

Chiral Surfaces: Accomplishments and Challenges

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Chirality is a property of objects and fields that can exist at all length scales. A simple manifestation of chirality is as a geometric property of objects that are nonsuperimposable on their mirror images. These exist as nonsuperimposable enantiomers of one another. From the chemist's perspective, interest arises from the fact that all biologically important molecules are chiral and exist in nature only as one of these two possible enantiomers. Such molecules include amino acids, proteins, sugars, and DNA: the building blocks of life. The origins of the homochirality of life on Earth are unknown, but the consequences are significant. The two enantiomers of chiral compounds ingested into the human body have vastly different physiological impacts, simply because they have different chemical interactions with the homochiral biomolecules of living organisms. Thus, in order to produce enantiomerically pure bioactive molecules, such as pharmaceuticals and agrochemicals, chemical processes must be devised that are enantioselective.

Chirality in Two Dimensions: Chiral Surface Chemistry. Enantioselective chemical processing requires the development of chiral media. Given the important role that surfaces play in many chemical processes (adsorption, catalysis, crystallization, and so forth), there is ample reason to develop chiral surfaces and an understanding of their enantioselectivity. Perhaps the earliest chiral surfaces of practical significance were the chiral stationary phases developed for chiral chromatography.¹ Another area of significant interest and activity is that of enantioselective heterogeneous catalysis. Several such catalysts are known, but the origin of their enantioselectivity is still the subject of study.²⁻⁴

Two basic problems need to be addressed by the field of chiral surface chemistry: the preparation of chiral surfaces, and

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the fundamental understanding of enantioselective chemistry and enantiospecific interactions of chiral molecules with such surfaces. What does it take to render a surface chiral? In order to be enantioselective in their chemistry, chiral surfaces must have atomic features that are chiral at the nanometer or molecular scale. More importantly, what does it take to render a surface enantioselective? This problem is complicated by the fact that the enantiospecific energy differences in interactions between chiral molecular species tend to be small, on the order of a few kilojoules per mole. As a consequence, chiral surfaces must exhibit a high degree of homogeneity. If the surfaces expose multiple binding sites of different or opposite intrinsic enantioselectivity, no net enantioselectivity will be observed.

The study of chiral metallic surfaces has largely developed over the past decade. It should be pointed out that there is a long history of the study of the surfaces of chiral organic crystals and of chiral minerals.⁵ It is only over the past decade, however, that the tools of surface science have been developed to the point that the study of large and relatively complex chiral organic species on metal surfaces has become feasible. Many

ABSTRACT Chiral surfaces serve as media for enantioselective chemical processes. Their chirality is dictated by atomic- and molecular-level structure, and their enantioselectivity is determined by their enantiospecific interactions with chiral adsorbates. This Perspective describes three types of chiral metal surfaces: those modified by adsorption of chiral molecules, those templated by chiral lattices of adsorbed species, and those that are naturally chiral. A new paper in this issue of *ACS Nano* offers insight into the intermolecular interactions that govern chiral templating of surfaces. This Perspective then outlines three major challenges to the field of chiral surface science: development of methods for detection of enantiospecific interactions and enantioselective surface chemistry, preparation of high-area chiral metal surfaces, and the development of a fundamental, predictive-level understanding of the origin of enantioselectivity on chiral surfaces.

See the accompanying Article by Bombis *et al.* on p 297.

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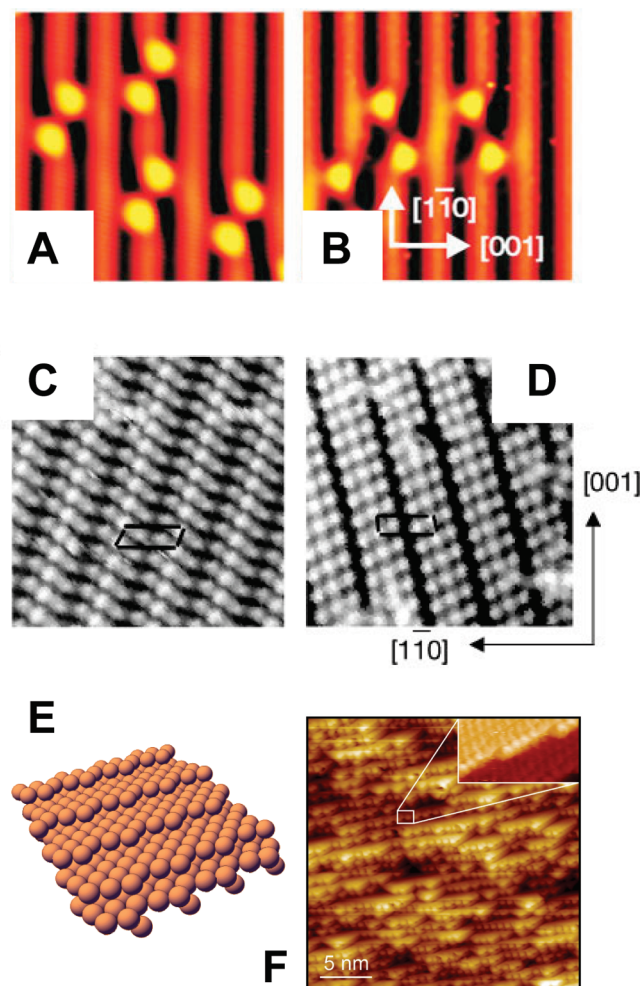


Figure 1. Manifestations of the three modes of inducing chirality at surfaces. (A,B) Adsorption of isolated chiral compounds onto surfaces renders them chiral and generates regions of local asymmetry in which adsorption is enantiospecific. The scanning tunneling microscopy (STM) images show dimers of (A) L-cysteine and (B) D-cysteine adsorbed on the (2×1) reconstructed Au{110} surface. The dimers are oriented asymmetrically with respect to the Au{110} rows oriented along the [110] direction. Reproduced with permission from ref 6. Copyright 2002 Nature Publishing Group (<http://www.nature.com/>). (C,D) Adsorbed species can form two-dimensional (2D) crystals with long-range order and asymmetric lattices. Such chiral surfaces can be created by adsorbates that are achiral in the gas phase, as in ref 11. The STM images reveal the ordered 2D overlayers generated by (C) (*R,R*)-bitartrate and (D) (*S,S*)-bitartrate adsorbed on the Cu{110} surface. Reproduced with permission from ref 11. Copyright 2000 Nature Publishing Group (<http://www.nature.com/>). The overlayer lattices lack mirror symmetry and exist in single enantiomer domains whose chirality is dictated by the chirality of the bitartrate. (E) Ideal structure of a high Miller index face-centered cubic (fcc) {643} plane. On such high Miller index planes, the kinked step edges that separate the low Miller index terraces lie along low symmetry directions of the bulk crystal lattice, and thus, the structure lacks mirror symmetry and exists in two enantiomeric forms: $\text{fcc}(hk\bar{l})^R$ and $\text{fcc}(hk\bar{l})^S$. (F) STM image of the Cu{643}^R surface revealing the kinked step structure. Reproduced with permission from ref 16. Copyright 2008 American Chemical Society. The STM image also reveals that these surfaces retain their low symmetry and net chirality, despite being subject to thermal roughening.

such investigations have been made possible by the widespread use of scanning tunneling microscopy (STM) to image adsorbed molecules on surfaces and have been aided significantly by the improve-

ments in molecular-scale simulation of adsorbates on metal surfaces.

The bulk structures of all metals are based on highly symmetric lattices such as face-centered cubic

(fcc), body-centered cubic (bcc), and hexagonal close-packed (hcp), and thus, the bulk structures of metals are achiral. However, there are three ways in which metal surfaces can be made chiral. The first is simply by adsorption of a chiral molecule onto the surface. Once adsorbed, the molecule breaks the symmetry of the surface, and if it was achiral, it is rendered chiral. The simple example of cysteine adsorption on the Au{110} surface is illustrated in Figure 1A,B.⁶ The Au{110} surface has an achiral row and trough structure with a (2×1) reconstruction. The ridges in the surface structure are readily observable in the STM image of Figure 1A,B. Adsorbed cysteine dimerizes enantiospecifically and breaks the mirror symmetry of the surface; the dimers of D-cysteine and L-cysteine are non-superimposable mirror images of one another. As a consequence, a second molecule adsorbing near the cysteine dimers will experience a chiral interaction with the surface.⁷ In order for such a surface to be enantioselective, there must be a fairly high coverage of these chiral modifiers, but they need not be organized into a chiral lattice, or even be organized into a lattice at all.

The second method for rendering a metal surface chiral is by adsorption of species that form chiral templates on the surface, two-dimensional overlayer lattices with long-range order but lacking mirror symmetry. There have been many observations of such structures.^{8,9} In this issue, Bombis *et al.* present one of the most systematic studies yet of the effects of adsorbate molecular structure on chiral templating of an achiral metal surface.¹⁰ Figure 1C,D illustrates a chirally templated surface: Cu(110) templated with (*R,R*)-bitartrate or (*S,S*)-bitartrate generated by adsorption of the corresponding tartaric acids.¹¹ The bitartrates themselves are inherently chiral, so templating of the surface with enantiomerically pure tartaric acids leads to ordered homochiral overlayers which extend across the

entire surface. The structures are clearly nonsuperimposable mirror images of one another. What may not be obvious is that molecules that are achiral in the gas phase can also adsorb on surfaces in such a way that they render the surface chiral. Bombis *et al.* have used achiral molecular species with planar structures, but adsorption breaks the mirror symmetry of the molecular plane and, thus, the adsorbed species can exist as one of two enantiomers. Of course, if there is no asymmetric driving force, one gets an equimolar or racemic mixture of the two enantiomers. Furthermore, adsorbed species can form ordered overlayer lattices that are chiral, even if the adsorbate has no chirality on the surface or in the gas phase. Even atoms can adsorb to form chiral ordered overlayers on achiral substrates; all that is required is that the symmetry of the overlayer breaks the symmetry of the substrate. Common examples would include the $(\sqrt{5} \times \sqrt{5})R26^\circ$ overlayer formed on square fcc(100) surfaces or the $(\sqrt{7} \times \sqrt{7})R19^\circ$ overlayer found on many hexagonal fcc(111) surfaces.¹² These form large, extended domains that are locally chiral; however, in the absence of asymmetric driving forces, equal areas of both enantiomeric structures are obtained across the surface.

The work of Bombis *et al.* presented in this issue explores the formation of chiral templates by achiral adsorbates and is extremely informative in a number of ways. They use a set of molecules with the generic, planar structure shown in Figure 2 and adsorb these onto the achiral Au{111} surface. The key feature of their work is the systematic inclusion or elimination of the substituents *tert*-butyl, hydroxyl, and aldehyde (A, B, and C in Figure 2) in order to ascertain which intermolecular interactions have the greatest influence on the structures of the chiral templates formed by these adsorbates. The backbone of the molecule is planar, but once ad-

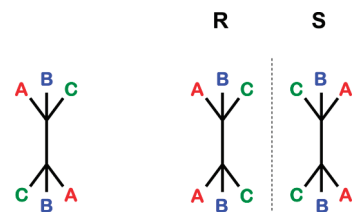


Figure 2. Generic structure of the species used by Bombis *et al.* in ref 10. These are planar, and in the gas phase, they are free to undergo intramolecular conformational inversion by rotation about the molecular axis. Although this molecule is achiral in the gas phase, adsorption can result in the three conformers illustrated. One is achiral; however, the other two are chiral enantiomers of each other, with their chirality induced by the presence of the surface. The absolute configurations of individual enantiomers have been determined by Bombis *et al.* In addition, these species form structures with long-range order and lattices that may also be chiral. The key observations are that the interactions of the substituents A, B, and C can be used to control both the frequency of occurrence of molecular conformations and the long-range chirality of the overlayers.

sorbed on the surface, it is rendered in three conformers, one achiral and an enantiomeric pair. One of the beautiful features of this study is the fact that the nature of the substituents and the quality of the STM imaging allow the authors to assign the absolute configuration of the adsorbed molecules. They are able to show that chiral templates are created by adsorbates that can interact *via* intramolecular hydrogen bonding. Furthermore, these chiral templates are formed from adsorbates all of the same

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chirality. This provides some insight into the design of species that will form chiral templates.

The third type of chiral metal surface is that which is intrinsically chiral. Given that the bulk structures of metals are achiral, it may not be obvious that one can make a clean metal surface that is intrinsically chiral. However, this is no more difficult than terminating the bulk lattice along a low symmetry plane, as in the case of the high Miller index fcc(643) surface illustrated in Figure 1E.^{13–15} The ideal structure of this surface is formed of (111) terraces separated by kinked, monatomic step edges. This structure is nonsuperimposable on its mirror image and thus chiral. Figure 1F shows a STM image of the Cu{643}^R surface. The real structure is complicated by the fact that it has undergone thermal roughening and diffusion of atoms along the step edges. Nonetheless, it retains the basic chiral terrace-step-kink structure and the net chirality of the ideal surface structure.¹⁶ Over the past decade, there have been a number of demonstrations of the enantioselective interactions of these naturally chiral metal surfaces with chiral adsorbates.^{17–26}

Enantioselectivity in Two Dimensions: Challenges. As mentioned above, the preparation of chiral surfaces is one of the key steps in the development of the field of chiral surface chemistry. The vast majority of the published efforts in this area have focused on chiral templates and their structures.^{8,9} As illustrated by the work of Bombis *et al.*, this effort is reaching the point that concepts for rational design of such templates are being proposed and tested. Without suggesting that chiral surface structures are fully understood, there remain three key challenges to developing chiral surface science to the point that it has practical impact: (1) study of enantioselectivity on chiral surfaces, (2) preparation of chiral surfaces in high surface area form, and (3) ultimately developing

a predictive understanding of the origins of enantioselectivity.

While there is a significant body of work that has identified chirally modified, chirally templated, and naturally chiral metal surfaces, there is comparatively little published work on the enantiospecific interactions of chiral adsorbates with these surfaces. Chiral surfaces themselves are only half of the equation; understanding enantioselectivity requires a chiral surface, a chiral probe molecule, and some measurement that is sensitive to the enantiospecificity of their interactions. As mentioned above, there are a small number of demonstrations of enantioselectivity on naturally chiral metal surfaces. These include demonstrations of enantiospecific adsorption energetics, enantioselective separations, enantiospecific adsorbate orientations, and enantioselective

electrochemistry.^{17–26} There are also a number of recent measurements of enantiospecific interactions of chiral probe molecules with templated chiral surfaces.^{27–29} The problem is that enantioselectivity is perhaps the most subtle form of chemical selectivity. Enantiospecific energy differences between pairs of chiral species are often of the order of a few kilojoules per mole or less. An energy difference of 2 kJ/mol yields a difference of a factor of 2 in reaction rates or equilibrium constants at room temperature, so even at this level one can achieve useful enantioselectivities. Thus, these enantiospecific interactions with chiral surfaces are measurable, but they require care and the appropriate use of control measurements and demonstrations of diastereomerism. Unfortunately, achieving accurate predictions of

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energy differences of this magnitude is beyond the capabilities of the best electronic structure calculations.³⁰ Nonetheless, these challenges must be addressed as the field moves forward.

If chiral metal surfaces are to be of practical value, then they must be prepared in significant quantities. Applications such as enantioselective catalysis and separations require high surface areas.

Applications such as enantiospecific sensors may be feasible with low surface area materials. Preparation of chiral surfaces by chiral modification or templating can easily be envisioned on a large scale. In fact, heterogeneous catalysts having a high surface area have been prepared and have demonstrated enantioselectivity for some classes of hydrogenation reactions.^{2–4}

Large-scale preparation of naturally chiral metal surfaces has received little attention, although if achieved, these might provide some significant advantages over modified and templated surfaces, including a higher thermal stability. To date, all naturally chiral metal surfaces have been prepared by cleaving single crystals of metals along low-symmetry planes.

There have been some indications that one might be able to prepare naturally chiral metal surfaces with a high surface area. For instance, it is possible to prepare naturally chiral surfaces through molecular imprinting. One often thinks of molecular imprinting as applicable to soft materials such as polymers; however, metal surfaces are in fact quite pliable at the

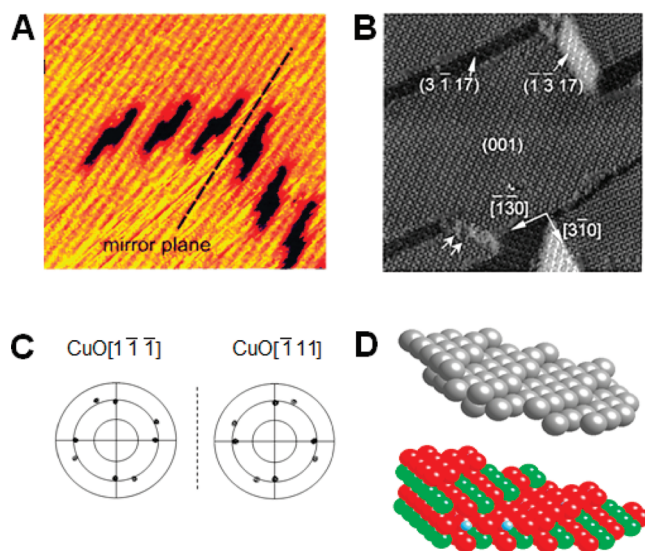


Figure 3. Four manifestations of the enantiospecifically controlled preparation of chiral inorganic surfaces. (A) Adsorption of chiral 2,5,8,11,14,17-hexa(*tert*-butyl)decacyclene onto Cu{110} results in the extraction of atoms from the rows of Cu atoms at the surface. The STM image shows the chiral holes remaining in the surface after removal of the adsorbate and reveals that the chirality of the holes is dictated by the chirality of the adsorbate. Reproduced with permission from ref 31. Copyright 2001 John Wiley & Sons, Inc. (B) Adsorption of L-lysine onto the Cu{100} surface results in the formation of high Miller index (3,1,17) facets. The four facets observed on the Cu{100} surface are homochiral with their chirality dictated by that of lysine. Reproduced from ref 32. Copyright 2000 American Chemical Society. (C) Electrodeposition of CuO onto the Au{100} surfaces from solutions of Cu^{II}(*R,R*-tartrate) results in the growth of CuO[$\bar{1}\bar{1}\bar{1}$] planes, while Cu^{II}(*S,S*-tartrate) results in the growth of CuO[111] planes. These CuO surfaces are enantiomorphs, as revealed by the X-ray diffraction (XRD) pole figures. The four diffraction features along the high-symmetry directions arise from the Au{100} substrate. Reproduced with permission from ref 33. Copyright 2003 Nature Publishing Group (<http://www.nature.com/>). (D) Schematic illustration of the homochiral, heteroepitaxial growth of a Pt{621} film on a SrTiO₃(621) substrate. The Pt film retains the chirality of the substrate.³⁴

atomic scale. Figure 3A shows a STM image of a Cu{110} surface with chiral pockets or holes that have been generated by adsorption and then removal of a chiral adsorbate.³¹ Figure 3B shows a STM image of a Cu{100} surface that has reconstructed in the presence of adsorbed L-lysine to expose a homochiral set of [3,1,17] facets.³² These demonstrate, at least in principle, that chirality can be imparted to a metal surface not just by adsorption of achiral compounds but by imprinting of chirality into the atomic structure of the surface. Figure 3C illustrates the X-ray diffraction (XRD) pole figures obtained from two CuO films deposited by epitaxial electrodeposition on the Au{100} surface from solutions of Cu^{II} tartrate.³³ The CuO[111] and CuO[111] surfaces are chiral enantiomers of one another, and their chirality is dictated by the chirality of the tartrate precursor used in electrodeposition. Finally, Figure 3D illustrates schematically the deposition of a chiral Pt{621} film onto a chiral SrTiO₃(621) surface, the first demonstration of homochiral heteroepitaxial film growth.³⁴ These examples represent the first hints that the growth of naturally chiral materials can be achieved with control over chirality, offering possible routes to the production of high area naturally chiral surfaces.

Finally, there is the grand challenge: understanding enantioselective interactions on surfaces with predictive accuracy. This is an extremely difficult problem. Given the very small energy differences that are typical of enantiospecific interactions and the fact that these are beyond even the limits of accuracy of modern computational chemistry, it is clear that tremendous strides will need to be made in order to develop any useful intuitive understanding of enantioselective surface chemistry. This perspective is not given to detract from the importance of the problem, simply to indicate its difficulty. The work of Bombis *et al.* is a solid first step and

demonstrates that some useful insights can be gained into various aspects of the problem, in this case the preparation of a chiral template.

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