated with this goal are described below.

It was demonstrated that the unique resonant electronic transitions existing at Pt-CO interfaces, which do not exist at Pt-O bonds could be exploited to control the outcome of the preferential CO oxidation reaction. In this reaction a small amount of CO in an H_2 rich stream is desired to be oxidized by O_2 to produce a highly pure H_2 stream for fuel cell applications. We demonstrated that 450 nm photoexcitation of 2.3 nm Pt nanoparticles operating preferential CO oxidation induced a 40% increase in CO_2 production selectivity (from 40 to 80%), Figure 4(A). A similar impact was not observed on larger particles, or off resonant excitation, corroborating our hypothesized mechanism of selectivity control by photoexcitation of targeted bonds. Detailed measurements of the CO_2 and H_2O production pathways during these experiments show that the primary influence of photons was to promote CO_2 production uniquely on the smallest Pt nanoparticles, Figure 4(B). This provides very strong evidence that photons can be used to control the outcome of catalytic processes at small metal nanoparticle surfaces via selective energy deposition into targeted reaction pathways.

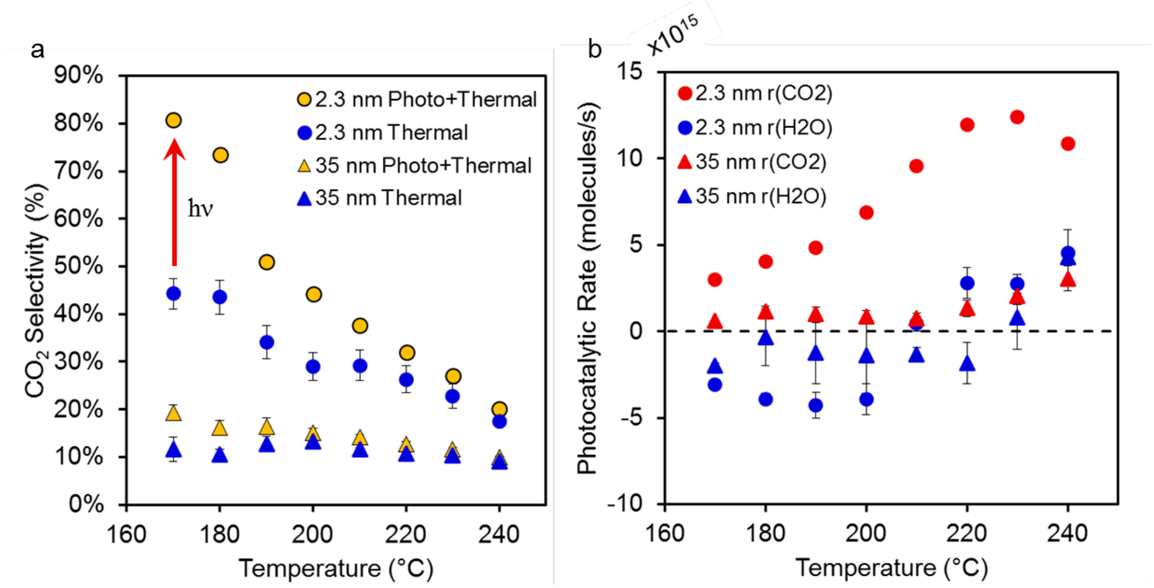

Figure 4. Controlling selectivity in preferential CO oxidation via photon excitation. (A) CO_2 selectivity, H_2O is the other possible product, as a function of operating temperature for 2.3 and 35 nm Pt particles in the dark and under 450 nm illumination. (B) Photocatalytic rate of CO_2 and H_2O formation as a function of reaction temperature for the measurements shown in (A). Adapted from *Nano Letters*, **2014**, 14, 5405-5412.

The findings associated with the induced optical effects caused by O and CO adsorption on Pt clusters and the resulting use of this to efficiently drive and control catalysis was then expanded to more complicated reactions such as benzyl alcohol dehydrogenation, benzyl amine oxidative coupling and heck coupling demonstrating the use of this approach to control a range of chemistries over small metal nanoparticles (*Journal of Physical Chemistry Letters*, **2017**, 8, 2526-2534). Various features of this mechanism and applications for driving catalysis were also described in the following publications (*J. Phys. Chem. C*, **2014** 118, 28017-28031; *Annual Review of Physical Chemistry*, **2017**, 68, 379-398).

Following our achievement of the primary project goals, we were interested in understanding how the local geometry of metal sites creating bonds with the adsorbates influenced the photoexcitation process. Before addressing this question we needed to develop quantitative insights into the nature and distribution of exposed metal sites on metal nanostructures. This issue is complicated by the reconstruction of metal surfaces that is induced reactive adsorption. To address this we developed approaches to quantitatively measure the distribution of different exposed metal (Pt) site geometries on nanoparticles of varying size before and after molecular (CO) adsorption.

A quantitative IR spectroscopy approach was developed to identify the fraction of exposed Pt sites existing as well-coordinated and under-coordinated Pt atoms, by exploiting site specific vibrational frequencies of CO bound to each type of site, deconvoluting and integrating the contributions of site specific vibrational stretches to the IR spectra and normalizing the relative intensities by the site-specific extinction coefficients for each stretch, Figure 5(A). Using this measurement approach we calculated that at room temperature 1.8 nm Pt nanoparticles have 39% of exposed atoms existing as well-coordinated sites and 61% as under-coordinated sites, whereas 17 nm Pt particles have 77% terrace sites and 23% defect sites, in quantitative agreement with predictive geometric models. The agreement between IR based analysis of site distributions and the predictive geometric model justifies the quantitative nature of the approach.

Using our approach, it was identified that as temperature was raised for Pt nanoparticles with saturation coverage of CO, the IR stretch associated with adsorption on under-coordinated Pt sites increased in intensity, suggesting reconstruction that is consistent with particle roughening, Figure 5(B). The roughening increased defect site density by 5-20% dependent on particle size and conditions. By exploiting quantitative IR measurements under CO oxidation conditions where the Pt surface was poisoned in CO the well-coordinated Pt site density on working catalysts was correlated to turn over frequency for the reaction, conclusively demonstrating that CO oxidation occurs on well coordinated Pt atoms when operating at CO saturation conditions (these conditions are common in PEM cells with >100 PPM CO, in automotive catalytic convertors and were used for our photocatalysis studies), Figure 5(C).

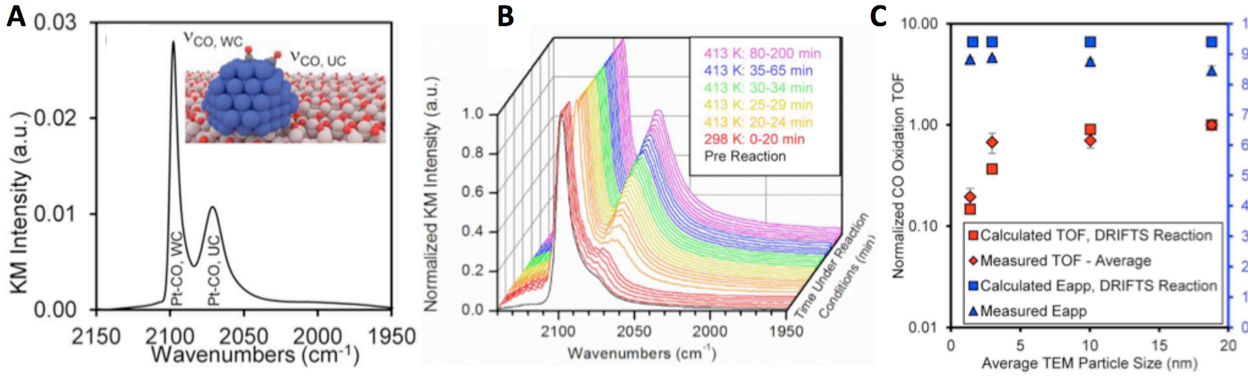

Figure 5. (A) FTIR measurement of CO adsorbed at saturation coverage to Pt clusters, showing a stretch associated CO on well-coordinated (WC) Pt atoms and undercoordinated (UC) Pt atoms. (B) *In-situ* IR measurements on CO covered Pt nanoparticle showing the increase in the band associated with CO on UC sites, suggesting Pt reconstruction. (C) A comparison between the measured and model predicted (from IR measurements and DFT calculations) CO oxidation

turn over frequency (TOF) and activation energy Ea as a function of Pt particle size. Adapted from *ACS Catalysis*, **2016**, 6, 5599-5609.

To understand the CO induced Pt nanoparticle surface reconstruction at an atomic level, DFT calculations of Pt surface energies for various facets as a function of CO coverage were executed. The driving force for adsorbate-induced reconstruction is the reduction in surface free energy of normally high energy facets due to strongly exothermic adsorption, Figure 6(A). Coverage increased above 1 for higher index facets, because a coverage of 1 correlates to CO saturation of all the lowest coordination number exposed adsorption sites for each facet. It is seen from these calculations that for the bare Pt surface, the (111) and (100) facets are most stable and thus will comprise most of the catalyst surface area. However, at CO saturation coverage (the lowest energy coverage on each facet) the (111) is still the most stable facet, while the (100) facet now competes with "roughened" higher miller index facets, Figure 6(B). Images of the various surface facets at CO coverage identified as the minimum energy are shown in Figure 6(C).

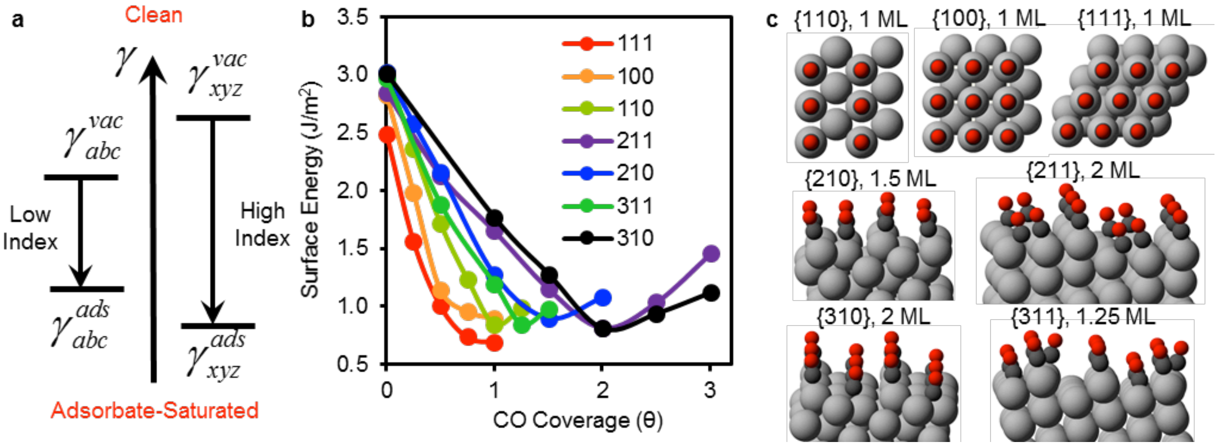

Figure 6. Calculation of bare and CO-saturated surface free energies for various Pt facets. **A)** Schematic diagram depicting the driving force for adsorbate-induced reconstruction of surfaces through modification of competing facet surface energies. **B)** DFT-calculated CO coverage dependent surface energy of various Pt surface facets. **C)** Models of various Miller indices of Pt slabs at the identified saturation CO coverage. Adapted from *Journal of the American Chemical Society*, **2017**, 139, 4551-4558.

To visually corroborate the predications *in-situ* scanning transmission electron microscopy (STEM) was utilized to observe Pt nanoparticle reconstruction due to CO adsorption. Wulff constructions (thermodynamic energy minimization of particle shape based on the surface energies of competing surface facets) for a clean and CO covered Pt particle are shown in Figure 7(A) and (B) respectively. It is clearly seen that DFT calculations predict a facet selective reconstruction of {100} facets into higher miller index planes, while (111) facets are largely intact. It is also observed that the {100} reconstruction causes the growth of a new atomic layer of Pt on top of the particle. It is seen that in agreement with the DFT predictions, a facet selective CO induced reconstruction is observed via *in-situ* STEM imaging upon the adsorption of CO to a Pt nanoparticle that results in the growth of a new layer of Pt atoms on the top {100} facet. The simulated STEM images associated with the CO induced reconstruction, based on DFT calculated Wulff constructions, are in excellent agreement with the experimental STEM.

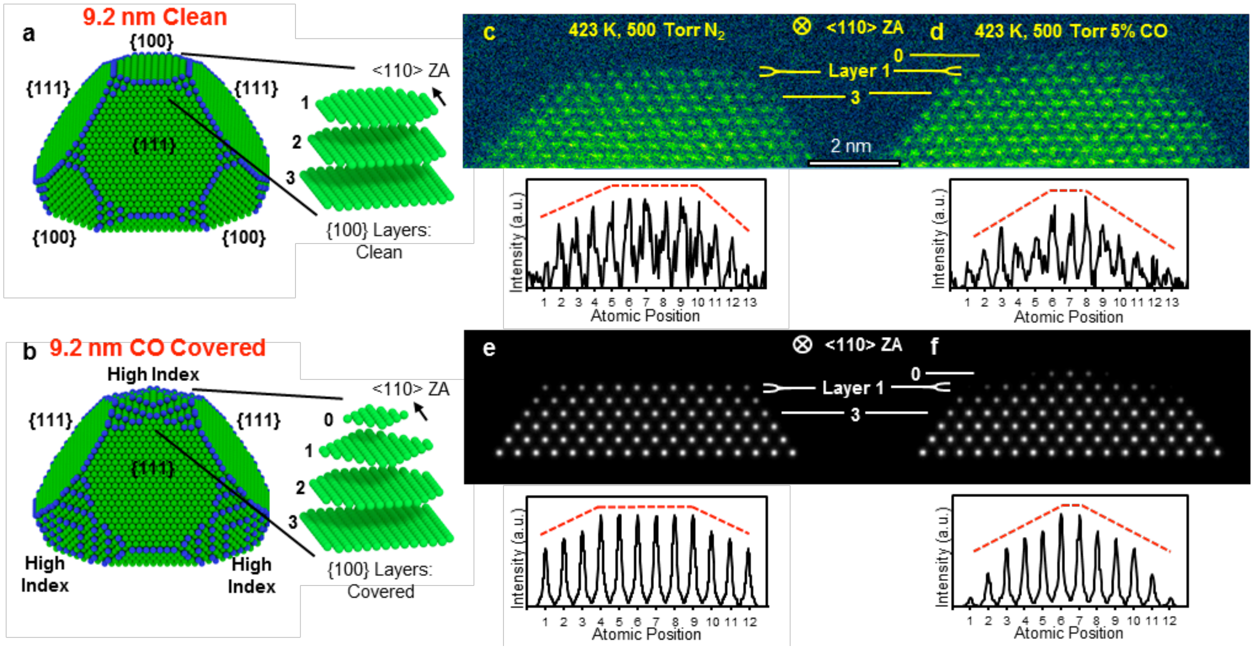

Figure 7. Visual comparison of DFT-calculated and *in-situ* STEM measurements of facet-specific CO induced Pt nanoparticle surface reconstruction. Wulff constructions of a 9.2 nm Pt particle based on DFT calculated surface free energies for **A)** bare surfaces, and **B)** CO saturated surfaces. Both images are tilted slightly off the <110> zone axis (ZA). The green atoms represent WC Pt atoms, and the blue atoms represent UC Pt edge and corner atoms. The layers to the right are the top 3-4 {100} layers of the particle model, with the <110> zone axis going into the page. STEM images of a 9 nm Pt particle taken along the <110> zone axis **C)** at 423 K in 500 Torr N_2, and **D)** at 423 K in 500 Torr of 5% CO in Ar (25 Torr CO). Layers 0 (for **D** only), 1, and 3 are labeled in each image for comparison. Below each image is the intensity analysis for layer 1 of each corresponding image. Each peak corresponds to an atomic column along the <110> zone axis. Simulated STEM-HAADF image based on layers 0-6 of the {100} facets of the **E,** clean and **F,** CO saturated 9.2 nm Wulff constructions, along with the corresponding intensity analysis of layer 1 for each particle. Adapted from *Journal of the American Chemical Society*, **2017**, 139, 4551-4558.

These results were further corroborated by using quantitative IR, examining the reconstruction of Pt particles of varying size due to the adsorption of CO, Figure 8 (A-C). All spectra show clear evidence of CO induced roughening of Pt surfaces due to increase in the intensity of the low frequency mode. Figure 8(D) shows a quantitative agreement between the IR measurements and DFT predictions of CO induced reconstruction as a function of particle size. The quantitative agreement between calculations and IR measurements, accompanied by the visual agreement between calculations and microscopy provide convincing evidence that we have completely described the structure of Pt nanoparticles following CO induced roughening, where (100) facets reconstruct into higher index facets, while (111) facets remain intact.

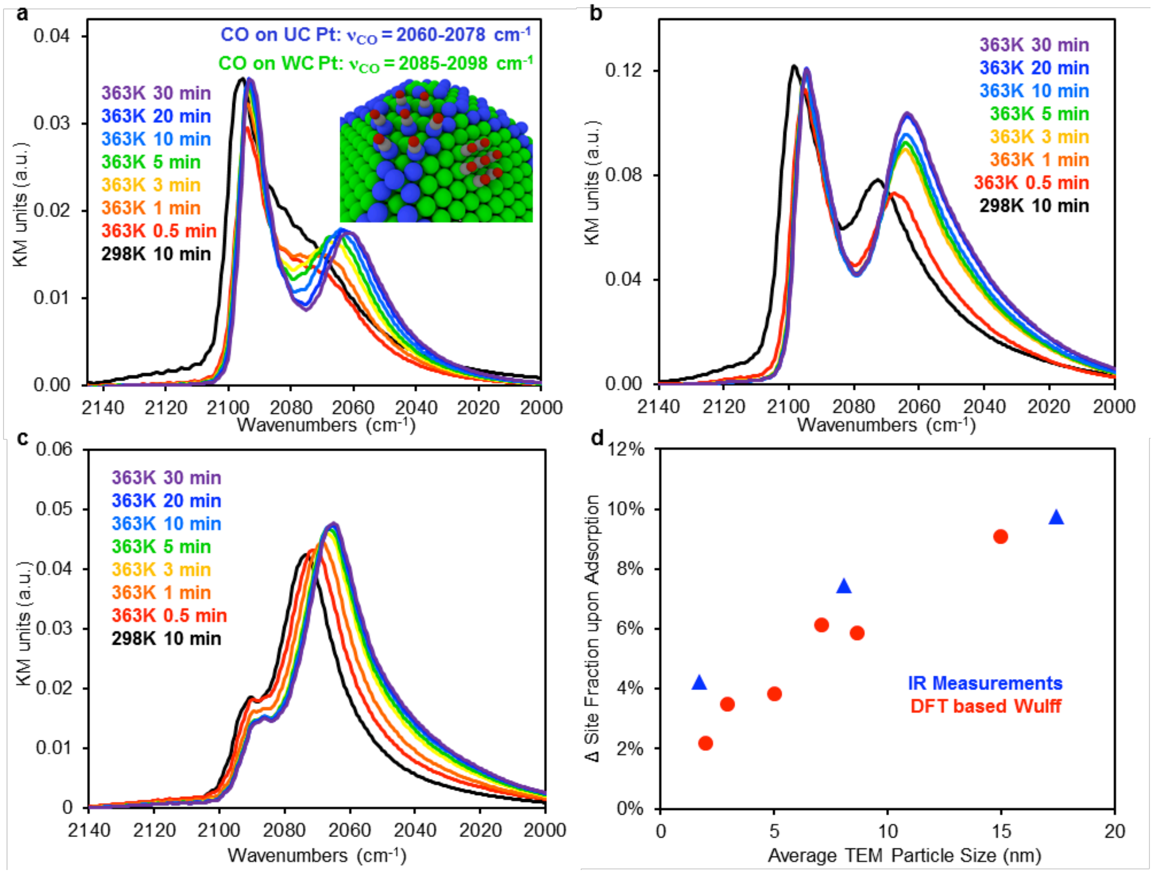

Figure 8. Quantitative correlation between IR measurements and DFT predictions of CO-induced Pt nanoparticle surface reconstruction. *In-situ* IR spectra associated with a time evolution of **A,** a pre-reduced 17 ± 9 nm Pt/Al_2O_3 catalyst **B,** a pre-reduced 8.1 ± 6.2 nm Pt/Al_2O_3 catalyst, and **C,** a pre-reduced 1.8 ± 0.3 nm Pt/Al_2O_3 catalyst in a stream of 1% CO/He at room temperature (black) followed by a fast temperature ramp (1-2 minutes) to 363K (colors) which was maintained for 30 minutes. All spectra are non-normalized and are presented in KM units. The inset in **A** shows example linear adsorption geometries of CO on a Pt nanoparticle on WC (green) and UC (blue) atoms, and the assigned vibrational frequencies (ν_{CO}). Additional CO molecules are excluded in this illustration for clarity. **D,** The change (Δ) in fraction of Pt surface atoms existing as UC Pt atoms, caused by CO induced reconstruction, as a function of particle size calculated from the DFT based Wulff construction models, and measured by IR for the three considered catalysts. Adapted from *Journal of the American Chemical Society*, **2017**, 139, 4551-4558.

These result associated with analyzing the reconstruction of Pt nanoparticles due to CO adsorption strongly suggest that in our examination of photons activating Pt-CO bonds through resonant photoexcitation, we were observing photochemistry associated with CO molecules adsorbed to (111) facets.

Summary

To summarize, in this project it was identified that unique photon mediated mechanisms for driving and controlling catalytic processes exist on small metal nanoparticle surfaces. Specifically, the adsorption of molecules to metal nanoparticle surfaces creates hybridized metal-molecule orbitals that can be directly photoexcited to induce chemical conversions. These electronic transitions are unique to each molecule, both in terms of the excitation energy and oscillator strength of the transition, and this can be exploited to selectively deposit the energy of a photon flux into a targeted reaction pathway. This was demonstrated for the case of targeted activation of Pt-CO bonds instead of Pt-O bonds and to control selectivity in the preferential CO oxidation pathway through targeted photoexcitation of small (< 5 nm diameter) Pt nanoparticle catalysts. To more deeply understand whether photoexcitation of Pt-CO bonds associated with control over catalytic processes was occurring on well or undercoordinated Pt atoms detailed analysis of the surface structure of Pt particles with CO saturated surfaces was executed. It was demonstrated that under saturation coverage of CO, (111) facets of Pt do not reconstruct while (100) facets roughen. This was used to infer that the photo-excitation process that enabled selective energy deposition into Pt-CO bonds likely occurred on (111) facets of Pt nanoparticles.