ES Materials & Manufacturing

Highly Stretchable Self-Healing Nanocomposite Hydrogel Reinforced by 5 nm Particles

Xiaosai Hu,[1] Rui Liang,[1] Jun Li,[2] Zhengping Liu[2*] and Guoxing Sun[1*]

This study firstly reports that low content of non-aggregated calcium hydroxide (Ca(OH)$_2$) nano-spherulites (CNS) (200 ppm, diameters <5 nm) acting as cross-linkers pioneers highly stretchable self-healing PAA/CNS nanocomposite hydrogel (NC gel). Such NC gel exhibits increased mechanical properties (2300 % of tensile strain, 72 kPa of tensile strength, 0.611 MJ/m^3 of toughness), excellent self-recovery (high recoverability against elongation of up to 1800% with tensile stress of 35 kPa), and most notably, remarkable self-healing ability (extensibility of 2100 % and toughness of 0.599 MJ/m^3), suggesting even a small amount of CNS helps to establish a high stretchable and outstanding self-healing hydrogel.

1. Introduction

Self-healing materials have recently gained increasing interests because of their self-repair capabilities after damage, which properties are highly desirable for widely applications from weather resistant surfaces to robust electronics. Inspired by this self-healing capacity, smart hydrogels have always been an interesting topic in the gel science field because of their stimuli-responsive properties to external environment like temperature,[1] conductivity,[2] pH value,[3] strain,[4] and especially their self-healing properties.[5-6] Among these interesting properties, self-healing ability is one outstanding property of hydrogel. Endowing self-healing capability for damaged hydrogel is a promising way to extend the hydrogel-based devices life cycle. Up to date, various strategies like hydrogen bonds, host-guest interaction, metal coordination, dynamic chemical bonds, hydrophobic associations and ionic interactions, have been applied to fabricate self-healing hydrogel.[7-10] Despite extensive studies on improving self-healing efficiency of hydrogel, limitations imposed by poor mechanical behavior still have a negative impact on its application scope.[11-13] Highly stretchable self-healing hydrogel is still rarely reported. Meanwhile, to design hydrogels possessing high stretchable and excellent self-healing properties play a role in the emerging fields including tissue scaffolds,[14] drug delivery,[15] cell supports[16] and actuators.[17] Darabi[18] designed a mechanical and self-healing hydrogel through dynamic ionic interactions between COOH groups of PAA and Fe^{3+}. Though the mechanical performance of such hydrogel can recover to original state after 2 min, this design suffered from low stretchability (1500 %) and low strength (6 kPa). Kang[19]

developed a dual-network self-healing chitosan/PAA hydrogel through Fe^{3+} ion coordination and hydrogen bonds between chitosan molecular and PAA. The break and reform of dynamic Fe^{3+} ion coordination bonds can occur during the tensile testing by means of unfolding and sliding of polymer chains, endowing such hydrogel with mechanical property and self-healing efficiency. Though this self-healed hydrogel possessed high elongation up to 2390 % at break by adjusting Fe^{3+} contents, its tensile strength only reached 20 kPa. Thus, it is still meaningful to develop hydrogels with desirable mechanical strength and self-healing behaviors. As far as we knew, PAA-based self-healing hydrogel with more than 2000 % tensile strain at rupture for both original and healed hydrogel is rarely reported. Low mechanical and self-healing properties still could damage prospects for tissue engineering, heavy ions detection, sensor, supercapacitor and drug delivery.

Greatly improved mechanical property and self-healing efficiency of PAA-based hydrogel could be successfully achieved if appropriate cross-linkers can be selected. Until now, most of the reported self-healing hydrogel did not achieve improved self-healing ability and enhanced mechanical performance simultaneously. The self-healing hydrogel generally showed poor mechanical properties. The aim of this work was to use a novel cross-linker to design well-cross-linked three-dimensional network for PAA-based nanocomposite hydrogel with advantages of good mechanical property and self-healing efficiency. In our work, a novel highly stretchable self-healing PAA-based nanocomposite hydrogel (NC gel) achieved by employing 200 ppm CNS as cross-linkers of hydrogel was achieved. Without any other cross-linker, the introduction of CNS as cross-linker triggered the robust and flexible three-dimensional polymer framework in the NC gel, endowing them with outstanding self-healing efficiency and admirable mechanical properties simultaneously. To study the self-healing property, as-obtained PAA/CNS NC gel was cut with a blade, and then freshly-cut parts of NC gel re-contacted and healed with the support of acid. The resulting hydrogel showed remarkable stretchable self-healing properties, such as high tensile elongation (2300 %), excellent self-recoverability at a high strain of 1800 %, and notable self-healing efficiency (>91 % of tensile strain and >98 % of toughness). The

[1] Joint Key Laboratory of the Ministry of Education, Institute of Applied Physics and Materials Engineering, University of Macau, Avenida da Universidade, Taipa, Macau, 999078, China
[2] College of Chemistry, Beijing Normal University, Beijing, 100875, China
*E-mail: gxsun@um.edu.mo ; lzp@bnu.edu.cn

hydrogen bonds between COOH groups of PAA polymer chains and CNS were possibly ascribed to these improved self-healing capability and mechanical strength. According to our knowledge, it was firstly reported that PAA-based self-healing NC gel simultaneously showed elongation of more than 2000 % for original and healed gel even under low cross-linker content (200 ppm). The present work had a great potential to help pave the way for designing a highly stretchable self-healing hydrogel.

2. Experimental section

Materials
Acrylic acid (AA), urea, ammonium persulfate (APS), sodium sulfocyanate (NaSCN), calcium carbonate, N,N,N',N'-tetramethyl-ethylenediamine (TEMED), sodium hydroxide (NaOH) and silica were provided by Sigma-Aldrich Chemical Reagent Co.Ltd. .These chemicals were of analytical grade and used without further purification. Deionized water was employed in the entire polymerization process.

Fabrication of stretchable self-healing NC gel
The fine Ca_3SiO_5 powders were prepared according to literatures.[20-21] The highly stretchable self-healing NC gel was synthesized by free radical polymerization. To begin with, Ca_3SiO_5 powders (0.03 g) was dispersed in water (20 ml) with magnetic stirring in ice water bath for 30 min and then maintained for another 3 days to produce enough CNS. Subsequently, AA (6 ml) and NaOH (3 g) dispersed in water (15 ml) was added into above CNS solution with strong stirring in ice water bath for 30 min under N_2 protection. Finally, APS (0.24 g) and TEMED (250 ul) were successively added until the polymerization was completed. As for comparison, pure PAA hydrogel was also prepared with no CNS.

Characterizations
The FEI Talos F200X Transmission electron microscopy (TEM) was used to characterize CNS. The Zeiss Zigma high-resolution scanning electron microscope (SEM) was employed to study freeze-dried swollen PAA/CNS NC gel and Ca_3SiO_5 powders. The surface elements of Ca_3SiO_5 were studied by using Energy-Dispersive Spectroscopy (EDS). Fourier transform infrared spectroscopy (FTIR) spectra of the hydrogels was carried out on a Nicolet iS10 FTIR spectrometer within the frequency range $(3600-500 \ cm^{-1})$ at a resolution of 4 cm^{-1}. A Rigaku Smartlab high resolution X-ray diffraction (HRXRD) pattern was used to analyze Ca_3SiO_5 within 2θ range (10−80°).

Mechanical tests
Mechanical properties of hydrogels were evaluated on a MTS (model E44, EXCEED) testing machine at room temperature (25 °C). Tensile testing for the samples (6 mm × 3mm ×20 mm) was performed at a strain rate of 1 mm/s with a 50 N load cell. The residual strain (r) was defined as the change in final length (L) after the releasing of loading against initial gauge length (L_0) of samples (r=(L-L_0)/L_0×100 %). The area under the stress-strain curves was defined as toughness. The area of the hysteresis loop encompassed by the loading-unloading curve represented the dissipated energy for each cycle.

Rheological tests
Rheological behavior of cylindrical hydrogels (20 mm in diameter and 2 mm in height) was observed by using Anton Paar MCR 301 rheometer. Oscillatory strain amplitude (0.01-300%) was carried out at an angular frequency of 2 rad/s and 25 °C. Frequency sweep tests at 0.5 % strain and 25 °C in a linear viscoelastic range were studied over the angular frequency of 0.1~100 rad/s. Temperature sensitivity was investigated by heating the gels at temperature range of 10 to 80 °C with a heating rate of 2 °C/min at 2 rad/s and 0.5 % strain.
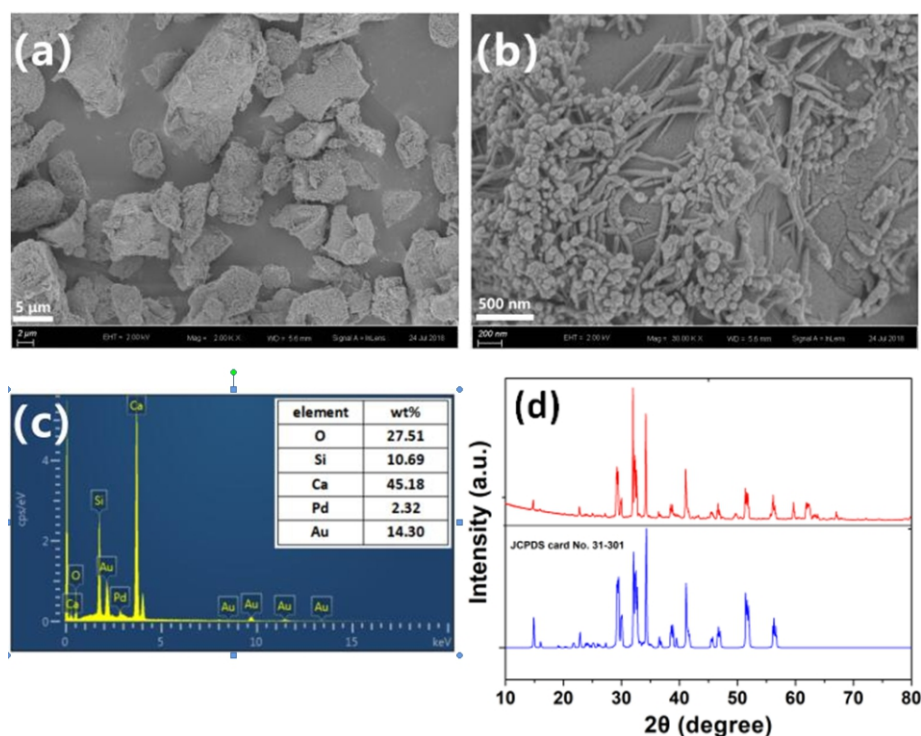

Fig. 1 SEM images (a-b), EDS spectra (c) and XRD pattern (d) of as-prepared Ca_3SiO_5 particles.

3. Results and discussion

In our work, the hydration process of tricalcium silicate (Ca_3SiO_5) was employed to produce CNS. Herein, SEM, EDS and XRD were firstly used to prove as-obtained fine Ca_3SiO_5 particles. It was clear that Ca_3SiO_5 exhibited irregular block shape and furthermore rod-like structures were also found on the surface of Ca_3SiO_5 (Fig. 1a, b). The EDS spectrum suggested that O, Si and Ca were main components of as-obtained Ca_3SiO_5 (Fig.1c). Additionally, Au and Pd were mainly ascribed to the coating material. Several strong diffraction peaks were observed in XRD pattern of as-prepared Ca_3SiO_5, indicating high crystallinity degree for Ca_3SiO_5 (Fig. 1d). Characteristic XRD patterns of as-obtained Ca_3SiO_5 (29.5°, 32.2°, 34.3°, 41.1° and 51.8°) were consistent with that of triclinic-Ca_3SiO_5.[22-23] XRD and SEM-EDS suggested the formation of high pure triclinic-Ca_3SiO_5 particles.Tables 1 will be located at the top or bottom of the column following their first citation in the text during production (unless they are equations, which appear in the flow of the text). They can be single column or double column as appropriate and require appropriate captions. Text is not wrapped around any of the graphics.

The proposed preparation mechanism for highly stretchable self-healing PAA/CNS NC gel was shown in Fig. 2. To begin with, fine Ca_3SiO_5 powders were dispersed in water under stirring for 30 min in an ice water bath and then maintained for another 3 days (Fig. 2a, b). Ca^{2+} would release from the surface of Ca_3SiO_5 particles in the meantime (Fig. 2a) and crystallize to produce CNS (Fig. 2b).[20] This can be clearly found in Fig. 3a, showing a TEM photograph of particles with diameters around 5 nm. Three days later, 200 ppm of CNS was obtained.[20] This can be clearly found in Fig. 3a, showing a TEM photograph of particles with diameters around 5 nm. Three days later, 200 ppm of CNS was obtained.[20] Then, AA buffered by NaOH was added with constant stirring for 30 min in ice water bath under N_2 atmosphere (Fig. 2c). Subsequently, APS and TEMED were successively added into above suspension under strong stirring until a uniform solution was obtained. Three days later, highly stretchable self-healing PAA/CNS NC gel was obtained. Physically cross-linked PAA polymer chains constituted this skeleton of NC gel (Fig. 2d and Fig. 4). Correspondingly, SEM images exhibited that freeze-dried swollen NC gel was of porous structures (Fig. 3b-d), suggesting the existence of framework and interconnected channels within internal structure for as-obtained NC gel by using CNS as cross-linkers.

Meanwhile, it was found that neutralization degree of AA had a great impact on the mechanical performance of NC gel during this procedure. When the value of neutralization degree increased up to 90 %, at which the pH value of mixture was around 6.2, our NC gel possessed optimum stretchable self-healing properties. However, further increase of neutralization degree led to worse mechanical performance. These results indicated moderate neutralization degree would promote mechanically enhancement for NC gel, which was attributed to partially ionization of COOH groups of AA. Ionization of COOH groups was helpful for the swelling of hydrogel. It was proposed that the diffusion of polymer chains and residual−COOH of AA were conducive to the hydrogen bonding interactions between COOH groups of PAA polymer chains and the oxygen-containing groups of CNS. Therefore, sufficient hydrogen bonding between polymer chains and CNS would be formed, resulting in three-dimensional cross-linked framework for our NC gel and further highly stretchable self-healing properties of NC gel. However, further increased ionization of COOH group possibly caused great damage on the formation of hydrogen bond due to the complete disappearance of COOH in polymer chains. In addition, NaOH also played a role in adjusting PH value of mixture. Partially ionization of AA would increase the pH value of solution, and moderate PH may promote stable existence of CNS in mixture. As a result, we found that
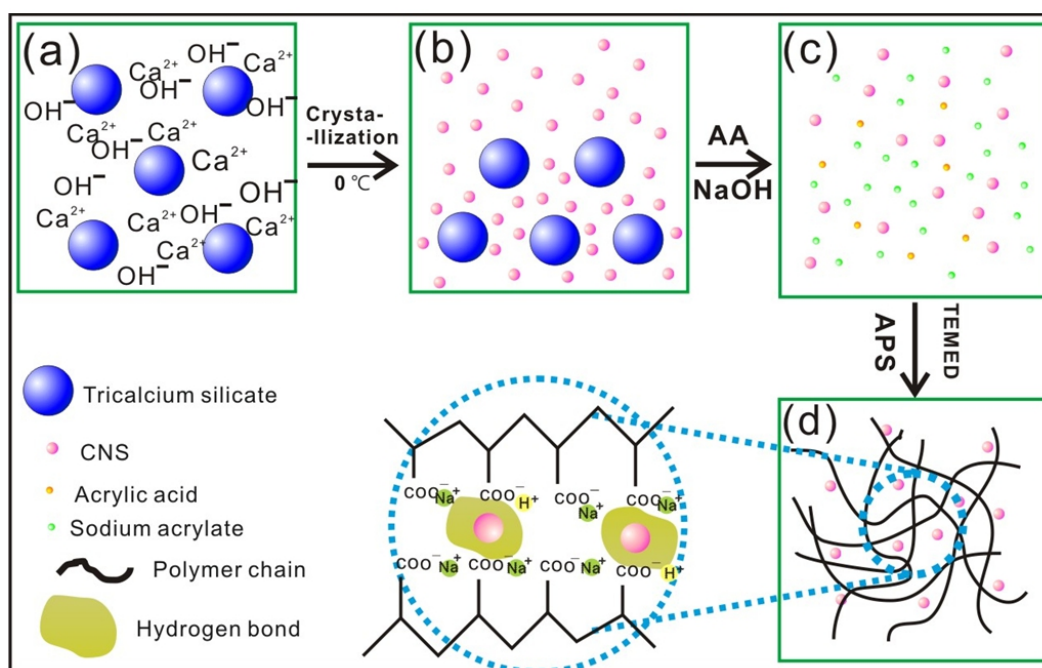

Fig. 2 Schematic diagram of stretchable and self-healing PAA/CNS NC gel. (a) Ca^{2+} released from surface of tricalcium silicate (Ca_3SiO_5); (b) Ca^{2+} crystallized to produce calcium hydroxide ($Ca(OH)_2$) nano-spherulites (CNS, diameters < 5 nm); (c) acrylic acid (AA), sodium acrylate and CNS were well blended; (d) Formation of highly stretchable self-healing NC gel cross-linked by CNS through hydrogen bonds.

NC gel had a maximum mechanical performance and self-healing ability when 90% of AA was neutralized. Meanwhile, we also found that pure PAA gel would dissolve in adequate water solution, meaning that poor structure for this gel.

The hydrogen bonds within polymer chains and between the polymer chains and CNS, mainly take responsibilities for mechanical and self-healing properties of our PAA/CNS NC gel. Meanwhile, the physical entanglement of polymer chains can not be neglected to some extent. To detect the role of hydrogen bonding across the interface of two damaged PAA/CNS NC gel, the healed gel was immersed into hydrogen-bonds-breaking solvents (urea or NaSCN) and pure water solution. The healed NC gel showed similar swelling behavior in urea and pure water solution, but it was largely swelled in NaSCN solution. Meanwhile, two cut halves of NC gel could be repaired only under acid conditions but not alkaline conditions, meaning that the formation of COOH in polymer chain was favourable for the re-construction of hydrogen bonds at the interface and further conducive to the self-healing behavior. These results indicated that hydrogen bonding significantly impacted on the self-healing efficiency. Furthermore, FTIR spectroscopes was also employed to prove hydrogen bonds in our NC gel. The FTIR spectra of the hydrogels was displayed in Fig. 4. For pure PAA gel, the bands located at 3417 cm^{-1} were the O-H stretching vibration from COOH groups of PAA polymer chains. The C-C vibration observed at 1000 cm^{-1} and 860 cm^{-1} and the stretching vibration of C$-$O$-$C around 1125 cm^{-1} suggested the formation of PAA polymer chains. The band around 2940 cm^{-1} was ascribed to the stretching vibration of C-H. Furthermore, the bands at 1619 cm^{-1} and 1445 cm^{-1} were corresponding to the stretching vibration of C=O in COOH and COO$-$, respectively. In addition, the O-H bending vibration observed at 1383 cm^{-1} and 910 cm^{-1} confirmed the existence of COOH in polymer chains. As for FTIR spectrum of PAA/CNS NC gel, the
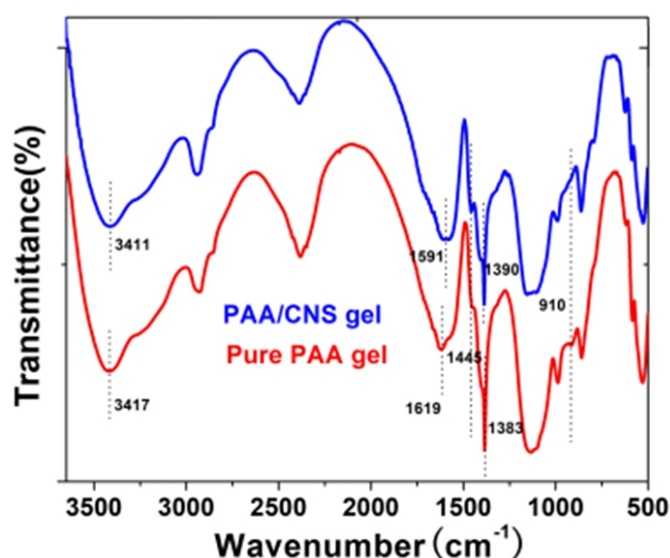

Fig. 4 FTIR spectra of PAA/CNS NC gel and pure PAA gel using KBr pellets.

peak at 3417 cm^{-1} for O-H had obviously shifted to 3411 cm^{-1}. The bands around 1619 cm^{-1} for C=O stretching vibration of COOH shifted to 1591 cm^{-1}. The peak corresponding to O$-$H bending vibration of COOH showed a slight shift from 1383 cm^{-1} to 1390 cm^{-1}. These shifts suggested the hydrogen bonding interactions between PAA polymer chains and CNS.

CNS acting as cross-linkers had a positive effect on the mechanical performance of hydrogels. Thus, as-obtained NC gel were flexible and strong to sustain high elongation of up to 2000 % by hand,
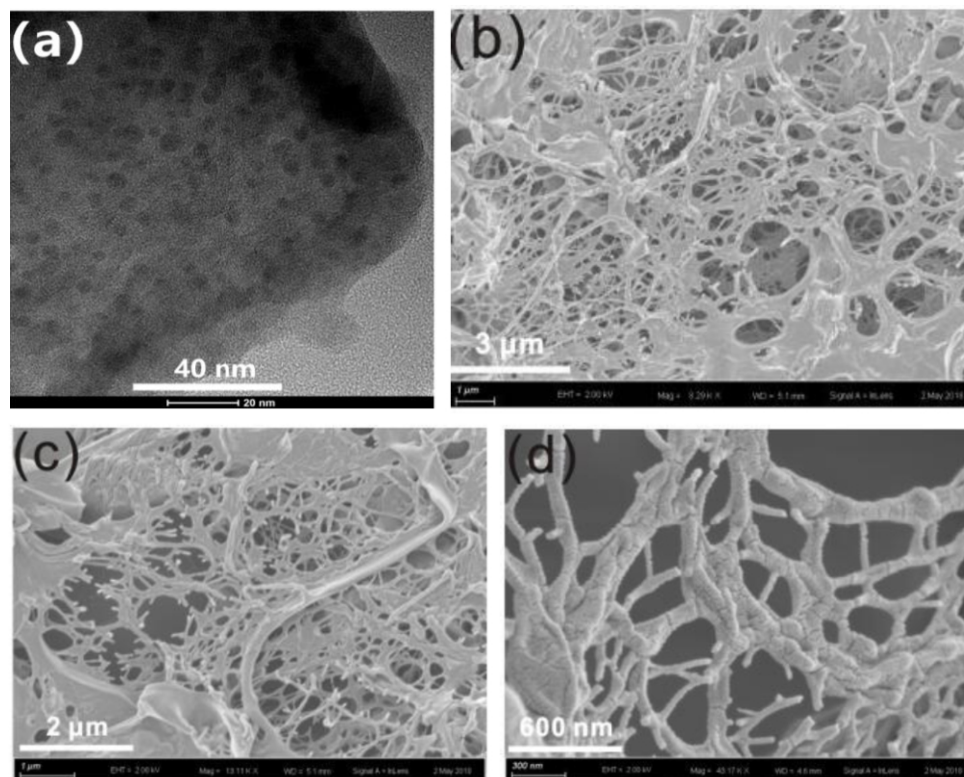

Fig. 3 (a) TEM image of CNS and (b-d) SEM images of as-obtained freeze-dried swollen PAA/CNS NC gel.

which could recover to its original length in one second with no visible deformation after the loading was released (Fig. 5a). To determine this enhanced mechanical behavior, hydrogels were subjected to uniaxial tensile. As displayed in Fig. 5b-c, the representative stress–strain curves showed that PAA/CNS NC gel exhibited a remarkably increased elongation of up to 2300 % at rupture along with a tensile strength of 72 kPa. The toughness of this NC gel was 0.611 MJ/m³. To the best of our known, PAA-based self-healing NC gel possessing such novel mechanical properties mainly through hydrogen bonding interactions between PAA polymer chains and cross-linker was reported for the first time. However, as for pure PAA hydrogels without any cross-linker, the stretch ratio and corresponding strength at break were lowered to 800% and 21 kPa, respectively. Both results indicated that CNS could greatly enhance mechanical properties of PAA-based self-healing hydrogels.

Meanwhile, the residual strain (r) can be considered as an index of recoverability. It was found that NC gel could revert to 15 % strain relative to the initial gauge length after being stretched 23 times, and a residual deformation ratio for pure PAA gel was 430 %, indicating good recoverability for PAA-based hydrogels cross-linked by CNS. Cyclic uniaxial tensile tests at a strain of 1800 % without any resting time for recovery between each cycle were further performed to analyze recoverability of our NC gel (Fig. 5d-e). The sample was firstly loaded to 1800 % strain at a speed rate of 3 mm/s, and subsequently the loading was released at the same speed. A small hysteresis area and less obvious residual deformation ratio were observed, indicating a good elasticity for NC gel. After 5 cycles following the first cycle without any time delay, the hysteresis loop did not show an clear change and reached similar level, indicating that desirable self-recoverability against
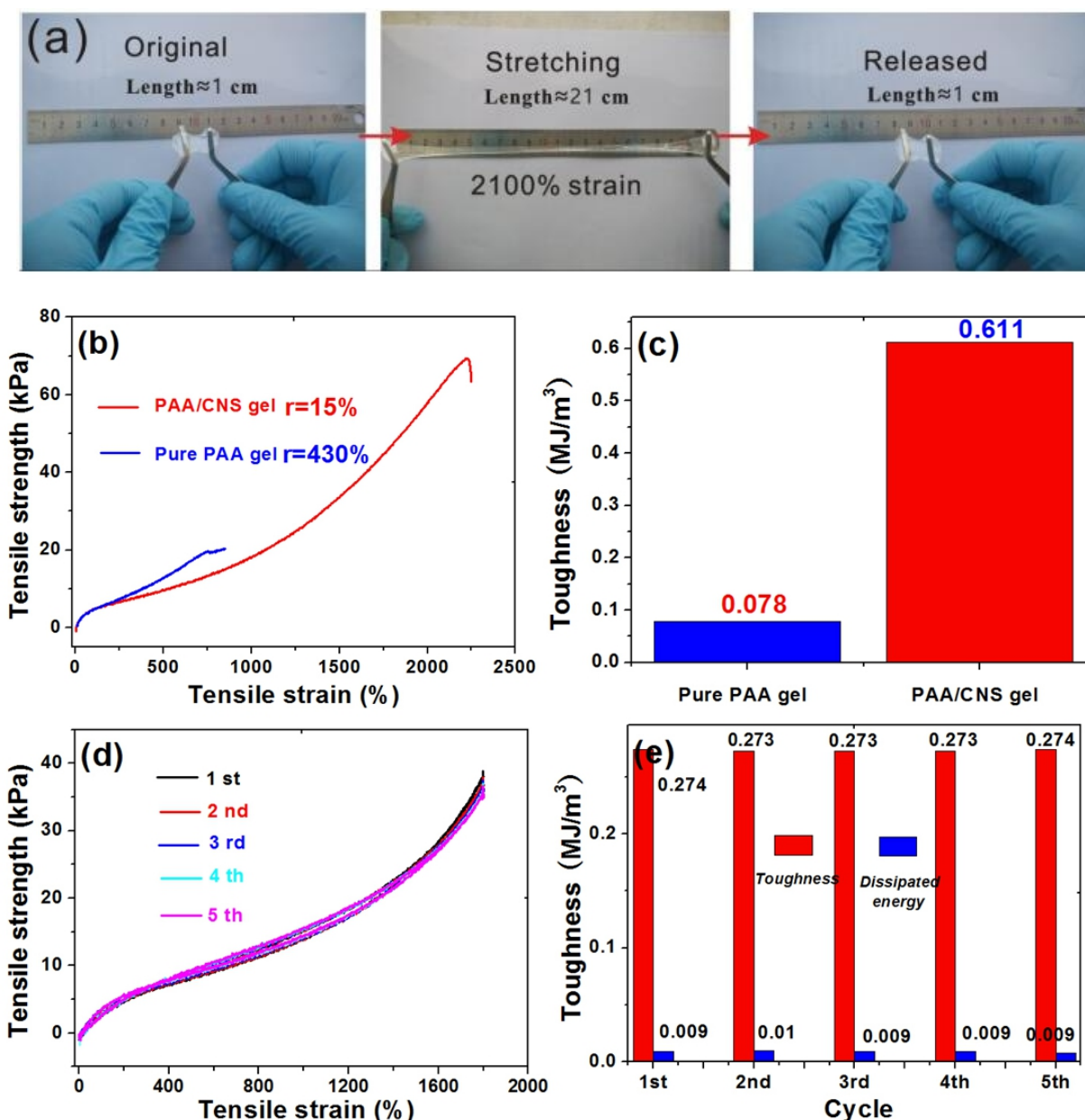

Fig. 5 (a) Photograph of NC gel sustaining elongation of up to 2,000% by hand; (b) Tensile stress-strain curves of PAA/CNS NC gel and pure PAA gel and (c) its corresponding toughness; (d) Cyclic loading-unloading tensile tests curves of PAA/CNS NC gel at a strain of 1,800% and (e) its corresponding toughness.

up to 1800 % strain could be achieved. It was suggested that the energy dissipation during load-unload process could be attributed to the dissociation of hydrogen bonding between COOH groups of PAA polymer chains and CNS, and these hydrogen bonds could reform almost entirely over time, leading to the complete recovery of mechanical performance for our NC gel. To be more quantitatively, toughness and dissipated energy were calculated on the basis of area of stress-strain curves under loading and area of the hysteresis loop, respectively. It could be found that the NC gel can recovery its toughness by 100 % and dissipated energy by 100 % after 5 cycles, suggesting the reliable mechanical performance for hydrogels cross-linked by CNS. Correspondingly, CNS could be employed as cross-linkers to improve mechanical properties of PAA-based hydrogels.

The self-healing property is an another important feature for our PAA/CNS NC gel. Initially, one piece of sample was sliced into two halves. Next, the separated pieces were brought into contact with aid of one drip of HCl solution. Finally, the sample re-formed an integrated one after 2 weeks later at room temperature (Fig. 6a). Furthermore, it also observed that two separated halves could not be repaired to form integration under NaOH solution. Under HCl condition, it was suggested that the transform of COO− to COOH in PAA polymer chain was conducive to the hydrogen bonding interactions at the interface

along with excellent self-healing behavior. Visual inspection exhibited that the self-healed NC gel could be stretched up to 2,000 % strain under the support of HCl solution. Additionally, when two separated pieces of NC gel were put together by pressure with absence of HCl, the self-healed NC gel could be stretched only to 300 % strain. It could be proposed that HCl solution was helpful for the formation of hydrogen bond across the fracture interface of NC gel, leading to re-establishment of the loose and weak contacts at the two separated halves. Thus, strong mechanical performance for self-healed NC gel could be achieved once again. It was clear that self-healed NC gel exhibited a stretching ratio of up to 2100 % with the tensile strength of 56 kPa at fracture (Fig. 6b). The toughness for healed NC gel reached 0.599 MJ/m³ (Fig. 6c). Correspondingly, the healing efficiency on the base of elongation and toughness were 91 % and 100 %, respectively. Consequently, the introduction of CNS can significantly improve self-healing efficiency for our PAA/CNS NC gel without sacrificing their mechanical properties.

Hydrogels are viscoelastic materials with the properties of storing and dissipation of energy. The energy stored in gel system under the oscillatory stress are indexed by storage modulus (G') and loss modulus (G''), respectively. In our work, the storage modulus (G') and loss modulus (G'') also are employed to study rheological properties of
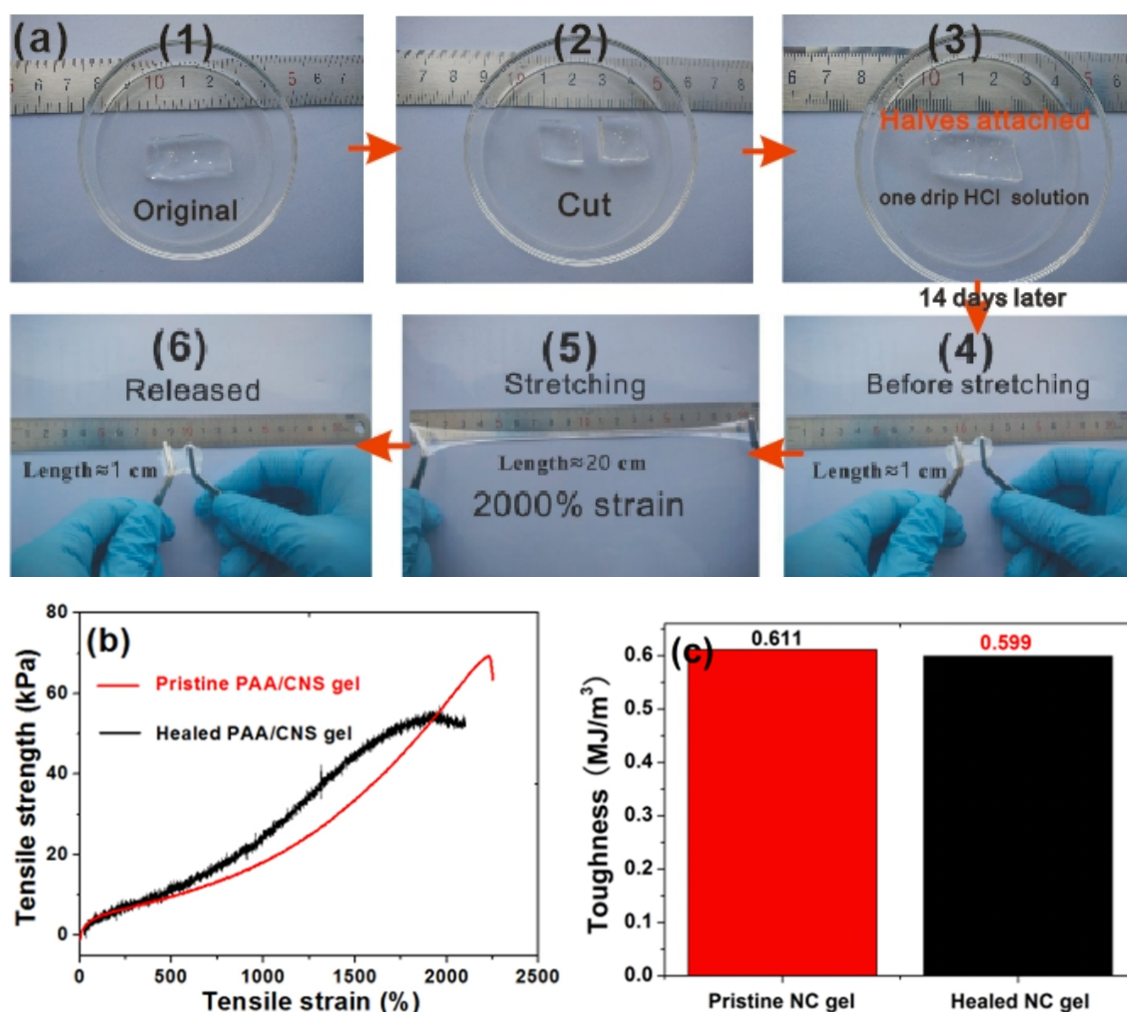

Fig. 6 Self-healing property of PAA/CNS NC gel. (a) Photograph showed that the healed NC gel could be stretched to 2,000 % strain after two separated halves re-formed an integrated one; (b) Tensile stress-strain curves of self-healed NC gel and (c) its corresponding toughness.

PAA/CNS NC gel (Fig. 7). Fig. 7a plotted the G' and G" as a function of shear strain (0.01-300 %). The NC gel displayed a significant strain-dependent viscoelastic response. At lower shear strain (0.01-100 %), the NC gel exhibited linear viscoelastic behavior. The value of G' was higher than that of G", indicating the hydrogel framework was preserved under low oscillatory strain. At higher shear strain (100-300 %), the physical bonds of NC gel dissipated and relaxed leading to the decreased values of G' and G".[24] In the frequency ranging 0.1 to 100 rad/s, the value of G' remained higher than that of G", indicating the ability to withstand external forces and remain solid elasticity property (Fig. 7b). Meanwhile, G' and G" were also plotted against temperature (Fig. 7c). A temperature-dependent behavior was found, in which G' was shown to be higher than G", representing that the gelled state can be maintained at selected temperature range. The increased values of G' and G" in 65-72 °C may be caused by the dramatically loss of water of the PAA/CNS NC gel. At this temperature range (65-72 °C), the PAA polymer chains may greatly shrink, squeezing out water from the cross-linked structures of NC gel. In our work, the addition of CNS into cross-linked network of PAA hydrogels was responsible for above-mentioned rheological results, leading to the maintenance of gel state but not sol state for our self-healing NC gel.

4. Conclusions

In summary, the present work first demonstrated that the highly stretchable self-healing PAA-based nanocomposite hydrogel using non-aggregated CNS as cross-linkers was achieved. The robust and flexible three-dimensional polymer network structures in the PAA/CNS NC gel was created by the introduction of CNS into polymer chains, further endowing them with outstanding self-healing efficiency and admirable mechanical performances simultaneously. Therefore, the interesting stretchable self-healing properties, such as high tensile elongation (2300 %), excellent self-recoverability at a high strain of 1800 %, and notable self-healing efficiency (>91 % of tensile strain and >98 % of toughness), were obtained for our NC gel. The hydrogen bonding interactions between PAA polymer chains and CNS were helpful for this high stretchable and outstanding self-healing efficiency properties of the NC gel. This new design of NC gel opened avenues to create hydrogels with advantages of high stretchable and excellent self-healing efficiency. It was anticipated that this simple strategy to design highly stretchable self-healing NC gel made them promising candidates for practical applications, such as soft robotics, stretchable sensors, tissue scaffolds, drug delivery, and actuators.

Conflict of interest

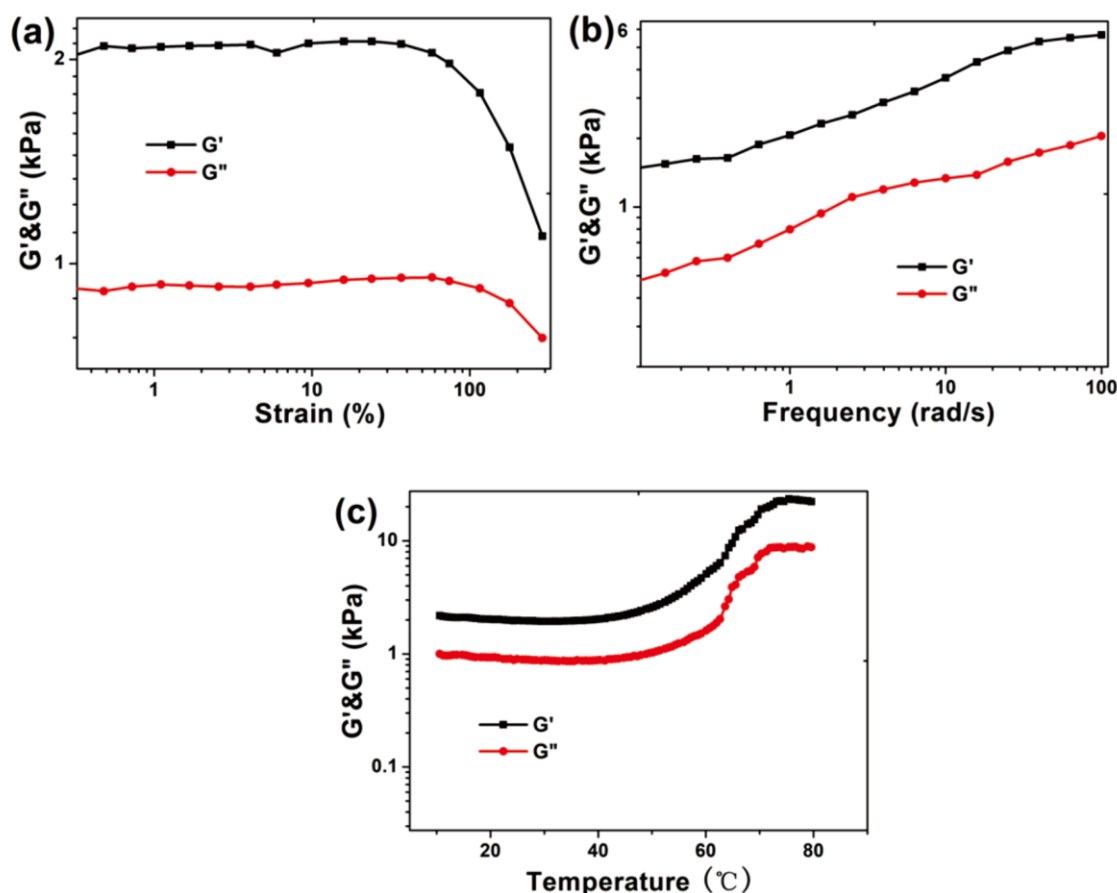The authors declared no conflict of interests.

Fig. 7 Storage modulus (G') and loss modulus (G") as (a) a function of shear strain (0.01-300 %) with a frequency of 2 rad/s and 25 °C; (b) a frequency (0.1-100 rad/s) at 0.5 % strain and 25 °C; (c) a temperature (10-80 °C) at a heating rate of 2 °C min^{-1} with a frequency of 2 rad/s and 0.5 % strain, for our PAA/CNS NC gel.

References

1. H. Kim, K. Kim, S. Lee, *NPG Asia Mater.*, 2017, **9**, 445-453.
2. Y. Shi, M. Wang, C. Ma, Y. Wang, X. Li, G. Yu, *Nano Lett.*, 2015, **15**, 6276-6281.
3. H. Zhang, C. Wang, G. Zhu, N. Zacharia, *ACS Appl. Mater. Interfaces*, 2016, **8**, 26258-26265.
4. G. Cai, J. Wang, K. Qian, J. Chen, S. Li, P. Lee, *Adv. Sci.*, 2017, **4**, 1600190-1600196.
5. C. Pan, L. Liu, Q. Chen, Q. Zhang, G. Guo, *ACS Appl. Mater. Interfaces*, 2017, **9**, 38052-38061.
6. G. Singh, K. Damarla, P. Sharma, A. Kumar, T. Kang, *ACS Sustainable Chem. Eng.*, 2017, **5**, 6568-6577.
7. A. Uzumcu, O. Guney, O. Okay, *ACS Appl. Mater. Interfaces*, 2018, **10**, 8296-8306.
8. N. Yuan, L. Xu, H. Wang, Y. Fu, Z. Zhang, L. Liu, C. Wang, J. Zhao, J. Rong, *ACS Appl. Mater. Interfaces*, 2016, **8**, 34034-34044.
9. I. Jeon, J. Cui, W. Illeperuma, J.Aizenberg, J.Vlassak, *Adv. Mater.*, 2016, **28**, 4678-4683.
10. Y. Cao, T. Morrissey, E. Acome, S. Allec, B. Wong, C. Keplinger, C. Wang, *Adv. Mater.*, 2017, **29**, 1605099-1605108.
11. H. Chen, Y. Liu, B. Ren, Y. Zhang, J. Ma, L.Xu, Q.Chen, J. Zhang, *Adv. Funct. Mater.*, 2017, **27**, 1703086-1703092.
12. Z. Lu, D. Hou, L. Meng, G. Sun, C. Lu, Z. Li, *RSC adv.*, 2015, **5**, 100598-100605.
13. E. Palleau, S. Reece, S. Desai, M. Smith, M. Dickey, *Adv. Mater.*, 2013, **25**, 1589-1592.
14. M. Cushing, K. Anseth, *Science*, 2007, **316**, 1133-1134.
15. J. Zhao, X. Zhao, B. Guo, P. Ma, *Biomacromolecules*, 2014, **15**,3246-3252.
16. H. Cong, P. Wang, S. Yu, *Chem. Mater.*, 2013, **25**, 3357-3362.
17. K. Parida, V. Kumar, J. Wang, V.Bhavanasi, R.Bendi, P. Lee, *Adv. Mater.*, 2017, **29**, 1702181-1702188.
18. M. Darabi, A. Khosrozadeh, R. Mbeleck, Y. Liu, Q. Chang, J. Jiang, J. Cai, Q. Wang, G. Luo, M. Xing, *Adv. Mater.*, 2017, **29**, 1700533-1700540.
19. M. Kang, S. Liu, O. Oderinde, F. Yao, G. Fu, Z. Zhang, *Mater. Des.*, 2018, **148**, 96-103.
20. G. Sun, Z. Li, R.Liang, L. Wen, L. Zhang, *Nat. Commun.*, 2016, **7**, 12095-12102.
21. X. Hu, R.Liang, G. Sun, *J. Mater. Chem. A*, 2018, **6**, 17612-17624.
22. J. Taylor, L. Aldridge, *Powder Diffr.*, 1993, **3**, 138-144.
23. Z. Lu, H. ASAD, C. Ning, H. Shao, R. Yin, Z. Li, *Mater. Des.*, 2016, **127**, 154-161.
24. G.Song, Z. Zhao, X. Peng, C. He, R. Weiss, H. Wang, *Macromolecules*, 2016, **49**, 8265-8273.