FULL PAPER

Wet and Dry Adhesion Properties of Self-Selective Nanowire Connectors

By *Hyunhyub Ko, Zhenxing Zhang, Yu-Lun Chueh, Johnny C. Ho, Jongho Lee, Ronald S. Fearing,* and *Ali Javey**

Here, the wet and dry adhesion properties of hybrid Ge/parylene nanowire (NW) connectors are examined. The ability of the NW connectors to bind strongly even under lubricating conditions, such as mineral oil, sheds light on the dominant role of van der Waals interactions in the observed adhesion. The superhydrophobic surface of the NW connectors enables the wet, self-cleaning of contaminant particles from the surface, similar to the lotus effect. In addition, the effect of NW length on the shear adhesion strength, repeated usability, and robustness of the connectors, all critical properties for applications that require reversible binding of components, is examined.

1. Introduction

The evolution of biological systems has resulted in hierarchical nano- and microfibrillar structures with diverse mechanical, optical, and sensing functionalities.[1,2] These excellent and unique structure-related properties found in biological systems have inspired researchers to generate artificial materials mimicking, for example, the amazing adhesion abilities of gecko feet,[3–8] the self-cleaning superhydrophobic surface of the lotus leaf,[9,10] or hairy fluid sensor arrays on the body of fish[11] or crickets.[12] In particular, the nanofibrillar structures of synthetic gecko adhesives enable binding to almost any surface by van der Waals (vdW) interactions.[13] More recently, we reported self-selective connectors based on nanofibrillar structures that enable efficient binding with self-similar surfaces but weak adhesion towards other surfaces. The connectors consist of inorganic/organic, core/shell nanowire (NW) forests with the inorganic core serving as the rigid backbone and the organic shell providing a soft surface for conformal contact. Since the hybrid NWs are relatively stiff as compared to those used in most gecko adhesives, minimal adhesion is observed when brought in contact with flat surfaces (i.e., they are poor adhesives). However, the contact area, and therefore the vdW interactions, is drastically enhanced (~1000× enhancement) when the NW forests are engaged with self-similar surfaces, resulting in high shear strength with relatively low engagement/disengagement forces.[14] This selective binding with self-similar surfaces is one of the major differences between a connector and an adhesive.

In order to investigate the suitability of NW connectors for real-life applications it is necessary to characterize their adhesion properties and robustness in various ambient conditions. In this regard, here we report the performance of hybrid NW connectors under various dry and wet conditions while elucidating the interaction forces involved in the binding of NW connectors. We also examine the effects of surface contamination and self-cleaning via the lotus effect on the adhesion properties. In addition, we investigate the effect of NW length on the shear adhesion, repeated usability, and robustness, which are all critical properties for connector applications that require reversible binding of components.

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DOI: 10.1002/adfm.200901178

2. Results and Discussion

To study the length-dependent shear adhesion abilities of NW connectors, we utilized Ge NW forests (diameter $d = 20–30$ nm) with different lengths, $L \approx 5–100$ μm, as the inorganic backbone of the chemical connectors and subsequently deposited a thin parylene layer with a thickness $t_p = 200$ nm to make hybrid Ge/parylene core/shell NW arrays (Fig. 1). The geometric configuration of the NW forests varies as a function of the NW length. For instance, NW arrays with $L \approx 10$ μm are more vertical and straight compared to longer NWs, as evident from scanning electron microscopy (SEM) analyses (Fig. 2a–f). The top-view optical microscope images (Fig. 2g–i) also indicate that the effective

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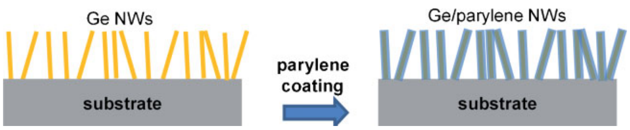

Figure 1. Fabrication procedure of hybrid Ge/parylene core/shell NW forests.

surface density of NWs at a fixed focal plane decreases with increasing NW length, attributed to the random bending observed for the longer NWs.

To study the effect of NW geometry on the shear adhesion of NW connectors, we measured macroscopic shear adhesion strength of hybrid NW connectors as a function of NW length (5, 7, 10, 30, and 100 μm). The shear adhesion strengths were measured by sequential procedures of applying a normal preload stress (3.1 N cm^{-2}), applying a shear stress, and finally removing the normal stress on the engaged connectors (Fig. 3a). The failure shear stress of the connectors corresponds to the maximum shear adhesion strength. As can be seen in Figure 3b, the shear adhesion strength is strongly affected by the length of the NWs. Specifically, the shear adhesion strength at first increases with increasing NW length, peaking at ~30 N cm^{-2} for $L \approx 10$ μm, beyond which a drop in the shear strength is observed (Fig. 3b). The strong shear adhesion strength arises from vdW interactions amplified by the large contact area between the interpenetrating NWs. For $L < 10$ μm, the interpenetration depth and therefore the contact area is directly proportional to the NW length. However, when the NW length is too large (i.e., $L > 10$ μm), the NWs tend to bend or collapse (Fig. 2b–c). As a result, the efficiency of the NW interpenetration is reduced.

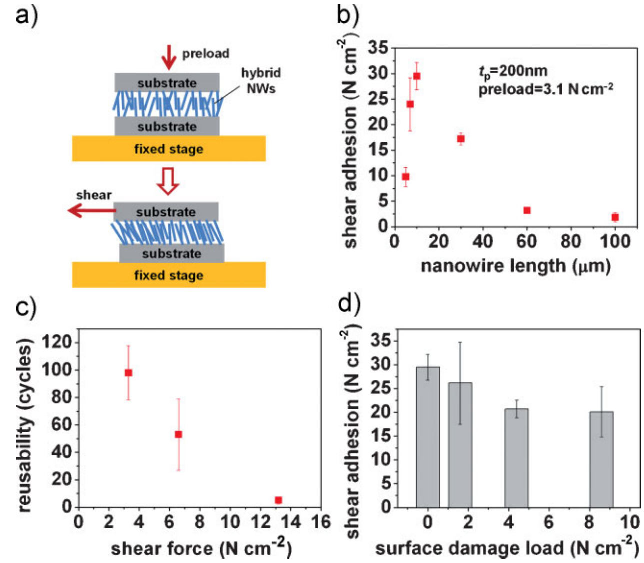

Figure 3. Shear adhesion strength and repeated usability of NW connectors as a function of the NW length. a) Schematic of shear adhesion measurements. b) Shear adhesion strength of NW connectors at preload of 3.1 N cm^{-2}. c) Reusability (repeated attach/detach cycles) of NW connectors with a preload and shear stress of ~3.1 N cm^{-2}. d) Mechanical robustness of NW connectors showing shear adhesion strengths of NW connectors after intentionally inducing mechanical damage on the surface of the NW forests by dragging substrates against a flat glass surface for a distance of ~15 mm with different surface damage loads (normal loads during drag).

The repeated reusability of NW connectors is one of the critical factors to consider for applications requiring reversible binding of components. We tested repeated usability of NW connectors by repeating multiple attach/shear/detach cycles with known preload (3.1 N cm^{-2}) and shear load (3.1 N cm^{-2}) until the NW connectors failed (Fig. 3c). The repeated usability of NW connectors showed ≈98 times for $L \approx 10$ μm, which is well over the few cycles of most synthetic gecko adhesives.[15,16] Another factor to consider for NW connectors in practical applications is the mechanical robustness since the nanofibrillar structures are seemingly very susceptible to external scratching or impact. We tested the mechanical robustness of NW connectors against external mechanical damage by measuring the shear adhesion strength after inducing controlled mechanical damage on the surface of NW forests by applying a frictional load (Fig. 3d). In this approach, the NW forests were first dragged on a planar glass substrate with different normal loads (1.6, 4.4, and 8.6 N cm^{-2}) to intentionally induce mechanical damage, and subsequently tested for shear adhesion. NW connectors showed acceptable mechanical robustness with minimal decrease of shear adhesion strength (~30% decrease) after

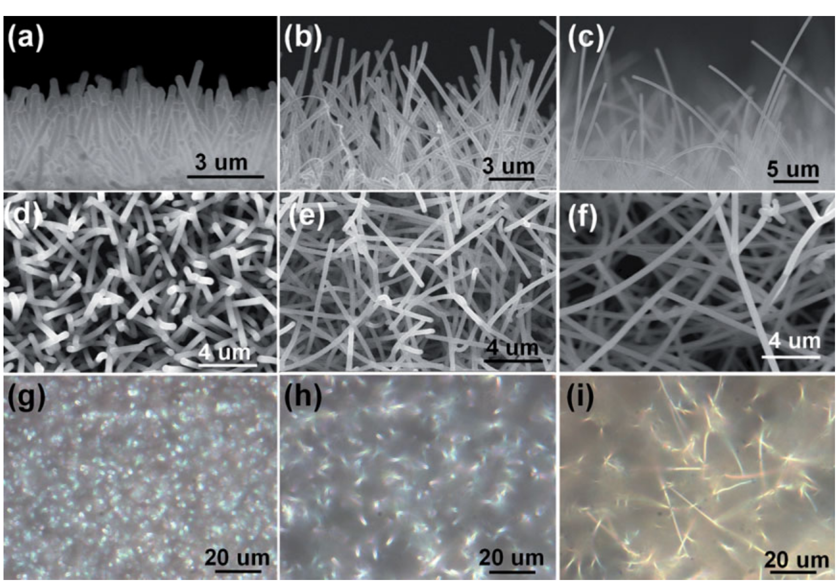

Figure 2. Comparison of hybrid Ge/parylene core/shell NW forests with different NW lengths. Cross-sectional SEM (a–c), top-view SEM (d–f), and top-view optical (g–i) images of hybrid NW forests with NW lengths of 10 (a, d, g), 30 (b, e, h), and 60 μm (c, f, i). Parylene shell thickness is $t_p = 200$ nm with a Ge core diameter of 20–30 nm.

surface damage with normal load up to 8.6 N cm^{-2} during drag of NW arrays.

A generic concern for most common adhesives is particulate contamination on the surface. At first glance, the NW connectors may seem highly vulnerable to surface contamination given their fibrillar geometry. However, owing to their superhydrophobic surface behavior, hybrid NW connectors exhibit the so called wet self-cleaning phenomenon, in which, similar to the lotus effect,[9] the contaminant particles on the surface are efficiently removed by the rolling of water droplets. The superhydrophobic characteristic of the hybrid NWs (Fig. 4a–c) arises from the hydrophobic behavior of the parylene shell, which is further amplified by the surface morphology of the high aspect ratio NW forests.[17,18] To study the wet self-cleaning mechanism, micrometer-sized particles (mixture of silica and alumina particles with diameters 1–11 μm) were spread over the surface of NW connectors (Fig. 4d). These particles were readily removed from the surface by rolling a water droplet (Fig. 4e and f and Video S1 in the Supporting Information). The ability of surface-contaminated NW connectors to restore their adhesion strengths after the wet self-cleaning process is depicted in Figure 4g. As evident in this figure, the shear adhesion of NW connectors with particulate surface contamination is reduced by ~3× due to the less intimate contact between the interpenetrating NWs in the engaged mode. However, the NW connectors nearly regain their full shear adhesion strength, matching that of the neat state, after the application of the wet self-cleaning procedure (Fig. 4g).

Of particular interest to a number of connector applications is the ability to retain binding abilities in different liquid environments. For instance, such adhesion properties may enable underwater assembly of components. In the past, surface-modified synthetic gecko adhesives have been demonstrated to operate in water or physiological conditions for possible use as medical adhesives.[19,20] To examine the binding ability of NW connectors for operation in wet environments, we tested shear adhesion strength under different liquid environments including water, isopropyl alcohol (IPA), octane, and mineral oil (Fig. 5). During the adhesion tests, we noted that the surface of superhydrophobic NW connectors could get wet when they are completely immersed in water under external pressure (i.e., applied preload stress). This phenomenon has been previously observed for Cassie–Wenzel wetting transition induced by pressure

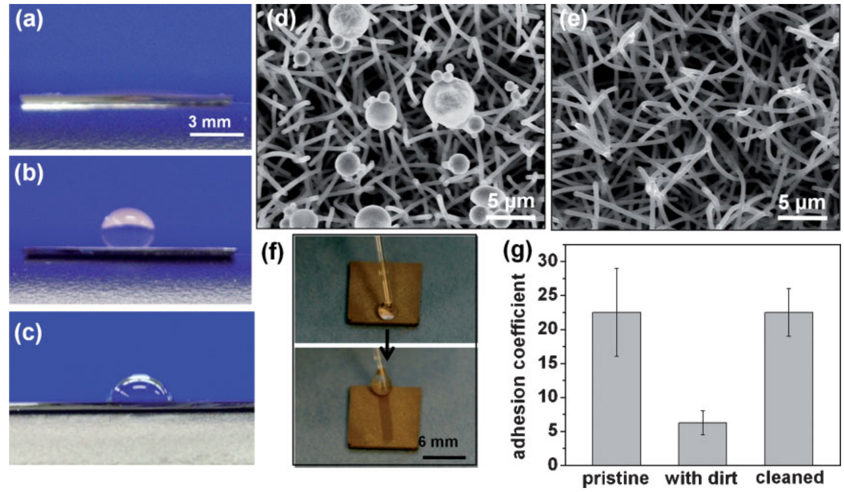

Figure 4. Wet self-cleaning of superhydrophobic NW connectors. Contact angle measurements for a) pristine Ge NW arrays, b) parylene coated Ge NW arrays, and c) parylene coated Si substrate. The optical images illustrate a water droplet placed on the surface of each substrate. SEM images of NW forests d) contaminated with alumina and silica particles (~1–11 μm) and e) cleaned with rolling a water droplet. f) Wet self-cleaning procedure on surface-contaminated NW forests, in which a water droplet is gently rolled on the surface by a glass rod during which contaminants are efficiently removed from the surface by the lotus effect. g) Comparison of the adhesion coefficient (shear to preload ratio) of pristine, contaminated, and cleaned NW connectors.

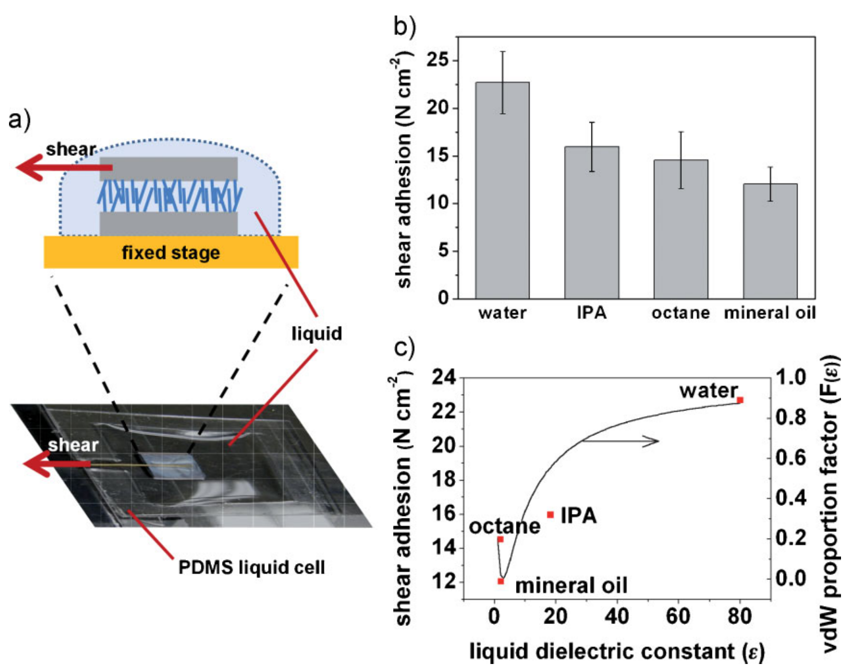

Figure 5. Wet shear adhesion strength of NW connectors under different liquid environments (water, isopropyl alcohol, octane, and mineral oil). a) Schematic of wet adhesion test of NW connectors under water environments. b) Comparison of wet adhesion strength of NW connectors under different liquid environments for a preload stress of 3.1 N cm^{-2}. c) Comparison of wet adhesion strength of NW connectors as a function of the dielectric constant of the liquid environment. The solid line shows the vdW proportion factor, $F(\varepsilon) = [(\varepsilon_1 - \varepsilon_2)/(\varepsilon_1 + \varepsilon_2)]^2$, where ε_1 is dielectric constant of parylene and ε_2 is the dielectric constant of the liquid.

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or vibration force.[21,22] We also noted that NW connectors are completely wettable to IPA, octane, and mineral oil without any external pressure. The NW connectors showed underwater shear adhesion strength of $\sim$23 N cm^{-2}, $\sim$77% of the dry adhesion strength. When the NW connectors were engaged under different organic liquids, such as IPA and octane, the shear adhesion strength was reduced to $\sim$15 N cm^{-2}, $\sim$50% of the dry adhesion strength. Interestingly, NW connectors still maintain their adhesion capabilities even when they are engaged in extremely lubricating liquids, such as mineral oil (shear adhesion of $\sim$12 N cm^{-2}, Fig. 5b).

We propose that vdW interactions between the interpenetrating NWs is the main binding force that result in the observed wet adhesion properties of the connectors. Previous studies have shown that vdW interactions between two identical surfaces with dielectric constant of ε_1 in a medium with dielectric constant of ε_2 is proportional to $[(\varepsilon_1-\varepsilon_2)/(\varepsilon_1+\varepsilon_2)]^2$.[23,24] A similar trend is also expected for the NW connectors if the vdW interactions are the dominating binding force. In fact, as can be seen in Figure 5c, the observed wet adhesion trend under various liquid environments (i.e., adhesion strength for water > IPA > octane > mineral oil) is approximately consistent with vdW proportion factor, $F(\varepsilon)=[(\varepsilon_1-\varepsilon_2)/(\varepsilon_1+\varepsilon_2)]^2$ (solid line in Fig. 5c), where ε_1 is the dielectric constant of parylene ($\varepsilon_1=2.65$) and ε_2 is the dielectric constant of liquids between parylene surfaces (ε_2, water = 80; IPA = 18.3; octane = 2; mineral oil = 2.1). The viscosity of the liquids may also affect the binding strength, for instance, by the viscous drag force or by determining the separation distance between the interpenetrating NWs and affecting the vdW interactions. However, the observed adhesion trend does not correlate with the viscosity of the liquids (water: 1 cP; IPA: 2.4 cP; octane: 0.5 cP; mineral oil: $\sim$30 cP). The results suggest that the viscosity does not play a dominant role on the shear stress, at least for the viscosity range and the normal preload stresses explored in this study. In addition to the vdW interactions, capillary forces may contribute to the wet adhesion of the NW connectors. However, capillary forces are known to be greatly reduced when substrates are completely submerged in liquid environments due to the reduced probability of capillary bridge formation that requires air/liquid interfaces.[8] Hydrophobic effects could also play a role in the adhesion properties, especially for the measurements performed under water, although, as previously stated, the wetting properties highly depend on the applied external forces. Finally, mechanical entanglement of randomly aligned NWs cannot be ruled out although our previous study of the dry adhesion has shown that the mechanical interactions are not the dominating force in NW connectors.[14] Most likely, the wet adhesion properties of NW connectors arise from multiple interaction forces listed above with the vdW interactions being the dominant force. The wet adhesion ability of NW connectors combined with strong solvent stability and chemical resistance arising from the parylene shell[25] may enable the exploration of novel applications utilizing NW connectors.

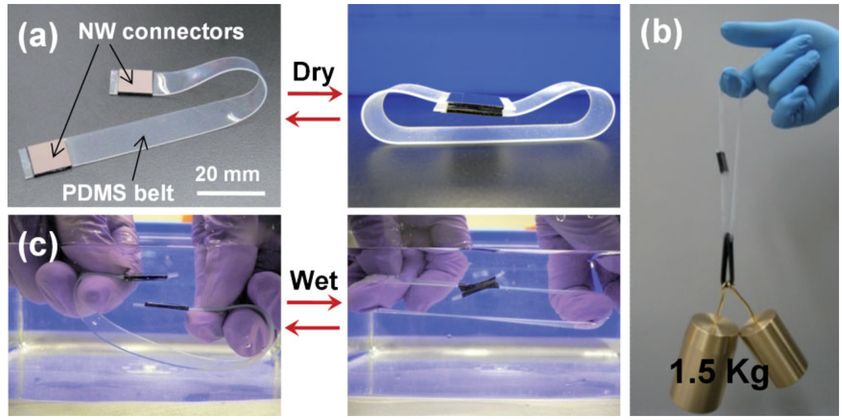

Figure 6. Macroscale wet and dry adhesion performances of NW connectors attached to the ends of a stretchable PDMS belt. a) Reversible dry NW connectors. b) Dry NW connectors holding 1.5 kg of weight. c) Reversible wet NW connectors, operating under water.

To demonstrate the feasibility of the NW connectors for macroscale applications, two connector mates were attached to the ends of a stretchable polydimethylsiloxane (PDMS) belt (Fig. 6 and Video S2 in the Supporting Information). In this experiment, the unisex NW connectors were engaged/disengaged multiple times by hand in both dry and wet environments to simulate a potential real-life usage of the connectors. Figure 6a and b shows the reversible dry adhesion and Figure 6c shows the underwater adhesion for the same NW connector sample, demonstrating the versatility of NW connectors without significant degradation over multiple cycles of operation, regardless of the ambient.

3. Conclusions

In summary, we demonstrate hybrid inorganic/organic core/shell NW forests as highly versatile and reusable connectors with strong shear adhesion strengths in both dry and wet environments, arising from their high aspect ratios that generate large contact areas in the engaged mode. In addition, we show that the adhesion strength, repeated reusability, and mechanical robustness of the NW connectors strongly depend on the geometric configuration of the NW forests with an optimal NW length of $\sim$10 μm. These NW connectors could potentially be used for a wide range of applications, including those involving underwater assembly of components. In the future, NW forests grown on flexible backing (such as a Kapton substrate) may be explored as ultrathin connectors to further enhance their functionality.

4. Experimental

Ge/parylene Core/Shell NW Arrays: Ge NWs with diameter d = 20–30 nm and length $L\approx$ 5–100 μm were grown in a chemical vapor deposition chamber on Si/SiO_2 ($\sim$50 nm, thermally grown) support substrates by a vapor–liquid–solid process as previously reported elsewhere [26]. By controlling the growth time, the NW length was readily tuned to the desired length (5–100 μm). Subsequently, parylene-N was deposited on Ge NW forests following the procedure described earlier and the parylene shell thickness was maintained constant at $\sim$200 nm for all experiments reported in this work.

Macroscopic Dry and Wet Adhesion Test: The macroscopic dry adhesion tests were performed by first applying a normal preload stress to the NW connectors ($\sim 0.5 \times 0.6\,cm^2$) followed by applying a shear stress, and finally removing the preload to measure the pure shear stress strength. The wet adhesion tests were performed by immersing the NW connectors inside various wet environments in a PDMS liquid cell. For the feasibility test of NW connectors for macroscale applications (Fig. 6 and Videos in Supporting Information), the back sides (i.e., the Si support substrate) of the NW connectors were attached to the two ends of a stretchable PDMS belt (0.79-mm thick, BISCO HT-6240, Rogers Corporation) by a double sided carbon tape, and subsequently tested for reversible wet and dry adhesions.

Acknowledgements

H. Ko, Z. Zhang contributed equally. We thank B. E. Schubert and R. Kapadia for insightful discussions. This work was supported by DARPA/DSO, NSF Center of Integrated Nanomechanical Systems, and Berkeley Sensor and Actuator Center. Z. Z. acknowledges a fellowship from the China Scholarship Council. The nanowire synthesis part of this project was supported by a Laboratory Directed Research and Development grant from Lawrence Berkeley National Laboratory. Supporting Information is available online from Wiley InterScience or from the author.

Received: April 19, 2009
Revised: June 13, 2009
Published online: August 25, 2009

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