



Concepts, instruments, and model systems that enabled the rapid evolution of surface science

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ARTICLE INFO

Article history:

Available online 8 January 2009

Keywords:

Surface chemistry
Molecular beam surface scattering
Low energy electron diffraction
Sum frequency generation vibrational spectroscopy
Scanning tunneling microscopy
Reaction intermediates
Nanoparticles
Catalytic nanodiode

ABSTRACT

Over the past forty years, surface science has evolved to become both an atomic scale and a molecular scale science. Gerhard Ertl's group has made major contributions in the field of molecular scale surface science, focusing on vacuum studies of adsorption chemistry on single crystal surfaces. In this review, we outline three important aspects which have led to recent advances in surface chemistry: the development of new concepts, *in situ* instruments for molecular scale surface studies at buried interfaces (solid–gas and solid–liquid), and new model nanoparticle surface systems, in addition to single crystals. Combined molecular beam surface scattering and low energy electron diffraction (LEED)- surface structure studies on metal single crystal surfaces revealed concepts, including adsorbate-induced surface restructuring and the unique activity of defects, atomic steps, and kinks on metal surfaces. We have combined high pressure catalytic reaction studies with ultra high vacuum (UHV) surface characterization techniques using a UHV chamber equipped with a high pressure reaction cell. New instruments, such as high pressure sum frequency generation (SFG) vibrational spectroscopy and scanning tunneling microscopy (STM) which permit molecular-level surface studies have been developed. Tools that access broad ranges of pressures can be used for both the *in situ* characterization of solid–gas and solid–liquid buried interfaces and the study of catalytic reaction intermediates. The model systems for the study of molecular surface chemistry have evolved from single crystals to nanoparticles in the 1–10 nm size range, which are currently the preferred media in catalytic reaction studies.

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1. Introduction

Over the last several decades, surface science has undergone revolutionary advances that reveal on the atomic- and molecular-level structural, dynamic, compositional, and thermodynamic properties of surfaces that are utilized in chemical process development along with adsorption and reaction rates and catalytic selectivity to deliver desired chemical properties [1–9]. In this review, we highlight recent studies in developing instrumentation, concepts, and model systems that permitted the rapid evolution of surface science. Surface science evolved such that new instruments for surface analysis on the molecular scale could be used in a vacuum or at realistic conditions such as high pressures and at solid–liquid interfaces where chemical processes typically operate (bridging the pressure gap) [10]. Surface science also led to studies of new nanomaterials which have increased reaction rates

and improved chemical selectivity (bridging the materials gap) [8,9]. Through molecular scale investigations, new concepts were developed to understand how catalysts work at the molecular scale [11].

We demonstrate important surface phenomena revealed by vacuum studies on single crystal surfaces in Section 2. We outline the development of *in situ* instruments for molecular scale surface analysis in Section 3. Section 4 discusses concepts uncovered by surface science studies at high pressure. We highlight the evolution of model systems from single crystal surfaces to colloid nanoparticle systems in Section 5. Finally, in Section 6, we provide future directions of surface science that include the role of hot electrons in surface chemistry and heterogeneous catalysis, and molecular adsorption at hydrophobic and hydrophilic surfaces in water which are important in the chemistry of biointerfaces.

2. Phenomena revealed by surface science studies in vacuum

Vacuum studies on single crystal surfaces revealed a number of important surface phenomena, leading to new concepts in surface science. The instrumentation techniques developed for

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surface studies [12] include photon-in/electron-out (X-ray photoelectron spectroscopy (XPS)), electron-in/electron-out (low energy electron diffraction (LEED) surface crystallography and Auger electron spectroscopy (AES)), atomic, molecular beams, and ion beam in/ions out (secondary ion mass spectrometry (SIMS) and inelastic ion surface scattering (ISS) techniques). All of these techniques have high scattering cross sections that would not survive the presence of high pressure gas or liquid at the interfaces. In a vacuum, or at low pressures that permit high enough mean free paths for the exiting particle surface probes to be detectable, one could determine the surface composition with less than 1% of a monolayer sensitivity, electronic structures and oxidation states of surface atoms, and the surface structures of clean surfaces and adsorbed atoms and molecules with their bond distances and bond angles [13]. Single crystals were usually used as model surfaces in these studies. Fig. 1 shows a photograph of a Pt(111) single crystal sample in the high pressure reactor cell ((a) in the open and (b) closed position) in an ultra high vacuum chamber. This chamber is equipped with LEED and AES for surface science studies in vacuum.

Many major discoveries were made by these vacuum studies. Clean surface reconstruction of semiconductors and metals showed that surface structures are very different from structures in the bulk. This holds true for alkali halides, oxides and even ice. Adsorbed atoms and molecules occupy sites of stronger bonding on surfaces and cause further restructuring of surface atoms [14–16]. Fig. 1c shows the Pt(111) single crystal surface and ethyldyne-induced surface restructuring of Pt(111) upon adsorption of ethylene. It was discovered that surfaces have defects, atomic steps (often periodic) and kinks in the steps that are chemically active, leading to site selectivity for molecular adsorption [17,18] or dissociation of adsorbing molecules [19]. Surface thermodynamic studies using calorimetry and thermal desorption revealed that the heat of adsorption (desorption) depends on the coverage of

adsorbing molecules due to the presence of adsorbate-adsorbate interactions [20]. Bimetallic or multi-component systems show surface segregation as the lower surface free energy component accumulates on the surface [21,22]. Segregation at the surface is also affected by adsorption as the chemical bonds between adsorbed atoms and the substrate change the surface composition. Molecular and atomic beam scattering studies revealed the nature of energy transfer at the surface during a single collision [23–25].

In order to demonstrate that chemical reaction studies at high pressures are essential, we focus on the chemical behavior of various single crystal surfaces of platinum. A stepped surface exhibits unique chemical activity. When one of the simplest reactions, H_2/D_2 exchange, was investigated by molecular beam scattering the dissociation of hydrogen molecules to atoms had a reaction probability of unity – that is, every hydrogen molecule was dissociated when scattered from the stepped platinum surface [19,26]. When a defect-free platinum (111) crystal face was prepared, the dissociation probability of molecular hydrogen was below the detection limit of 10^{-3} , as shown in Fig. 2a and b. At elevated pressures, however, where the collision rate of H_2 molecules with the metal surface was high H_2/D_2 exchange was readily detectable even from the (111) crystal face of the metal. We consider another chemical dissociation reaction, the breaking of carbon hydrogen bonds by dissociation of methane, CH_4 . When methane was incident on the Pt(111) surface the dissociation probability to produce carbon and hydrogen, which ultimately deposited a layer of carbon on the platinum surface, was below 10^{-8} [27]. This type of C–H bond breaking reaction cannot be detected at low pressures or in ultra high vacuum. We need at least 1 Torr of methane colliding continuously with the platinum single crystal surface to detect the deposition of carbon atoms within 60 s. Such high pressure is absolutely essential to detect the formation of CH_3 molecules, and the subsequent rearrangement to C– CH_3 , C–H, and C_2H molecular segments on the surface by vibrational spectroscopy. Thus, the surface is

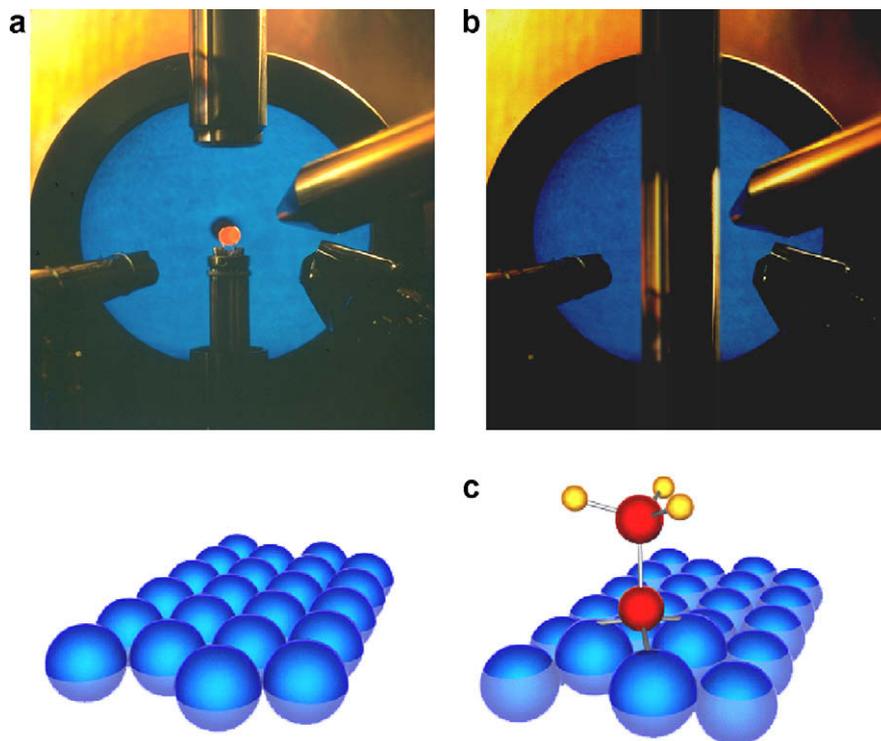


Fig. 1. Photograph of UHV high pressure cell apparatus with Pt single crystal (a) in open position and (b) in closed position. The vacuum chamber is equipped with low energy electron diffraction, Auger electron spectroscopy, and mass spectrometry for surface science studies in vacuum. (c) Ethyldyne-induced restructuring of platinum (111) surface during ethylene hydrogenation.

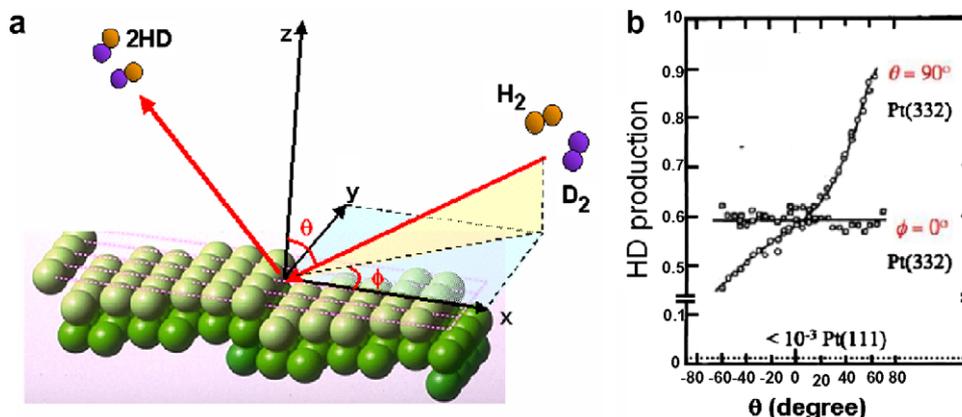


Fig. 2. Molecular beam scattering studies of H₂–D₂ exchange on Pt(332) surface, showing that atomic steps on metal surfaces break chemical bonds, in this case hydrogen–hydrogen bonds, with a reaction probability of unity. (a) Schematic defining the geometry of the incident angle (polar θ and azimuthal ϕ) of the molecular beam with respect to a stepped surface. (b) HD production as a function of angle of incidence θ of the molecular beam normalized to the incident D₂ intensity. The plot was taken at the beam modulation frequency of 10 Hz and the surface temperature of 800 °C.

populated by sites where reaction probabilities to break or rearrange chemical bonds vary by orders of magnitude and, to access both the active and less active sites, high reactant pressures are needed. These results demonstrate the importance of surface science studies at high pressure.

3. Development of high pressure instruments – bridging the pressure gap

In this section, we highlight three in situ high pressure instruments, a high pressure–ultra high vacuum combined system, sum frequency generation (SFG) vibrational spectroscopy, and scanning tunneling microscopy (STM). Fig. 1a shows the high pressure cell which is in open position, equipped with LEED, AES, and mass spectrometry, allowing us to study the surface composition and surface structure in vacuum. In the closed position shown in Fig. 1b, the sample surface is enclosed by the high pressure cell and the rates of catalytic turnover at high pressures can be monitored.

One of the most useful techniques for high pressure studies is non-linear laser optics based SFG vibrational spectroscopy (Fig. 3a) [3,28–31]. This is a surface specific technique that was developed in Berkeley, based on the principle of second harmonic generation [30]. One or both laser frequencies are tuned and spa-

tially and temporally overlapped. By scanning one of the lasers in the infrared frequency regime a sum frequency signal, and thus a visible vibrational spectrum is obtained. Such a signal is forbidden from a centrosymmetric medium, such as the bulk of face centered cubic crystals or an isotropic high pressure gas or a liquid. However, at a surface which is not centrosymmetric, the second order susceptibility is non-zero, and the surface yields a vibrational spectrum with monolayer sensitivity. It is also able to give vibrational frequencies of adsorbed molecules at pressures ranging through 10–12 orders of magnitude. It was found that vibrational spectra of carbon monoxide and ethylene on Pt(111) surface are virtually pressure independent for these molecules adsorbed on a metal surface [32,33].

Another technique that can be used equally well at high pressures and in an ultra high vacuum is STM (Fig. 3b) [5,34–37]. Although most researchers use this technique at low pressures, when it is used around 150 Torr one can see ordered surface structures of carbon monoxide that are not seen at low pressures. Due to the close packing of these molecules on the surface, there is an increase in repulsive interaction among molecules that leads to ordering, which is not observable at low pressures. In addition, the adsorption of various gases at high pressures often induces reconstruction of the surface due to the high coverage of strongly adsorbed atoms or molecules.

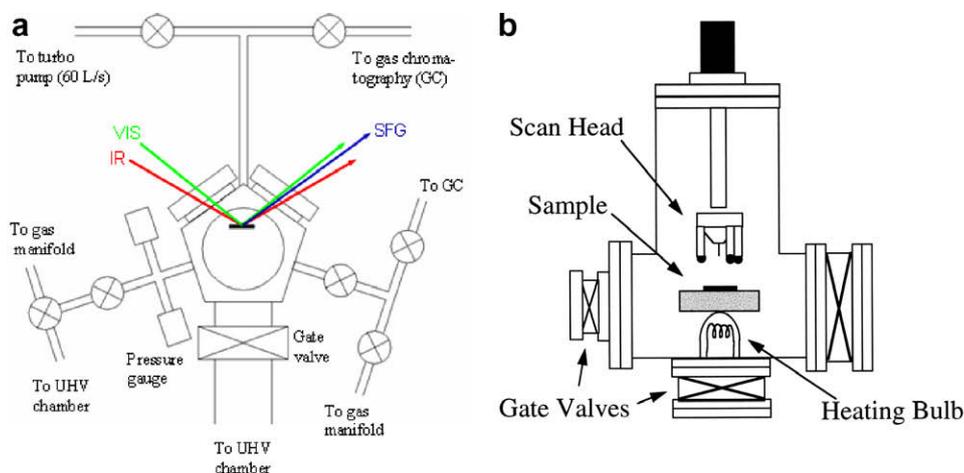


Fig. 3. (a) Schematics of high pressure sum frequency generation (HP-SFG) vibrational spectroscopy and (b) high pressure scanning tunneling microscopy (HP-STM).

4. Surface science concepts at high pressures

The development of new instrumentations at high pressure has enabled new studies, such as detection of *reaction intermediates* and measurement of the *mobility of adsorbate molecules*. In this section, we focus on two chemical reactions, ethylene hydrogenation to ethane, hydrogen/deuterium exchange, and their poisoning with carbon monoxide. Fig. 4a shows an SFG spectrum that reveals three *reaction intermediates* of ethylene hydrogenation: ethylidyne, π -bonded ethylene, and di- σ ethylene [28]. By using carbon isotopes, ethylidyne was found to be a strongly adsorbed spectator that covered 96% of the platinum surface and stayed on the surface a million times longer than the turnover rate of ethylene hydrogenation. The study of the surface structure of ethylene reveals that π -bonded ethylene is a weakly adsorbed intermediate, as compared to di- σ ethylene and ethylidyne. Thus, it is π -bonded ethylene that turns over and forms ethane during ethylene hydrogenation.

As the surface is scanned at a speed of about 10 nm per millisecond, high pressure STM shows no structural features under ethylene hydrogenation, as shown in Fig. 4b [38]. This indicates that the adsorbed molecules under reaction conditions are mobile on the surface, and they have a *mobility* higher than the scanning rate of our STM tip. However, when we add another molecule to the surface, carbon monoxide, it acts as a poison, the reaction stops and the STM picture shows a high level of order on the surface, as shown in Fig. 4c. It appears that the ordering of CO prohibits the *mobility* of the reactants and catalysis is inhibited due to this, according to several different reaction studies. Using high pressure STM, we always find that the adsorbed layer is mobile on the catalytically active surface while ordered structures form if the reaction is inhibited by another adsorbate that poisons the catalytic reaction.

Catalytic hydrogen/deuterium exchange on a platinum (111) single crystal and its poisoning with carbon monoxide was also studied using STM and mass spectrometry at reaction conditions at pressures ranging from mTorr to atmospheric range [39]. STM images acquired at room temperature under reaction conditions (200 mTorr H₂, 20 mTorr D₂) show a surface with no discernible order (Fig. 5a) as the adsorbate species are diffusing much faster than the scanning rate of our instrument (10 nm per millisecond). After introducing 5 mTorr of CO to poison the reaction, however, STM images reveal an ordered surface with hexagonal symmetry (Fig. 5b), which is similar to that formed by pure CO on Pt(111) in this pressure range. The structure is incommensurate with that of the Pt(111) lattice and has a coverage of about 0.6 monolayer. A schematic of the proposed structure is shown in Fig. 5c.

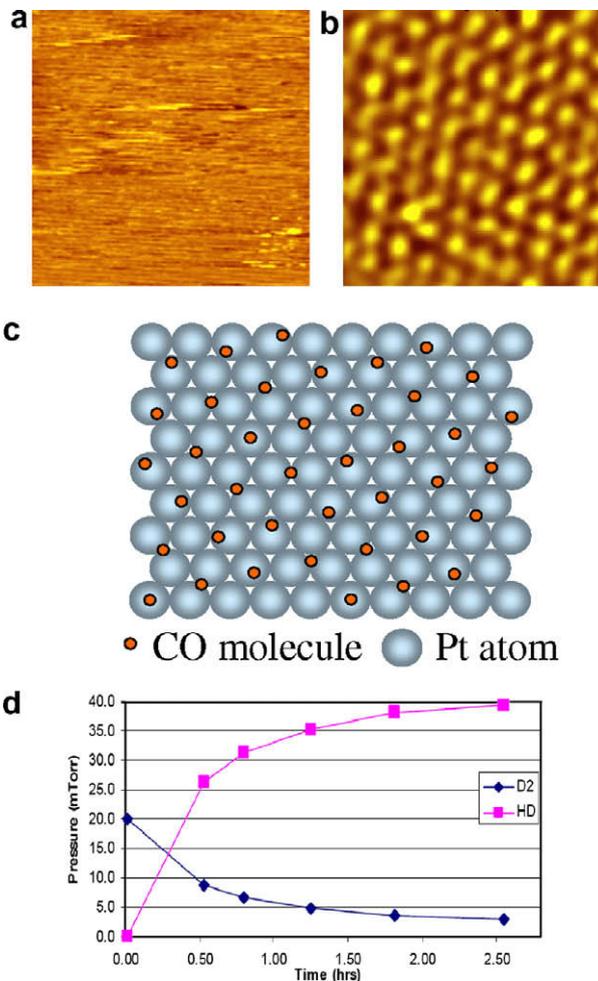


Fig. 5. (a) $90 \text{ \AA} \times 90 \text{ \AA}$ STM images of catalytically active Pt(111) at 298 K: (a) in the presence of 200 mTorr H₂ and 20 mTorr D₂. (b) In the presence of 200 mTorr H₂, 20 mTorr D₂, and 5 mTorr CO. (c) CO molecules are represented by the small circles and color coded according to their proximity to a top site (dark) or to a bridge site (light). (d) D₂ and HD were monitored with mass spectrometry at 296 K, 200 mTorr H₂, and 20 mTorr D₂. The evolution of D₂ and HD partial pressure indicates that Pt catalyst surface is actively producing HD, consistent with the STM image (a).

It was found that at room temperature and in the presence of 200 mTorr of H₂ and 20 mTorr of D₂, the surface is catalytically active, producing HD at a rate of 4.3 molecules/site/s as shown in

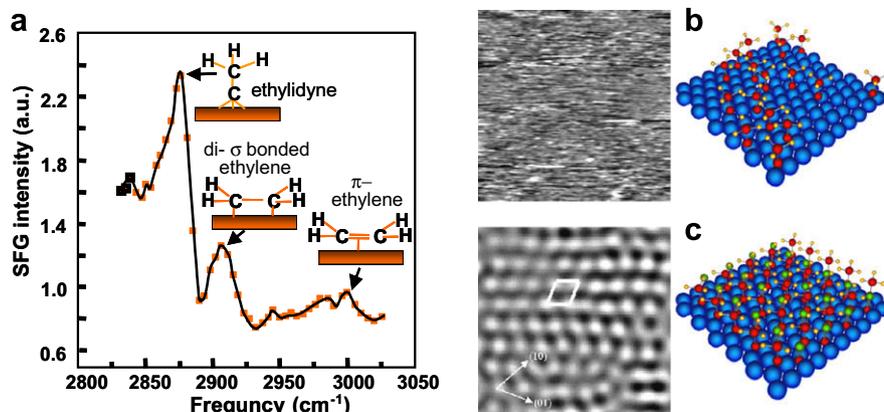


Fig. 4. (a) SFG spectrum of the Pt(111) surface during ethylene hydrogenation revealing reaction intermediates, ethylidyne, di- σ bonded ethylene, and π -ethylene. The spectrum was measured with 100 Torr of H₂, 35 Torr of C₂H₄, and 615 Torr of He at 295 K, (b) $10 \text{ nm} \times 10 \text{ nm}$ STM images of Pt(111) surface at 20 mTorr H₂ and 20 mTorr C₂H₄, (c) $10 \text{ nm} \times 10 \text{ nm}$ STM images of Pt(111) surface at 20 mTorr H₂, 20 mTorr C₂H₄, and 5 mTorr CO.

Fig. 5d. Upon introduction of 5 mTorr of CO, however, the production of HD dropped below the detection limit of our mass spectrometer. At 345 K, the turnover frequency in the absence of CO increased to 39 molecules/site/s, which is about 10 times higher than that at room temperature. Addition of 5 mTorr of CO at this temperature decreased the reactivity dramatically, but unlike in the room temperature case, catalytic activity was still observed at the rate of 0.03 molecules/site/s. This implies that the immobile and ordered monolayer of CO molecules forms an incommensurate structure relative to the Pt(111) substrate. Removing a small fraction of the CO layer by heating the sample allowed the surface to become mobile and catalytically active. It was also found that the activation energy for the H₂/D₂ exchange reaction in the absence of CO is 5.3 kcal/mol. The introduction of CO into the system causes the activation energy to more than triple to 17.4 kcal/mol. The activation energy after CO poisoning was also observed for ethylene hydrogenation on Pt(111), where it increased from 9.6 kcal/mol for the clean surface to 20.2 kcal/mol for the CO-poisoned surface [40,41].

Surface science studies at high pressure also suggest that *adsorbate-induced restructuring at high pressures* is a more facile and more dominant phenomena. The dynamic surface under high pressure condition undergoes rapid adsorbate-induced restructuring on the time scale of chemisorption as adsorbate bonds form or break. This concept of surface science at high pressure can be applied to emerging surface materials, such as nanoparticles. Catalysis may take place more easily in a nanoparticle form, where less atoms and molecules participate in the restructuring during catalytic turnover.

5. Development of a model system – bridging the materials gap

Chemically active surfaces are not single crystals, but are frequently nanoparticles 1–10 nm in size. The use of single crystals as model catalytic systems has shed light on many surface concepts and phenomena, as shown in Section 2 and Section 4. Industrial catalysts, however, do not just consist of metal, but are made up of metal particles 1–10 nm range dispersed in a high surface area support, as shown in Fig. 6. They are produced by synthesizing the metal particles and support separately and then dispersing the

metal clusters onto the support by techniques such as wet-impregnation, co-precipitation, or ion-exchange. Thus, single-crystalline metals used for modeling industrial catalysis inherently lack the complexity needed to uncover many of the factors important to catalytic turnover and selectivity on nanoparticles. Considerations such as metal-support interactions and the importance of metallic cluster size are of extreme importance to catalytic applications.

In order to bridge this materials gap, several new model systems have been proposed and utilized, as shown in Fig. 6. The first approach involves the fabrication of Pt nanoparticles and nanowires with lithography techniques. Pt nanoparticle arrays 30 nm in size were fabricated with electron beam lithography [42], which utilizes high-resolution pattern writing and an electron-sensitive resist/etching. Disadvantages of electron beam lithography are low throughput and high cost. Thus, we utilized size reduction lithography (SRL) and nanoimprint lithography (NIL) [43,44]. Several repetitions of size reduction lithography can reduce the size of the mold to ~7 nm silicon nanowire. The nanowire pattern is transferred into poly methylmethacrylate (PMMA) under high pressure and high temperature by using nanoimprint lithography. Then, a thermal oxide layer formed by oxygen-plasma etching on the residual PMMA is removed, with the final product being a nanoscale mold. Pt atoms can be deposited by electron beam evaporation to form Pt nanowires. Fig. 6 shows an SEM image of the Pt nanowire arrays on a silicon oxide surface with a width of 30 nm. Thermal treatment in a vacuum, hydrogen, or oxygen crystallized the Pt nanowires. Catalytic reactions including ethylene hydrogenation and CO oxidation were carried out on Pt nanowires on oxide supports [45]. It was found that the turnover rate of ethylene hydrogenation is proportional to the oxide-metal periphery area, even though the nanoparticles are poisoned, suggesting the oxide-metal interface functions as a reactive site [41].

Nanoparticles are prepared by colloid synthesis, and in this circumstance they are capped with a polymer to prevent their aggregation in the solution. These can be monodispersed with uniform size and shape and can be deposited as a two-dimensional film using the Langmuir–Blodgett technique [46]. The nanoparticles can also be deposited in a mesoporous three-dimensional oxide framework at much higher surface concentrations [47–50]. The particle size and shape and the interface sites between the metal

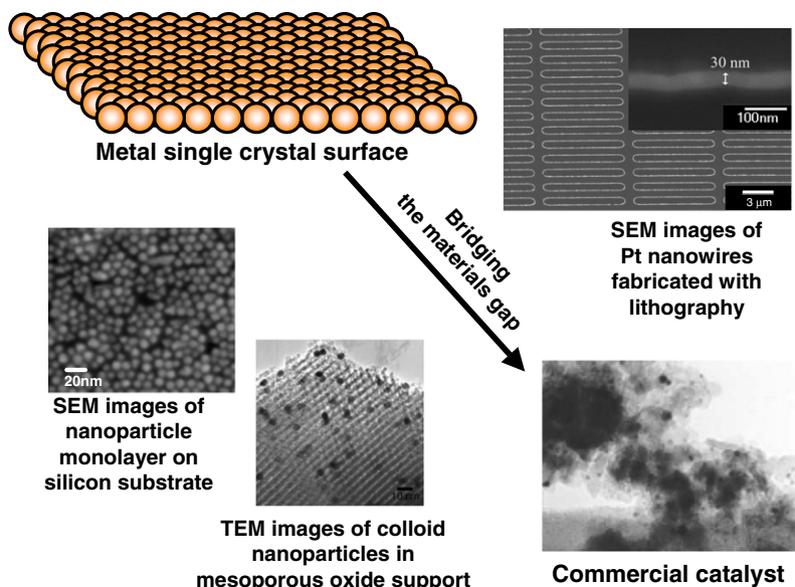


Fig. 6. Schematic showing new model catalyst systems to bridge the materials gaps from a single crystal metal surface to a commercial catalyst. New model systems include two-dimensional Pt nanoparticle arrays, colloid Pt nanoparticles encapsulated into a mesoporous oxide support, and Pt nanowire arrays fabricated with lithography.

particles and the oxide where they are deposited are important aspects that control reaction selectivity [46,51]. The development of new model systems permit us to study phenomena associated with reduced dimensions, such as chemical activity and reaction selectivity variation due to metal nanoparticle size and shape, as well as the role of oxide-metal interfaces, which are fundamental questions in surface chemistry.

6. Future directions of molecular surface science

Two examples of future directions in molecular surface science are the study of surface science at liquid–solid interfaces and hot electron detection. Studying liquid–solid interfaces is an important task in bridging the pressure gap because the liquid has a thousand times higher density than gas in one atmosphere. We highlight the recent study of the detection of hot electrons generated on metal thin films or nanoparticles during exothermic catalytic reactions by using a metal–oxide Schottky diode.

6.1. Surface science at liquid–solid interfaces – surface electrochemistry, and biointerfaces

The ability to monitor the surface structure and orientation of adsorbed molecules with SFG as a function of applied potential is a unique feature of surface electrochemistry. The potential dependent structure of a water/acetonitrile mixture was explored on Pt(111) with SFG. Fig. 7a shows the orientation change of acetonitrile as a function of the potential of the platinum electrode [52]. The CN group is directed toward the metal at potentials where the metal has a positive charge. As the surface becomes less positively charged, the acetonitrile orientation flips 180°, with the CH₃ group pointing toward the surface.

From a surface science perspective, the human body may be viewed as a biopolymer–water interface with a layer of adsorbed proteins. Bioimplants, from contact lenses to stents to open arteries and replacements for heart valves, are tools to increase

life expectancy and improve quality of life. The challenge is how to make implant materials biocompatible to prevent rejection of artificial replacement organs or devices. Important aspects of biointerface research are studies of the adsorption of proteins and peptides, their surface structure and orientation, which appear to correlate with biocompatibility. These studies are carried out in biologically relevant conditions in aqueous solutions.

Proteins and shorter chain peptides are made up of amino acid molecular building blocks [53]. Hydrophobic surfaces that are mostly polymers (such as polystyrene or collagen) or hydrophilic surfaces (such as silica) are used as interfaces most frequently in studies that orient the amino acids in the peptide chains differently. For example, the SFG of a 14 amino acid containing peptide at the hydrophilic (silica/buffer) and hydrophobic (deuterated polystyrene/buffer) interfaces is shown in Fig. 7b. This peptide contains leucine (non-polar) and lysine (polar), amino acids. At the hydrophobic polystyrene interface, the non-polar leucines adsorb and are ordered (and hence seen in the SFG spectra), whereas at the hydrophilic interface, an N–H mode is observed (attributed to the polar lysine side-chains) [54,55]. Hydrogels, which are polymers that adsorb water in large volumes, are an intensive area of biointerface research because of their use in contact lens technology [56].

6.2. Hot electron chemistry – the role of hot electrons in catalytic reactions

One important site for reaction activity and selectivity is the oxide–metal interface, which deserves special attention. It has been known for decades in chemical science and applications that when a metal nanoparticle catalyst is deposited on surfaces of certain oxides that are not chemically active, the reaction rate of the catalyst on a high surface area support is much improved (over tenfold), as compared to the metal alone [57,58]. This phenomenon was utilized empirically in catalysis science and the chemical industry by pairing certain oxides with metals to optimize this effect.

The origin of this strong metal–support interaction has been attributed to either geometric or electronic effects. The electronic effect involves the generation of hot electrons at metal surfaces that transfer through the metal–oxide interface. During exothermic chemical processes, energetic charge carriers can be generated through non-adiabatic electronic dissipation of chemical energy. Experimental evidences indicating the presence of energetic electrons, known as “hot” electrons, have been reported.

A pulse of energetic photons can generate hot electrons on femtosecond time scales that can be detected by monitoring their kinetic energy in a vacuum, where a large fraction of the photon energy is deposited in the metal. Interestingly, vibrationally excited NO molecules also show very large energy losses (>1.5 eV) when they are scattered from gold surfaces, while they do not undergo any chemical change. The vibrational deexcitation provides energy transfer to the metal, which yields hot electrons. As shown by comparison, lithium fluoride shows no vibrational energy transfer [23] because it has no free electrons.

We constructed a so called catalytic nanodiode [59–61], which is composed of a metal of thickness less than the mean free path of hot electrons, deposited on a semiconductor surface, as shown in Fig. 8a. When exothermic catalytic chemical reactions occur, we find that the heat transferred is converted to a hot electron flow that can pass through the metal film into the semiconductor which has a Schottky barrier [62,63], which allows the passage of energetic electrons in one direction but not in the other direction.

We place the diode into a catalytic reactor and we measure simultaneously the hot electron flow, which is often called “chem-

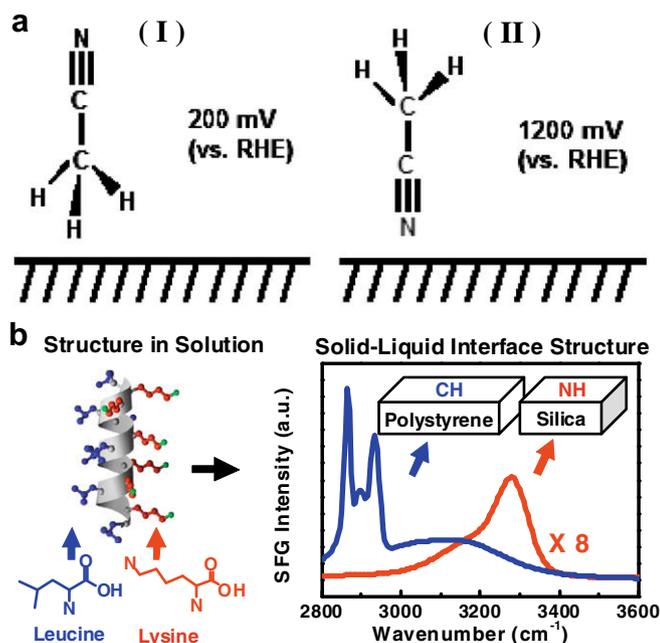


Fig. 7. (a) Possible orientations of acetonitrile at Pt(111) electrode. (I) methyl group toward metal (observed at 200 mV with respect to the reference hydrogen electrode (RHE)). (II) Nitrogen lone pair electrons interacting with metal (observed at 1200 mV). (b) SFG spectrum of a 14 amino acid leucine–lysine containing peptide adsorbed onto polystyrene and silica.

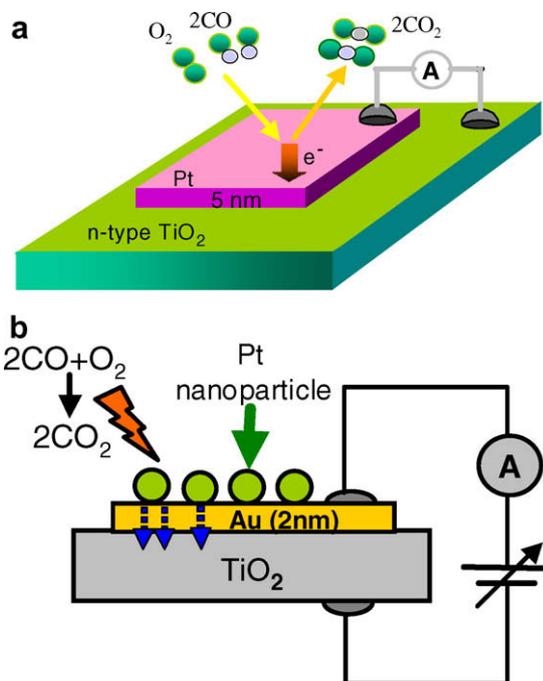


Fig. 8. (a) Schematic of hot electron generation in Pt/TiO₂ Schottky diode and (b) schematic of hot electron generation in nanoparticles on Au/TiO₂ Schottky diode.

icurrent”, and the turnover rate. We found that the turnover rate and the chemicurrent are correlated as a function of temperature. The influence of physical and chemical properties of Pt/TiO₂, Pd/TiO₂, and Pt/GaN metal-semiconductor Schottky diodes on the yield of collected hot electron flow (number of hot electrons per product molecule) was investigated [64]. It was found that the metal-semiconductor interface structure (roughness, grain size, and step-terrace) is important in controlling the magnitude of the chemicurrent yield.

Recently, we found that hot electrons generated on colloid nanoparticles can be directly detected on Au/TiO₂ diodes [65]. The scheme of this device is shown in Fig. 8b. The role of Au/TiO₂ diodes is to have a catalytically inactive template diode with a continuous, thin Au layer that ensures that the metal nanoparticles are electrically connected to the device, permitting us to collect hot electrons during exothermic catalytic reactions. Furthermore, the influence of capping layers on the number of hot electrons collected per product molecule generated, also known as the chemicurrent yield, has been investigated. This detection scheme can be used to elucidate the role of the metal-oxide interface in heterogeneous catalysis for practical catalytic systems that involve highly dispersed nanoparticles deposited on an oxide.

The mechanism of how hot electron flows influence catalytic activity is being investigated. This shows it is possible to use hot electron flow to control catalytic activity, while the exothermic catalytic reaction provides the hot electron flow. Hot electron generation can be utilized as a new method for chemical energy conversion.

Acknowledgement

This work was supported by the Director, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geological and Biosciences and Division of Materials Sciences and Engineering of the US Department of Energy under Contract No. DE-AC02-05CH11231.

References

- [1] G. Ertl, H.J. Freund, *Physics Today* 52 (1999) 32.
- [2] C.T. Campbell, *Surface Science Reports* 27 (1997) 1.
- [3] H.J. Freund, H. Kuhlbeck, J. Libuda, G. Rupprechter, M. Baumer, H. Hamann, *Topics in Catalysis* 15 (2001) 201.
- [4] A.T. Bell, *Science* 299 (2003) 1688.
- [5] G.A. Somorjai, K.M. Bratlie, M.O. Montano, J.Y. Park, *Journal of Physical Chemistry B* 110 (2006) 20014.
- [6] G.A. Somorjai, J.Y. Park, *Catalysis Letters* 115 (2007) 87.
- [7] G.A. Somorjai, J.Y. Park, *Physics Today* 60 (2007) 48.
- [8] R. Narayanan, M.A. El-Sayed, *Nano Letters* 4 (2004) 1343.
- [9] J.Y. Park, Y. Zhang, M. Grass, T. Zhang, G.A. Somorjai, *Nano Letters* 8 (2008) 673.
- [10] G.A. Somorjai, R.L. York, D. Butcher, J.Y. Park, *Physical Chemistry Chemical Physics* 9 (2007) 3500.
- [11] G.A. Somorjai, A.M. Contreras, M. Montano, R.M. Rioux, *Proceedings of the National Academy of Sciences of the United States of America* 103 (2006) 10577.
- [12] D.P. Woodruff, T.A. Delchar, *Modern Techniques of Surface Science*, Cambridge University Press, Cambridge, 1986.
- [13] G.A. Somorjai, *Introduction to Surface Chemistry and Catalysis*, Wiley, New York, 1994.
- [14] M.A. Van Hove, G.A. Somorjai, *Journal of Molecular Catalysis A: Chemical* 131 (1998) 243.
- [15] C.T. Campbell, G. Ertl, H. Kuipers, J. Segner, *Surface Science* 107 (1981) 220.
- [16] X. Bao, J.V. Barth, G. Lehmppuhl, R. Schuster, Y. Uchida, R. Schlögl, G. Ertl, *Surface Science* 284 (1993) 14.
- [17] U. Schneider, G.R. Castro, K. Wandelt, *Surface Science* 287 (1993) 146.
- [18] K. Wandelt, J. Hulse, J. Kupfers, *Surface Science* 104 (1981) 212.
- [19] M. Salmeron, R.J. Gale, G.A. Somorjai, *Journal of Chemical Physics* 67 (1977) 5324.
- [20] S. Westerberg, C. Wang, G.A. Somorjai, *Surface Science* 582 (2005) 137.
- [21] N. Toshima, T. Yonezawa, *New Journal of Chemistry* 22 (1998) 1179.
- [22] J.A. Rodriguez, D.W. Goodman, *Science* 257 (1992) 897.
- [23] Y.H. Huang, C.T. Rettner, D.J. Auerbach, A.M. Wodtke, *Science* 290 (2000) 111.
- [24] A. Bottcher, R. Imbeck, A. Morgante, G. Ertl, *Physical Review Letters* 65 (1990) 2035.
- [25] D.N. Denzler, C. Frischkorn, C. Hess, M. Wolf, G. Ertl, *Physical Review Letters* 91 (2003) 226102.
- [26] M. Salmeron, R.J. Gale, G.A. Somorjai, *Journal of Chemical Physics* 70 (1979) 2807.
- [27] A.L. Marsh, K.A. Becraft, G.A. Somorjai, *Journal of Physical Chemistry B* 109 (2005) 13619.
- [28] P.S. Cremer, X.C. Su, Y.R. Shen, G.A. Somorjai, *Journal of the American Chemical Society* 118 (1996) 2942.
- [29] G. Rupprechter, *MRS Bulletin* 32 (2007) 1031.
- [30] Y.R. Shen, *Nature* 337 (1989) 519.
- [31] X.C. Su, P.S. Cremer, Y.R. Shen, G.A. Somorjai, *Journal of the American Chemical Society* 119 (1997) 3994.
- [32] P. Cremer, S. Stanners, J.W. Niemantsverdriet, Y.R. Shen, G. Somorjai, *Surface Science* 328 (1995) 111.
- [33] X.C. Su, P.S. Cremer, Y.R. Shen, G.A. Somorjai, *Physical Review Letters* 77 (1996) 3858.
- [34] B.L.M. Hendriksen, J.W.M. Frenken, *Physical Review Letters* 89 (2002).
- [35] J.A. Jensen, K.B. Rider, M. Salmeron, G.A. Somorjai, *Physical Review Letters* 80 (1998) 1228.
- [36] B.J. McIntyre, M. Salmeron, G.A. Somorjai, *Journal of Vacuum Science & Technology A: Vacuum Surfaces and Films* 11 (1993) 1964.
- [37] M. Montano, D.C. Tang, G.A. Somorjai, *Catalysis Letters* 107 (2006) 131.
- [38] D.C. Tang, K.S. Hwang, M. Salmeron, G.A. Somorjai, *Journal of Physical Chemistry B* 108 (2004) 13300.
- [39] M. Montano, K. Bratlie, M. Salmeron, G.A. Somorjai, *Journal of the American Chemical Society* 128 (2006) 13229.
- [40] K.S. Hwang, M.C. Yang, J. Zhu, J. Grunes, G.A. Somorjai, *Journal of Molecular Catalysis A: Chemical* 204 (2003) 499.
- [41] J. Grunes, J. Zhu, M.C. Yang, G.A. Somorjai, *Catalysis Letters* 86 (2003) 157.
- [42] J. Grunes, J. Zhu, E.A. Anderson, G.A. Somorjai, *Journal of Physical Chemistry B* 106 (2002) 11463.
- [43] X.M. Yan, S. Kwon, A.M. Contreras, J. Bokor, G.A. Somorjai, *Nano Letters* 5 (2005) 745.
- [44] X.M. Yan, S. Kwon, A.M. Contreras, M.M. Koebel, J. Bokor, G.A. Somorjai, *Catalysis Letters* 105 (2005) 127.
- [45] A.M. Contreras, X.M. Yan, S. Kwon, J. Bokor, G.A. Somorjai, *Catalysis Letters* 111 (2006) 5.
- [46] H. Song, F. Kim, S. Connor, G.A. Somorjai, P.D. Yang, *Journal of Physical Chemistry B* 109 (2005) 188.
- [47] H. Song, R.M. Rioux, J.D. Hoefelmeyer, R. Komor, K. Niesz, M. Grass, P.D. Yang, G.A. Somorjai, *Journal of the American Chemical Society* 128 (2006) 3027.
- [48] A. Corma, *Chemical Reviews* 97 (1997) 2373.
- [49] R.M. Rioux, H. Song, J.D. Hoefelmeyer, P. Yang, G.A. Somorjai, *Journal of Physical Chemistry B* 109 (2005) 2192.
- [50] D. Zhao, P. Yang, N. Melosh, J. Feng, B.F. Chmelka, G.D. Stucky, *Advanced Materials* 10 (1998) 1380.
- [51] K.M. Bratlie, H. Lee, K. Komvopoulos, P. Yang, G.A. Somorjai, *Nano Letters* 7 (2007) 3097.

- [52] S. Baldelli, G. Mailhot, P.N. Ross, G.A. Somorjai, *Journal of the American Chemical Society* 123 (2001) 7697.
- [53] J. Kim, G.A. Somorjai, *Journal of the American Chemical Society* 125 (2003) 3150.
- [54] O. Mermut, D.C. Phillips, R.L. York, K.R. McCrea, R.S. Ward, G.A. Somorjai, *Journal of the American Chemical Society* 128 (2006) 3598.
- [55] O. Mermut, R.L. York, D.C. Phillips, K.R. McCrea, R.S. Ward, G.A. Somorjai, *Biointerphases* 1 (2006) P5.
- [56] Q. Chen, D. Zhang, G. Somorjai, C.R. Bertozzi, *Journal of the American Chemical Society* 121 (1999) 446.
- [57] K. Hayek, M. Fuchs, B. Klotzer, W. Reichl, G. Rupprechter, *Topics in Catalysis* 13 (2000) 55.
- [58] A. Boffa, C. Lin, A.T. Bell, G.A. Somorjai, *Journal of Catalysis* 149 (1994) 149.
- [59] X.Z. Ji, A. Zuppero, J.M. Gidwani, G.A. Somorjai, *Journal of the American Chemical Society* 127 (2005) 5792.
- [60] J.Y. Park, J.R. Renzas, A.M. Contreras, G.A. Somorjai, *Topics in Catalysis* 46 (2007) 217.
- [61] J.Y. Park, G.A. Somorjai, *Chemphyschem* 7 (2006) 1409.
- [62] H. Nienhaus, *Surface Science Reports* 45 (2002) 3.
- [63] H. Nienhaus, H.S. Bergh, B. Gergen, A. Majumdar, W.H. Weinberg, E.W. McFarland, *Physical Review Letters* 82 (1999) 446.
- [64] J.Y. Park, J.R. Renzas, B.B. Hsu, G.A. Somorjai, *Journal of Physical Chemistry C* 111 (2007) 15331.
- [65] J.Y. Park, H. Lee, J.R. Renzas, Y. Zhang, G.A. Somorjai, *Nano Letters* 8 (2008) 2388.