MICROSCOPY

# A nanotube molecular tool

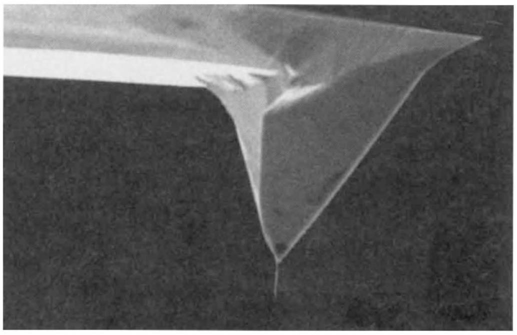
*David Keller*

SINCE their invention in the early 1980s, scanning probe microscopes have become the tool of choice for probing and manipulating the nanoscale world. Smalley and colleagues (Dai *et al.*, page 147 of this issue[1]) have now given the brush a finer point by securing a single carbon nanotube to the tip of a scanning force microscope (SFM). The nanotube tip can gain access to deeper recesses of surface structure than can the very much blunter pyramidal tip of a standard device.

With the advent of the scanning tunnelling microscope (STM), it became possible (in principle) to build structures on the atomic scale in the same way that we do on the macroscopic scale: by putting together individual components (atoms or molecules) one at a time. The dramatic experiments of Eigler and others, who used an STM to assemble tiny rings, letters and other complex structures from individual adsorbed atoms on metal surfaces[2], showed that even single atoms can be visualized and manipulated. Many other experiments have demonstrated a wide range of measuring, imaging and nanofabrication capabilities on somewhat larger scales[3,4].

The STM (or the related SFM) is uniquely suited to these kinds of 'single molecule' experiments because it combines the ability to visualize individual atoms and molecules with the ability to manipulate them. Both feats are accomplished by bringing an atomically sharp probe tip very close to the sample surface and measuring some sort of tip–sample interaction (the actual quantity measured depends on the type of experiment). Then, by scanning the probe over the surface, a high-resolution image can be created; or, by changing the tip–sample interaction (say, by bringing the probe tip closer or by applying a voltage pulse), the tip can be used as a tiny tool to alter the same sample it previously imaged. A second image shows the results of the operation.

Clearly, the probe tip is the crucial element in any such experiment. Both the resolution of the STM when used as a microscope, and the ability to control the outcome when used as a nano-manipulator, depend on the size, shape, chemical composition and surface properties of the tip. But in the vast majority of experiments done today, the tip is a very crude instrument. STM tips are usually metal wires etched to a sharp point or simply snipped off with a pair of scissors. SFM tips are most often microfabricated pyramids of silicon or silicon nitride. In either case, the end of the probe is at least tens and usually hundreds of ångströms across. The STM and SFM can achieve high resolution with such blunt tips because they sometimes have well-placed, atomic-scale protrusions, and it is these 'asperities' that make the primary contact with the sample. Unfortunately, even when such protrusions exist, their size, shape and chemical composition are completely unknown, and frequently change during the course of an experiment.


H. Dai

Tipped off — a carbon nanotube (some 10 nm in diameter and 100 nm long) stuck on the end of a conventional silicon probe used in scanning force microscopy. The probe and its associated cantilever arm are made of silicon. The nanotube tip is attached by coating the larger probe with glue and then bringing it in contact with a bundle of nanotubes; on pulling the probe away, a single tube can be left stuck on the probe's end.

Needless to say, the lack of reliable probe tips is a serious impediment to progress in either nano-manipulation or straight microscopy. The ideal probe would be sharp (from a few ångströms to a few nanometres), with a well-defined, reproducible geometry on the atomic scale. It would also be chemically inert, conductive (for STM experiments or electrically stimulated manipulation experiments), easy to build, and cheap. For SFM experiments with biomolecules, it should be hydrophobic.

Virtually all of this wish list is satisfied by the new probe reported by Dai *et al.*[1]. Fabrication of the probe is simplicity itself: a glue-coated SFM or STM tip is brought up to a preparation of multiwalled fullerene nanotubes, touched to a nanotube bundle, and then pulled away. Under favourable circumstances the bundle separates from the other nanotubes leaving a single, slender tube, with a diameter of between 5 and 20 nm and length of up to several micrometres, extending from one end. High-resolution electron micrographs show that the nanotube end is usually closed by an inert, hydrophobic fullerene cage. Single-walled nanotubes, with diameters of only 14 Å and capped by a hemispherical fullerene dome, can also be attached.

Somewhat surprisingly, such tips are strong enough to function as SFM probes, and even survive catastrophic crashes with the surface, apparently by flexing instead of breaking as a normal tip would. This flexing also limits the maximum force that can be applied to the sample, so nanotube tips have a built-in 'soft-touch' feature that should make them preferable for use on delicate samples that might be damaged by stiffer conventional tips. As a final bonus, nanotubes are conductive, and so can be used as STM tips, or, in SFM experiments, to measure electrochemical currents or to modify samples by applying voltage pulses. For example, Dai *et al.* use a voltage pulse to create a 40-nm dot on a gold surface in an SFM experiment, and also use a nanotube tip in an atomic-resolution STM experiment on a tantalum disulphide surface.

This is the first reported example of what might be called a 'molecular tool': a single, well-defined molecular structure connected to a macroscopic control device. Three features of the fullerene nanotubes combine to make such a microscopic tool possible. First, the nanotubes themselves are small and self-assembling, and their natural shape is nearly ideal for an STM or SFM probe. Second, they occur in large bundles with dimensions on the micrometre scale, which can be viewed with a light microscope and handled with micromanipulators. Finally, and somewhat fortuitously, the large bundles break apart in a way that leaves single tubes exposed.

The idea of using a fullerene as a probe tip for the SFM or STM has been bandied about in the probe microscope community for years, but has not been realized until now. The new nanotube tips give us the first opportunity to probe molecular-scale samples with a known molecular structure, and thus to reliably control the tip–sample interaction. The immediate benefit is likely to be an increase in the resolution and reliability of SFM experiments, where the need for good probe tips is acute. Further refinement of the basic idea (perhaps by chemically modifying the tip end, or by adding layers of insulation to the nanotube, or by attaching other molecules) should make many more such molecular tools possible, and open new avenues of research in which the properties of matter can be measured and manipulated directly, one atom at a time. □

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