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Photodetachable Adhesion

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Peeling from strong adhesion is hard, and sometimes painful. Herein, an approach is described to achieve both strong adhesion and easy detachment. The latter is triggered, on-demand, through an exposure to light of a certain frequency range. The principle of photodetachable adhesion is first demonstrated using two hydrogels as adherends. Each hydrogel has a covalent polymer network, but does not have functional groups for bonding, so that the two hydrogels by themselves adhere poorly. The two hydrogels, however, adhere strongly when an aqueous solution of polymer chains is spread on the surfaces of the hydrogels and is triggered to form a stitching polymer network in situ, in topological entanglement with the pre-existing polymer networks of the two hydrogels. The two hydrogels detach easily when the stitching polymer network is so functionalized that it undergoes a gel–sol transition in response to a UV light. For example, two pieces of alginate–polyacrylamide hydrogels achieve adhesion energies about 1400 and 10 J m^{-2}, respectively, before and after the UV radiation. Experiments are conducted to study the physics and chemistry of this strong and photodetachable adhesion, and to adhere and detach various materials, including hydrogels, elastomers, and inorganic solids.

Adhesives have been used in a sophisticated manner since antiquity.[1] Many recent advances involve adhesives for soft and wet materials in medicine and engineering. Examples include soft electronics,[2–4] biomedical devices,[5,6] wound dressing,[7–9] drug delivery,[10–12] and hydrogel ionotronics.[13–16] On-demand detachment is also important in many applications.[17–20] Upon completing the function, some components need be taken apart. For expensive or vulnerable adherends, the adhesion must be removed without harming the adherends.[21–23] Strong adhesion usually requires covalent bonds,[14,16,24] physical interactions,[25–27] or their combinations.[15,28,29] Adhesion through covalent bonds is typically hard to remove. Adhesion through physical interactions may be detachable, but usually requires solvents to act at the bonding front[25,30]; the operation can be time-consuming and environmentally harmful. Some traditional adhesives are chemically modified to be detachable upon a change in temperature (e.g., epoxy)[31,32] or an exposure of light (e.g., pressure-sensitive adhesive),[23,33] but they are usually cytotoxic and ineffective for wet materials like hydrogels and living tissues. Some bioinspired adhesion systems also use noncontact stimuli like temperature or magnetic field to trigger detachment.[34–36] Nevertheless, their adhesions rely on specific materials with special surface geometry, or generate low adhesion energy (1–10 J m^{-2}). Achieving both strong adhesion and easy detachment has been a challenge.

Here we describe an approach to achieve both strong adhesion and light-triggered easy detachment. We first describe the principle of strong and photodetachable adhesion using two hydrogels as adherends (**Figure 1**). Each hydrogel aggregates water molecules and a covalent polymer network. The polymer networks in the two hydrogels have no matching functional groups for bonding, so that the two hydrogels by themselves adhere poorly. We achieve strong adhesion by spreading an aqueous solution of polymer chains on the surfaces of the two hydrogels, and triggering the polymer chains to cross-link into a third polymer network in situ, in topological entanglement with the preexisting polymer networks of the two hydrogels. The third polymer network acts as a molecular suture that stitches the two preexisting polymer networks of the hydrogels together. This process is called topological adhesion, or topohesion for short.[25] We achieve photodetach by functionalizing the stitching polymer network for photodetach, and triggering the network to dissociate upon an exposure to light of a certain frequency range.

The principle described above requires two triggers. The first trigger, which we call the topohesion-trigger, causes the stitching polymer chains to cross-link into a new polymer network in topological entanglement with the preexisting polymer networks of the two hydrogels. The second trigger, which we call the photodetach-trigger, causes the stitching network to dissociate in response to light of certain frequency range. Conceivably the two triggers can be realized with various chemistries. Here we demonstrate topohesion and photodetach using two facts of chemistry: 1) Fe^{3+} ions and carboxyl groups form coordination complexes,[37,38] and 2) the coordination complexes

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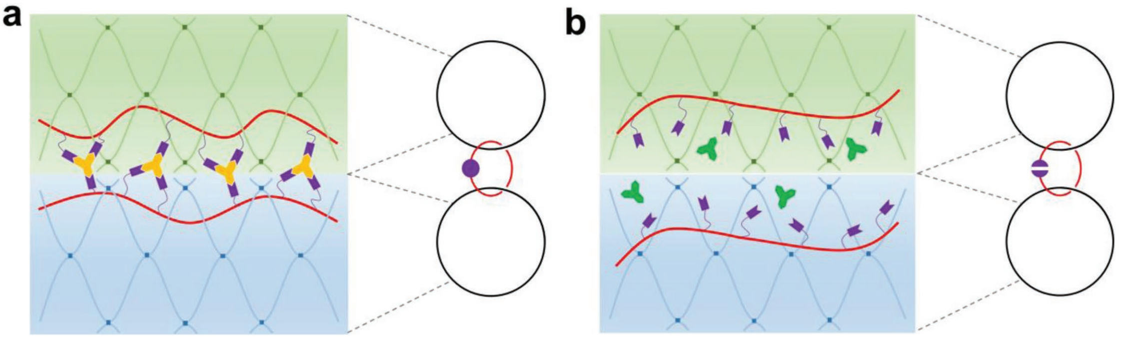

Figure 1. Principle of strong and photodetachable adhesion. The principle is illustrated using two pieces of hydrogels of covalent polymer networks as adherends, and an aqueous solution of polymer chains as an adhesive. a) For the two hydrogels to adhere strongly, the stitching polymer chains form a network in situ, in topological entanglement with the pre-existing polymer networks of the two hydrogels. b) For the two hydrogels to detach easily, a light of a certain frequency range breaks the stitching polymer network.

dissociate when the Fe^{3+} ions are reduced to Fe^{2+} ions upon an exposure to ultraviolet (UV) light.[39–41]

In our initial experiments, we spread an aqueous solution of poly(acrylic acid) (PAA) chains on the surfaces of two pieces of polyacrylamide (PAAm) hydrogel, and waited for some time for the PAA chains to diffuse into the hydrogels to small depths (**Figure 2**a). We then added an aqueous solution of Fe^{3+} and citric acid with controlled pH on one piece of hydrogel, and immediately pressed the other piece of hydrogel on top (Figure 2b). The Fe^{3+} ions diffused into the hydrogel, and formed the coordination complexes with the carboxyl groups on the PAA chains, which cross-linked into a PAA network, in topological entanglement with the two preexisting PAAm networks of the hydrogels. For the on-demand detachment, we exposed the adhered hydrogels to UV light (365 nm, 60 mW cm^{-2}) for a few minutes, so that Fe^{3+} ions were reduced to Fe^{2+} ions, and the PAA network dissociated (Figure 2c, Movie S1, Supporting Information).

To confirm topohesion and photodetach, we obtained SEM images of the interface of the two hydrogels. Without Fe^{3+}, the PAA polymer chains barely affected the networks of the two hydrogels. The SEM image showed a homogeneous porous structure in each hydrogel, along with a clear interface between the two hydrogels (Figure 2d). With Fe^{3+}, a dense interfacial zone formed, of thickness ≈10 µm (Figure 2e). The Fe^{3+} ions cross-linked the PAA chains into a network, which was anchored by the two preexisting PAAm networks through topological entanglement. After the UV radiation, the Fe^{3+}-cross-linked PAA network dissociated into polymer chains again. The dense interfacial zone disappeared, and a clear interface reappeared (Figure 2f).

To further confirm topohesion and photodetach, we measured adhesion energy using the peeling test. Without Fe^{3+}, the PAA chains did not form a network, and the two hydrogels peeled easily along the interface, giving a low adhesion energy of ≈10 J m^{-2} (Figure 2g). With Fe^{3+}, the PAA chains turned into a network in topological entanglement with the networks of the two hydrogels, and the two hydrogels peeled by cohesive failure, generating a high adhesion energy of ≈200 J m^{-2} (Figure 2h, Figure S1a and Movie S2, Supporting Information). After an exposure to the UV light, the PAA network dissociated, and the two hydrogels peeled easily along the interface, giving again a low adhesion energy of ≈10 J m^{-2} (Figure 2i, Figure S1b and Movie S3, Supporting Information). We note that the adhesion energy of two pieces PAAm hydrogels without any treatment is ≈10 J m^{-2}, and the fracture energy of the PAAm hydrogel is ≈200 J m^{-2}.

The topohesion was strongly affected by the rheology of PAA gelation. We controlled the gelation of the PAA solution by adding an aqueous solution of Fe^{3+} and citric acid with controlled pH. Each molecule of citric acid has three carboxyl groups, and the protonation of citric acid in an aqueous solution increases with pH (Figure S2 Supporting Information).[42–44] Consequently, citric acid and PAA chains compete for Fe^{3+} ions to form coordination complexes. This competition affects the Fe^{3+}-triggered sol–gel transition of PAA. We measured the storage modulus and loss modulus as functions of time (Figure S3, Supporting Information). Without citric acid, the free Fe^{3+} caused a rapid gelation of PAA and high storage modulus. With citric acid, and as pH increased, the gelation time expanded and the equilibrium storage modulus decreased. At pH = 6, PAA chains no longer cross-linked.

We next studied the physics and chemistry of the topohesion and photodetach by measuring the adhesion energy as a function of several variables (**Figure 3**). In a typical experiment, we spread 2 ml PAA solution (20 wt%, 24 W M_w) on the surfaces of the two PAAm hydrogels, waited for 20 min, added 100 µL of the aqueous solution of Fe^{3+} and citric acid with a pH of 3 on one hydrogel surface, and pressed the two hydrogels together with a strain d/L of 10% for 30 min. To detach, we exposed the adhered hydrogels to UV light (365 nm, 60 mW cm^{-2}) for 3 min. For each curve in Figure 3, we changed variable and fixed all other variables to the conditions above. The experiment for each value of the variable was repeated with at least three samples.

The rheology of PAA gelation correlated well with the adhesion energy (Figure 3a). Without citric acid, the Fe^{3+} solution on the PAA-coated hydrogel only produced an adhesion energy of ≈40 J m^{-2}, far less than the fracture energy of PAAm hydrogel (≈200 J m^{-2}). The gelation was too fast that a hard shell of PAA gel formed immediately on the surface between the two PAAm hydrogels, resulting in heterogeneous bonding interface. When we stretched two adhered hydrogels, the rigid plaques could be seen obviously at the interface (Figure S4a, Supporting Information). In comparison, a solution of Fe^{3+} and citric acid

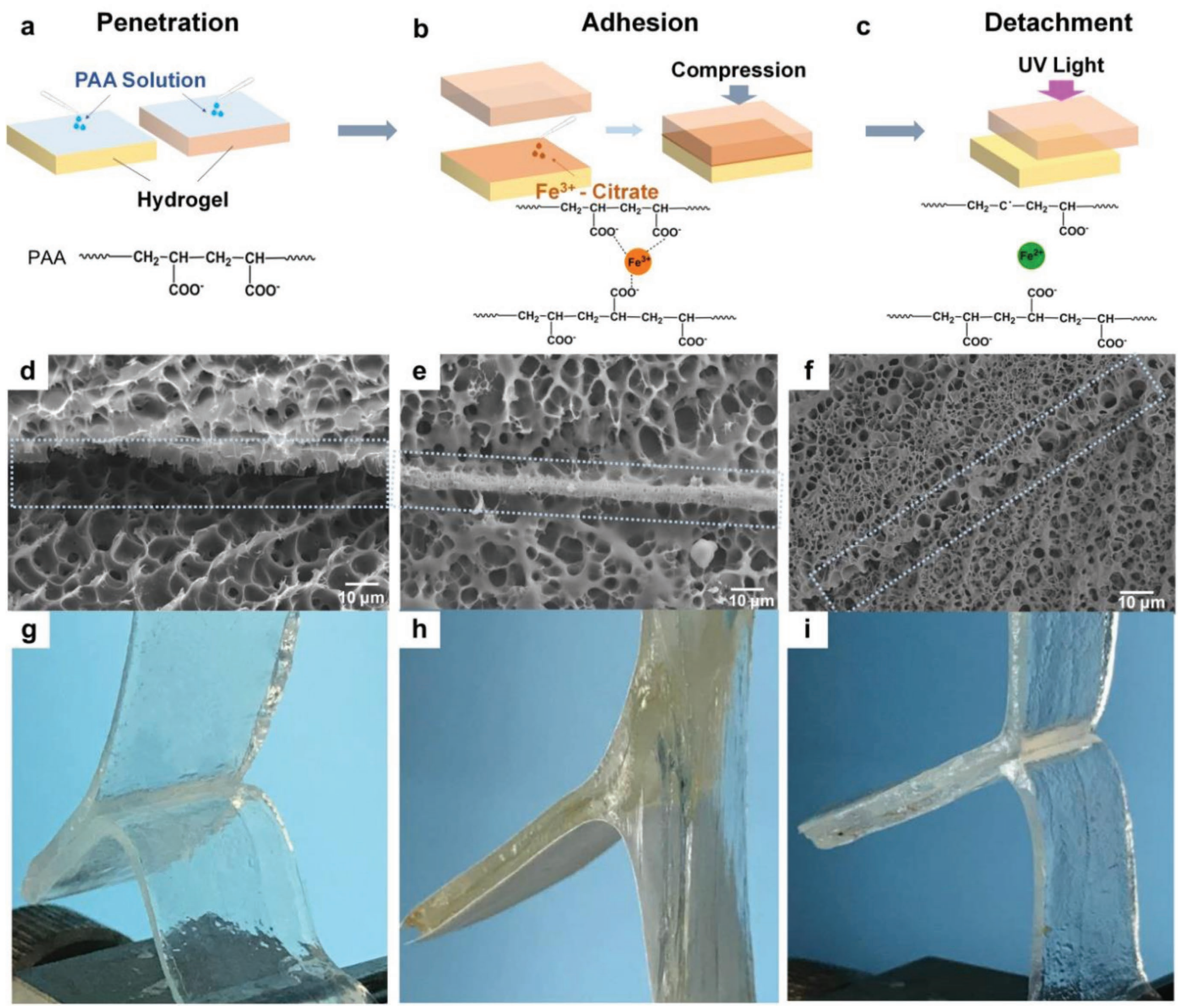

Figure 2. Photodetachable adhesion of two pieces of polyacrylamide (PAAm) hydrogels. a) Spread an aqueous solution of polyacrylic acid (PAA) on both PAAm surfaces, and let the PAA chains diffuse into the PAAm hydrogels. b) Spread an aqueous solution of Fe^{3+} and citric acid with controlled pH on one PAAm surface, and compress the other piece of hydrogel on top. The Fe^{3+} ions diffuse into the hydrogels and cross-link the PAA chains into a network, in topological entanglement with the two PAAm networks, so that the two PAAm hydrogels adhere strongly. c) Shine a UV light on the adhered hydrogels, reduce Fe^{3+} to Fe^{2+}, and decarboxylate PAA, so that the two PAAm hydrogels detach easily. d–f) SEM images of the interface. g–i) Photos of peeling tests.

with pH of 1.5 on the PAA-coated hydrogel slightly increased the adhesion energy. Lowering the gelation rate ensured Fe^{3+} to diffuse deeper into the hydrogels and cross-link PAA chains more uniformly. The maximum adhesion energy of 200 J m^{-2} was achieved when the solution of Fe^{3+} and citric acid had a pH of 3. A gelation time of 4 min was enough to form a PAA network thick enough in the two hydrogels. The relatively high equilibrium storage modulus indicated that this PAA gel network was strong enough to entangle with the PAAm networks and pull them during the peeling. Under this condition, a transparent interface could be seen when we stretched two adhered hydrogels (Figure S4b, Supporting Information). Further increasing the pH decreased adhesion energy, as the complexes of Fe^{3+} and citric acid would diffuse into the hydrogels without cross-linking the PAA chains. With a pH = 6, the adhesion energy dropped to ≈10 J m^{-2}.

The photodetach was closely related to the power and frequency of light. We found that UV light (365 nm) was highly effective to trigger easy detachment. Under a 3 min' UV exposure, the final adhesion energy decreased as the intensity increased (Figure 3b). However, the adhesion was stable in natural light: over 120 h of exposure in natural light caused no measurable decline in adhesion energy (Figure 3c). Thus, the detachment could be triggered on demand under specific stimuli, and avoided undesirable loss of adhesion during long-time services. In practical applications, to avoid unwanted degradation of adhesion, a UV blocking layer may be added to the surface.

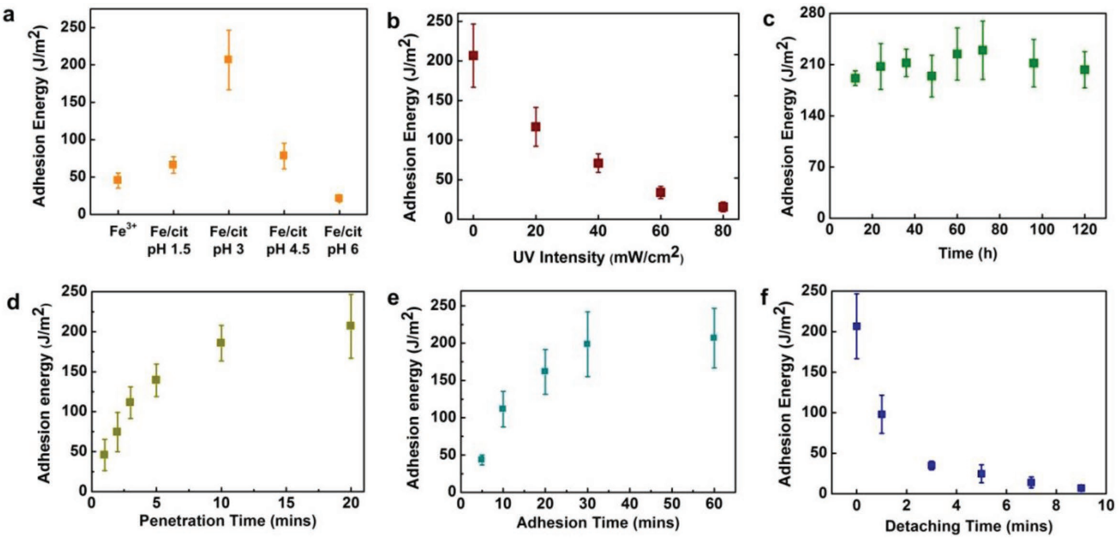

Figure 3. Adhesion energy as a function of several variables. Generally, PAA solution first penetrated for 20 min to PAAm hydrogels, then the two hydrogels were adhered for 30 min by adding Fe^{3+}/citric acid aqueous solution with a pH of 3. To detach, the adhered hydrogels were exposed to UV light (365 nm, 60 mW cm^{-2}) for 3 min. The effect of each variable was measured by changing the one variable with all others fixed. a) Adhesion energy changes with the initial pH of the aqueous solution of Fe^{3+} and citric acid. b) Final adhesion energy decreases as the UV intensity increases. c) Adhesion energy remains stable for a long period of time after exposed to sunlight. d) Adhesion energy increases with penetration time. e) Adhesion energy increases with adhesion time. f) Adhesion energy decreases with UV radiation time.

To characterize the kinetics of topohesion and photodetach, we measured the adhesion energy as functions of three durations of time: the time for PAA penetration, for PAA gelation, and for UV exposure. As the time increased between the spreading of the PAA solution and the spreading of the Fe^{3+}/citric-acid solution, the PAA chains diffused deeper into the hydrogels, and resulted in a higher adhesion energy. By 10-minute penetration, the PAA chains in hydrogel were concentrated enough to generate the maximum adhesion energy (Figure 3d). The PAA gelation started when we added the Fe^{3+}/citric-acid solution on the PAA-coated PAAm hydrogel. The adhesion energy increased as the PAA gelation progressed, reached ≈50 J m^{-2} after 5 min of gelation, and achieved the maximum value in 30 min (Figure 3e). This time-sequence of the adhesion energy tracked well with the time sequence of the storage modulus during the gelation of PAA (Figure S3c, Supporting Information). In photodetach, the adhesion energy dropped by 50% after 1 minute of UV radiation (60 mW cm^{-2}), and by over 90% after 3 min (Figure 3f).

In addition to PAA, other carboxyl-containing polymers like alginate, carboxymethyl cellulose (CMC), hyaluronic acid (HA) can also enable photodetachable adhesion. The adhesion energies achieved by these polymers were lower than that by PAA (**Figure 4**a). The natural polysaccharides (such as CMC and alginate) contain a lot of —OH and —COOH on their polymer chains. Hydrogen bonds are easy to form between each other. These solutions have high viscosity, and the affinity between the stitching polymers make them more difficult to penetrate into hydrogel. In addition, the carboxyl groups for Fe^{3+} binding on their chains may be not as abundant as those on PAA. Nevertheless,

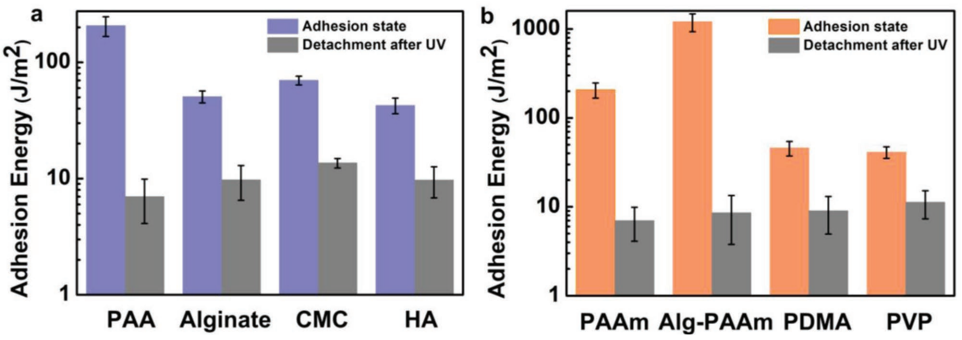

Figure 4. Adhesion energies before and after UV radiation for various stitching polymers and hydrogels. a) Two pieces of PAAm hydrogels adhered by using several kinds of stitching polymers: PAA, alginate, carboxymethylcellulose (CMC), and hyaluronic acid (HA). b) PAA chains were used to adhere several kinds of hydrogels: two pieces of PAAm hydrogels, two pieces of alginate–PAAm hydrogels, two pieces of PDMA hydrogels and two pieces of PVP hydrogels.

these polymers still gave rise to adhesion energy of 60–90 J m^{-2}, which might be strong enough for many practical applications. Furthermore, after an exposure of the UV light (60 mW cm^{-2}, 3 min), the adhesion energies all reduced to ≈10 J m^{-2}.

Strong and photodetachable adhesion was also achieved between various kinds of hydrogels (Figure 4b). In particular, an alginate–polyacrylamide (Alg-PAAm) hydrogel had two interpenetrating networks: the network of polyacrylamide chains cross-linked by covalent bonds, and the network of alginate chains cross-linked by ionic bonds. When stretched, the covalent cross-links remained intact, but the ionic cross-links unzipped, so that the Alg-PAAm hydrogel was highly dissipative.[45] We adhered two pieces of the Alg-PAAm hydrogel using the Fe^{3+}-cross-linked PAA network. The PAA network was in topological entanglement with the PAAm networks in the hydrogels, and was strong enough to elicit energy dissipation in a large volume of the hydrogels, leading to a high adhesion energy of ≈1400 J m^{-2} (Figure S1, Supporting Information). The adhesion energy was comparable to the fracture energy of the hydrogel, so that peeling caused cohesive failure. By contrast, after 3 min of UV radiation (60 mW cm^{-2}), the PAA network dissociated, and peeling no longer elicited the energy dissipation in the bulk of

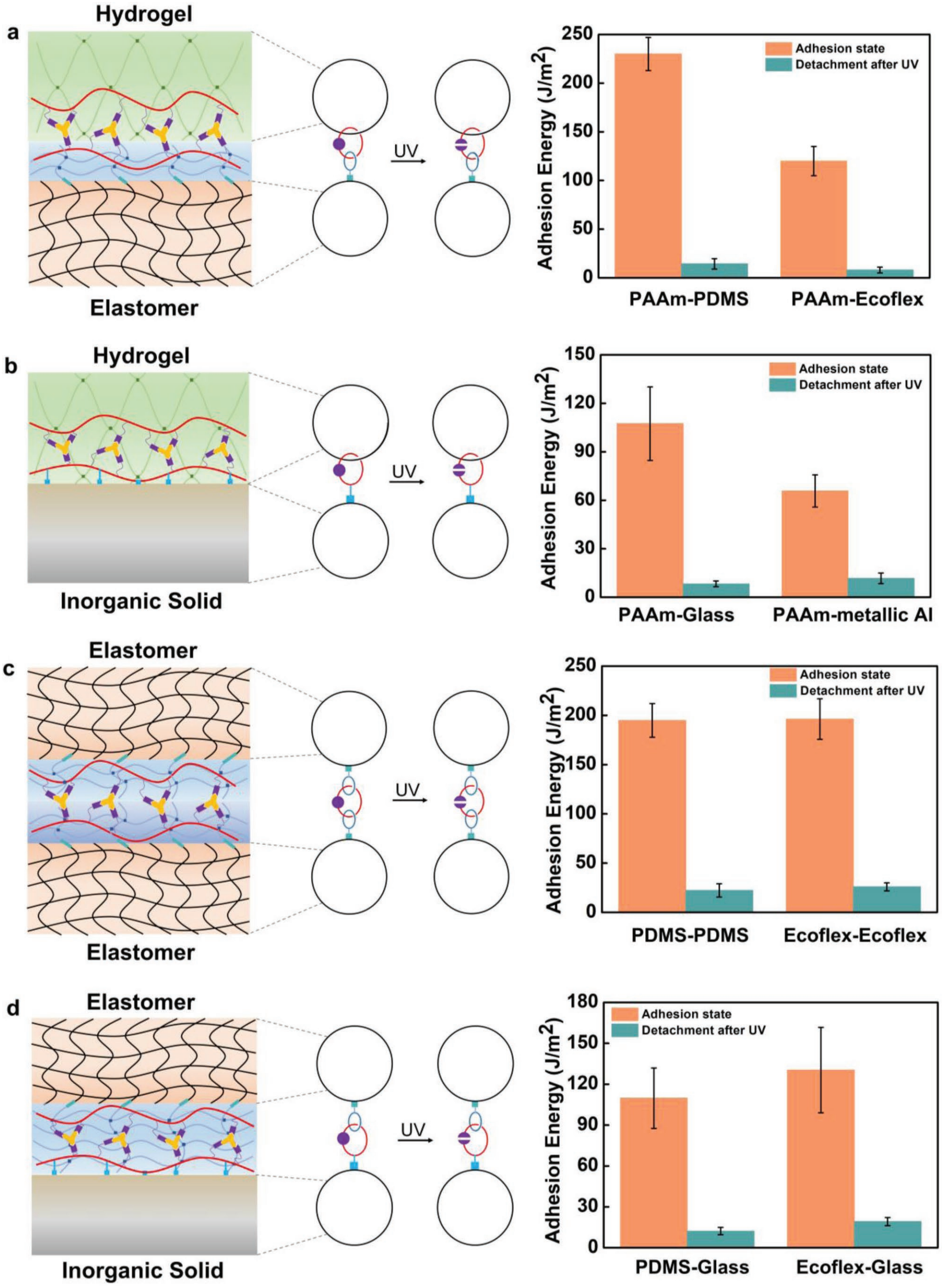

Figure 5. Photodetachable adhesion between various adherends: a) hydrogel–elastomer; b) hydrogel–inorganic solid; c) elastomer–elastomer; d) elastomer–inorganic solid.

the hydrogels. The adhesion energies dropped to ≈10 J m^{-2}, which ensured easy detachment along the interface. Two other kinds of hydrogels, Poly(*N*,*N*-dimethylacrylamide) (PDMA) and Poly(*N*-vinyl-2-pyrrolidone) (PVP), were less dissipative than Alg-PAAm. Nonetheless, they both achieved significant difference in adhesion energies before and after UV exposure. As the skin and organs are permeable matrix similar to hydrogel, adhesion between hydrogel and these living materials can also be achieved (Figure S5, Supporting Information). We adhered PAAm hydrogel to porcine skin and liver (purchased from a local grocery store) by the Fe^{3+}-cross-linked PAA network. The tissue is less permeable than the hydrogel. We achieved relatively high adhesion energy by using PAA polymer of smaller molecular weight (5000 M_w). As expected, the PAAm hydrogel could also be easily detached from tissue surfaces after UV exposure.

We now consider photodetachable adhesion for adherends of all kinds: elastomers, inorganic solids, as well as hydrogels. The stitching network connects the adherends through three basic modes: topological entanglement with the network of an adherend, topological entanglement with a network that is chemically bonded to an adherend, and direct bond to an adherend. The three basic modes in various combinations will enable the iron-carboxyl chemistry to realize photodetachable adhesion between adherends of all kinds. This versatility is illustrated with several examples (**Figure 5**). We achieved photodetachable adhesion between a hydrogel and a hydrophobic elastomer. We coated a thin layer of hydrogel on the surface of the elastomer using benzophenone (Figure S6, Supporting Information),[16] and then stitched the hydrogel-coated elastomer and a piece of hydrogel together by a Fe^{3+}-cross-linked PAA network. We also achieved photodetachable adhesion between hydrogels and inorganic solids. We used oxygen plasma to add -OH groups on the solid surface, and then used silanes to anchor PAA chains to the solid surface (Figure S7, Supporting Information). These PAA chains participated in the formation of a stitching network, in topological entanglement with the preexisting network of the hydrogel. We similarly achieved photodetachable adhesion between two elastomers, as well as between an elastomer and an inorganic solid. In the last two examples, because adherends are all dry solids, it may be desirable to develop nonaqueous photodetachable adhesion. This development will require us to abandon the iron-carboxyl chemistry, and will not be pursued here.

Strong and photodetachable adhesion may enable broad applications. As a first example, in wound dressing and transdermal drug delivery, strong adhesion between a hydrogel and the skin may be required for intimate contact without limiting the movements of the patient. Noninvasive and painless detach is also required when the function of the hydrogel is completed. Compared with traditional pressure sensitive adhesive tape or bioinspired adhesive pad using microstructures such as microsuction cups,[46] adhering a hydrogel to skin using our adhesion approach may be more time-consuming. However, this strategy has the advantages such as water-resistant strong adhesion, painless detach, and wound healing benefited from the hydrogel environment. As a second example, in manufacturing flexible devices, the transfer of thin films of devices from a donor to a target substrate requires strong adhesion and easy detach between plastic and metals. As a third example, strong adhesion detachable in response to light of different frequency ranges can be designed. For example, near-infrared (nIR) light detachable adhesion may be realized by introducing the nIR light cleavable moiety like o-nitrobenzyl or coumarin into the backbone of the stitching polymer.[47] As the nIR light is not significantly absorbed by most biomaterials, detachment in response to nIR light may enable new medical procedures. All these examples motivate further development of photodetachable adhesion.

In summary, we have demonstrated photodetachable adhesion between various materials. Whereas photodetachable adhesion can be realized using various chemistries, here we demonstrate the principle using the iron-carboxyl chemistry. This chemistry provides two triggers: a topohesion-trigger for strong adhesion, and a photodetach-trigger for easy detachment. It is hoped that the combined characteristics of strong adhesion and easy detachment will be developed using various chemistries to open doors to innovation in medicine and engineering.

Experimental Section

Details on the materials and methods are available in the Supporting Information.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

hydrogels, light-triggered, photodetachable adhesion, topological adhesion

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