

Inducing Nonlocal Reactions with a Local Probe

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Since its invention, the scanning tunneling microscope (STM) has expanded the boundaries of surface science.¹ It has provided unparalleled new insights into semiconductor and metal surface structure and a deeper understanding of nucleation and film growth and of the physical and chemical properties of interfaces. The highly localized nature of the probe enables quantitative access to electronic and topographic information from aperiodic and isolated features,² while tip–sample interactions open the possibility for local surface modifications with atomic-scale precision.^{3–5} The STM has also proven to be a useful tool to measure surface-state characteristics, including hole and electron lifetimes and effective masses, which can be investigated *via* the standing waves caused by scattering of surface electrons.^{6,7} The local imaging capability of the STM confers a distinct advantage for these types of measurements because it can be used to identify defect-free regions of surfaces. Thus, carrier lifetimes, for example, can be accurately measured without attenuation due to defect scattering.^{8,9}

Using the STM tip as a hot-electron source introduced the possibility to initiate reactions on a spatially localized scale and to subsequently study the reaction products one molecule at a time.

An emerging area of surface science research is the study of organic/inorganic interfaces,¹⁰ which are important for a number of applications, including catalysis,¹¹ biocompatibility,¹² nanoelectronics, organic electronics, photonics, and photovoltaics,^{13–17} as well as for increasing a fundamental understanding of surface chemistry. A key challenge in studying these interfaces lies in correlating their morphologies with their physical and chemical properties, in particular, their electronic structure. The STM provides an excellent tool for this purpose, both because it enables physical and electronic characterization^{18,19} and because it can be used to induce and to observe reactions in a controlled fashion at the atomic scale.

Initiating Reactions with “Hot Electrons”. The STM tunneling current is a highly localized stream of electrons with energy determined by the bias voltage, whose polarity dictates whether electrons are to be injected into the tip or into the sample. In either case, conservation rules dictate that the electrons must originate from and terminate in allowable energy states. Electrons injected from the tip to the sample are called “hot electrons” because they possess energies greater than the Fermi energy, E_F . Prior to the advent of the STM, photochemical studies involving hot-electron processes necessitated an optical source to excite electrons from occupied states, with momentum transfer arising solely from the crystal.²⁰ Using the STM tip as a hot-electron source introduced the possibility to initiate reactions on a spatially localized scale and to subsequently study the reaction products one molecule at a time. Early work investigating the interactions between STM-injected hot electrons and molecules exploited the tunneling current to induce molecular dissociation.^{21–24} Later, it was shown that chemical bonds could be created in the same manner.²⁵ More recent work has led to striking demonstrations of the use of

ABSTRACT The scanning tunneling microscope (STM) has evolved continually since its invention, as scientists have expanded its use to encompass atomic-scale manipulation, momentum-resolved electronic characterization, localized chemical reactions (bond breaking and bond making) in adsorbed molecules, and even chain reactions at surfaces. This burgeoning field has recently expanded to include the use of the STM to inject hot electrons into substrate surface states; the injected electrons can travel laterally and induce changes in chemical structure in molecules located up to 100 nm from the STM tip. We describe several key demonstrations of this phenomenon, including one appearing in this issue of *ACS Nano* by Chen *et al.* Possible applications for this technique are also discussed, including characterizing the dispersion of molecule–substrate interface states and the controlled patterning of molecular overlayers.

See the accompanying Article by Chen *et al.* on p 3684.

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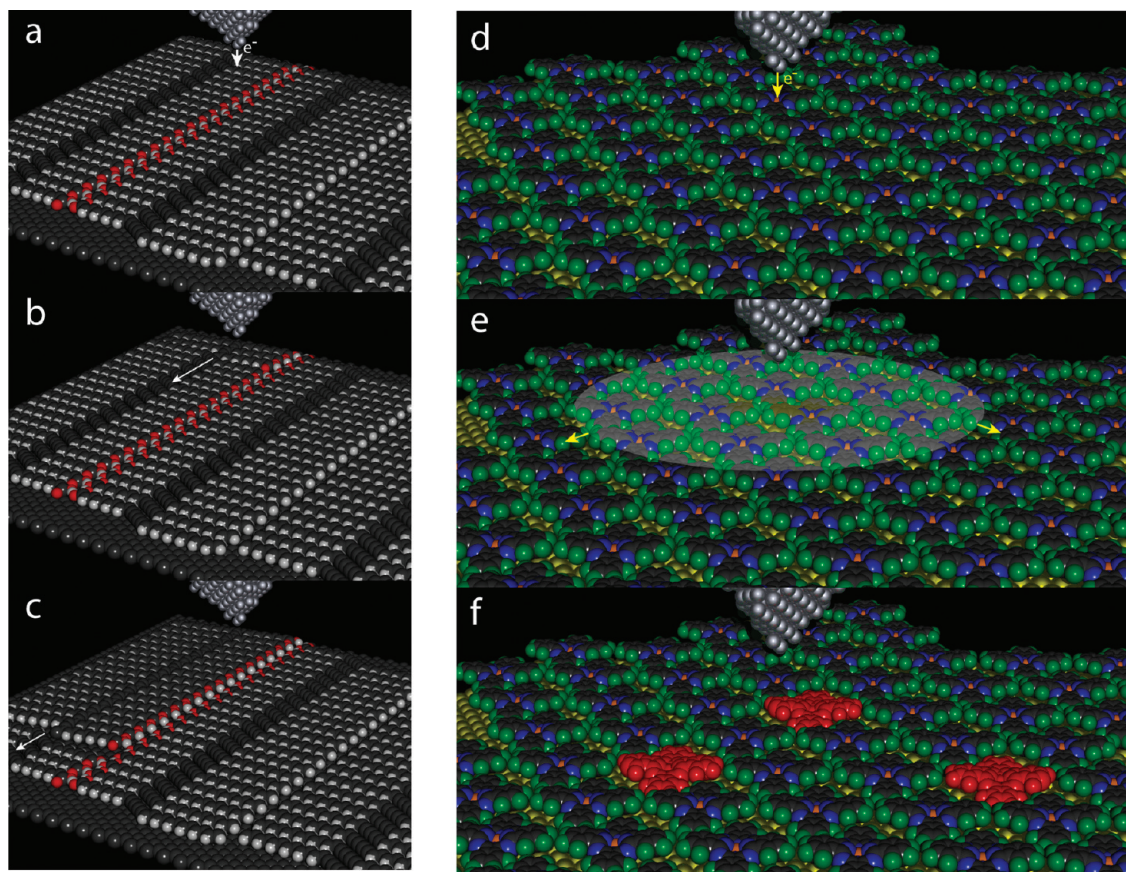


Figure 1. Schematic mechanisms of two different examples of using hot electrons from the STM tip to induce reactions over an extended region in a molecular overlayer. The schematic on the left shows a chemical chain reaction, wherein the localized injection of electrons (a) induces a reaction that propagates from molecule to molecule along a defined direction (b,c). The schematic on the right shows the chemical reaction induced *via* the injection of electrons through a molecule/metal interface (d) into a surface state (e), from which the electrons can back-transfer into molecules away from the injection site, inducing a chemical change (f).

the STM to manipulate reactants into proximity with one another, followed by initiation of chemical bond formation with injected electrons.^{25–27}

These localized reactions provide an elegant proof-of-principle of the efficacy of initiating chemistry with electron injection from the STM tip and represent an ideal testing ground for investigating systems relevant for single-molecule electronics (for example) as well as for a fundamental description of chemical reactions. However, the localized nature of the reaction currently limits its applicability to extended molecular films and networks since initiating reactions one molecule at a time over an entire film is too slow to become a scalable, technologically viable approach.

Molecular chain reactions at surfaces^{28–30} have attracted attention because they can create nanoscale patterns with a fast, parallel approach. STM-induced chain reactions provide a possible method to bridge the spatial difference between localized tunneling electrons and an extended two-dimensional layer since electrons from the STM tip can initiate a reaction that will propagate through the molecular overlayer (Figure 1). Aono's group demonstrated this concept in a self-assembled molecular network of diacetylene-containing molecules on highly ordered pyrolytic graphite (HOPG).^{31,32} By injecting electrons into a single molecule, they initiated the chain polymerization of adjacent diacetylene moieties in the network, effectively extending the sphere of influence of the tip well

beyond the region of injected current. However, this type of tip-induced polymerization has so far been uniquely applied to diacetylene, which undergoes a vibrationally coupled chain reaction. In this system, the practical constraints of the topochemical polymerization and the stabilization of the molecular network on HOPG have so far been met with molecules containing a diacetylene moiety flanked by alkyl chains, which form an interdigitated network with a geometry that strictly confines the polymerization process to one dimension.

A different type of linearly propagating chain reaction induced by the STM tip was recently demonstrated by Maksymovych and co-workers.³³ In this system, chains of dimethyldisulfide (CH_3SSCH_3) mol-

ecules on either Au(111) or Au(100) are induced to dissociate sequentially into CH_3S fragments and subsequently to re-form into new CH_3SSCH_3 molecules (*i.e.*, $n(\text{CH}_3\text{SSCH}_3) \rightarrow \text{CH}_3\text{S} + (n-1)(\text{CH}_3\text{SSCH}_3) + \text{CH}_3\text{S}$, with $n \leq 10$). The reaction propagates with only negligible energy barriers following the cleaving of the initial S–S bond.

Inducing Nonlocal Reactions. In this issue, Chen *et al.* take a different approach to inducing changes to chemical reactivity and initiate reactions within a two-dimensional area in a molecular overlayer by injecting hot electrons from the STM tip into a metal–molecule interface state (Figure 1).³⁴ After propagating laterally, some proportion of the hot electrons back-transfer into molecular orbitals, inducing chemical reactions at distances up to 12 nm from the STM tip. In addition to inducing nonlocal chemical reactions using a local probe, this novel approach provides a direct method to study reaction dynamics at organic/inorganic interfaces.

Chen *et al.* have studied this hot-electron process on molecular monolayers of copper hexadecafluorophthalocyanine (F_{16}CuPc) on the (111) faces of Ag and Au. On both metal substrates, the application of a voltage pulse over a single molecule results in a visible change in symmetry of the four-fold symmetric F_{16}CuPc complexes at various distances from the STM tip, which is attributed to defluorination. By analyzing the relationship between the tunneling current and reaction yield, the authors are able to confirm that the reaction originated from hot-electron injection and to extract the reaction order on each surface (~ 4 for Ag, ~ 2 for Au); consideration of the radial distribution of the reacted molecules further allows elucidation of the lateral decay length of the hot-electron current (6 nm on Ag(111), 1.2 nm on Au(111)).

Chen *et al.* propose a four-step mechanism for the lateral hot-electron propagation in $\text{F}_{16}\text{CuPc}/$

metal interface states.³⁴ The hot electron is initially captured by the π^* orbital of one of the benzene rings of F_{16}CuPc . At this point, the electron may be transferred into the σ^* orbital, breaking a C–F bond in the molecule directly below the STM tip. However, most of the anions undergo fast electron detachment, and the hot electron is resonantly transferred through the hybridized molecule–metal state and into a surface state. From this state, the electron has a finite probability of back-transferring into the π^* orbital of a distant molecule to induce a defluorination reaction outside of the vicinity of the STM tip.

The nature of the metal–molecule interface state has important implications for this hot-electron process. By comparing quantities measured on Ag and Au, insight can be gained into the differences between the interfaces formed on each surface. The reaction on Ag has higher quantum yield; density functional theory (DFT) calculations show that the overlap of the F_{16}CuPc carbon orbitals with the Au (d_{xz}, d_{yz}) orbitals is stronger than for the Ag (p_x, p_y) orbitals, leading to a lower anion lifetime, which limits the quantum yield. The larger spatial extent of the orbitals on Ag(111) should correlate with increased delocalization of the surface state, and this is consistent with the longer lateral decay length observed for this surface. DFT also reveals the energy of these hybridized states, which agree with the experimentally observed onset voltages for reaction on each of the surfaces (1.9 eV for Ag, 2.4 eV for Au).

The mechanism described by Chen *et al.* builds on previous work by Maksymovych and co-workers, who injected hot electrons directly into substrate surface states (or surface resonances) on Au(111), Cu(111), Cu(110), and Au(100) and observed the dissociation of isolated CH_3SSCH_3 molecules at distances up to 50 nm (Figure 2a).³⁵ By analyzing the radial

distribution of the reacted molecules for various electron currents, and through experiments where the tip–sample distance was increased to eliminate the possibility of electric field effects, Maksymovych *et al.* were able to attribute the reaction unequivocally to the hot-electron current.³⁵ Similar work by Nouchi and collaborators³⁶ demonstrated reversible polymerization of C_{60} molecules in a multilayer on Si(111). Subsequent to electron (or hole) injection, the authors observe a ring-shaped region of polymer, with units bonded both laterally and along the substrate axis. The diameter of the ring-shaped region is dependent both on the height and sign of the pulse voltage, and its propagation is attenuated by defects or domain boundaries. The authors argue that the polymerization is due to the presence of the carriers, finding conclusive evidence against any effects arising from the electric field or the geometry between tip and sample. The formation of the rings is described in terms of Joule heating through carrier-phonon scattering and implies that the carriers must induce both the assembly and dissociation of C_{60} oligomers. This experiment provides a unique probe of both empty and filled states, and comparisons can be made accordingly between electron and hole transport in the organic crystal. For example, due to electron–phonon coupling, the electrons dissipate energy faster than the holes, leading to shorter lateral decay.

OUTLOOK

The STM provides a unique opportunity for inducing reactions, characterizing molecule/metal surface states, and linking the photochemistry of adsorbed molecules with STM-induced reactions.³⁵ Hot-electron injection into surface states provides a new avenue to this end. Nonlocal reactions are conceptually different from local excitations occurring directly in the STM tunneling junction; in the latter case, the electronic states of the tip overlap

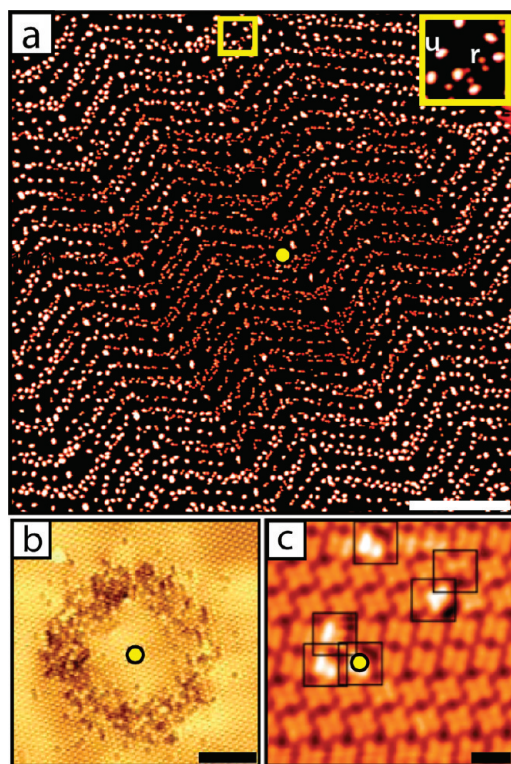


Figure 2. Three examples of hot-electron-induced non-local reactions. In all cases, the yellow dot indicates the location of the hot-electron charge injection. (a) Maksymovych and co-workers' dissociation of isolated CH_3SSCH_3 molecules on Au(111), resulting from a 2.5 V, 1.0 nA, 200 ms pulse. The inset (yellow box) shows reacted (r) and unreacted (u) molecules. Scale bar is 20 nm. Image reprinted with permission from ref 35. Copyright 2007 The American Physical Society. (b) Polymerization is induced in a thin film of C_{60} by a 3.3 V pulse, as described by Nouchi *et al.* Scale bar is 10 nm. Image reproduced with permission from ref 36. Copyright 2006 The American Physical Society. (c) Defluorination of F_{16}CuPc on Ag(111) resulting from a 3.0 V, 3.5 nA pulse, as described by Chen *et al.* in ref 34. Copyright 2009 American Chemical Society. The reacted molecules are indicated by boxes. Scale bar is 2 nm.

with molecular states and resonances, whereas in the former case, molecular excitation is mediated by surface resonances.³⁵ These initial results lay a solid foundation for possible extension and application to other model systems. While the limits to possible future experiments are bounded only by the imaginations of synthetic chemists and surface scientists, we describe a few interesting potential opportunities hereafter.

Although Chen *et al.* limited their considerations to the $\bar{\Gamma}$ point of the surface Brillouin zone, the observation of nonlocal reactions could conceivably be extended to investigate the dispersion of the

molecule–metal states, which is known to vary significantly from the dispersion expected for an isolated organic layer.³⁷ Traditionally, the dispersion of unoccupied states along given crystalline directions is obtained with spectroscopic techniques such as two-photon photoemission (2PPE)³⁸ or *k*-resolved inverse photoemission,^{39,40} although scanning tunneling spectroscopy (STS) analysis of electron standing waves in nanoscale molecular islands has also recently been employed for this purpose.³⁷ Probing molecular overlayer states by observing changes in chemical reactivity following STM hot-electron injection could also provide useful, albeit indirect, information. For instance, flat dispersion along a given direction in the Brillouin zone would correlate with a lack of reacted molecules along the corresponding direction on the surface. It might also be possible to infer reaction rates based on effective electron masses obtained by the aforementioned spectroscopic techniques, combined with the interface state lifetimes.

High-reaction-yield hot-electron injection experiments could prove to be a useful approach for nanoscale patterning of molecular overlayers. To promote the formation of uniform reacted regions, the choice of molecular species, and its corresponding reaction, is crucial. Under appropriate conditions, the single-electron dissociation of CH_3SSCH_3 demonstrated by Maksymovych *et al.*³⁵ occurred in 100% of molecules within the lateral extent of the hot-electron current, whereas the two- and four-electron defluorination processes described by Chen *et al.*³⁴ produced much lower reaction yields. Defining a useful pattern would obviously demand control over the proportion of reacted molecules as well as the lateral extent of the reaction. This lateral extent can be augmented through the controlled use of a chain reaction. In their most recent work, Maksymovych *et al.*³³ combined the non-

local reactivity induced by hot electrons with the chemical chain reaction responsible for sequentially dissociating and re-forming CH_3SSCH_3 molecules. By applying a voltage pulse to the bare substrate, they induced the chain reaction in molecular chains in the surrounding region. This type of reaction could present a controlled path to extending the lateral dimension of the reacted area beyond the decay length of the hot-electron current.

The emerging body of work describing nonlocal reactions induced by the STM suggests exciting new opportunities and directions that will enable improved understanding of organic/inorganic interfaces, with the possible consequence of enhanced device performance in the areas of organic electronics, photonics, and photovoltaics. Hot-electron injection has already been shown to initiate reactions of isolated molecules on metal surfaces,^{33,35} in organic thin films,³⁶ and, now, at metal/organic interfaces formed in molecular monolayers.³⁴ In addition to providing new insight into the transport properties of metal/organic interfaces, this technique could address the problem of using the STM tip to react relatively large regions of molecules spontaneously and simultaneously. We have primarily confined the discussion to organic/metal interfaces; however, we note that semiconductor substrates present another pos-

High-reaction-yield hot-electron injection experiments could prove to be a useful approach for nanoscale patterning of molecular overlayers.

sible domain for hot-electron experiments, which could yield further interesting results and new opportunities.

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