Nanocellulose-mediated electroconductive self-healing hydrogels with high strength, plasticity, viscoelasticity, stretchability, and biocompatibility toward multifunctional applications

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ABSTRACT: Conducting polymer hydrogels (CPHs) emerge as a fascinating class of smart soft matters important for various advanced applications. However, achieving the synergistic
characteristics of conductivity, self-healing ability, biocompatibility, viscoelasticity and high mechanical performance still remains a critical challenge. Here we develop for the first time a type of multifunctional hybrid CPHs based on a viscoelastic polyvinyl alcohol-borax (PB) gel matrix and nanostructured CNF-PPy (cellulose nanofibers-polypyrrole) complexes that synergizes the biotemplate role of CNFs and the conductive nature of PPy. The CNF-PPy complexes are synthesized through \textit{in situ} oxidative polymerization of pyrrole on the surface of CNF templates, which are further well-dispersed into PB matrix to synthesize homogeneous CNF-PPy/PB hybrid hydrogels. The CNF-PPy complexes not only tangle with PVA chains though hydrogen bonds, but also form reversibly crosslinked complexes with borate ions. The multi-complexation between each component leads to the formation of hierarchical 3D network. The CNF-PPy/PB-3 hydrogel prepared by 2.0 wt\% of PVA, 0.4 wt\% of borax and CNF-PPy complexes with a mass ratio of 3.75/1 exhibits the highest viscoelasticity and mechanical strength. Due to a combined reinforcing and conductive network inside the hydrogel, its maximum storage modulus (~0.1 MPa) and nominal compression stress (~22 MPa) are 60 and 2240 times higher than those of pure CNF/PB hydrogel, respectively. The CNF-PPy/PB-3 electrode with a conductivity of 3.65±0.08 S m\(^{-1}\) has a maximum specific capacitance of 236.9 F g\(^{-1}\), and its specific capacitance degradation is less than 14% after 1500 cycles. The CNF-PPy/PB hybrid hydrogels also demonstrate attractive characteristics, including high water content (~94\%), low density (~1.2 g cm\(^{-3}\)), excellent biocompatibility, plasticity, pH sensitivity and rapid self-healing ability without additional external stimuli. Taken together, the combination of such unique properties endows the newly developed CPHs with potential applications in flexible bioelectronics and provides a practical platform to design multifunctional smart soft materials.
1. INTRODUCTION

Nowadays, the rapid development of soft, stretchable and flexible electronic components expands the applications of electronic devices.¹ Multifunctional electroconductive components are centrally important in developing advanced “smart” devices, such as wearable electronics, implantable biomedical devices and portable electronic equipment.²-⁵ To realize practical soft electronics, the fixed shape and inflexibility of the conductive component is a particular limiting factor. Therefore, the adoption of moldable, flexible and elastic materials would be a promising solution.⁶ Hydrogels are stretchable, compressible and cross-linked three-dimensional networks of hydrophilic polymer with tunable amounts of water and switchable mechanics, while maintaining their structural integrity during deformation.⁷-⁸ Due to their high biocompatibility and hydrophilic property, hydrogels can adapt to complex environments and have been explored for various applications where “smart” soft materials are required.⁹ Because the water contained in hydrogels can dissolve ions, hydrogels are also considered as ideal ionic conductors.¹⁰

As a special class of intelligent hydrogels, conducting polymer hydrogels (CPHs) synergize the advantageous features of organic conductors and hydrogels, allowing both materials to retain their respective unique properties.¹¹ CPHs with continuous conductive backbones and intrinsic 3D network micro/nano structures can provide an electrically conductive yet mechanically robust framework, thus facilitating the transport and diffusion of electrons, charges, ions and small molecules.¹² Due to their excellent conductivity, biocompatibility, mechanical flexibility and tissue-like softness, CPHs are regarded as a powerful material platform and provide a new route to design soft bioelectronics and flexible energy storage/conversion devices,¹³-¹⁴ such as wearable and implantable devices,¹⁵ flexible supercapacitors,¹⁶ biosensors,¹⁷ electro-stimulated drug release devices and electronic skin.¹⁸
As a class of functional polymers that have a delocalized p-system backbone along the polymeric chains, conducting polymers are emerging as a mechanically soft and electrically conducive platform for cell integration, making the CPHs suitable candidates as flexible bioelectronics for improving both the interface between biological and synthetic systems and the performance of medical devices. Among conductive polymers, polypyrrole (PPy), the intrinsically conductive polymer with highly π-conjugated polymeric chains, has attracted significant attention due to the ability to efficiently switch between the redox states, distinguished in vitro/vivo cytocompatibility, excellent ion-exchange property, controllable electrical conductivity (varying from $10^{-4}$ to $10^2$ S cm$^{-1}$), thermal and environmental stability. Recently, great efforts have been dedicated to developing functionalized CPHs using PPy. Wallace et al. developed a cytocompatible PPy/PEDOT hydrogel for use in an Mg biobattery. By introducing a two-step crosslinking process, PPy was electrochemically deposited onto PEDOT gel, forming a robust CPH with good electrochemical properties and biocompatibility. Takeuchi et al. demonstrated a tunable 3D nanostructured conductive gel electrode based on PPy gel and Fe$_3$O$_4$ nanoparticles. The multifunctional PPy gel framework was adopted as both binder and 3D conductive network, significantly improving the performance of active inorganic nanoparticle-based electrodes in the next-generation high-capacity lithium ion batteries.

However, the delocalized π-electron system along the backbone of conjugated polymers causes rigid polymeric chains of PPy. When incorporated into hydrogel individually, PPy is generally difficult to disperse and even tend to form separate domains of aggregations, probably due to the inaccessibility, rigidity and dense layers of PPy. Not surprisingly, most previously reported CPHs based on PPy suffer from mechanical brittleness and rigidity, thus they cannot bear large deformation, which limits their practical application in soft electronics. In addition, the
noncontinuous conductive PPy network within gel matrix severely degrades the electrochemical performance of CPHs.\textsuperscript{20, 25} Therefore, it remains a challenge to fabricate homogeneous CPHs with high conductive, elastic and flexible nature using PPy.

Fortunately, direct polymerization of pyrrole monomers on flexible template materials can overcome above-mentioned problems.\textsuperscript{20} Among various flexible substrates, cellulose nanofibers (CNFs), derived from the most abundant and renewable biomass on earth-cellulose, are particularly promising and desirable because of their appealing properties, such as intrinsic flexibility, high strength (modulus in the range of 134-140 GPa), high aspect ratio and excellent biocompatibility.\textsuperscript{26-30} These distinguished characteristics of CNFs endow them as ideally suitable templates to enhance the flexibility, toughness and electrochemical properties of the brittle PPy.\textsuperscript{24} The CNF carriers are expected to serve the dual function of mechanically toughening the fragile PPy and increasing the conductivity through providing a continuous 3D scaffold of high porosity.\textsuperscript{31} Based on the issues above, it is reasonable to assume that CNFs functionalised with PPy could be applied for reinforcing and supporting 3D conductive network of hydrogel to create stable, tough and flexible CPHs with properties that can be optimised both with respect to their electrochemical property and mechanical integrity.\textsuperscript{32}

In our previous study, we have prepared hybrid hydrogels with enhanced viscoelasticity, strength and toughness by incorporated well-dispersed nanocellulose to the polyvinyl alcohol (PVA)-borax gel matrix via cross-linking between nanocellulose and PVA-borax (PB) system in an aqueous medium.\textsuperscript{33-34} Inspired by their appealing features, we believe that PB hydrogels with hierarchically 3D framework can serve as an ideal matrix for the introduction of a second conductive network, thus potentially providing continuous pathways for electron transport and forming multifunctional CPHs by introducing CNF-carried PPy.\textsuperscript{23} To the best of our knowledge,
we are unaware of any reports on the multifunctional CPHs based on PB system and CNF-templated PPy.

In the present work, we report a novel type of multifunctional smart CPHs that possess synergistic characteristics, including low density, decent viscoelasticity, inherent plasticity, adequate conductivity, fast self-healing ability, intrinsic biocompatibility and pH sensitivity. Specifically, PPy was firstly in situ polymerized onto the surface of CNF biotemplates to synthesize conductive CNF-PPy complexes, which were further uniformly dispersed into PB gel matrix to form homogeneous CNF-PPy/PB hybrid hydrogels with hierarchical 3D network structure. Through microscopic observation, mechanical, dynamic rheological and electrochemical measurements, a successful in situ polymerization of pyrrole monomers onto CNFs was verified, and the regulating effects of CNF-PPy complexes on the viscoelasticity, conductivity, mechanical properties and electrochemical performances of hybrid CPHs were investigated in detail. The multi-complexation of each component within hydrogel, the relationships between hydrogel microstructure and performances, as well as the plausible mechanism for hierarchical 3D network formation of hydrogel were also described. By combining desirable properties of conductive CNF-PPy complexes and PB hydrogel matrix, we demonstrated that this kind of CPHs could be practically used to fabricate flexible, biocompatible and fast self-healable bioelectrodes or strain sensors with excellent electrochemical performances.

2. EXPERIMENTAL SECTION

Materials. Bleached wood pulp (BWP, W-50 grade of KC Flock, Tokyo, Japan) was dried for 12h at 60ºC, and sulfuric acid (98 wt%, Nanjing Chemical Reagent Co., Ltd., China) was diluted to a concentration of 48 wt% before use. Pyrrole monomers (C₄H₅N, M₀=67.09 g mol⁻¹) and Iron (III) chloride (FeCl₃, M₀=162.2 g mol⁻¹) were purchased from Aladdin Industrial Co. Polyvinyl
alcohol (PVA, M_w = 146,000-186,000 g mol⁻¹, 99.0% hydrolyzed) and sodium tetraborate decahydrate (borax, Na₂B₄O₇·10H₂O, ≥99.5%, M_w = 381.37 g mol⁻¹) were obtained from Aldrich Chemical Co. Deionized water was used in the preparation of all solutions. All solvents and reagents used were of analytical grade.

**Preparation of CNFs and CNF-PPy Complexes.** CNFs were extracted from BWP using acid hydrolysis followed by an ultrasonication as previously described in our work (detailed preparation process is given in Supporting information).³⁵-³⁶ CNF-PPy complexes were synthesized via an *in situ* oxidative polymerization of pyrrole monomers using CNFs as biotemplate and FeCl₃ as oxidant in an acid aqueous medium. Before use, the pyrrole monomers were distilled under reduced pressure to prevent their oxidization in air. Based on the preliminary experiments, the feeding mass ratio of pyrrole monomers to CNFs were 1.25/1, 2.50/1, 3.75/1, 5.00/1 and 6.25/1 w/w, and the corresponding CNF-PPy complexes were labeled as CNF-PPy-1, CNF-PPy-2, CNF-PPy-3, CNF-PPy-4 and CNF-PPy-5, respectively. Typically, CNF-PPy-1 was synthesized as follows. Pyrrole (2.5 g, 0.036 mol) and virgin HCl (0.050 mol, 1.0 M) were added into the CNF aqueous suspension (200 g, 1.0 wt%). After magnetic stirring in ice-water for 1h, a solution of FeCl₃ (2.9 g, 0.018 mol) in 50 mL deionized water, used as oxidant catalyst, was added into the suspension, and the polymerization proceeded in an ice-water bath for 2h. The obtained product was filtered and rinsed with water several times to a neutral pH value. The solid contents of the CNF-PPy complex suspension from No.1 to No.5 were measured 4 times, and the average values were 1.3±0.04, 2.1±0.06, 2.9±0.02, 3.5±0.04, 4.2±0.03 wt%, respectively. Neat PPy was
prepared via an oxidative synthetic approach without CNFs, and all other processing conditions
were in accordance with CNF-PPy complexes.

**Preparation of CNF-PPy/PB Hybrid Hydrogels.** The hybrid hydrogels with 2.0 wt% of PVA,
0.4 wt% of borax and different CNF-PPy complexes were prepared as follows. Firstly, borax
powder (0.8 g) was dissolved in CNF-PPy aqueous suspension (195.2 g) with continuous stirring
at room temperature for 20 min. Subsequently, PVA powder (4.0 g) was slowly added into the
stirred aqueous solutions. After a complete swelling of PVA powder, the solutions were heated
to 90°C and stirred for 2h. As the temperature increased, the PVA powder began to dissolve and
the mixture gradually became viscous. After the PVA was completely dissolved, homogeneous
PVA-borax (PB) solutions with well-dispersed CNF-PPy complexes were formed. As the
temperature decreased, the solutions started to present viscoelastic performance. The solutions
were further cooled slowly to room temperature to form the final CNF-PPy/PB hydrogels. A
series of hybrid hydrogels with different CNF-PPy complexes were designated as CNF-PPy/PB-1,
CNF-PPy/PB-2, CNF-PPy/PB-3, CNF-PPy/PB-4 and CNF-PPy/PB-5, respectively. As a
reference, the hydrogel synthesized in the absence of PPy was marked as CNF/PB. The weight
ratio of CNF in all the hydrogels were kept at 1.0 wt%.

**Characterizations.** Fourier transform infrared spectrometry (FTIR) was conducted using a
VERTEX 80v spectrophotometer (Thermo Fisher Scientific inc. USA) with the samples mixed
with KBr. Transmission electron microscopy (TEM) was performed using a transmission electron
microscope (JEM-1400, Japan) with an accelerating voltage of 80 kV. Scanning electron
microscopy (SEM) was carried out on JSM-7600F field emission scanning electron microscopy
(FE-SEM, JEOL, Japan) at 5.0 kV.

The densities ($\rho$, g cm$^{-3}$) of the hydrogels were determined from the dimensions and weights
of the samples. Each sample (initial weight=\(W_i\)) was dried in a vacuum oven at 50°C until a constant weight (\(W_d\)) was reached. The water contents (\(W_c\)) of the hydrogels were calculated from eq 1.

\[ W_c = \frac{W_i - W_d}{W_i} \times 100\% \]  

(1)

**Dynamic Oscillation Measurement.** The dynamic rheological behaviors, including dynamic strain sweep, dynamic frequency sweep, continuous step strain and dynamic temperature sweep, were investigated with an HAAKE RheoStress 600 (Thermo Fisher Science Inc. USA) using a plate-and-plate geometry (diameter 35 mm, gap 100 \(\mu\)m).

**Dynamic Strain Sweep.** Before the dynamic viscoelastic measurements, the dynamic strain sweep from 0.01 to 100\% at \(\omega=1.0\) Hz was performed, and the storage modulus was recorded to define the linear viscoelastic region in which the storage modulus was independent to the strain amplitude. A strain (\(\gamma\)) of 1.0\% was selected in the subsequent oscillation tests to ensure that the dynamic oscillatory deformation of each sample was within the linear viscoelastic region.

**Dynamic Frequency Sweep.** The viscoelastic parameters (log mode), including shear storage modulus (\(G'\)) and loss modulus (\(G''\)) as functions of angular frequency (\(\omega\)) were measured over the \(\omega\) range of 0.1-100 rad s\(^{-1}\) at \(\gamma = 1\%\) at 25°C. The complex modulus (\(G^*\)) and complex viscosity (\(\eta^*\)) were calculated based on the values of \(G'\) and \(G''\) (\(G^* = \sqrt{G'^2 + G''^2}\), \(\eta^* = G'/\omega\)).

**Continuous Step Strain.** To investigate the self-healing properties of the hydrogels in response to applied shear forces (expressed in terms of strain), a 1h-programmed procedure was used as follows (strain\% and duration in parentheses): 1.0\% (700 s) \(\rightarrow\) 80\% (700 s) \(\rightarrow\) 1.0\% (700 s) \(\rightarrow\) 80\% (700 s) \(\rightarrow\) 1.0\% (900 s), and the \(G'\) and \(G''\) dependence of time was recorded in continuous step strain measurements at \(\omega = 1.0\) Hz and at 25°C. For the test, CNF-PPy/PB-3 was selected as a representative hydrogel.
Mechanical Measurements. Compression stress ($\sigma$)-strain ($\varepsilon$) measurements were performed on the cylindrical hydrogel samples (35 mm in diameter and 10 mm in height) using a universal mechanical testing machine (CMT4304, SANS Test Machine Co. Ltd., Shenzhen, China) at a crosshead speed of 10 mm/min. The compression for all samples ended when the normal force reached the maximum loading capacity (30 kN). The energy absorption ($E_a$) under uniaxial compression was defined as the area below the stress-strain curve. The specific compressive stress ($\sigma_s$) was calculated by dividing densities. The compression results were averaged over three specimens per group. Tensile stress-strain tests were carried out with a universal testing machine (TY-8000B, China) at a pulling rate of 25 mm/min. The samples in a size of 30mm $\times$ 15mm $\times$ 5mm were nipped to the tensile machine while testing. Then the hydrogels were cut into halves, and the two separate parts were contacted in air and underwater without any external stimulus during the healing process. The tensile tests were repeated to calculate the healing efficiency.

Conductivity. In a two-electrode system, the hydrogel samples with a size of 1.0cm $\times$ 0.5cm $\times$ 0.5cm were sandwiched between two platinum plate electrodes. The measurements were carried out on an electrochemical workstation (CHI760E, China). The resistance was calculated from the current-time curve by eq 2.

$$R = \frac{U}{I}$$  \hspace{1cm} (2)

where $R$ was the resistance ($\Omega$), $U$ was the open circuit potential of the conductive hydrogel (viewed in the open circuit voltage-time curve) (V), and $I$ was the current corresponding to the open circuit potential (A). The conductivity was calculated by eq 3.

$$\sigma = \frac{1}{RS}$$  \hspace{1cm} (3)

where $L$, $S$ and $R$ were the hydrogel thickness in cm, the electrode area in cm$^2$, and the hydrogel resistance in $\Omega$, respectively.
**Electrochemical Properties.** The electrochemical measurements were carried out on a three-electrode system using an electrochemical workstation (CHI760E, China). The hydrogel sample (12 mg), a Pt wire and a saturated calomel reference electrode were used as the working electrode, counter electrode and reference electrode, respectively. All measurements were performed in a 6.0 M KOH electrolyte. Cyclic voltammetry (CV), galvanostatic charge/discharge (GCD), cycling performance and electrochemical impedance spectroscopy (EIS) were conducted to examine electrochemical performance of hybrid hydrogels. CV tests were performed with 20, 50, 80 and 100 mV s\(^{-1}\) scan rates in a potential window of -0.6–0.4 V. The GCD experiment was carried out in the potential range from 0 to 0.4 V with applied current density of 0.5, 1.0 and 2.0 A g\(^{-1}\). The EIS tests were conducted over the frequency range from 0.01 Hz to 100 kHz using a sine wave with alternate signal amplitude of 5 mV. The cell specific capacitance \(C_s\) was calculated from the slope of the linear region of GCD curves, using the following eq 4.

\[
C_s = \frac{I \cdot \Delta t}{m \cdot \Delta V}
\]  

(4)

where \(I\), \(\Delta t\) and \(\Delta V\) was charge/discharge current in A, discharge time in s, potential drop during discharge in V, respectively, and \(m\) was the mass of active material within electrode in g.

**In Vitro Cell Culture.** L-929 cells (mouse fibroblast cells) were selected as the testing cell model. L-929 cells were routinely cultured in culture flasks with High Glucose-Dulbecco’s Modified Eagle’s Medium (HG-DMEM), supplemented with 10% fetal bovine serum. The cells were then incubated at 37°C in 5% CO\(_2\) and 95% air. Once the cells became nearly confluent, they were washed three times with phosphate buffer saline (PBS). Subsequently, the cells were released by treating with trypsin-EDTA solution for 3 min at 37°C, and then they were resuspended in fresh complete culture media with a final concentration of 1.5×10\(^5\) cells mL\(^{-1}\).

**In Vitro Cytotoxicity Assays.** The effects of the hybrid hydrogel on cell viability were
assessed by MTT [3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide] colorimetric assays (detailed assay process is given in Supporting information). The optical density values of the blank group, control group and experimental group were measured at 490 nm using Full-wavelength microplate reader and marked as $OD_b$, $OD_c$, and $OD_e$, respectively. The cell viability was calculated using the eq 5.

$$Cell\,\,viability\,\,[\%] = \frac{OD_e - OD_b}{OD_c - OD_b} \times 100\%$$ (5)

**SEM of Cell Adhesion and Morphology.** The morphology and cellular state of CNF-PPy/PB hydrogels were examined using SEM (Quanta 200). Before observation, the hydrogels were sterilized by UV irradiation for 30 min, and then the cells were seeded on the hydrogels surface in 24-well tissue-culture plates. After 24h in culture, the hydrogels were rinsed three times using PBS to remove non-adherent cells. The adherent cells were fixed with 2.5% glutaraldehyde for 2d at 4°C, followed by a dehydration in graded ethanol series (50, 70, 80, 90, and 100%). After a vacuum drying, the samples were sputter-coated with a thin Au layer and then observed under SEM.

**Fluorescent Staining.** Cell apoptosis was observed by fluorescence staining with fluorescence microscopy (OLYMPUS IX53). After 1d of culture with extract liquid, a certain amount of Hoechst 33342 live cell staining solution (100X) (Shanghai Beyotime Biotechnology Co., Ltd) was added and adjusted to the final concentration of cell staining solution 1X. Then the sample was incubated for 10 min at 37°C, followed by a removal of the mixed solution. Afterwards, the cell was washed with PBS three times and observed.
3. RESULTS AND DISCUSSION

3.1. Synthesis Process and Formation Mechanism of CNF-PPy/PB Hybrid Hydrogels

Figure 1. (a) Schematic illustration of preparation and synthesis process of CNF-PPy/PB hydrogels. (b) CNF-PPy/PB hydrogels molded into various shapes. (c) Formation mechanism of integrated 3D network within CNF-PPy/PB hydrogels. (d) Multi-complexation between PVA, CNF-PPy and borax.

The facile two-step synthesis process of CNF-PPy/PB hydrogels is schematically illustrated in Figure 1a. A stable aqueous suspension of CNFs was firstly prepared through acid hydrolysis and ultrasonication. Because of their excellent dispersibility and nanoscale dimension, CNFs were applied as a stable and robust nanocarrier to disperse PPy in water. CNF-PPy complexes were then synthesized via an in situ oxidative chemical polymerization of pyrrole monomers using FeCl₃ as oxidant and CNFs as biotemplate in an acid aqueous medium. The water-dispersed
CNF-PPy complexes were successfully achieved by the grown of PPy coating on the surface of individual CNF. Subsequently, the well-dispersed CNF-PPy complexes were incorporated into PB matrix to form CNF-PPy/PB hybrid hydrogels. CNFs acted as a biotemplate and guide the growth of PPy into compact CNF-PPy complexes with ideal dispersity, which enabled the formation of a hierarchical 3D conductive network structure in PB gel matrix. Interestingly, the obtained hybrid hydrogels exhibited high water content (~94%) and low density (~1.2 g cm$^{-3}$). These homogeneous, stable and moldable hydrogels could be readily and repeatedly remolded into various 3D shapes after gelation (Figure 1b).

A schematic illustration of hierarchical 3D network formation of CNF-PPy/PB hybrid hydrogels is proposed in Figure 1c. In a dilute solution, borax ($\text{Na}_2\text{B}_4\text{O}_7\cdot10\text{H}_2\text{O}$) dissociated into equal quantities of trigonal planar $\text{B(OH)}_3$ and tetrahedral $\text{B(OH)}_4^-$ that quickly interchanged in water, and the authentic concentration of $\text{B(OH)}_4^-$ was nearly twice the initial borax concentration. More importantly, the $\text{B(OH)}_4^-$ ion was shaped like a tetrahedron (four sides, each side an equilateral triangle) with the boron in the center and the four -OH groups at each corner, which could form various complexes with cis-diol sites of PVA chains and/or CNF-PPy hybrids (Figure 1d).\textsuperscript{27} In this way, borax acted as a cross-linker between the PVA chains and CNF-PPy complexes, resulting in strong interactions between these components and $\text{H}_2\text{O}$ molecules. As a result, the coexistence of multi-complexation, $\text{H}_2\text{O}$ interpenetration, chain entanglement of CNF-PPy hybrids and PVA, as well as inter- and intramolecular hydrogen bonding systems between them led to the formation of an integrated 3D network within the hybrid hydrogels.

3.2. Synthesis Process and Dispersion State of CNF-PPy Complexes in Aqueous Suspensions

The FTIR spectra of CNFs, PPy, CNF-PPy-3 complexes and CNF-PPy/PB-3 hydrogel are shown in Figure 2a. For CNFs, the characteristic bands at 3338 and 2889 cm$^{-1}$ were attributed to
the O-H stretching and C-H asymmetrically stretching, respectively.\textsuperscript{37} The small bands around 1432 cm\textsuperscript{-1} were due to the -CH\textsubscript{2} stretching and -CH bending, and the absorption band at 1035 cm\textsuperscript{-1} originated from C-O stretching vibration.\textsuperscript{38-39} For neat PPy, the peaks at 3428 and 2923 cm\textsuperscript{-1} were attributed to N-H stretching vibration. The peaks at 1549 and 1463 cm\textsuperscript{-1} corresponded to C=C and =C-N symmetric and asymmetric ring stretching, respectively. The peak at 1047 cm\textsuperscript{-1} and the band at 885 cm\textsuperscript{-1} were ascribed to C-H vibration and C-H out-of-plane vibration, respectively.\textsuperscript{40} After the \textit{in situ} polymerization, the spectrum of CNF-PPy-3 complexes was similar to that of pure PPy, indicating a successful polymerization of pyrrole monomers onto the CNF templates. Particularly, all the major peaks of CNF-PPy-3 complexes shifted to lower wavenumbers, which might be caused by the formation of hydrogen bonding between N-H in the pyrrole ring and the -OH groups of CNFs, suggesting the existence of PPy coating layer on the surface of CNFs. After hydrogelation, the entire spectrum of CNF-PPy/PB-3 hydrogel was similar to that of CNF-PPy-3 complexes. Specifically, the peak around 3436 cm\textsuperscript{-1} slightly shifted to a lower wavenumber at 3425 cm\textsuperscript{-1}, which probably indicated the formation of interactions between PVA chains, CNF-PPy complexes and those involved in molecular bonding. In addition, the peaks at 1329 and 831 cm\textsuperscript{-1} were attributed to the asymmetric stretching relaxation of B-O-C and B-O stretching from residual B(OH)\textsubscript{4}\textsuperscript{-}, suggesting the presence of borax and borate. These results confirmed the occurrence of multi-complexation and crosslinking between PVA chains, CNF-PPy hybrids and borate, as well as the presence of B(OH)\textsubscript{4}\textsuperscript{-} within the hydrogels.\textsuperscript{41}
**Figure 2.** (a) FTIR spectra of CNFs, PPy, CNF-PPy-3 complexes and CNF-PPy/PB-3 hydrogel. (b) Photographs of pure PPy and CNF-PPy aqueous suspensions after standing for 24h. (c) The chemical interaction between PPy and CNFs. TEM images of (d) CNFs, (e) pure PPy and (f) CNF-PPy-3 complexes. The insert of (f) confirming the specific morphology of CNF-PPy-3 complexes.

As shown in **Figure 2b**, the neat PPy and CNF-PPy complexes were dispersed well after a 30-min stirring. After 24h, the pure PPy particles were aggregated together in aqueous suspension due to their intrinsic intermolecular interactions, while the aqueous suspension of CNF-PPy complexes still remained stable without any precipitates, indicating that CNF templates were ideally suitable dispersant for PPy. The interaction between PPy and CNFs might ascribe to the hydrogen bonding between N-H in the pyrrole ring and the O-H functional groups of CNFs (**Figure 2c**). In addition, the UV-Vis spectra of PPy and CNF-PPy-3 complexes further proved
the good dispersibility of CNF-PPy (Figure S1). Due to the poor dispersibility and a large aggregation, the absorption peak of neat PPy suspension was much weaker than that of the CNF-PPy-3 complexes, which further demonstrated that the incorporation of CNFs significantly improved the dispersibility of PPy in water. The CNF-PPy-3 complexes had two absorption peaks at 342 and 730 nm, which could be explained by the $\pi-\pi^*$ interband transition, the polaron and bipolaron band transition of PPy, respectively.\textsuperscript{42} These results confirmed the successful polymerization of PPy on CNFs.

The morphology of CNFs, pure PPy and CNF-PPy-3 complexes are shown in Figure 2d-f. CNFs with high aspect ratio dispersed homogeneously in water and formed a stable colloidal suspension without visible aggregation (insert of Figure 2d). The average length and diameter of CNFs were 732±208 nm and 21±7 nm, respectively (Figure 2d), while the near-spherical PPy particles synthesized through directly oxidative polymerization were dozens of nanometers in diameter and densely compacted with each other (Figure 2e). As expected, the polymerization of PPy on CNF templates maintained the integrity of CNFs. The PPy grew along the templates to avoid the aggregation, and thus the PPy carried by CNF templates were uniformly dispersed in aqueous medium to build an interconnected conductive network (Figure 2f). The morphology of CNF-PPy complexes can be clearly observed in the insert of Figure 2f, indicating the successful coating of PPy shell on CNFs. It was worth noting that the continuous conductive PPy network supported by CNF templates and excellent dispersity of CNF-PPy complexes was a prerequisite for the synthesis of the CPHs with good electrical conductivity and enhanced mechanical performances.
3.3. Linear Viscoelastic Region Determined by Dynamic Strain Sweep

**Figure 3.** Dynamic viscoelasticity performance at 25°C and thermo-reversibility of the hydrogels at \( \gamma = 1\% \): (a) strain dependence of \( G' (\omega = 1.0 \text{ Hz}) \); (b) frequency dependence of \( G' \) and \( G'' (\omega = 1.0-100 \text{ Hz}) \); (c) frequency dependence of \( G^* \) and \( \eta^* (\omega = 1.0 \text{ Hz}) \); (d) Stretching demonstration of CNF-PPy/PB-3 hydrogel (more than 600% of the original length).

**Figure 3a** shows the curves for \( G' \) as a function of \( \gamma \) based on the results from dynamic strain sweep tests, demonstrating a typical elastic response of hybrid hydrogels. The strain sweep tests were conducted to confirm the linear viscoelastic region of hydrogels, where \( G' \) and \( G'' \) were independent of the applied \( \gamma \) (from 0.01 to 100%). The \( G' \) value of all samples was relatively stable within \( \gamma = 1.0\% \), so \( \gamma = 1.0\% \) was selected in the subsequent oscillation tests to ensure that...
the following dynamic oscillatory deformation of each hydrogel was within linear viscoelastic region. As expected, the addition of a small amount of CNF-PPy complexes pronouncedly increased the viscoelasticity and toughness of hydrogel. All CNF-PPy/PB hybrid hydrogels exhibited considerably higher $G'$ values than CNF/PB hydrogel, indicating a more significant reinforcing effect of CNF-PPy complexes than CNFs. Compared with the other hydrogels, CNF-PPy/PB-3 present the highest $G'_{\text{max}}$ value ($\sim 10^5$ Pa), which was almost 60 times higher than that of CNF/PB hydrogel ($G'_{\text{max}} \approx 1700$ Pa) and three orders of magnitude greater than that of pure PB hydrogel ($G'_{\text{max}} \approx 100$ Pa).\(^{34}\)

### 3.4. Dynamic Viscoelasticity of Hybrid Hydrogels

The $G'$ (elasticity) and $G''$ (viscosity) of CNF-PPy/PB and CNF/PB hydrogels as a function of angular frequency ($\omega = 0.1-100$ rad s\(^{-1}\)) within linear viscoelastic region are shown in Figure 3b. It was clearly observed that the $G'$ and $G''$ curves of these hydrogels basically followed a comparable trend. Unlike the permanently cross-linked gels that was frequency-independent,\(^4^3\) PB-based hydrogels with dynamically cross-linked network demonstrated frequency-dependent moduli. As $\omega$ proceeded, there was an initial regional monotonic increase in both moduli. Within the latter part of the curves, $G'$ continued to increase to reach a plateau region that was indicative of polymer entanglements, whereas $G''$ reached its peak and then began to decrease. Over the entire $\omega$ range, the $G'$ values of all hydrogels were always higher than their corresponding $G''$ values, which indicated that a permanent elastic network was formed in the solid-like hydrogel.\(^4^4^\)

\(^{45}\) It was generally deemed that the existence of crossover point where $G' = G''$ was the sign of gelation. We previously found that the pure PB hydrogel held this type of crossover point, and it exhibited quasi-liquid behavior at low frequency ($G' < G''$) and solid-like behavior ($G' > G''$) at high frequency.\(^{34}\) Interestingly, it was noticed that the moduli curves of CNF-PPy/PB hydrogels
only showed a rubbery-like behavior over the accessible frequency window ($\omega = 0.1$-100 rad s$^{-1}$), revealing that their intersection point located out of $\omega$ window and the gelation occurred at a lower $\omega$, much earlier than PB and CNF/PB hydrogels. This result demonstrated the formation of the elastic 3D network with both entangled chains and reversible cross-links was achieved.

As noted from the graph, the $G'$ values of all CNF-PPy/PB hydrogels gradually increased with the increasing content of PPy. Compared with CNF/PB hydrogel, an increase of almost 100-fold in $G'$ (high-frequency plateau of $G'$) was generated for CNF-PPy/PB-3. However, excessive PPy would hinder the formation of 3D network within hydrogel, thus leading to the decline of $G'$ values. Therefore, CNF-PPy/PB-3 possessed the most outstanding viscoelasticity among these hydrogels. The plots of complex modulus ($G^*$) and complex viscosity ($\eta^*$) as a function of $\omega$ provided a sharper contrast of these hydrogels (Figure 3c), where CNF-PPy/PB-3 exhibited the highest $G^*$ and $\eta^*$ within the whole $\omega$ range. As shown in Figure 3d, a block of elastic CNF-PPy/PB-3 hydrogel could be stretched beyond 600% strain into a thin film without damage, exhibiting its excellent stretchability, efficient energy dissipation behavior and damage-tolerant ability. Its elastomeric nature was probably attributed to the entanglements of PVA chains and flexible CNF-PPy complexes through physical junctions and hydrogen bonds with the presence of borax. In this view, the homogeneously dispersed CNF-PPy complexes in PB matrix could be considered as multifunctional cross-linkers and reinforcing nanofillers.

3.5. Self-healing Behavior of the Hydrogels under Continuous Step Strain

Because all hydrogels were self-healable at room temperature, CNF-PPy/PB-3 was representatively selected to demonstrate the self-healing ability of these hydrogels. In Figure 4a, the hydrogel demonstrated the autonomous recovery of its viscoelasticity after a large-amplitude oscillatory collapse. When applying a small-amplitude oscillatory force ($\gamma = 1.0\%$), the hydrogel...
presented a solid nature with a $G'$ of 30.0 kPa and a $G''$ of 18.0 kPa. During the following large-amplitude one ($\gamma = 80\%$), the $G'$ values decreased considerably to 7.8 kPa that was lower than $G''$ (~12 kPa), indicating a transient transition of hydrogel from quasi-solid to quasi-liquid state. When $\gamma$ was decreased once again to 1.0%, the $G'$ and $G''$ instantly returned to their original values, and the hydrogel recovered the original solid state, suggesting the thixotropic nature and intrinsic self-recovery property of hydrogel.

Figure 4. (a) $G'$ and $G''$ dependence of time in continuous step strain measurements for CNF-PPy/PB-3 hydrogel. (b) Demonstration of merging CNF-PPy/PB and CNF/PB hydrogels together. (c) Demonstration of self-healing ability for CNF/PB. (d) Schematic illustration of in situ self-healing and dynamic reversible cross-links of hydrogels.

To evaluate the self-healing ability of the hydrogels, two blocks of freshly prepared CNF-PPy/PB (black) and CNF/PB hydrogels (white) were put together, their surfaces could adhere to
each other without any external force, and eventually they were autonomously self-healed to form one integral hydrogel block within 20s (Figure 4b). It can be clearly observed that the interface between CNF-PPy/PB and CNF/PB was completely merged together, which could not be pulled apart under stretching. To further demonstrate the self-healing behavior, two freshly prepared CNF/PB hydrogels with two different colors (the blue one was stained with methylene blue) were brought into contact. After about 20s, they completely merged together to form one integral hydrogel (Figure 4c). In Figure 4d, just after the fresh hydrogel was cut into two pieces, the two parts of the hydrogel were put together and then contacted in situ for about 20s. As expected, they automatically self-healed in the same way, which indicated the excellent self-healing property of dynamic borate-associated network inside hydrogels.

One possible explanation for the self-healing property of CNF-PPy/PB hydrogel was attributed to the inter- and intra-molecular hydrogen bonds and the dynamically reversible bonds formed through the complexation of borate ions and hydroxyls within the hydrogels. Particularly, the complexation of borate ions and hydroxyl groups on the adjacent polymer chains was exceedingly fast, and these reversible cross-links in hydrogels were readily broken and reformed, so CNF-PPy/PB could completely self-recover after contacting or deformation only for a few seconds.46 Consequently, the sufficient mobility of polymer chains, free hydroxyl groups and dynamic interactions within the network could illuminate the fast self-healing ability of CNF-PPy/PB hydrogel without any stimuli or healing agents.41 Introducing CNF-PPy complexes into the PB gel matrix rendered it electric conductivity and enhanced its stiffness. Nevertheless, the prepared CNF-PPy/PB hybrid hydrogel retained its viscoelasticity, and because of the low viscosity of PB gel matrix, the CNF-PPy complexes were mobile and respond to deformation in a time-dependent manner. In particular, the hydrogel formed mobile networks that dynamically broke and reformed
during mechanical deformation or damage, which probably led to the development of a soft sensing material.  

Interestingly, the hydrogels also presented pH-sensitive ability due to the dynamically reversible bonds (Figure S2). This pH-sensitive sol-gel transition behavior was probably attributed to the cross-linking reaction between borate ion and hydroxyl groups of PVA or CNF-PPy, known as reversible didiol complexation, the balance of which could be shifted through changing pH value. When the tetrahedral borate form was stabilized with pH around 9.5, the efficient cross-linking occurred and the formation of hydrogel network was thus facilitated, while the acid caused the dissociation of didiol-borate complex. Therefore, CNF-PPy/PB hydrogel with pH-sensitive sol-gel transition behavior could be potentially applied in biological sensors and smart drug-delivery systems.

3.6. Tensile Stress-strain Behavior and Self-healing Ability in Multiple Environments

More importantly, after each self-healing process, the hydrogels could basically maintain their original characteristics and performances, which was beneficial to their long-term applications. To further assess the self-healing ability, the tensile tests were carried out to characterize the self-healing behavior both in air and underwater (Figure 5). Figure 5a shows the tensile stress-strain curves of CNF/PB and CNF-PPy/PB hydrogels before and after a 20s self-healing in air. It can be observed that the tensile fracture stress of hydrogels was significantly enhanced with the addition of CNF-PPy complexes. The maximum tensile fracture stress of CNF-PPy/PB-3 (~62.8 kPa) was two times larger than that of CNF/PB (~30.4 kPa). The corresponding rupture strain of hydrogels was decreased with the increasing CNF-PPy loading, and the rupture strain of CNF-PPy/PB-3 could reach up to 600%. After being cut into two pieces and a 20s self-healing in air, the tensile stress-strain curves of the self-healed hydrogels were almost identical to the original
counterparts (Figure S3). Figure 5b shows the stress histogram of CNF/PB and CNF-PPy/PB hydrogels before and after a 20s healing in air. For CNF/PB hydrogel, the maximum fracture stress of original sample was 29.8±2.1 kPa, and the maximum fracture stress of self-healed sample was 28.5±1.4 kPa. After a 20s healing in air, the tensile stress of CNF/PB hydrogel could recover to 95.6%. For CNF-PPy/PB-3 hydrogel, the original fracture stress was 62.8±2.2 kPa. After a 20s healing in air, and the fracture stress was 61.0±1.2 kPa. Therefore, its self-healing efficiency was about 97%, indicating an excellent self-healing ability.

![Graphs and images showing stress-strain curves and healing efficiency](image)

**Figure 5.** (a) Tensile stress-strain curves of original CNF/PB and CNF-PPy/PB hydrogels. (b) Stress histogram of CNF/PB and CNF-PPy/PB hydrogels before and after a 20s healing in air. (c)
Tensile stress-strain curves of CNF-PPy/PB-3 before and after a 60s healing in air and underwater. (d) Stress histogram of CNF-PPy/PB-3 after various self-healing time underwater. (e) Demonstration of the underwater self-healing ability of the hydrogels at room temperature without external intervention.

Interestingly, the hydrogels also exhibited self-healing property underwater. The rupture stress and rupture strain of CNF-PPy/PB-3 after a 60s self-healing underwater were lower than those healed in air (Figure 5c). Figure 5d shows the fracture stress histogram of CNF-PPy/PB-3 after various self-healing time underwater. After a 20s healing, the stress was 15.2±2.5 kPa. In the case of 60s, the stress was increased to 37.9±2.7 kPa. After a longer healing time of 90s, the stress was further increased to 54.9±3.8 kPa. The underwater healing efficiency of the hydrogel after a 90s healing was about 87%, indicating a good underwater self-healing ability of the hydrogels. Figure 5e illustrated the underwater self-healing ability of the hydrogels. In particular, two pieces of CNF-PPy/PB hydrogel were contacted for 90s underwater, and the healed integral hydrogel could be stretched without any damage along the contact interface. The underwater self-healing ability of the hydrogels probably resulted from the diffusion of borate in water, and the dynamic cross-linking within the hydrogel network still maintained. Consequently, the hydrogels could still heal even in a water environment. However, due to the lower borate concentration and the insufficient contact of hydrogels, the self-healing process underwater became slower than that in air.46

3.7. Uniaxial Compression Stress-strain Behavior and Microstructure of Hydrogels
**Figure 6.** Typical compression stress-strain curves of (a) CNF-PPy/PB-3, (b) CNF-PPy/PB-2, (c) CNF-PPy/PB-1, (d) CNF-PPy/PB-4, (e) CNF-PPy/PB-5 and (f) CNF/PB hydrogels as the dependences of nominal $\sigma_{\text{nom}}$ and true stresses $\sigma_{\text{true}}$ on the deformation ratio $\lambda$. Purple circles representing the points of failure in the hydrogel samples.

The compression properties of hydrogels were essential to their target applications, so the hydrogels were subjected to uniaxial compression tests to assess their mechanical performance. Compressive stress consisted of nominal stress ($\sigma_{\text{nom}}$) and true stress ($\sigma_{\text{true}}$), which were the forces acting per unit undeformed and deformed area of the hydrogel specimen, respectively. It was given by $\sigma_{\text{true}} = \lambda \sigma_{\text{nom}}$, where $\lambda$ was the deformation ratio (deformed length/initial length). Figure 6 shows the stress-strain curves of CNF-PPy/PB and CNF/PB hydrogels as the dependences of nominal $\sigma_{\text{nom}}$ and true stresses $\sigma_{\text{true}}$ on the deformation ratio $\lambda$. It was observed that the fracture stress and fracture strain obtained from $\sigma_{\text{nom}}$-$\lambda$ plots did not match with those obtained from $\sigma_{\text{true}}$-$\lambda$ plots. For example, the fracture stresses obtained from $\sigma_{\text{nom}}$ vs $\lambda$ curves of CNF-PPy/PB and CNF/PB were 41.1, 36.6, 36.7, 32.1, 4.4 MPa and 70.6 kPa at 100%, 99%, 99%, 96%, 100% and 98% strains, respectively, while the corresponding $\sigma_{\text{true}}$ vs $\lambda$ curves passed through maximum
values below the strains. It was probably due to the possibility that the samples could still support the stress even with microscopic cracks or the nonisotropic deformation of the hydrogels under large strain. Therefore, the fracture stresses were 19.6, 15.9, 17.1, 25.0, 1.5 MPa and 37.6 kPa at the breaking points calculated from the maxima in $\sigma_{\text{true}} - \gamma$ plots, as indicated by the purple circles.

![Graphs showing stress-strain and energy absorption-strain curves](image)

**Figure 7.** (a) Nominal stress-strain and (b) corresponding energy absorption-strain curves of hydrogels. (c) CNF-PPy/PB-3 hydrogel loaded with 500g weight. (d) Idealized 3D hydrogel network. SEM of CNF-PPy/PB-3 at low (c, $\times$4000) and high magnifications (f, $\times$10000) and (g, $\times$15000).
The typical $\sigma_{\text{nom}}$-$\varepsilon$ curves and the corresponding energy absorption-strain curves of hydrogels are shown in Figure 7. The mechanical properties were compared by the nominal stress and the energy absorption at a 90% strain level, respectively. As expected, the addition of CNF-PPy complexes pronouncedly increased the compressive strength of composite hydrogel. All CNF-PPy/PB hydrogels exhibited a much higher compressive strength than CNF/PB hydrogel (Figure 7a). At first, the $\sigma_{\text{nom}}$ values of CNF-PPy/PB hydrogels gradually increased with the increasing content of CNF-PPy complexes. Compared with CNF/PB hydrogel, an increase of almost two to three orders of magnitude in $\sigma_{\text{nom}}$ was generated for CNF-PPy/PB-1 to CNF-PPy/PB-3. With a moderate content of PPy, the CNF-PPy complexes could form sufficient bonds with PB matrix. However, at a higher content of PPy, the excessive PPy would obstruct the reaction of sufficient -OH groups from CNFs with PB matrix and decrease the effective crosslinking between CNF-PPy and PB, resulting in a low crosslinking density and the weakening of mechanical properties for CNF-PPy/PB-4 and CNF-PPy/PB-5. Obviously, CNF-PPy/PB-3 possessed the highest compressive strength among these hydrogels. In particular, the $\sigma_{\text{nom}}$ of CNF-PPy/PB-3 at $\varepsilon = 90\%$ was almost 2240-fold higher than that of CNF/PB (Table 1). Taking into consideration their real densities, the specific compressive stress ($\sigma_s$) ($\sim 18.5$ MPa cm$^3$ g$^{-1}$) of CNF-PPy/PB-3 was 1850-fold higher than that of CNF/PB ($\sim 0.01$ MPa cm$^3$ g$^{-1}$). The improved mechanical strength was mainly attributed to the numerous hydrogen bonds and chemical interactions between PB matrix and CNF-PPy complexes, causing the chain entanglement and the formation of the 3D networks. Specifically, the movement of the PVA chains was inhibited by the hydrogen bonds between PVA and CNF-PPy complexes. The existence of borax also led to strong interactions between CNF-PPy and PVA chains as well as chemically crosslinked hydrogel network.33 CNFs chains coated with PPy molecules were the reinforcement fillers of the hybrid hydrogels. Under external force,
the well-dispersed PPy carried by CNFs within hydrogels played a key role in the enhancement effect through transferring the stress from polymer chains to CNF-PPy complexes.

Not surprisingly, it was further observed that among all hydrogels, CNF-PPy/PB-3 showed the highest energy absorption ($E_a$) throughout the whole $\varepsilon$ range, especially at high $\varepsilon$ levels (Figure 7b). Specifically, the $E_a$ value of CNF-PPy/PB-3 ($262.9 \pm 0.3$ kJ m$^{-3}$ at $\varepsilon = 90\%$) was about 560 times higher than that of the CNF/PB hydrogel (Table 1), demonstrating a significant elevation of toughness and strength. The CNF-PPy/PB-3 cake (weight $\approx 8.4$ g) with a high water content ($W_c \approx 93.9\%$) did not display any obvious deformation under a static loading of 500g, supporting more than 60 times of its own weight (Figure 7c). The reason of enhanced mechanical strength was that the -OH and -NH on the CNF-PPy complexes associated with PB matrix to construct a chemical and physical cross-linking network inside the hybrid hydrogel via multi-complexation.

Table 1. Physical and compression properties of hydrogels

<table>
<thead>
<tr>
<th>Hydrogels</th>
<th>$\sigma_{\text{room}}$ at $\varepsilon=90%$ $[\text{MPa}]$</th>
<th>$E_a$ at $\varepsilon=90%$ $[\text{kJ m}^{-3}]$</th>
<th>Water Content $W_c$ $[%]$</th>
<th>Density $\rho$ $[\text{g cm}^{-3}]$</th>
<th>$\sigma_s$ $[\text{MPa} \cdot \text{cm}^{-3} \text{g}^{-1}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNF-PPy/PB-1</td>
<td>10.8 $\pm$ 0.3</td>
<td>73.5 $\pm$ 0.1</td>
<td>95.4 $\pm$ 0.1</td>
<td>1.17 $\pm$ 0.12</td>
<td>$\sim$9.23</td>
</tr>
<tr>
<td>CNF-PPy/PB-2</td>
<td>13.4 $\pm$ 0.5</td>
<td>116.3 $\pm$ 0.3</td>
<td>94.6 $\pm$ 0.2</td>
<td>1.19 $\pm$ 0.09</td>
<td>$\sim$11.26</td>
</tr>
<tr>
<td>CNF-PPy/PB-3</td>
<td>22.4 $\pm$ 0.2</td>
<td>262.9 $\pm$ 0.3</td>
<td>93.9 $\pm$ 0.1</td>
<td>1.21 $\pm$ 0.05</td>
<td>$\sim$18.51</td>
</tr>
<tr>
<td>CNF-PPy/PB-4</td>
<td>7.6 $\pm$ 0.4</td>
<td>42.1 $\pm$ 0.5</td>
<td>93.2 $\pm$ 0.2</td>
<td>1.24 $\pm$ 0.08</td>
<td>$\sim$6.13</td>
</tr>
<tr>
<td>CNF-PPy/PB-5</td>
<td>1.1 $\pm$ 0.3</td>
<td>11.2 $\pm$ 0.6</td>
<td>92.5 $\pm$ 0.2</td>
<td>1.27 $\pm$ 0.11</td>
<td>$\sim$0.87</td>
</tr>
<tr>
<td>CNF/PB</td>
<td>$\leq$ 0.01</td>
<td>0.5 $\pm$ 0.1</td>
<td>95.8 $\pm$ 0.1</td>
<td>1.15 $\pm$ 0.07</td>
<td>$\sim$0.01</td>
</tr>
</tbody>
</table>

In comparison, the as-synthesized CNF-PPy/PB-3 hydrogel could bear more compressive stress than most CPHs previously reported. In particular, the compression strength of CNF-PPy/PB-3 ($\sigma \approx 10$ MPa at $\varepsilon = 80\%$) was about 3.3, 167 and 1.4 times greater than that of chitosan/polyacrylamide-PANI hydrogel ($\sigma \approx 3$ MPa at $\varepsilon = 80\%$),\textsuperscript{49} PPy-grafted chitosan/poly(acrylic acid) double-network conductive hydrogel ($\sigma \approx 60$ kPa at $\varepsilon = 80\%$) and
[EMIm][DCA]/PAMPS double-network conductive ionogel ($\sigma \approx 7.7$ MPa at $\varepsilon = 92\%$),\textsuperscript{50-51} respectively. Consequently, the introduction of CNF-PPy complexes with high toughness and flexibility significantly improved the strength and elasticity of PB gel matrix, building a combined reinforcing and conductive network inside the hybrid CNF-PPy/PB hydrogel.

The idealized 3D network structure and the microstructure of hybrid hydrogels observed by SEM at different magnifications are presented in Figure 7d to 7g, clearly illustrating the stable 3D interconnected network formed by CNF-PPy complexes and PB matrix. All hydrogels exhibited a highly interconnected and porous structure with pores of sub-micrometer to several micrometers in size. The chain entanglement of CNF-PPy complexes and PVA resulted in the formation of the porous structure enabled by molecular interactions. Additionally, this architecture could effectively facilitate the diffusion of electrons, ions and molecules inside the hybrid hydrogel. In the case of CNFs, the primary advantages were their renewability, flexibility, mechanical strength and biocompatibility. CNFs served as nanotemplates for PPy and the hydrogen bonds between them acted as traction force to assist the polymerization of pyrrole monomers \textit{in situ}, thus promoting the formation of continuous PPy conductive network in the hybrid hydrogels. The efficient PPy network was beneficial to the construction of electrically conductive pathways, which probably contributed to enhancing the electrical conductivity due to the uniform dispersion of PPy in PB matrix without any visible aggregates with the assist of CNFs.\textsuperscript{52} Consequently, it was demonstrated by this work that the architecture of the filling phase in the gel matrix and design of gel network structure were vital for achieving desired performance of hybrid hydrogel. This 3D interconnected porous structure had a positive influence in improving mechanical and conductive performances of the hydrogels, thus enabling their potential application as bioelectrode in flexible supercapacitor.\textsuperscript{53}
3.8. Electrochemical Performances of Hydrogels

**Figure 8.** (a) Conductivity transition of CNF-PPy/PB hydrogels with different mass of pyrrole. (b) Relative resistance variation ($\Delta R/R_0$) of CNF-PPy/PB-3 at different strains and luminance variation of an LED as a function of applied strains. (c) Current change of CNF-PPy/PB-3 hydrogel during cyclic cutting and self-healing process. (d) Luminance variation of an LED during cutting and self-healing processes.

The conductivity of CNF-PPy/PB hydrogels with different mass of pyrrole monomers added for polymerization are shown in **Figure 8a**. The conductivity of these hydrogels, ranging from 1.5 to 4.8 S m$^{-1}$, exhibited a nonlinear increase with the increase of pyrrole content. The maximum
conductivity of CNF-PPy/PB was determined to be 4.74±0.05 S m⁻¹, which was much higher than that of Pectin/PANI aerogels (up to 0.1 S m⁻¹) by a supercritical CO₂ drying,⁵³ self-assembled graphene hydrogels (up to 0.5 S m⁻¹) via a convenient one-step hydrothermal method,⁵⁴ and even pure PPy hydrogels (up to 1.7 S m⁻¹).⁵⁵ It was reported that CNFs could provide pathways for ion and electron transport when applied in electrochemical materials.⁵⁶ Compared to the bulky PPy, CNFs with fine structure facilitated the efficient dispersion of PPy and significantly enhanced the surface area by forming a continuous porous conductive network.⁵⁷ Therefore, the well-dispersed CNF-templated PPy created efficient conductive paths in the PB matrix, endowing the hybrid hydrogels with high conductivity. The multi-complexation of CNF-PPy, borax and PB system also gave rise to additional conductive paths through the hydrogel which could facilitate the charge transport.⁵²

The high stability, elasticity and conductivity of CNF-PPy/PB hydrogels made them suitable for fabricating sensing materials. To assess their strain-sensing property, the measurements of relative resistance changes (ΔR/R₀=(R₀−R)/R₀, where R₀ and R were the resistance without and with stretch, respectively) versus strains were carried out. During the stretching process, the increased distance between PPy network led to the elongating tunneling of charges transferred between adjacent PPy chains.⁵⁸ Therefore, ΔR/R₀ value raised with the increasing stretching strain (Figure 8b). The inserts of Figure 8b demonstrated the luminance transition of the LED under different strains. It can be clearly seen that the hydrogel was still conductive after being stretched to 300% strain, indicating that the conductive network of hydrogels was essentially stable and highly stretchable.

In addition, the self-healing ability of CNF-PPy/PB-3 hydrogel was further demonstrated by a current test (Figure 8c). After the first cutting, the current was almost disappeared and the circuit
became open. When the two fractured surfaces were physically connected to each other for about 20 s, the circuit current immediately recovered to its initial value, demonstrating a complete reconstruction of an integrated 3D conductive network for the self-healed hydrogel. As shown in Figure 8d, the hydrogel could cause illumine a LED bulb in a closed loop. When the hydrogel was cut into two parts, the circuit became open and the bulb was extinguished. After a 20 s self-healing, the circuit was re-established and the bulb was lighted again without any reduction in conductivity, indicating the self-recovery of electrical performance of the hybrid hydrogels. More importantly, the hydrogel could repeatedly self-recover its normal conductivity each time after damage. With the smart self-healing ability that gave priority to repair damages, the CNF-PPy/PB could maintain its original shape, conductivity, strength and other functions after every self-healing process. Because of dynamic association or dissociation of various borax-based complexes in hydrogels, their smart, efficient and repeatable self-healing behavior could be achieved at room temperature without any external stimuli. The hybrid hydrogels based on a highly conductive CNF-PPy network and a self-healable PB network exhibited high mechanical strength and elasticity due to their unique reversibly complexed network structure, providing the possibility for the fabrication of highly self-healable and flexible bioelectric devices.59

To evaluate the electrochemical performance of hydrogels, CV, GCD and EIS measurements were performed in a conventional three-electrode system. Figure 9a illustrated the typical rate-dependent CV curves of the hydrogel-based electrode in the voltage range from -0.6 to 0.4 V at 20, 50, 80 and 100 mV s⁻¹ scan rates. The current densities increased along with increasing scan rates, exhibiting a good rate capability.60 As the scan rate increased, the cathodic peaks right-shifted high voltages and the anodic peaks shifted to the low values, which was caused by the inherent resistance of the electrode materials.61 Moreover, the hydrogel-based electrode showed
a high degree of electroactivity, with transitions from reduced to oxidized forms demonstrating
the intrinsic redox feature of conducting polymers.\textsuperscript{62} The typical oxidation and reduction peaks
pointed out the ideal pseudocapacitive feature of hydrogel electrode.

**Figure 9.** Electrochemical performance of CNF-PPy/PB-3 hydrogel-based electrode: (a) CV
curves at various scan rates of 20-100 mV s\textsuperscript{-1}; (b) representative GCD profiles at current densities
of 0.5-2.0 A g\textsuperscript{-1}; (c) EIS curves and enlarged region of high frequency; (d) capacitance retention
versus cycle number at high current rate of 7.5 A g\textsuperscript{-1} and the first 21 cycles of GCD curves.

**Figure 9b** shows the GCD profiles at varied current densities of 0.5, 1.0, and 2.0 A g\textsuperscript{-1}. For the
charge-discharge procedure, the time needed gradually decreased with the increase of current
density, which was similar to the supercapacitors previously reported.\textsuperscript{63} It was noticed that the
GCD curves were not symmetrical triangles and did not follow a linear relationship, which might be attributed to the presence of pseudo-capacitance caused by the surface-confined Faradaic reaction of PPy. The specific capacitance ($C_s$) of the hydrogel-based electrode calculated from GCD curves were as high as 236.9, 141.3 and 62.8 F g$^{-1}$ at the current density of 0.5, 1.0 and 2.0 A g$^{-1}$, respectively, which were comparable to that of various electrodes in previous reports, such as pectin/PANI aerogels (~184 F g$^{-1}$ at 0.5 A g$^{-1}$), pure PPy (~90 F g$^{-1}$ at 0.01 V s$^{-1}$) and graphene hydrogels (~160 F g$^{-1}$ at 1.0 A g$^{-1}$). The capacitances decreased along with the increase of scan rates, which further proved the ion diffusion effect in the hydrogel electrode. The exceptional electrochemical performance of CNF-PPy/PB electrode was attributed to the appropriate combination of CNFs and PPy that could greatly enhance the electrochemical properties of PPy itself. Firstly, the renewable and sustainable CNFs with a large specific surface area and an extremely low density were suitable templates for PPy. They could construct a flexible reinforcing scaffold that supported the continuous PPy conductive network within the PB gel matrix, and the PPy carried by CNFs could be well-dispersed in the gel system, providing the hydrogel electrode with a more stable and higher conductivity for electrical signal transmission. Secondly, the beneficial polymerization of pyrrole monomers on the CNF biotemplates formed a porous nanostructure of CNF-PPy complexes within the hydrogel electrode that facilitated electron transport. Thirdly, the uniform dispersion of CNF-PPy complexes within PB matrix could help to provide a larger specific surface area of electrode/electrolyte interface to improve utilization of PPy for redox reactions.

The Nyquist plots obtained from EIS are summarized in Figure 9c. The inset plot is an enlargement of EIS in the area of high frequencies. The semicircle at higher frequencies corresponded to the electron-transfer reaction at the electrolyte/electrode interface. The linear
part in the low frequency region represented the Warburg impedance associated with the charge diffusion process in the electrode materials, indicating an ideal capacitive behavior. It should be noted the smaller of the charge transfer resistance ($R_{ct}$) that was calculated by the diameter of semicircle, the lower the charge transfer resistance and the better the conductivity of the electrode. The intercept of the semicircle at the real axis represented the internal resistance ($R_s$) deriving from the active materials and the electrolytic resistance. The $R_{ct}$ and $R_s$ of the hydrogel-based electrode were 6.5Ω and 3.5Ω respectively, indicating a high conductivity of the hydrogel electrode.

The cyclic stability of the hydrogel-based electrode was tested through GCD curves at a current density of 7.5 A g⁻¹, and its cell specific capacitance degradations were less than 14% after 1500 cycles (Figure 9d). Calculated from the capacitance retention curves (columbic efficiency (%) = (discharge capacity/charge capacity) × 100%), the average columbic efficiency of hydrogel-based electrode during 100 cycles was about 80.3%. This ideal electrochemical stability of the electrode could be assigned to the strong interactions between CNFs and PPy as well as the stable 3D network structure within hydrogels, which could restrict the structural change of PPy and stabilize the electrochemical sites of PPy during the electrochemical cycles. The capacitance decreases during charge-discharge cycling was probably attributed to the destruction of PPy, which was caused by the shrinkage and expansion of PPy during doping and dedoping along the cycling. In addition, the structural change and instability of the electrochemical sites of PPy during the electrochemical cycles also caused the imperfect cycling properties. Figure S4 shows the flexible hydrogel-based symmetric supercapacitor. The supercapacitor was prepared by a CNF/PB gel electrolyte sandwiched between two CNF-PPy/PB electrodes (insert of Figure S4). The assembled symmetric supercapacitor exhibited good cycling stability and mechanical endurance.
when suffering from mechanical deformations such as bending, folding, and twisting. Due to the fast self-healing ability, the healing efficiency of the supercapacitor calculated by the ratio of capacitance retention was about 97.2% after 10 cutting/healing cycles (Figure S5). Because of their excellent electrochemical performance and other appealing functions mentioned above, these CNF-PPy/PB hydrogels thus showed great potential as multifunctional electrode materials for smart flexible supercapacitors.

3.10. **In Vitro Biocompatibility and Cell Attachment of Hydrogels**

**Figure 10.** (a) Cell viability assays of the CNF-PPy/PB-3 hydrogel using L-929 cells by MTT colorimetric assays. (b) Fluorescent staining images of L-929 cell incubated for 24h with 100%
hydrogel extract liquid. SEM of the cell adhered to the CNF-PPy/PB-3 hydrogel after 24h in the culture at low (c) and high (d) magnifications.

Due to the excellent biocompatibility of CNF, PVA and PPy, the biocompatibility of CNF-PPy/PB hydrogels were highly expected. Therefore, the cytotoxicity of representative CNF-PPy/PB-3 hydrogel was evaluated using L-929 cells by MTT colorimetric assays (Figure 10). As shown in Figure 10a, the remaining cell viability was larger than 90% for different concentrations of hydrogel extracts incubated for 24h. The increase of the concentration of extracts nearly had no effect on cell viability which still maintained a high level. It was thus proved that these hydrogels were biocompatible. As shown in the live/dead fluorescence staining in Figure 10b, L-929 cells were well spread and reached high confluence at 24h after seeding, and these cells maintained a high viability with the large majority of living cells and few dead cells, indicating a nontoxic nature of hydrogels. The cell attachment on hydrogels was investigated by SEM. Figure 10c and 10d show the images of the cell adhesion to the CNF-PPy/PB-3 hydrogel after 24h in culture at low and high magnifications. The cells appeared to be extensively dispersed and successfully attached on the hydrogel surface. Additionally, cells seeded on CNF-PPy/PB-3 hydrogel were spread and appeared confluent. This result suggested that the hydrophilic surface of CNF-PPy/PB hydrogels provided a more compatible environment for cell attachment and proliferation. These results demonstrated that this class of CNF-PPy/PB hydrogel provided a compatible substrate for L-929 cells. Taken together, the excellent biocompatibility and cell attachment ability made CNF-PPy/PB hydrogels ideal candidates to build a bio-device interface to create implantable bioelectronics.
4. CONCLUSIONS

In summary, we demonstrated a novel strategy to design and develop a type of multifunctional CPHs based on a viscoelastic PB gel matrix and nanostructured CNF-PPy complexes that synergized the biotemplate role of CNFs and conductive nature of PPy. CNFs served as a biotemplate and guided the growth of PPy into compact CNF-PPy complexes with ideal dispersity, while borax acted as a dynamic cross-linker between the PVA chains and CNF-PPy complexes. Following the two-step design strategy, the CNF-PPy complexes, which not only imparted high conductivity to the CNF-PPy/PB hydrogel but also reinforced the hydrogel network, were homogeneously incorporated into the hydrogel to establish a combined reinforcing and conductive network. The coexistence of multi-complexation, H₂O interpenetration, chain entanglement of CNF-PPy complexes and PVA, as well as inter- and intramolecular hydrogen bonding systems among them led to the formation of an integrated 3D network within the CNF-PPy/PB hybrid hydrogels. The final homogeneous, stable and moldable hydrogels with high water content (~94%) and a low density (~1.2 g cm⁻³) exhibited high strength (σ, up to 18.5 MPa cm³ g⁻¹, σₘᵋᵣᵣ up to 22 MPa at ε=90%), decent viscoelasticity (G' max up to 0.1 MPa) and excellent conductivity (up to 4.74 S m⁻¹). They could be repeatedly remolded into various 3D shapes and support more than 60 times of its own weight. Because of dynamically reversible network formed via various borax-based complexes, the hydrogels demonstrated pH-sensitive sol-gel transition behavior, as well as fast (within 20s), efficient and repeatable self-healing ability at room temperature without any external stimuli. CNF-PPy/PB hydrogels also exhibited excellent biocompatibility and cell attachment ability, making them ideal candidates to build a bio–device interface. The CNF-PPy/PB-3 hydrogel-based electrodes showed a high specific capacitance of 236.9 F g⁻¹ at a current density of 0.5 A g⁻¹ and excellent cyclic stability with a capacitance
retention of 86% after 1500 cycles. In conclusion, this study illustrated a new pathway for the fabrication of CPHs with multifunctionality, opening up a number of future research directions and applications, particularly in intelligent bioelectronics devices, such as bioelectrodes, biosensors and implantable devices.

ASSOCIATED CONTENT

Supporting Information. The preparation of CNFs and characterization of in vitro cytotoxicity assays, UV-Vis of neat PPy and CNF-PPy-3 complex suspensions, pH-responsive ability of hydrogels, tensile stress-strain curves of the original and healed hydrogels, and the specific capacitance variation of the hydrogel supercapacitors were supplied as Supporting Information.

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