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A thermo-responsive dual-crosslinked hydrogel with ultrahigh mechanical strength

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Abstract Tough poly (N-isopropylacrylamide-co-acrylic acid) (P(NIPAM-co-AA)) hydrogel has been engineered by a hybrid covalently cross-linked P(NIPAM-co-AA) and an ionic (COO)₃Fe(III) coordinated network. The tough dual crosslinked hydrogel exhibited ~6 MPa of tensile strength, 69.8 MPa of compressive strength and 330% of elongation at break. The temperature sensitive swelling behaviors depended significantly on the hydrogel architectures.

Stimuli-responsive polymeric hydrogels could respond automatically to the changes of external stimuli, such as temperature, pH, light, redox.¹⁻⁹ These smart soft materials have great potential applications in the areas of tissue engineering, microlenses, forth.^{10, 11} sensors and so Among the stimuli-responsive hydrogels, temperature-responsive ones are the most attractive, because temperature variation is very easily controlled as an external stimulus. Poly (N-isopropylacrylamide) (PNIPAM), as a typical thermo-responsive polymer, is mostly studied with a negative thermal response around 32 °C.¹²⁻²¹ Traditional PNIPAM hydrogels that were prepared by free-radical copolymerization of the monomer NIPAM and a chemical organic crosslinker are usually fragile with low strength of \sim 5 kPa ²² and modulus of ~ 10 kPa.²³ The applications of PNIPAM-based hydrogels, thus far, are limited mainly to the cases where stress level is rather low. Enhancing the mechanical performance will extend the application area of the hydrogels to the soft machine. For example, in many practical applications such as temperature-controlled soft robots, both significant responsive-bending property and excellent mechanical property are indispensable for the temperature responsive hydrogels.

Recent progress in developing tough hydrogels has provided promising potential in

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this type of soft materials. During the last decades, many toughing methods have been developed in this regard by overcoming the intrinsic weakness and brittleness of the traditional hydrogels, including double-network (DN) hydrogel,^{24, 25} nanocomposite (NC) hydrogels,²⁶ slide-ring hydrogels,²⁷ microgel reinforced hydrogels,²⁸ macromolecular microsphere composite (MMC) hydrogels²⁹. The mechanical strength of these hydrogels was significantly promoted owing to the effective energy dissipation in their distinctive structures. For example, PNIPAM-based double network hydrogel achieved 17.5 MPa of comporessive strength;³⁰ PNIPAM/clay NC hydrogel exhibited approximately 1 MPa of tensile strength;³¹ nanostructured PNIPAM hydrogel showed ~240 KPa of tensile strength.³² Nevertheless, it is still challenging to design a hydrogel that exhibited ultrahigh strength.

Some metal cations can coordinate with appropriate ligands, such Ca²⁺/SA, and this interaction could serve as a non-covalent crosslinking point in fabricating DN tough hydrogels.²⁵ While Machida-Sano et al. found Fe-alginate gels could be used as a culture substrate for human dermal fibroblasts.³³ Besides Fe³⁺/SA pair, it was also reported by Tong et al. that the poly(acrylic acid) (PAA) gelation could be induced by Fe (III) through the binding of Fe (III) to the carboxyl groups.³⁴ It was proved that this trivalent ionic interaction was more effective in enhancing the mechanical properties than mono-/divalent interactions.³⁵ Very recently, Wang et al. developed a dual network poly(acrylamide-co-acrylic acid) (p(Am-co-AA)) hydrogel: a chemical cross-linked network and an ionic coordinated network. The resultant hydrogels exhibited mechanical strength with long elongation and good self-recovery.³⁶ The reported work provided a feasible way to construct a high-strength hydrogel with a dual network protocol. Very few efforts, to our best knowledge, have been conducted to construct a thermal responsive hydrogel with ultrahigh strength by this method.

Inspired by the effective $(COO)_3Fe(III)$ coordination interaction and previous tough p(Am-co-AA) hydrogels, in this contribution, we demonstrate a thermal responsive mechanically strong hydrogel with a two-level network structure. The first layer of the network was fabricated by a covalently crosslinked P(NIPAM-co-AA) network by a crosslinking agent (N, N'-methylenebis-acrylamide, BIS), on which the secondary

layer of the network crosslinked by coordination between acrylic groups on PAA and Fe(III) was built. This coordinating process was conducted by immersing the P(NIPAM-co-AA) hydrogel into the FeCl₃ solution. The hydrogel with the optimal composition, i.e. molar ratio of AA to NIPAM=25%, showed ultrahigh tensile strength (~6 MPa), high compressive strength (~69.8 MPa) and promoted elongation at break (330%). Endowed with the PNIPAM moiety, the dual crosslinked hydrogels exhibit thermal responsive swelling behaviors, showing a lower critical solution temperature (LCST) of 32 °C.

The P(NIPAM-co-AA) dual crosslinked hydrogel was prepared via a two-step strategy, as shown in Scheme 1. In the first step, free radical polymerization was conducted with NIPAM and AA as monomers, BIS as a crosslinker, APS as an initiator at room temperature (Scheme 1(i)) for obtaining a covalently crosslinked P(NIPAM-co-AA) hydrogel. Here, NIPAM served as a thermal responsive moiety and AA acted as the secondary cross-linking point for the coordination with Fe(III). Then in the second step, the chemical crosslinked hydrogel was immersed in 0.06 M Fe(III) solution for the coordination between acrylic groups and Fe(III) (Scheme (ii)). Thus, PAA can be cross-linked by stable Fe-carboxylic coordination bond between Fe(III) and acrylic acid groups (Fe(COO)₃), and a reddish brown tough Fe-P(NIPAM-co-AA) hydrogel was obtained. It has reported that a very small amount of crosslinkers (0.0216 % relative to AAm and AAc) were used in preparing P(AAm/AAc) chemical crosslinked hydrogel.³⁶ The corresponding D-hydrogel showed optimal mechanical properties. In the current work, the dual crosslinked hydrogel was fabricated by the similar method Therefore, a C-hydrogel with a small quantity of chemical cross-linker BIS (0.04 % molar ratio of AA and NIPAM) was chosen and demonstrated. Excessive FeCl₃ solution was used in this process to ensure enough Fe(III) could coordinate with AA in the hydrogel. Therefore, it should be mentioned here that an immersion process in water is necessary to remove superfluous Fe(III), which was evidenced by the color change of the water observed when the dual crosslinked hydrogel was immersed in water from colorless to light yellow. The coordination process was confirmed by FT-IR as shown in Fig. S1. In the

spectrum of D-hydrogel 25, The peaks ascribed to carboxyl and hydroxyl groups at 3457 and 1716 cm⁻¹ weakened compared with the those in C-hydrogel 25, which indicated that –COO⁻ in PAA coordinated with Fe(III). It is reported by Ding et al ³⁷ that three carboxyl groups in PAA could coordinate to Fe(III) and form a complex with coordination number of 6. Considering the same ligand and the similar treatment method, it is reasonable to infer that Fe (III) form a (PAA)₃Fe(III) complex with PAA. The hydrogels in this paper are denoted as C-hydrogel X or D-hydrogel X (C refers to covalent cross-linking, D refers to dual cross-linking, X refers to the molar ratio of AA/NIPAM: 5%, 15%, 25% and 30%). The detailed experimental information was available in Supporting Information. The feed compositions of the C-hydrogels were supported by FT-IR spectra of C-hydrogels with varying feed compositions in Fig. S2, which showed that the intensity of C=O stretching vibration at 1716 cm⁻¹ in AA gradually increased when the AA molar ratio was increased from 5 to 30.



Scheme 1 Possible schematic diagram of the formation of D-hydrogels: (i) Formation of first layer of P(NIPAM-co-AA) hydrogel network. (ii) The schematic illustration of the dual-crosslinked hydrogel.



Fig. 1 Tensile strength (a), tensile stress-strain curve (b) and compressive strength(c) of D-hydrogels, compressive strength (d) of C-hydrogels.

The NIPAM/AA molar ratio is continuously varied to achieve the optimal synthesis conditions of the D-hydrogels. Fig. 1 (a) and (b) present the tensile strength and stress-strain curve of the D-hydrogels with the varying NIPAM/AA molar ratios. The NIPAM/AA molar ratio affects the critical stretches obviously, and the tough D-hydrogel 25 exhibits the highest tensile stress of 6 MPa and the elongation at break of 330%. Intrinsically, the NIPAM/AA molar ratio represents the crosslinking density of the secondary network. Thus, the molar ratio dependent tensile behaviors could be understood as follows. When the NIPAM/AA molar ratio is too low, the hydrogel networks become too compliant and unable to sustain stress. In the other extreme, the cross-linking density is too high, and the hydrogel networks become too compact and unable to sustain deformation. On the contrary, the C-hydrogels with the single network were too fragile to carry out the tensile tests.

The tough hydrogel can exhibit even superior properties in compression (Fig. 1(c) and (d)). D-hydrogel 25 can sustain a 69.8 MPa of compressive stress when

compressed at 95%, which is ~ 2.8 times that of the C-hydrogel 15 (24.9 MPa), the latter exhibits the best compressive performance among the C-hydrogels. Moreover, D-hydrogel 25 showed excellent recovery after compression (Fig. 2 (a-c)), which did not break under high compression and quickly recovered its original shape after the release of the load in a few seconds. Figure 2(d) shows that a strip of D-hydrogel 25 could lift up a steel block of with a weight of ~ 1.5 kg, which further demonstrates the excellent mechanical strength of the D-hydrogel 25. It could be observed that C-hydrogel 15 and D-hydrogel 25 showed higher compressive strength in their respective sample groups. For the C-hydrogels, the carboxyl groups in NIPAM and hydroxyl groups in AA may interact with each other by hydrogen bonding³⁸. The strong intermolecular interaction will facilitate the energy dissipation during compression. In C-hydrogel 15, the interaction was strong and the compressive strength was the maximum. Further increasing the AA ratio may induce the stress concentration because of the high intermolecular interaction. For the D-hydrogels, the trends in compressive strength could be ascribed to the increasing crosslinking density of the second network. When the NIPAM/AA molar ratio is too low, the hydrogel networks were too compliant to sustain stress. In the other extreme, the cross-linking density is too high, and the hydrogel networks become too compact and unable to sustain deformation.



Fig. 2. D-hydrogel could sustain a high compression. (a)-(c) D-hydrogel 25 during the compression test, (d) D-hydrogel 25 strip lifts up a steel block of ~1.5 kg in weight.

The tough D-hydrogel outperforms overwhelmingly as compared with the C-hydrogel, showing substantial increase in tensile and compressive strength, recoverability and elongation at break. Many tough hydrogels, including

supramolecular hydrogels^{34, 39}, particle filled gels^{26, 40} and DN hydrogels,²⁵ were intrinsically common in the mixing weak and strong bonds in the hydrogel structure. The possible toughening mechanism was that the combination of the two networks with different structures and densities could contribute collaboratively to relaxation of locally applied stress and dissipation of the crack energy. For example, in alginate-polyacrylamide hybrid gel reported by Suo et al.²⁵ when a notched hybrid hydrogel was stretched, the polyacrylamide and alginate networks were believed to bear loads cooperatively: the polyacrylamide bridged the crack and stabilized deformation, enabling the alginate network to unzip over a large region of the gel. The unzipping the alginate network, in its turn, reduced the stress concentration of the polyacrylamide network ahead of the notch. In this paper, the reason behind the remarkable enhancement of the mechanical properties of the D-hydrogels was possibly attributed to the typical two-level network structure. The Fe(III) ions crosslink PAA via electrostatic interaction with COO⁻ on PAA polymer chains. The physical cross-linking between Fe(III) and PAA is reversible. Decross-linking ionic bonding dissipates energy under large deformation; coexisting of both chemical and physical cross-links and interpenetrating of long chain PNIPAM networks increase the elasticity of the hydrogels, which contributes to the recovery of its original configuration after deformation. The synergy of these two mechanisms enhances the mechanical performance of Fe-P(NIPAM-co-AA) hydrogel.

The hydrogel samples were freeze-dried to observe their inner structures by SEM as shown in Fig. 3 to provide some possible explanations behind the high strength of the D-hydrogels. It is interesting to find that C-hydrogel 25 and D-hydrogel 25 networks display distinct morphologies. For C-hydrogel 25, the inner structure of the network was characterized by a common sponge like large-pore morphology with the pore size of 100~300 μ m (Fig. 3(a) and (b)). On the contrary, a two-level structural hierarchical porous morphology with pore sizes at both the micro- and nanometer scales of the D-hydrogel 25 could be confirmed in Fig. 3(c). Inside the microporous structure, a large number of filamentous structures are present Fig. 3(d). It was reported that a LDH/PAM NC hydrogel presented a hierarchical network morphology

with a two-level porous structure and contributed to the unexpected yielding phenomenon in the mechanical results of LDH/PAM NC hydrogel.⁴¹ Therefore, we deduced that the present unusual hierarchical porous morphology with interconnected pore sizes at micro- and nanometer scales contributes significantly to the high mechanical strength of the D-hydrogels. In terms of the pore size, the pore size of D-hydrogel 25 was smaller than that of the C-hydrogel 25, indicating a denser structure of D-hydrogel 25. Moreover, it was found in the sample preparation process that the volume of the D-hydrogel 25 shrank to 70% of the original C-hydrogel 25 taken freshly out of the tube (inset in Fig. 3(a) and (b)). The evidence indicates that the cross-linking density of the dual cross-linked hydrogel, i.e. D-hydrogel 25 becomes higher and the inner structure is more compact.



Fig. 3. Typical SEM images of C-hydrogel 25 (a), (b) and D-hydrogel 25 (c), (d). Inset shows pictures of C-hydrogel 25 hydrogel taken freshly from the tube, D-hydrogel after being immersed in FeCl₃ solution for 24 h, respectively.



Fig. 4. Swelling ratio of (a) C-hydrogel and (b)D-hydrogel as a function of temperature. Error bars represent one standard deviation about the mean of measurements.

Besides the high strength, another functionality of the hydrogels was their thermal responsiveness owing to the incorporation of the PNIPAM moiety. The swelling behaviors of single network and dual network hydrogels at various temperatures were recorded to investigate the thermal responsiveness of the hydrogels. To our expectation, both C-hydrogels and D-hydrogels presented the obvious temperature dependent swelling behaviors (Fig. 4 (a) and (b)): both hydrogels showed sensitive swelling ratios toward temperatures; and the swelling ratio of the D-hydrogels decreased more sharply than that of the C-hydorgels. It could also be judged that the lower critical solution temperature (LCST) of D-hydrogels was 32 °C. The C-hydrogels showed a temperature dependent swelling behavior, that is, the swelling ratio decreased with the elevation of the temperatures. It can be seen that a LCST of ~45 °C was observed for C-hydrogel 5 and C-hydrogel 15. However, for C-hydrogel 25 and C-hydrogel 30 samples, the changes in the swelling ratio with the elevation of the temperature were inconspicuous. This may be associated with the hydrophilic nature of PAA. It is known that the hydrophilic/hydrophobic transition of PNIPAM could be ascribed to the varying hydrogen bonding strength with water with the increasing temperatures. At lower temperatures, PNIPAM is hydrophilic because the hydrogen bonding between amide group on the PNIPAM chains and water is strong. With the increasing temperatures, the hydrogen bonding strength becomes weak and

hydrophobic interactions turns strong and PNIPAM chains collapse. PAA is highly hydrophilic and the solubility is independent of the environmental temperature. With the increasing PAA concentration in the C-hydrogels, the copolymer hydrogel became more hydrophilic. This will hinder the conformational transition to the hydrophobic state of the PNIPAM chains to a great extent. For C-hydrogel-25 and C-hydrogel 30 samples, the PAA concentration was higher and the LCST was not pronounced, although the swelling ratio declined with the elevating temperatures. Moreover, the dual crosslinked hydrogels exhibited a much lower swelling ratio than the covalently crosslinked counterpart. For example, for C-hydrogel 30 and D-hydrogel 30 with the similar compositions, the value of the swelling ratio declined sharply from \sim 232 g/g to \sim 2.4 g/g, which indicated a more compact network structure of the D-hydrogel.





Fig. 5 shows the swelling ratio of C-hydrogels and D-hydrogels at 20°C with the prolonging time, to record the swelling kinetics of the hydrogels. The D-hydrogels presented faster rates of absorbing water than the C-hydrogels: the D-hydrogels achieved swelling equilibrium within about 24 hours (Fig. 5(b)), while the C-hydrogels took ~100 hours till the swelling ratio turned constant (Fig. 5(a)). As indicated in SEM observations in Fig. 3, the D-hydrogel 25 was characteristic of a hierarchical network structure, which was composed of a two-level porous network. The featured structure actually increased the specific surface area of the hydrogel. Therefore, it was believed that this structure hierarchy was helpful in the delivery of the water molecules into the inner network during swelling.

It should also be noted that great differences in the swelling ratios could be observed for the two groups of hydrogels. It is well known that the swelling behavior of the hydrogel depended greatly on the cross-linked density of the gel network. C-hydrogels were mildly crosslinked by a very small amount of chemical cross-linkers, and the crosslinking density was low and the corresponding swelling ratio was higher. On the other hand, D-hydrogels were dually crosslinked both by covalent bonding and coordinate bonding. For the hydrogel samples with different networks, i.e. C-hydrogel 30 and D-hydrogel 30, the higher amount of hydrophilic PAA in C-hydrogel 30 would result in a higher swelling ratio, whereas the counterpart D-hydrogel 30 with the same amount of PAA would mean that the secondary crosslinking was higher. These collaborative factors led to a large gap in the values of swelling ratio of the two groups of the hydrogels. The swelling behaviors with varying pH values from 2 to 8 were also tested to indicate the influence of pH values (Fig. S3). C-hydrogel 15 was selected as a typical sample. It could be observed that the swelling ratio of C-hydrogel 15 increased when the pH values was raised from 2 to 6. Further increasing pH values will result in a small decrease of the swelling ratio. It is known that the pKa of PAA is 4.75. In the current system, however, the critical transition in swelling ratio occurred at pH=3. This may be caused by the interaction between PNIPAM and PAA. In the acid medium, PAA is protonated and may interact with the amide groups in PNIPAM by the hydrogen bonding interaction. This effect will decrease the hydrogen bonds within the PAA chains. Thus, the critical pKa of PAA was decreased to obtain stronger interactions between themselves.

In summary, a novel functional dual-crosslinked hydrogel was designed by combining the covalent crosslinking and the multivalent ion paring of acrylic acid and Fe(III). The resulting hydrogels exhibited very high mechanical strength and the mechanical properties could be tuned by varying the concentration of acrylic acid. The ion coordination interaction served as a weak and dynamic bonding, and facilitated the effective energy dissipation when the load was applied. Moreover, the swelling ratios of the dual crosslinked hydrogels showed sensitiveness toward temperatures, and the LCST of \sim 32 °C could be observed. The present hydrogels were

endowed with desirable high strength and thermal responsiveness, and if designed rationally and subtly, they might have promising potential as soft robotics, manipulators, sensors and tissues.

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Notes and References

- D. J. Pochan, J. P. Schneider, J. Kretsinger, B. Ozbas, K. Rajagopal and L. Haines, J. Am. Chem. Soc., 2003, 125, 11802-11803.
- L. Peng, H. J. Zhang, A. C. Feng, M. Huo, Z. L. Wang, J. Hu, W. P. Gao and J. Y. Yuan, *Polym. Chem.*, 2015, 6, 3652-3659.
- S. Keun, K. Sung, W. Young, H. Jin, Y. Ji and H. Soon, *Biomaterials*, 2004, 25, 2393-2398.
- A. Gutowska, Y. H. Bae, H. Jacobs, J. Feijen and S. W. Kim, *Macromolecules*, 1994, 27, 4167-4175.
- H. J. Zhang, Q. Yan, Y. Kang, L. L. Zhou, H. Zhou, J. Y. Yuan and S. Z. Wu. Polymer, 2012, 53, 3719-3725.
- 6. C. Tsitsilianis, Soft Matter, 2010, 6, 2372-2388.
- X. L. He, S. Yu, Y. Y. Dong, F. Y. Yan and L. Chen, J. Mater. Sci., 2009, 44, 4078-4086.
- G. T. Gotzamanis, C. Tsitsilianis, S. C. Hadijyannakou, C. S. Patrickios and R. Lubetsky, *Macromolecules*, 2006, **39**, 678-683.
- 9. H. J. Zhang, X. J. Pang and Y. Qi, RSC Adv., 2015, 5, 89083-89091.
- 10. Z. X. Zhang, K. L. Liu and J. Li, Angew. Chem., Int. Ed., 2013, 52, 6180-6184.
- 11. J. Li and X. J. Loh, Adv. Drug Delivery Rev., 2008, 60, 1000-1017.
- F. Zhang, G. H. Hou, S. J. Dai, R. Lu and C. C. Wang, *Colloid Polym. Sci.*, 2012, 290, 1341-1346.

- Y. P. Lu, T. Q. Chen, A. X. Mei, T. Y. Chen, Y. W. Ding, X. H. Zhang, J. T. Xu, Z.
 Q. Fan and B. Y. Du, *Phys. Chem. Chem. Phys.*, 2013,15, 8276-8286.
- 14. T. Wu, G. Zou, J. M. Hu and S. Y. Liu, Chem. Mater., 2009, 21, 3788-3798.
- Y. F. Zhang, H. LIU, H. F. Dong, C. H. Li and S. Y. Liu, J. Polym. Sci. Part A: Polym. Chem., 2009, 47, 1636-1650.
- Y. Z. Pan, H. Q. Bao, N. G. Sahoo, T. F. Wu and L. Li, *Adv. Funct. Mater.*, 2011, 21, 2754-2763.
- Z. Q. Yu, D. Y. Tang, H. T. Lv, Q. Feng, Q. N. Zhang, E. Y. Jiang, Q. D. Wang, Colloids Surf. A Physicochem. Eng. Asp., 2015, 471, 117-123.
- B. Y. Du, A. X. Mei, Y. Yang, Q. F. Zhang, Q. Wang, J. T. Xu and Fan Z. Q, *Polymer*, 2010, **51**, 3493-3502.
- R. Zhu, G. Wu, X. H. Liu, D. D. Shi, B. Cao, R. C. Gu, J. W. Xiao and H. Liao, *RSC Adv.*, 2015, 5, 28023-28029.
- J. C. Chen, M. Z. Liu, C. M. Gao, S. Y. Lu, X. Y. Zhang and Z. Liu, *RSC Adv.*, 2013, 3, 15085-15093.
- 21. Z. W. Wang and P. Y. Wu, RSC Adv., 2012, 2, 7099-7108.
- 22. K. Haraguchi, T. Takehisa, S. Fan, *Macromolecules*, 2002, 35, 10162-10171.
- 23. X. Z. Zhang, D. Q.Wu, C. C. Chu, Biomaterials, 2004, 25, 3793-3805.
- J. P. Gong, Y. Katsuyama, T. Kurokawa and Y. Osada, *Adv. Mater.*, 2003, 15, 1155-1158.
- J. Y. Sun, X. H. Zhao, W. R. K. Illeperuma, O. Chaudhuri, K. Hwan Oh, D. J. Mooney, J. J. Vlassak and Z. G. Suo, *Nature*, 2012, 489, 133-136.
- 26. K. Haraguchi and T. Takehisa, Adv. Mater., 2002, 14, 1120-1124.
- 27. Y. Okumura and K. Ito, Adv. Mater., 2001, 13, 485-487.
- J. Hu, K. Hiwatashi, T. Kurokawa, S. M. Liang, Z. L. Wu and J. P. Gong, Macromolecules, 2011, 44, 7775-7781.
- T. Huang, H. G. Xu, K. X. Jiao, L. P. Zhu, H. R. Brown and H. L. Wang, *Adv. Mater.*, 2007, **19**, 1622-1626.
- R. C. Fei, J. T. George, J. Park, A. K. Means, M. A. Grunlan, *Soft Matter*, 2013, 9, 2912-2919.

- 31. K. Haraguchi, H. J. Li, Angew. Chem., Int. Ed., 2005, 44, 6500-6504.
- L. W. Xia, R. Xie, X. J. Ju, W. Wang, Q. Chen, L. Y. Chu, *Nat. Commun.*, 2013, 4, 2226.
- I. Machida-Sano, S. Ogawa, H. Ueda, Y. Kimura, N. Satoh, and H. Namiki, Int. J. Biomater., 2012, 820513.
- F. Peng, G. Z. Li, X. X. Liu, S. Z. Wu and Zhen Tong, J. Am. Chem. Soc., 2008, 130, 16166-16167.
- 35. C. H. Yang, M. X. Wang, H. Haider, J. H. Yang, J. Y. Sun, Y. M. Chen, J. X. Zhou and Z. G. Suo, ACS Appl. Mater. Interfaces, 2013, 5, 10418-10422.
- 36. P. Lin, S. H. Ma, X. L. Wang and F. Zhou, Adv. Mater., 2015, 27, 2054-2059.
- Z. Z. Ding, Y. C. Dong, B. Li and M. Li, *Acta Phys. -Chim. Sin.*, 2013, 29(1), 157-166.
- 38. S. T. Sun and P. Y. Wu, J. Mater. Chem., 2011, 21, 4095-4097.
- M. A. Haque, T. Kurokawa, G. Kamita and J. P. Gong, *Macromolecules*, 2011, 44, 8916-8924.
- K. J. Henderson, T. C. Zhou, K. J. Otim and K. R. Shull, *Macromolecules*, 2010, 43, 6193-6201.
- 41. Z. Q. Hu and G. M. Chen, Adv. Mater., 2014, 26, 5950-5956.

Table of Contents

A thermal-responsive hydrogel with ultrahigh mechanical strength was engineered by a covalently cross-linked and an ionic coordinated network.

