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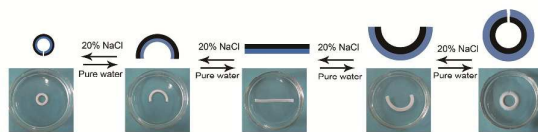
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Graphical Abstract

TiO₂ cross-linked nanocomposite hydrogel bilayer with bidirectional bending and shape switching behaviors was reported.



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High strength nanocomposite hydrogel bilayer with bidirectional bending and shape switching behaviors for soft actuators†

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We report on a type of TiO₂ cross-linked nanocomposite hydrogel bilayer with bidirectional bending and shape switching behaviors that could be used as soft actuators.

Stimuli-responsive hydrogels have become the focus of hydrogel research for the past decades because of their ability to show volume changes in response to external stimuli such as temperature¹, pH², salt³, electric field⁴ and light⁵. They have been widely used as building blocks in various applications including tissue engineering⁶, controlled drug delivery⁷, cell releasing⁸ as well as biosensors⁹. In recent year, stimuli-responsive hydrogels showing shape changing behaviors (e.g., bending and twisting) other than simple homogeneous swelling/de-swelling have aroused new scientific interests for their great potential to be used as soft actuators in biomedical application¹⁰. For example, Gao et al reported electric-sensitive graphene oxide/polyacrylamide hydrogels which exhibited bending behaviors in an electric field¹¹. Stark et al prepared a kind of magnetic field-driven actuators by direct incorporation of metal nanoparticles into the backbone of hydrogels¹². Lee et al synthesized near-infrared light-driven hydrogel actuators by interfacing genetically engineered elastin-like polypeptides with reduced-graphene oxide sheets¹³. Despite their unique properties, the actuation of these hydrogels can only be realized in directional fields due to their macroscopically homogeneous structures, which badly limited their biomedical applications under non-directional stimuli. Therefore, it remains a big challenge to fabricate hydrogel based soft actuators which could reveal shape changing ability in isotropic environments.

It is well-known that some plants are able to display bending or twisting behaviors by simple taking up or releasing of water due to their inhomogeneous structures¹⁴⁻¹⁶. Inspired by these plants, researchers have developed some hydrogel materials that can display bending behaviors based on bilayer structures. This method was first reported by Hu et al, who prepared a kind of spatial modulated bigel by limiting interpenetration of part of polyacrylamide (PAM) gel network with poly (N-isopropylacrylamide) (PNIPAA) gel network. The obtained bigel strip could bend almost into a circle in response to increased temperature¹⁷. In another study, Gracias et al described the fabrication of photopatterned actuators consisting of stimuli-

responsive hydrogel bilayers made from N-isopropylacrylamide (NIPAM), acrylic acid (AA) and polyethylene oxide diacrylate (PEODA)¹⁸. The resulting actuators could fold and unfold into three dimensional (3D) structures in response to the changing of aqueous conditions. Recently, Sun et al also prepared a bigel strip showing a bending behaviour in response to a temperature increase, via a direct combination through molecular recognition of two individual hydrogel strips with different temperature sensitivity¹⁹. Shim et al fabricated a chemo-responsive bilayer actuator film showing reversible curling/un-curling actuation in both water and ethanol due to the expansion and contraction of the polymer layer in the respective solvents²⁰. However, although these hydrogel bilayer materials successfully achieved stimuli-induced shape bending behaviors, they could only response to one type of stimulus and achieve unidirectional bending. Furthermore, all of these bilayers were prepared from conventional chemically cross-linked hydrogels with poor mechanical properties, which greatly limited their utilization as soft actuators in load-bearing systems.

Recently, we have demonstrated that TiO₂ nanoparticles (TiO₂ NPs) could be employed as inorganic cross-linking agents to prepared high strength nanocomposite hydrogels via in situ free radical copolymerization of N, N-dimethylacrylamide (DMAA) with acrylic acid (AA) or acrylamide (AM)^{21, 22}. The cross-linking mechanisms were contributed to the complexations and hydrogen bonds between -COOH and -NH₂ on polymer chains with -OH on the surface of TiO₂ NPs, respectively. It was found that the swelling ratios of the prepared hydrogels could be adjusted by changing the monomer ratios in the initial solutions. Thus, it is reasonable to believe that bilayers fabricated from TiO₂ cross-linked hydrogels with different initial compositions could display bending behaviors when placed in water. However, in order to achieve bidirectional bending, we need to find another force to induce bending towards the opposite direction.

In this study, we synthesized a new type of TiO₂ cross-linked nanocomposite hydrogels (TAN gels) by using AM and NIPAM as comonomers with the same procedure described in ref. 21. The TAN gels prepared by varying AM/NIPAM ratios were denoted as TANx gels, where x represents mole ratio of AM in total monomer amount ($100 \times [\text{AM}] / ([\text{AM}] + [\text{NIPAM}])$). The detailed compositions of TAN gels were listed in **Tab. S1** (See Supporting Information). The

resultant TAN gels also exhibited outstanding mechanical properties that can withstand large deformations, such elongation after knotting and compression, without breaking (**Fig.1**). Since it has been proven that the NIPAM cannot be used as the single monomer to prepare TiO₂ cross-linked nanocomposite hydrogels²³, the cross-linking mechanism of TAN gels is also contributed to the hydrogen bonds between –NH₂ groups on the polymer chains and –OH groups on TiO₂ surface²². Thus the relationship between mechanical properties and the monomer ratios (**Tab.1**) is the same as that of hydrogels reported in ref. 22. That is, as the decreasing of AM ratio, the cross-linking density decreased, leading to the increasing of toughness of hydrogels. For example, the TAN100 gel, which was prepared by using only AM as monomer, can only be stretched to 234% of its original length. When it was compressed 95% of their original height, some cracks appeared after compression although the sample still looked like intact. By decreasing the AM ratio and introduction of NIPAM in the initial solutions, the elongations at break gradually increased and the cracks on hydrogels after compression also became smaller and smaller. For the TAN50 gel, TAN40 gel and TAN30 gel, the elongations at break increased to 1309%, 1970% and 2494%, respectively, showing tensile strengths ranging from around 40kPa to more than 200kPa. In addition, all of these gels can be compressed 95% without any sign of cracks, displaying compressive strengths between 1.9MPa and 8.8MPa. These values of mechanical properties were much higher than conventional chemically cross-linked hydrogels and comparable to those of nanocomposite hydrogels cross-linked by clay^{24, 25} and other nanomaterials²⁶⁻²⁸. This new type of nanocomposite hydrogel with excellent mechanical toughness and strength provides an ideal candidate for preparing soft actuators.

The introduction of NIPAM in the initial solutions not only increased the mechanical toughness of the obtained TAN gels, but also influenced their swelling properties in different media. **Fig. 2** displays the time-dependent swelling ratios of TAN gels in pure water and 20% NaCl solution. As anticipated, the TAN gels with higher NIPAM ratios showed higher swelling ratios in pure water due to the decreasing of cross-linking densities. However, when the TAN gels were immersed in 20% NaCl solution, all the NIPAM-contained TAN gels started to shrink instead of swell. The reason for this phenomenon can be contributed to the salt (NaCl)-induced decreasing of volume phase transition temperature (VPTT) of NIPAM-contained copolymer hydrogels²⁹. Here, it should be noted that TAN100 gel showed similar swelling behaviors in both pure water and 20% NaCl solution, indicating that the osmotic pressure has little influence on the shrinking behaviors of TAN gels in NaCl solution. Under the NaCl solution of 20%, the VPTTs of TAN gels were lower than room temperature (about 25 °C), therefore, hydrogels excluded inside water and shrank. Since the VPTTs of TAN gels were originated from the NIPAM unit in the copolymer matrix, the increasing of NIPAM ratio (decreasing of AM ratio) in hydrogel formulation would decrease the VPTTs of TAN gels under the same NaCl concentration. Thus, the TAN gels prepared from higher NIPAM ratios can release more water and show lower swelling ratios.

From the swelling and shrinking curves of TAN gels measured in pure water and 20% NaCl solution, it can be found that TAN gels (e.g., TAN30 gel and TAN50 gel) which showed higher swelling ratios in pure water displayed lower swelling ratios in 20% NaCl solution, whereas hydrogels (e.g., TAN70 gel and TAN100 gel) showing lower swelling ratios in pure water maintained higher swelling ratios in 20% NaCl solution. Taking advantage of this finding, we designed and synthesized a hydrogel bilayer, using the formulation of TAN50 gel and TAN30 gel, which could show different stimuli-responsive bending behaviors in pure water and

20% NaCl solutions. As shown in **Fig. 3**, when the bilayer strip was placed in pure water, both of the two layers would swell while TAN30 gel showed larger swelling ratio than TAN50 gel. These uneven swellings of each layer led to the bending of bilayer strip towards the side of TAN50 gel, and ultimately formed a swelling hydrogel circle. In contrast, when the bilayer was immersed in 20% NaCl solution, it bended towards the side of TAN30 and forms a shrinking hydrogel circle because the TAN30 displayed lower swelling ratio compared with TAN50 gel. That is to say, the bilayer strip is able to show bidirectional bending responding to different stimuli, which is more prospective to be used as soft actuators than bilayer hydrogels mentioned above¹⁸⁻²⁰. Furthermore, because the swelling and shrinking behaviors of TAN gels are reversible, the formed hydrogel circles were able to automatically switch between each other when they were placed in pure water and 20% NaCl solution, alternately, showing reversible shape switching property.

Fig.4 demonstrates the utilization of prepared hydrogel bilayer strip as soft actuators to deliver a Teflon ring from 20% NaCl solution to pure water. Two pieces of bilayer strips were tied together on an iron hook and hung over a glass beaker with a Teflon ring between two strips. When the beaker was filled with 20% NaCl solution, the bilayer strip bended upwards into a circle and held the ring. After the circled strips were transferred to pure water alone with the iron hook, the Teflon ring was released as the bilayer strip swelled and started to bend to the other direction. Because of their reversible shape switching property, the bilayer strips can be reused to deliver another Teflon ring, which means that the bilayer strip could actuate repeatedly by transferring it between those two media.

In summary, we have prepared a novel type of hydrogel bilayer with unique bidirectional bending and shape switching behaviors based on high strength TiO₂ cross-linked nanocomposite hydrogels. The hydrogel bilayer is able to bend to opposite directions to form hydrogel circles in pure water and 20% NaCl solution due to the different swelling and shrinking behaviors of each layer. The formed hydrogel circles could reversible switch between each other when they were placed in pure water and 20% NaCl solution, alternately. This novel kind of bilayer with high mechanical strength and unique properties would have great potential to be used as soft actuators in load-bearing system

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Notes and references

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Tab.1 Mechanical Properties of TAN gels.

Hydrogels	Elongation at break/%	Tensile strength/kPa	Young's modulus/kPa	Compressive strength/MPa	Compressive modulus/KPa
TAN100	234.3±10.6	93.1±8.9	41.85±1.51	5.16±0.3	109.15±2.56
TAN90	340.1±13.8	111.1±10.2	35.38±1.42	5.89±0.4	92.83±2.05
TAN80	490.1±17.4	120.9±11.3	32.61±1.34	6.20±0.3	75.49±1.95
TAN70	663.3±18.4	128.3±11.9	30.82±2.03	6.77±0.2	61.36±1.56
TAN60	1111.5±22.6	140.2±12.8	26.98±1.91	7.21±0.4	52.98±1.26
TAN50	1309.5±27.0	197.2±15.9	21.03±2.14	8.81±0.8	42.53±1.35
TAN40	1970.7±30.6	136.3±11.5	14.37±1.59	5.78±0.5	33.32±1.22
TAN30	2494.4±41.2	41.2±9.6	3.47±1.05	1.94±0.2	11.84±1.03

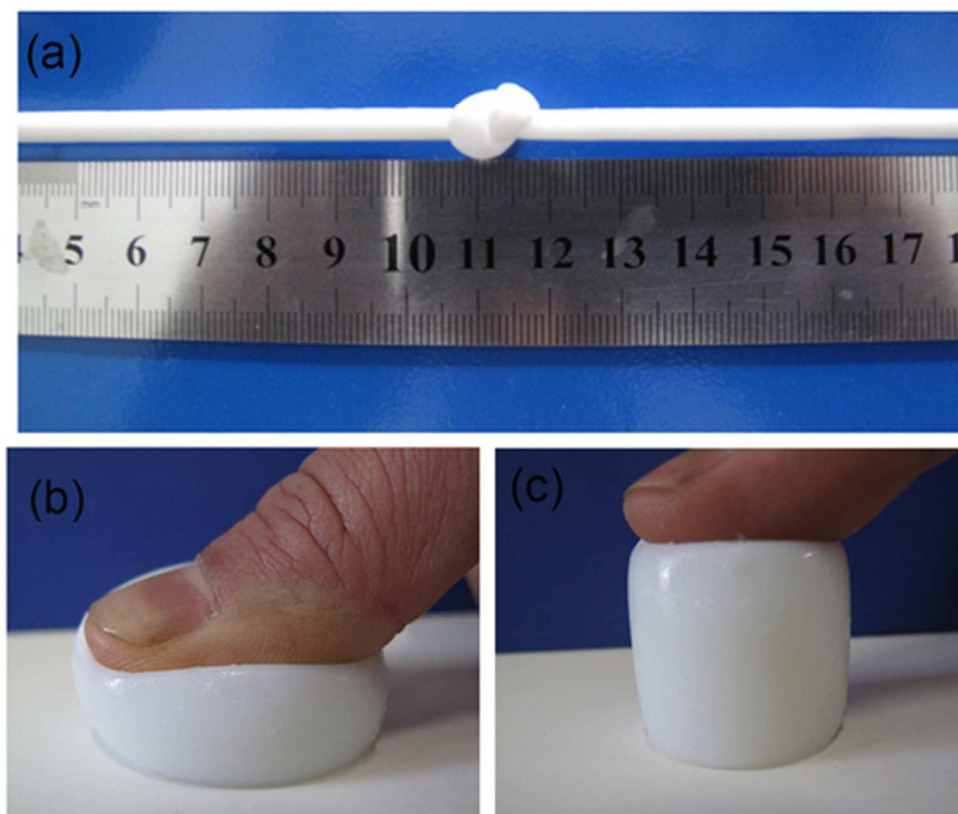


Fig. 1 Photographs of TAN gels. (a) Elongation after knotting; (b) under compression; (c) after compression
44x36mm (300 x 300 DPI)

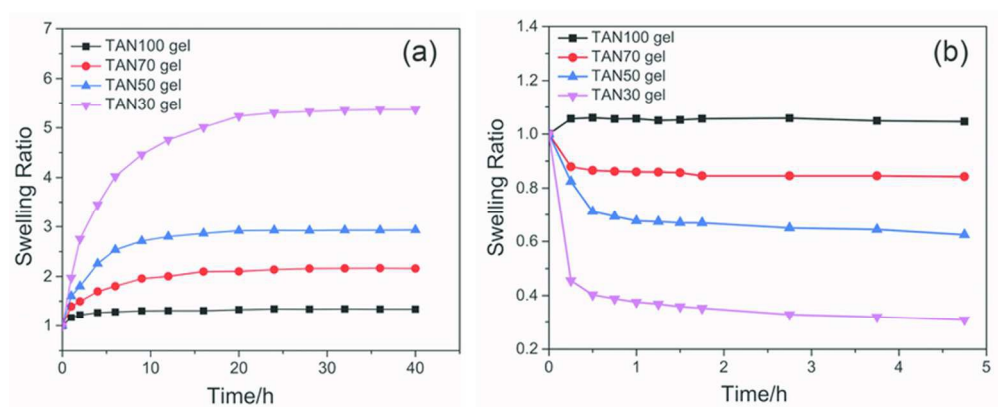


Fig. 2 Time-dependent swelling ratios of TAN gel in (a) pure water and (b) 20% NaCl solution 36x15mm (600 x 600 DPI)

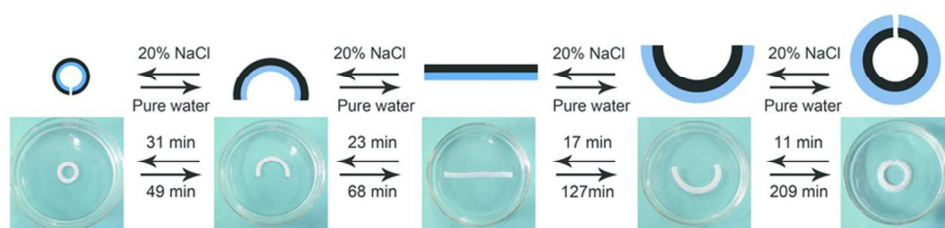


Fig. 3 Schematic representation of bidirectional bending and shape switching behaviors of hydrogel bilayer (Black layer: TAN50gel; Blue layer: TAN30 gel)
38x9mm (600 x 600 DPI)

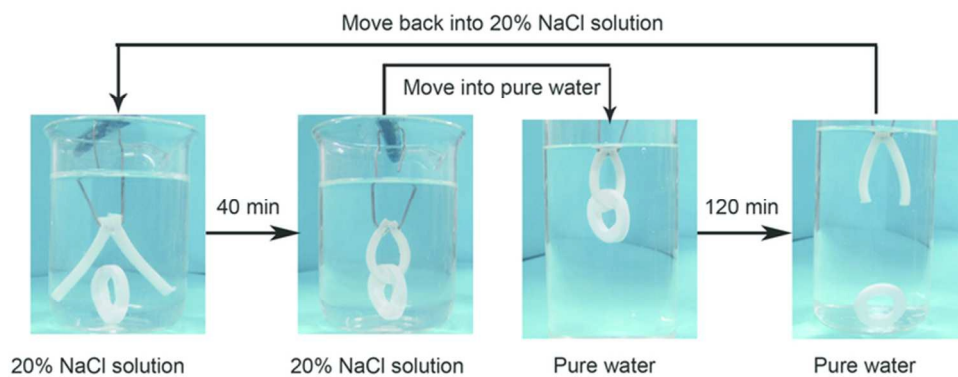


Fig. 4 Illustration of potential application of hydrogel bilayer used as soft actuators
34x13mm (600 x 600 DPI)