E-BEAM PHOTORESIST AND CARBON NANOTUBES AS BIOMIMETIC DRY ADHESIVES

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ABSTRACT

This paper presents the fabrication and characterization of nano-fibrils mimicking gecko foot-hairs for enhanced dry adhesion. High contact area ratio of the polymer and carbon nanotube fibrils is achieved, respectively, using e-beam lithography and chemical vapor deposition. The adhesion forces from gecko foot-hairs and the artificial fibrils are measured with a customized AFM tip to evaluate the effects of different materials and surface density. With the water-vapor assisted deposition, the surface density of the carbon nanotubes is optimized for comparable adhesion forces to gecko foot-hairs.

1. INTRODUCTION

Recently, the exceptional climbing capability of the biological examples such as small insects and geckos has drawn tremendous research attention for the development of dry adhesives [1-7]. The biological dry adhesion is attributed to the high-surface-density fibrils of animal's skin which provide sufficient contact area on rough surfaces.

To determine the dimensions of these biological fibrils, the fingers of a typical Taiwan house gecko (Hermidactylus frebatus) ware examinated, as shown in Fig. 1. There are leaf-like arrays (lamellae) on the gecko's toe pads. Each lamella is composed of millions of keratinous foot hairs (setae). The setae are about 30-130μm in length. Their diameter starts from about 5 μm on the base (stalks) and decreases to 100-200 nm by branching on the top, which is referred to as spatular stalks [8,9]. When gecko climbs on a wall, it is the spatular stalks making contact with the rough surface utilizing capillary force or van der Waals force [10,11].

Many efforts have been taken to mimick the nano-fibrils of the spatular stalks for the enhancement of dry adhesion. The adopted microfabrication approaches include PDMS molding [5], ion reactive etching on polyimide [6], and chemical synthesis inside porous membrane [7]. These methods produce either submicron fibrils with low surface density [5,6] or nano-hairs lying horizontally on the substrate [7]. The surface density is defined as the total number of nano-fibrils per unit area. In this work, we have successfully fabricated polymer nano-fibrils and vertically aligned carbon nanotubes (CNT) with high surface density and provided a large variety of contact area ratios for different adhesion forces.

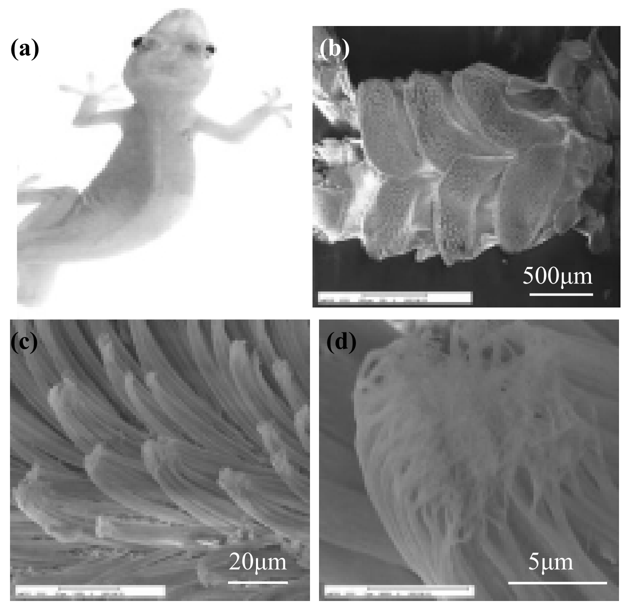

Figure 1: Photographs and SEM images of a typical house gecko. (a) Hermidactylus frebatus; (b) Lamellae; (c) Setae; (d) Spatular stalks.

2. DESIGN AND FABRICATION OF NANO-FIBRILS

In this work, the polymer nano-fibrils were fabricated using e-beam lithography. Although it is time-consuming to perform large-area e-beam writing, the dimensions of the submicron patterns can be readily controlled. To compare the adhering surfaces of different materials, CNT fibrils were synthesized by chemical vapor deposition (CVD). The detailed design and fabrication of the nano-fibrils of different materials are given below.

E-BEAM LITHOGRAPHY

The polymer nano-fibrils were patterned by performing e-beam lithography on a silicon substrate, as shown in Fig. 2. The positive e-beam photoresist, ZEP-520A from ZEON CSC Corp., were used as the fibril material. 450nm ZEP-520A was coated on the substrate with 5000 rpm spin rate for 90 seconds, followed by 180^{o}C softbake on a hotplate for 2 minutes. Then the patterns were defined by an e-beam lithography system, ELS-7500EX. For producing 100nm line width, the field size was 600µm^{2}. The dose time was 0.7µs, and the beam current was 100pA. The development was carried out in ZED-N50 solution for 3 minutes. The developer was thermostatically maintained at 23^{o}C, for 3 minutes.

The spacing between adjacent photoresist pillars were controlled at about 100nm. The width of these pillars was changed from 100nm to 2840nm, and hence the contact area ratio from 16% up to 90.3% was obtained. The dimensions of the pillars are listed in Table I. For 100nm wide nano-pillars, the significant residual stress inside photoresist peeled off the pillars and hence reduced the contact area ratio form 25% down to 16%. Although these nano-pillars have been patterned in square, they were self-modified to possess circular cross-section due to non-negligible surface tension, as shown in Figure 2a.

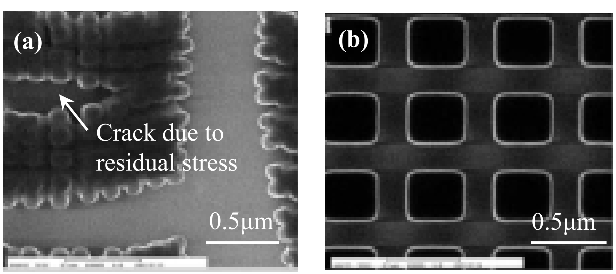

Figure 2: SEM and AFM images of polymer nano-fibriis. (a) Fibrils with 100nm width and 100nm spacing. (b) Fibrils with 410nm width and 190nm spacing.

CARBON NANOTUBES

To synthesize CNT, iron catalyst of 1-2nm thickness was applied to an oxidized silicon surface by e-beam evaporation. The temperature of the CNT chemical vapor deposition was controlled at 750^{o}C. The gases in the deposition were ethylene (100ccm), hydrogen (400ccm), argon (600ccm), and water vapor, respectively. Three different concentrations of the water vapor (300ppm, 600ppm and 721ppm) were used to vary the CNT surface density. Previous result [12] has shown that there is no positive correlation between the water concentration and the surface density. For our deposition condition, 600ppm concentration results in the lowest density while 721ppm concentration results in the highest, as shown in Fig. 3.

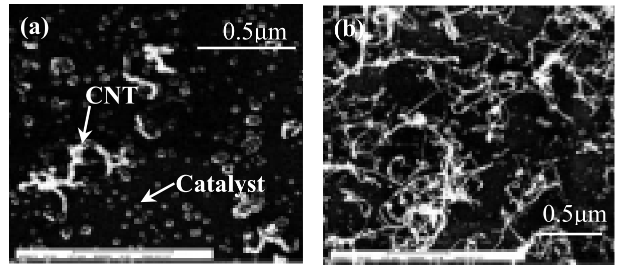

Figure 3: SEM images of CNT with different water vapor concentrations in deposition. (a) 600ppm. (b) 721ppm.

Table 1: Design parameters of polymer nano-fibers.

Sample	Fibril width (nm)	Spacing (nm)	Contact area ratio (%)	Adhesion force (N/cm^{2})
1	100	100	16.00	0.10
2	240	160	64.00	0.14
3	320	80	64.00	0.16
4	410	190	46.70	0.12
5	900	100	81.00	0.37
6	1900	100	90.30	0.84
7	2370	130	89.90	Out of range
8	2840	169	89.60	Out of range

3. ADHESION TEST

An atomic force microscope (AFM), DI Multimode from Vecco Instrument Inc., was used to measure the total adhesion forces of the fabricated fibrils in contact. A plateau tip of 5µm diameter, as shown in Fig. 4, from NanoWorld AG was used to provide sufficient contact area. The measurement was carried out in a laboratory environment with 23^{o}C and 70% relative humidity.

The force mode of the AFM was used to measure the adhesion force between the silicon tip and the sample. Before the measurement, the stage was rotated about 11 degrees along the X-axis to compensate the deflection of the AFM cantilever in contact with the sample. As a result, contact was made perpendicular to the sample surface.

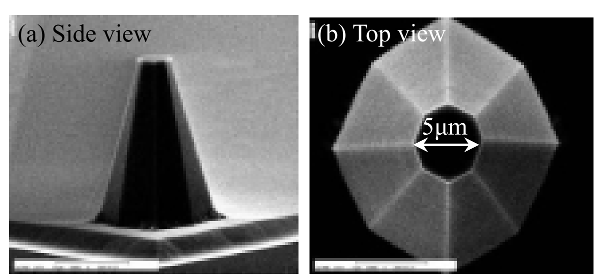

Figure 4: SEM images of the AFM plateau tip.

For 100nm-wide polymer fibrils, the force-displacement curve in Fig. 5a shows that these fibrils work as a bundle to provide single adhesion force. For the CNT characterization, the force-displacement curve in Fig. 5b shows that there exist at least two maximum adhesion forces, which result from different length of the CNT grown under identical deposition condition. The interaction between the tip and the nano-fabrils is sketched in Fig. 6. and is described in the following. (1) AFM tip approaches CNT. (2) AFM tip compresses CNT for intimate contact. (3) AFM tip moves up, and shorter CNT are fully stretched. (4) AFM tip keeps moving up and breaks its contact with the shorter CNT. (5) AFM tip moves up, and the longer CNT are fully stretched. (6) AFM tip moves up to break the contact with all CNT. In the evaluation, all the peak values of the adhesion forces are added based on the assumption that all the CNT could contribute to a single adhesion force when they had uniform height. This assumption is consistent with the calculation approach in [6].

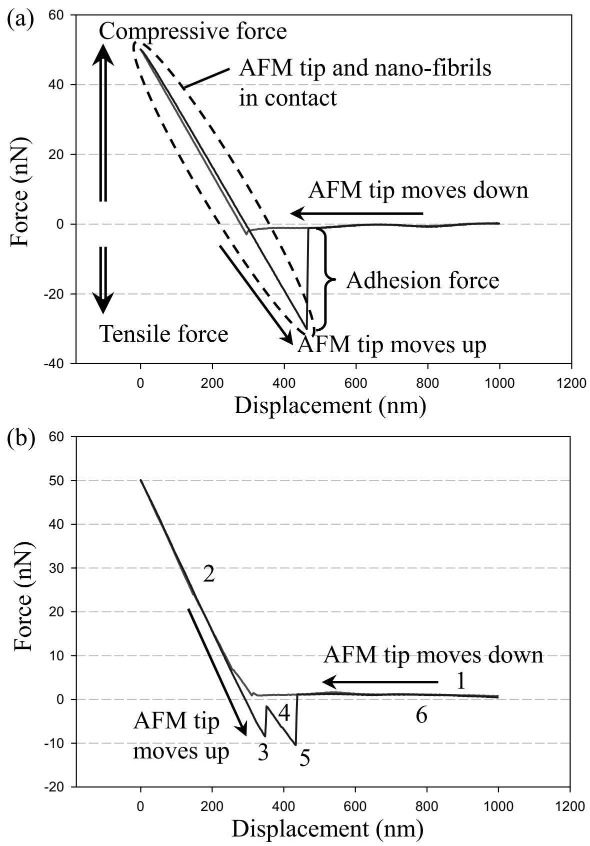

Figure 5: AFM force-displacement measurement of artificial nano-fibrils. (a) ZEP 520A nano-fibrils (100nm width and 100nm spacing). (b) CNT.

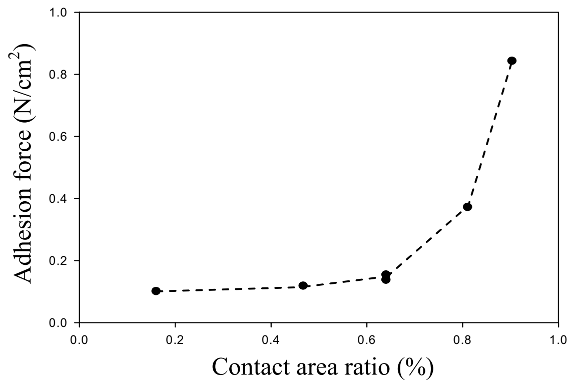

Figure 7: Measured adhesion forces of polymer nano-fibrils as a function of contact area ratio.

4. RESULT AND DISCUSSION

For the polymer fibrils, the testing results are summarized in Table 1. By fixing the spacing, larger contact area ratio was obtained by increasing the fibril width. The testing results in Fig. 7 show that the adhesion force increases quadratically with the contact area ratio and is independent of the aspect ratio. These results all agrees with the conclusion in [6].

Because the diameter of the deposited CNT is fixed within 30nm and 50nm, we increased the contact area ratio by increasing surface density. The AFM measurement in Fig. 8 shows that CNT with higher surface density provides larger adhesion force.

Furthermore, the CNT provides larger adhesion forces than the polymer fibrils for the whole range of contact area ratio. For comparison, we also measured the adhesion forces of the foot-hairs from a typical house gecko, which is shown in Fig. 1. It is found that the adhesion force of the CNT with 1nm-thick catalyst and 721ppm water vapor (2.25 N/cm^2) is comparable to that of the gecko's foot hairs (about $4N/cm^2$).

5. CONCLUSION

In this paper, we have investigated the performance of the biomimetic dry adhesives which were made of e-beam photoresist and CNT, respectively. Nano-fibrils with high surface density were fabricated by e-beam lithography and chemical vapor deposition. The AFM plateau was used to measure the adhesion force of the micrometer-scale contact area. It was found that the adhesion force increases with

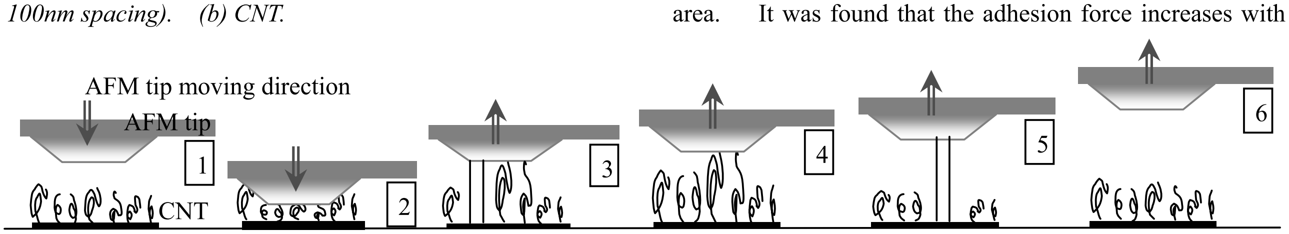

Figure 6: Stretching mechanisms of CNT during AFM measurement.

the contact area ratio of the polymer nano-fibrils. The adhesion force of the CNT with 721ppm water vapor was found to be 2.25 N/cm^2. This adhesion force is sufficient to suspend a human about 70 kg with the contact area of 305 cm^2, which is slightly larger than the surface area of a pair of palms. Generally, CNT provides larger adhesion force than the photoresist does. However, it is easier for the photoresist to generate nano-frbrils of uniform height.

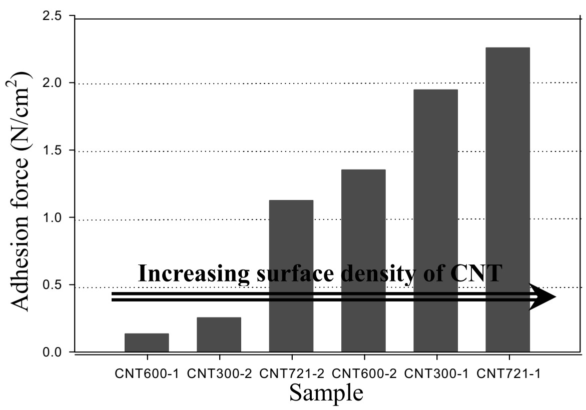

Figure 8: Measured adhesion force of CNT.

6. ACKNOWLEDGEMENT

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