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Carbon nanotube forests: a non-stick workbench for nanomanipulation

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Abstract
The ubiquitous static friction (stiction) and adhesion forces comprise a major obstacle in the manipulation of matter at the nanoscale (Falvo *et al* 1999 *Nature* **397** 236; Urbakh M *et al* 2004 *Nature* **430** 525). In this work it is shown that a surface coated with vertically aligned carbon nanotubes—a nanotube forest—acts as an effective *non-stick* workbench for the manipulation of micro-objects and fibres/wires with one or more dimensions in the nano-range. These include organic nanofibres (Balzer and Rubahn 2001 *Appl. Phys. Lett.* **79** 3860) and microsized latex beads, which adhere strongly even to a conventional low surface-energy material like Teflon. Although organic nanofibres are attractive as device components due to their chemical adaptability, adhesion forces nearly always rule out manipulation as a route to assembly of prototype devices based on such materials, because organic materials are soft and fragile, and tend to stick to any surface. We demonstrate here that the nanotube forest due to its roughness not only exhibits very low stiction and dynamic friction; it also acts as a springy and mechanically compliant surface, making it possible to lift up and manipulate delicate nanostructures such as organic nanofibres in ways not possible on planar, rigid surfaces.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

In order to realize the potential of nanotubes and nanowires as components in electronic devices or other microsystems, methods for reliable pick-and-place assembly must be established. Manipulation may offer a fast and straightforward path to functional prototypes, whereas fabrication for industrial purposes requires a different approach, such as *in situ* growth of nanostructures on microelectrodes [1, 2]. A major obstacle for the pick-and-place assembly method is the delicate balance required between the adhesion forces acting between the object to be manipulated, and the surface and the manipulation tool, respectively [3, 4]. Controlling the balance of these forces is a key issue [5–7].

In this work it is demonstrated that the stiction and adhesion forces acting on objects, such as micron-sized latex beads and organic nanofibres [8], are extremely small on a vertically aligned multiwalled carbon nanotube forest compared to other surfaces such as gold, Teflon, diamond-like carbon (DLC) thin films [9], and crystalline silicon. We propose that such nanotube forests allow significantly more reliable pick-and-place assembly of 1D nanostructures. Manipulation of objects in the 100 nm range and below is often carried out inside the chamber of a scanning

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electron microscope (SEM) for visualization purposes, due to the limited resolution of optical microscopes [5]. In this environment, van der Waals forces are mainly responsible for the overall stiction and adhesion, although capillary forces can also contribute despite the low pressure in the SEM sample chamber (10^{-5} mbar). Electrostatic forces, due to charging from the electron beam, can also be present, either in an attractive or repulsive way. In this work it is observed that the initial stiction of objects on most surfaces is significantly higher than the subsequent stiction and dynamic friction. The adhesive forces may be enlarged by drying residues gathering around the objects after a liquid dispersion. For successful nanomanipulation, the forces between the objects, manipulation surfaces and manipulation tool need to be balanced. Since adhesion forces such as van der Waals and capillary forces depend on the contact area, these forces will be reduced on a rough surface. In this work a nanotube forest, to be considered as very rough, is compared to various smooth surfaces, which represent typical choices for dispersion of nanowires or fibres.

2. Experimental details

To evaluate the stiction and dynamic friction properties of nanotube forests in comparison to other substrates, microfabricated cantilevers were pushed against microbeads, supported on the various substrates, using a piezo-electrically actuated xyz manipulator. Both the manipulator and the substrates were located inside an SEM. The principle is illustrated in figure 1(A), where a 225 μm long cantilever is deflected against a 20 μm polystyrene (latex) microbead. As the cantilever base is moved to the left, the cantilever bends because of the stiction between the microbead and the underlying surface. The cantilever base is moved until the microbead is released. In theory, the maximum deflection of the cantilever before release is a measure of the stiction force. When the microbead is kept in constant motion, or when sliding comes to rest, the deflection gives a measure of the dynamic friction force.

The force is calculated from the measured deflection of the cantilever. It can be assumed that the deflection force can be treated as a point force acting on the tip of the cantilever. In such a situation the force is given by $F = \Delta X \cdot 3EI/L^3$, where ΔX is the deflection of the cantilever, L is the length of the cantilever, E is the elastic modulus of the cantilever material, and $I = w \cdot t^3/12$ is the plane moment of inertia for a rectangular beam with thickness t in the lateral direction of deflection and width w [10]. It should be noted that in our experimental set-up the terms thickness and width are interchanged as compared to common terminology of cantilevers. The cantilevers used were made from silicon dioxide, with E about 94 GPa. When multiple cantilevers are pushed against a single object, the total applied force is estimated as the sum of the individual bending forces on the cantilevers.

Five different substrates were used for the latex bead stiction studies: (I) gold, (II) Teflon, (III) silicon, (IV) diamond-like carbon, and (V) a nanotube forest. The gold substrate was prepared by depositing 100 nm of gold by e-beam evaporation onto a 500 μm thick silicon wafer. Similarly,

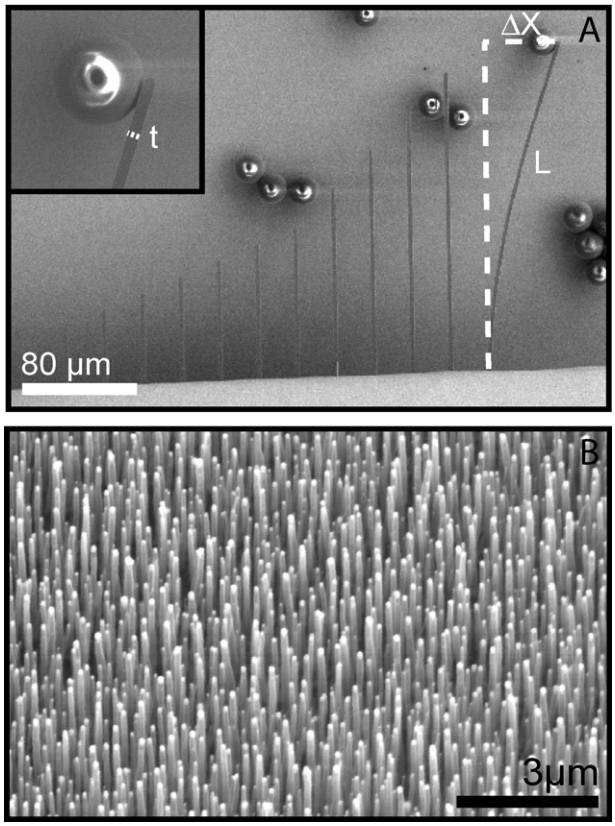

Figure 1. (A) Determination of the force exerted on a microbead. This picture shows a cantilever deflecting against a 20 μm diameter latex bead on a gold surface. The deflection ΔX is illustrated, as well as the length L of the cantilever being deflected. The inset shows a close-up of the cantilever and the bead. Here, the thickness t of the cantilever is illustrated. (B) A SEM micrograph of a typical carbon nanotube forest.

the Teflon substrate was made by deposition of a 80 nm thick Teflon-like coating from a C_4F_8 plasma onto a 500 μm thick silicon wafer [11]. The silicon substrate was taken as a clean, untreated 500 μm thick silicon wafer, and the diamond-like carbon substrate was made by depositing a 70 nm DLC film onto a 500 μm thick silicon wafer using an S-bend filtered cathodic vacuum arc system [9]. Finally, the substrate with the nanotube forest was prepared by a plasma enhanced chemical vapour deposition (PECVD). Here, a 4 nm thick nickel catalyst film was first deposited by evaporation onto an oxidized (15 nm thick) silicon wafer (500 μm thick). The carbon nanotubes were then grown by PECVD at 650 °C from a 50:200 sccm mixture of acetylene:ammonia for 5 min. This yielded about 1 μm tall nanotubes; see figure 1(B). Due to the electrical field present in the plasma sheath region, the nanotubes are automatically vertically aligned in the PECVD process [12–14]. All the substrates, except the nanotube forest, were rinsed in ethanol and blow-dried with nitrogen. Subsequently, an aqueous solution of latex microbeads was deposited on the different samples in small droplets using a micropipette. The solvent was evaporated by low-power heating for 20 min.

For the three-dimensional nanomanipulation experiment, we chose to manipulate organic nanofibres [8, 17], as these

Table 1. Forces obtained with a 225 μm long, 1 μm wide, 3 μm thick cantilever on individual 20 and 5 μm beads. It was impossible to release the large 20 μm beads on all substrates except the nanotube forest, due to excessive bending of the cantilever. This was also the case for 5 μm beads on silicon and gold. The values are averaged. The value for initial stiction of 5 μm beads on Teflon is for one group of three beads that released simultaneously. Several other individual beads were unable to release even when applying a force greater than 1.4 μN (maximum possible force from the excessive bending of cantilevers).

	20 μm beads		5 μm beads	
Substrate	Initial stiction (μN)	Dynamic friction (μN)	Initial stiction (μN)	Dynamic friction (μN)
Nanotube forest	0.9	0.3	0.2	0.1
Diamond-like carbon (DLC)	>1.4	No release	0.8	0.1
Teflon	>1.4	No release	1.1	0.4
Silicon	>1.4	No release	>1.4	No release
Gold	>1.4	No release	>1.4	No release

by experience represent well the difficulties inherent in mechanical manipulation of soft and fragile nanostructures. The nanofibres break at a shear stress of just 20 MPa [15]. This makes these structures excellent benchmark objects for evaluating the usefulness of our nanotube forest as a nanomanipulation workbench. In this experiment, the sample was prepared by depositing an aqueous solution of the nanofibres on the nanotube forest with subsequent drying in air. The experimental set-up was similar to the previous one, but rather than a microchip equipped with cantilevers an electrochemically etched tungsten tip was used as the manipulation tool. The tip was also mounted on the xyz manipulator inside the SEM. By nanomanipulation, nanofibres were picked up from the substrate and moved to another microchip with microfabricated electrode vias. Here, the nanofibres were put down in the desired positions—allowing subsequent electrical characterization by employing a special shadow mask technique described elsewhere [16].

3. Results and discussion

By releasing and moving the microbeads with the cantilever structure shown in figure 1, we were able to compare the initial stiction and friction forces on the nanotube forest substrate with the other substrates. The silicon dioxide cantilever used had a length of 225 μm, a width of 1 μm, and a thickness of 3 μm. This large ratio between length and cross-sectional dimensions makes this cantilever very flexible. We first compared the behaviour of 20 μm diameter microbeads on the different substrates. Only on the nanotube forest was it possible to release the 20 μm microbeads with this cantilever, whereas on all other substrates the microbead adhered too well; see table 1. In fact, on the nanotube forest it was possible to release clusters of several beads and move them around with a very small cantilever deflection. It was hard to tell the difference between initial stiction and dynamic friction on this substrate. For comparison we also examined a 5 μm diameter microbead on all five substrates. Similar behaviour was observed; however, in this case it was possible to release some 5 μm beads on the DLC substrate and the Teflon substrate as well as the nanotube forest substrate. It was found that the beads on the nanotube forest had the lowest average initial stiction force of 0.2 μN, as compared to 0.8 μN on DLC. In most cases it was impossible to release the beads on the Teflon substrate before the cantilever would break. However, in one case three beads were released simultaneously by applying a force of only 1.1 μN. In table 1 these values are listed, but the value for the Teflon substrate is not considered to be representative. It was not possible to release any beads on the silicon and gold substrates due to excessive bending of the cantilever, which in this case corresponds to an applied force of about 1.4 μN. For the successfully released beads, it was possible to estimate the dynamical friction as well. In both cases the nanotube forest exhibits the lowest friction, although for 5 μm beads the dynamic friction is more comparable to DLC and Teflon. The behaviour on the different substrates is shown in figure 2 with several SEM micrographs.

A different, less flexible cantilever probe was also used to obtain values of the stiction on the Teflon, silicon and gold substrates for 5 μm latex beads. Apart from this, exactly the same procedure and set-up were used. Figure 3 illustrates the behaviour of the different substrates in this case. On gold, the initial stiction prevented the release of a 5 μm latex bead even with an applied force of 100 μN. Thus this gives a lower limit for the initial stiction. The latex beads had a very similar behaviour on both the silicon substrate (not shown) and the Teflon coated substrate. Micrographs (C) and (D) in figure 3 show the manipulation experiment on a Teflon surface. In figure 3(C) the cantilevers push mainly on the lower bead. The force estimated as about 30 μN is just one third of the force used on the latex bead on gold. However, in this case, a slight increase in the force resulted in a sudden release of all four beads from the surface. Due to the built-up tension in the cantilevers, the beads are pushed instantly outside the field of view upon release. A similar result was achieved on a silicon substrate, but here a force of 70 μN per bead was necessary to release a group of five latex beads. The situation is quite different on the substrate covered with a nanotube forest. Figure 3(E) shows three cantilevers approaching a small cluster of three latex beads. It was possible to push all the beads simultaneously, without any visual deflection of the cantilevers. The experiments show that the nanotube forest exhibits low stiction and dynamic friction as compared to the other investigated substrates, particularly with respect to initial stiction. This is an important observation, which has also been noted before [15]. The difference between the initial stiction and the stiction after the first release is probably caused by the liquid deposition method, that may leave drying residues after evaporation. This behaviour is difficult to avoid as samples of nanostructures are often provided as liquid dispersions. However, the experiments clearly show that nanotube forests can minimize or even eliminate the effects of such residues.

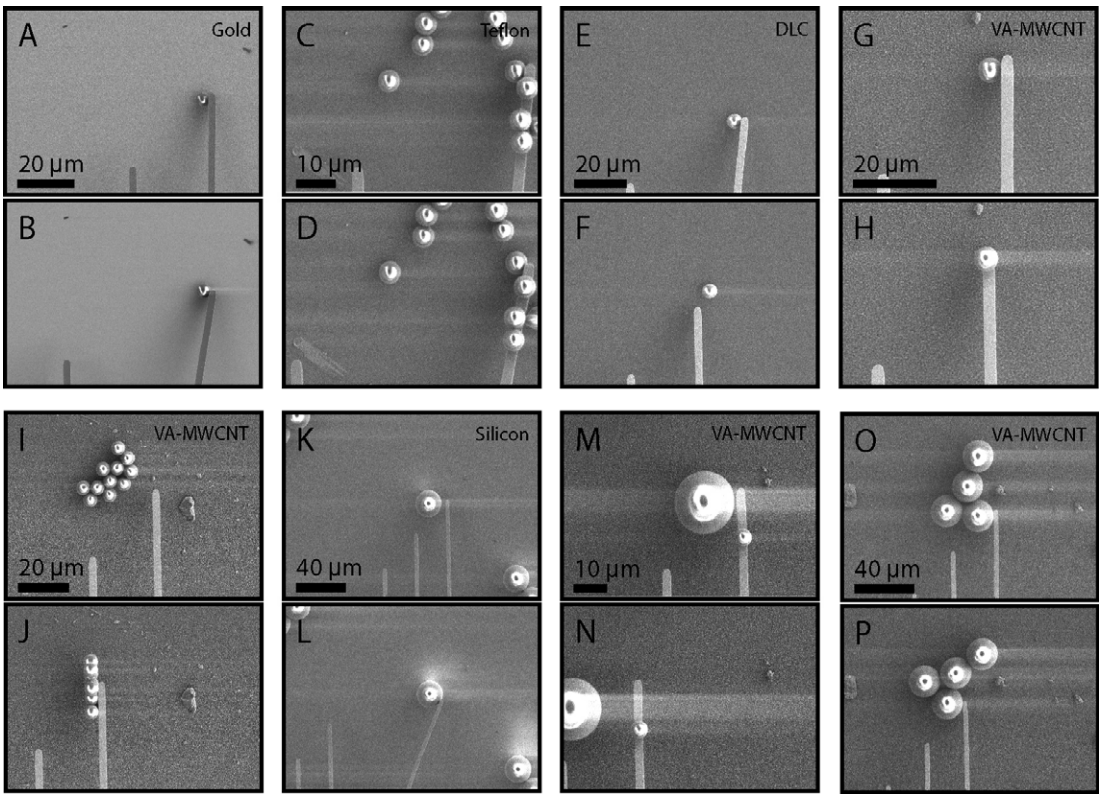

Figure 2. (A), (B) Cantilever unable to release a 5 μm bead on the gold substrate (1.4 μN). (C), (D) Cantilever unable to release a 5 μm bead on the Teflon substrate (1.6 μN). (E), (F) With only a moderate deflection, the cantilever releases a 5 μm bead on the DLC substrate (0.8 μN). (G), (H) The cantilever deflects even less with beads on the nanotube forest, when easily releasing a 5 μm bead (0.1 μN). (I), (J) On the nanotube forest, even large clusters of latex beads easily detach from the substrate surface without observable deflection of the cantilever and even transfer to the manipulation tool. (K), (L) On the silicon substrate, the cantilever is unable to release a 20 μm bead due to excessive bending. (M), (N) On the nanotube forest, the 20 μm beads are released easily. (O), (P) Even clusters of several 20 μm beads are moved easily on the nanotube forest.

Not only does the nanotube forest exhibit low static and dynamic friction, but also the small contact area between the objects and the nanotube forest results in a low adhesion force. This is demonstrated by the vertical lifting of an organic nanofibre, facilitated both by the compliant nature and the low adhesion of the nanotube forest. Organic nanofibres, such as para-hexaphenylene (*p*-6P) nanofibres, show great promise as components in future nanophotonic applications [17], for instance as waveguides, lasers and blue-light nanosized LEDs. However, their soft and fragile structure makes manipulation very challenging. Once dispersed on a Teflon-like surface, only short pieces of these 50 nm tall and 300 nm wide nanofibres could be pushed along the surface using the tip of an atomic force microscope [15], analogous to the lateral pushing of beads. Lifting of such nanofibres using an AFM tip is in that case practically impossible. In contrast, the organic nanofibres adhere only very lightly to the nanotube forest. Moreover, the mechanically compliant nanotube forest allowed us to push the tip slightly into the nanotube forest, under the nanofibre, and finally to lift it, without any visible damage to the fibre or the substrate. This lifting sequence is not possible with the other substrates examined here. In fact, in some cases, it was possible to lift off the nanofibres simply by touching them from above, indicating that the adhesive forces between the nanofibre and the manipulation tool were stronger than the forces between the nanofibre and the nanotube forest.

A manipulation sequence of a *p*-6P nanofibre on the nanotube forest is shown in figure 4. In figure 4(A) an electrochemically etched tungsten tip is moved underneath the nanofibre, and the concept is illustrated in figure 4(B). By lifting the tip, the nanofibre is successfully released from the surface as seen in figure 4(C), and it is now attached to the tip. Once adhering to the tip, the nanofibre could easily be moved to another microchip and placed controllably onto electrode supports, where the much larger adhesion forces, as compared to the nanotube forest, are sufficient to keep it in place. This is shown in figures 4(D), (E). In figure 4(D) the fibre is placed controllably onto electrode supports on another microchip, and the tip is successfully retracted as seen in figure 4(E). Although the nanotube forest solves the problem with initial stiction, the nanostructure may stick in an unfavourable position when placed on the smooth target substrate. The experiments indicate that this stiction can be expected to be much smaller than the initial stiction. It may still be necessary to minimize the adhesive properties of the target substrate to make fine-positioning possible. However, in our case the precision is adequate for subsequent fabrication of electrical connections. The manipulation method has a potential risk of contaminating the manipulated nanostructure with nanotubes from the nanotube forest, in particular if the nanotubes do not adhere strongly to the surface. However,

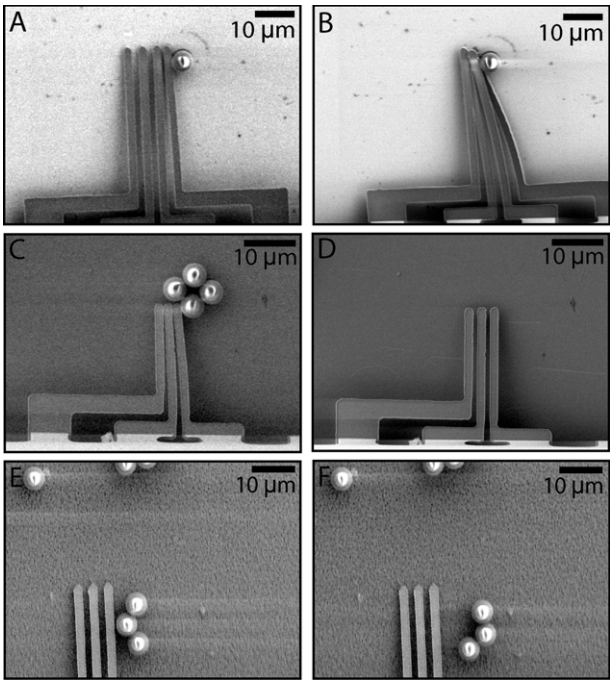

Figure 3. (A) A micro four point probe is moved in contact with a latex bead resting on a gold covered surface. (B) Even by applying a force in the order of 100 μN it is not possible to move the latex bead. (C) A force around 30 μN is applied to one latex bead situated in a small cluster on a Teflon coated silicon surface. (D) By increasing the force slightly, all the latex beads detach and abruptly disappear from view, due to the built-up tension in the cantilevers. (E) Latex beads resting on top of a nanotube forest are approached by a microchip with three cantilevers. (F) Without any visible deflection of the cantilevers, the latex beads are moved around on the surface.

the purity of the nanostructure can be inspected in the SEM directly after placement, and we have in no cases found any nanotubes in unwanted places. Tests of the mechanical properties further showed that the nanotube forest adhered very strongly to the surface for the samples used in this work. In addition, a custom-built manipulation set-up [16] was used to perform equivalent manipulations in ambient conditions under an optical microscope. In this set-up similar stiction properties of the different substrates were observed. The success rate of vertical picking strongly depends on the tip geometry. With a sharp tip (radius of curvature around 50 nm) around half of the picking trials were successful, whereas a duller tip reduced the rate of success significantly.

Once the organic nanofibre is successfully placed in the desired position on the electrode supports, it is possible to do electrical characterization of this particular nanostructure. Figure 5 shows a fluorescence microscope image of another manipulated *p*-6P nanofibre, emitting blue light under UV radiation. With a nanomanipulation-based, resistless shadow mask technique described elsewhere [16], electrical contact can be made to the nanofibre to characterize its electrical properties. This is accomplished without further manipulation of the nanofibre. Figure 5(B) shows the electrical characteristics of a single *p*-6P nanofibre, electrically contacted with two electrodes via manipulation in SEM and nanowire shadow masking. Electrical measurements and interpretations thereof are described in more detail in [16].

A careful study of the electrical properties of such nanofibres in terms of carrier injection from the metal electrode to the nanofibre as well as carrier transport inside the nanofibre is essential for the development of nanofibre-based devices. As demonstrated in figure 5(B) we can contact and study individual nanofibres manipulated onto a target structure; however, the analysis and interpretation requires invoking additional theoretical models, which are beyond the scope of this paper.

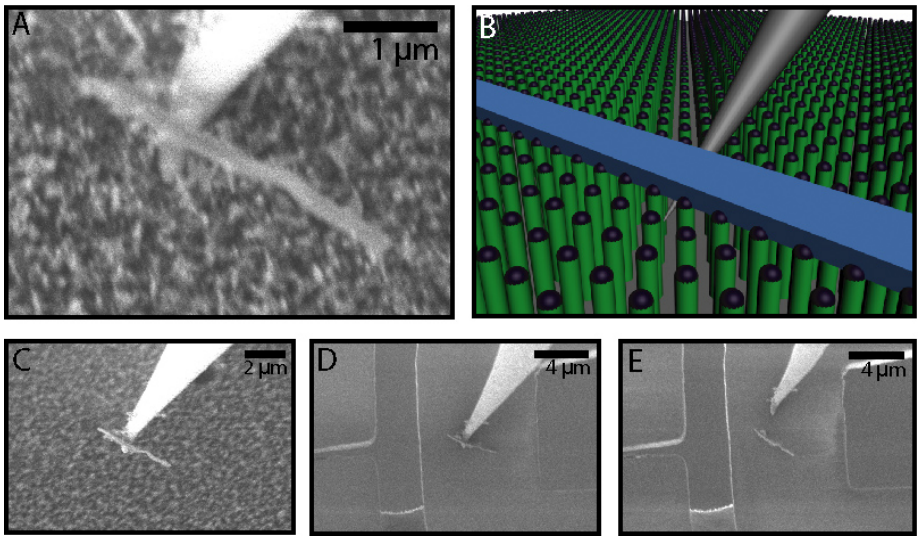

Figure 4. (A) A tungsten tip approaches a *p*-6P nanofibre resting on top of a nanotube forest, and moved underneath the fibre. (B) Illustration of the technique used for manipulation of fragile organic nanofibres. An electrochemically etched tungsten tip is moved beneath the nanofibre slightly into the mechanically compliant nanotube forest. The nanofibre may then be lifted by pulling the tip vertically up. (C) The nanofibre is lifted off the nanotube forest by pulling the tip up. (D) The nanofibre is then placed onto electrode supports on another microchip. (E) By pulling the tip away, the nanofibre remains on the electrode support, as it has been moved from a surface with low adhesion to a surface with higher adhesion.

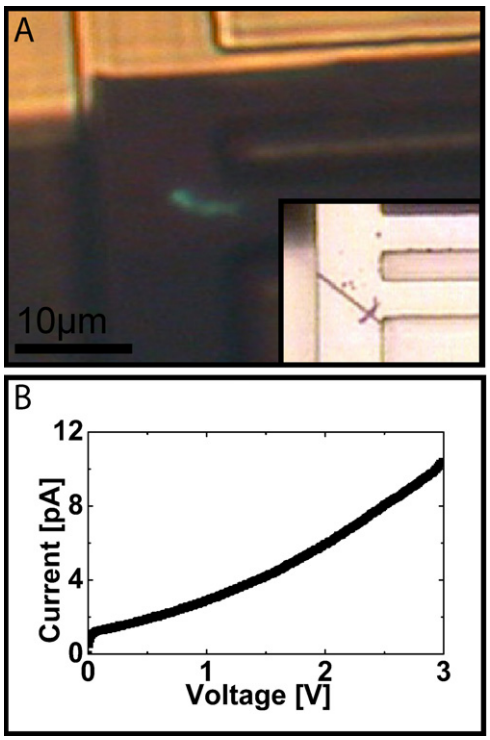

Figure 5. (A) Optical image of a different *p*-6P nanofibre placed onto electrodes. In ultraviolet light the nanofibre is seen to have retained its fluorescent properties. The inset shows the nanofibre after deposition of the electrode material using the shadow mask technique [16]. Notice the discontinuous metal coating across the nanofibre. (B) Electrical characteristics of a *p*-6P nanofibre mounted via assembly in a SEM. The measurement shown is consistent with other *p*-6P measurements, made using manipulation as well as other methods [18].

4. Conclusion

In general, adhesive and frictional forces depend on the effective surface area in contact between two objects. Uniquely, when using the nanotube forest, only the nanotube tips are in contact with the object, minimizing the effective contact area greatly (as illustrated in figure 4(B)) and hence lowering the total stiction and adhesion forces. By deflecting a microcantilever against latex microbeads on various surfaces including the nanotube forest, we examined both the initial stiction and the dynamic friction and found that on the nanotube forest these are a few tenths of a micronewton, which is at least four to eight times lower than on the other traditionally low friction surfaces. Furthermore, the ability of each individual carbon nanotube to bend in any direction as a response to an applied force makes the nanotube forest mechanically compliant, expanding the possibilities for three-dimensional manipulation compared to existing techniques. This allowed the first demonstration of pick and place of soft, fragile nanofibres dispersed on a surface from a liquid dispersion. In comparison, such a manipulation on surfaces such as gold or Teflon is practically impossible. Thus, surfaces coated with vertically aligned carbon nanotubes are highly suitable as a workbench for the manipulation, assembly and characterization of novel prototype nanodevices.

Acknowledgments

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