Highly Anisotropic Adhesive Film Made from Upside-Down, Flat, and Uniform Vertically Aligned CNTs

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ABSTRACT: We have created a multifunctional dry adhesive film with transferred vertically aligned carbon nanotubes (VA-CNTs). This unique VA-CNT film was fabricated by a multistep transfer process, converting the flat and uniform bottom of VA-CNTs grown on atomically flat silicon wafer substrates into the top surface of an adhesive layer. Unlike as-grown VA-CNTs, which have a nonuniform surface, randomly entangled CNT arrays, and a weak interface between the CNTs and substrates, this transferred VA-CNT film shows an extremely high coefficient of static friction (COF) of up to 60 and a shear adhesion force 30 times higher (12 N/cm²) than that of the as-grown VA-CNTs under a very small preloading of 0.2 N/cm². Moreover, a near-zero normal adhesion force was observed with 20 mN/cm² preloading and a maximum 100-μm displacement in a piezo scanner, demonstrating ideal properties for an artificial gecko foot. Using this unique structural feature and anisotropic adhesion properties, we also demonstrate effective removal and assembly of nanoparticles into organized micrometer-scale circular and line patterns by a single brushing of this flat and uniform VA-CNT film.

KEYWORDS: anisotropic adhesion, high static friction, low adhesion, vertically aligned carbon nanotubes, transfer process

INTRODUCTION

Carbon nanotubes (CNTs) are considered among the stiffest materials in the world, with single-walled CNTs exhibiting a Young’s modulus of up to 1 TPa in axial loading, well beyond the performance envelopes of traditional metals and alloys.1-3 The principal source of this strength, which stems from the C=C bonds on the CNT surface, also results in surprisingly poor stiffness in bending loads.4 The upshot of this nontraditional behavior is the simultaneous stiffness and exceptional flexibility of CNTs depending on the loading direction. This highly anisotropic behavior of CNTs is amplified when they are aligned together vertically, resulting in vertically aligned carbon nanotubes (VA-CNTs) that can exhibit an out-of-plane effective Young’s modulus as small as 100 kPa.4,5 This low value of modulus puts VA-CNTs firmly in the property envelopes of soft viscoelastic materials according to the well-known Dahlquist criterion.7,8 and thus makes them suitable for applications as pressure-sensitive adhesives (PSAs).

However, because of their inherent fibrillar structure, resembling the gecko foot structure well-known to simultaneously exhibit strong shear binding and weak normal adhesion, VA-CNT systems hold tremendous promise as transient adhesives that can be applied and reapplied repeatedly, unlike traditional PSAs. Particularly at the nanometer scale, the remarkable adhesion force resulting from van der Waals forces is up to 200 times higher than that of gecko setae.9 Table 1 compares the adhesion forces obtained using VA-CNTs with different preloading and unloading directions.

Qu et al.10 fabricated adhesive films based on vertically aligned multiwalled CNTs (VA-MWCNTs) with entangled tops and found substantial differences between the normal and shear binding forces. In particular, these VA-MWCNTs films, applied with a preloading of ~120 N/cm², exhibited high shear adhesion forces with a strong dependence on the length of the CNTs that increased substantially with increasing CNT length. This high shear adhesion force is attributed to two components: the interaction between CNTs and a target substrate and the length-dependent bending moment along the

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CNT caused by the shear loading. In contrast, the normal adhesion force showed only a weak dependence on the length, in which case a higher normal adhesion force of 29 N/cm² was observed for the same preloading. Ge et al. also reported VA-MWCNT-based synthetic gecko tapes that mimicked the seta array structure of gecko feet with aligned and patterned MWCNTs. The shear strengths measured after a preloading of 25–50 N/cm² were better than those of gecko feet and also exhibited a marked dependence on CNT height. From scanning electron microscopy (SEM) images, the authors deduced that cohesive binding between the CNTs and the substrate is the primary mechanism for the high performance of these tapes. However, a high preloading force, 50 N/cm², often resulted in severe deformation of the CNT films and limited their repeatable use.

In this article, we demonstrate the design and fabrication of high-performance and multifunctional dry adhesive films using transferred VA-CNTs structured by converting the relatively flat bottom of VA-CNTs directly grown on atomically flat silicon wafer substrates into the top surface of the adhesive layer. This unique surface of VA-CNTs maximizes the contact between the nanotubes and the substrate with a small loading, leading to a coefficient of static friction (COF) of 40–60, which is ~30 times higher than that of the as-grown VA-CNTs, while exhibiting a shear adhesion force comparable to that of gecko feet and a near-zero normal adhesion strength under extremely low preloading conditions. By harnessing these highly anisotropic adhesion properties along with a flat and uniform surface morphology and nanoscale high-density aligned nanotube structure, we were also able to clean and assemble nanoparticles into various highly organized micropatterns with a simple one-time brushing. This contrasting directional anisotropy, as well as the multifunctional behavior on the macro-, micro-, and even nanoscale dimensions, could prove to be important for a number of industrial applications such as an end effector for reusable tape, robot hands, micro-electromechanical systems (MEMS), and biomedical devices, as well as in applications requiring increasing mobility in space, where high static friction and lower adhesion properties with small preloading are required.

### RESULTS AND DISCUSSION

To fabricate high-performance and multifunctional dry adhesive films, high-density VA-CNTs were synthesized on a polished silicon oxide wafer by a thermal chemical vapor deposition (CVD) method. Most of the CNTs grown were single-walled CNTs (SWCNTs) and a few double-walled CNTs (DWNTs), as confirmed by high-resolution transmission electron microscopy (HR-TEM) and Raman spectroscopy (Figure S1). During the initial period of growth, the CNT network had no long-range order and grew randomly. Under this initial ‘randomly ordered crust layer’, well-aligned CNTs began to form as a result of their high-packing-density nucleation and growth, particularly when the thickness was greater than 10 μm. As shown in Figures 1, 2a, and S1, the typical as-grown VA-SWCNTs film exhibits an intrinsic concave shape at the free end, especially when the aligned SWCNTs are continuous and without cracks on the surface. Both the inhomogeneity arising from the initial crust layer underneath and the overall concave shape of the VA-CNT films often result in irregular contacts with the surface, thereby concentrating the contacting surfaces to a limited proportion of the total CNTs film area. This would lead to both undesirable friction properties of the film and high susceptibility of the CNTs to damage, rendering the film useless.

To overcome these challenges, we employed a simple but highly effective transfer process that inverts the VA-CNT film, thereby exposing the better aligned, flat, and uniform lower end of the CNTs. The entire transfer process is illustrated in Figure 1. First, a continuous 1-μm-thick Cr layer was deposited on the top surface of the as-grown VA-CNT film, where the CNTs were randomly formed into a crust layer (Figure 2a,b), using a dc sputter coater. This Cr layer was infused into a CNT crust to take hold of the top surface of the entangled VA-CNTs. To proceed with the transfer, we also prepared a receiving substrate, which consisted of a flat polished Si wafer with a
thickness of 380 μm covered with a drop-casted layer of epoxy resin. The as-grown VA-CNT film was then inverted, and a top Cr-infused crust layer was placed inside an epoxy resin on the receiving substrate, after which the assembly was cured at 100°C for 2 min for better mechanical integrity of the upside-down VA-CNT film. The role of the Cr layer is critical, as, in its absence, up to 80% of the volume of the VA-CNTs can be densified by capillary action of the epoxy resin, resulting in a...
loss of their elasticity. Therefore, the metal interlayer acted as a separator that prevented any capillary action as well as a binder for an entangled CNT crust layer. Finally, the SiO₂ wafer substrate used for nanotube growth was removed from the inverted VA-CNT film, resulting in a flat, uniform, and highly aligned surface of VA-CNTs, as shown in Figure 2c,d.25 Such a transfer process was previously used to expose the soft bottom CNTs.26 However, we obtained both the soft bottom CNTs and overall flatness on a large scale (Figure 2c). We confirmed the well-developed multilayer VA-CNTs/Cr layer/epoxy adhesive structure, as shown in Figure 2e.

The frictional properties of our transferred VA-CNT film were tested first through its (static) COF. To determine the COF of the VA-CNTs, we selected an atomically flat 3-in. Si wafer, 380 μm in thickness and 20 g in weight, as a target substrate. This wafer was balanced over three 6 mm × 6 mm VA-CNT films that were affixed to another flat plate using a commercially available glue. The plate was then tilted until the supported wafer began sliding (or breaking contact), as shown schematically in Figure 3a. The COF was calculated using a balance of forces on the wafer at the moment of sliding. Furthermore, if Coulomb’s friction law is assumed, the COF can be calculated as the tangent of the inclination angle.27 We used three different types of friction films of identical area made of as-grown VA-CNTs; transferred VA-CNTs; and polydimethylsiloxane (PDMS), which is widely used for adhesion purposes, as a control. Each type of VA-CNT film had four specimens of differing heights between 100 and 500 μm. The heights of the VA-CNT films were controlled by the CNT growth time during the CVD process (Figure S1d). To make a uniformly flat PDMS surface, PDMS solution was cured on a polished Si wafer. The inclination angle of impending sliding for both the as-grown and transferred VA-CNT films was measured multiple times for consistency.

Figure 4. Adhesion force measurements. (a) Schematic of experiments. (b) Comparison of adhesion force between PDMS and transferred VA-CNT film with a pulling speed of 2.25 μm/s. (c) Dynamic adhesion (or breaking) force measurements of PDMS film with different pulling speeds. (d) Relationship between pulling speeds and adhesion force of the PDMS film, except the fastest pulling speed. (Note that, to examine the effect on the adhesion force for the most extreme displacement scenario possible, a step function was applied to the piezoelectric stage. Piezo actuators have response times on the order of several microseconds. For this experiment, the actuator ideally traveled 90 μm in 0.01 s, yielding a velocity of 9000 μm/s.) (e) Dynamic adhesion force measurement of the transferred VA-CNT film with different pulling speeds.
Panels b and c of Figure 3 show the changes in COF of the as-grown and transferred VA-CNT films, respectively, for different CNT heights. Our results indicate a positive correlation between the COF and the height of the CNTs, although the improvement was more pronounced and consistent for transferred VA-CNT films. More strikingly, the transferred VA-CNT films with the greatest CNT height of 500 \( \mu \text{m} \) exhibited an extremely high static COF of up to 60, which is about 30 times higher than that of the as-grown VA-CNTs and close to the value exhibited by the PDMS pads, as shown in Figure 3d, which shows the average COF of all measurements under the best conditions. The calculated maximum shear adhesion force of the transferred VA-CNT film was 12 N/cm\(^2\), which is equivalent to or greater than that of natural gecko feet.

It is also very important to note that the weight of the wafer produced a normal pressure (preloading for initiating contacts between the nanotubes and the substrate for shear adhesion) of about 0.2 N/cm\(^2\) on the substrates with the greatest CNT height of 500 \( \mu \text{m} \). Furthermore, through repeated measurements, we also found that, in contrast to the transferred VA-CNT films, the as-grown VA-CNT films were easily broken and detached from the growth substrate (Figure S2). This poorer overall performance of the as-grown VA-CNTs can be attributed to the localized force on the CNTs due to the previously discussed concave shape of the end surface and the weak interface between the CNTs and the growth substrate.

In addition to friction properties, we also explored the normal adhesive behavior of transferred VA-CNTs using PDMS as a control. In Figure 4a, the motion of the target substrate in the normal direction is controlled by the piezoelectric stage affording a small preloading on the millinewton level and up to 100 \( \mu \text{m} \) of displacement. The as-grown VA-CNT films were found to be too fragile for this test and easily disintegrated. To compare the adhesive performance of transferred VA-CNT films with that of PDMS, the PDMS sample was preloaded to a maximum compression force equal to that of the transferred VA-CNT samples, and a subsequent pull-off rate of 2.25 \( \mu \text{m/s} \) was used. This was compared to the results from the slowest VA-CNTs pull-off measurement, for which the adhesion force was plotted as a function of the piezoelectric-stage displacement or time. As shown in Figure 4b, the transferred VA-CNT film showed near-zero normal adhesion force, whereas perceptible adhesive forces (approximately 0.88 mN, as an average of multiple measurements (Figure S3d)) were clearly observed for the PDMS sample. Furthermore, a linear increase in adhesion force with increasing pulling speed was clearly observed for the PDMS sample (Figure 4c,d). This linearity conforms to a similar linearity observed in the case of tacky films. On the other hand, the transferred VA-CNT film exhibited a near-zero adhesion force for all pull-off speeds (Figure 4e).

In addition to frictional properties, the unique structural features of VA-CNT films, such as the flat surface and the nanosized (10–15-nm) gap between the aligned CNTs, could also be used to manipulate and remove nanoparticles on flat surfaces with very high accuracy through a brushing action. We found that the strong adhesion force between the high-density CNTs and the nanoparticles was higher than the adhesion force between the nanoparticles and the substrate. This strong adhesion force between the CNTs and the nanoparticles would be useful for removing nanoparticles and even constructing micropatterned nanoparticle assemblies, which is imperative for building nanoparticle-based functional devices. To test the efficacy of this approach, a sweeping of the brush on nanoparticles dispersed on flat and patterned substrates (Figures 5 and S4) were performed. To this end, fluorescent silica nanoparticles with a diameter of 200 nm were initially sprayed evenly at a thickness of about one particle layer (confirmed by SEM) over the patterned SiO\(_2\) (400 nm)/Si substrate, where 10-\( \mu \text{m}\)-diameter, 400-nm-deep cylindrical
cavities were spaced at 20 μm; the depth was sufficient to hold only about two nanoparticles vertically (Figure 5a–c). Figure 5d–f shows a striking example of arrays of organized microassemblies of silica nanoparticles achieved by a single sweeping of a transferred VA-CNT brush. During the brushing action, the transferred VA-CNTs maximized contacts with the fluorescent nanoparticles on the flat surface and moved in the shear direction, leading to the highly effective removal of the nanoparticles as a result of the higher static friction force between the CNTs and the nanoparticles than between the nanoparticles and the substrate (Figure 5d–f). However, the silica nanoparticles sitting on the bottom of the microcavities remained in place, as the VA-CNT arrays did not touch nanoparticles inside the 400-nm-deep cylindrical micropatterns, as shown in Figure 5f (compare with Figure 5c). SEM micrographs (Figure 5g,h) showed that, during brushing with the VA-CNT film, the removed nanoparticles were attached to the ends of the aligned CNTs, clearly demonstrating the strong static friction force between the CNTs and the nanoparticles. We also tested the effectiveness of this unique dry particle cleaning and patterning technique for various sizes of nanoparticles (10–500 nm in diameter). It was observed that nanoparticles with diameters smaller than the depth of cavities (400 nm in this case) could be removed efficiently while leaving nanoparticles inside the microcavities undisturbed. However, nanoparticles with diameters larger than the depth of the cavities (i.e., 500 nm and greater) were moved along the brushing direction by the CNTs, as the larger nanoparticles protruded from the cavities (Figure 5i).

**CONCLUSIONS**

In summary, we successfully fabricated a highly anisotropic multifunctional adhesive film by creating upside-down, flat, and uniform VA-CNT films. These adhesive films exhibited a pronounced contrast between frictional and normal adhesive behaviors. The measured shear adhesion force was substantial (12 N/cm²), whereas a near-zero normal adhesion force was exhibited under astonishingly small preloading of 0.2 N/cm², demonstrating the ideal properties of an artificial gecko foot. Using these unique nanostructures and adhesive properties, we were also able to demonstrate the selective removal and formation of microassemblies of nanoparticles. These highly anisotropic and unique multiple functions of the reported CNT films have immediate and immense implications for the development of multifunctional platforms for robot hands, reusable tapes, end effectors, brushes for removing nano-/microscale contamination, organized assembly of nanoparticles, and MEMs, among other applications.

**EXPERIMENTAL DETAILS**

VA-CNT samples were synthesized by a thermal CVD process using anhydrous ethanol (Sigma-Aldrich, 99.95%) as the carbon source. Si(100) wafers (p-doped, University Wafer) with 100-nm SiO₂ layers were used as growth substrates. An aluminum thin film was used as the buffer layer and was prepared using an argon sputter coater for 90 s with rotation at a power of 1.5 kW. This buffer layer was annealed for 3 days in the air. As a catalyst metal, cobalt was deposited by electron-beam evaporator for 3–5 s at a 1 A/s deposition rate. The prepared growth substrate was carried by an alumina boat and placed in the middle of a horizontal quartz tube. The reaction chamber was heated to 850 °C under a 150 sccm (i.e., cubic centimeters per minute at standard temperature and pressure) gas flow of 5% hydrogen balanced with argon. The pressure was fixed at 700 Torr by a needle valve with a rotary pump. The ethanol source was induced by bubbling a carrier gas of 5% H₂ balanced with argon. A carbon nanotube forest with a length of about 500 μm was achieved in 30–45 min. The length was proportional to the reaction time until the Co catalyst was deactivated for certain reasons, namely, Oswald ripening and poisoning by amorphous carbon deposited on the catalyst surface (Figure S1d,e). The HR-TEM instrument was operated at 200 kV (2010F, Jeol, Figure S1f). Raman spectra of the VA-CNT films were obtained using a Raman spectrometer (LabRAM HR-800 with a 532-nm YG laser, Horiba; Figure S1g). For the transfer process, we deposited 1.2 μm of Cr on the VA-CNT surface using an MRC 8867 instrument. We used a power of 500 W, a base pressure of 3 × 10⁻⁷ Torr, and an Ar flow rate of 15 sccm for 10 min. The deposited metal penetrated several hundred of nanometers into the VA-CNTs, as confirmed by SEM. An epoxy resin (Epon-812, SPI Supplies) was applied to the Si wafers at a hot-plate temperature of 100 °C for 2 min. The growth substrates were removed after curing of the epoxy resin. To measure the surface roughness of our transferred VA-CNT films, we conducted atomic force microscopy (AFM) characterization (Figure S5).

Three 6 mm × 6 mm as-grown and transferred VA-CNT pads were placed on an incline. Each pad supported the same normal force, and the normal force was only the mass of a Si wafer, namely, 20 g. The three normal forces are labeled N1, N2, and N3 in Figure 3a, and each normal force on each pad is equal to one-third of the total weight of the Si wafer (W/3). The relative humidity of the measurement conditions was about 40%. The angle of the incline was measured with an accelerometer. We increased the tilt angle slowly and stopped it when the Si wafer started sliding. We measured the angle five times for each set of conditions.

For the adhesion force measurements, a labeled image of the experimental setup is shown in Figure S3a–c. The setup for the adhesion force measurements consists of a manual xyz stage, an active xy piezoelectric stage, a composite load cell for measuring contact forces in both the X (shear) and Y (compression/adhesion) directions, a support structure for holding the target substrate, and a base plate to which all of the major components are mounted. To ensure good contact between the target substrate and the adhesion pads, we applied a rotary compliance at the mount. Although there was some potential for a minute moment to be imparted to the sample-holding element of the load cell, the sample holder was mounted in such a way as to be compliant in the rotary direction but rigid in the transverse direction (normal). In this way, any strain measurement errors due to concentrated moments at the load cell tip were reduced by several orders of magnitude relative to the dominant, concentrated point load. The validity of this measurement technique was verified during calibration. The load cell consisted of two beam-style, full-bridge load cells mounted at right angles to one another to simultaneously measure compression/adhesion and shear forces. The signals are amplified with a two-channel instrumentation amplifier and fed into a dSpace data acquisition system. In addition, both the load cells and the instrumentation amplifier were supplied with 10 V from a low-noise power supply, and the piezoelectric stage was controlled with a Physik Instrumente piezoelectric amplifier/controller using an output signal from the dSpace system. To measure the adhesion force for all samples, the compression/pull-off procedure reported in Table S1 was used for the various pull-off rates (3–2.25 μm/s).

For the brush experiments, the patterned silicon oxide wafer was prepared by a photolithography process. The circular pattern was 10 μm in a diameter, and the strip pattern was 4.5 μm in width. The thickness of the oxide was 400 nm, and it was etched with HF solution. Fluorescent silica nanoparticles were dispersed in ethanol and spread on a patterned silicon oxide wafer with a spray gun. VA-CNT films were fixed using a stand, and the stage was controlled with an x- and y-axis motor. First, VA-CNT films were made flush with the substrate. Then, we moved the stage using the motor.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.6b10395.
Experimental details of materials, a piezoelectric stage setup, failure images of as-grown VA-CNTs, adhesion force measurement data at different pulling speeds, and nanoparticles brushing results for different sizes and patterns (PDF)

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Notes
The authors declare no competing financial interest.

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