The advent of conductive self-healing (CSH) hydrogels, a class of novel materials mimicking human skin, may change the trajectory of the industrial process because of their potential applications in soft robots, biomimetic prostheses, and health-monitoring systems. Here, the development of a mechanically and electrically self-healing hydrogel based on physically and chemically cross-linked networks is reported. The autonomous intrinsic self-healing of the hydrogel is attained through dynamic ionic interactions between carboxylic groups of poly(acrylic acid) and ferric ions. A covalent cross-linking is used to support the mechanical structure of the hydrogel. Establishing a fair balance between the chemical and physical cross-linking networks together with the conductive nanostructure of polypyrrole networks leads to a double network hydrogel with bulk conductivity, mechanical and electrical self-healing properties (100% mechanical recovery in 2 min), ultrastretchability (1500%), and pressure sensitivity. The practical potential of CSH hydrogels is further revealed by their application in human motion detection and their 3D-printing performance.

Nature has provided countless inspirations to develop biomimetic synthetic materials.[1] Repeatable autonomous self-healing systems together with pressure sensitivity are considered as essential components for mimicking the human skin.[2] Despite extensive studies on developing self-healing materials, only a few attempts were made to capture other functional features such as conductivity. Developing hydrogels with autonomous self-healing property and electrical conductivity are vital for the advancement of emerging fields such as artificial skins,[2] medical devices,[3] soft robotics,[4] and flexible devices.[5] However, designing a material engaging multiple functionalities still remains a big challenge. A summary of studies on synthesizing conductive self-healing (CSH) materials is provided in Table S1 (Supporting Information).[6–10] The mechanical and electrical recovery efficiencies are defined as the strain ratio and the electrical restoration before cut and after healing, respectively. Autonomous and repeatable self-repairing materials can be developed by employing dynamic covalent interactions[11] or alternatively by designing a supramolecular system using noncovalent interactions, including hydrogen bond,[12] host–guest interaction,[3] hydrophobic association,[13] crystallization,[14] metal–ligand interactions, and ionic interactions.[15] Tee et al.[16] developed a composite capable of restoring its mechanical and electrical properties through the supramolecular polymeric hydrogen-bonding network. The proposed self-healing electronic skin demonstrated a good ability to sense mechanical forces. However, the efficiency of mechanical recovery was only 41% after 10 min followed by mechanical damage. Peng et al.[10] proposed hybrid hydrogels produced from a commercial superabsorbent polymer and reduced graphene oxide for a potential candidate in soft moisture-related resistors-sensor systems, whereas it cannot sense the mechanical force, a key factor for electrical skin. Using a polymer network and single-walled carbon nanotubes connected through host–guest interactions, Guo et al.[9] designed a composite revealing bulk electrical conductivity, proximity and humidity sensitivities. The specimen was self-healed after 5 min under ambient conditions and was able to recover 90% of its mechanical and electrical properties. However, this design suffers from low conductivity (5 S m−1) and low pressure sensitivity. Shi et al.[8] developed a self-healing hybrid hydrogel in which the dynamic assembly/disassembly nature of metal–ligand supramolecules contributes to self-healing property and the conductive nanostructure of polypyrrole (PPy) aerogel contributes to...
reach bulk conductivity. However, the conductivity was relatively low \((10 \text{ S m}^{-1})\) and stretchability was limited to 67%. Although dynamic noncovalent approaches enhance the time and efficiency of the healing, the applicability of the most proposed self-healing hydrogels is questionable, mainly due to their poor mechanical performance. One approach to address this shortening is establishing a fair balance between chemical and physical cross-linking networks.[16]

Here, we synthesized a mechanically and electrically self-healing hydrogel with pressure and extension sensitive features, introducing a promising candidate for wearable sensors. The hydrogel was prepared with physically and chemically cross-networked through a two-step synthesis. In the first step, PPy is grafted to the double-bond decorated chitosan (DCh) to form PPy-grafted chitosan (DCh-PPy). In the second place, acrylic acid (AA) monomers were chemically polymerized in the presence of DCh-PPy and ferric iron, to form poly(acrylic acid) (PAA) double network with physically and chemically cross-linked polymers. The reversible ionic interactions between carboxylic groups of PAA and NH groups of PPy, and ferric iron contribute to an eye-catching autonomous self-healing property (100% mechanical recovery in 2 min; electrical recovery with 90% efficiency in 30 s). The covalent cross-linking between PAA and N,N′-methylenebis-acrylamide (MBAA) is responsible for strengthening the mechanical performance of the hydrogel. Another feature of our hydrogel is the injectability which enables to print a CSH hydrogel for the first time. The noncovalent and reversible bonds can be disrupted and reformed by an introduction and removal of an external force, respectively.[17] Furthermore, we revealed that the current CSH hydrogel has the ability to monitor human motions with fast resistance response.

The chemical illustration for the preparation of the conductive component and CSH hydrogel was drawn in Figure S1 (Supporting Information). First, chitosan was decorated by using methacrylic anhydride to obtain DCh. A nuclear magnetic resonance spectroscopy was performed to confirm the presence of double bond in chitosan (Figure S2 and S3, Supporting Information). DCh was grafted with PPy to synthesize DCh-PPy. Herein, DCh-PPy with two different compositions was prepared as listed in Table S2 (Supporting Information). To further examine the chemical structure, Fourier transformed infrared spectra of chitosan, DCh, and DCh-PPy20 were presented in Figure S4 (Supporting Information).

The CSH hydrogels were prepared via free radical polymerization of AA in the presence of FeCl₃, covalent cross-linker (MBAA) and conductive compound (DCh-PPy) as shown in Figure S5 (Supporting Information). This polymerization gives chemically cross-linked PAA chains that form the backbone of the hydrogel and preserve the permanent hydrogel network. On the other hand, there is the secondary network as a physical cross-link within the hydrogel (Figure S1, Supporting Information). The network polymer obtained is due to mainly the noncovalent ionic interaction of Fe³⁺ ions with carboxylic groups of PAA and NH groups of PPy.[18] In addition, the presence of plenty of −OH and −NH₂ groups in chitosan structure forms strong inter- and intramolecular hydrogen bonds, therefore stabilizing the resulting hydrogel formed.[19]

Owing to the conjugation with chitosan, PPy-chitosan complex become much more stable in the solution. In comparison, using PPy (prepared with the same formula without chitosan) as a conductive component in hydrogel solution led to self-polymerization and ultimately aggregation of PPy (Figure S6, Supporting Information). Hydrogels with different compositions listed in Table S3 (Supporting Information) were prepared with different covalent cross-linking concentrations and different mass ratios of DCh-PPy. For instance, H2010h1 contains 100 µL of AA, 400 µL of water, 0.25 mol% of MBAA, 10 mg of DCh-PPy20 and 0.005 g of ammonium per sulfate (APS). Hydrogels were further tested to evaluate the conductivity and self-healing time (Table S4, Supporting Information). According to Table S4 (Supporting Information), hydrogels prepared by DCh-PPy20 had higher conductivity compared to those by DCh-PPy10 which means rising the ratio of PPy to chitosan led to higher conductivity. Also, for a given amount of DCh-PPy loading, the covalent cross-linking density in the hydrogel did not significantly impact the conductivity.

Generally, two mechanisms are contributing to the conductivity of our hydrogel; one is the existence of Fe³⁺ ions in the hydrogel which results in ionic conductivity and another one is the effect of PPy conductive polymer. Specifically, ionic solution led to rich conductivity in the hydrogel and induction of PPy relatively enriched the conductivity.[17]

Furthermore, the effect of the ferric ions concentration on the gelation and mechanical structure of the hydrogel was also discussed in Table S5 and Figure S7 (Supporting Information). Figure 1 studies the self-healing behavior of the CSH hydrogels. According to Figure 1a, H2010h1 was cut into two halves. Then, two halves were brought into a contact and the healing time was recorded. It was found that H2010h1 was self-healed completely after only 2 min (no specific changes were observed in cut area after 2 min, Movie S1, Supporting Information). The proposed self-healing mechanism was schematically shown in Figure 1b. When two halves were brought into a contact, dynamic ionic interactions between PAA and PPy functional groups enabled ferric ions to migrate from one side to another leading to the hydrogel healing. Furthermore, hydrogen bonding between chitosan and PAA can also contribute to improve the self-healing property.

Similarly, other entries in Table S3 (Supporting Information) were tested and the recovery times were recorded (Table S4, Supporting Information). According to Table S4 (Supporting Information), the concentration of the covalent cross-linker can significantly affect the healing time. The self-healing times for H2010h1, H2010h2, and H2010h3 hydrogels (containing 25%, 30%, and 35% of MBAA (MBAA/AA mol%), respectively) were 2, 4, and 10 min, respectively. Hence, a higher percentage of MBAA increases the healing time. For example, H2010h4 hydrogel with 40% of the MBAA was found to recover after 5 h. Figure 1c reveals the effect of the chemical cross-linking density on the self-healing recovery efficiency through comparing the strain ratio before and after cut (strain rate was 2 mm s⁻¹). It was seen that with an increase in the MBAA concentration, the strain ratio decreased with an increasing rate, reaching almost a complete loss of self-healing for H2010h4 hydrogel corresponding to 40% of MBAA. For H2010h1, the strain rate before and after the cut was almost the same, signaling a complete self-healing. When MBAA was less than 25 mol%, the mechanical properties of the hydrogel become poor and unable
to keep its shape. Accordingly, the chemical cross-linking was shown to be a significant parameter to preserve the mechanical strength and stable shape of the conductive hydrogel. H2010h1 hydrogel revealed to be mechanically stable with highly efficient self-healing ability. Capability of the electrical recovery after cut was demonstrated in Figure 1d, showing 90% of electrical recovery in 30 s. Also, it was seen that after 1 min, the electrical recovery efficiency was 96%.

The dynamic oscillatory frequency sweep of the H2010h1 hydrogel was studied for frequencies ranging from 0.1 to 100 rad s\(^{-1}\) and the storage (\(G'\)) and loss moduli (\(G''\)) were illustrated in Figure 1e. A frequency-dependent behavior was observed,
in which for frequency values less than 0.5 rad s\(^{-1}\), \(G'\) and \(G''\) increased dramatically. Over the studied frequency range, \(G'\) was shown to be bigger than \(G''\), representing the gel-like property. To evaluate the self-healing properties of the H2010 hydrogel, the strain amplitude sweep test was performed and was shown in Figure 1f. It was seen that the critical strain of the storage and loss moduli (strains where both moduli experience a dramatic drop and the hydrogel fails) were 200% and 100%, respectively, of which the network of the hydrogel was not damaged yet. However, the hydrogel tended more into the liquid phase.\(^{[3]}\) The collapse of the hydrogel occurs when the value of \(G'\) and \(G''\) interact at the oscillatory strain amplitude of 400%. In order to determine the recovery of mechanical property of H2010h1 hydrogel after network failure at high strains, \(G'\) and \(G''\) of the hydrogel under continuous strain sweep with alternate low (1%) and high (500%) oscillation excitations were demonstrated in Figure 1g. At first sequence, when the hydrogel was subjected to the small amplitude oscillatory shear (1%) for 60 s, the storage modulus was constantly about 1700 Pa and always higher than the loss moduli (500 Pa). This fact shows that the hydrogel network was conserved adequately under low oscillatory strains. After that, the hydrogel was subjected to a high amplitude oscillatory shear (500%). It was found that \(G'\) decreased considerably to around 250 Pa which was lower than \(G''\) with 390 Pa, implying that the hydrogel network lost its gel-like character. Subsequently, when the strain amplitude was decreased to the previous value (1%), the \(G'\) and \(G''\) both recovered instantaneously to primary values promptly, proving the robust self-healing property of the hydrogel and fast recovery of the hydrogel network after the damage. This process was repeated for multiple times and our results indicated that the recovery of the hydrogel network and self-healing property are repeatable with the same efficiency.

**Figure 2** investigates the mechanical properties and morphology of hydrogels with different cross-linking ratios when
samples were subjected to uniaxial stress. Figure 2a shows the optical image of H2010h1 sample with the length of 15 mm without stretch and with a stretch of 250 mm (more than 1500% of the original length). According to the stress–strain curves (Figure 2b), the elongation at fracture was reduced and the yield strength was improved with an increase in the cross-linking ratio. Moreover, at a specific strain ratio, the tensile strength of the hydrogel with a higher cross-linking ratio was larger. The reason why ultimate strengths of lower cross-linked hydrogels were larger than those with higher one might be due to the water evaporation of hydrogel. For H2010h1 sample, 39% of the water content was evaporated during 25 min of the tensile test. When hydrogels lose their water content, they shrink, since the space between chains becomes smaller when water molecules leave the hydrogel, resulting in a stronger hydrogel structure.

Low cross-linked hydrogels had higher elongation percentages at break, leading to an increased surface area which has direct bearing on the hydrogel dehydration. Scanning electron microscopy (SEM) images of hydrogels with different covalent cross-linker ratios (H2010h1, H2010h2, and H2010h3) were shown in Figure 2e–g. The nanostructured morphologies of PPy networks were also shown in the inset. Hydrogels with lower amount of MBAA, had larger porosity. It is evident that increasing the MBAA ratio enhanced the number of covalent bonds and interchain connections, and hence leading to the foundation of more mechanically strengthened hydrogels. This behavior is also observable in compressive stress–strain curves and elasticity moduli reported in Figure 2c,d, respectively. H2010h3 has higher degree of chemical cross-linking and higher Young’s modulus.

In order to investigate the effect of PPy on the modulus and mechanical strength, samples with 8 mm diameter and 10 mm length containing 10, 15, and 20 mg DCh-PPy were prepared for compressive test and Young’s modulus were obtained as $E = 774$, $498$, and $237$ kPa, respectively (test speed $= 20$ mm min$^{-1}$). According to Figure S10 (Supporting Information), both mechanical strength and elastic modulus were decreased as the weight of DCh-PPy increased. PPy was utilized to assist the conductivity and improve self-healing property rather than improving the mechanical strength (Figure S10, Supporting Information). According to our observations and experiment, the hydrogel was clearly stronger without the application of PPy. Although PPy is considered a hard segment, it did not increase the strength of the hydrogel since the hydrogen and ionic bonding between the PPy and the host gel was weaker than covalent bonds present in the hydrogel. Also, ionic cross-linking of iron and PAA network contributed greatly to gel’s modulus. Since PPy had interaction with Fe$^{3+}$ ions, introduction of PPy in hydrogel network partially interacted with iron in replace of carboxylic groups of PAA and led to less PAA ionic cross-linking network density.

Figure 3 is the dependency of the resistance with an applied compression. It was seen that with an increase in the applied pressure, the conductivity raised correspondingly (Figure 3a). This behavior was further illustrated in Figure 3b (Movie S2, Supporting Information). By using the hydrogel, we designed a complete circuit composed of a light-emitting diode (LED) bulb. Increasing the pressure led to a brighter light in the LED bulb. This is mainly owing to the fact that with applying compression force, the distance between the conductive particles inside the hydrogel network decreases leading to more interconnections. To examine the pressure sensing performance by using the INSTRON machine and two-probes digital multimeter, the corresponding resistance variation due to the cyclic compression was captured while the length of the hydrogel was repeatedly changing to 25% and 50% of the original length of the specimen (Figure 3c and Movie S3 (Supporting Information)). It was seen that at both strains of 25% and 50%, the resistance of hydrogel ideally responded to the applied loading and unloading process.

![Figure 3](image-url)
A hydrogel with following components was prepared: 400 µL water, 10 mg DCh-PPy20, 1.25 mol% Fe(Cl3)/AA, 0.25 mol% MBAA/AA, 100 µL AA, and 0.0025 g of APS, which compared to H2010h1, half of initiator (APS) was used. In the 3D printing process, two steps of solidification were performed to achieve higher printing efficiency and enable the hydrogel to pass through the needle. The second initiator becomes active when the APS-contained gelatin membrane liquefies, since the APS is incubated inside the gelatin membrane. Additionally, it was found that gelatin membrane is the best candidate for a printing substrate compared to glass slides, poly(dimethylsiloxane) (PDMS), and Petri dishes. One challenge regarding the printing substrate was that the hydrogel was sliding when printing on glass slides, PDMS, and Petri dishes.

Graph shown in Figure 4a presents the effect of high shear rates on the CSH hydrogel viscosity. The background image shows the conductive ink for printing, and the index image is the 3D printing nozzle while printing the hydrogel on gelatin membrane. It was seen that the viscosity decreased at higher shear rates, signaling a shear-thinning behavior. Thus, while the hydrogel passes through the needle, the dynamic network of the hydrogel breaks down. On the other hand, the self-healing property resulted from ionic transition helps the hydrogel to heal again. Shear-thinning behavior of H2010h1

Figure 4. 3D printing characterization, preparation, and application. a) Shear-thinning behavior. b) Preparation of 3D printed wearable sensor with the CSH hydrogel. c) A real-time bodily motion monitoring system using smart phones and a 3D printed CSH wearable and flexible sensor. d) Resistance variation of the CSH hydrogel strip (left), and 3D printed sensor (right) attached on the index finger, as the finger was subjected to repeated bending and relaxing from 0° to 20°, 45°, and 90°.
hydrogel and the one prepared for 3D printing was compared in Figure S11 (Supporting Information) and it can be seen that the hydrogel with less initiator provided better shear-thinning behavior.

The 3D printing process is illustrated in Figure 4b (Movie S4, Supporting Information). In the first step, the CSH hydrogel was printed on the APS-contained gelatin membrane which is the sacrificial layer. Afterward, the gelatin together with 3D pattern was placed on a thin PDMS membrane from the printed side. Hot water was added to wash the gelatin; and it was found that duration of 2 min was enough to wash the gelatin. Meanwhile, the second solidification occurred, since APS initiator was incubated in gelatin membrane and released in the presence of hot water. Two-sided copper tapes were used to connect the ends of printing for collecting signals. Another PDMS membrane was used to cover the 3D printed pattern. The rheological experiments were repeated for the hydrogel made with the same process explained above (APS initiator was added in two steps, one with the 3D printing ink and the other one activated when gelatin dissolved; Figure S12, Supporting Information). Similar to H2010h1 hydrogel, a frequency-dependent behavior was observed in which $G'$ was bigger than $G''$, showing a gel-like property. For H2010h1, $G'$ increased from 600 to 6000 Pa when the frequency was increased to 200 rad s$^{-1}$ which this behavior is very similar to $G'$ from 3D printed hydrogel where $G'$ increased from 300 to 6000 Pa. According to oscillatory strain amplitude, it was seen that the critical strain of the storage and loss moduli were 100% and 200%, respectively. The collapse of the hydrogel occurred when the value of $G'$ and $G''$ interact at the oscillatory strain amplitude around 500%. Regarding continuous strain sweep with alternate low (1%) and high (500%) oscillation excitations, results indicated that the recovery of the hydrogel network and self-healing property are repeatable with the same efficiency.

A real-time bodily motion monitoring system was designed using smart phones and 3D printed CSH hydrogel. Current wearable and flexible device was used for human motion detection and data were appeared in smart phone by Bluetooth (Figure S13, Supporting Information). As shown in Figure 4c, the sensor was adhered to the chest for respiration monitoring and the electrical changes associated with inhalation and exhalation were recorded for slow and deep breathing. The signal of deep breathing was of higher frequency and larger amplitude than that of slow one. Also, CSH sensor was used to record wrist pulses; each cycle signifies a pulse. The results completely conformed to the realistic physiological behaviors. Relative changes in resistance for index finger and bicep motions were also depicted (Movie S5, Supporting Information). The peaks and valleys are assigned to the stretching and relaxing muscles, respectively. Figure 4d shows the CSH hydrogel strip and 3D printed hydrogel attached on the index finger. The resistance variations were collected while the finger was repeatedly bent and 90% of electrical recovery in 30 s). Autonomic repeatable self-repairing capability after damage and shear-thinning behavior enables these hydrogels to be used as 3D printing materials. Conductive nanostructure of PPy networks offers new applications in strain and pressure sensing devices. To demonstrate the potential of the CSH hydrogel in wearable devices, a stretchable wireless human motion detector was fabricated. Relative change of resistance of the respiratory, pulse, and muscle motions were collected which outcomes complied with human physiological aspects. Considering the superb sensing performance pairing with self-healing property, 3D printability, and stretchability, the developed material offers superior functionalities compared with the previously reported ones (Table S1, Supporting Information).

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

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