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Carbon nanotube tips for atomic force microscopy

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The development of atomic force microscopy (AFM) over the past 20 years has had a major impact on materials science, surface science and various areas of biology, and it is now a routine imaging tool for the structural characterization of surfaces. The lateral resolution in AFM is governed by the shape of the tip and the geometry of the apex at the end of the tip. Conventional microfabrication routes result in pyramid-shaped tips, and the radius of curvature at the apex is typically less than 10 nm. As well as producing smaller tips, AFM researchers want to develop tips that last longer, provide faithful representations of complex surface topographies, and are mechanically non-invasive. Carbon nanotubes have demonstrated considerable potential as AFM tips but they are still not widely adopted. This review traces the history of carbon nanotube tips for AFM, the applications of these tips and research to improve their performance.

The impact of scanning probe microscopy (SPM) over the past 20 years has been dramatic: its invention was, for example, recently rated the second most important advance in materials science of the past 50 years[1]. Breakthroughs in fields as wide ranging as cell biology and semiconductor research have been driven by SPM through its ability to map not only surface topography, but also material properties at the nanoscale. SPM techniques are diverse in their nature but share common features, in particular the use of a probe to detect a spatially localized signal. In most cases it is the probe that limits the spatial resolution of the technique.

The most common form of SPM is atomic force microscopy (AFM)[2] where the probe is a sharp tip, usually mounted on a microscale cantilever that acts to transduce the tip–sample force (the localized signal). A map of surface topography is constructed by scanning the tip across the substrate. The resultant image is a convolution of the tip geometry with the surface topography. Commercial AFMs can have sub-ångström noise levels, but the realizable lateral spatial resolution is limited by the tip geometry and is typically around two orders of magnitude larger. For an ideal AFM tip, the exact tip geometry and chemistry should be known, the tip dimensions should be as small as possible without sacrificing rigidity, and the probe should be capable of imaging over a long lifetime, while maintaining a constant geometry.

Attempts have been made to create 'ideal' tips using methodologies such as focused ion-beam structuring of the tip apex[3]. However, the above requirements are perhaps best met by carbon nanotubes: cylindrical shells of graphene with diameters as small as 1 nm (ref. 4). Indeed, carbon nanotubes show great promise as AFM tips despite the substantial challenges involved in their fabrication. This article reviews the progress that has been made in the production and application of carbon nanotube AFM tips since their arrival on the SPM scene in 1996 (ref. 5).

AFM probes have come a long way since the use of a diamond shard glued onto a hand-cut gold foil cantilever[6]. The breakthrough in tip technology came with the application of microfabrication techniques to mass produce AFM tips[7]. Silicon and silicon nitride can now be processed routinely to form cantilevers with the appropriate spring constants and resonance frequencies and integrated pyramidal (or conical) tips for imaging. Although this top-down microfabrication route has many advantages, there are limitations, such as control over the exact geometry at the very apex of the tip. Tip geometry can be characterized by deconvolution of images of defined sample structures. However, this is of limited applicability as most AFM-based techniques involve contact with the sample at least intermittently, which can result in damage to the tip apex and a changing geometry over time. The tip apex is also crucially important in quantifying tip–sample forces. Beyond the tip apex, the aspect ratio of the probe is also significant. The cone angle of a tip is defined by the microfabrication process[7], and for samples with high-aspect-ratio features, such as trench structures common in semiconductor processing, the ability of microfabricated tips to accurately map the topography is limited[8].

The defining features of carbon nanotubes are their nanometre-scale diameters and high aspect ratio. They also show remarkable mechanical and electrical properties associated with the graphene sheet from which they are formed — in particular, exceptionally high Young's modulus, toughness and electrical and thermal conductivity[4]. Carbon nanotubes come in two forms: single-walled nanotubes (SWNT), which have only one shell and typical diameters of 1–3 nm, and multiwalled nanotubes (MWNT), which have multiple concentric cylinders with typical diameters of 5–100 nm. The cylindrical nature of the nanotubes confers stiffness perpendicular to their axis, and their toughness means they reversibly buckle rather than break when subjected to axial compression[9]. Combined, these properties make nanotubes a near-ideal imaging probe, and it was only five years after their discovery that they were first used as AFM tips[5]. As expected, they showed not only high spatial resolution but also robustness and wear resistance.

Nanotube tip fabrication

There are two key aspects to the fabrication of nanotube AFM tips: attachment — the nanotube(s) must be fixed to the AFM probe so that they become the imaging point; and modification. Several stages may be involved; for example, the attachment may require strengthening, the nanotube(s) may need to be shortened for imaging purposes and chemical functionality may need to be added.

The resulting nanotube tip is characterized by its length, l_{nt}, radius, r_{nt}, and orientation (angle with respect to the surface, θ) — factors that determine the rigidity, resolution and imaging characteristics of the tip, as discussed in Box 1. Importantly, control over these parameters allows optimization of the tip for different AFM applications. For widespread use, reproducible fabrication processes for a variety of nanotube tips must be developed at prices competitive with standard microfabricated tips. Here we review some of the

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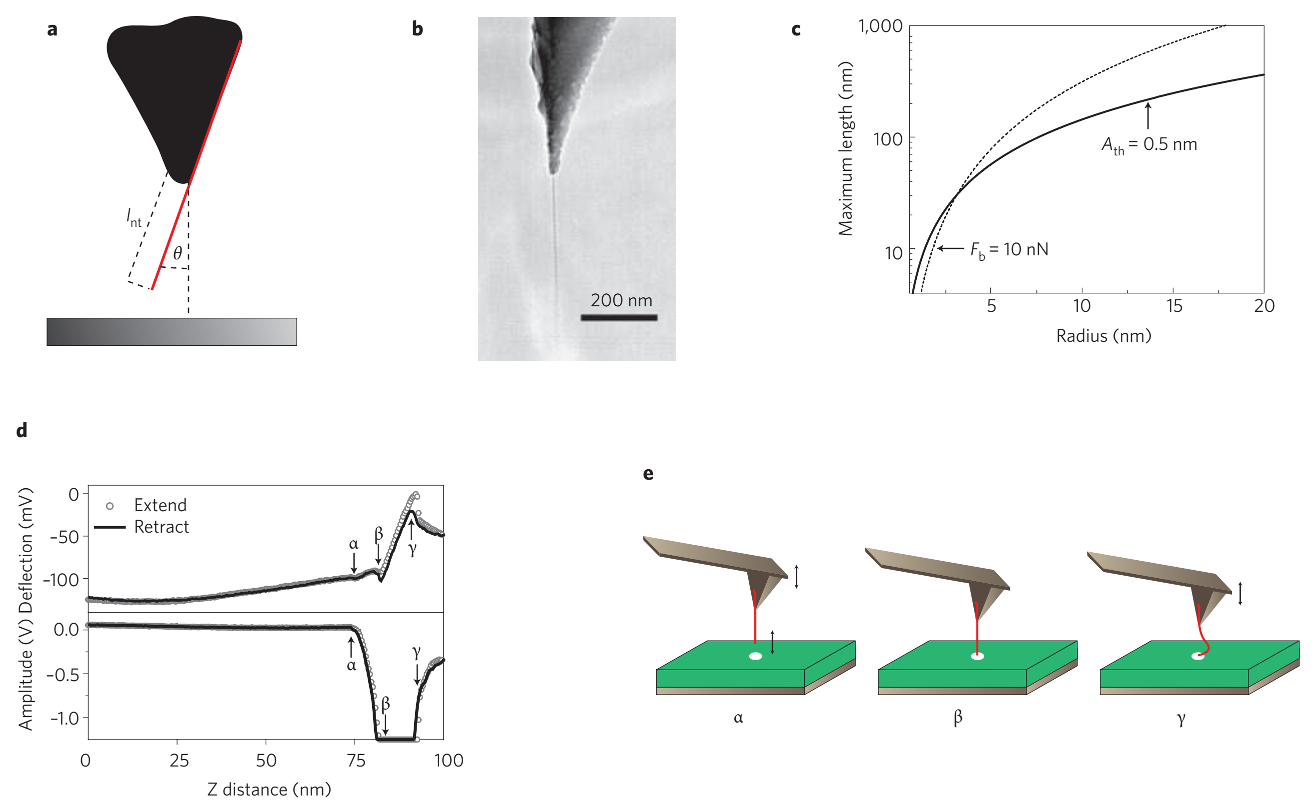
Box 1 | Characterizing a nanotube tip



Nanotube tips are characterized by their length, l_{nt}, and angle relative to the surface, θ (panel **a**). The nanotube radius, r_{nt}, limits the spatial resolution and has an impact on the usable length of the nanotube tip. The nanotube acts as a beam clamped at one end, and as such it will buckle when the axial load exceeds the buckling force, F_b. Panel **b** shows a transmission electron microscope (TEM) image of a nanotube tip[89]; the blurring of the lower portion of the nanotube is due to thermally induced oscillations (with amplitude A_{th}). Combining continuum mechanics and the equipartition theory, it is trivial to find the following parameters:

$$F_b = \frac{\pi^2 \alpha_{nt}}{l_{nt}^2}, \quad k_l = \frac{3\alpha_{nt}}{l_{nt}^3}, \quad \alpha_{nt} = \frac{Y_{nt}\pi r_{nt}^4}{4}, \quad A_{th} = \sqrt{\frac{k_B T}{k_l}},$$

where k_l is the nanotube's lateral spring constant, α_{nt} the flexural rigidity, Y_{nt} Young's modulus, k_B Boltzmann constant and T the temperature. For robust imaging, $A_{th} < 0.5$ nm and $F_b > 10$ nN; these constraints are plotted in **c** using $Y_{nt} = 1$ TPa and $T = 300$ K.

This simple model is only a guide. However the constraints on the usable length are clear: a nanotube with $r_{nt} = 0.5$ nm should be shortened to $l_{nt} \leq 10$ nm, whereas at $r_{nt} = 10$ nm, $l_{nt} \leq 1$ μm. For a nanotube tip composed of a bundle of nanotubes, the effective Young's modulus is much lower than 1 TPa (ref. 90), however the trend of a thicker bundle allowing greater l_{nt} holds true. Coating the nanotube tip increases the flexural rigidity and so also allows greater l_{nt} (refs 38, 85).

The tapping mode force–distance curve characteristic of a nanotube tip[89] (**d**) and a corresponding schematic (**e**) are shown. 'Extend' and 'retract' refer to the tip being moved towards and away from the surface, respectively. At point α the nanotube tip contacts the surface at the bottom of the tip oscillation. As it is lowered further the amplitude decreases until at β the oscillation is damped completely and the cantilever deflects. The axial force on the nanotube increases until at point γ the force exceeds F_b, the nanotube buckles and the tip oscillates again. The reversibility of the buckling, evident from the observation that 'retract' matches 'extend', is a distinctive signature of a nanotube tip[5].

more common fabrication techniques and evaluate their promise for achieving this goal.

Direct manipulation. The first nanotube tips were made by direct manipulation of MWNTs onto standard microfabricated AFM probes[5]. Silicon tips, coated with an adhesive and under direct view in an optical microscope, were brought into contact with a small bundle of MWNTs. After attachment, it was often observed that one nanotube, typically with a diameter of 5–20 nm, extended from the bundle to form the tip apex. Using this simple approach both high-resolution topographic AFM imaging and atomic-resolution scanning tunnelling microscopy imaging were demonstrated with the same nanotube tip. However, this process was limited as the thicker, more easily visible, bundles were selected preferentially for attachment. Further work extended the technique using nanomanipulators inside an electron microscope[10,11], which allowed greater control over the length, diameter and orientation of the nanotube tip (usually a MWNT). Controlling l_{nt} by cutting with nanomanipulators has been demonstrated[12,13], as has 'nanowelding' — that is, using the electron beam to fix the nanotube to the tip[14]. Direct manipulation in this way controls many of the critical parameters. However, it is

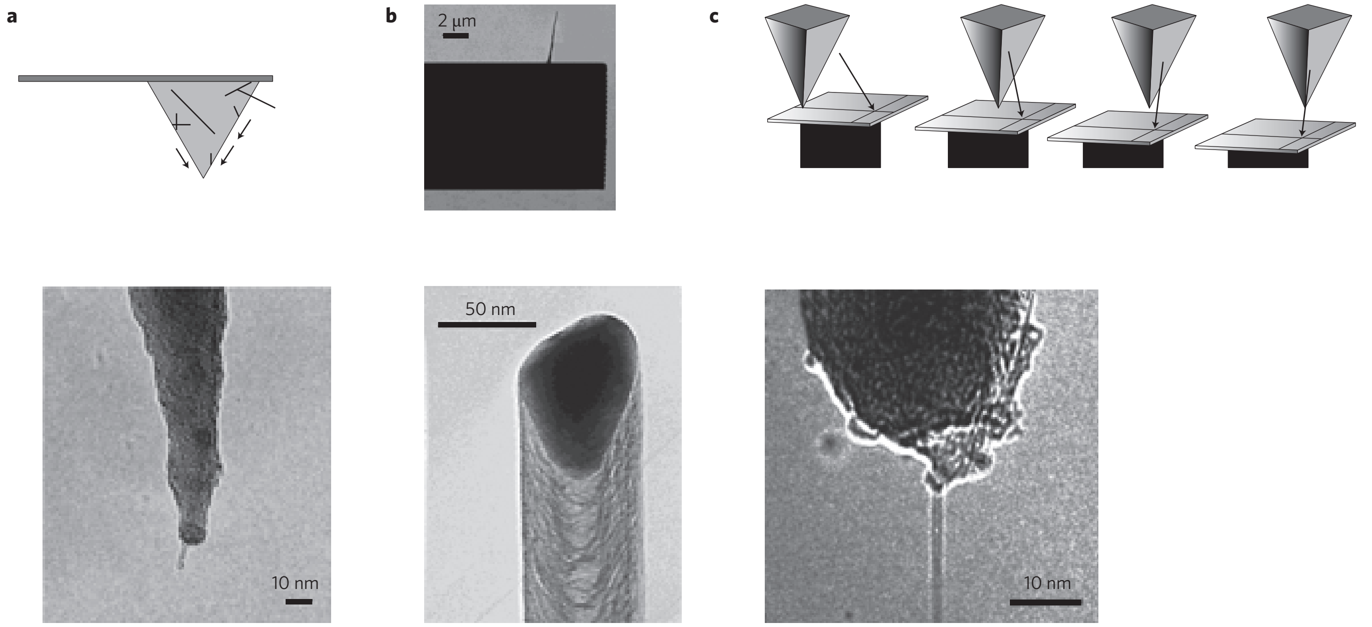


Figure 1 | Preparation of nanotube tips. a, Surface growth cCVD nanotube tip preparation. Top: Schematic of the growth process. Bottom: TEM image of an individual SWNT tip produced using this technique. Reproduced with permission from ref. 49 (© 2000 Elsevier). **b**, Cross-sectional TEM images of an individual bamboo morphology nanotube on a cantilever produced by directional-growth plasma-enhanced CVD. Top: 90° side view with ×1,500 magnification. The nanotube has a 60-nm tip diameter, is 5 µm long, and has a tilt angle of 13° with respect to the cantilever. Bottom: Nanotube tip end. The nickel catalyst wrapped within thin graphite layers is clearly visible. Reproduced with permission from ref. 24 (© 2004 ACS). **c**, Nanotube attachment through 'pick-up'. Top: Schematic depicting the process by which a microfabricated pyramidal tip picks up a vertically aligned carbon nanotube. Bottom: TEM image of a 0.9-nm-diameter SWNT tip produced by 'pick-up'. Reproduced with permission from ref. 21 (© 2001 Elsevier).

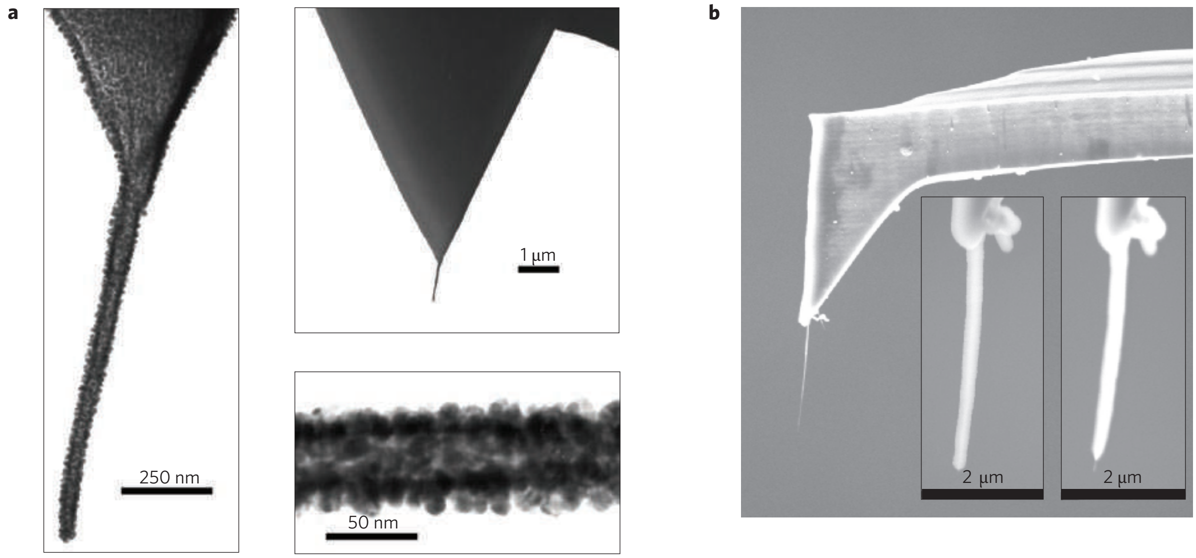


Figure 2 | Coated nanotube AFM probes. a, TEM images of a gold nanowire probe formed by sputtering onto a nanotube tip (left) and an enlarged view of the nanowire (top and bottom right). Reproduced with permission from ref. 38 (© 2003 ACS). **b**, Polymer (Parylene C)-coated nanotube tip, with the apex exposed using a laser (right inset). Reproduced with permission from ref. 85 (© 2004 ACS).

difficult to envisage how the process could be scaled up to provide commercially available nanotube tips at competitive prices, given the time-consuming and serial nature of the process.

Chemical vapour deposition growth. A major breakthrough in carbon nanotube research came in 1998 through the use of catalysed chemical vapour deposition (cCVD) for the growth of nanotubes from transition-metal catalyst particles[15–17]. A year after its development cCVD was used for the fabrication of MWNT tips[18], and then SWNT tips[19], by growing the nanotubes *in situ* onto catalyst-coated silicon tips, as shown in Fig. 1a. The key advantage of direct growth onto the tip is the easy route to batch fabrication; wafer-scale growth of SWNT tips for high-resolution imaging was demonstrated as early as 2002 (ref. 20). Although the nanotube

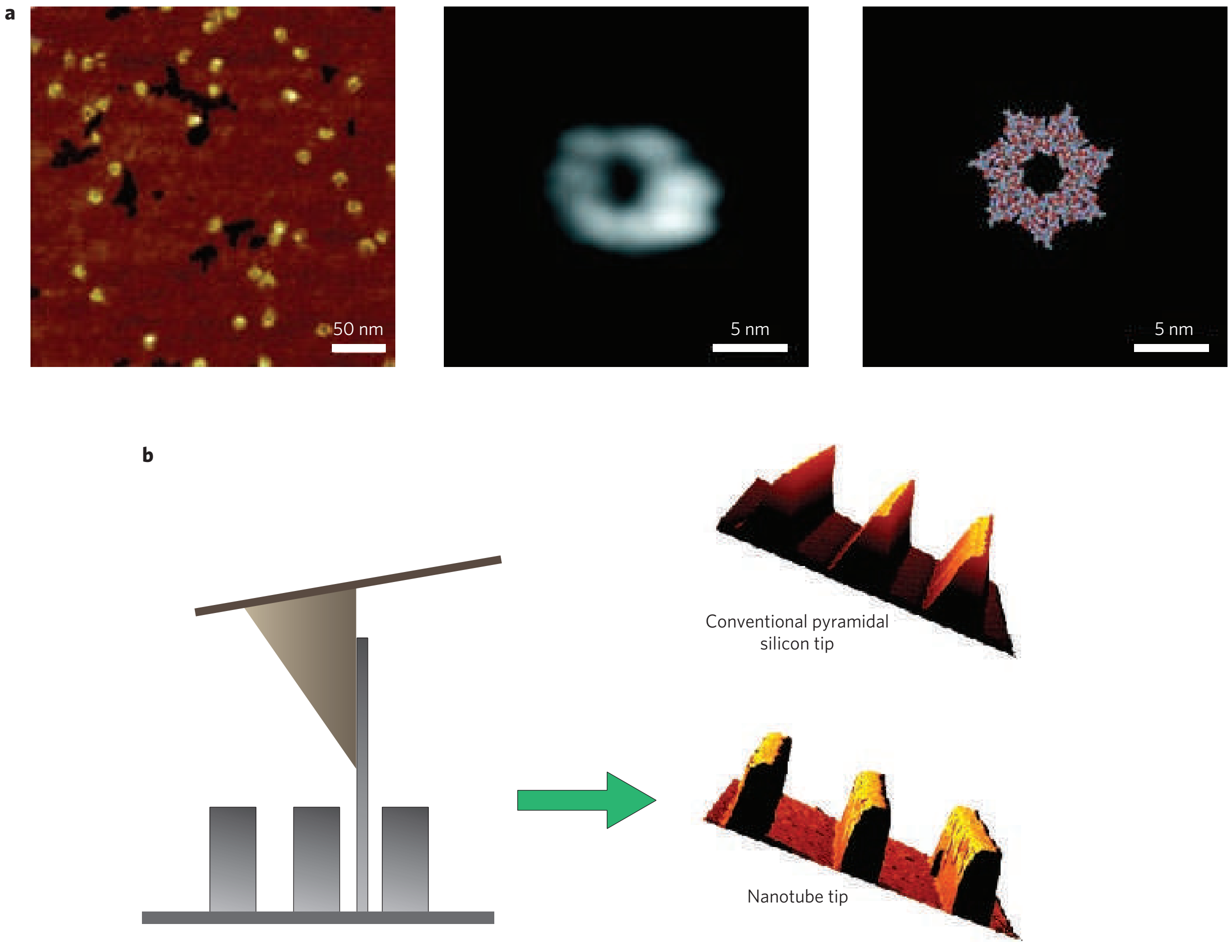


Figure 3 | Topographical demonstrations with nanotube tips. a, High-resolution imaging. The chaperonin protein GroES, imaged with a cCVD surface-grown SWNT tip. The large scan area in the left image shows both 'dome' and 'pore' conformations, representing the two sides of GroES facing up. A higher resolution image of the pore side (middle) shows the heptameric symmetry, which matches well with the crystal structure shown on the right. Reproduced with permission from ref. 52 (© 2000 PNAS). **b**, A comparison of AFM images of 280-nm-spaced, 300-nm-deep trenches in photoresist obtained with a conventional silicon probe and a nanotube probe. The improvement in the ability of the nanotube tip to map surface topography is clearly evident. Adapted with permission from refs 58 and 91.

growth step itself is relatively cheap and simple, reproducibility seems to be problematic. To grow tips composed of just one nanotube at high yield, statistics dictate that nanotube growth must be controllable at the single nanotube level, which is challenging. Bundles of nanotubes, however, are easier to grow controllably and so it is possible that nanotube bundle AFM tips could be reproducibly fabricated by this technique in the near future.

Control over l_{nt} is critical for the application of nanotube tips for imaging (see Box 1), but this is difficult to achieve in the growth process. Instead, l_{nt} can be controlled by post-growth shortening, usually by electrical etching[12,21]. The diameters can also be controlled (to an extent) by adjusting the growth conditions, however orientation is harder to manipulate. Alignment during cCVD growth has been demonstrated by the application of electric fields[22]. This has most successfully been applied for nanotube tip growth through the use of plasma-enhanced CVD[23]. The most noteworthy example has been by Ye *et al.*[24], who achieved wafer-scale growth of AFM tips, each consisting of a single MWNT, 40–80 nm in diameter and 2–6 μm in length, grown directly onto a tipless silicon cantilever, at angles of 10–20° with respect to the beam. Using plasma-enhanced CVD, it was thus possible to gain control over the length, diameter and orientation of the MWNT, as shown in Fig. 1b, to create nanotube tips optimized for critical dimension imaging.

Pick-up. SWNTs grown on smooth silicon oxide surfaces by cCVD mostly lie flat on the substrate, owing to the strong van der Waals interactions between them. However occasional nanotubes grow upwards with only their base in contact with the surface. Lieber and co-workers found that when scanning such surfaces (termed 'pick-up' plates), if the AFM tip touched an upstanding nanotube, van der Waals forces attached the two so strongly that the nanotube was 'funnelled' through the tip apex to maximize contact, thus creating a nanotube tip (Fig. 1c)[21]. This is a quick, flexible and reproducible technique. Multiple nanotubes can be picked up by scanning larger areas to create bundle nanotube tips; owing to high aspect ratio and small diameters, the van der Waals interactions between nanotubes are also strong (~ 1 eV nm^{-1} for SWNTs[25]) resulting in their aggregation to form well-aligned, close-packed bundles that are stiffer than individual nanotubes[26]. With care, just one nanotube can be attached; however, bundle tips often show greater stability owing to the greater attachment area over which the van der Waals interactions act. As in direct growth, there can be little control over the orientation of the nanotube tip.

With 'pick-up', AFM tips pre-coated with almost any material can be used. In this way it is therefore possible to provide a good electrical connection to the nanotube using metal-coated tips[27,28], or to increase adhesion using polymer-coated tips[21,29]. The present limitation is the availability of 'pick-up' substrates. Even though each substrate can be used to make thousands of nanotube tips, there is, as yet, no commercial source of high-quality 'pick-up' samples[21,30].

Solution-based approaches. The challenge of solubilizing nanotubes is critical to their widespread use in areas from composites to biosensors[31]. Once in solution, a range of processing techniques become available, such as separation of nanotubes according to electronic[32,33] and/or physical[34] structure. Controlled deposition from solution to substrates with specified position and orientation has been achieved by surface modification[35] and dielectrophoresis[14]; for nanotube tip fabrication dielectrophoresis is particularly promising as it gives control over the orientation, length, and to some extent the diameter of the nanotube tip[36,37]. So far, however, there have been few demonstrations of nanotube tips fabricated in this way. The processing required for solubilization shortens the nanotubes to lengths of around 100 nm (decreasing the van der Waals attachment strength to the tip) and can damage them significantly. However, as processing techniques improve this may become a more fruitful fabrication route.

Nanotube tip modification. Modification of AFM tips is essential to push beyond the study of topography to material properties such as conductivity, electrochemical activity and chemical functionality at the nanoscale. Modification typically involves either physically coating the AFM tip or chemically modifying it, and these approaches can be applied equally well to nanotube tips. Metal-coated nanotube tips have been used for conducting AFM[38,39], scanning surface potential microscopy[40] and magnetic force microscopy[41,42], and the addition of an insulating layer can lead to the creation of nanoelectrodes[43], as shown in Fig. 2. These coatings, applied post-nanotube-tip fabrication, bind the nanotubes more securely to the AFM tip, increasing stability and rigidity. The increase in diameter of the probe decreases the spatial resolution (unless the tip is deliberately re-sharpened at the apex)[40], but the increase in functionality opens up new avenues of research, such as combined topographic and electrochemical imaging; see below[43].

Many different chemical modifications to the nanotube structure can also be made. The majority involve opening the nanotube end, typically by electrical pulse shortening in air (often creating carboxyl groups[44,45]) and/or chemical derivatization using either gases[44], carbodiimide chemistry (covalent)[45], or π-π stacking (non-covalent)[46]. The well-defined chemistry of nanotubes is vital for their application as chemically specific nanoscale probes, as discussed below.

Outlook. An AFM tip must bridge the gap from the nanoscale tip apex to the microscale cantilever. The combination of top-down cantilever microfabrication with bottom-up fabrication of a nanotube as the imaging tip allows control and reproducibility at both these length scales; the challenge is the rational integration of the two. With the fast-paced advances in the growth and processing of carbon nanotubes it is almost inevitable that the problems associated with direct growth, pick-up and solution-based approaches will be overcome. Both the direct growth and solution-based approaches show great promise for scale-up, particularly for nanotube tips composed of bundles of nanotubes. The greatest challenge will surely be the reproducible production of nanotube tips composed of individual SWNTs, especially given the control required over l_{nt}. It is likely that the yield for these tips will always be low, and hence their cost high. However, given their potential applications, this may be a small price to pay.

Nanotube tip application

Nanotube tips have many advantages over conventional AFM tips, beyond the obvious increase in topographic resolution. Here we review some of the applications that have been demonstrated so far. In most cases nanotube tips are used in 'dynamic' mode because, despite their high rigidity, the nanotubes are prone to deformation under lateral forces.

Figure 4 | Nanolithographic writing with a nanotube AFM tip. Tip writing was carried out in tapping mode on a hydrogen-terminated silicon surface. Under a negative tip bias, oxide structures are created (white), which show a height increase against the H–Si background (black). Reproduced with permission from ref. 77 (© 1998 AIP).

Topographic imaging. The original motivation behind the fabrication of nanotube tips was high-resolution topographic imaging. This drove fabrication towards probes composed of individual SWNTs, with diameters on the nanometre scale and lengths shortened to <20 nm (see Box 1). The high aspect ratio and small diameter minimize attractive tip–surface interactions[47], facilitating imaging both in the repulsive regime — where resolution is maximized — and at reduced oscillation amplitudes[47]. The reduced tip–sample attraction allows less invasive imaging — high tip–surface forces lead to deformation, and in some instances damage, of soft samples. Thus nanotube tips are ideally suited to high-resolution imaging of biological complexes and have the potential to impact significantly on structural biology[14,29,48–51]. For example, Fig. 3a shows an AFM height image of the chaperonin protein, GroES (involved in protein folding) taken with a cCVD-grown SWNT tip[52]. The improved resolution capabilities of the nanotube tip enables both conformations of the isolated biomolecule — a ring-like structure (11 nm outer diameter) with heptameric symmetry, and a dome-shaped structure of the same diameter — to be imaged for the first time. This characteristic of SWNT tips has also made the identification of structural intermediates possible — for example, in amyloid fibril formation[53] (linked to Alzheimer's disease) — among other applications, as detailed in ref. 49.

In principle, the technique is also amenable to real-time *in vitro* work in physiologically relevant environments, offering an alternative characterization approach for those molecules whose structures cannot be obtained using techniques such as X-ray diffraction. However, one of the biggest challenges for nanotube tips is low-force high-resolution imaging under solution. Decreased van der Waals forces, and the higher impact forces typically involved in dynamic-mode imaging under solution, mean that many of the nanotube tip preparation routes described in this review are not suitable for fluid

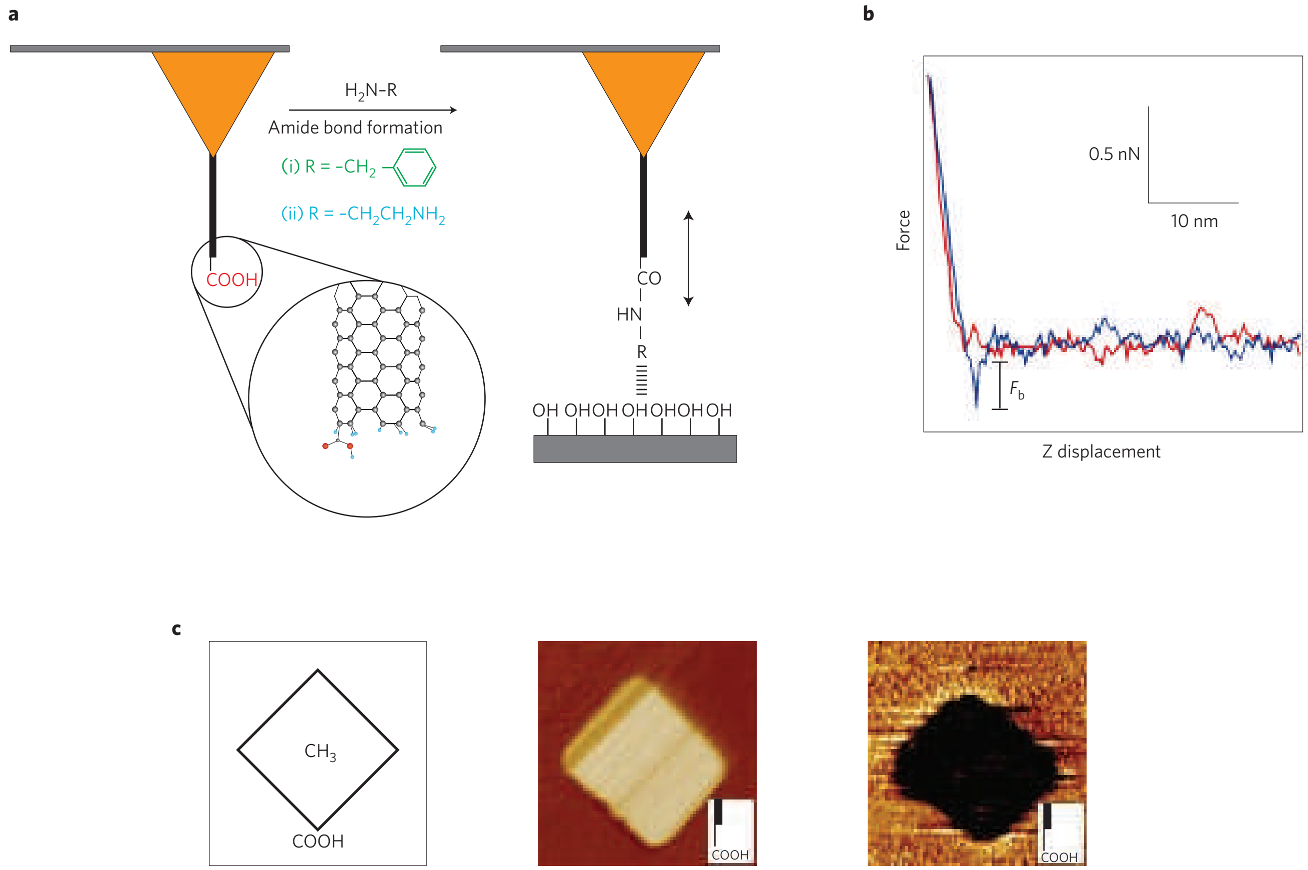


Figure 5 | Production and application of chemically functionalized nanotube tips. a, Schematic of the opened end of an oxidized SWNT tip and the carbodiimide coupling chemistry used in one form of chemical derivatization. **b**, A representative force–distance curve obtained with a biotin-modified SWNT tip on a streptavidin surface in solution; note that the binding force measured (~200 pN; blue line is the retract curve) corresponds to a single biotin–streptavidin chemical bond. **c**, Chemical imaging with functionalized nanotube tips. Left: Schematic of a patterned self-assembled monolayer terminating in methyl (CH_3) and carboxyl (COOH) end groups. Middle: Tapping-mode phase image of the patterned self-assembled monolayer shown in the left panel, obtained with a COOH-terminated tip. Right: Phase image of the same area obtained with a C_6H_5-terminated tip. Note the inversion in contrast. Figure reproduced with permission from ref. 49 (© 2000 Elsevier).

imaging. Attachment forces between the nanotube and tip that are sufficient in air are often not strong enough under fluid to prevent the nanotube being removed during immersion and/or imaging. Thus extra care must be taken when adhering the nanotube to the tip. The first demonstrations of imaging under solution involved relatively long MWNTs imaging through a shallow water layer so that only a portion of the tube was submerged, which minimized the effects of hydrodynamic damping[5,54]. More recently, techniques to strengthen the attachment of the tip to the surface have been developed — for example, the use of electron-beam-deposited carbon[55], pre-coating the tip with an adhesive before SWNT 'pick-up'[21] or coating the tip with a polymeric film post attachment[56]. Using these techniques several groups have demonstrated both force-curve analysis and high-resolution imaging under solution[21,55,56].

Tip damage is a common problem in AFM, with quantitative image analysis complicated by tip degradation over time. However, with nanotube tips this effect is significantly reduced, with reports of at least a 20 times improvement in the lifetime over conventional silicon probes[57]. The superior wear characteristics result from the reduced tip–sample forces, the strong carbon–carbon bonding within the nanotube, and the reversible buckling and bending characteristics. However, nanotube tips are not immune to degradation through contamination (for example, attachment of surface debris) during imaging — a problem common to all AFM tips. The robustness of nanotubes is also important in the application of nanotube tips to critical dimension metrology, particularly in semiconductor processing. For this, the primary goal is to accurately profile high-aspect-ratio features on substrates, rather than to achieve high lateral resolution, as shown in Fig. 3b[58]. The exceptional nanotube stiffness allows the use of MWNTs (or bundles of SWNTs) with micrometre lengths and aspect ratios of ~100 (see Box 1), enabling the probing of structures inaccessible to conventional silicon tips. Control over the length and orientation of the nanotube is desirable to obtain faithful representations of surface topography and prevent imaging instabilities[30,59–62].

In AFM it is important to understand the forces and dynamics involved, not only to aid the interpretation and optimization of images, but also as a route for probing interactions on the nanoscale. Theoretical work has shown that with nanotube tips, the influence of tip–sample forces not only has an impact on the amplitude response, and hence imaging capabilities in air and solution during dynamic AFM[47,63,64], but can also elastically deform the nanotubes creating imaging artefacts[65]. Nanotube orientation has also been shown to effect image resolution[66]. Further work is required to understand the optimal operating conditions for nanotube tips to maximize their potential impact.

Electrical and magnetic probing. A variety of AFM-based techniques have been developed to investigate electrical properties on the nanoscale, and the remarkable electrical conductivity of nanotubes makes many of these techniques accessible with nanotube tips. By attaching nanotubes to a metal-coated AFM tip,

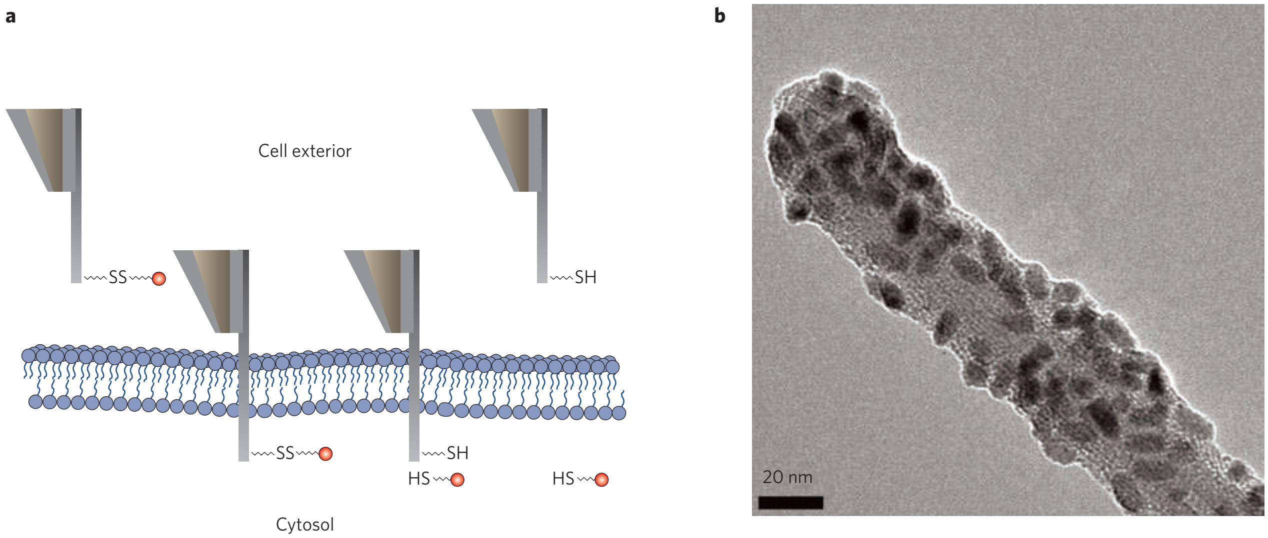


Figure 6 | Schematic of the 'nanoinjection' procedure. a, A MWNT–AFM tip with its cargo attached penetrates a cell membrane. On chemical stimulation the cargo is released and the nanoneedle is retracted. **b**, TEM image of a MWNT–AFM tip derivatized with quantum dots (the 'cargo'). Figure reproduced with permission from ref. 46 (© 2007 PNAS).

a stable electrical contact is created[27,28]. For electrical measurements made in contact mode, it is often necessary to stiffen the nanotube tip to reduce lateral bending of the nanotube. This can be done by using thicker nanotube tips[39,67] or by sputter-coating with metal[40]. The latter process results in probes robust enough for contact mode and conducting AFM imaging[38], with increased longevity over conventional probes.

Electrostatic force microscopy (EFM)[68] is a group of dynamic SPM techniques sensitive to the long-range electrostatic forces, which are useful in the study of active semiconductor devices, trapped charges and work function differences in heterogeneous materials. Interpretation of EFM images is complicated by the long-range nature of the electrostatic force, which results in significant contributions to the image from the tip beyond the tip apex. This effect can be reduced by using high-aspect-ratio probes, making nanotube tips ideal EFM probes[69,70]. For similar reasons nanotube tips are also suited to high-resolution magnetic force microscopy, which has been demonstrated with nanotube tips using either the magnetic catalyst particle, located at the end of a MWNT[71], or by filling/coating nanotubes with magnetic material[41]. Selective placement of magnetic material at the tip apex removes all long-range contributions of the tip cone and cantilever, providing the most localized and least invasive magnetic force microscopy probe[71].

Nanolithography. AFM is not just a tool for imaging, but also for manipulation. AFM nanolithography has found widespread application in fields such as data storage and device fabrication, as well as being of interest in fundamental materials research[72,73]. The interactions are typically electrostatic, electrochemical or thermal (all of which usually require a conductive probe), and/or nanomechanical. Surface modification requires a strong interaction, which can result in damage or deterioration of conventional AFM probes, and hence inconsistent features. Nanotube tips have the obvious advantage of finer resolution lithography owing to their approximately nanometre diameter[74]. They also have other benefits such as prolonged lifetimes and reduced electromigration, resulting from the high carbon–carbon bond strengths[75]; hydrophobicity, which reduces the effect of humidity[76]; and low work function, which aids in local oxidation and field emission[77,78].

Typically, nanotube tips are operated in tapping mode; in contact mode, instabilities in the tip can affect the resulting shape of the feature produced on the surface[79] unless the probe has been deliberately stiffened — for example, by the addition of a coating layer[28]. However, even with tapping mode, care must be taken to minimize the lateral bending force during writing. Furthermore, the angle at which the nanotube protrudes from the tip is also important as this can have a role in defining the resultant structure[80]. However, with a nanotube tip it is possible to generate very small reproducible features, for instance, by using a SWNT tip: bit densities of 1.6 Tbits in^{-2} (8-nm-diameter, 1-nm-height bits) were produced by locally oxidizing titanium[74]; 6.8-nm-diameter bits in ferroelectric thin films were formed through localized domain polarization[28]; and tunnel junctions <10 nm in size for use in single electron transistors were created by oxidizing aluminium[81]. By 'reading' with the same tip, convolution effects are also minimized. Longer writing lifetimes are possible and as long as the nanotube is correctly orientated from the tip, the resultant pattern is a faithful representation of the movement of the AFM piezoelectric positioners, as shown in Fig. 4 (ref. 77).

Chemical sensing. Specific molecular and intermolecular interactions are vital for many fundamental processes, especially in the life sciences. Examples include molecular recognition between receptor and ligand, host and guest, antibody and antigen, and complementary DNA strands. The nanonewton-scale forces involved make chemically modified AFM tips an ideal tool for exploring these interactions[82] and it is even possible to chemically map surface functionality. Conventional chemical force microscopy is typically limited in its ability to sense individual molecular interactions as the standard silicon, and particularly silicon nitride, tips can be difficult to chemically functionalize. Thus, chemical modification usually involves pre-coating the tip with gold, followed by the addition of a self-assembled monolayer terminated with the appropriate chemistry, which results in an increase in the size of the effective tip. This often means that multiple molecular interactions are probed at a time, making quantification difficult. In contrast, with nanotube tips not only is it possible to directly functionalize the carbon itself, but the nanometre-scale diameter of a SWNT allows measurement of interactions at the single-molecule level[45].

So far SWNT tips have been used to directly measure the binding force between single protein–ligand pairs[45] and map surface chemistry (Fig. 5)[45]. More recently, nanotube tips derivatized with nanoparticles[83] and quantum dots have been used as carriers and 'nanoinjectors'[46] (Fig. 6). In the latter work, the needle-like geometry of the nanotube tip was used to 'inject' protein-coated quantum dots into live human cells, crucially without significant physical disruption to the cell membrane or the nanotube. The controlled release of a small number of target molecules into cells without physical damage could have far reaching implications for medical science and biotechnology.

Chemical detection of species is also possible using electrochemistry: electroactive species show characteristic oxidation and reduction potentials. By using an electrochemically active AFM tip, biased at the appropriate potential, it is possible to correlate the structure of a surface with its (electro)chemical activity. This is important in corrosion, ion-channel mapping, neurotransmitter release from synapses, and so on[84]. The smaller the electrode, the higher the electrochemical resolution. Preliminary work demonstrated the use of vapour-phase deposited polymers and plasma-deposited silicon oxide to electrically insulate a SWNT tip such that only the end was exposed to solution[85–87]; however no electrochemical imaging was demonstrated. Further work used metal-templated nanotube tips coated in an electrodeposited polymer to simultaneously image the structure and activity of approximately micrometre-size electroactive sites[43,88], paving the way for ultrahigh-resolution (electro)chemical and topographical imaging.

Conclusions and outlook

A readily available source of nanotube tips would further open up the AFM imaging world, increasing tip longevity, reducing tip imaging artefacts, increasing resolution and decreasing tip–surface forces. It would also have a significant impact in key research areas such as structural biology, biotechnology, metrology and nanoelectronics. The question then remains, why are nanotube tips not being used routinely for AFM imaging and characterization? The answer lies in the fabrication. Even though carbon nanotubes have superior material properties, in order to make the transition to mainstream applicability, nanotube tips must become an off-the-shelf product with an accessible price tag. Although microfabrication has proven to be an effective technique for mass production of AFM probes, the challenge lies in creating an equally efficient process for the integration of nanotubes onto these tips. With commercial routes limited at present, most users are unlikely to invest time and effort into making their own nanotube tips when sharper silicon tips, which compete favourably in terms of lateral resolution, are now readily available. Progress in this area is being made, but obstacles still remain, and it is yet to be seen whether these issues are surmountable. However, the significant rewards waiting will ensure that this remains an active area for the foreseeable future.

References

1. Wood, J. The top ten advances in materials science. *Mater. Today* **11,** 40 (2008).
2. Wiesendanger, R. *Scanning Probe Microscopy and Spectroscopy* (Cambridge Univ. Press, 1994).
3. Ximen, H. & Russell, P. E. Microfabrication of AFM tips using focused ion and electron beam techniques. *Ultramicroscopy* **42–44,** 1526–1532 (1992).
4. Saito, R., Dresselhaus, G. & Dresselhaus, M. S. *Physical Properties of Carbon Nanotubes* (Imperial College Press, 1998).
5. Dai, H. *et al.* Nanotubes as nanoprobes in scanning probe microscopy. *Nature* **384,** 147–150 (1996).
6. Binnig, G., Quate, C. F. & Gerber, Ch. Atomic force microscope. *Phys. Rev. Lett.* **56,** 930–933 (1986).
7. Albrecht, T. R., Akamine, S., Carver, T. E. & Quate, C. F. Microfabrication of cantilever styli for the atomic force microscope. *J. Vac. Sci. Technol. A* **8,** 3386–3396 (1990).
8. Nguyen, C. V., Ye, Q. & Meyyappan, M. Carbon nanotube tips for scanning probe microscopy: fabrication and high aspect ratio nanometrology. *Meas. Sci. Technol.* **16,** 2138–2146 (2005).
9. Wong, E. W., Sheehan, P. E. & Lieber, C. M. Nanobeam mechanics: Elasticity, strength, and toughness of nanorods and nanotubes. *Science* **277,** 1971–1975 (1997).
10. deJonge, N., Lamy, Y. & Kaiser, M. Controlled mounting of individual multiwalled carbon nanotubes on support tips. *Nano Lett.* **3,** 1621–1624 (2003).
11. Martinez, J. *et al.* Length control and sharpening of atomic force microscope carbon nanotube tips assisted by an electron beam. *Nanotechnology* **16,** 2493–2496 (2005).
12. Kim, D.-H. *et al.* Shortening multiwalled carbon nanotube on atomic force microscope tip: Experiments and two possible mechanisms. *J. Appl. Phys.* **101,** 064317 (2007).
13. Jiang, A. N. *et al.* Amplitude response of multiwalled carbon nanotube probe with controlled length during tapping mode atomic force microscopy. *J. Phys. Chem. C* **112,** 15631–15636 (2008).
14. Nishijima, H. *et al.* Carbon-nanotube tips for scanning probe microscopy: Preparation by a controlled process and observation of deoxyribonucleic acid. *Appl. Phys. Lett.* **74,** 4061–4063 (1999).
15. Kong, J. *et al.* Synthesis of individual single-walled carbon nanotubes on patterned silicon wafers. *Nature* **395,** 878–881 (1998).
16. Kong, J., Cassell, A. M. & Dai, H. Chemical vapor deposition of methane for single-walled carbon nanotubes. *Chem. Phys. Lett.* **292,** 567–574 (1998).
17. Hafner, J. H. *et al.* Catalytic growth of single-wall carbon nanotubes from metal particles. *Chem. Phys. Lett.* **296,** 195–202 (1998).
18. Hafner, J. H., Cheung, C. L. & Lieber, C. M. Growth of nanotubes for probe microscopy tips. *Nature* **398,** 761–762 (1999).
19. Hafner, J. H., Cheung, C. L. & Lieber, C. M. Direct growth of single-walled carbon nanotube scanning probe microscopy tips. *J. Am. Chem. Soc.* **121,** 9750–9751 (1999).
20. Yenilmez, E. *et al.* Wafer scale production of carbon nanotube scanning probe tips for atomic force microscopy. *Appl. Phys. Lett.* **80,** 2225–2227 (2002).
21. Hafner, J. H., Cheung, C. L. Oosterkamp, T. H. & Lieber, C. M., High-yield assembly of individual single-walled carbon nanotube tips for scanning probe microscopies. *J. Phys. Chem. B* **105,** 743–746 (2001).
22. Zhang, Y. *et al.* Electric-field-directed growth of aligned single-walled carbon nanotubes. *Appl. Phys. Lett.* **79**, 3155–3157 (2001).
23. Ren, Z. F. *et al.* Growth of a single freestanding multiwall carbon nanotube on each nanonickel dot. *Appl. Phys. Lett.* **75,** 1086–1088 (1999).
24. Ye, Q. *et al.* Large-scale fabrication of carbon nanotube probe tips for atomic force microscopy critical dimension imaging applications. *Nano Lett.* **4,** 1301–1308 (2004).
25. Girifalco, L. A., Hodak, M. & Lee, R. S. Carbon nanotubes, buckyballs, ropes, and a universal graphitic potential. *Phys. Rev. B* **62,** 13104–13110 (2000).
26. Salvetat, J.-P. *et al.* Elastic and shear moduli of single-walled carbon nanotube ropes. *Phys. Rev. Lett.* **82,** 944–947 (1999).
27. Wilson, N. R., Cobden, D. H. & Macpherson, J. V. Single-wall carbon nanotube conducting probe tips. *J. Phys. Chem. B* **106,** 13102–13105 (2002).
28. Tayebi. N. *et al.* Nanopencil as a wear-tolerant probe for ultrahigh density storage. *Appl. Phys. Lett.* **93,** 103112 (2008).
29. Carnally, S. *et al.* Ultra-resolution imaging of a self-assembling biomolecular system using robust carbon nanotube AFM probes. *Langmuir* **23,** 3906–3911 (2007).
30. Snow, E. S., Campbell, P. M. & Novak, J. P. Atomic force microscopy using single-wall C nanotube probes. *J. Vac. Sci. Technol. B* **20,** 822–827 (2002).
31. Lin, Y. *et al.* Advances toward bioapplications of carbon nanotubes. *J. Mater. Chem.* **14,** 527–541 (2004).
32. Strano, M. S. *et al.* Electronic structure control of single-walled carbon nanotubes functionalization. *Science* **301,** 1519–1522 (2003).
33. Zheng, M. *et al.* DNA-assisted dispersion and separation of carbon nanotubes. *Nature Mater.* **2,** 338–342 (2003).
34. Zheng, M. *et al.* Structure-based carbon nanotube sorting by sequence-dependent DNA assembly. *Science* **302,** 1545–1548 (2003).
35. Keren, K. *et al.* DNA-templated carbon nanotube field-effect transistor. *Science* **302,** 1380–1382 (2003).
36. Tang, J. *et al.* Rapid and reproducible fabrication of carbon nanotube AFM probes by dielectrophoresis. *Nano Lett.* **5,** 11–14 (2005).
37. Kim, J. E., Park, J. K. & Han, C. S. Use of dielectrophoresis in the fabrication of an atomic force microscope tip with a carbon nanotube: experimental investigation. *Nanotechnology* **17**, 2937–2941 (2006).
38. Wilson, N. R. & Macpherson, J. V. Single-walled carbon nanotubes as templates for nanowire conducting probes. *Nano Lett.* **3,** 1365–1369 (2003).
39. Ishikawa, K. & Cho, Y. Using an electroconductive carbon nanotube probe tip in scanning nonlinear dielectric microscopy. *Rev. Sci. Instrum.* **77,** 103708 (2006).
40. Zhao, M. *et al.* Ultrasharp and high aspect ratio carbon nanotube atomic force microscopy probes for enhanced surface potential imaging. *Nanotechnology* **19,** 235704 (2008).
41. Deng, Z. F. *et al.* Metal-coated carbon nanotube tips for magnetic force microscopy. *Appl. Phys. Lett.* **85,** 6263–6265 (2004).
42. Winkler, A. *et al.* Magnetic force microscopy sensors using iron-filled carbon nanotubes. *J. Appl. Phys.* **99,** 104905 (2006).
43. Burt, D. P. *et al.* Nanowire probes for high resolution combined scanning electrochemical microscopy — Atomic force microscopy. *Nano Lett.* **5,** 639–643 (2005).

44. Wong, S. S., Woolley, A. T., Joselevich, E. & Lieber, C. M. Functionalization of carbon nanotube AFM probes using tip-activated gases. *Chem. Phys. Lett.* **306,** 219–225 (1999).
45. Wong, S. S. *et al.* Covalently functionalized nanotubes as nanometre-sized probes in chemistry and biology. *Nature* **394,** 52–55 (1998).
46. Chen, X., Kis, A., Zettl, A. & Bertozzi, C. R. A cell nanoinjector based on carbon nanotubes. *Proc. Natl Acad. Sci. USA* **104,** 8218–8222 (2007).
47. Chen, L., Cheung, C. L., Ashby, P. D. & Lieber, C. M. Single-walled carbon nanotube AFM probes: Optimal imaging resolution of nanoclusters and biomolecules in ambient and fluid environments. *Nano Lett.* **4,** 1725–1731 (2004).
48. Li, Y. *et al.* Controlled assembly of dendrimer-like DNA. *Nature Mater.* **3,** 38–42 (2004).
49. Woolley, A. T., Cheung, C. L., Hafner, J. H. & Lieber, C. M. Structural biology with carbon nanotube AFM probes. *Chem. Biol.* **7,** R193–R204 (2000).
50. Chen. L., Haushalter, K. A., Lieber, C. M. & Verdine, G. L. Direct visualization of a DNA glycosylase searching for damage. *Chem. Biol.* **9,** 345–350 (2002).
51. Wong, S. S. *et al.* Single-walled carbon nanotube probes for high-resolution nanostructure imaging. *Appl. Phys. Lett.* **73,** 3465–3467 (1998).
52. Cheung, C. L., Hafner, J. H. & Lieber, C. M. Carbon nanotube atomic force microscopy tips: Direct growth by chemical vapor deposition and application to high-resolution imaging. *Proc. Natl Acad. Sci. USA* **97,** 3809–3813 (2000).
53. Harper, J. D., Wong, S. S., Lieber, C. M. & Lansbury, P. T. Assembly of A beta amyloid protofibrils: An in vitro model for a possible early event in Alzheimer's disease. *Biochemistry* **38,** 8972–8980 (1999).
54. Moloni, K., Buss, M. R. & Andres, R. P. Tapping mode scanning force microscopy in water using a carbon nanotube probe. *Ultramicroscopy* **80,** 237–246 (1999).
55. Jarvis, S. P. *et al.* Local solvation shell measurement in water using a carbon nanotube probe. *J. Phys. Chem. B* **104,** 6091–6094 (2000).
56. Stevens, R. M., Nguyen, C. V. & Meyyappan, M. Carbon nanotube scanning probe for imaging in aqueous environment. *IEEE Trans. Nanobiosci.* **3,** 56–60 (2004).
57. Larsen, T. *et al.* Comparison of wear characteristics of etched-silicon and carbon nanotube atomic-force microscopy probes. *Appl. Phys. Lett.* **80,** 1996–1998 (2002).
58. Nguyen, C. *et al.* Carbon nanotube tip probes: stability and lateral resolution in scanning probe microscopy and applications to surface science in semiconductors. *Nanotechnology* **12,** 363–367 (2001).
59. Wade, L. A. *et al.* Correlating AFM probe morphology to image resolution for single-wall carbon nanotube tips. *Nano Lett.* **4,** 725–731 (2004).
60. Nguyen, C. V. *et al.* Carbon nanotube scanning probe for profiling of deep-ultraviolet and 193 nm photoresist patterns. *Appl. Phys. Lett.* **81,** 901–903 (2002).
61. Stevens, R. *et al.* Improved fabrication approach for carbon nanotube probe devices. *Appl. Phys. Lett.* **77,** 3453–3455 (2000).
62. Solares, S. D. Characterization of deep nanoscale surface trenches with AFM using thin carbon nanotube probes in amplitude modulation and frequency-force-modulation modes. *Meas. Sci. Technol.* **19,** 015503 (2008).
63. Kutana, A., Giapis, K. P., Chen, J. Y. & Collier, C. P. Amplitude response of single-wall carbon nanotube probes during tapping mode atomic force microscopy: Modeling and experiment. *Nano Lett.* **6,** 1669–1673 (2006).
64. Solares, S. D., Esplandiu, M. J., Goddard, W. A. & Collier, C. P. Mechanism of single walled carbon nanotube probe sample multistability in tapping mode AFM imaging. *J. Phys. Chem. B* **109,** 11493–11500 (2005).
65. Shapiro, I. R. *et al.* Influence of elastic deformation on single-wall carbon nanotube atomic force microscopy probe resolution. *J. Phys. Chem. B* **108,** 13613–13618 (2004).
66. Solares, S. D., Matsuda, Y. & Goddard, W. A. Influence of the carbon nanotube probe tilt angle on the effective probe stiffness and image quality in tapping-mode atomic force microscopy. *J. Phys. Chem. B* **109,** 16658–16664 (2005).
67. Ishikawa, K., Honda, K. & Yasuo. C. Resolution enhancement in contact-type scanning nonlinear dielectric microscopy using a conductive carbon nanotube probe tip. *Nanotechnology* **18,** 084015 (2007).
68. Martin, Y., Abraham, D. W. & Wickramasinghe, H. K. High-resolution capacitance measurement and potentiometry by force microscopy. *Appl. Phys. Lett.* **52,** 1103–1105 (1988).
69. Wilson, N. R. & Macpherson, J. V., Enhanced resolution electric force microscopy with single-wall carbon nanotube tips. *J. Appl. Phys.* **96,** 3565–3567 (2004).
70. Arnason, S. B., Rinzler, A. G., Hudspeth, Q. & Hebard, A. F. Carbon nanotube-modified cantilevers for improved spatial resolution in electrostatic force microscopy. *Appl. Phys. Lett.* **75,** 2842–2844 (1999).
71. Arie, T. Nishijima, H., Akita, S. & Nakayama, Y. Carbon-nanotube probe equipped magnetic force microscope. *J. Vac. Sci. Tech. B* **18,** 104–106 (2000).
72. Kalinin, S. & Gruverman, A. *Scanning Probe Microscopy Electrical and Electrochemical Phenomena at the Nanoscale: Fundamentals and Applications* (Springer, 2007).
73. Tseng, A. A., Notargiacomo, A. & Chen, T. P. Nanofabrication by scanning probe microscope lithography: A review. *J. Vac. Sci. Technol.* B **23,** 877–894 (2005).
74. Cooper, E. B. *et al.* Tetrabit-per-square-inch data storage with the atomic force microscope. *Appl. Phys. Lett.* **75,** 3566–3568 (1999).
75. Austin, A. J. & Nguyen, C. Electrical conduction of carbon nanotube atomic force microscopy tips: Application in nanofabrication. *J. Appl. Phys.* **99,** 114304 (2006).
76. Kuramochi, H., Tokizaki, T., Yokoyama, H & Dagata, J. A. Why nano-oxidation with carbon nanotube probes is so stable: I. Linkage between hydrophobicity and stability. *Nanotechnology* **18,** 135703 (2007).
77. Dai, H., Franklin, N. & Han, J. Exploiting the properties of carbon nanotubes for lithography. *Appl. Phys. Lett.* **73,** 1508–1510 (1998).
78. Jian, S.-R. & Juang, J.-Y. Scanned probe oxidation of p-GaAs(100) surface with an atomic force microscopy. *Nanoscale Res. Lett.* **3,** 249–254 (2008).
79. Kuramochi, H. *et al.* Nano-oxidation and in situ faradaic current detection using dynamic carbon nanotube probes. *Nanotechnology* **15,** 1126–1130 (2004).
80. Park, J. G., Zhang, C., Liang, R. & Wang, B. Nano-machining of highly orientated pyrolytic graphite using conductive atomic force microscope tips and carbon nanotubes. *Nanotechnology* **18,** 405306 (2007).
81. Gotoh, Y., Matsumoto, K. & Maeda, T. Room temperature coulomb diamond characteristic of single electron. Transistor made by AFM nano-oxidation process. *Jpn J. Appl. Phys.* **41,** 2578–2582 (2002).
82. Noy, A. Chemical force microscopy of chemical and biological interactions. *Surf. Interf. Anal.* **38,** 1429–1441 (2006).
83. Vakarelski, I. U., Brown, S. C., Higashitani, K. & Moudgil, B. M. Penetration of living cell membranes with fortified carbon nanotube tips. *Langmuir* **23,** 10893–10896 (2007).
84. Gardner, C. E. & Macpherson, J. V. Atomic force microscopy probes go electrochemical. *Anal. Chem.* **74,** 576A–584A (2002).
85. Patil, A., Sippel, J., Martin, G. W. & Rinzler, A. G. Enhanced functionality of nanotube atomic force microscopy tips by polymer coating. *Nano Lett.* **4,** 303–308 (2004).
86. Esplandiu, M. J., Bittner, V. G., Giapis, K. P. & Collier, C. P. Nanoelectrode scanning probes from fluorocarbon-coated single-walled carbon nanotubes. *Nano Lett.* **4,** 1873–1879 (2004).
87. Narui, Y., Ceres, D. M., Chen, J., Giapis, K. P. & Collier, C. P. High aspect ratio silicon dioxide coated single walled carbon nanotube scanning probe nanoelectrodes, *J. Phys. Chem. C* **113,** 6815–6820 (2009).
88. Burt. *et al.* Developments in nanowire scanning electrochemical atomic force microscopy (SECM-AFM) probes. *IEEE Sensors* **1–3,** 712–715 (2007).
89. Wilson, N. R. *Electronic Transport in Single Walled Carbon Nanotubes and Their Application as Scanning Probe Microscopy Tips.* PhD Thesis, Univ. Warwick (2004).
90. Jaroenapibal, P., Luzzi, D. E., Evoy, S. & Arepalli, S. Transmission-electron-microscopic studies of mechanical properties of single-walled carbon nanotube bundles. *Appl. Phys. Lett.* **85,** 4328–4330 (2004).
91. Valcarcel, V., Cardenas, S. & Simonet, B. M. Role of carbon nanotubes in analytical science. *Anal. Chem.* **79,** 4788–4797 (2007).