

## Jay A. Switzer – Summary of Research

I have dedicated most of my career to research on the electrodeposition of nanostructured metal oxide ceramics. Although the electroplating of *metal* films is a mature field, our group has focused on the electrodeposition of *metal oxide ceramics*, such as nanostructured metal oxide semiconductors, magnetic materials, and catalysts. The goal of this research is not to imitate vapor deposition, but to exploit the “wet” aspects of electrodeposition to produce architectures which may not be accessible to UHV methods. Our current emphasis is on the epitaxial electrodeposition of metal oxide ceramics for energy conversion and storage.

### *Electrodeposited Metal Oxides for Energy Applications*

The focus of our work will be the electrodeposition of metal oxide films for solar energy and battery applications. All of these materials will be produced as nanostructured films from aqueous solution. This work is supported by the U.S. Department of Energy, Office of Basic Energy Sciences under Grant No. DE-FG02-08ER46518 (four years, \$700,000).

We plan to produce epitaxial nanostructures of ZnO (see, *Langmuir* **22**, 10535 (2006)), Cu<sub>2</sub>O and Bi<sub>2</sub>O<sub>3</sub> for use in photovoltaic and photoelectrochemical applications. One possible architecture is an ordered nanocomposite of ZnO nanowires with Cu<sub>2</sub>O electrodeposited between the nanowires. The ZnO wires are single crystalline, which minimizes electron-hole recombination at grain boundaries. The Cu<sub>2</sub>O is a lower bandgap material, which helps maximize the absorption of the solar spectrum.

We have previously shown that we can deposit layered nanocomposites of Cu<sub>2</sub>O and Cu metal in a self-assembling reaction produced by electrochemical oscillations (*J. Am. Chem. Soc.* **120**, 3530 (1998)). These films are highly absorbing due to the surface plasmon resonance of the nanocrystalline Cu. We plan to study the photovoltaic response of these materials to determine whether the surface plasmon absorption can be coupled with the valence to conduction band absorption of the Cu<sub>2</sub>O to produce a highly absorbing semiconductor. The nanophase Cu would function as an inorganic sensitizer – which should be much more photostable than organic dyes.

Several years ago, we showed that epitaxial films of  $\delta$ -Bi<sub>2</sub>O<sub>3</sub> can be electrodeposited onto single-crystal Au (*Science* **284**, 293 (1999)). Although the interest in this material is usually for an electrolyte in solid oxide fuel cells, we wish to explore the photoelectrochemical response of the material. The monoclinic form of Bi<sub>2</sub>O<sub>3</sub> has been used for photoelectrochemical water splitting. A problem with this (yellow) material is that the bandgap is too large to produce efficient solar cells. The cubic, delta form is black, with a bandgap of only about 1.2 eV.

We have recently shown in unpublished work that thin films of NaMnO<sub>3</sub> can be electrodeposited from aqueous solution. We plan to extend this work to the deposition of LiMnO<sub>3</sub> – an important material for Li-ion batteries. A beauty of the electrochemical method is that both electrical contact and crystallographic orientation should be uniform throughout the film. We are especially interested in producing materials for thin-film microbatteries for medical applications.

## *Chiral Electrodeposition*

The best example of the use of “wet” electrodeposition to produce unique architectures is our recent work on the electrodeposition of chiral surfaces (*Nature* **425**, 490 (2003)). Chiral surfaces of CuO were electrodeposited onto achiral Au substrates using solution templating agents such as tartaric acid and amino acids to direct the chiral growth (see Figures 1&2 below). This was an unexpected result, because the surface of the electrodeposited CuO was chiral, but CuO does not crystallize in a chiral space group. Chiral surfaces offer the possibility of developing heterogeneous enantioselective catalysts that can more readily be separated from the products and reused than the presently used homogeneous catalysts. In addition, such surfaces can serve as electrochemical sensors for chiral biomolecules and pharmaceuticals (*Chem. Mater.* **16**, 4232 (2004)). Implantable sensors could be used to monitor drug levels in the body, and post-chromatographic chiral electrochemical sensors will obviate the need for chiral separation prior to chemical detection.

We have been supported by AstraZeneca to develop chiral electrochemical sensors. We are exploring the chiral recognition of molecules such as tartaric acid, malic acid, L-dopa, and various amino acids by cyclic voltammetry. Recent results with L- and D-dopa are very encouraging. In the future, we plan to use non-Faradaic techniques such as surface plasmon resonance and differential capacitance, or to follow mass changes due to molecular adsorption with the electrochemical quartz crystal microbalance (EQCM).

We are also working under NSF funding (grant #DMR-0504715, four years, \$452,000) to better understand the mechanism of chiral recognition, to produce new chiral surfaces, and to use “electrochemical biomineralization” to produce chiral habits of materials such as calcite. For the mechanistic studies, we are using in-situ techniques such as EQCM, STM, and vibrational spectroscopy to understand how the tartrate ions or amino acids serve as templates to produce the chiral films. To produce new chiral films, we have determined by symmetry considerations which surfaces (i.e., which values of **h**, **k**, and **l**) lack mirror symmetry for a given point group. We can then deposit oxides of inorganic materials with these orientations in the presence of chiral ligands such as tartrate or amino acids. We have recently found, for instance, that sea-shell-like chiral habits of calcite can be produced by “electrochemical biomineralization” if calcium carbonate is crystallized on a surface in the presence of tartrate ion. The calcium carbonate is produced from calcium bicarbonate by the generation of base at the electrode surface. We are also using this technique to deposit thin films of hydroxyapatite. There are considerable similarities between electrodeposition and biomineralization. In both cases solid materials are produced from solution precursors, and solution additives (such as chiral amino acids) can have profound effects on the resulting deposit.

## *Electrodeposition of Metal Oxide Nanostructures*

We have been involved with the deposition of metal oxide nanostructures since 1990, when we electrodeposited ceramic superlattices (*Science* **247**, 444 (1990)). Our research in this area is supported by NSF (grant #CHE-0243424, three years, \$345,000). Superlattices are nanometer-scale layered structures with coherent stacking of atomic planes. They are usually produced by ultra-high-vacuum techniques like molecular beam

epitaxy. Our group was the first to show that ceramic superlattices can be produced at room temperature by the simple and inexpensive electrodeposition method. In 1992, we showed that superlattices can be imaged in real space in the scanning tunneling microscope (*Science* **258**, 1918 (1992)), and in 1994 we developed a new type of superlattice called a defect-chemistry superlattice (*Science* **264**, 1573 (1994)). We also have emphasized producing nanomaterials which have unique size-dependent properties. In 1998, we showed that layered metal/metal oxide nanostructures which exhibit negative differential resistance at room temperature due to quantum confinement can be self-assembled in a chemically oscillating system (*J. Am. Chem. Soc.* **120**, 3530 (1998)).

Our present research is on the electrodeposition of nanometer scale magnetic oxides such as  $\text{Fe}_3\text{O}_4$  for the production of spintronic devices (see Fig. 3 below) and resistive random access memory (RRAM)(see Fig. 4 below). Our focus is on producing superlattices based on iron oxides in which the alternating layers in the superlattice are produced by pulsing the applied potential during deposition. We have very recently shown (*J. Am. Chem. Soc.*, 2010) that defect chemistry superlattices based on magnetite show low-to-high and high-to-low resistance switching that may be applicable to the fabrication of resistive random access memory (RRAM). The fact that multiple resistance states can be accessed by simply varying the applied bias voltage opens up new possibilities for multibit data storage and retrieval.

### *Epitaxial Electrodeposition of Metal Oxides*

In 1999, we showed that it is possible to electrodeposit single crystal films of metal oxides (*Science* **284**, 293 (1999)). We have deposited epitaxial films of  $\text{Cu}_2\text{O}$ ,  $\text{CuO}$ ,  $\text{AgO}$ ,  $\text{Fe}_3\text{O}_4$ , Prussian Blue,  $\delta\text{-Bi}_2\text{O}_3$ ,  $\text{PbO}_2$ ,  $\text{Ti}_2\text{O}_3$ ,  $\text{PbS}$ ,  $\text{KBi}_x\text{Ba}_{(1-x)}\text{O}_3$ , and  $\text{ZnO}$  onto single-crystal  $\text{Au}$ ,  $\text{Cu}$ ,  $\text{Si}$ , and  $\text{InP}$  substrates. These materials have included catalysts (*J. Am. Chem. Soc.* **126**, 488 (2004)), fuel cell materials (*Science* **284**, 293 (1999)), oxide semiconductors (*Chem. Mater.* **13**, 508 (2001) & *Langmuir* **22**, 10535 (2006)), molecular magnets (*J. Am. Chem. Soc.* **125**, 14998 (2003)), and magnetic oxides used for spin-dependent tunneling (*J. Am. Chem. Soc.* **124**, 7604 (2002) & *J. Mater. Res.* **21**, 293 (2006)). We have shown that the size and shape of epitaxial films of  $\text{Cu}_2\text{O}$  can be controlled by changing the solution conditions such as pH (*J. Phys. Chem. B* **106**, 4027 (2002)), and that epitaxial films of metal oxide semiconductors can be directly deposited onto  $\text{Si}$  (*J. Phys. Chem. B* **106**, 12369 (2002)) and  $\text{InP}$  (*Appl. Phys. Lett.* **83**, 1944 (2003)) wafers. The deposition of epitaxial oxides onto semiconductors such as  $\text{Si}$  and  $\text{InP}$  is extremely important, because there is an active search for alternatives to the native oxide on  $\text{Si}$  for the manufacture of nanometer-scale electronic devices.

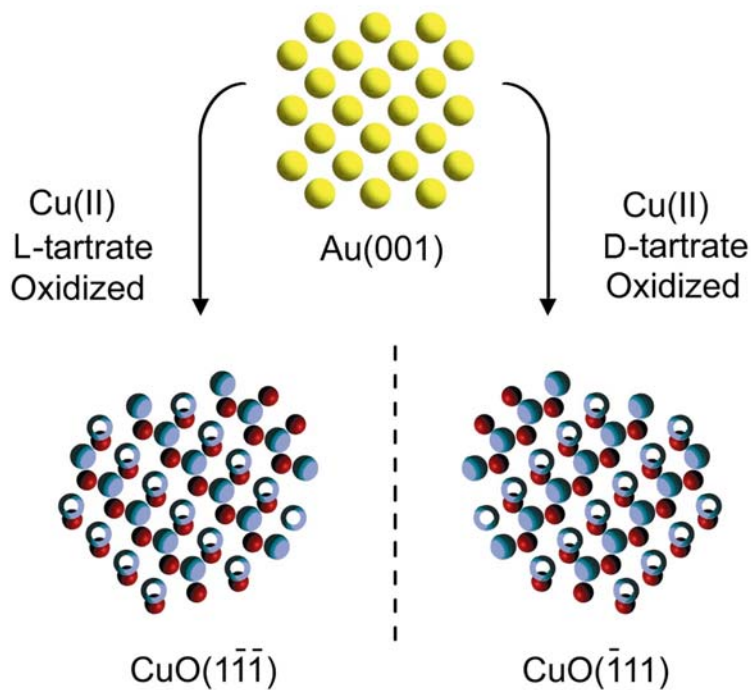
Our future emphasis in this area will be on shape control in epitaxial electrodeposition. In this case the out-of-plane and in-plane orientation of the electrodeposited metal oxide is determined by the single crystal substrate, but the shape is determined by additives in solution that selectively adsorb on specific crystal faces. Besides producing deposits with fascinating morphologies, this work will lead to some very interesting surface chemistry studies.

## *Unleaded Drinking Water*

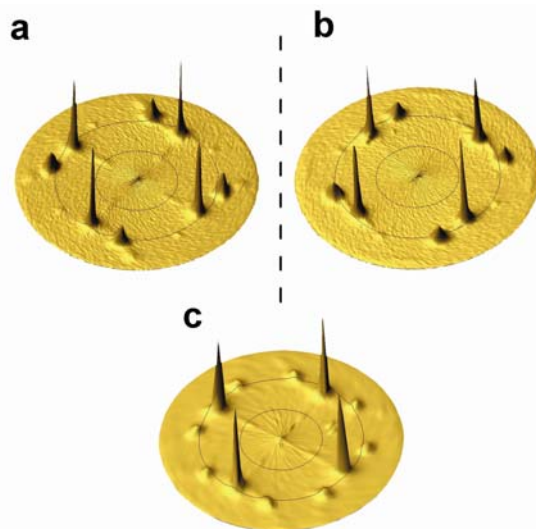
Many water districts have recently shifted from free chlorine (in the form of  $\text{OCl}^-$ ) to monochloramine ( $\text{NH}_2\text{Cl}$ ) as a primary disinfectant for drinking water in order to lower the concentration of chlorinated hydrocarbon by-products in the water. There is concern that the use of  $\text{NH}_2\text{Cl}$  disinfectants may lead to higher Pb levels in drinking water. NSF (grant #CHE-0437346, one year, \$150,000) asked us to study this problem because very little is understood about the chemistry of the problem. In our initial study (see, *Environmental Science and Technology* **40**, 3384 (2006)), the electrochemical quartz crystal microbalance (EQCM) was used to compare the effects of these two disinfectants on the dissolution of Pb films (see Figure 4 below). A  $0.5\ \mu\text{m}$  thick Pb film nearly completely dissolves in a  $\text{NH}_2\text{Cl}$  solution, but it is passivated in a  $\text{OCl}^-$  solution. X-ray diffraction analysis shows that the  $\text{NH}_2\text{Cl}$  oxidizes Pb to Pb(II) species such as  $\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$ , whereas the stronger oxidant  $\text{OCl}^-$  oxidizes Pb to Pb(IV) as an insoluble  $\text{PbO}_2$  conversion coating. Although  $\text{NH}_2\text{Cl}$  may produce less chlorinated hydrocarbons than  $\text{OCl}^-$  when used as a disinfectant, it may lead to increased Pb levels in drinking water.

There is still a lot of research that needs to be done on this topic. We plan to study whether the  $\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$  layers that deposit on Pb in the presence of  $\text{NH}_2\text{Cl}$  can be converted to passivating layers of  $\text{PbO}_2$  in the presence of  $\text{OCl}^-$ . We will determine whether the  $\text{PbO}_2$  conversion layers on Pb are epitaxial. The kinetics of electrochemical reduction of both  $\text{OCl}^-$  and  $\text{NH}_2\text{Cl}$  will also be studied. The electron-transfer pathways of these deceptively simple oxidizing agents are not well understood. For example, although both  $\text{OCl}^-$  and  $\text{NH}_2\text{Cl}$  are thermodynamically capable of oxidizing Pb to Pb(IV), only  $\text{OCl}^-$  oxidizes Pb to  $\text{PbO}_2$ . Our experience in electrochemistry and materials characterization should allow us to provide a fresh perspective on this important problem.

Our research has always been at the interface between chemistry, electrochemistry, materials science, and solid-state physics. Our research group reflects this diversity, and typically consists of chemists, chemical engineers, materials scientists and physicists. Students in the group become experienced in electrochemistry, STM, AFM, X-ray diffraction, and electron microscopy. They are well prepared for academic or industrial careers in electrochemistry, inorganic materials chemistry, or materials science. Ongoing research projects include i) chiral electrodeposition, ii) chiral sensing, iii) nanostructured metal oxides, iv) spintronic devices, v) epitaxial electrodeposition, and vi) studies to lower lead levels in drinking water.



**Figure 1:** Outline of the chiral electrodeposition scheme (from, *Nature* 425, 490, (2003)). CuO with either a left-handed or right-handed orientation is electrodeposited onto achiral Au(001) in the presence of left-handed or right-handed tartaric acid. The chiral CuO was shown to function as a chiral electrochemical sensor.



**Figure 2:** CuO(111) pole figures for films of CuO on Au(001) grown from solutions of (a) L-tartaric acid, (b) D-tartaric acid, and (c) DL-tartaric acid. The film grown from L-tartaric acid has a  $(1\bar{1}\bar{1})$  orientation, while the film grown from D-tartaric acid has a  $(\bar{1}11)$  orientation. The film deposited from DL-tartaric acid has nearly equal amounts of the two chiral orientations.

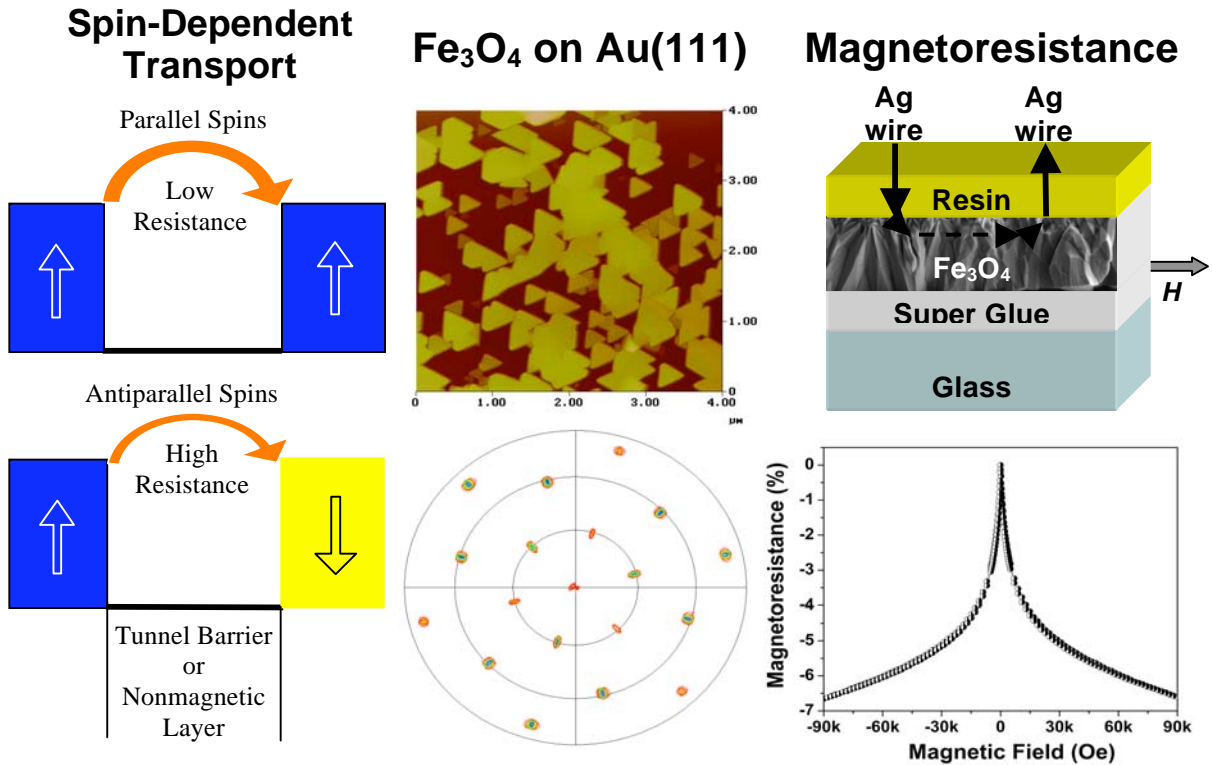


Figure 3 Electrodeposition of epitaxial  $\text{Fe}_3\text{O}_4$  onto Au(111) and the production of spintronic devices.

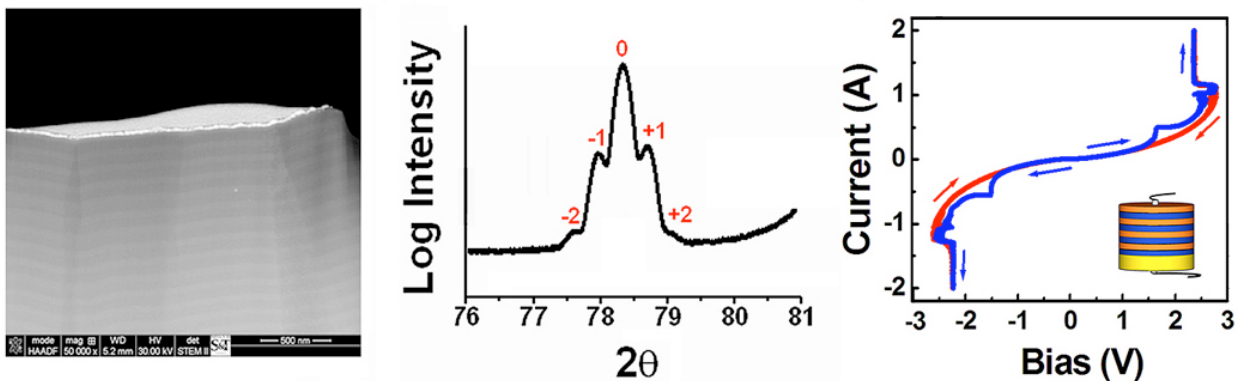


Figure 4 - Defect-chemistry magnetite superlattices and compositional superlattices in the magnetite/zinc ferrite system are electrodeposited as epitaxial films onto single-crystal Au(111). The defect-chemistry superlattices have alternating nanolayers with different Fe(III)/Fe(II) ratios, whereas the compositional superlattices have alternating nanolayers with different Zn/Fe ratios. The electrochemical/chemical (EC) nature of the electrodeposition reaction is exploited to deposit the superlattices by pulsing the applied potential during deposition. The defect-chemistry superlattices show low-to-high and high-to-low resistance switching that may be applicable to the fabrication of resistive random access memory (RRAM). (*J. Am. Chem. Soc.*, 2010)

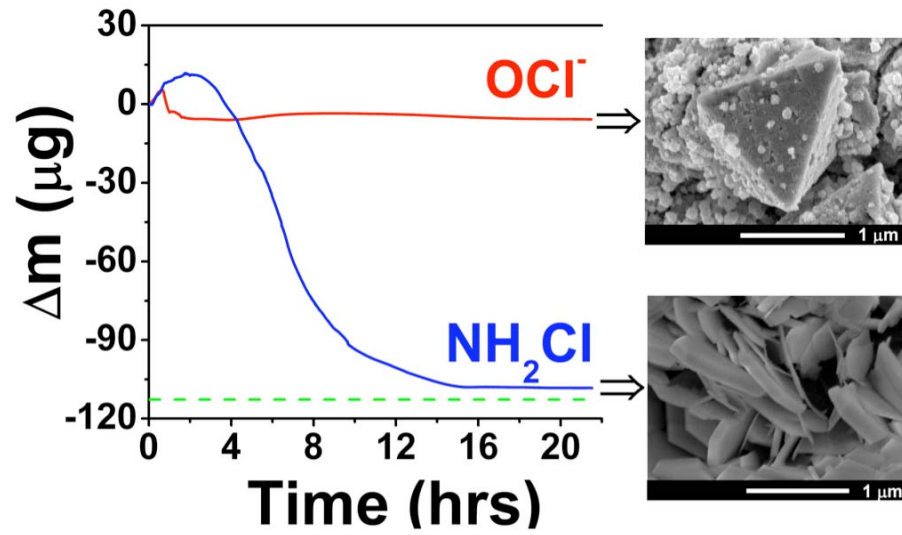


Figure 5: EQCM evidence that monochloramine disinfectants could lead to elevated Pb levels in drinking water. A Pb film nearly dissolves in monochloramine, but it is passivated with lead dioxide in hypochlorite (*Environmental Science and Technology* 40, 3384 (2006)).