Synthetic gecko foot-hairs from multiwalled carbon nanotubes

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We report a fabrication process for constructing polymer surfaces with multiwalled carbon nanotube hairs, with strong nanometer-level adhesion forces that are 200 times higher than those observed for gecko foot-hairs.

The mechanism that allows a gecko lizard to climb any vertical surface and hang from a ceiling with one toe has attracted considerable interest and awe for over two millennia. Recent studies have discovered that the gecko’s ability to defy gravity comes from its remarkable feet and toes.1 Each five-toed foot is covered with microscopic elastic hairs called setae. The ends of these hairs split into spatulas which come in contact with the surface and induce enough intermolecular [van der Waals, (VdW)] forces to hold them in place. Similarly, the same VdW forces act between our two hands when they are held together, but in this case they do not stick to each other. The reason is that the roughness of our hands prevents them from coming close to each other at separations relevant for VdW forces. On the other hand, based on the gecko’s foot anatomy, if our hands were made up of tiny elastic structures that were able to deform or bend at different length scales in accordance with the contact surface and correct for the roughness, then perhaps our hands could also adhere to the surfaces we touch.

This achievement is not far away. There have been recent attempts to fabricate surface patterns with polymers to mimic the structure of setae and spatulas.2,3 However, these synthetic systems are not comparable to nature’s precision. Gecko foot-hairs have the proper aspect ratio, thickness, stiffness, and structure to adhere to any type and shape of surface with enough density to provide high adhesion forces. Here, we report a novel structure, based on multiwalled carbon nanotubes (MWNT) constructed on polymer surfaces with strong nanometer level adhesion, that can serve as a dry adhesive similar to or stronger than gecko foot-hairs.

The first step of our approach involves the growth of 50–100 micron MWNT on quartz or silicon substrates through chemical vapor deposition.4 A gaseous mixture of ferrocene (0.3 g), as a catalyst source, and xylene (30 mL), as a carbon source, is heated to over 150 °C and passed over the substrate for 10 min which is itself heated to 800 °C in a quartz tube furnace. The MWNT grow selectively on the oxide layer with controlled thickness and length. The oxide layer of the substrate can be patterned by photolithography followed by a combination of wet and/or dry etching in order to create various patterns of MWNT.5 A scanning electron microscope (SEM) image of typical MWNT grown on silicon is shown in Fig. 1a. These tubes are vertically aligned with a typical diameter of 10–20 nm and length of 65 μm. The samples, with the MWNT side facing up, are then gently dipped in a beaker containing methyl methacrylate monomer (60 mL) and polymerized using a 2,2’-azobisisobutyronitrile initiator (0.17 g) and a 1-decanethiol chain transfer agent (30 μL) in a clean room. After the completion of polymerization in a water bath at 55 °C for 24 h, the samples are taken out by breaking the beaker. The MWNT are completely embedded and stabilized in the PMMA matrix. The PMMA–MWNT sheets are peeled off from the silicon substrates forming a very smooth surface. The MWNT are exposed from the silicon-facing side of the PMMA matrix by etching the top 25 μm with a good solvent (acetone or toluene) for 50 min and subsequently washing with deionized water for 10 min. The exposure length of the MWNT can be controlled by varying the solvent etching time. As a control, blank PMMA films prepared using the same procedure, were etched with solvent and observed to maintain a very smooth surface. Fig. 1b shows MWNT brushes on PMMA films. Any pattern of MWNT on silicon can be exactly transferred on the top of the polymer surface. The brushes are mostly aligned vertically and in general form entangled bundles (50 nm diameter) due to the solvent drying process. This creates surface roughness which in turn enhances the adhesion as shown below.

The adhesive behavior of the MWNT brushes was measured with a Digital Instruments Nanoscope IIIa multimode scanning probe microscope (SPM). SPM has been used before as a powerful technique for measuring mechanical and interfacial properties of carbon nanotubes.6–10 Standard rectangular silicon probes (MikroMasch) with typical radius of curvature <10 nm and spring constant of 3.5 N m−1 (with an accuracy of 10% according
Carbon nanotubes, this complete length can be taken as an approximation for the maximum penetration depth. At the slope of a gecko foot-hair. The typical adhesive force in a setae corresponds to $10^{-4} \text{nN nm}^{-2}$, as estimated from a single setae attached to the cantilever of a micro-electromechanical system. Since the adhesive forces depend on the preloading of the setae, this number is also likely to be an underestimate. Conservatively, our experiments assume that the contact area is equivalent to that of a cone with the height equal to the maximum penetration depth determined from Fig. 2. The calculated minimum force/area is $1.6 \pm 0.5 \times 10^{-2} \text{nN nm}^{-2}$, which is much greater than the estimated value of a gecko’s setae.

What really is the origin of these astonishing values of adhesion forces? We postulate that these forces are a combination of VdW forces and energy dissipation during the elongation of the carbon nanotubes which comes from their material properties. The VdW forces originate from contact with multiple nanotubes and/or from large contact areas with a single nanotube, while the energy dissipation is due to their exceptionally high strength and extraordinary flexibility under large strains. Our force magnitudes are significantly different from that of a previous observation with a multiwalled carbon nanotube carpet, where the nanotubes do not form a dense phase but lie flat on the surface with nanotube free areas. This situation corresponds to one of our low adhesion areas. An analysis of the adhesion forces at various scan rates, from 0.5 Hz up to 14 Hz, shows a velocity independent behavior. This shows that, in this velocity region, there is no detectable change in the energy dissipation and contact area. We have also performed control experiments with blank PMMA samples and MWNT grown on quartz. The values of adhesion forces are negligible in the case of PMMA, eliminating the possibility of PMMA chains affecting the adhesion forces. On the other hand, the MWNT on quartz exhibit adhesive behavior similar to the MWNT brushes on PMMA, indicating that the adhesion forces are not influenced by the chemical composition of the solid substrate.

In summary, we have successfully demonstrated that structures found in gecko feet can be fabricated on polymer surfaces by using multiwalled carbon nanotubes. These structures have remarkable adhesion forces at the nanometer level, 200 times higher than that of a gecko foot-hair, and offer excellent potential as dry adhesives for microelectronics and space applications. The polymer used is a glassy PMMA but this approach can be applied to elastomeric
polymers with different moduli and flexibility. This will provide the flexibility to deform at many different length scales compared to that of gecko foot-hair. We are currently extending our procedure to optimize the nanotube structures, to obtain macroscopic contact areas with high adhesion and different polymer matrices.

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Notes and references