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Ultrathin tough double network hydrogels showing adjustable muscle-like isometric force generation triggered by solvent

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Ultrathin double-network hydrogels, which have super-high toughness under micro-scale thickness (elastic elongation ε_b > 1000%, tensile strength σ_b > 2 MPa and tearing energy G ~ 600 J/m^2), and solvent-triggered fast and high isometric stress generation, were synthesized by coupling the salt-controlled swelling process and polymer chain pre-reinforced technique.

Researches in artificial-muscle have been focused on designing "strong and flexible", "smart response to stimuli", and "fast and high force output" materials that mimic the energy-conversion functions observed in real muscle.[1-3] Polymer gels, which are soft-wet and show stimuli-response capability, have emerged impressively in this field since 1990's. Sensing and actuating of polymer gels are usually showed *via* its volume changes in response to a wide range of stimuli of light, temperature, pH, chemical reactions and even antibody-antigen interaction. [4-8] Field-induced contraction, motion and bending of polymer gels provide also other possibilities for energy conversion, where the real muscle fails. [9-11] Even so, several problems associated with the extensive use of gel-based artificial muscle, however, still remain unsolved. Among them, the weak mechanical strength and slow response are two main issues. Because of this, polymer gels are limited to systems where the mechanical strength and the response speed are not important issues, such as drug delivery devices, [12] gel actuators with walking capability, [9, 13] smart "on-off" valves and sensors. [14] The strong mechanical-related capabilities that really access the natural performance of the real muscle, namely, high and fast force generation or output, is lacking and have been rarely explored yet.

In the past several years, we have developed a double network (DN) principle that offers bulk polymer gels with mechanical strength (σ_b > 1 MPa) and toughness (fractural energy ~ 10^3 J/m^2) as high as that shown by real cartilage.[15, 16] This tough feature of the DN gels has dramatically changed our understanding that a hydrogel was a mechanically weak material, and makes it possible to be used as the load-bearing artificial muscles. According to the theoretical prediction, the contraction kinetics of a gel is determined by the cooperative diffusion, and the characteristic time τ is related to the characteristic size of the specimen h as $\tau \sim h^2$. Therefore, one of the approaches to improve the response rate is to work with ultrathin DN hydrogels.

Herein we describe a facial strategy to synthesize ultrathin poly(2-acrylamido-2-methylpropane-sulfonic acid) / polyacrylamide (PAMPS/PAAm) double-network (UTDN) gels having super-high toughness under micro-scale thickness. In this strategy, the salt effect and the polymer chain pre-reinforced technique were firstly coupled to control the swelling behavior and to adjust the mechanical strength of the weak precursor gels, that is, ultrathin PAMPS gels. It is truly critical to avoid osmotic-pressure-induced break and to obtain self-peeling and direct manipulation of the precursor gels during the synthesis process. As the first example, these UTDN hydrogels are designed as fast-response artificial muscle and its muscle-like force generation is further explored for experimentally measuring their applicability to this field.

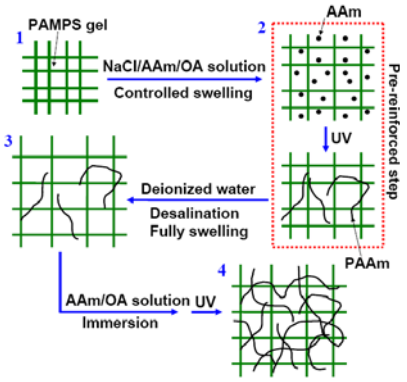

Fig. 1. Synthesis procedures of the UTDN gels.

The procedure for synthesizing the UTDN gels is performed by multi-step UV-light-initiated polymerization (UVIP) (Fig. 1). Using two glass plates spaced with 15, 25 and 50 μm polyethylene film, we first synthesized ultrathin PAMPS gels by the UVIP, where 2-acrylamido-2-methylpropane-sulfonic acid (1 M, Tokyo Kasei, Japan) was used as monomer, *N*, *N*'-methylenebis(acrylamide) (0.04 M, Tokyo Kasei, Japan) as crosslinking agent, and 2-oxoglutaric acid (OA) (0.001 M, Wako, Japan) as an initiator. Then, the PAMPS gels were immersed in acrylamide (AAm) (4M, Wako, Japan)/OA (0.001 M) aqueous solution, containing 0.08 M NaCl. The presence of salt prevents the PAMPS gels from the dramatic swelling due to the high ionic osmotic pressure exerted on the polyelectrolyte networks. The swelling degree of the PAMPS gels in 0.08 M NaCl aqueous solution is only about half to that in pure water (Fig. S2, ESI‡). At the same time, self-peeling of the gels from the substrate was achievable in the solution. Following this step, another UVIP to the partial-swelled PAMPS gels was performed to introduce

PAAm chains to PAMPS network. The PAMPS gels were thus pre-reinforced (step 2) to a level that permits us to directly manipulate the PAMPS gels at its fully swelling state in water (Fig. 2c, curve 1). Finally, the enhanced PAMPS gels were washed till free from NaCl by distilled water. They were then immersed in AAm (2 M) /OA (0.001 M) solution for 10 h and UVIP was applied to obtain the UTDN hydrogels. According to our previous works, the molar ratio between the PAAm and PAMPS was about 20:1. [17] Although we did not add crosslinking agent in polymerizing AAm, the effective crosslinking density of PAAm was 5×10^{-2} mol% (in relative to PAAm repeated units) due to the inter-connection of PAAm to the PAMPS network through the residual crosslinking agent. [18]

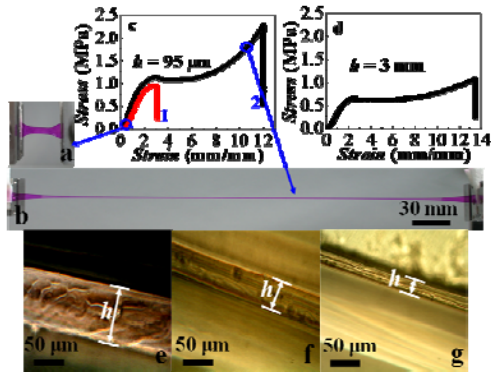

Fig. 2. The UTDN gel at (a) its free-standing state and (b) the stretching state at a strain of ~ 11 mm/mm, the gel was here dyed for a clear visibility; (c) Stress-strain curves of the pre-reinforced ultrathin film PAMPS gel (1) and the UTDN gels (Thickness $h \approx 95$ μm) (2); (d) Stress-strain curve of the bulk DN gels with thickness of $h = 3$ mm; Cross-section images of the UTDN gels with the thickness h of (e) ~ 100 μm, (f) ~ 55 μm, and (g) ~30 μm obtained by phase contrast microscope equipped with ×20 objective lens.

Fig. 2a and 2b show, respectively, the pictures of the UTDN gels at its initial state and highly stretching state. Comparing the stress-strain curve 1 and 2 in Fig. 2c, it is not difficult to judge that the final UTDN gel (curve 2) is tougher than the pre-reinforced PAMPS gel (curve 1). The values of fracture stress σ_b, fracture strain ε_b, and fracture energy G reach 2.3 MPa, 12 mm/mm and 620 J/m^2, respectively. These performances are comparable to that of the bulk DN gels (Fig. 2d). This result demonstrates that the DN principle is still effective for creating strong DN gel at micro-scale. Actually, we observed the similar necking phenomenon and damage zone at the crack tip as that of bulk DN gels (data not shown), indicating the toughening mechanism of the UTDN gel is the same as that of the bulk DN gels. [20, 21] Fig. 2(e-g) presents the cross-section images of the UTDN gels and their thickness after fully swelled by water. It was observed that, with the initial space of 15, 25, and 50 μm, the thickness of the UTDN gels after fully swelled in water is ranged from ~30 to ~110 μm. The water content of these gels is ~90 wt%.

To explore the applicability of the UTDN hydrogels to artificial muscle, its solvent-triggered force generation was studied in ethanol (EtOH) and EtOH/water mixture under a constant pre-strain of 100% (Experiment, Fig.S1, See ESI‡). Fig. 3a presents the cyclic changes in the isometric stress of the UTDN gels alternately triggered by water and EtOH. The magnification of one of the cycles (800 ~ 1300 s) is shown in Fig. 3b. In EtOH, the stress of the UTDN gels firstly decreased from the initial value σ_0 in water to a valley σ_l, and then increased rapidly to a stress plateau (σ_p) that is higher than the initial value σ_0. Setting here $\sigma_0 = 0.48$ MPa as the base line, the "contractile stress", $\Delta\sigma = \sigma_p - \sigma_0$, can reach about 0.25 MPa. This value is competitive to ~ 0.1 MPa of the real muscle in response to Ca^{2+} signal and 0.2 MPa of electrostatic silicone rubber triggered by strong electric field (144 V/μm). [1a, 1b, 3, 19] Moreover, the UTDN gels showed a monotonous decrease in the isometric stress to a stress plateau (σ_n),when triggered with 50 wt% water / 50 wt% EtOH mixture (EtOH-50) (Fig. 3c). The isometric contractile stress, $\Delta\sigma = \sigma_n - \sigma_0$, in EtOH-50 was about -0.23 MPa. We observed that this adjustability in $\Delta\sigma$ is continuous over a wide range through changing the solvent component. For example, the UTDN gels in 20 wt% water / 80 wt% EtOH mixture (EtOH-80) only give $\Delta\sigma$ of about -0.12 MPa.

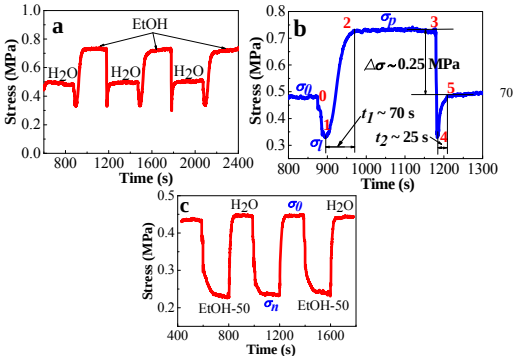

Fig. 3. (a) Response in the isometric stress of the UTDN gels periodically triggered by EtOH and water; (b) Magnification of the response cycle located at 800 ~ 1300 s presented in (a); (c) Response in the stress of the UTDN gels periodically triggered by EtOH-50 and water. Thickness of the UTDN gels used here was about 100 μm. The isometric contraction was performed at a tensile pre-strain of 100%.

This adjustability in $\Delta\sigma$ is explainable according to the solvent-induced changes in the length and elastic modulus (E_x, x = water, EtOH, EtOH-50 and EtOH-80) of the UTDN gels. At free-standing state, we observed that the UTDN gels greatly contracted when being immersed in the above solvents. Both the length contraction ratios $\Delta\varepsilon$ and E_x depend on the solvent component. $\Delta\varepsilon$ in EtOH-80 and EtOH-50 are about 33.5% and 28.7%, respectively, which are higher than that obtained in EtOH (25.1%). It suggests that the UTDN gels can contract more in EtOH-80 and EtOH-50 due to the presence of water. Comparing to $\Delta\varepsilon$, E_x changed contrarily and more remarkably responding to the change in the solvent component. The elastic modulus in pure EtOH, E_{EtOH} reached 133 MPa, which was more than two orders in the magnitude higher than that in pure water ($E_{water} = 0.3$ MPa). The significant increase in the modulus in pure EtOH is probably due to that the EtOH is poor solvent for PAAm chains but not for PAMPS network. With the introduction of 20 wt% water to EtOH, elastic modulus of the UTDN gels dramatically decreased with the order of ~10^3 to $E_{EtOH\text{-}80} = 0.22$ MPa. A further decrease of

the modulus to $E_{EtOH\text{-}50}$ = 0.093 MPa is obtained in EtOH-50. It implies a softening of the gels in the mixture solvent. This dependence of E_x on the solvent component well agrees with that exhibited by $\Delta\sigma$. Regardless of the larger contraction ratio in EtOH-50 and EtOH-80, the negative response and adjustability of $\Delta\sigma$ is therefore primarily determined by the solvent-induced dramatic changes in E_x.

Further, the response behavior of our system is very fast and well reversible. As shown in Fig. 3b, clearly, two peak-like transitions 0→1→2 and 3→4→5, which denote the fast response of the gels to the solvents, are observed. We attribute the sharp drop of σ_0 to σ_1 in 0→1 to the rapid softening process of the UTDN gels due to the presence of residual water. At the very beginning of the solvent alternation, it causes a transient EtOH/water mixture on/near the surface of the gels and thereby the gels give a low modulus. 1→2 denotes the hardening of the gels in response to the solvent change from the EtOH/water mixture to pure EtOH. With the characteristic contraction time of $\tau_{1\rightarrow2}$ = 14.8 s, this process is mainly controlled by the diffusion of water molecule outward the gel (Fig. S3a, ESI‡). Following 1→2, $\Delta\sigma$ reaches its maximum at the time scale of t_1 = 50 ~ 80 s and keeps almost constant until re-relaxed in water. The fast responses 3→4 and 4→5 are the fast re-softening of the contracted UTDN gels from EtOH to the transient EtOH/water mixture and the relative re-hardening to the pure water, respectively. In 4→5, the fast drop of $\Delta\sigma$ from about 0.25 MPa to zero can be completed within t_2 = 20 ~ 30 s. Exponent fitting analysis indicates that, the characteristic relaxation time $\tau_{4\rightarrow5}$ is about 10 s, which is relatively shorter than that in the process 1→2 (Fig. S3b, ESI‡). This different response time between 1→2 and 4→5 suggests a different hindrance for the diffusion of water in the gels. Our results imply that, as a typical soft and wet muscle-like material, the UTDN gels used here can serve as an artificial-muscle to execute force-generations as the real muscle behaves in living systems.

In summary, we have successfully developed a facial strategy to synthesize tough UTDN hydrogels through embracing the salt-controlled swelling process and the polymer chain pre-reinforced technique. Under micro-scale thickness, the UTDN hydrogels synthesized by this method showed super-high toughness with σ_b > 2 MPa, ε_b > 1000% and G ~ 600 J/m^2. Further, as an example for its application, our UTDN gels have demonstrated very fast and high solvent-triggered force generation. Within several decade seconds, $\Delta\sigma$ of the UTDN gels could reach 0.25 MPa, which is competitive to ~ 0.1 MPa of the real muscle.[19] Moreover, the value $\Delta\sigma$ was well adjustable over a wide range by simply changing the solvent component. The solvent-induced dramatic changes in the elastic modulus of the UTDN gels were considered as the main reason to cause this response in the contractile stress. Our successful synthesis to the tough UTDN gels and their striking muscle-like behavior responding to the solvent stimuli are expected to give rise to more applications in smart valves, actuators, robots, separation and even devices for controlling interfacial reaction. Experiments along this line will be performed and reported in due course.

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‡Electronic Supplementary Information (ESI) available: Additional experimental data and details and description of testing methods and setup.

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