Nanohydrogel Brushes for Switchable Underwater Adhesion

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Abstract

In nature, living systems commonly adopt the switchable friction/adhesion mechanism during locomotion. For example, geckos can move on ceilings relying on the reversible attachment and detachment of their feet on substrate surfaces. Inspired by this, scientists have used different materials to mimic natural dynamic friction/adhesion systems. However, synthetic systems usually cannot work in water environments and are also limited to single contact interfaces, while nature has provided living systems with complex features to perform energy dissipation and adhere on multiple contact interfaces. Here, for the first time, we report the design, synthesis and testing of a novel double-sided synthetic construct that relies on nanohydrogel brushes to provide simultaneous friction switching on each side of the membrane that separates the nanohydrogel fibers. This highly tunable response is linked to the swelling and shrinkage of the brushes in basic/acid media. Such a system shows three different friction states, which depend on the combination of pH control of the two membrane sides. Importantly, each side of the membrane can independently provide continuous but stable friction switching from high to ultra-low friction coefficients in a wet environment under high load conditions. An in-depth theoretical study is performed to explore the mechanisms governing the hydration state responsible for the observed switching. This novel design opens a promising route for the development of new solutions for intelligent devices, which can adapt to multi-stimulus responsive complex environments.
Introduction

Lessons learnt from Nature,1-6 have led to the construction of novel responsive actuating systems whose behavior is regulated by mechanisms that take place at the micro-scale, all the way down to molecular level,7-16 and which can perform intelligent functions for various applications, such as solid-liquid transportation,16 chemical motors or switches,17-24 and controlled release.25 These systems are particularly interesting when they are linked to the control of friction and lubricating mechanisms,26-29 which are not only responsible for energy dissipation but also control much of our daily life.30

Inspired by the reversible adhesion ability of gecko’s feet that benefit from dynamic van der Waals interaction,31-33 numerous gecko-inspired synthetic adhesives have been recently developed,34-38 including stimulus-responsive (temperature, light, magnetic field, etc.) adhesives.39-42 Although the switching performance of such synthetic gecko adhesives are impressive, developing effective switching adhesives underwater still remains a scientific and technical challenge. This is particularly interesting, especially when considering the fact that geckos can easily perform attachment and detachment on various surfaces that are frequently exposed to rainfall and/or high humidity atmosphere. Thus, obvious gaps remain between synthetic man-made systems and their natural counterparts. To date, very few adhesives allow dynamic adhesion switching underwater;43-44 the difficulty in achieving such task could be attributed to several scientific results showing that gecko adhesion is greatly diminished upon full immersion in water and surface wettability plays a significant role in gecko adhesion underwater.45-47 In 2007, Lee and co-workers48 for the first time fabricated a high adhesion gecko array underwater by integrating a dopamine-containing copolymer on array. Although this composite array possesses excellent adhesion strength underwater, it does not show reversible switching capabilities.
This prompts a very intriguing research challenge: can we engineer a nano-fibre synthetic adhesive capable of reversible adhesion and/or friction switching underwater? Both high and low friction are useful in daily life. For example, high friction enables manipulations of objects, heat generation, power transmission and braking, while low friction is beneficial for e.g. anti-wear, drag-reduction and object transportation. Performance of intelligent switching based on controlling frictional and interfacial forces is challenging and difficult to achieve but has promising application in automotive, micro-electromechanical systems (MEMS), transportation, and chemical sensors.\textsuperscript{8, 11, 49-51} One promising strategy to construct intelligent systems is the use of responsive materials, such as hydrogels, which are ideal candidates for artificial joints and soft tissue mimics,\textsuperscript{52-53} and for the fabrication of intelligent frictional interfaces.\textsuperscript{24, 54-55} This is due to the high degree of polymer hydration and volume changes,\textsuperscript{56-59} which make such synthetic constructs sensitive to environment stimulus,\textsuperscript{60} including pH,\textsuperscript{61} temperature,\textsuperscript{62} light,\textsuperscript{63} and magnetic field.\textsuperscript{64}

Our group has recently developed a general approach to integrate nanostructured hydrogel fibers (brushes) into ordered inorganic porous membrane,\textsuperscript{65} and the resulting composite surface showed a strong pH-dependence of friction under wet conditions and high applied loads (note that for soft materials high loads corresponds to contact pressures at the interface above the 1-100 kPa range, typically varying from order 1 kPa for hydrogels to 100 kPa for e.g. PDMS rubber contacts). This provides a great opportunity to develop new synthetic adhesives made of nanohydrogel fibers, which can switch static friction underwater. However, just like the traditional gecko-inspired adhesives, the adhesive surface only shows one-sided wet adhesive properties. In typical experimental processes, when the adhesion properties of one side are measured, the other side of the adhesive (i.e. the non-structured side of the substrate) must be fixed to a surface by using chemical bonding or glue. This means that it is difficult for the sample to be easily detached from the surface after the measurements have been carried out
and chemical fixation implemented; this implies that often the functionality of the “active” side is also lost. So can we construct a pH-sensitive double-sided adhesive capable of multiple-interface adhesion and/or friction switching? In the present work, double sided hydrogel nanofibrillar structures are constructed to solve this problem.

Nature often provides living systems with asymmetric or complex features to perform complicated functions. Inspired by this, we aim to confer more design flexibility to adhesive materials that can allow us to perform friction or adhesion actuation in different regimes on multiple contact-interfaces in a wet environment. In this work, for the first time, we report the design, synthesis, characterization and testing of a novel double-sided construct (DSA – double-sided adhesive) that relies on nanohydrogel brushes to provide simultaneous friction switching on each side of the membrane that separates the nanohydrogel fibers. We also provide a systematic theoretical investigation that sheds light on the mechanisms responsible for the tunability and the switching characteristics of the construct. This highly tunable response is linked to the swelling and shrinkage of the brushes in basic/acid media. Thus, such a system could show three different friction states, which depend on the combination of pH control of the two membrane sides: low friction (LF)low friction (LF), low friction (LF)high friction(HF) [and high friction(HF)low friction (LF)], high friction(HF)high friction(HF); it should be noted that the two states (LF¶HF and HF¶LF) provide identical relative frictional response. However, the same provide two independent actuation channels (thus, totally four actuation channels), a feature of utmost importance for e.g. locomotion purposes. Overcoming some of the limitations of traditional double-sided tape (once used, it is difficult to release from the surface; furthermore, the adhesive properties of double-sided tape would largely be weakened once immersed into water), the DSA system is a chemically-responsive double-sided gecko-inspired synthetic adhesive. As a whole, DSA provides a platform for multi-interfaces friction
regulation. Considering the multiple friction states generated in response to pH-controlled media, to which both sides of the construct can be exposed, a typical DSA system has the potential to be adopted for truly-underwater/wet applications, such as pH-sensing, pH-activated locomotion and pH-activated structural stiffening/damping of composites (see Figure S1 to S3, Supporting Information). The various steps of our investigation are reported in the next sections, starting with the fabrication and characterization techniques described in the Experimental Methods section. This is followed by the Results and Discussion section in which the performance of the new construct is thoroughly assessed and theoretical insight is provided to explain the principles governing its performance.
Experimental Methods

Fabrication of PAA Double-sided Nanohydrogel Brushes

To fabricate the double-sided nanohydrogel brushes, we first prepared a double-faced non-through AAO membrane by a two-step anodic oxidation method. After removing bubbles by blowing N₂ for 10 min, the mixed water solution of N,N'-Methylenebisacrylamide (BIS, Sinopharm Chemical Reagent Co. Ltd., China), potassium persulfate (KPS, Tianjin Chemical Reagents Corp.) and acrylic acid (AA, J&K Chemical Ltd.) obtained using a certain mass ratio (AA: 1.5 g; BIS: 0.01 g; KPS: 0.02 g; water 20 mL) was poured into the asymmetric mold. Then the reaction system was moved to a vacuum dryer oven (at room temperature) for 2 h, and this was followed by polymerization in an oven (80°C) for 7 h in N₂ atmosphere. After a short period of cooling, the bulk hydrogel layer formed on the surface of the AAO pores was removed with a sharp blade, and the residual part was removed by the aid of the N₂ gas flow or peeled off in air.

Experimental Characterization of Double-sided Nanohydrogel Brushes

In order to perform field emission scanning electron microscopy (FESEM) characterization, the sample was frozen in a drying oven first, and was then transferred to a conductive substrate for gold coating. Observation was performed on JSM–6701F (Japan) using constant imaging voltage of 5 kV. For in situ monitoring of the evolution of the nanohydrogel brushes in liquid environment, atomic force microscopy (AFM) measurements were performed on an Agilent Technologies 5500 AFM using a MacMode Pico SPM magnetically driven dynamic force microscope. Images were taken using commercially available type II MAC levers with a nominal force constant of 2.8 N/m at a driving frequency of 24 KHz in liquid environment. We first fixed the sample of 9 mm² into the cell, then the acid media (pH=2) was injected. The morphology was observed after 30 min. Finally, the acid media was removed and basic liquid (pH=12) was in situ injected into the cell for morphology monitoring.
**Force Measurement**

Surface force measurement was conducted using a Nanoscope Maltimode 8.0 AFM (Bruker Co. GER) with a vendor-supplied fluid cell. Polydimethylsiloxane-coated Si$_3$N$_4$ tips along with cantilevers (Digital Instruments, CA) were used as AFM probes. In typical case, the Si$_3$N$_4$ tips were immersed into a mixture solution containing 1.0 g commercial silicone elastomer kit (SYLGARD 184 silicone elastomer), 0.1 g curing agents (Dow corning, Midland, MI, USA), 2 g hexane for 2-3 min, and then pulled out quickly. This was followed by polymerization in vacuum drying oven at 80 °C for 3 h, resulting in a very reproducible PDMS coated tips preparation process. The coating does not strictly affect the geometry of the AFM tips (see Supporting Information, Figure S16). The force measurement and calibration for the spring constant of each cantilever was performed on the basis of standard methods. Prior to the measurements, both the probes and brush surfaces were immersed into the corresponding test liquid to allow at least 30 min equilibration. For each liquid test in acid (pH=2) or basic media (pH=12), the force measurement was perform at least at five different locations and each test is the statistical average determined using at least 100 retraction force profiles. The adhesive force is defined as the pull-off force measured when the probe detaches from the surface of the specimen. The experiments are conducted at room temperature (25 ± 1 °C).

Non-conformal contact geometry friction tests were performed on a conventional pin-on-disk reciprocating tribometer by recording the friction coefficient ($\mu$) (Tribometer UMT-2, CETR). Elastomeric poly-dimethylsiloxane (PDMS) hemispheres with a diameter of 6 mm were employed as pins to slide against the composite interface in different media. The stroke length was 5 mm and test were run at constant frequency of 1 Hz; the friction coefficient was determined by dividing the friction force by the applied normal load through the acquisition software provided with the tribometer. For static friction force measurements under plane contact geometry, the sample was independently
wetted by different media for 30 minutes on each side and then was used for testing. Then measurements were performed using 5 mm sliding distance under constant load of 50 g using a 14-FW Stat-namic tribometer (HEIDON Co., Ltd.) operated in a face-to-face contact mode.

Application of Load in the Demonstrative Experiment

Demonstrative experiments were carried out to showcase the applicability of the nanohydrogel brushes construct to realistic loading scenarios (see also the sub-section Performance of Hydrogel Constructs in the Results and Discussion section). A magnetic field was generated from two commercial magnets with middle magnetic field of 2.07 mT; this was used to provide the normal force to be applied to clamp the DSA between PDMS layers, determining the constant normal load applied to the construct. The force was measured by HANDPI Digital Push & Pull HP-50 Tester (full-scale reading: 50 N; minimum reading: 0.01 N) as 12 N, under fixed distance of 12 mm between two magnets separated by PDMS blocks of nominal contact area of 1 cm². After the membrane carrying the double-sided nanohydrogel brushes was sandwiched between the PDMS blocks, weights were applied to the construct after the two sides of the DSA had been wetted by different liquid media to demonstrate the response of the system in different configurations.
Results and Discussion

Preparation of The Double-sided Adhesive

The preparation of the double-sided nanohydrogel brushes membrane (see also Experimental Section) was achieved by infusing the monomer solution into the double-sided nanoporous alumina (Figure S4, Supporting Information), polymerization of each side of the construct, and stripping of surface gel layer (Figure 1a). The experimental setup in Figure 1b indicates that modification of both sides can be operated at the same time without interference with each other. This provides the possibility of preparing either symmetric fiber brushes or asymmetric gel brushes simultaneously. After polymerization and drying upon exposure to nitrogen flow, the gel layers formed on the two surfaces were easily separated from the AAO substrates. Thus, after brittle fracture of the bulk hydrogel, the final surface became very smooth and clean (Figure 1c). Both sides of the porous substrate were successfully infused with nanohydrogel fibers, which protrude from the AAO surface and form a “film” whose out-of-the-pores thickness is about 3-5 µm (Figure 1c). The fibers constituting each brush show a certain orientation linked to the direction of the nitrogen flow. The formed gel fibers extend to the bottom of each side in the channels (Figure S5, Supporting Information). The gel fibers have an average diameter of about 100 nm on both sides. Each fiber is stretched out from the specific pore and is independent from the others, forming brush structure. Moreover, it is observed that the nanohydrogel fibers confined in the nanoporous channels are characterized by highly flexibility and low adhesion with the walls of the pores (Figure S6, Supporting Information).
**Figure 1.** (a) Schematic showing the preparation of the double-sided PAA nanohydrogel brushes membrane. (b) Experimental setup. (c) The as-prepared membrane after peeling off surface gel layer, its cross-section profile on both sides and SEM images of ordered nanohydrogel brushes in large area and magnified gel nanofibers bundles – scale bars = 1 µm for all SEM images apart from the bottom right image, where the scale bar = 500 nm.

**Friction Test under Point Contact Macro-geometry**

The as-prepared gel nanofiber brushes were immersed into the basic media (pH=12) for 30 min to allow the conformation conversion of polymer chains from polyacrylic acid (PAA) to polyacrylic acid sodium (PAAs). When employing a poly-dimethylsiloxane (PDMS) ball as the friction counterpart using the UMT-2 friction test platform (Figure S9, Supporting Information), each side of the composite membrane shows high coefficient of friction (COF) of about 0.3-0.4 in acid media of pH=2 under load of 3 N (Figure 2a). By contrast, each side of the composite membrane remains in ultra-low friction state, characterized by COF<0.01, under the same load in basic media of pH=12 (Figure 2b). It is also observed that each side of the composite membrane can remarkably achieve
this very low friction state ($\text{COF}<0.01$) under heavy load of 40 N in basic media of pH=12 (Figure S11, Supporting Information). These results indicate that both sides are pH responsive, which means that each side can be used to tune the fiction independently. The interface shows high COF when exposed to a 20 µL solution of pH=2 medium under a 3N load; this value decreases suddenly when 5 µL of basic medium (pH=12) is added in the contact zone. Finally, the interface keeps ultra-low friction state after the third injection (pH=12) (Figure 2c). This indicates that our samples are ideally designed to perform in situ friction switching. Moreover, it is observed that the interface changes very rapidly from ultra-low friction to high friction state upon adding 10 µL acid liquid (Figure 2d, first and second red arrows), and then the COF drops quickly after injecting 5 µL basic liquid (Figure 2d, first yellow arrow), once again the friction coefficient rises when wet by 10 µL acid liquid (Figure 2d, second red arrow) and finally falls back to ultra-low friction state after injecting 20 µL basic liquid (Figure 2d, second yellow arrow). In both cases, once the media is injected on the interface, friction switching would rapidly take place without stagnation. Similar considerations apply (in situ friction switching) under a relatively higher load (40 N), with Hertzian contact pressure of ~1.8 MPa (Figure 2e).

In order to assess the durability of the friction switching, continuous shift between the two states is initiated by alternately wetting the interface with 20 µL acid (pH=2) and basic (pH=12) media. When increasing the disturbance time intervals for friction switching from 50-80 s (Figure 2f, black curve) to 150-200 s (Figure 2f, red curve), and then to 300-400 s (Figure 2f, green curve), fast and stable friction switching could be maintained in all cases.

A common issue encountered when dealing with composite hydrogels and, more in general, soft matter materials is that they may be easily damaged when they are subjected to high frictional forces and normal loads due to the generation of high shear stresses within the contact region. In the present
work, our samples are capable of preserving their switching function for long time without failure, which has significant implications for different applications.

Figure 2. Friction properties of the double-sided PAA nanohydrogel brush membrane. Plots of COF vs. time when both sides of the gel fiber brushes are exposed to (a) acid media (pH=2) under a 3 N load and (b) basic media (pH=12) under a 40 N load – red and black data points represent the two sides of the construct. (c) Curve of COF vs. time when the basic media (pH=2) wetted surface was repeatedly supplied with 5 μL basic media (pH=12) under a 3 N load. (d) Plots of COF vs. time when
the surface was wetted by 20μL basic media \((t=0-210\ s)\) and then was perturbed by the following sequence: 10 μL acid media at \(t=210\ s\) (red arrow-\(a\)); 10μL acid media at \(t=300\ s\) (red arrow-\(b\)); 5μL basic media at \(t=390\ s\) (yellow arrow-\(c\)); 10μL acid media at \(t=390\ s\) (red arrow-\(d\)); 5μL basic media at \(t=430\ s\) (yellow arrow-\(e\)). (e) Reversible friction switching between acid media (pH=2) and basic media (pH=12) under a 40 N load. (f) In-situ friction switch between low and high friction induced by alternatively injecting 20 μL acid (pH=2) and basic (pH=12) media using different time intervals: (black curve) 50-80 s, (red curve) 150-200 s, (green curve) 300-400 s under a 3 N load.

The realization of stable, fast and durable friction switching under high loads suggests the potential use of our constructs as e.g. intelligent actuating interfaces. Indeed, our tests show that the composite membrane could sustain switching between low and high frictional states without undergoing significant changes in its response for over 4 hours, i.e. about 10000 reciprocating sliding cycles. Subsequently, the wear track is observed for the insight of morphology evolution in the sliding interface. After getting through 300 reciprocating friction cycles in basic liquid (pH=12), the interface reaches a steady low friction state while the surface morphology gradually evolves from the ordered gel fiber array shown in Figure 1c to a gel thin-film structure (Figure S7, Supporting Information). After performing in situ friction switching and 10000 reciprocating cycles the ordered gel brushes becomes a dense thin gel film (Figure S8, Supporting Information).

This reversible friction switch is caused by the fast transition of surface hydration in acid-basic media. As shown in Figure 3a, due to the formation of inter-molecular hydrogen bonds between carboxyl and water molecules, PAA gel fibers assume a fully swollen state when wetted by basic liquid (pH=12). By contrast, due to the formation of intra-molecular hydrogen bond among carboxyl groups, the fibers contract when exposed to acid liquid (pH=2). This dynamic mechanism could be correlated with the surface morphology evolution as probed by AFM (Figure 3b). Gel fibers keep
hydrated and sustain a swollen state in basic media (pH=12); this leads to merging of the fibers to form a uniform and smooth surface characterized by a low roughness of ~5.6 nm (measured over a 5.0 µm × 5.0 µm domain). Conversely, these gel fibers are dehydrated and tend to shrink in acid liquid (pH=2), leading to high surface roughness of ~172 nm (measured over a 5.0 µm × 5.0 µm domain).

**AFM Characterization of the Pull-off Adhesion**

Furthermore, the AFM tips have been coated by PDMS and then used for detecting the interfacial interaction at the microscopic level (Figure S16, Supporting Information). Successful modification of the AFM tips with silicone is confirmed by the XPS and EDS characterizations. As shown in Figure S17 (Supporting Information), after the tips have been coated with PDMS, the signal corresponding to carbon increases, while that corresponding to silicon decreases; at the same time we witness the appearance of characteristic peaks with Si-O and Si-C bonds in the PDMS coated samples (Figure S18, Supporting Information), which are not recorded for the bare tips (Figure S19, Supporting Information). Similar results are also obtained to confirm the functionalization of the tips (see SEM-EDS pictures shown in Figure S20-21, Supporting Information).

In consideration of realistic wet applications of such adhesives, such as for the process of locomotion on wet surfaces, both manipulation of the normal and lateral surface forces are needed. In this work, our paper places special emphasis on lateral (frictional) forces, rather than on the adhesion behavior. However, unlike dry friction/adhesion mechanisms, friction and adhesion of soft materials in aqueous solution are never independent. For friction of polyelectrolyte hydrogel system, macroscopic friction force can be always related to the microscopic adhesion mechanism, and this is supported by theories based on of repulsion–adsorption models.

As a typical result, when exposed to basic media, two negatively-charged surfaces (PDMS
indenter and gel fibers) give rise to strong double-layer repulsion effects and, consequently, low adhesive forces are recorded (Figure 3c). By contrast, the surface of the fibers presents high adhesive forces from the electrostatic attraction effects induced by exposure of the hydrogel to acid media (Figure 3d). Microscopic adhesion force measurement results showed a good correlation with the macroscopic friction testing results, which in turn supports the polymer repulsion–adsorption model. In our work, we obtained results in perfect agreement with this theory. In brief, by changing the pH value of the solution, the charge on PAA gel fibers surface can be regulated as well. Below the pKa (~4) of the PAA s, the carboxyl groups in PAA s polymer chains are protonated, resulting in the dehydration of the gel fibers in the composite surface; in this case the interface is mainly dominated by electrostatic adsorption/van der Waals interaction, leading to high adhesion and friction. Above the pKa of the PAA s, the carboxyl groups in PAA s polymer chains are deprotonated and the gel fibers array is highly hydrated. Here strong electrostatic repulsion against PDMS occurs, resulting in the ultralow friction. Finally we stress that whilst PDMS is hydrophobic, polymer surfaces do typically show a surface charge often coming from unknown sources, or simply because of the fabrication techniques (e.g. through electrification). In our system, the PDMS surface may be partially oxidized as a consequence of exposure to environment or, as recently deduced, the surface charge may arise from the enhanced autolysis of water (at the hydrophobic surface), with the preferential adsorption of hydroxide ion.

**Friction Tests under Plane Contact Macro-geometry**

By using different wetting media on each side of the composite membrane, our system could present three different friction responses: LF∥LF, LF∥HF (or HF∥LF), HF∥HF; these correspond to four different actuation (and hydration) states at the interface as: swelling∥swelling, swelling∥deswelling, deswelling∥swelling, deswelling∥deswelling (Figure 3e). The friction force at
different friction states can be captured using the 14-FW friction test platform in a typical flat-on-flat contact mode (Figure S10, Supporting Information).
Figure 3. (a) Schematic showing the molecular conformation change in acid (pH=2) and basic media (pH=12). (b) Surface morphology probed by AFM in liquid environment. Normalized adhesive force curve as a function of separation distance between PDMS coated tip and hydrogel brushes, (c) in basic (pH=12) or (d) acid media (pH=2); the black curve represents that probe approaches substrate surface while the red curve represents that probe retracts from the substrate. (e) schematic four different hydration models of the double side membrane as swelling|swelling, swelling|deswelling, deswelling|sweling, deswelling|desweling, corresponding to three friction states as: LF (on)∥LF (on), LF (on)∥HF(off) [or HF(off)∥LF (on)], HF(off)∥HF(off). Blue: double-through AAO template; green: PAA gel fibers; gray: PDMS specimens. The gel fibers were confined into the template as a whole to slide against the PDMS specimens. (f) Plots of real-time friction force (Ff) vs. time for four different states (contact area: 1 cm²; load: 0.5 N). a: in HF(off)∥HF(off) state (both sides were wetted by pH=2 acid media); b: in HF(off)∥LF(on) state (on side was wetted by pH=2 acid media while the other side was wetted by pH=12 basic media); c: in LF(on)∥HF(off) state (on side was wetted by pH=12 basic media while the other side was wetted by pH=2 acid media); d: in LF(on)∥LF(on) state (both sides were wetted by pH=12 basic media). (g) The static friction force (F_s) vs. normal load under four different states. (h) The calculated ratio between of static friction force obtained in the four states and the results obtained for the reference swelling|swelling state.

For freshly prepared samples, it is found that the friction coefficient gradually decreases with increasing immersion time in basic media (pH=12, Figure S12, Supporting Information), while increases with increasing immersion time t in acid media (pH=2, Figure S12, Supporting Information). In particular, we observed $\Delta \tau_w \approx \tau_0 e^{-b*t/t_1}$, where b is an order one factor and $\Delta \tau_w$ represents the module of the variation of the shear frictional shear stress with respect the initial value. $t_1 \approx 0.05$ min and $t_1 \approx 0.09$ min for, respectively, the acid and basic solution, in perfect agreement with the
theory (see Supporting Information, Figure S12). Once the charges diffusion dynamics reaches the steady configuration, and thus the conformation conversion of polymer chains is completed [e.g. from polyacrylic acid (PAA) to polyacrylic acid sodium (PAAs) upon basic solution immersion], the friction force converges to the pH-related asymptotic value (Figure S13, Supporting Information). Thus, under a normal load of 0.5 N, the system keeps a high static friction force of ~1.5 N when both DSA sides are wetted by the acid media (corresponding to HF\|HF state, blue curve of Figure 3f). When one side is wetted by acid media while the other by basic media, the system shows LF\|HF or HF\|LF state and the friction force decreases at about one order of magnitude (Figure 3f, red and green curves). When both DSA sides are wetted by the basic media, the system keeps almost zero friction force in the LF\|LF state (Figure 3f, black curve). Furthermore, when the normal load increases from 0.1 N to 2 N, the static friction force ($F_s$) increases slightly, but still remains at a very low value of ~$10^{-2}$ N in swelling\|swelling state (Figure 3g, black points). This is not the case for the other three states, for which a sharp increase in friction is observed (Figure 3g). The ratio of static friction force recorded in the deswelling\|deswelling state to that obtained in the swelling\|swelling state, which reaches 38 under 0.1 N load, significantly increases to ~100 under 2 N load (Figure 3h). All of the above results indicate that the performance of each side of the construct can independently be tuned in terms of friction and that the response of the system is highly sensitive to acid-base stimuli at the two interfaces exposed to contact.

Given an order 1N squeezing load with contact area of 1.0 cm$^2$, the nominal frictional shear stress of our acidic-actuated DSA (~0.75 N/cm$^2$) is typically much higher than natural gecko’s values in wet conditions, and in particular are comparable with the gecko’s adhesive shear stresses measured in fully dry conditions, with normal load naturally provided by the lizards weight. This demonstrate the superior performances of the nano-fibers gel array. Furthermore, and this goes
beyond the gecko’s capabilities, our DSA will show ultra-low shear stresses when actuated in basic solution, thus providing an extreme adhesion switching property. As expected, in consideration of the effect of solution pH on hydration degree and surface charge of the gel fibers array, our DSA would show a pH-induced surface morphogenesis (see AFM surface topography acquisition, as well as theoretical insight section). With the rising of the solutions pH, the surface roughness of DSA decreases corresponding (from the acid to the basic case), leading to a strong reduction in the true contact area under the applied normal loads, with consequent reduction of the measured nominal frictional shear stresses (Figure S13).

*Theoretical Insight*

The PAA-hydrogel/PDMS quasi-static friction force can be theoretically predicted as follows. We first observe that, under relatively small values of sliding speed, the hydrodynamic lift induced by the combined deswelling and sliding kinematics can be neglected, since the interaction occurs under DLVO (Derjguin-Landau-Verwey-Overbeek) roughness-mediated boundary conditions. Moreover, the high fibril area density characterising the constructs studied in the present work justifies the adoption of the uniform hydrogel coating assumption, as shown in the model below. We note that it has been experimentally demonstrated that this assumption becomes exact for sliding interactions, upon the execution of the run-in stage.

We consider here the case of plane-to-plane contact geometry, as shown in the experimental setup of Figure S10 (Supporting Information). However, the model below can be applied to non-conformal interactions as well. The nominal contact pressure \( \sigma_0 \) is assumed constant throughout the nominal contact area \( A_0 \), whereas, due to the PAA-hydrogel/PDMS asperity-asperity contacts, the true asperity projected contact area \( A_c \) will be a fraction of \( A_0 \), and it will be characterized by a locally varying contact pressure. Thus, the friction force \( F_T = \tau_w A_c (1 + H)^{-1} \), where \( \tau_w \) is the shear stress.
originating from the bonding-debonding process of polymer chains (see Figure 4a) and $(1 + H)^{-1}$ takes into account that the swelling further reduces the true polymer contact area $A_p$ by a factor $A_p/A_c \approx V_0/V_c = (1 + H)^{-1}$, where $V_0$ and $V_c$ are, respectively, the gel volume in the unswollen and swollen state, and $H$ is the hydration. Finally, the friction coefficient $\mu$ can be written as

$$\mu \approx \tau_w A_c/(\sigma_0 A_0)(1 + H)^{-1}. \quad (1)$$

In (1) the contact pressure dependence of both $\tau_w$ and $A_c/A_0$ needs to be calculated. According to the standard Schallamach process of molecular bonding/debonding (see Figure 4a for a schematic representation of such mechanism), $\tau_w \approx N_0 M v_0 \bar{t}$, where $N_0$ is the (average) nominal number of live bonds, $\bar{t}$ is the bond age, and $M$ is the bond elastic stiffness (where from the scaling theory of polymers, the polymer elongation stiffness $M \approx E r_b$, where $r_b$ is the size corresponding to an average polymer blob radius, and $E$ the elastic modulus). The number of live bonds $N_0$ is affected by the double layer pressure $p_r$ (proportional to $\zeta_{gel} \zeta_{PDMS}$, where $\zeta_{gel}$ and $\zeta_{PDMS}$ are, respectively, the surface potential of both hydrogel and PDMS counter-surface) through the solution pH, and in particular it will increase (decrease) depending on the decrease (increase) of the average bond energetic barrier, $\Delta U_e$, as caused by the double layer. In particular, one can estimate the energetic barrier variation with $\Delta U_e = r_b^3 p_r$, where $p_r \propto \zeta_{gel} \zeta_{PDMS}$ is the double layer pressure (positive when repulsive). Thus we get $N \approx N_0 e^{-r_b^3 p_r/(k_B T)}$, resulting into

$$\tau_w = \tau_0 e^{-r_b^3 p_r/(k_B T)}. \quad (2)$$

Such an exponential dependence of the wall shear stresses originating from the Schallamach dissipation mechanism has been recently demonstrated.

We now show how to determine the contact pressure dependence of $A_c/A_0$. We consider first the limiting case of low contact pressures. We observe that, given the small contact pressure dependence of $\tau_w$ and $(1 + H)^{-1}$ at low contact pressures, (1) shows that at constant pH the friction
is roughly proportional to $A_c/(\sigma_0 A_0)$. For adhesionless interactions, or for interactions characterized by a negligible length-scale dependence of the average detachment stress, $\sigma_a$, the normalized contact area $A_c/A_0 \approx k(\sigma_0 + \sigma_a)$ in the linear contact regime, where $k$ is a constant. Thus, in the linear contact regime (or low contact pressure regime) and for $\sigma_0 + \sigma_a \gg 0$ (small work of adhesion), (1) predicts a constant friction coefficient. However, for $\sigma_0 + \sigma_a \approx 0$, or for more general contact conditions, the projected contact area $A_c/A_0$ has to be calculated, e.g. recurring to a multiscale contact mechanics theory with adhesion, as shown in the following (such a pressure dependence of the true contact area can be also calculated recurring to numerical models, however with much larger computational effort). In particular, here we assume JKR-limit interactions to occur along the whole range of roughness length scales (the accuracy of such assumption can be evaluated by calculating the scale dependent Tabor number characterizing the contact), since the spatial extend of the wall-wall interaction potential can be usually neglected for soft interactions. To summarize, the theory focuses on the probability distribution $P(\sigma, \zeta)$ of stresses $\sigma$ (acting at the interface when the system is studied at the magnification $\zeta$) which is determined from an approximate diffusion equation of motion in $P(\sigma, \zeta)$. The projected area of real contact $A_c$ can then be calculated for any magnification $\zeta$, $A_c(\zeta)$, and normalized by the nominal contact area $A_0$, to obtain

$$A_c(\zeta)/A_0 = \int_{-\sigma_a(\zeta)}^{\infty} dP(\sigma, \zeta),$$

where $A_c = A_c(\zeta_1)$, with $\zeta_1$ the largest roughness magnification.

As an example, for $\sigma_a(\zeta) \approx 0$ (adhesiveless interactions), (3) simplifies into

$$A_c(\zeta_1)/A_0 = \text{erf}\left(\frac{1}{2\sqrt{G}}\right),$$

where $G = 2\pi/(8\sigma_0^2) \int_{q_0}^{q_1} dq q^3 C(q)|E_c|^2$. $C(q) = \sum C_i(q)$ is the combined roughness power spectral density ($C_i(q) = \frac{3-D_F}{\pi} \left(\frac{q}{q_0}\right)^{2(4-D_F)}$ for a self-affine isotropic roughness with fractal dimension $D_F$) of the interface, $q_0$ and $q_1 = \zeta_1 q_0$ are, respectively, the large- and small-scale cut-off
frequencies of the roughness power spectral density and $\sigma_0$ is the externally applied nominal pressure.

$E_c$ is the combined interfacial visco-elastic modulus\textsuperscript{65} which in our case can be written as:

$$E_c(q)^{-1} = E_{r, gel}(\pi v_0/a_H)^{-1} S(q) + E_{r, PDMS}^{-1},$$

with $E_{r, gel}(\omega) = E_{r, gel-0}(1 - i\omega\tau_{r, gel})$, and

$$S(q) = \frac{(3-4\nu_{gel})\sinh(2qt)-2qt}{(3-4\nu_{gel})\cosh(2qt)+2(qt)^2-4\nu_{gel}(3-2\nu_{gel})+5}. \tag{6}$$

$E_{r, gel-0}$ and $\tau_{r, gel}$ are, respectively, the hydrogel rubbery elastic modulus and relaxation time, related to the squeeze-out dynamics of the solvent\textsuperscript{65} through the hydrogel slab. In (5) $S(q)$ takes into account of the finite thickness, $t \approx 1\mu m$, of the hydrogel, whereas in the most general case $a_H$ is the nominal contact length and $v_0$ the sliding speed\textsuperscript{65}. $v_0 \approx 0$ in our case.

For adhesive interactions, instead, (3) has to be solved numerically.\textsuperscript{75, 78} The AFM pull-off experiments show that the contact area formation, between the coated AFM tip and the hydrogel coating, results in some interfacial bonding energy $-\Delta \gamma A$ (where $\Delta \gamma = \gamma_1 + \gamma_2 - \gamma_{12}$ is the change in the interfacial energy per unit area upon contact) for the acid solution (pH=2, see Figure 3d). Considering a JKR-limit interaction (Johnson-Kendall-Roberts) to apply for the AFM experiments, the force needed to remove the ball from the flat (the pull-off force) is given by $F_c = 3\pi \Delta \gamma R/2$ (note that the latter is a factor of $3/4$ times smaller than predicted by the DMT (Derjaguin-Muller-Toporov) theory, thus the following results are approximately insensitive to the correct modelling of the AFM adhesion dynamics). In our case, considering a tip radius of about $\approx 1\mu m$ (see Figure S16, Supporting Information) and an average measured pull-off force of $\approx 50 nN$, the work of adhesion (for acid solution) can be estimated as $\Delta \gamma_{pH=2} \approx 0.01 N/m$. For the basic solution (pH=12, see Figure 3c), instead, we adopt $\Delta \gamma_{pH=12} \approx 0$, i.e. we assume an adhesionless interaction to occur. Moreover, the measured acid-pH (basic-pH) hydrogel roughness can be approximated by a self-affine isotropic roughness with root-mean square roughness $h_{rms} \approx 0.17 \mu m$ ($h_{rms} \approx 5.6 \text{ nm}$), fractal
dimension $D_F = 2.2$, small cut-off frequency $1.26 \times 10^6 m^{-1}$ and large cut-off frequency $1.26 \times 10^8 m^{-1}$.

**Figure 4.** (a) Schematic representation of the bonding/debonding molecular process occurring at the polymer length scale; (b) The calculated normalized area of real contact as a function of the nominal pressure for the acid-pH solution; (c) Magnification of (b) displayed in term of nominal load (the nominal contact area adopted in the experiment $A_0 \approx 1 \text{ cm}^2$); (d) Friction force as a function of the normal load, as predicted by the theory with (dashed line) and without (solid line) adhesion, compared with the experimental results of Figure 3g. We have assumed $\tau_w \approx 0.6 \text{ MPa}$ for the acid-pH solution and $\tau_w \approx 0$ for the basic-pH solution.

In Figure 4b we show the calculated normalized area of real contact $A_c/A_0$ as a function of the nominal pressure for the acid-pH solution, whereas in Figure 4c we show a magnification of Figure 4b in terms of nominal load (the nominal contact area adopted in the experiment $A_0 \approx 1 \text{ cm}^2$). Note
in Figure 4c that, under the experimentally-adopted loading conditions, only a small percentage of normalized contact area is generated for the acid-pH solution. Moreover, the local electrostatic interactions, resulting in an effective work of adhesion, play a strong role on the asperity contact formation, and in particular the contact area (dashed line) is almost doubled with respect to the ideal adhesionless (solid line) interaction, for the acid-pH solution. It should be noted here that the effective work of adhesion must take into account irreversible processes, e.g. all those occurring during crack opening for polymers (e.g. flash temperature at crack tip, cavitation in soft polymers, polymers chain extractions, etc…). For hydrated hydrogels, the dissipation occurring during solution ejections from the polymer matrix (a poroelastic effect) are also part of the effective work of adhesion and should be considered for a more accurate estimation of the work of adhesion; this should result in a velocity dependence, e.g. scaling with the viscosity of the solution.

Finally, in Figure 4d we show the friction force as a function of the squeezing load, as predicted by the theory with (dashed line) and without (solid line) adhesion, compared with the experimental results of Figure 3g (note that the HF||HF results have been halved to account for the individual contribution of each side of the double-sided construct). For the acid-pH solution we have assumed $\tau_w \approx 0.6 \, MPa$, whereas we neglect the friction contribution coming from the basic-pH actuated side. The adopted contact parameters are described above. The agreement between the model and the experiments is remarkable, supporting the proposed mechanism of adhesion.

Finally we note that the roughness increase under the acid-solution actuation (with respect to the basic case) determines a strong reduction in the true contact area (see Fig. 4c) in the range of applied normal loads, with consequent reduction of the measured nominal frictional shear stresses. Hence, a more detailed investigation would be particularly useful to relate fiber structures and surface morphology to the solution pH, a research activity that will be the subject of future investigations.
**Performance of Hydrogel Constructs**

Demonstrative experiments were performed by placing the double-sided nanohydrogel brushes between two PDMS blocks, which were pressed together by the means of a constant magnetic field (~12 N) (Figure 5a). When loaded with weights, the DSA senses friction forces ($F_f$) from both sides of the hydrogel construct and the downward pull force ($F_p$) in the vertical direction (Figure 5b). The composite brushes slides downward once the weight applied to the system overcomes the maximum static friction force. When both sides of the brushes are wetted by acid media (pH=2), the system was capable of supporting a book weighing 695 g with a normal load of ~12 N (Figure 5c). When one side is wetted by basic media (pH=12) and the other by acid media (pH=2), the load bearing capacity of the system reduces to less than 290g (Figure 5d-e). The system could only support a 20 g weight when both sides of the brushes were wetted by basic media (pH=12) (Figure 5f).

In order to display different friction actuating states on the double interfaces more intuitively, a commercial stainless steel tweezers is decorated by coating one layer of PDMS film for picking up the wetted double-sided gel composites piece (Figure 6a). After immersing into acid media (pH=2) for 30 min, gel fibers brushes on each side of the piece shrink sufficiently. As a result, the PDMS modified tweezers could easily pick up the wetted construct loaded using a 228 g weight (Figure 6b, Movie 1). However, after immersing into basic media (pH=12) for 30 min, gel fibers on both sides of the piece swell sufficiently to produce a hydrated state corresponding to very low friction.
Figure 5. (a) Demonstrative model of the loading experiments. The normal load was applied by a constant magnetic field ($H_{\text{middle}}=2.07$ mT, Load: 12N). (b) Photo shows the demonstrative setup and corresponding force analysis. (c) Weight loading photo of the double-sided nanohydrogel brushes when wetting both sides with acid media (pH=2); (d,e) wetting one side with acid media (pH=2) while the other side with basic media (pH=12); (f) wetting both sides with basic media (pH=12).

As a result, it is difficult for the PDMS-modified tweezers to hold the wetted hydrogel construct subjected to the weight corresponding to a 4 g stainless steel ball (Figure 6c, Movie 2). Similar demonstrations have also been performed when the testing system was completely immersed into aqueous solution, in which the friction force can be indirectly obtained by assessment of the load weight on the movable pulleys (Figure S14, Supporting Information, Movie 5). In details, when immersed into the acid media (pH=2), the double-sided construct can easily support a 178.2 g weight (Figure S15, left). However, when the same sample is immersed into the basic media (pH=12) it can hardly sustain the weight of 4.08 g steel ball when the same normal load is applied to clamp the
double-sided specimen (Figure S15, right). Interestingly, it is also found that the basic-pH wetted DSA also keeps very low friction when loaded against rubber; when sandwiched between two rubber sheets and subjected to the normal load corresponding to the weight of a person (~56 kg, see Figure 6d), the basic-pH wetted DSA was pulled out very easily, using a maximum force of only 2 N (Figure 6e, Movie 3 and Movie 4).

**Figure 6.** (a) Photo showing PDMS coated tweezers. (b) Photo showing that the double-sided nanohydrogel membrane could be easily clamped by the tweezers supporting a mass of ~228 g if both sides were wetted by acid media (pH=2) for 30 min, but could not hold ~4 g when wetted by basic media (pH=12) for 30 min (c). (d) Photos showing the double-sided gel composite film (wetted by basic media) and the rubber sheet used to clamp the double-sided construct, followed by application of foot contact with body’s normal load of 56 kg. (e) Demonstration for easy removal (200g drag) of the double-sided gel composite specimen when subjected to the full load, with the pull off force measured by the tensimeter.
Conclusions

Inspired by geckos’ capabilities to adhere to surfaces in both dry and wet environments, we have presented here a novel double-sided nanohydrogel fiber brushes infused composite membrane that could realize friction switching underwater when changing pH from basic (pH=12) to acid (pH=2) media. The composite membrane can show in situ, stable, fast and durable friction switching under high loads of 40 N (contact pressure: ~2.0MPa) between low and high frictional states without undergoing significant changes in its response for over 4 hours, i.e. about 10000 reciprocating sliding cycles in the testing configuration adopted in this investigation. Moreover, it is shown that four different states, corresponding to three different frictional and adhesive responses can be obtained by switching the behavior of the two sides of the composite construct, which was proven by supporting weight experiments. We have realized, for the first time, a synthetic double-sided gecko’s foot made from responsive hydrogels that has the capabilities to work underwater. We have also provided theoretical explanation for the mechanisms governing the hydration state responsible for the switching mechanisms. The agreement between the model and the experiments is remarkable and supports the proposed mechanism of adhesion. This novel design with symmetric or asymmetric modification opens great opportunities for developing intelligent interface actuated devices, which can adapt to multi-stimulus responsive complex environments, with wide potential applications in e.g. underwater robots, sensors and other bionic devices.
Supporting Information

Supporting Information Available: Description of the characterization, frictional testing and potential applications of the DSA construct. This material is available free of charge via the Internet at http://pubs.acs.org

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