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Conducting hydrogels with enhanced mechanical strength

Tingyang Dai, Xutang Qing, Yun Lu*, Youyi Xia

Department of Polymer Science and Engineering, State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, PR China

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ABSTRACT

Mechanically strong triple-network (TN) hydrogels composed of poly(acrylic acid) (PAA) and poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT-PSS) have been fabricated with conductive PEDOT-PSS hydrogel acting as the third network. As-prepared PAA/PEDOT-PSS TN hydrogels display a compressive fracture stress as high as 1.8 MPa and still keep the electrical functionality of the conducting component. The success of PEDOT-PSS hydrogel in strengthening the materials is ascribed to the entangled microstructure of the triple networks and the variable molecular structure of the conducting polymer. A preliminary strengthening mechanism is proposed based upon the experimental results and the DN and/or TN theories. In addition, the applicability of the TN hydrogels in electrosensors and supercapacitors is briefly discussed. The present findings have successfully demonstrated the functionalization of mechanically strong hydrogels, and are of crucial significance in the development of DN and TN hydrogels both academically and practically.

1. Introduction

Hydrogels are a class of condensed matter crosslinked with chemical bonds or physical nodes and characterized by the existence of a three-dimensional hydrophilic polymer network over macroscopic distances that immobilizes a large amount of water [1]. Hydrogels based on conducting polymers have been attracting increasing attention in the past decade because the materials exhibit the mechanical and swelling properties of hydrogels added to the specific transport properties of conducting polymers, originating from their unique π-conjugated systems [2,3]. Nowadays, the most obvious but intractable problem for conducting polymer hydrogels is probably the lack of mechanical toughness, hindering their extensive applications in the fields from electrosensor and capacitor to electromechanical actuator and artificial muscle, which is likely the most important application for this class of materials [4–7]. An alternative method to solve this problem is blending conducting polymers with conventional insulating hydrogels to prepare materials keeping the mechanical characteristics of the latter [8]. Unfortunately, such a blending process usually alters the physical properties of the insulating matrix and as-prepared composite hydrogels are still mechanically weak with a typical fracture stress in the range from 5 KPa to 50 KPa [9,10].

During the past several years, gel scientists have invented and developed a novel method for obtaining hydrogels with extremely high mechanical strength, namely double-network (DN) or triple-network (TN) method [11,12]. The point of this discovery is that the mechanically strong hydrogels are composed of not only a stiff, brittle first network (highly crosslinked), but also a combination of soft, ductile second and even third networks (loosely crosslinked). Different theories for the origin of the unexpected mechanical strength have been discussed, among which a composite model similar to that applying to hard composites toughened with rubber particles is believed to be the most promising [13–15]. That is, DN gels can be regarded as a type of interpenetrating polymer network (IPN) in a limiting condition that the extensive cracks in the rigid polymer network are held together by the chains of the flexible polymer network extended across the crack, resulting in remarkable energy dissipation when an external stress is applied [16–19].

Recently, we have reported an effective and versatile approach for the facile synthesis of conducting polymer hydrogels via supramolecular self-assembly between polymer chains and multivalent cations [20]. The multivalent cations play a dual role of initiating the polymerization as the oxidant and promoting the gelation as the ionic crosslinker. In the present work, as-prepared physically-crosslinked conducting polymer hydrogels are applied as the third network, and the mechanically strengthened hydrogels are fabricated on the basis of the TN method. Such TN hydrogels, containing 90 wt-% water, exhibit a compressive fracture stress as high as 1.8 MPa and still possess the outstanding electrical functionality of the conducting component. Besides the mechanical

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* Corresponding author. Tel.: +86 25 83686423; fax: +86 25 83317761.
E-mail address: yunlu@nju.edu.cn (Y. Lu).

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toughness, the rheological properties, electrical properties, microstructures and molecular structures of the TN hydrogels are also characterized. Based on the experimental results, the mechanism for the strengthening effects of the third network is discussed. Additionally, the applicability of these mechanically strong conducting hydrogels in electrosensors and supercapacitors is briefly demonstrated. The novelty of this work lies in the combination of the mechanical robustness of TN hydrogels and the electrical activity of conducting polymers, thus demonstrating an effective approach for the functionalization of the mechanically strong hydrogels, which is a significant step in the development and applications of DN and TN hydrogels [21].

2. Experimental section

2.1. Materials

Acrylic acid (AA) (monomer; Tianjin Chem. Co., China) was distilled under reduced pressure before use. *N*,*N*′-Methylene bisacrylamide (MBAA) (crosslinking agent; Beijing Chem. Co., China) was recrystallized from ethanol. 3,4-Ethylenedioxythiophene (EDOT) and poly(sodium 4-styrenesulfonate) (NaPSS, M_w 70,000) were purchased from Aldrich. All other chemicals (analytical grade) were obtained from Shanghai Chem. Co. (China) and used as received.

2.2. Fabrication of PAA/PEDOT-PSS TN hydrogels

Poly(acrylic acid) (PAA) single-network (SN) hydrogel (the first network) was prepared by chemically crosslinking at 80 °C for 6 h from an aqueous solution of 1.5 M AA monomer containing 6 mol-% MBAA as the crosslinker and 0.05 mM potassium peroxysulfate (KPS) as the initiator. The SN hydrogel was then cut into cuboidal samples with a dimension of 10 mm × 10 mm × 4 mm and immersed in an aqueous solution of 6 M AA containing 0.1 mol-% MBAA and 0.2 mM KPS for 24 h until equilibrium was reached. After crosslinking at 80 °C for another 6 h in a hermetical container with similar dimensions to the hydrogel samples (to avoid the evaporation of the solvent), the second network was synthesized. As-prepared PAA DN hydrogel was then immersed in an aqueous solution containing 0.48 M EDOT and 0.1 M NaPSS under severe stirring (to ensure the uniform dispersion of EDOT) for 24 h and a solution of 2 M $Fe(NO_3)_3 \cdot 9H_2O$ at 25 °C for 12 h in sequence to accomplish the polymerization of EDOT and the formation of the third network. Finally, the TN hydrogel was purified in a large amount of distilled water for at least 1 week until the sample reached the equilibrium state. As-prepared TN hydrogels displayed good homogeneity throughout the samples.

2.3. Characterization

The mechanical strength of the hydrogels was tested by both the compressive and the tensile stress–strain measurements (INSTRON 4466, Instron Co., England). For compression tests, cuboidal samples with the dimension of 10 mm × 10 mm × 4 mm were set on the lower plate and compressed by the upper plate, which was connected to a load cell, at a strain rate of 10% min^{-1}. Tensile tests were carried out by uniaxially stretching specimens of 20 mm length, 4 mm breadth and 3 mm height at a strain rate of 10% min^{-1}. The strain λ under compression (or stretching) is defined as the change in the thickness (or length) divided by the thickness (or length) of the freestanding state. Stress is defined as the force divided by the area of the samples vertical to the direction of the force. Such definitions have been described in detail in the literature [22].

Rheological properties were characterized by dynamic mechanical thermo analysis (DMTA, Rheometric Scientific DMTA V) in the shear deformation mode with a strain amplitude of 0.1% in the frequency range from 0.1 to 10 Hz at 20 °C.

The morphologies of the freeze-dried hydrogels were observed by scanning electron microscopy (SEM, LEO-1530 VP, JEOL Co., Japan).

The molecular structures of PAA/PEDOT-PSS TN hydrogel at its freestanding and compressive ($\lambda = 70\%$) states were determined using Fourier transform Raman spectroscopy (Bruker MultiRAM, using 1064 nm laser as the excitation source). The hydrogel sample with a thickness of 5 mm was placed between two quartz plates. The distance between the plates was adjusted to 5 mm and 1.5 mm, corresponding to the freestanding and compressive states of the TN hydrogel, respectively. After equilibrium for 2 h, the sample was investigated in situ via Raman spectroscopy.

The electrical conductivities were measured via the four-probe method [23] at room temperature by inserting the four probes into cuboidal samples with the dimension of 5 mm × 5 mm × 1 mm (RTS-8 4-point probes resistivity measurement system, Probes Tech., China).

Water content of the hydrogels was evaluated from the following equation:

$$\text{Water content} = (W_s - W_d)/W_s \tag{1}$$

where W_s and W_d are the fully swollen and dry weight of each sample, respectively.

Electrochemical experiments were conducted in a three-electrode system (Autolab PGSTAT 30, Ecochemie, Netherlands), using a glassy-carbon electrode (GCE, 3 mm in diameter) as the working electrode, a coiled platinum wire as the auxiliary electrode and a saturated calomel electrode (SCE) as the reference electrode. The modified electrode was prepared through in situ synthesis of the TN hydrogel on the surface of the working electrode, and a film sample with the thickness of about 15 μm was coated on the electrode.

3. Results and discussion

The TN hydrogel investigated in this work is prepared by using PAA hydrogels as both the first and the second network, with crosslinking concentrations [11] of 6 mol-% and 0.1 mol-%, respectively. The combination of the third network, poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT-PSS) hydrogel physically-crosslinked with Fe^{3+} ions [20], makes the TN hydrogel so tough that it is resistant to a compressive stress in the order of megapascals (MPa) and a compressive strain higher than 75%, despite containing about 90 wt-% water (Fig. 1). This is in stark contrast to most common hydrogels, which are easily broken either by pressing with a finger or pulling with the hands. In our experiments, TN hydrogels with good homogeneity can be facilely prepared even when the thickness of the samples is as high as 15 mm. Comparing with the results of the previous reports on the fabrication of conducting polymer hydrogels [9], this unexpected phenomena possibly results from the low polymerization rate of EDOT [24], which prevents the blockage of the pores on the surface of the samples, and/or the high concentration of the oxidant in the polymerization process (See Experimental section), which ensures effective diffusion of the oxidant inside the hydrogels and uniform polymerization of EDOT in the whole samples.

Fig. 2 shows the typical stress–strain curves of PAA/PEDOT-PSS TN hydrogel as well as the corresponding PAA SN and PAA DN hydrogels under compression. It can be seen that PAA SN and DN hydrogels break at a stress of 0.1 and 0.6 MPa, respectively, while

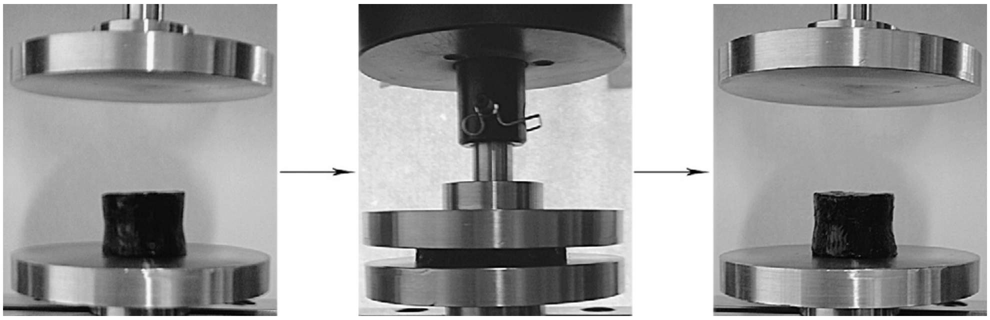

Fig. 1. Photographs demonstrating the strength of a PAA/PEDOT-PSS TN hydrogel under compression. PEDOT-PSS content: 18.4 wt-%, water content: 92 wt-%, fracture stress: 1.8 MPa, fracture strain: 78%.

PAA/PEDOT-PSS TN hydrogel sustains a stress of 1.8 MPa, which is 18 times and 3 times that of the corresponding SN hydrogel and DN hydrogel, respectively. The fracture strain λ of the TN hydrogel is up to 78%, much higher than that of both the SN hydrogel ($\lambda = 37\%$) and the DN hydrogel ($\lambda = 61\%$). The stress–strain curve of the TN hydrogel overlaps well with that of PAA DN hydrogel in the wide range before the fracture of the DN hydrogel and extends to a higher stress–strain point, suggesting that the third network actually takes effect as the strengthening agent after the double networks of PAA collapse under a critical stress. For comparison, an articular cartilage is a hydrogel that contains 70 wt-% water and exhibits a fracture stress from several to a hundred megapascals [25]. Hence, from the aspect of the mechanical strength, as-prepared TN hydrogel can serve as a candidate for artificial articular cartilage. The tensile strength and extension at failure of PAA/PEDOT-PSS TN hydrogel is also much greater than that of the corresponding DN hydrogel: the TN sample can sustain up to $\lambda = 89\%$ stretching and breaks at a stress of 0.041 MPa, while PAA DN hydrogel breaks at $\lambda = 57\%$ and a stress of 0.023 MPa (Fig. 3).

The content of the conducting component in the TN hydrogels can be facilely modulated by adjusting the concentration of the EDOT monomers during the preparation of the third network (See Experimental Section). As shown in Table 1, with the increase of the PEDOT-PSS content (defined as the weight percentage of PEDOT-PSS in the dry weight of the TN hydrogels) from 8.0 wt-% to 18.4 wt-%, the TN hydrogels display enhanced mechanical toughness as well as improved electrical conductivity. For all the samples with the PEDOT-PSS content in this range, the compressive fracture stress is above 1.0 MPa, while the electrical conductivity is in the order from 10^{-4} S/cm to 10^{-3} S/cm. As-prepared TN hydrogels actually possess both ionic and electronic conductivities, in which the ionic counterpart is contributed by the polyelectrolytes, PAA and PSS. It is measured that the conductivity of PAA DN hydrogel is only $\leq 10^{-5}$ S/cm, more than an order lower as compared to the TN hydrogels. Therefore, it is reasonable to believe that the observed conductivity in the TN samples is mainly accounted for the presence of the PEDOT-PSS component, which could enhance the conductivity both electronically and ionically. Herein, it should be noticed that when the PEDOT-PSS content is higher than 17 wt-%, the TN hydrogel can reach an electrical conductivity in the same order that of pure PEDOT-PSS hydrogel [20]. Samples with more PEDOT-PSS component can be hardly prepared due to the low solubility of EDOT in water [26].

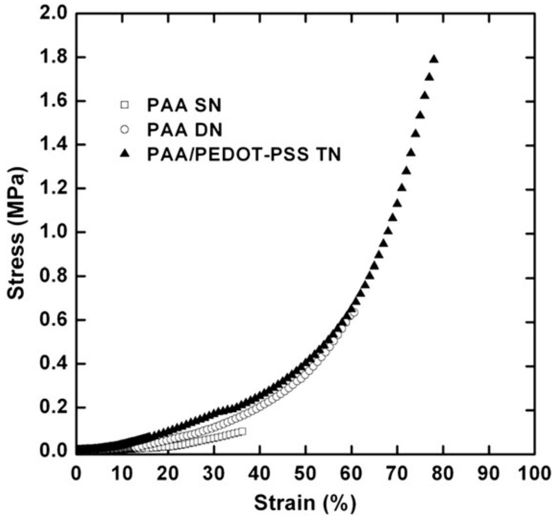

Fig. 2. Stress–strain curves for PAA SN, PAA DN and PAA/PEDOT-PSS TN hydrogels under compression. The crosslinking concentration of PAA SN hydrogel is 6 mol-%. The crosslinking concentrations of the first and second networks of PAA DN hydrogel is 6 mol-% and 0.1 mol-%, respectively. The PEDOT-PSS content of PAA/PEDOT-PSS TN hydrogel is 18.4 wt-%. Water contents of the SN, DN and TN hydrogels are 90 wt-%, 87 wt-% and 92 wt-%, respectively.

Fig. 4 displays a rheological characterization of the DN and TN hydrogels in the shear deformation mode with a strain amplitude of 0.1%. For both of the samples, the elastic (storage) modulus is much higher than the viscous (loss) modulus in a frequency range from 0.1 to 10 Hz, indicating that the bulk response of both hydrogels to an applied deformation is nearly elastic within the range [27]. Moreover, the elastic modulus keeps the same value in the small deformation region when the third network is combined,

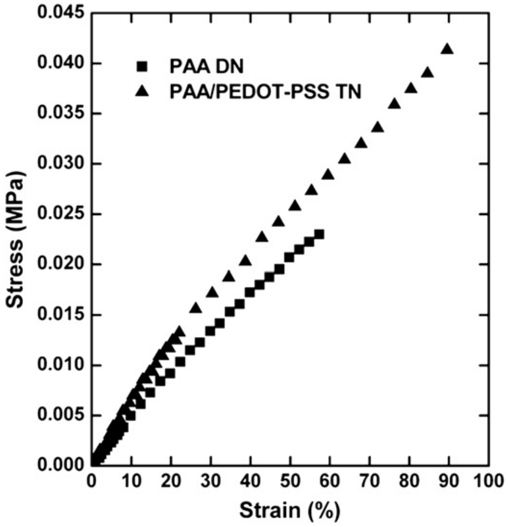

Fig. 3. Stress–strain curves for PAA DN and PAA/PEDOT-PSS TN hydrogels measured by elongation method.

Table 1
Mechanical and electrical properties of the SN, DN, and TN hydrogels.

Hydrogels	PEDOT-PSS content[a] (wt-%)	Water content[b] (wt-%)	Fracture stress[c] σ_{max} (MPa)	Fracture strain[c] λ_{max} (%)	Electrical conductivity[d] (S/cm)
PAA SN	–	90.1	0.1	37	–
PAA DN	–	86.8	0.6	61	–
PAA/PEDOT-PSS-8 TN	8.0	88.7	1.0	68	6.7×10^{-4}
PAA/PEDOT-PSS-12 TN	12.2	89.4	1.1	70	8.3×10^{-4}
PAA/PEDOT-PSS-15 TN	15.8	89.2	1.3	72	9.1×10^{-4}
PAA/PEDOT-PSS-17 TN	17.3	90.3	1.6	73	1.1×10^{-3}
PAA/PEDOT-PSS-18 TN	18.4	92.1	1.8	78	1.2×10^{-3}

[a] PEDOT-PSS content is defined as the weight percentage of PEDOT-PSS in the dry weight of the TN hydrogels.
[b] Water content is the weight percentage of water in saturated hydrogels.
[c] Mechanical properties of the hydrogels were tested in the compressive mode.
[d] Electrical conductivities were measured using the four-probe technique at room temperature.

in agreement with the measurements of the stress–stain curves. The increase of the loss modulus for the TN hydrogel implies the potential function of the third network to promote the dissipation of the fracture energy, which will be discussed in the following text.

The microstructures of PAA DN hydrogel and PAA/PEDOT-PSS TN hydrogel are investigated by scanning electron microscopy. Although two sequent polymerizations have been performed in the preparation of the DN hydrogel, there are still lots of voids in the sample, reflected from the coarseness of the cross section (Fig. 5a). Comparatively, the TN hydrogel presents a much more compact and homogeneous texture (Fig. 5b), suggesting that PEDOT-PSS hydrogel, as the third network, grows into PAA DN hydrogel, twists with the PAA component and fills up the existent voids. Such a microstructure makes it possible for the PEDOT-PSS component to act as a strengthening agent [28,29].

Raman spectra are used to determine the molecular structure of PAA/PEDOT-PSS TN hydrogel before and after the compression (Fig. 6). An obvious red-shift from 1431 cm^{-1} to 1417 cm^{-1} is observed for the strong band located between 1400 and 1500 cm^{-1}, which corresponds to the $C_\alpha{=}C_\beta$ symmetric stretching vibration of the five-member thiophene ring on the PEDOT chains [30]. Because of the contribution of the two conjugated π-electrons on the $C_\alpha{=}C_\beta$ bond in the benzoid structure, the symmetric $C_\alpha{=}C_\beta$ stretching vibration band will have a red-shift when the structure changes from the benzoid to the quinoid structure (Fig. 6, insets). We accredit the change of the chemical structure to the conformational variation of the PEDOT chains from the coil conformation to the linear or expanded-coil conformation, because in the linear or expanded-coil conformation, the neighboring thiophene rings on the PEDOT chains are oriented almost in the same plane so that the conjugated π-electrons can be delocalized over the whole chain [31]. Such a conformational change of PEDOT chains has also been observed experimentally during the redox processes of PEDOT-PSS films [32,33] and indicates the manner by which the PEDOT-PSS component strengthens the hydrogel materials.

Based on the above experimental results and the theories characterized in the DN and/or TN method [13–19], a preliminary mechanism to account for the strengthening effects of the PEDOT-PSS component is proposed. The physically-crosslinked PEDOT-PSS hydrogel, which fills in the voids of PAA DN hydrogel and entangles with the PAA component, enhances the loss modulus of the material. When the applied stress exceeds a critical value, the double networks of PAA collapse, accompanied by the extensive formation of cracks. At the same time, the PEDOT-PSS component entangled with PAA bridges the neighboring fracture surfaces and dissipates the local crack-energy by the change of the polymer chains from the coil conformation to a more expanded conformation, thus preventing the cracks growing to a macroscopic level. In concise words, PEDOT-PSS component takes strengthening effects by holding together the cracks existent in the PAA networks. Such a “holder” function is closely related to both the entangled microstructure of the triple networks and the variable molecular structure of the conducting component. Although as-proposed mechanism is still within the framework of the DN and/or TN theory, the electrical activity is introduced into the system for the first time. In our experiments, however, we failed to directly

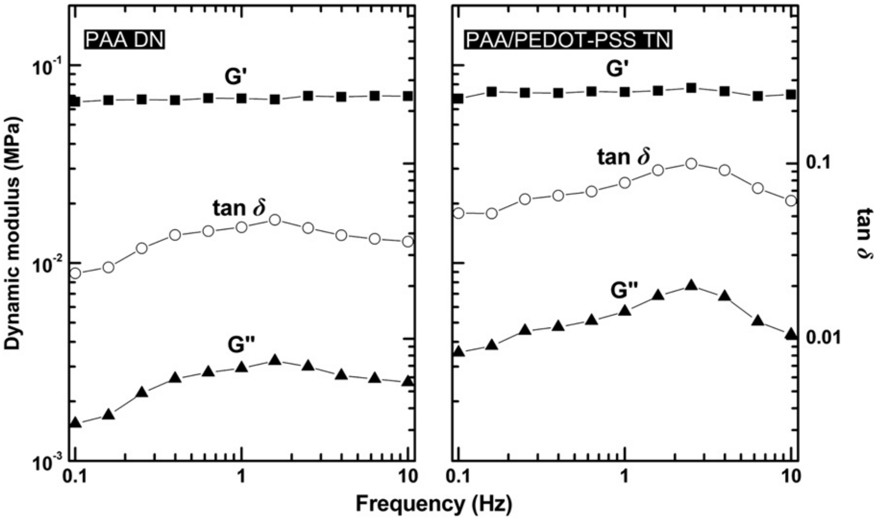

Fig. 4. Rheological determination of the storage modulus (G′), the loss modulus (G″) and the loss tangent (tan δ) as a function of frequency for PAA DN and PAA/PEDOT-PSS TN hydrogels. The rheological properties were measured in the shear deformation mode with a strain amplitude of 0.1% at 20 °C.

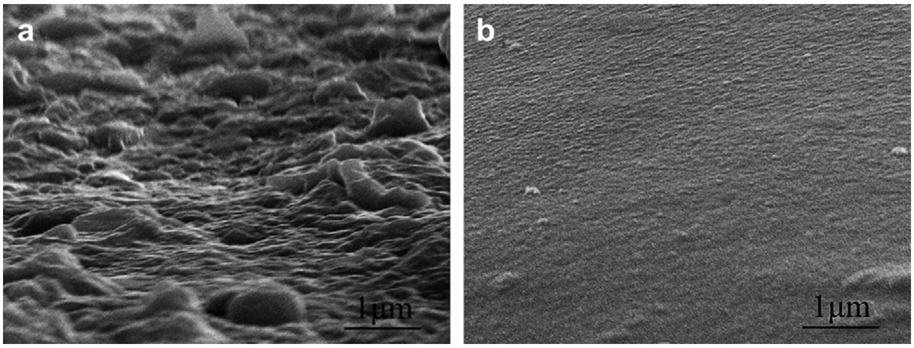

Fig. 5. Scanning electron microscopy images of the cross sections of freeze-dried PAA DN hydrogel (a) and PAA/PEDOT-PSS TN hydrogel (b).

strengthen PAA SN hydrogel by using PEDOT-PSS hydrogel as the second network. Actually, an IPN hydrogel [34] with a compressive fracture stress of 0.1 MPa and a fracture strain of 39% is obtained, which shows no substantial improvement in the mechanical toughness comparing with PAA SN hydrogel. It seems that this kind of ion-crosslinked physical hydrogels is only suitable to be employed as the third network.

Despite containing only less than 20 wt-% conducting component, PAA/PEDOT-PSS TN hydrogel can be successfully applied in electrosensors and supercapacitors [35,36]. When a TN hydrogel-modified electrode is used to record the cyclic voltammograms of an aqueous redox, 0.5 mM potassium ferricyanide (KHCF) in 0.1 M potassium nitrate (KNO_3), a 17 times increase in the peak currents can be observed compared to that obtained using a bare glassy-carbon electrode under the same conditions (Fig. 7a). This indicates the increase in the effective surface area of the electrode due to the coating of the conducting hydrogel, which is swellable, porous, and three-dimensional. Such characteristics also promote the material applicable in supercapacitors because of the high ionic mobility of the hydrogel matrix as well as the high electrical conductivity resulting from the conducting component. Cyclic voltammograms of PAA/PEDOT-PSS TN hydrogel have a rectangular shape, characteristic for a capacitor, even at high scan rates, revealing the high rate of the electrochemical process (Fig. 7b). The calculated specific capacitance [37] of the TN hydrogel is as high as 4.8 F/g, much larger than that of the ordinary commercial capacitors (in the order of mF/g) [38], showing the potential use of such conducting hydrogel as supercapacitor materials. Comparing with conventional conducting polymer hydrogels that have been employed in electrosensors and supercapacitors [39,40], PAA/PEDOT-PSS TN hydrogels not only maintain the remarkable electrochemical properties of PEDOT-PSS hydrogel (the third network), but also possess the excellent mechanical strength, which is probably more important in the applications of flexible electronics [21,41]. Research is now under way to investigate the behaviors of the mechanically strong conducting hydrogels as artificial muscle materials.

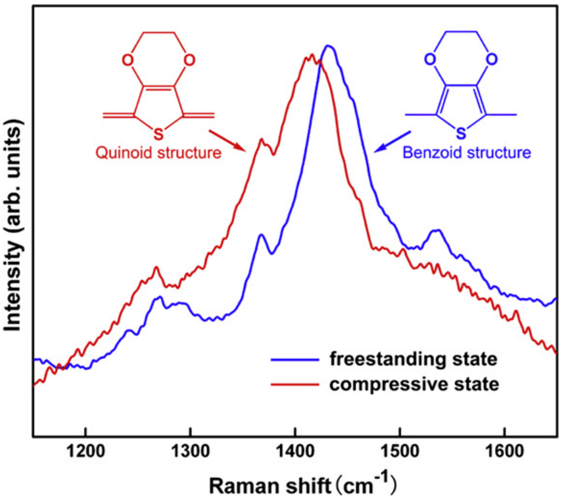

Fig. 6. Raman spectra of PAA/PEDOT-PSS TN hydrogel at its freestanding and compressive ($\lambda = 70\%$) states. Insets: benzoid and quinoid structures of a unit of PEDOT.

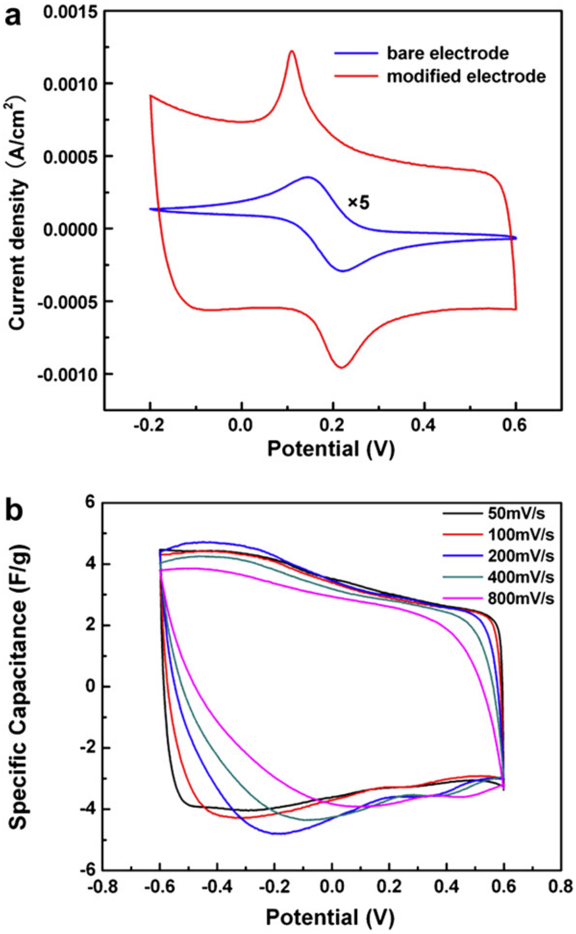

Fig. 7. (a) Cyclic voltammograms of 0.5 mM KHCF, in 0.1 M KNO_3 aqueous solution using bare glassy-carbon electrode (plot has been 5 time magnified) and electrode modified with PAA/PEDOT-PSS TN hydrogel. Scan rate: 100 mV/s. (b) Cyclic voltammograms of PAA/PEDOT-PSS TN hydrogel at different scan rates in 1 M Na_2SO_4 aqueous solution.

4. Conclusions

In summary, we have described an effective approach for the fabrication of mechanically strengthened hydrogels with conducting polymer hydrogels as the third network via the TN method. As-prepared PAA/PEDOT- PSS TN hydrogels exhibit a fracture stress in the order of megapascals and still keep the electrochemical activity of the conducting component. The PEDOT-PSS component fills up the voids of PAA DN hydrogel, twists with the PAA component, and promotes the increase of the loss modulus for the material. When the double networks of PAA collapse under the external stress, the PEDOT-PSS component is capable of holding together the fracture surfaces across the cracks by the conformational change of the polymer chains, thus dissipating the local crack-energy and endowing the TN hydrogel with a higher mechanical strength. Such TN hydrogels can be successfully utilized as electrosensor and supercapacitor materials.

This work is a successful demonstration for the functionalization of the hydrogel materials, which is an important step in the development of DN and TN hydrogels both academically and practically. Significantly, the present findings have testified the possibility for the preparation of mechanically strong hydrogels using the fragile physical hydrogels as the strengthening agent, and thus may provide a versatile solution for the mechanical problems of physical hydrogels in practical applications.

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