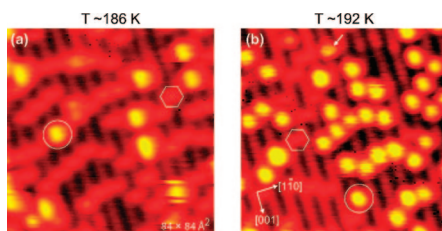


Now Starring: Reaction Intermediates on an Oxide Surface

■ Surface chemists have long sought to “watch” chemical reactions taking place at the atomic scale, and scanning tunneling microscopy (STM) is thought to be the most likely technique to enable reaching this goal. STM has previously been used to gain insight into the diffusion of small molecules, adatoms, and large organic molecules, as well as spontaneous dissociation reactions and reactions induced by tunneling electrons from the STM tip. However, STM studies showing complete surface-catalyzed reactions that include all the intermediate species are rare, and those for reactions on oxide surfaces are rarer still.

Seeking to gain better understanding of the individual steps and species



involved in these types of reactions, Matthiesen *et al.* (p 517) used high-resolution STM to make a set of time-lapsed images, stringing together movies that display unprecedented details of the intermediate steps of a surface-catalyzed reaction. They compared these images to density functional theory calculations to identify the species present in the images.

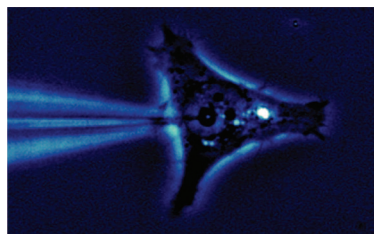
The researchers focused on the oxidation of H adatoms by O₂ molecules on the rutile TiO₂(110) surface, a reaction with both fundamental interest and practical applications in heterogeneous catalysis and photocatalysis. By monitoring the different morphologies and mobilities of species that appear in the resulting movies, the researchers were able to follow the individual reaction intermediates HO₂, H₂O₂, and H₃O₂, and the final reaction products as O₂ adsorbed and successively reacted with adatoms on the oxide surface. The authors suggest that such STM results will enhance our understanding of reaction intermediates and may be important for designing better catalysts.

World's Smallest Pipette Also World's Smallest Patch Clamp

■ Getting an accurate read on cell electrophysiological behavior in real time and with high spatial resolution is a key goal for understanding cellular machinery and evaluating individual cells' responses to various drugs. To that end, experimental cell biologists and pharmacologists often use electrolyte-filled glass micropipettes or microelectrodes that access intracellular domains to measure how a stimulus affects the flow of ions through or changes the electrical potential across the cell membrane. Though these probes are versatile and widely used, they come with a host of problems, including the propensity to rupture the cell membranes with the pipettes' tips or damage cell interiors as the electrolyte solution diffuses inside.

To overcome these problems, Schlaue *et al.* (p 563) tested the ability of carbon nanopipettes (CNPs) they had previously developed for intracellular injection to take electrical recordings. The researchers constructed CNPs by integrating carbon nanopipes, with diameters ranging from tens to hundreds of nanometers and lengths ranging from hundreds of nanometers to hundreds of microns, into the tips of pulled glass capillaries. Using mouse hippocampal cells as a model system, the scientists inserted

CNPs into the cells' interiors, allowing cell membranes to form a tight seal around the probes' tips. They then used



these probes to test cellular responses to various extracellular stimuli, ultimately showing that the CNPs could accurately measure changes in potentials resulting from ionic enrichment

and the pharmacological agent γ -aminobutyric acid (GABA). The researchers plan to evaluate whether CNPs can simultaneously measure electrophysiological responses to stimuli that these devices inject into cells.

Polymer Vesicles: Formed and Functionalized

■ Polymer vesicles have been gaining interest as possible vehicles for encapsulation and controlled delivery of drugs. Composed of closed bilayer membranes with hollow cavities and similar to liposomes, the structures of these “polymerosomes” can be manipulated on both

polymeric and supramolecular levels to tune their properties, including size, response to external stimuli, mechanical properties, membrane permeability, and *in vivo* fate. However, though researchers have been developing and studying polymer vesicles since the mid-1990s, most designs have consisted of amphiphilic block copolymers with limited functionalities for chemical transformations after vesicle assembly. Some researchers have reported surface functionalization through reactions with the functional groups inserted at the chain ends of the hydrophilic segments, though few have reported modifying the wall domains of polymerosomes.

Seeking to change this paradigm, Sun *et al.* (p 673) constructed polymer vesicles bearing benzaldehyde functionalities within the vesicular walls. The researchers developed these polymerosomes through self-assembly of an amphiphilic diblock copolymer precursor in water. Us-

ing microscopy and light scattering techniques to characterize the vesicles, the scientists showed that these polymerosomes ranged in size from 100 to 600 nm in diameter. They demonstrated the reaction of embedded benzaldehyde functionality using reductive amination to cross-link individual vesicles, as well as using a one-pot approach to incorporate fluorescent dyes. These fluorescent vesicles were found to associate with cells effectively, with insignificant cytotoxicity. The researchers plan to investigate the chemistry of these synthetic and reactive vesicles further, including optimizing the reaction efficiency and incorporating other labels and ligands, to enable a general approach for *in vivo* delivery of drugs and other therapeutics.

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