

Surface chemistry: Key to control and advance myriad technologies

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This special issue on surface chemistry is introduced with a brief history of the field, a summary of the importance of surface chemistry in technological applications, a brief overview of some of the most important recent developments in this field, and a look forward to some of its most exciting future directions. This collection of invited articles is intended to provide a snapshot of current developments in the field, exemplify the state of the art in fundamental research in surface chemistry, and highlight some possibilities in the future. Here, we show how those articles fit together in the bigger picture of this field.

adsorption | surface science | nanoscience | materials science | soft matter chemistry

The field of surface chemistry has undergone an explosive development in the period marked by its two Nobel prizes—1932 (Irving Langmuir) to 2007 (Gerhard Ertl). Indeed, many years went by after Langmuir before modern surface measurement techniques began to develop significantly (in the 1960s) as a result of the need to understand semiconductor surface chemistry and physics for applications to emerging electronic devices. The period after 1960 witnessed the development of ultrahigh vacuum techniques for probing surfaces using electrons, ions, photons, and heat as probes of chemistry on single-crystal metal, semiconductor, and insulator surfaces. These new measurement methods were often the product of the work of surface physicists, and the term surface science began to be used to encompass developments in the field that mixed chemistry and physics. The journal of the same name was established and quickly achieved prominence with high-impact factors. At the same time, modern quantum theory began to be applied to surface problems with increasing accuracy, because theoretical methods developed to a point where chemical accuracy became possible, allowing the prediction of the course of chemical processes on surfaces. At the present time, surface chemistry is an endeavor that combines theory and experiment, often to generate new concepts and principles that are predictive, a desired but unachieved goal for much of the early history of the field. In addition to the advent of accurate predictions of surface behavior in the last 25 years, the field of surface chemistry has expanded from studies focused on hard materials to investigations of the surface properties of soft matter, connecting to problems in biochemistry and materials science of organic films, polymers, and liquids. Thus, surface chemistry is now a well-developed field where the understanding of surface phenomena can often be reduced to the

knowledge of the behavior of electrons, molecules, and excitations at the Angstrom and femtosecond level.

In parallel to the development of the fundamental basis of surface chemistry, there has been a tremendous impact of this knowledge on technology of many sorts. At the beginning of the era bounded by Langmuir and Ertl, the improvement of the incandescent lamp was a major technological driver, and the interest in the chemistry on tungsten filaments spread quickly to related interests in the behavior of molecules adsorbed and reacting on transition metal surfaces, forming the underpinnings of fundamental heterogeneous catalysis. As interest in semiconductor surfaces blossomed in the 1960s, fundamental understanding of the role of surface structure affected both catalyst and semiconductor science. For many years, a substantial portion of the world's GDP has involved surface chemistry, and the wide range of high-impact applications of surface chemistry has been a driver in the development of the field. Among the most important are the electronics industry, the petrochemical industry, the conversion of air into fixed-nitrogen substances such as fertilizers, and the automotive catalyst technology. Emerging areas include the photovoltaic industry and the wide range of energy conversion technologies.

In the 1990s, a new descriptor was coined—nanoscience. At that time, surface scientists (chemists, physicists, and materials scientists) were already at work at the nanometer level of dimensional control, but the advent of nanoscience showed a widening of interest beyond quantum dots and conjugated organic systems of variable size. Because nanometer-sized materials contain mostly surface atoms, it was natural for leaders in surface science to be among the leaders of the new field of nanoscience, lending surface analysis, scanning tunneling, and electron microscopes as well as theory to the emerging area.

This special feature of PNAS on surface chemistry provides a snapshot of current developments in the field through a group of invited articles in surface chemistry written by some of its best practitioners. Our goal is to exemplify the state of the art in fundamental research in surface chemistry and highlight its most exciting future directions and applications. We start with a perspective (Somorjai group) that summarizes the many applications of surface chemistry and reviews some surface measurement methods followed by reports of exciting developments in understanding the surface chemistry of heterogeneous catalysis, including the simulation of surface processes (King, Goodman, Norskov, and Jonsson groups). This is followed by two papers dealing with chemistry on semiconductor surfaces (Polanyi and Bent/Teplakov groups). The transient and excited-state electronic behavior of surfaces and adsorbed molecules forms a separate area, coupling to the behavior of adsorbates, nanostructures, ultrathin films, and interfaces as electronic components in molecular electronic, optoelectronic, photovoltaic, or photocatalytic devices (Berndt, Zhu, and Echenique groups). Physical studies of soft surfaces involving polymers follow in the work of Sibener's group. Then, Hamers and his group describe methods for functionalizing diamond surfaces for biomaterials or biosensing applications. Finally, important relationships between the kinetic processes occurring during thin film growth and the structural features of the resulting films are explored by the groups of Evans and Thiel.

Applications of Surface Chemistry

Surface chemistry holds a very special position in the development and

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nitrogen adatoms on Fe(111), with and without coadsorbed potassium promoter, which cleanly shows a rate enhancement by K for the combined elementary steps that occur after N₂ dissociation (i.e., the stepwise hydrogenation of nitrogen adatoms to ammonia). This is an elegant demonstration of combining a high-pressure reactor directly to an ultrahigh vacuum (UHV) surface analysis system, where well-defined adsorbate-covered surfaces can be prepared and coverages quantified. Because some of the elementary steps are too slow to observe under UHV, this approach has been very powerful in the surface chemistry of catalysis.

The Holy Grail in catalysis is to understand the relationship between surface structure and catalytic activity or selectivity well enough to design better catalysts. Above, we mentioned only two aspects of structure/function relationships in catalysis: the active metal site geometry and the role of promoters. Other crucial aspects include the role of the second metal in alloy or bimetallic catalysts, the role of particle size in supported metal catalysts, and the role of different support materials (different oxides, carbons, etc.). The paper from McClure et al. (Goodman group) (22) shows the quantitative effect of rhodium nanoparticle size on the rates of C₂H₄ hydroformylation (C₂H₄ + CO + H₂) for the synthesis of aldehydes through CO insertion over silica-supported Rh. The Rh particles were prepared on a planar model silica support, and their size was characterized by STM, chemisorptions, and other reaction rates for CO oxidation and C₄H₁₀ hydrogenolysis. Again, the rates were measured in an attached high-pressure cell—in this case, equipped with *in situ* infrared spectroscopy. The latter reaction's selectivity is closely coupled to the fraction of undercoordinated Rh sites and confirms the STM size measurements. The hydroformylation reaction (H₂ + CO) rate also correlates strongly with the number of undercoordinated Rh sites until the particle size drops below 2 nm, where IR spectra show the Rh particles atomically disperse across the silica surface in the form of Rh gem dicarbonyls or carbonyl hydride, causing dramatic loss of catalytic activity.

This represents an experimental tour de force in clarifying metal particle size effects. The gem dicarbonyl of Rh was first discovered on high-area Al₂O₃ surfaces by IR spectroscopy by Yang and Garland (23). Its route of production by the facile oxidation of small Rh metal clusters by surface hydroxyl groups was discovered on Al₂O₃ surfaces (24). Except for Ni(CO)₄, the Rh(I)(CO)₂ species is one of the most prominent links between surface chemistry and organometallic chemistry.

Driven by the exciting experimental results of the types outlined above, theory has made many important corresponding contributions to these same goals, with theorists in the best cases working hand-in-hand with experimentalists. No theorist shows that spirit better than Jens Norskov, whose group's contribution here (25) highlights the essential role played by density functional theory (DFT) with periodic boundary conditions in the surface chemistry of catalysis. Although such contributions can range from something as straightforward as aiding the interpretation of surface spectral assignments, which itself is very important, Norskov et al. (25) show that these calculations have already reached a level of accuracy and speed where they have actually been able to make predictions about better materials for achieving specific catalytic effects, sometimes using a combinatorial computational chemistry approach. That group's d-band center model and identification of key descriptors for reaction performance have revolutionized the ways to use theory to advance fundamental understanding in catalysis and search for better catalysts.

Norskov et al. (25) point out that the accuracy of DFT is still lacking and that the promise of surface chemistry will only be fully realized when calculations can make predictions of the energies of surface structures with more reliable accuracy. Measurements of adsorption energies in one of our own groups also have revealed some real problems in the accuracy of state of the art DFT. Such calculations underestimate measured values for benzene and naphthalene on Pt(111) by 80 and 110 kJ/mol, respectively (26), and no DFT results can come close to reproducing measured values for linear alkanes up to 10 carbons long on Pt(111), graphite(0001), or MgO(100) (27). Thus, in the future, we should place heavy emphasis also on new theoretical developments that improve accuracy and broaden the range of phenomena that can be addressed. The contribution here by Jonsson (28) summarizes some of the important new directions that are being pursued to achieve these goals. That paper also highlights recent improvements in calculating dynamical effects, such as accurately finding transition states, computing preexponential factors, and predicting tunneling rates (which Jonsson (28) shows to only be important below ~300 K). The description of transition states plays a dominant role in understanding the all important rates of catalytic reaction steps. Because of their transient nature, transition states are elusive to experimental characterization (except in energy), and therefore, it is really only through such calculations that we can hope to understand their true nature.

Chemistry on Semiconductor Surfaces

We turn from metal surfaces to semiconductor surfaces. Here, one envisions the surface as an interrupted covalent solid with dangling bonds projecting into vacuum. These bonds possess high chemical reactivity and rich surface chemistry results, including the localized anchoring of adsorbed organic molecules, the production of thin oxide and other compound layers, and the preservation of surface electronic states with observable properties. The self assembly of molecules on such surfaces poses two interesting molecular questions: (i) the mobility of the physisorbed layer before chemical reaction with the surface, and (ii) the anchoring of this layer at covalent sites related to dangling bonds. Early work on the chemisorption of ethylene and acetylene on the Si(100) 2 × 1 surface showed both of these characteristics. The mobility of a mobile precursor model was invoked to explain the coverage-independent sticking coefficient of near unity value, and the formation of a monolayer of adsorbate at dangling bond sites was verified by the measurement of the equivalence of the number of adsorbate molecules in the saturated layer to the known surface density of dangling bonds (29). As described herein, Harikumar et al. (30) have used STM to observe the self-assembly of weakly bound 1-chloropentane molecules on Si(100)-2 × 1 surfaces and then, covalently anchored these molecules by heat, electrons, or photochemistry. The transition state visualized involves a breaking C–Cl bond and a forming C–Si bond in the same region of the surface, locking the physisorbed molecule to a site and activating a neighbor dangling bond site on the silicon dimers for the attachment of neighbor molecules, much as a zipper closes. The acronym invented by the Polanyi group is molecular scale imprinting (MSI). MSI may have broad applicability to fields such as silicon wafer lithography and molecular electronics.

The paper by Bent et al. (31) reports that well-established ideas about the basicity of different amines connect to measurements of reactivity of these amines when adsorbed dissociatively (by N–H bond scission) on either Si(100) 2 × 1 or Ge(100)-2 × 1. A probe transamination reaction was used to measure the reactivity of dissociatively adsorbed ethylamine and dissociatively adsorbed aniline, where the electron withdrawing power of the phenyl group in the aniline-based species produces a higher pK_b than does the ethyl group in the ethylamine-derived species. The reaction with a model organometallic reagent, tetrakis(diethylamido) titanium or ((CH₃)₂N)₄Ti (TDMAT), was studied. The reaction, replacing a single dimethylamino group of TDMAT occurs

with adsorbed NH_2 and the ethylamine-exposed surface but not with the aniline-exposed surface on $\text{Si}(100)\text{-}2 \times 1$. This trend is in accordance with the higher pK_a expected for the aniline-related species compared with the ethylamine-related species. In contrast to the nonreactivity of the aniline-based species on $\text{Si}(100)\text{-}2 \times 1$, the reaction with dissociatively adsorbed aniline was observed on $\text{Ge}(100)\text{-}2 \times 1$, showing that the electronic character of the underlying semiconductor is also involved in controlling the surface reactivity of the functionalized surface. This investigation nicely shows that model reactions may be used to sense reactivity trends on functionalized semiconductor surfaces and that expectations based on homogeneous reactivity trends are seen also for semiconductor-anchored groups. However, the observation of reactivity is a relatively crude tool unless it is coupled with coverage-dependent studies and other investigations to deconvolute steric effects. Also, the use of surface spectroscopies that are not exactly molecule-specific can give an incorrect impression of a specific reaction taking place, which the authors (31) correctly indicate.

Transient Electronic Excitations at Surfaces

The transient electronic excitation of surfaces constitutes a current frontier area of surface chemistry, especially surface photochemistry. The field has recently been reviewed (32). Often in the past, electronic decoupling of a molecule from a surface has been accomplished by building spacer layers. As described herein, Matino et al. (33) have used a cyclophane molecule that exposes one aromatic ring system to the metal surface while projecting another almost similar aromatic ring system into vacuum, decoupling it from the metal. STM studies of the adsorbed molecule reveal intense vibronic excitation of the upper ring's carbonyl ($\text{C}=\text{O}$) functionalities, indicating its successful electronic isolation from the underlying metal substrate that otherwise would quench the vibronic transition efficiently. The strong vibronic coupling is localized in the region occupied (near the molecular boundaries) by the carbonyl groups. These observations may provide future workers with concepts for building molecular-electronic structures where molecular motion in an isolated moiety is a trigger to charge transfer and hence, an energy-dependent molecular switch. They also suggest a potential way for getting quantum dots and other chromophores to maintain their special optical and electronic properties at metal surfaces, which is important in many potential applications.

The work of Tisdale and Zhu (34) deals with the interaction of semiconducting quantum dots with macroscopic semicon-

ductors. The interaction may be strong as the two semiconductors touch or weaker if intervening functional groups (often used in capping colloidal semiconductor particles) are present at the interface. The quantum dot can be electronically tuned by adjustment of its size so that one has a near continuum of electronic properties at hand. In addition, it can exhibit a high absorptivity for light. Tisdale and Zhu (34) discuss the size-dependent localization of excitons and electron-hole pairs in such systems. They discuss charge transfer between quantum dots and semiconductors, showing that, at close separations, tunneling is dominant, whereas at larger separations caused by intervening molecules, electron-hopping dominates. Their results closely correspond to issues in photovoltaic device behavior, where maximizing charge transfer across macroscopic distances is paramount. Also, the design of molecular electronic devices of the future will hinge on the ideas developed in this area.

The femto- and subfemtosecond dynamics of excited electrons in solids forms the topic discussed here by Muino et al. (35). The understanding and adjustment of the survival time of excited electrons are the key to the control of processes at surfaces caused by charge transfer. The frontier of this field involves shorter lifetimes, smaller systems, and electron spin effects. The question is how electronic excitations are created in time and how the environment reacts in time (or how electronic screening builds in as a function of time). It is found that screening of localized charges occurs in attoseconds; collective excitations transfer their perturbations over longer distances on longer timescales. The theoretical results relate to the frontier of experimental measurements, where attosecond time scales are probed.

Soft Surfaces and Interfaces: Polymer Surfaces

Polymer surfaces are extremely important in many applications. Much of the recent basic research excitement in this area has been associated with their applications in organic electronic and photovoltaic devices. This area was recently reviewed, with an emphasis on energy-level alignment across polymer interfaces (36, 37). Recent calorimetric measurements have begun to elucidate the strength of chemical bonding at polymer/metal interfaces (38).

The dynamical properties of polymer surfaces are quite different from those of the other types of surfaces discussed above, and these properties may help us understand the dynamical properties of other soft-matter surfaces such as liquids, thick organic layers, or living cells. The use of He atom scattering to understand the dynamical behavior of solid surfaces is a historical highlight of the development of

surface science. The technique has now been extended to soft surfaces such as liquids, organic layers, and thin polymer films. Becker et al. report here (39) an extension of this method to measure the surface vibrational dynamics of a polymer undergoing crystallization that can be monitored by FTIR spectroscopy. Thermal attenuation measurements provided the perpendicular and parallel mean square displacements for two different crystallinities of a polymer film. The primary result is that the mean square displacements perpendicular to the surface are softer than those parallel to the surface. Also, the semicrystalline polymer surface is softer than the amorphous polymer film in the perpendicular direction. Parallel mean square displacements were found to increase with increasing temperature by an order of magnitude over the perpendicular displacements for both polymer films. The surface dynamics information provided by He scattering complements bulk dynamical measurements by X-ray and neutron scattering and quantitatively enhances polymer materials science.

Surface Functionalization and Bio-Recognition at Surfaces

Surface functionalization was one of the earliest applications of surface chemistry and remains of extremely high importance today. The goal here is to take a material whose surface chemistry is initially dictated by that material's intrinsic surface composition and surface properties and attach to it specific chemical functional groups, especially well-defined organic functional groups or biochemical functionalities, to impart the appropriate physical, chemical, or biochemical properties to that material's surface. The goal can be to improve the material's frictional or optical properties, its wear resistance, hydrophobicity, or hydrophilicity, or its pK_a or to introduce specific functional groups chosen to react in controlled ways with molecules in the fluids with which it is in contact. This can include the introduction of receptors for adding chemical or biochemical specificity to a sensor surface or spots on the surface of a sensor array. The desired receptor can be proteins like antibodies, DNAs, RNAs, aptamers, etc., that, when spotted in microarrays, can lead to high-throughput assays for biochemical activity with applications in fundamental biochemistry or biophysical chemistry, gene sequencing, biomarker or drug discovery, and disease diagnosis.

Early success in the organo-functionalization of surfaces was achieved with oxide surfaces, particularly silica, using so-called silane-coupling agents (40, 41). Later came the development of alkylthiol- and disulfide-based strategies for func-

tionalization of gold surfaces, with the evolution of the concept of self-assembled monolayers (SAMs) (42, 43) and the amazing opportunities that they offer for surface patterning (44). More recently came methods for organo-functionalizing silicon surfaces (31, 45), which opened up applications involving semiconducting electronic devices.

Carbon-based surfaces are attractive for use in vivo because of their biocompatibility, mechanical hardness, electrical properties, and extraordinary chemical robustness. The article here by Stavis et al. (46) highlights some recent developments in methods for imparting biological compatibility and bio-recognition to diamond and other carbon surfaces and measurements that determine the success of those efforts. Their results show that photochemical grafting of short ethylene glycol (EG) oligomers to diamond surfaces produces a layer whose EG unit density is comparable with that for EG-based self-assembled monolayers on gold, which substantially reduces the nonspecific binding of proteins (to less than 3% of a monolayer). This may provide a route to make diamond and other carbon coatings, which already have very good biocompatibility, even more compatible with biological systems and tissue. Their results further show that the outstanding performance of diamond as a substrate for biological studies can be extended to include antibody-modified surfaces, which show improved chemical stability. Finally, their results suggest that more nonspecific binding of proteins occurs on surfaces whose roughness is on a similar size scale to protein size.

The interactions of proteins with surfaces are of great importance in many areas and are a topic of rapidly developing frontier research. Recently, a thermodynamic study of protein adsorption energy and entropy was performed on a system where the adsorbed protein's structure had also been characterized by NMR (47). That study focused on statherin adsorption on the mineral hydroxyapatite, which is important in understanding the role of this salivary protein in the growth of teeth and their biocompatibility. Adsorption here was found to be entropy-driven, with a heat of adsorption of only ~12 kJ/mol, tiny compared with energies usually measured in

ultrahigh vacuum adsorption calorimetry for much smaller molecules.

Dynamics of Thin Film Growth

The growth of thin films by physical vapor deposition has applications in a wide range of technologies, perhaps the most important of which includes fabrication of microelectronic, optical, opto-electronic, or electro-optic devices. The development of modern microelectronics and computers was greatly facilitated by the surface analysis of ultrathin films after or even during growth, which indeed served as one of the earliest drivers for the development of ultrahigh vacuum surface science. Usually, this brings to mind a flat film, but the sophistication of understanding in this field has led to remarkable control of the resulting structures such that one can now cite multiple examples where deposition instead leads to equally spaced nanoparticles and quantum dot arrays. For example, metal deposition onto the heringbone reconstruction of Au(111) starts with cluster nucleation at the same sites within this surface's large unit cell and eventually, leads to the beautifully controlled self-assembly of a periodic array of metal nanoparticles of nearly equal size (48). The growth of a SiGe alloy film on Si surfaces followed by Ge deposition can lead to spontaneous evolution of Ge quantum dots in a periodic array, which arises from the lattice strain because of lattice mismatch between SiGe and the underlying Si (49). Because this strain increases with particle size and then thickness when one mismatched material grows on top of another, it can lead to forces that limit the lateral spreading of particles and strongly distant-dependant particle-particle repulsions (50). The surface energy differences between the two materials and how they vary with surface curvature also introduce important forces. These forces all serve as tools that can be used to tune the self-assembly of such sophisticated nanostructures.

The kinetics of nucleation and growth also serve as powerful tools for controlling self-assembly during vapor deposition of one material onto another. Particularly important here are rates of monomer and small-cluster migration across the surface, their up-stepping and down-stepping at

step edges, and the creation and decomposition of small clusters. The article by Duguet et al. (51) highlights the importance of these elementary step kinetics in controlling the resulting nanostructure evolution. Specifically, they show the self-assembly of metal nanostructures during metal deposition onto a binary alloy surface, NiAl(110). This article also exemplifies the power of STM for monitoring these processes, especially when coupled with quantitative analyses and detailed kinetic modeling (in this example, backed by DFT input of energy barriers).

Conclusions

This snapshot of some of the frontiers of surface chemistry has missed many important areas of research activity, partially because of space limitations in this journal. It is hoped that this assembly of representative research articles together will serve as a stimulus to young workers to have a look at surface chemistry, now a well-developed field of science. They will find broad vistas that are currently flourishing as a result of the influence of surface chemistry on emerging areas, such as the biosciences, optical sciences, nanoscience, materials science, energy-related sciences, and environmental control. Surface chemistry has historically benefited from enormous developments in our ability to measure at surfaces coupled with enormous advances in theory. Refined surface measurement techniques are now being combined with equally refined methods for synthesis of useful surface layers of designed structure and functionality. Concepts resulting from the combination of advanced experiments and advanced theory now provide a comforting intellectual cohesiveness to the field. Most current developments in surface chemistry relate to man's needs in the 21st century in a technological world, dominated by surface processes undreamed of by Irving Langmuir.

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