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ALIGNED CARBON NANOTUBES FOR DRY ADHESIVES AND METHODS FOR PRODUCING SAME (Gecko Glue)

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Functionalized Aligned Carbon Nanotubes for Dry Adhesive Applications

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The amazing ability of geckos to climb on natural surfaces has inspired extensive interest of scientific research for centuries. Only in the past few years, has progress been made to understand and demonstrate the mechanism that the gecko defies the gravity and adheres himself on any surfaces. [1] The adhesive force mainly depends on the submicron feature of spatulae (0.2-0.5 μm in diameter) on setae (3-130 μm in length) covering the geckos' feet and their van der Waals interactions with target surfaces. [1] To carefully observe the toe of a gecko, we can also find the peculiar structure of alignment in the rows of setae, and each tip of seta is composed of ordered "spatulae". The three-dimensional hierarchical structure of aligned setae collects the miniscule van der Waals force from millions of spatulae in contact with the object surface, and induces a formidable adhesion of ~ 10 N cm^{-2}. Recently, attempts have been made to mimic the gecko feet by microfabricating the arrays of polymer pillars.[2,3] However, these synthetic specimen are not comparable to the geckos due to the inaccessibility to the fine structure of geckos' setae. A maximum adhesive force of 3 N cm^{-2} is obtained. [3]

Carbon nanotubes have high aspect ratio, extraordinary mechanical, electrical, and thermal properties.[4] According to the quantitative estimate based on JKR theory, it is possible to generate adhesive strengths of more than 500 N cm^2 between carbon nanotubes and glass surface,[4] indicating the potential of carbon nanotubes for dry adhesive application. Recently, Yurdumakan et al. [5] reported a strong nanometer-level adhesion forces that are 200 times higher than those observed for gecko foot-hairs by dipping an AFM tip into the PMMA supported aligned carbon nanotube bundles. However, this result will not be suitable for practically macroscopic condition due to the difficulty in access to the ideal case that all the nanotube tips contact with the target surface. In recent study, Zhao et al. [6] demonstrated that the as-grown aligned carbon nanotubes array can generate adhesion strength comparable to that of a gecko's foot in

macroscopic measurement. The strength for normal adhesion and shear adhesion is similar and no more than 11.7 N cm^{-2}. Considering the gecko's unusually strong adhesion force upon pulling seta parallel to the surface during attachment and weak adhesion force perpendicular to the surface during detachment,[7] it is highly desirable to control the difference of adhesion strength in parallel and perpendicular to the surface for strong adhesion on and easy separation from it like that gecko does.

Herein, we report the dry adhesive based on aligned carbon nanotube film, which not only possesses strong adhesion strength but also is easily taken off. The normal adhesion strength is comparable to that of geckos' feet, while the strength in the shear direction is up to 130 N cm^{-2}.

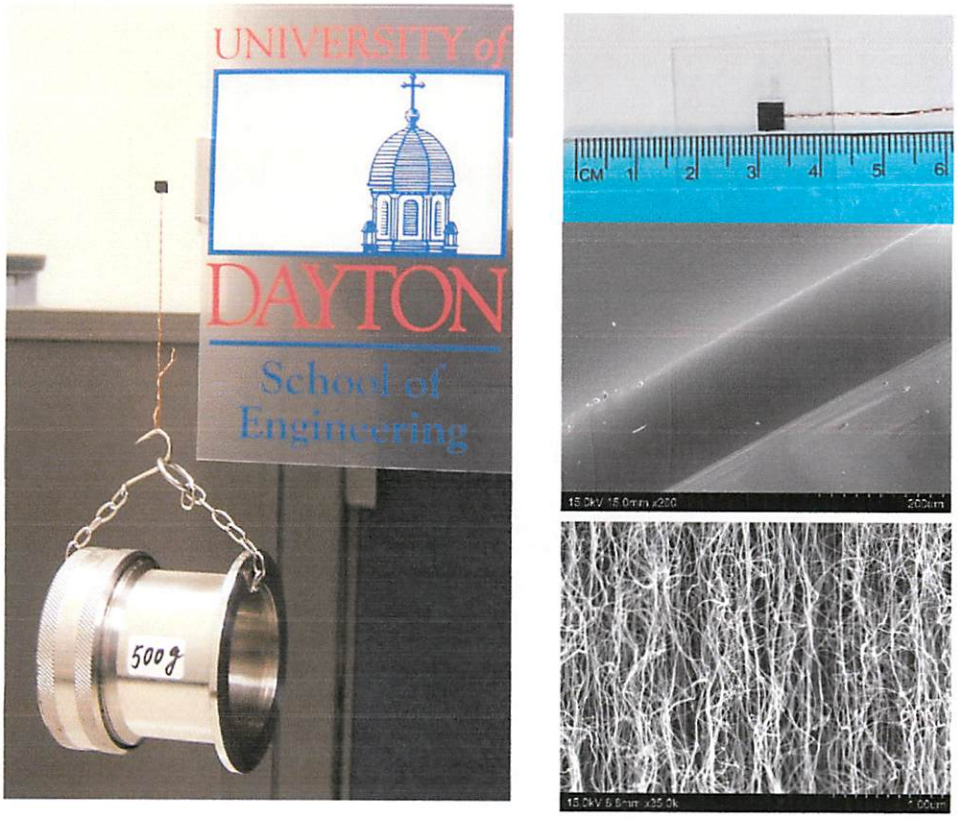

Figure 1 a) A photo that a stainless steel adapter of 500 g weight is hung through dry adhesion between the glass surface and an aligned CNT array film grown on Al-coated SiO_2 substrate. b) A photo indicating the size of CNT array film, 4× 4 mm^2. c and d) SEM images of aligned CNT film with different magnification.

As we can see in Figure 1a, an example is shown that a stainless steel ring of 500 g weight is clung to a glass slide through dry adhesion between the glass surface and an aligned CNT array film grown on Al-coated SiO_2 substrate. The area of this CNT film is as small as only 4 × 4 mm^2 (Figure 1b), corresponding to an adhesion of 30.6 N cm^{-2}. Figure 1c and d show the well-aligned CNT film used here has a length of 200 μm and uniform diameter of 10-15 nm.

The samples of aligned CNTs were grown on SiO_2 substrate. For the CNT film with length of 50 – 200 μm, the measured normal adhesion strength is 8±3 N cm^{-2} in the direction perpendicular to the surface, which is comparable to that of geckos', while, for the CNT film with height of ~200 μm, the shear adhesion strength is as high as 35 ±5 N cm^{-2} in the direction parallel to it, which is over 4 times higher than that of normal adhesion and is the highest value in macroscopic CNT film so far. The difference of adhesion in normal and shear direction provides the advantage that the dry adhesive tape of CNTs film can not only be strongly attached on the surface, but also be detached easily.

We investigate the adhesion capability of aligned CNT film with different length. As shown in Figure 2, the normal adhesion strength of CNT film on the glass slide reaches fairly stable value range of 5-11 N cm^{-2}, while the value of shear adhesion increases correspondingly with the increase of CNT length and up to the maximum of 40 N cm^{-2}.

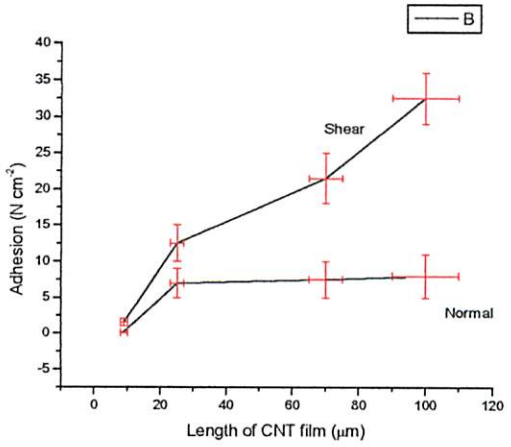

Figure 2 The dependence of the normal and shear adhesion forces on the nanotube length.

Due to the main contribution for the dry adhesion from the van der Waals (VDW) interactions between the contact surface of CNT film and the glass slide, the surface properties of aligned CNT film should have a great influence on the adhesion capacity. Surface and interface play an important role in controlling the properties of a broad range of materials, including the carbon nanotube/polymer nanocomposites. Carbon nanotube nanocomposites can be prepared through physical casting of appropriate polymers onto the aligned carbon nanotube arrays or chemically/electrochemically grafting polymer chains onto the nanotube structure. In both cases, a strong interface between the nanotube and polymer is essential. The surface modification covers two important aspects including: (1) modification of outerwall of the aligned carbon nanotubes for enhancing their compatibility with the polymer matrix and improving the adhesive properties; and (2) modification of the top tips of the aligned carbon nanotubes for regulating the adhesive performance.

For the sidewall modification, we will graft appropriate polymer chains onto plasma-induced functional groups on outerwall of the aligned carbon nanotubes to enhance their compatibility with the polymer matrix and to reversibly change the inter-tube distance by regulating the external stimulus (e.g. changing the temperature). In view of the importance of the interaction between the aligned carbon nanotube tips and substrate to the adhesive performance, we will also exploit the possibility of end-functionalization of the aligned carbon nanotube top tips with various chemical reagents of different properties. To start with, the tips of the polymer-supported aligned carbon nanotubes will be activated by plasma treatment under appropriate conditions. It is envisioned that the aligned carbon nanotube tip can be readily switched between hydrophilic and hydrophobic states by plasma treatments with and without oxygen-containing low-molecular-weight gases. Furthermore, we can use water plasma etching to open the nanotube top tip without damaging the aligned structure so that the adhesion properties for the closed and opened aligned carbon nanotubes can be compared.

Like that the orientation of the setae is the crucial to setal force capacity in the attachment and detachment process [7], the alignment of CNTs also takes an important role in

producing strong adhesion and controlling the discrepancy of adhesion strength in parallel and perpendicular to the surface.

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