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Tough Bonding, On-Demand Debonding, and Facile Rebonding between Hydrogels and Diverse Metal Surfaces

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Hybrid systems of hydrogels and metals with tough bonding may find widespread applications. Here, a simple and universal method to obtain strong adhesion between hydrogels and diverse metal surfaces, such as titanium, steel, nickel, tantalum, argentum, and aluminum, with adhesion energy up to >1000 J m^{-2} is reported. To achieve such, the metal surfaces are instantly modified with a linker molecule via soaking, dip-coating, or drop-casting. The designed linker molecule has a carboxylic acid group to bind with a metal surface, and a methacrylic group to crosslink with a hydrogel, thus bridging the interface between them. In addition, by introducing a stimulus-responsive disulfide bond into the linker molecule, the on-demand debonding between toughly bonded hydrogel and metal surface, which is enabled by reductive cleavage of the disulfide chemical linkage, is also demonstrated. More interestingly, after the reductive debonding, the resulting metal surface with free thiol groups can be easily rebonded with a second hydrogel without any further surface modification. The strategy may provide unique opportunities in designing hybrid devices that are suitable for complex and dynamic environments.

The human body is an integrated complex system of many dissimilar components. For instance, the bonding between tendon and cartilage to bone tissues is the structural basis for body movement. From a biomimetic viewpoint, combining materials with drastically different chemical compositions and mechanical characteristics might provide the hybrid systems with superior properties and functions. One good example could be the combination of hydrogels and metals, which has been suggested as promising candidates for designing advanced implants that unite the strong mechanical properties (stiffness, fatigue resistance, strength, and damping) of metals as the load-bearing components,[1,2] and the bioactivity of hydrogels for purposes such as delivery[3,4] and promotion of tissue healing.[5] Such metal–hydrogel hybrid implants might potentially facilitate the success of implant metal devices and biointegration of interfaces at the soft and hard tissues.[6–8] Moreover, it has been recently shown that the hybridization of hydrogels with metals and other solid substrates may produce new synergistic materials that possess unprecedented levels of structural and functional features,[9–13] which can be used for hydrogel painting,[14] sensors,[15] and soft robots,[16] among others. For these applications, one critical issue is to form tough and robust bonding between hydrogels and other solid substrates.

Due to their distinct mechanical and chemical properties, tough bonding of hydrogels to metal surfaces has been a challenge. Traditional methods include electrochemical[17] and photochemical[18] reactions as well as layer-by-layer depositions,[19] which result in complex adhesion mechanisms but only moderate interfacial adhesion energy. Frank and co-workers reported a silane chemistry-based procedure to chemically graft hydrogels to Ti surfaces via in situ photopolymerization.[6] By combining with recently developed tough hydrogels,[13,20–23] Zhao and co-workers extended this silane-based chemical anchoring strategy to various nonporous solid surfaces and achieved tough bonding between them with adhesion energy up to >1000 J m^{-2}, which exceeds the interfacial bonding of tendon and cartilage to bone tissues.[11] Such high interfacial adhesion is attributed to both the chemical anchorage of the long-chain polymer networks onto the solid surfaces, and the mechanical energy dissipation enabled by the double-network tough hydrogels.[11,20,24] This silane-based strategy is also applicable to interface engineering in hydrogel–elastomer hybrid systems with high adhesion energy.[11,12,25] Very recently, Suo and co-workers initiated a novel concept of "topological adhesion,"[26–28] and demonstrated bonding of hydrogels to

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metal surfaces via stitching polymer chains at the interfaces. However, introduction of such stitching polymer chains onto metal surfaces still required multiple processes with relatively harsh conditions.[26]

From previous reports, we noticed that there still lacks a general method for instant surface modification of diverse metals and tough bonding of hydrogels thereafter. Moreover, most previously reported methods will create permanent strong adhesion of hydrogels to other solid surfaces.[10–13,22,29] To our knowledge, subsequent on-demand debonding of the toughly bonded components is rare,[27,30] which, however, can provide a higher level of flexibility toward rational design of functional "smart" materials and devices for applications in dynamic and complex situations.[30]

Herein, we report a simple and universal approach for tough bonding and on-demand debonding of hydrogels to common metal substrates, including nickel (Ni), aluminum (Al), tantalums (Ta), argentum (Ag), stainless steel, titanium (Ti), and some of their alloys. Surface modification of metals and chemical anchorage of hydrogels to metal surfaces are realized via a designed linker molecule, which contains a carboxylic acid group to bind with metal surfaces and a methacrylic group to chemically connect with the polymeric hydrogel network (**Figure 1**). Binding of linker molecules to metal surfaces can be achieved within a few minutes via simple soaking, dip-coating, or drop-casting processes.[31] The resulting adhesion energy between hydrogels and metals can reach up to >1000 J m^{-2}, comparable to that between cartilage and bone of mankind. To debond, the chemical structure of the linker molecule is modified with a disulfide group, which can respond to reduction agents such as glutathione (GSH), a tripeptide containing a thiol group.[32] Upon breaking the disulfide bond in the linker molecules that bridge the interfaces of hydrogels and metals, the tough bonding can be released, which also enables facile reprocessing for further modification (e.g., rebonding) of the debonded metal substrates.

To form tough bonding of hydrogels to solid surfaces, a key challenge is the introduction of surface chemical anchors.[10] For metal and metal oxide surfaces, common surface modification methods reply on chemicals that can react or strongly interact with metal surfaces, such as silanes,[10] polydopamines,[33] phosphonates,[34] and carboxylic acids.[31,35] Among them, we selected the carboxylic acid group for surface modification due to the versatility, facile processing under mild conditions, and low cost (**Figure 2**a). Previous studies have also proved that carboxylate groups can bind strongly to the surfaces of a range of metals and metal oxides.[31,35]

A prototype Linker-1 molecule was prepared by one-step amidation reaction of 12-aminolauric acid and methacrylic anhydride (Scheme S1, Supporting Information), which can be easily scaled up to tens of grams (Figure S1, Supporting Information). To enhance the binding affinity, the Linker-1 molecule was converted to its ammonia salt by neutralization. Modification of diverse metal surfaces, including Ni, Al, Ta, Ag, stainless steel, Ti, and Ti alloy, was completed by simple drop-casting and washing processes (see the Supporting Information for details). The interaction between Linker-1 and metal surfaces is mainly attributed to the coordination of deprotonated carboxylate groups to metal ions, along with contributions from the electrostatic and hydrophobic interactions.[31,35]

Attachment of Linker-1 on metal surfaces was confirmed by X-ray photoelectron spectroscopy (XPS). As shown in Figure S2 of the Supporting Information, the XPS data revealed the characteristic peak of N elements, peaks of C elements with increased intensities, and in particular, peaks attributed to C elements in carboxylate groups. Moreover, in the attenuated

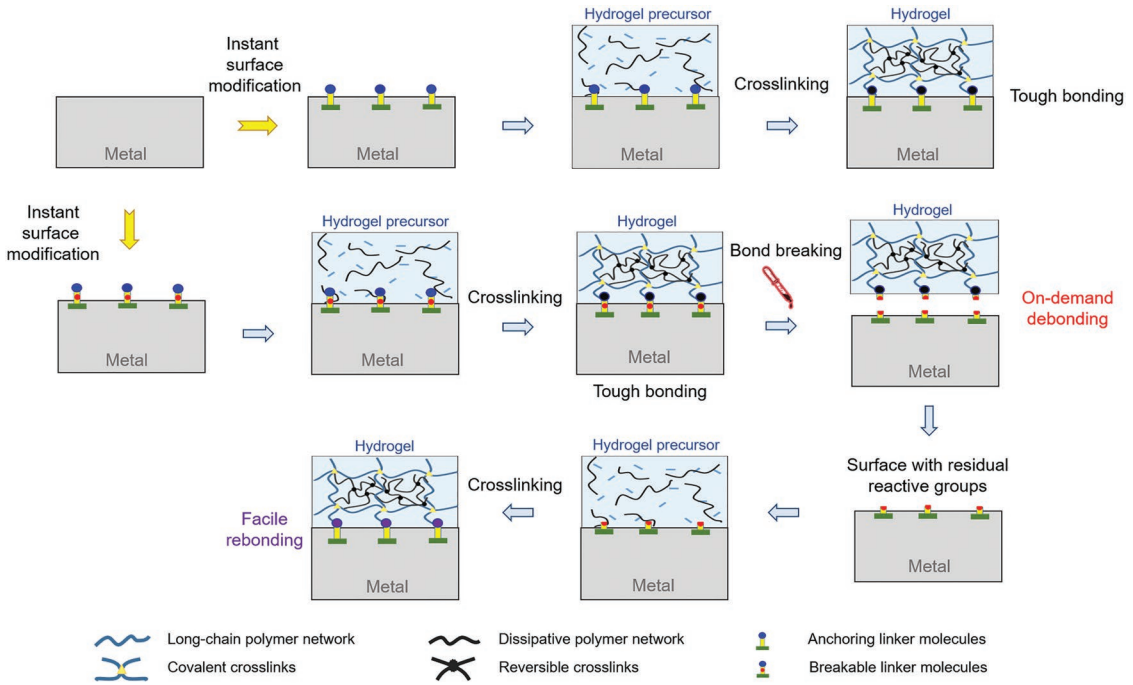

Figure 1. Design strategy for tough bonding, on-demand debonding, and facile rebonding of hydrogels to diverse metal surfaces.

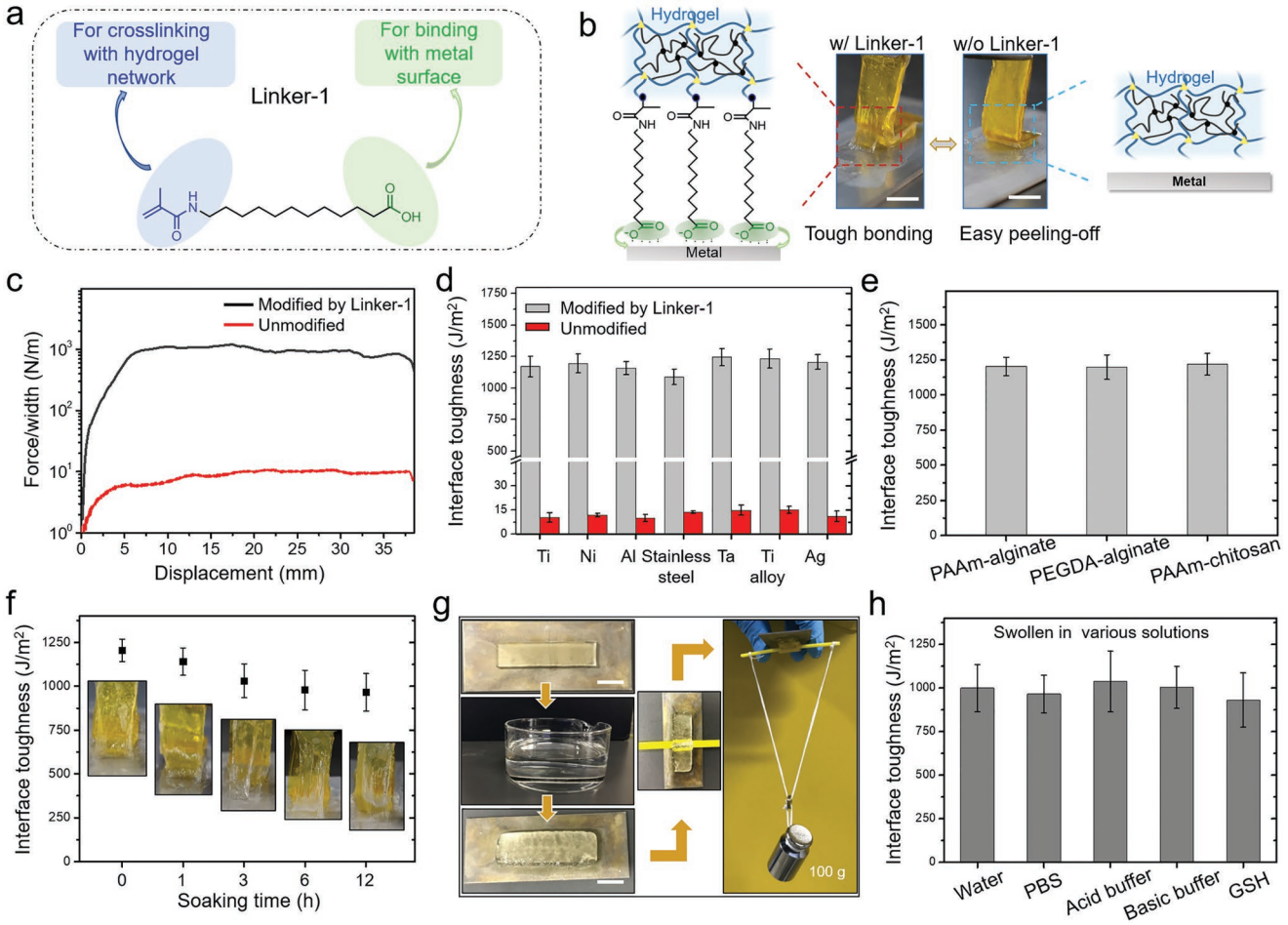

Figure 2. Tough bonding between hydrogels and diverse metal surfaces via Linker-1. a) Molecular structure of the Linker-1 as the bridge between hydrogels and metal substrates. b) Photographs of the 90° peeling tests of tough hydrogels bonded to Ti substrates (left) with and (right) without treatment by Linker-1. A yellow Kapton film was used as the stiff backing for hydrogels. Chemical anchoring of hydrogel networks via Linker-1 was the key for tough bonding. Scale bars: 5 mm. c) Representative force–displacement curves obtained from the 90° peeling tests of bonded hydrogel–metal systems with and without treatment by Linker-1. d) Measured interfacial toughness values of hydrogels bonded to diverse metals via Linker-1. e) Measured interfacial toughness values for different tough hydrogel systems chemically anchored to Ti substrates. f) Measured interfacial toughness at different soaking time in DI water. g) Image showing the capability of a swollen hydrogel attached to a Ti substrate to resist a weight of 100 g. Scale bars: 10 mm. h) Measured interfacial toughness values of PAAm-alginate hydrogels bonded to Ti substrates after swelling under different conditions.

total reflection Fourier-transform infrared spectroscopy (ATR FT-IR) data of the metal surfaces after treatment by Linker-1, characteristic peaks of C=O (in carboxyl groups) and C=C bonds appeared at 1750 and 1600 cm^{-1}, respectively (Figure S3, Supporting Information). From these results, we concluded that the surface modification successfully generated a monolayer of Linker-1 molecules at the metal surface,[35] which provided reactive methacrylic groups for chemical anchoring of hydrogels.

We then chose the well-documented tough hydrogel system based on alginate/Ca^{2+} and polyacrylamide (PAAm) or polyethylene glycol diacrylate (PEGDA) double networks as the model hydrogels[20] to bond with the treated metal surfaces. Precursor solutions were applied to modified metal surfaces and photo-crosslinked to form hydrogels. During the irradiation, the double bonds in the linker molecules, the acrylamide monomers, and the crosslinkers copolymerized to form one chemically interconnected network, which was fully penetrated by the physical network formed by complexation of alginate and Ca^{2+}. Untreated metal substrates were used as the control group to coat with hydrogels under otherwise identical conditions.

The standard 90° peeling test was then performed to measure the adhesion energy. A 70-µm-thick Kapton film was glued to the reverse side of the hydrogel sample as the backing to prevent elongation during peeling. For chemically bonded samples, we observed a typical cracking pattern as the peeling displacement increased (Figure 2b), which was similar to the reported system of tough hydrogels anchored by silanes.[10] Impressively, the measured bonding energy between the PAAm/alginate hydrogels and Linker-1-treated Ti surfaces reached as high as 1200 J m^{-2} (Figure 2c; Figure S4, Supporting Information), which was comparable to the strong bonding found between natural tendon or cartilage and bones.[36] For other metal substrates, the average bonding energies were similarly high (1000–1200 J m^{-2}, see Figure 2d). Moreover, other hydrogels, such as the PEGDA/alginate and the PAAm/chitosan hydrogels, could generate similar interfacial toughness

values (Figure 2e). On the contrary, hydrogels were found to bond poorly to untreated metal surfaces with typical measured values <100 J m^{-2} (Figure 2d).

To test the stability of tough bonding enabled by Linker-1, the bonded hydrogel–metal systems were immersed in deionized (DI) water, and the bonding energies were measured at different time points. Although slightly decreasing with immersing time, the recorded interfacial toughness values were still close to 1000 J m^{-2} after fully swollen for up to 1 week (Figure 2f–h; Figure S5, Supporting Information). Besides, swelling the bonded hydrogels in neutral (pH = 7), weakly acidic (pH = 5), and basic (pH = 9) buffer solutions for 12 h did not significantly lower the bonding energies (Figure 2h).

To further confirm that the methacrylic group in Linker-1 provides the chemical anchoring sites at the metal surface, we immersed Ti substrates treated by Linker-1 in DI water and an aqueous solution of lauric acid sodium salt (75 mg mL^{-1}). After 6 h, Ti substrates washed by DI water could still form tough bonding with hydrogels with similar bonding toughness (Figure S6, Supporting Information). However, after treatment by lauric acid sodium salt, the resulting substrates lost the capability to bond with hydrogels. These results indicated that lauric acid could also bind with metal surfaces to replace Linker-1 molecules via competing coordination interactions, forming a layer of lauric acid molecules without chemical anchors.

It is worth noting that although the dissociation energy of one carboxylate group binding to metal surfaces was relatively weak, the aggregation of many bonds together enhances the interaction and thus leads to collectively high bonding energy.[31,37] In this sense, the role of our linker molecules is very similar to the bridging polymers that act to strongly adhere tough hydrogels to wet tissue surfaces, as recently demonstrated by Mooney and co-workers.[38] Interestingly, although the chemical structures of alginate also contain carboxylate groups, they were not able to form strong binding with the metal substrates. This difference might be attributed to the different densities of chemical anchorage points at the hydrogel–metal interfaces. Without the linkers, the conformational rigidity of the polysaccharide backbone of alginate and the complexation of alginate with calcium ions prevented the formation of high-density chemical anchorage.

It has been suggested that the coordination interaction of carboxylate groups to metal surfaces is a pH-dependent phenomenon.[31,35] When the environmental pH was below the p*K*a value of Linker-1 (estimated as ≈4.4 from literature[39]), the carboxylate group would be protonated into a neutral carboxylic acid group and the interfacial coordination interaction with metal surfaces would be broken. Indeed, when the toughly bonded hydrogel–metal hybrids were immersed in a pH = 4.0 buffer for 6 h, we observed the debonding of hydrogels from the metal substrates, due to the loss of interfacial chemical anchoring (Figure S7, Supporting Information). Although not stable under acidic conditions of pH < 4.0, our Linker-1 molecule is still considered of great interest in achieving tough bonding between hydrogels and metal surfaces under physiological conditions.

Based on these results, it was reasoned that by eliminating the chemical anchorage via an external stimulus, on-demand debonding between hydrogels and metal surfaces could be realized. To achieve this under a milder condition, we modified the chemical structure of Linker-1 by introducing a breakable disulfide bond to prepare the Linker-2 molecule (Scheme S2 and Figure S8, Supporting Information). Both linker molecules share the carboxylic acid and double bond groups, while the disulfide bond render additional stimuli-responsive property to Linker-2 (**Figure 3**a). Similarly, we demonstrated that Linker-2 could also modify metal surfaces (see XPS data shown in Figures S2 and S9, Supporting Information, and FT-IR spectrum in Figure S10, Supporting Information), thus achieving tough bonding between hydrogels to diverse metal surfaces (Figures S10 and S11, Supporting Information). The measured interfacial adhesion energy values were indeed comparable to those obtained from Linker-1 (Figure 3c), indicating that this change in the chemical structures of linker molecules did not significantly alter the interfacial bonding toughness.

To debond, we treated the bonded hybrid system with a GSH solution (1.0 wt%). GSH is a reductive tripeptide containing a pendant thiol group, which has the well-known reactivity to break disulfide bonds into thiol groups under physiological conditions (Figure 3a).[34] In less than 30 min, the hydrogel layer could be easily removed from the metal surface since there were no longer chemical anchoring bonds at the interface (Figure 3b). Quantitatively, the 90° peeling tests revealed largely reduced adhesion energy (less than 100 J m^{-2}) for different tough hydrogels bonded to various metal surfaces via Linker-2 after GSH treatment (Figures S12 and S13, Supporting Information). On the contrary, when immersed in DI water or other buffer solutions, the bonding toughness of swollen hydrogel–metal systems did not show dramatic changes (Figure 3c,e, Figure S12, Supporting Information). In the FT-IR spectrum of the debonded Ti substrate, the absorption peak of C=C bonds disappeared, while weak absorption peaks at 2550–2590 cm^{-1} appeared, indicating the presence of thiol groups (Figure S10, Supporting Information). Therefore, we attributed the debonding by GSH treatment to the breaking of the disulfide bond in Linker-2 molecules. It is worth mentioning that after GSH treatment, efforts to rebond the peeled hydrogel back to the metal substrates via oxidation of thiol groups failed, probably due to the low efficiency to form interfacial anchoring in this manner. Such on-demand debonding of hydrogels and metals may offer new possibilities to design "smart" materials and devices.

The disulfide group (-S-S-) is also a possible ligand to bind with metal surfaces. To elucidate the interactions of Linker-2 with metal surfaces, we tested the competing binding capability of Linker-2 with both lauric acid and ethyl (R)-5-(1,2-dithiolan-3-yl) pentanoate, which contain only a carboxylic acid group and a disulfide group, respectively. We used the mixed solutions of Linker-2/lauric acid and Linker-2/ethyl (R)-5-(1,2-dithiolan-3-yl) pentanoate at a 1:1 molar ratio to modify Ti substrates, and then tested the bonding energy of hydrogels with the resulting Ti surfaces. It was shown that lauric acid was a strong competitor for Linker-2, but ethyl (R)-5-(1,2-dithiolan-3-yl) pentanoate with a disulfide group could not significantly affect the binding of Linker-2 with metal surfaces (Figure S14, Supporting Information).

More interestingly, after treatment by GSH, the residue part of the Linker-2 molecule bonded at the metal surfaces still

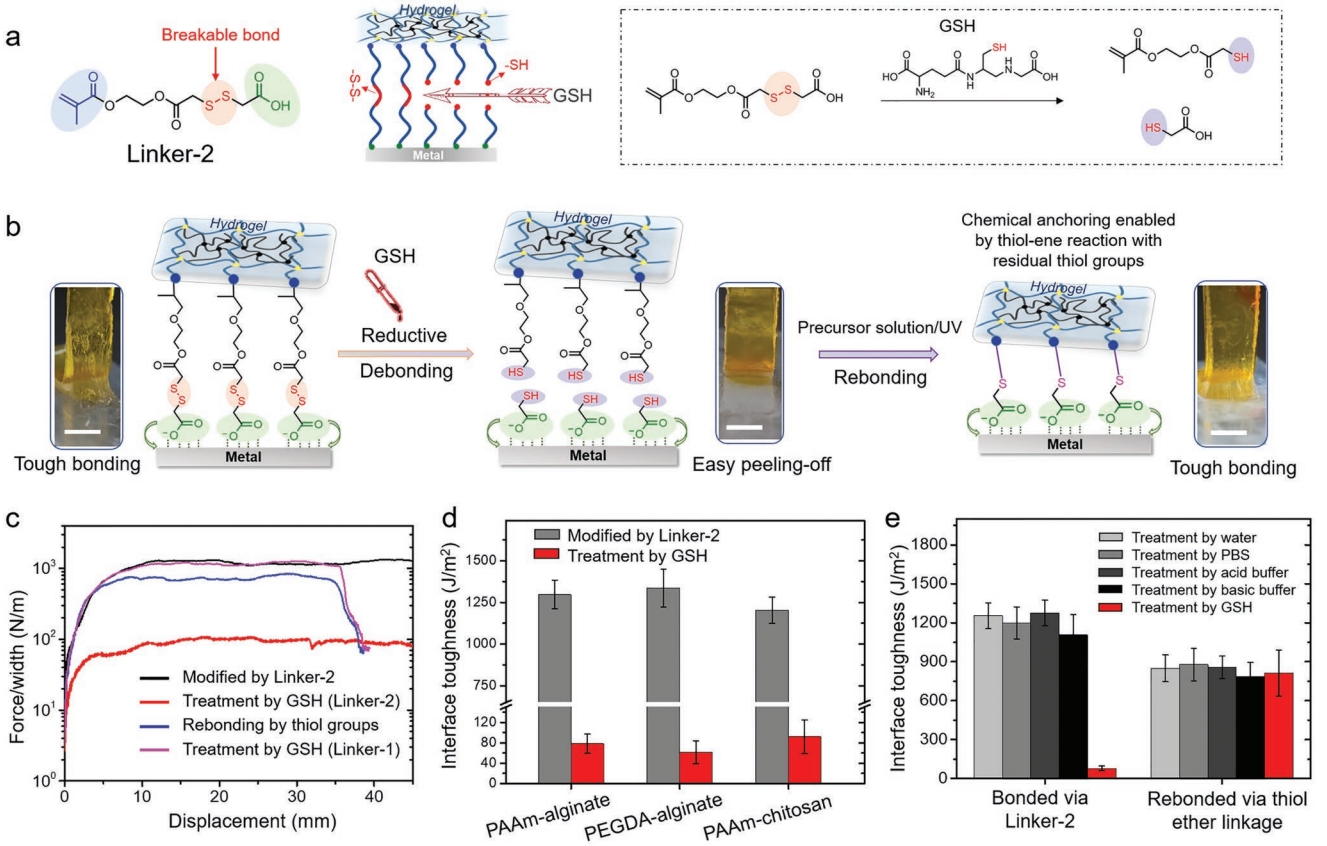

Figure 3. Tough bonding, on-demand debonding, and facile rebonding between hydrogels and metal surfaces via Linker-2. a) Molecular structure of Linker-2 (left) and the reductive cleavage of the disulfide chemical linkage by GSH (right). b) Schematic illustration of the experimental processes to achieve tough bonding, on-demand debonding, and subsequent in situ rebonding using Linker-2 as the interfacial bridge. Reduction of the disulfide bond in Linker-2 by GSH breaks the chemical anchoring. The residual thiol groups on debonded metal surfaces can also provide chemical anchors for rebonding without any further surface modification. Photos showing the 90° peeling tests of tough hydrogels initially bonded to a Ti surface via Linker-2 (left), after GSH treatment (middle), and after instant rebonding (right). A yellow Kapton film was used as the stiff backing for hydrogels. Scale bars: 5 mm. c) Representative force–displacement curves obtained from the 90° peeling tests of bonded hydrogel–Ti systems via Linker-2 (black like), after GSH treatment (red line), and after rebonding (blue line). Result from a control group of bonded hydrogel–metal system via Linker-1 indicated that GSH treatment did not significantly reduce its bonding energy (pink line). d) Measured interfacial toughness values for different tough hydrogel systems chemically anchored to Ti substrates with and without treatment by GSH. e) Measured interfacial toughness values of hydrogels bonded to Ti via Linker-2 and rebonded via thiol ether linkages after swelling in different conditions.

contained a free thiol group (Figure S15, Supporting Information), thus allowing further rebonding (Figure 3a,b). As an example, the same hydrogel precursor solution was again applied to the metal substrate and subsequently irradiated by UV light for photocrosslinking. Under this photoinitiated free radical polymerization condition, the surface thiol groups could also react with the double bonds via the thiol-ene addition mechanism to form thiol ether linkages.[40,41] As a result, the newly applied hydrogel network was again chemically anchored to the metal surface. Indeed, the 90° peeling test on this secondary hydrogel–metal interface bonded by thiol groups revealed an average interfacial toughness value of ≈800 J m^{-2} (Figure 3c,e). Although slightly smaller than those bonded by Linker-1 molecules or Linker-2 molecules at the first time of bonding, this value was still considered to represent toughly bonded interfaces. The lower bonding toughness could possibly indicate a lower density of chemical anchorage sites, which might be caused by the partial oxidative coupling between the thiol groups or by the partial washing-off of the residual linker molecules during the process.

To prove the role of thiol groups in the rebonding process, we directly treated Linker-2-modified Ti surfaces with GSH, breaking the Linker-2 molecules into thiol groups. The bonding energy of such Ti surfaces with hydrogels was ≈800 J m^{-2}, in good agreement with the values obtained from the rebonded hydrogel–metal hybrids (Figure S13, Supporting Information). Moreover, thiol groups are easily subjected to oxidation by common oxidative reagents. Therefore, when thiol-group-modified metal substrates obtained from GSH treatment were oxidized by a mixture of H_2O_2/NaI, the resulting metal substrates could not adhere to hydrogels. Exposure of thiol-group-containing substrates to air for 48 h would also significantly lower the bonding energy (Figure S16, Supporting Information), due to the slow partial oxidation of thiol groups by oxygen. These results, together with the known reactivity of thiol groups, confirmed the formation of thiol ether linkages

for tough bonding in the rebonding process. Since the thiol ether linkage is stable toward pH change or GSH treatment, the rebonded hydrogel–metal hybrids could resist swelling in DI water, buffers, and GSH solutions with no significant changes in bonding toughness (Figure S12, Supporting Information).

For many applications, simple and instant surface modification might be critical. We consequently investigated the effectiveness of three different surface modification methods, namely, long-time soaking (e.g., for overnight), instant dip-casting, and spraying on Ti substrates (Figure S17a, Supporting Information). As shown in Figure S17b (Supporting Information), Ti substrates treated with Linker-1 and Linker-2 via different methods did not show significant differences in water contact angle measurements. The measured water contact angles were slightly lowered to around 50°, compared to over 60° for the pristine substrates (Figures S17b and S18, Supporting Information), possibly due to the presence of polar bonds in the linker molecules. More importantly, we also tested the interfacial bonding toughness values of hydrogels to metal substrates obtained from different methods. Again, the measured values of interfacial toughness showed almost no difference in the 90° peeling tests (Figure S17c, Supporting Information). This experiment indicated the instant feature of our approach for simple yet effective surface modifications.

Considering that metal objects often possess irregular shapes with curved surfaces, we also assessed the feasibility to bond tough hydrogels to curved metal surfaces. **Figure 4**a–d illustrates the images of bonded hydrogels to several metal substrates with different arbitrarily distorted curvatures. Visually, the bonding seemed not affected by the curvature of the substrates. To quantitatively measure the bonding toughness, we adopted mechanical processing to deform the metal plates toward flat substrates and then tested them in 90° peeling experiments. As expected, the measured interfacial toughness values were all above 1000 J m^{-2} (Figure 4e), very similar to those obtained using flat substrates under otherwise identical conditions. Besides, our method could also be applied to modifying metal objects with complex 3D shapes. As shown in Figure 4f,g, after treatment by Linker-1, the hydrogels were successfully bonded to a 3D-printed Ta scaffold with a lattice structure and a 3D stainless-steel spherical object following a similar bonding procedure. Qualitatively, we showed that these bonded hybrid systems could bear loads of 350 and 369 g, respectively, without breaking the interfacial adhesions.

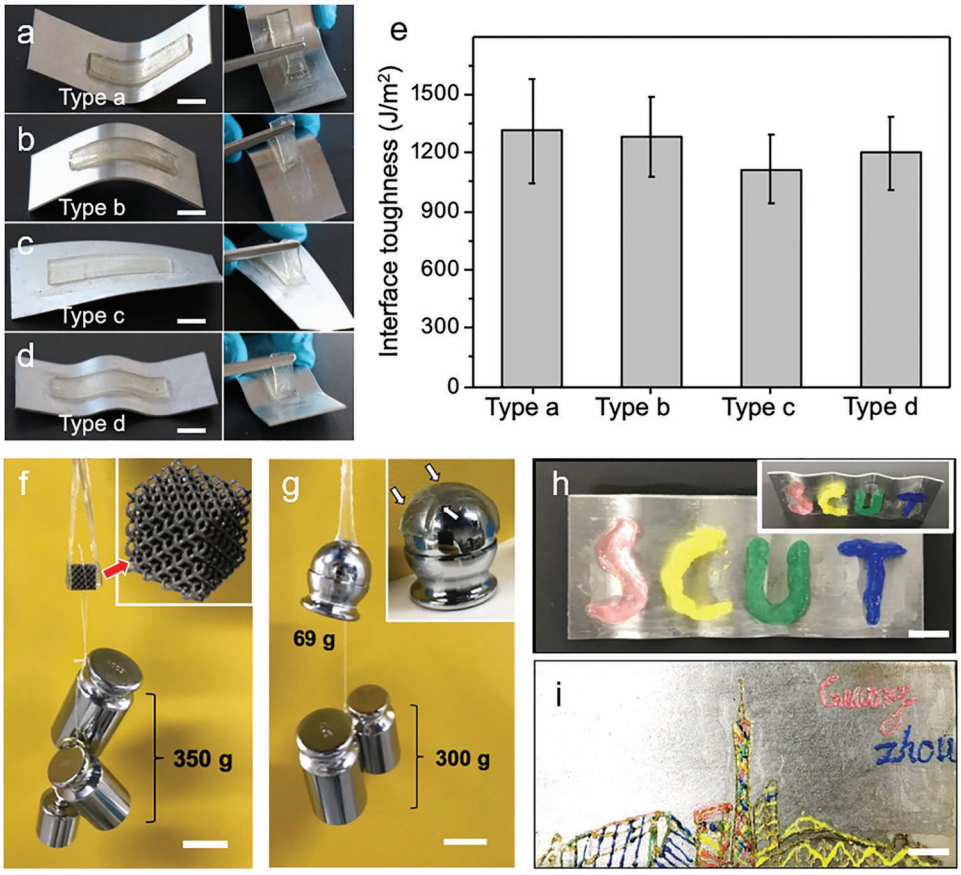

Figure 4. Tough bonding of hydrogels to metal substrates with curved and complex shapes. a–d) Images of bonded hydrogels to metal substrates with different arbitrarily distorted curvatures. e) Measured interfacial toughness values of hydrogels bonded to distorted substrates shown in (a–d) after mechanical processing to deform the metal plates toward flat substrates. f) The hydrogel bonded to a cubic Ta scaffold with a 3D-printed lattice structure holding a load of 350 g. g) The hydrogel bonded to a spherical stainless-steel object holding a weight of 369 g. h,i) Toughly bonded hydrogel coatings with moderate precision and complex patterns could be achieved. Scale bars: (d–g) 10 mm and (f–i) 20 mm.

Metal substrates modified with our linker molecules might also be used in other fabrication techniques, such as photomask patterning and bioprinting followed by photocrosslinking to bring in new functions, where hydrogel coatings with high precision and complex patterns could be achieved. For example, using simple extrusion deposition methods, we were able to draw, directly on the modified metal surfaces, hydrogel patterns of different compositions (Figure 4h,i). Lastly, to evaluate the compatibility of our linker molecules to cells, we seeded human umbilical vein endothelial cells (HUVECs) onto the Ti substrates modified by Linker-1 and Linker-2, with pristine unmodified Ti substrates as the control. As suggested in Figure S19 of the Supporting Information, the linker molecules did not show a negative effect on the proliferation and morphology of HUVECs during in vitro cell culture, which indicated good cytocompatibility for potential biomedical applications.

In summary, we demonstrated a simple and universally applicable method for instant chemical modification of diverse metal substrates and subsequent tough bonding of hydrogels to the metal surfaces to form hybrid systems. By applying a linker molecule as the interface bridge, the resulting interfacial toughness could reach up to >1000 J m^{-2}. In addition, by introducing a breakable disulfide bond into the linker molecule, we illustrated the on-demand debonding of the bonded hydrogels from the metal substrates, and the resulting metal surfaces with free thiol groups could be conveniently rebonded with the second hydrogel, as needed, without any further surface modification step. Considering the underlying principles, we believe that our approach is applicable to diverse metals of arbitrary shapes and tailored photocrosslinkable hydrogels with different compositions and functions,[29,30] which might provide the basis for developing next-generation biomimetic implantable devices composed of hydrogel–metal hybrids. Moreover, the demonstrated on-demand debonding features might inspire the development of functional smart materials, such as on-demand detachable tissue adhesives[38] and recyclable soft electronics.[30] It is also anticipated that our study might inspire new future strategies toward fully reversible strong hydrogel adhesion to diverse materials, which can endure multiple bonding–debonding cycles.

Supporting Information

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

Acknowledgements

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Conflict of Interest

W. Li and K. Yue are declared to be the inventors of a provisional patent application filed by the South China University of Technology related to the results reported here.

Keywords

hydrogels, on-demand debonding, stimuli-responsive, surface modification, tough bonding

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