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Triggering chemical reactions by Scanning Tunneling Microscopy: From atoms to polymers

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ABSTRACT

Besides its unique ability to image atoms and molecules at surfaces at unprecedented detail, a Scanning Tunneling Microscope can also be employed to manipulate matter at the nanoscale. This feature article focuses on the use of STM to induce chemical reactions at a surface, in particular involving small and larger assemblies of molecules. It will be shown that via local voltage pulses delivered by the STM tip (delivering charge carriers to the surface), by applying specific bias potentials between the STM tip and the sample, or through electrochemical control over a whole surface, a variety of chemical reactions can be induced. In this way, bonds between molecules can be broken or created, redox states can be changed, and well-defined polymerization reactions can be triggered, and the reaction components – starting materials, products, and in some cases also intermediates – can be identified in a highly appealing way: by imaging them.

1. Introduction

The invention of the Scanning Tunneling Microscope (STM) in 1981 [1–3] had a huge impact on scientific research. Suddenly it became possible to study materials at the atomic level by probing a surface with an atomically sharp tip, and to actually look at molecules with sub-ångström resolution. Over the years the technique was developed further, expanding its use from Low-Temperature (LT) Ultra-High Vacuum (UHV) environments to high temperature [4,5], high pressure atmospheres [4,6] and liquid [7] environments. STM is most commonly employed for *observing* surfaces. The presence of the metallic tip can disturb the surface, for example due to the strong inhomogeneous field it generates, and this influence of the tip is generally accepted as a necessary evil. However, it was quickly found that the presence of the tip can also be used to the advantage of the experimentalist: to *manipulate* the surface. One can use an STM tip, for example, to move single atoms around on the surface. Who does not know the letters of IBM spelled out by single xenon atoms [8]? This image (Fig. 1) has become a famous example of what the STM is capable of.

Besides manipulating atoms, an STM can also be used to induce and study chemical reactions, either on a single molecule or affecting a larger assembly of molecules [9–25]. This feature paper gives an overview of the exciting recent developments in this field, focusing mainly on triggering chemical reactions that affect small and large assemblies of molecules adsorbed at a surface.

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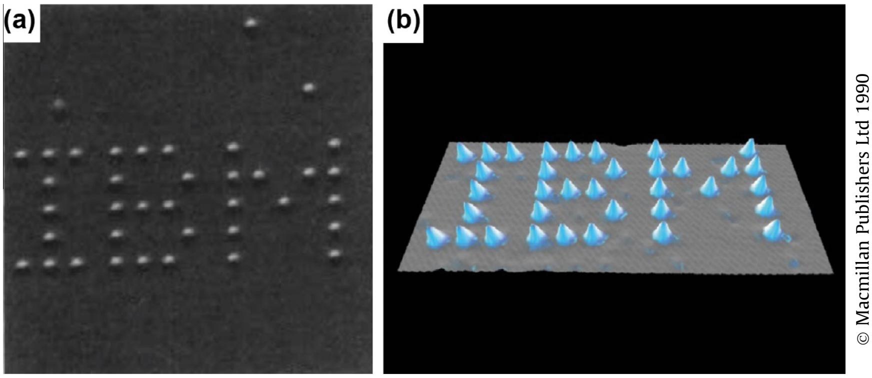

Fig. 1. (a) STM image of IBM spelled out by xenon atoms on a nickel surface, imaged and constructed by STM in a UHV environment at 4 K. (b) Three-dimensional representation of the data. Reprinted with permission from Macmillan Publishers Ltd: Nature, Ref. [8], Eigler, D. M.; Schweizer, E. K. *Nature* 1990, *344*, 524–526.

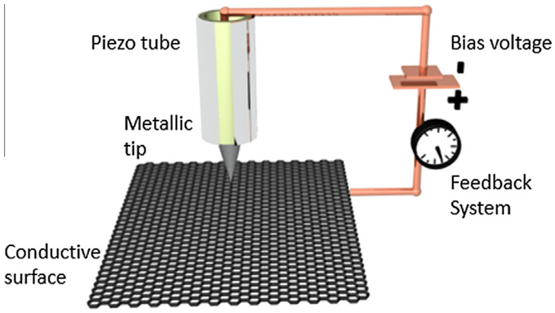

Fig. 2. Schematic representation of a Scanning Tunneling Microscope setup.

2. Scanning tunneling microscopy

The operating concept of an STM is relatively simple: the device consists of an atomically sharp tip of a conducting material, which is brought in close proximity of a conducting sample (Fig. 2). STM tips are generally fabricated by chemical etching or by the mechanical cutting of a wire. When the tip is close enough to the surface (at a distance of nanometers), electrons are able to tunnel from the tip to the sample and vice versa. Without an applied voltage between tip and surface, these currents cancel each other out, but as soon as a bias voltage is applied, a net tunneling current starts to flow. When the voltage of the surface is negative with respect to the tip, electrons will tunnel from the surface to the tip, and when the voltage of the surface is positive they tunnel in the opposite direction. The tunneling current depends exponentially on the distance between the electrodes, making it very sensitive to height differences between tip and surface. By mounting the tip in a piezo tube, this height can be very accurately controlled (in the sub-ångström range). In the so-called constant-current mode of measuring, a feedback system adjusts the height of the tip above the sample in such a way that the tunneling current remains constant while the tip scans the surface line by line, and a map of apparent height results. Alternatively, in the so-called constant height mode, the feedback is switched off and differences in current are measured during scanning while the distance between tip and sample remains constant.

In particular when the constant-current mode is employed one has to be careful in interpreting STM data, because the information present in the apparent height image is a convolution of the real height and the conductive properties of the surface. Because the tunneling current is used for the feedback, a more conductive part on the surface will appear higher in the STM topography. This additional feature makes it possible to use the STM for the analysis of the local density of states (LDOS) of the sample, or, in the case of molecules adsorbed to it, to visualize different orbitals or oxidation states.

3. Single molecule chemistry

The triggering of chemical reactions at the single molecule scale by STM has so far predominantly been studied under UHV conditions and at low temperatures. Chemical bonds within molecules can be broken, molecules or fragments can be pulled along by the STM tip, and new bonds can be formed. To overcome the energy barriers involved with these processes, typically a voltage pulse is applied. The voltage during this pulse (generally with a magnitude of several volts) is

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