Renatured hydrogel painting

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Hydrogel coatings pave an avenue for improving the lubricity, biocompatibility, and flexibility of solid surfaces. From the viewpoint of practical applications, this work establishes a scalable method to firmly adhere hydrogel layers to diverse solid surfaces. The strategy, termed as renatured hydrogel painting (RHP), refers to adhering dehydrated xerogel to a surface with appropriate glues, followed by the formation of a hydrogel layer after rehydration of the xerogel. With the benefits of simplicity and generality, this strategy can be readily applied to different hydrogel systems, no matter what the substrate is. Hydrogel adhesion is demonstrated by its tolerance against mechanical impact with hydrodynamic shearing at 14 m/s. This method affords powerful supplements to renew the surface chemistry and physical properties of solid substrates. In addition, we show that the RHP technique can be applied to living tissue, with potential for clinical applications such as the protection of bone tissue.

INTRODUCTION

Surface coatings are regarded as a key window to couple solid-state materials with external media. In the case of closely contacting with external media, the surface coatings are expected to exhibit adequate stability and durability against friction, corrosion, or other chemical and physical disturbances (1–3). Particularly for the sake of biomedical equipment and implantable devices, surface coatings can be hardly purified without reasonable lubricity and biocompatibility besides the consideration of other surface properties (4–9). For example, the surgery of partial hip replacement is an important treatment for femur head necrosis and some degenerative osteoarthrosis (10), in which artificial femur head is an essential substitute to the diseased one so as to restore the joint movement. However, the occurrence of rigorous friction between the artificial femur head and the original acetabulum generally gives rise to acetabular chondrocyte damage and inflammation. This disadvantage clinically weakens the tolerance against intense movements and also shortens the service life of the artificial joints (11–13). Coating the artificial femur head with a protective layer that satisfies the demands on good biocompatibility, lubricity, and appropriate flexibility has been recognized as a critical step in the success of partial hip replacement. Biocompatible and lubricated coatings are also essentially needed in many other medical items and marine objects, such as medical catheters (14) and ship hulls (15) where extraordinary lubricity may be beneficial to the prohibition of biofilms so as to obtain antibacterial or antifouling surfaces (16).

Hydrogels are rising as an innovative branch of soft materials with excellent lubrication (17, 18), biocompatibility (19, 20), and flexibility (21, 22) owing to their high water content. The diverse formulation and tunable porosity render the great possibilities to serve hydrogels as smart surface coatings with the ability of self-healing (23), transporting nutrients, accommodating cell proliferation (24, 25), and delivering cargos (26, 27). Although there have been tremendous progresses in pinning hydrogels on different substrates, which accordingly demonstrates the great potentials in clinical and marine applications (28–32), there remains a need for a more versatile method to firmly and scalably coat hydrogels on various solid substrates regardless of surface topology and material category. In hindsight, the ideally versatile hydrogel painting meets several challenges: (i) The painting method should exhibit excellent compatibility to numerous substrates with the use of various hydrogel formulations, and it should also minimize the dependence on the surface topology. (ii) The adhesion force between the hydrogel and the surface should be able to resist physical and chemical disturbances, particularly including the mechanical friction, the expansion and contraction in the process of hydrogel swelling and dehydration, and the erosion led by acid or alkali media. The hydrogel coatings would have longer lifetime and better durability if they can be self-healable. (iii) Intending for practical applications, the hydrogel painting ideally is a time-saving and inexpensive fabrication process, avoiding lengthy laboratory work and the use of aggressive solvents or energy costs.

Throughout the history of hydrogel painting, it is challenging to propose a hydrogel painting strategy that satisfies all those aspects as stated above at the same time. Water and oxygen loaded in the hydrogels are two main obstacles that hinder the substantial adhesion of hydrogels on solid substrates (29, 33–36). Specifically, the activity of hydrophilic moieties within the hydrogel is significantly weakened by the water-induced hydration effect (37–39), so strong bonding of hydrogel with solid surface is rarely facilitated in the case of direct hydrogel painting. The existence of oxygen can inhibit the free radical–based reactions, which is a fatal drawback for anchoring hydrogels on vinyl-functionalized surfaces via free radical polymerization (14). In this work, we innovatively proposed a concept of renatured hydrogel painting (RHP), referring to a two-step technology of sticking hydrogel layers on solid surfaces. Concretely, dehydrated xerogel particles were first stuck on solid surfaces with the help of special adhesive. Then, the xerogel particles were rehydrated in an aqueous medium, which led to the formation of a uniform hydrogel coating layer on the objective surface. The RHP method successfully enabled to coat hydrogels on large-area surfaces of metal, Teflon, ceramic, glass, wood, polyurethane (PU), polydimethylsiloxane (PDMS), and polyvinyl chloride (PVC) with the painting area readily up to 2.0 m². Different hydrogels could be firmly bonded on those surfaces, and the hydrogel layers did not lose their mechanical performance after compression with normal pressure up to 50 kPa. As a reference, the pressure of an adult applied on the ground is about 17.5 kPa. In addition to
mechanical compression in the vertical direction, the hydrogel coating layers could also endure the shearing force led by flowing water in lateral direction, with a water jet rate of 14 m/s, which is close to the speed of a cargo ship in an ocean.

RESULTS

Preparation and characterization of RHPs on solid surfaces

As schematically illustrated in Fig. 1A and fig. S1, the RHP technique involves two steps. First, an uncured fluidic adhesive is spread or sprayed on the surface of a specific substrate, followed by an immediate coverage of xerogel particles. The adhesive acts as a linker, bonding the xerogel particles with the underneath substrate. Second, a hydrogel layer comes into being after the xerogel particles are renatured in the presence of water. The preferred choice of adhesive relies on the substrate material. Taking glass as an exemplified substrate material, a classical adhesive is epoxy that is reactive with material consisting of polar groups. Both scanning electron microscopy (SEM) and confocal microscopy illustrate the stepwise preparation of a hydrogel painting consisting of polyacrylamide-alginate double network on a PU surface (see Fig. 1, B and C). Typically, uncured epoxy resin was diluted by acetone to facilitate spreading or spraying operations (figs. S2 and S3). After the evaporation of acetone, xerogel microparticles made of a polyacrylamide-alginate-Ca\textsuperscript{2+} double-network hydrogel were paved on the epoxy layer. It is supposed that the epoxy may cure together with the xerogel particles, and the “key-lock” structures along with the possible reactivity at appropriate temperature between the epoxy and xerogel particles may account for the stability of hydrogel layers against the rehydration process and mechanical operations in the following studies (see fig. S4). According to resolution of surface structures in Fig. 1B (ii and iii), the xerogel particles appear to be reshaped, from irregular spheres to tangled fibers, after rehydration in an aqueous environment (see fig. S5). This phenomenon of hydrogel reshaping is defined as a so-called renaturation process, accompanied by the diffusion and reorganization of polymer chains to form a new hydrogel network. The confocal microscopy image clearly demonstrates the formation of a hydrogel layer on the cured epoxy layer and the close combination between the two layers (Fig. 1C). It is noteworthy that the epoxy constituents are also interspersed in the hydrogel layer, which should also contribute to fastening the hydrogel coatings against water swelling and mechanical disturbance (40, 41).

Lubricity of RHP

Investigations are made for the lubricity of RHPs made of three kinds of xerogel particles with the same composition yet different sizes, including small particles (SP; 30 to 40 μm), medium particles (MP; 60 to 80 μm), and large particles (LP; 100 to 150 μm). As shown in Fig. 2A and figs. S6 and S7, both SEM and optical observations confirm that flatter hydrogel painting is obtained with the use of smaller xerogel particles. As assessed by the profilometer (Fig. 2B), the arithmetical mean deviations of the surface profile (R\textsubscript{a}), as the representative index of surface roughness, of the SP-RHP, MP-RHP, and LP-RHP are 4.90, 8.94, and 55.22 μm, respectively, fully agreeing

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**Fig. 1. Preparation and characterization of RHP.** (A) Schematic illustration of the RHP technique. (B) SEM images of the adhesive layer (i, epoxy resin), the xerogel microparticle layer before rehydration (ii), and the rehydrated hydrogel layer after lyophilization (iii). (C) Confocal microscope images of the layered structure of RHP. The entire thickness is about 20 μm. The adhesive and hydrogel layers are colorized with green and red fluorescence dyes, respectively.
with the fact that the RHP made of smaller xerogel particles has smaller surface roughness. It should be noted that the $R_a$ of three RHPs are all smaller than the size of their corresponding xerogel particles, further confirming the occurrence of renaturation in the rehydration process. It is assumed that the polymer chains within the smaller xerogel particles are easier to be relaxed from the particle interior once they are hydrated so as to reach a higher degree of chain interpenetration between neighbor particles.

An overwhelming majority of hydrogel coatings have remarkable lubricity in terms of the hydration layer on their surfaces. With respect to this intriguing event, the friction coefficients of the RHP made of xerogel particles with different sizes were evaluated by a rheometer under different pressures (Fig. 2C). Notably, a smaller xerogel particle corresponds to a hydrogel surface with lower friction coefficient, which accords with the higher flatness and lower surface roughness of SP-RHP relative to MP- and LP-RHPs (Fig. 2D). Therefore, the SP-RHP was chosen as the superior choice in the following experiments, unless otherwise indicated. It should also be noted that all three RHPs exhibit lower friction coefficients under higher pressure, which is not consistent with the behaviors of other hydrogel coatings (28) but similar to the shear-thinning performance of typical polymer solutions. It is supposed that the hydrogel chains of RHP resulting from xerogel particles are more unfettered than that of monolithic hydrogels, which should be the critical determinant for explaining the renaturation of SP-RHP. In this regard, higher shearing pressure may promote the orientation or unentanglement of polymer chains within RHPs so as to decrease the friction resistance. The reliable friction coefficient against cycles of rheological test between low pressure (12.7 kPa) and high pressure (50.8 kPa) confirms the excellent stability and repeatability of the lubricity, which has been recognized as an important factor for ensuring longer lifetime of surface coatings (Fig. 2E). It is worth noting that the pressure of 50.8 kPa is almost three times higher than the pressure on feet of an adult. To further verify the benefit of hydrogel for improving lubricity, we comprehensively compared the RHP with smooth PU and glass surfaces. As summarized in Fig. 2F, the friction coefficient of RHP is two and one orders of magnitude lower than that of PU and glass, respectively. Besides, contrary to RHP, both PU and glass surfaces suffer higher friction coefficient under higher shearing pressure.

**Robustness of RHP**

Following the same procedure for preparing RHP on glass, RHP was prepared on a metal slice that was subjected to a water jet to
assess the robustness of hydrogel coatings. As shown in Fig. 3A, the RHP was impinged by a water jet with a water flowing rate of 13 to 14 m/s. This flowing rate is equivalent to 25 to 27 knots/hour. As a reference, the average speed of cargo ships moving in water is about 15 to 20 knots/hour. After such a rigorous impingement, negligible damages were found throughout the whole RHP surface (Fig. 3A and movie S1). If the RHP was impregnated by silicone oil and then soaked in deionized water, then the exuviation of an “oil skin” was observed away from the RHP surface, indicating the wonderful preservation of integrity and oleophobicity of the RHP (figs. S8 and S9).

The durability of lubricity, as stated above, is also a character to demonstrate the robustness of RHPs. After being stored in acidic (pH = 3) or alkaline (pH = 11) solution for 24 hours, the friction coefficient of RHP at pH 3 remains almost unchanged, while the friction coefficient of RHP at pH 11 decreases gradually (fig. S10). It is assumed that the alkaline condition can cause the hydrolysis of polyacrylamide (PAM) (42), involving a nucleophilic addition reaction of hydroxide to the amide carbonyl and a subsequent elimination of the amide ion (−NH₂) to yield a carboxyl group (fig. S11A). The generation of carboxyl group increases the electrostatic repulsion between PAM chains, thus enabling surface polymer chains to be looser and more compliant. Meanwhile, the introduction of carboxyl groups also increases the surface hydrophilicity (fig. S11B), which is beneficial for improving lubrication. The friction coefficients of MP-RHP and LP-RHP decrease gradually, yet the friction coefficient of SP-RHP remains almost unchanged after being stored in deionized water for 6 weeks (see Fig. 3B). Incidentally, the xerogel particles, as a form of light and dry powder, are extremely suitable for storage and carriage. These unique features are favorable in moving forward with the commercialization of RHP technique, not to mention insusceptible to mildew (see fig. S12).

The volume change in the dehydration-renaturation process is another important factor to influence the RHP adhesion on solid surfaces. In principle, the hydrogel has a higher degree of deformation than the underneath substrate in response to humidity change (43, 44). This is a negative finding in the case of hydrogel coatings on nonswelling substrates. Yet, the results of both surface topography and friction coefficient indicate that RHPs are extremely stable against the dehydration-renaturation treatment (Fig. 3C and fig. S13). It is assumed that the adhesive interpenetrates among or into the xerogel particles, which may account for the stability of the coating in the hydration and dehydration process. In addition, the RHP also exhibits antiscratching performance. As illustrated in Fig. 3D, the RHP can fully restore to its original surface topography in 36 hours after it receives an incision by a knife. Such a self-healing capability is attributed to the refilling of hydrogel in the scratched area where the capillary effect may facilitate the extension and migration polymer chains in aqueous condition.

**Versatility of RHP**

The RHP technique is applicable to many substrates and diverse hydrogel formulas in Fig. 4. As exemplified in Fig. 4A and movie S2, RHP was also successfully fabricated on a Teflon substrate with the help of a cyanoacrylate adhesive. In contrast to the uncoated Teflon surface and the surface coated with cured adhesive that have water contact angles of 112° and 83°, respectively, the RHP-coated surface is much more hydrophilic with a water contact angle of 11°. This notable wettability difference was clearly specified by a patterned RHP on a Teflon film (see fig. S14 and movie S2). After getting splashed with an aqueous solution containing Rhodamine B, an “RUC” red pattern where RHP was coated was quickly distinguished from the surrounded Teflon matrix.

Other substrates like ceramics and wood could be also coated with RHPs, by which the surfaces were endowed with antifouling and lubricant performance. As shown in Fig. 4B and movie S3, the right side of a porcelain bowl was coated with RHP, while the left

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**Fig. 3. Robustness assessment of RHP.** (A) Impingement test of RHP on a metal slice against a water jet (flow rate is about 13 to 14 m/s). (B) The friction coefficient and optical images of RHPs soaked in phosphate-buffered saline solution over time. (C) Friction coefficient and SEM images of a typical RHP that receives a dehydration-renaturation treatment. (D) SEM images of a scratch on the RHP surface after 0, 6, and 36 hours in deionized water. Photo credit: (A and B) Zhaoxiang Yang and Yonglin He, Renmin University of China.
side was unmodified. When the oil contaminates the inner surface of the bowl, oil attached on the side with RHP could be easily cleared by deionized water, while the unmodified surface was fully stained with oil. Another example is a wooden board, which shows better lubricity after being coated with RHP. To vividly present the improved lubricity by RHP, we placed a wooden chess piece on two wooden boards with or without RHP at a specific tilting angle. The chess piece could easily slide off the RHP-modified surface at a tilting angle of 15°. However, the chess piece stays on the unmodified surface even at a tilting angle of 45° (see Fig. 4C and movie S4).

The RHP technique can be also extended to elastic substrates. Taking PDMS as an example, a silicone adhesive was used to firmly anchor RHP on PDMS surface. As a control, a hydrogel film was directly polymerized on PDMS surface without using adhesive. As shown in Fig. 4D, the RHP would be elongated together with PDMS when a tensile stretching was applied on two ends of the PDMS substrate, while the hydrogel film in a control group slipped instead of elongated with stretched PDMS. Water-soluble fluorescent dyes can be efficiently loaded in the RHP layer, which acts as a prober to help the direct monitoring of hydrogel elongation in this study. Meanwhile, loading cargos in RHP offers inspirations for drug delivery to the sites of interest if RHP technique can be applied on elastic catheters. Fluorescence photographs obviously confirm that the RHP exhibits no relative displacement with the PDMS substrate under the tensile strain ranging from 0 to 100% (fig. S15 and movie S5), which is indicative of the strong combination between PDMS and RHP. In addition, the surface wettability of RHP as represented by contact angle does not change after the tensile stretching operation (see fig. S16). Besides the studies of changing substrate materials, some other hydrogel formulas can be also formulated into RHPs (see fig. S17), confirming the generality and diversity of the RHP technology.

**Application of RHP in partial hip replacement**

As emphasized in Introduction, the lubricity between the artificial femur head and the original acetabulum is significantly important for the prognosis of the partial hip replacement. Among numerous attempts to reduce the friction in the hip joint, serum has been exploited as a popularly clinical lubricant, yet it is inevitably faced with the problems of rapid degradation and leakage from the joint (11, 13). Because of its unique characters of excellent lubricity and robustness, RHP may be ideally suited for playing a better role as lubricant in the repaired joints. A model surgery was presented in Fig. 5A, in which the RHP technique was applied to the hip joints of an adult domestic pig. The hip joint typically consists of two parts, including the acetabulum (A) and femur head (FH) (Fig. 5A, i). In the clinical surgery of partial hip replacement surgery, the necrotic femur head is generally replaced with an artificial femur head, and the healthy acetabulum is left unchanged. Two artificial femur heads were prepared by three-dimensional (3D) printing, according to the profiles of the natural femur heads that were reconstructed by a 3D scanner (fig. S18). As illustrated in Fig. 5A (ii) and movie S6, the artificial left femur head was coated with RHP, and the right one was unmodified as a reference sample. Keeping two acetabula (A-Left and A-Right) fixed, the friction test was done by rotating the artificial femur heads against the acetabulum under a given pressure in normal direction. Setting the pressure and rotation speed as the same, the cartilage on the left acetabulum was fully preserved after continuous rotation for 35 min, while notable damage...
was observed in the cartilage on the right acetabulum (Fig. 5B). Magnetic resonance imaging (MRI) was used to specifically identify the damage of the left and right acetabular. On the basis of the cross-sectional imaging of cartilages in a horizontal plane, unlike the serious loss of cartilage (white shadow) on the right acetabulum, the cartilage on the left acetabulum remains almost unchanged after the friction tests (Fig. 5C and movie S7). The distinct protection of the acetabular cartilage from abrasion suggests that RHP may become a promising choice in the efforts to lubricate joints. Referring to the high cell viability of MCF-7, it is confirmed that the cytotoxicity of cured epoxy resin is negligible (fig. S19). Through the choice of bio-compatible hydrogels, RHPs present great potential in applications with medical purposes.

**Large-area preparation of RHP**

RHP is a time-saving and inexpensive fabrication process, which avoids the use of aggressive solvents. It also does not rely on free radical–based polymerization and special treatment of substrate surfaces. In practice, both steps of adhesive coating and xerogel particle coating can be accomplished by means of spraying method. This technological innovation affords great convenience to prepare hydrogel coatings on a large-area substrate. As shown in Fig. 6A and movie S8, we demonstrated the possibility of preparing a hydrogel film on a 1 m–by–2 m PVC square by spraying epoxy adhesive, xerogel particles, and water in sequence. The success of RHP formation throughout the whole PVC sheet was convinced by the pronounced surface hydrophilicity. As a control, untreated PVC surface could not be wetted by the water loaded with red dyes (see Fig. 6B and fig. S20).

**DISCUSSION**

In summary, we developed a simple yet effective method, named renatured hydrogel painting (RHP), to prepare robust hydrogel coatings on various solid substrates. This hydrogel painting method involves the coating of adhesive and xerogel particles, followed by rehydration of xerogel into hydrogel. In addition to laboratory fabrication in small scale, each step can be readily scaled up with the combination of traditional spraying-based painting method. The adequate linkage by the cured adhesive enables the hydrogel coatings to accommodate arbitrary mechanical operations and volume changes in the dehydration-rehydration process. The excellent lubricity and notable robustness would attract interests in surface modification of both living and nonliving objects by means of RHP method. As far as we know, this is the first strategy for making hydrogel coatings that owns so many merits at the same time, including generality, high durability, acid and alkali resistance,
self-healing capability, convenience, low cost, no aggressive solvent, no surface pretreatment, and scalable fabrication. Besides the samples as investigated in this work, this method is readily applicable to a wide range of adhesives, hydrogel formulas, and substrate materials. Their reasonable combination could possibly produce special substrates where particular hydrogel coatings are needed.

MATERIALS AND METHODS

Materials

Epoxy adhesive (Ergo 7300), auxiliary product for cyanoacrylate adhesives (Ergo 5180), and one-component instant cyanoacrylate adhesives (Ergo 5400) were purchased from Ergo (Switzerland) as linkers. The solvent of acetone (C$_2$H$_6$O) was purchased from Beijing Chemical Works (Beijing, China). Sodium alginate (SA) was purchased from Lyntech (Beijing, China), which was extracted from brown algae according to the product introduction. Acrylamide (AM), gelatin (type B) was purchased from Aladdin Bio-Chem (Shanghai, China). N, N'-methylenebisacrylamide (97%) (MBAM) was obtained from Alfa Aesar. Calcium chloride (CaCl$_2$) was provided by Beijing Chemical Reagent Company (Beijing, China). N, N, N', N'-tetramethyl-ethylenediamine (TEMED) was supplied by J&K Scientific (Beijing, China). Silicone adhesive (DOW CORNING 3140 RTV) was purchased from Dow silicones Corporation.

Preparation and viscosity testing of linker solution

The epoxy resin components A and B were added to acetone with a ratio of 1:1, and they were fully stirred to form a uniform solution. The linker solution was freshly prepared just before use, but the component A or B solution could be stored separately for the long term. The viscosity of epoxy resin solution was measured by a rheometer (MCR 302, Anton Paar). The shear rate varied from $10^{-1}$ to $10^3$ s$^{-1}$. A steel parallel rotor with a diameter of 20 mm was used. The gap was kept at 50 µm, and the temperature was fixed at 25°C.

Preparation of RHP

PAM-alginate-Ca$_2^+$ hydrogel was prepared by curing a precursor solution [20 weight % (wt %) AM, 0.05 wt % MBAM, 2 wt % SA, 0.05 wt % (NH$_4$)$_2$S$_2$O$_8$, 0.34 wt % CaSO$_4$$2$H$_2$O, 0.1 wt % TEMED] for 12 hours at room temperature. The double-network xerogel was made by vacuum freeze-drying and then triturated into multisize xerogel microparticles by ball milling. Using ethanol as the solution, the multisize xerogel microparticles were filtered by size. After the evaporation of the ethanol, SP (30 to 40 µm), MP (60 to 80 µm), and LP (100 to 150 µm) were obtained. The substrates were first cleaned with deionized water and ethanol followed by drying under room temperature. The linker solution was coated on the surface of dry substrates. Then, the xerogel powder was sprayed on the intermediate layer prepolymers. After the polymerization of the linker, a uniform hydrogel coating was obtained, and then it was immersed in deionized water for 24 hours.

Confocal microscope images

The PAM-Alginate hydrogel labeled with Rhodamine B was prepared by curing a pregel solution, containing 20 wt % AM, 0.05 wt % MBAM, 2 wt % SA, 0.05 wt % (NH$_4$)$_2$S$_2$O$_8$, 0.34 wt % CaSO$_4$$2$H$_2$O, 0.1 wt % TEMED, and Rhodamine B (10$^{-5}$ g/ml), for 12 hours at room temperature. The xerogel containing Rhodamine B was punched into xerogel microparticles by ball milling. SPs with size approximately at 30 µm were screened out via rational filtration. The glass substrates were cleaned with deionized water and ethanol followed by drying under room temperature. Then, a linker solution containing epoxy resin prepolymers (1.0 g/ml) and petroleum fluorescent tracing dye (10$^{-5}$ g/ml) in acetone was coated on the surface of cleaned glass slide. Afterward, the xerogel powder was sprayed on the adhesive layer after its precuring for 15 min at 75°C. The sandwich-like sample was further placed in an oven with a temperature of 75°C for another 3 hours and then immersed in Rhodamine B solution (10$^{-5}$ g/ml) for 24 hours to allow the rehydration of xerogel particles.

Friction coefficient measurements

Friction coefficients of all samples were measured by a rotational rheometer (MCR 302, Anton Paar). Each sample (under water) was loaded on the rheometer, and a set of normal pressures (6.35 to 50.8 kPa) was applied to the sample with a shear rate of 0.5 s$^{-1}$.
From a rotational shearing test, the friction coefficient ($\mu_k$) is measured as

$$\mu_k = \frac{\tau}{P}$$

where $\tau$ is the shear stress and $P$ is the pressure applied to the surface.

**Antiscratching test of RHP**

The RHPs on a PU film were scratched by a knife in the water. The 0-hour samples were taken out immediately after scratched, and the remaining samples were taken out after 6 and 36 hours in water, respectively.

**Water jet impingement test of RHP**

First, the RHP coated on metal panel was put into the silicone oil to be fully impregnated, and the oil skin in the hydrogel coating was gradually removed when it was put into the deionized water, which proves the completeness and continuity of the hydrogel coating. Then, the RHP coated on metal panel was used for the water jet impingement test. Briefly, a high-pressure water gun was used to impact the RHP coated on metal panel. Last, the panel that had withstood an impact was subjected to the oil skin delamination experiment to verify the completeness of the hydrogel coating.

**Friction experiment between the artificial bone and the acetabulum in vitro**

The left and right hip joints were taken from the same domestic pig. The 3D structures of left femur head and right femur head were obtained by 3D scanner (OKIO 5M, TEN YOON). Then, a pair of femoral heads were reconstructed through 3D printing (Form 2, Formlab). A milling machine (Sieg Super X3, SIEGIND) was used for the friction experiments in vitro. First, the acetabulum was fixed on the worktable of the milling machine, and the artificial femur heads were fixed on the milling head. The same compression length of spring made the hip joint sustains the same normal force in each experiment. Then, the artificial femoral heads rubbed the acetabulum at rotational speed 300 rpm, and deionized water was continuously added to the hip joints to keep wetting. Last, MRI (Philips Achieva 3.0 T TX) was used to detect the damage degree of the left and right acetabular cartilages.

**Fabrication process of RHP on PVC**

Spraying the epoxy solution on the PVC substrate took about 5 min. The epoxy resin was allowed to be precured for 30 min at room temperature. Then, the xerogel powders were sprayed on the surface of partially cured epoxy resin, which took about 15 min. After further curing of the epoxy resin for 3 hours at room temperature, the RHP coating was immediately formed once the xerogel layer was rinsed by water.
30. R. Takahashi, K. Shimano, H. Okazaki, T. Kurokawa, T. Nakajima, T. Nonoyama, D. R. King, J. P. Gong, Tough particle-based double network hydrogels for functional solid surface coatings. Adv. Mater. Interfaces 5, 1801018 (2018).
31. W. Li, X. Liu, Z. Deng, Y. Chen, Q. Yu, W. Tang, T. L. Sun, Y. S. Zhang, K. Yue, Tough bonding, on-demand debonding, and facile reboning between hydrogels and diverse metal surfaces. Adv. Mater. 31, 1904732 (2019).
32. S. Pan, F. Zhang, P. Cai, M. Wang, K. He, Y. Luo, Z. Li, G. Chen, S. Ji, Z. Liu, X. J. Loh, X. Chen, Mechanically interlocked hydrogel–elastomer hybrids for on-skin electronics. Adv. Funct. Mater. 30, 190540 (2020).
33. J. Y. Chung, M. K. Chaudhury, Soft and hard adhesion. J. Adhes. 81, 1119–1145 (2005).
34. H. Lee, B. P. Lee, P. B. Messersmith, A reversible wet/dry adhesive inspired by mussels and geckos. Nature 448, 338–341 (2007).
35. H. Fan, J. Wang, Z. Tao, J. Huang, P. Rao, T. Kurokawa, J. P. Gong, Adjacent cationic–aromatic sequences yield strong electrostatic adhesion of hydrogels in seawater. Nat. Commun. 10, 5127 (2019).
36. H. Yuk, C. E. Varela, C. S. Nabzdzyk, X. Mao, R. F. Padera, E. T. Roche, X. Zhao, Dry double-sided tape for adhesion of wet tissues and devices. Nature 575, 169–174 (2019).
37. Q. Zhao, D. W. Lee, B. K. Ahn, S. Seo, Y. Kaufman, J. N. Israelachvili, J. H. Waite, Underwater contact adhesion and microarchitect in polyelectrolyte complexes actuated by solvent exchange. Nat. Mater. 15, 407–412 (2016).
38. S. Singla, G. Amarpuri, N. Dhopatkar, T. A. Blackledge, A. Dhinojwala, Hygroscopic compounds in spider aggregate glue remove interfacial water to maintain adhesion in humid conditions. Nat. Commun. 9, 1890 (2018).
39. J. Li, A. D. Celiz, J. Yang, Q. Yang, I. Wamala, W. Whyte, B. R. Seo, N. V. Vasilyev, J. J. Vlassak, Z. Suo, D. J. Mooney, Tough adhesives for diverse wet surfaces. Science 357, 378–381 (2017).
40. Z. Zhang, Z. Chen, W. Yang, J. Chi, Y. Wang, Y. Zhao, Bioinspired bilayer structural color hydrogel actuator with multi-environment responsiveness and survivability. Small Methods 3, 1900519 (2019).
41. J. Yang, R. Bai, B. Chen, Z. Suo, Hydrogel adhesion: A supramolecular synergy of chemistry, topology, and mechanics. Adv. Funct. Mater. 30, 1901693 (2020).
42. M. J. Caulfield, G. G. Qiao, D. H. Solomon, Some aspects of the properties and degradation of polyacrylamides. Biophys. J. 102, 3067–3084 (2002).
43. K. Saha, J. Kim, E. Irwin, J. Yoon, F. Momin, V. Trujillo, D. V. Schaffer, K. E. Healy, R. C. Hayward, Surface creasing instability of soft polyacrylamide cell culture substrates. Biophys. J. 99, 194–196 (2010).
44. M. K. Kang, R. Huang, Swell-induced surface instability of confined hydrogel layers on substrates. J. Mech. Phys. Solids 58, 1582–1598 (2010).

Acknowledgments: We are grateful to Y. Qiao and B. Hu from Institute of Microbiology, Chinese Academy of Sciences for help on the profilometer test and S. Lyu for help in MRI. X. Lian is acknowledged for help on contact angle measurement. Funding: This work was financially supported by the National Natural Science Foundation of China (22005336, 21825503, and 21674127). Author contributions: All authors discussed the results and revised the manuscript. Z.Y. led the project design and all the experiments under the supervision of Y.W. and Y.H. Y. assisted all the experiments in this project. S.L. assisted the fabrication of the artificial femur heads and the data analysis. Y.M. and X.T. helped with the large-area coating of RHP on PVC film. Competing interests: Y.W., Y.H., and Z.Y. are coinventors on a patent application for the use of RHP, filed by Renmin University of China (no. 201911335876.0, 23 December 2019). The remaining authors declare no competing interests. Data and materials availability: All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors.

Submitted 27 November 2020
Accepted 15 April 2021
Published 2 June 2021
10.1126/sciadv.abf9117

Citation: Z. Yang, Y. He, S. Liao, Y. Ma, X. Tao, Y. Wang, Renatured hydrogel painting. Sci. Adv. 7, eabf9117 (2021).